EPA/600/P-03/002F
November 2006

An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States for the Years 1987, 1995, and 2000

National Center for Environmental Assessment
Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC 20460

DISCLAIMER

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

The purpose of this document is to present a comprehensive inventory and overview of sources and environmental releases of dioxin-like compounds in the United States. The major identified sources of environmental releases of dioxin-like compounds are grouped into six broad categories: combustion sources, metals smelting, refining and process sources, chemical manufacturing sources, natural sources, and environmental reservoirs. Estimates of annual releases to land, air, and water are presented for each source category and summarized for reference years 1987, 1995, and 2000. The quantitative results are expressed in terms of the toxicity equivalence (TEQ) of the mixture of polychlorinated dibenzo-*p*-dioxin (CDD) and polychlorinated dibenzofuran (CDF) compounds present in environmental releases using a procedure sanctioned by the World Health Organization (WHO) in 1998. This TEQ procedure translates the complex mixture of CDDs and CDFs characteristic of environmental releases into an equivalent toxicity concentration of 2,3,7,8-tetrachorodibenzo-*p*-dioxin (2,3,7,8-TCDD), the most toxic member of this class of compounds. Using this WHO procedure, the annual releases of TEQ_{DF}-WHO_{98} to the U.S. environment over the three reference years are 13,965 g in 1987, 3,444 g in 1995, and 1,422 g in 2000. This analysis indicates that between reference years 1987 and 2000, there was approximately a 90% reduction in the releases of dioxin-like compounds to the circulating environment of the United States from all known sources combined. In 1987 and 1995, the leading source of dioxin emissions to the U.S. environment was municipal waste combustion; however, because of reductions in dioxin emissions from municipal waste combustors, it dropped to the fourth ranked source in 2000. Burning of domestic refuse in backyard burn barrels remained fairly constant over the years, but in 2000, it emerged as the largest source of dioxin emissions to the U.S. environment.

Preferred Citation:
U.S. EPA (Environmental Protection Agency). (2006) An inventory of sources and environmental releases of dioxin-like compounds in the United States for the years 1987, 1995, and 2000. National Center for Environmental Assessment, Washington, DC; EPA/600/P-03/002F. Available from: National Technical Information Service, Springfield, VA, and online at http://epa.gov/ncea.

CONTENTS

LIST OF TABLES xii
LIST OF FIGURES xxv
LIST OF ABBREVIATIONS AND ACRONYMS xxx
FOREWORD xxxiv
PREFACE xxxvi
AUTHORS, CONTRIBUTORS, AND REVIEWERS xxxvii
ACKNOWLEDGMENT xli
EXECUTIVE SUMMARY xlii

1. BACKGROUND, APPROACH, AND CONCLUSIONS 1-1
   1.1. BACKGROUND 1-1
      1.1.1. Reference Years 1-3
      1.1.2. Regulatory Summary 1-3
      1.1.3. Definition of Dioxin-Like Compound 1-4
      1.1.4. Toxicity Equivalence Factors 1-8
      1.1.5. Information Sources 1-11
   1.2. APPROACH 1-12
      1.2.1. Source Classes 1-12
      1.2.2. Quantitative Method for Inventory of Sources 1-23
      1.2.3. Confidence Ratings 1-27
         1.2.3.1. Rating Scheme 1-31
   1.3. CONCLUSIONS 1-37
      1.3.1. Total Environmental Releases 1-37
      1.3.2. Time Trends 1-42
      1.3.3. Sources Not Included in the Inventory 1-42
      1.3.4. Formation Theory 1-43
      1.3.5. Congener Profiles of CDD/CDF Sources 1-44

2. MECHANISMS OF FORMATION OF DIOXIN-LIKE COMPOUNDS DURING COMBUSTION OF ORGANIC MATERIALS 2-1
   2.1. MECHANISM 1 (PASS THROUGH): CDD/CDF CONTAMINATION IN FUEL AS A SOURCE OF COMBUSTION STACK EMISSIONS 2-3
   2.2. MECHANISM 2 (PRECURSOR): FORMATION OF CDDs/CDFs FROM PRECURSOR COMPOUNDS 2-4
   2.3. MECHANISM 3 (*DE NOVO* SYNTHESIS): SYNTHESIS OF CDDs/CDFs DURING COMBUSTION OF ORGANIC MATERIALS 2-12
   2.4. THE ROLE OF CHLORINE IN THE FORMATION OF CDDs/CDFs IN COMBUSTION SYSTEMS 2-20
      2.4.1. Review of Laboratory-Scale Studies 2-21
      2.4.2. Review of Full-Scale Combustion Systems 2-26
   2.5. POTENTIAL PREVENTION OF CDD/CDF FORMATION IN COMBUSTION SYSTEMS 2-28
   2.6. THEORY ON THE EMISSION OF PCBs 2-29

CONTENTS (continued)

2.7. SUMMARY AND CONCLUSIONS 2-31
2.7.1. Mechanisms of Formation of Dioxin-Like Compounds 2-31
2.7.2. Role of Chlorine 2-33
2.7.3. General Conclusion 2-34

3. COMBUSTION SOURCES OF CDDs/CDFs: WASTE INCINERATION 3-1
3.1. MUNICIPAL WASTE COMBUSTION 3-1
3.1.1. Description of Municipal Waste Combustion Technologies 3-2
3.1.1.1. Furnace Types 3-2
3.1.1.2. Air Pollution Control Devices 3-9
3.1.1.3. Classification Scheme 3-10
3.1.2. Characterization of MWCs in Reference Years 2000, 1995, and 1987 . . . 3-11
3.1.3. Estimation of CDD/CDF Emissions from MWCs 3-19
3.1.3.1. Estimating CDD/CDF Emissions from MWCs in Reference Year 2000 3-19
3.1.3.2. Estimating CDD/CDF Emissions from MWCs in Reference Years 1995 and 1987 3-21
3.1.4. Summary of CDD/CDF (TEQ) Emissions from MWCs for 2000, 1995, and 1987 3-23
3.1.5. Congener Profiles of Municipal Waste Combustion Facilities 3-31
3.1.6. Estimated CDDs/CDFs in MWC Ash 3-31
3.1.7. Recent EPA Regulatory Activities 3-40
3.2. HAZARDOUS WASTE INCINERATION 3-41
3.2.1. Furnace Designs for HWIs 3-42
3.2.2. APCDs for HWIs 3-44
3.2.3. Estimation of CDD/CDF Emission Factors for HWIs 3-45
3.2.4. Emission Estimates for HWIs 3-47
3.2.5. Recent EPA Regulatory Activities 3-51
3.2.6. Industrial Boilers and Furnaces Burning Hazardous Waste 3-51
3.2.7. Halogen Acid Furnaces Burning Hazardous Waste 3-53
3.2.8. Solid Waste from Hazardous Waste Combustion 3-55
3.3. MEDICAL WASTE INCINERATION 3-55
3.3.1. Design Types of MWIs Operating in the United States 3-55
3.3.2. Characterization of MWIs for Reference Years 1987, 1995, and 2000 . . . 3-57
3.3.3. Estimation of CDD/CDF Emissions from MWIs 3-59
3.3.4. Summary of CDD/CDF Emissions from MWIs 3-64
3.3.5. Recent EPA Regulatory Activities 3-65
3.4. CREMATORIA 3-65
3.4.1. Human Crematoria 3-65
3.4.1.1. Emissions Data 3-65
3.4.1.2. Activity Level Information 3-73
3.4.1.3. Emission Estimates 3-76
3.4.2. Animal Crematoria 3-76

CONTENTS (continued)

3.4.2.1. Emissions Data . . . 3-76
3.4.2.2. Activity Level Information . . . 3-76
3.4.2.3. Emission Estimates . . . 3-76
3.5. SEWAGE SLUDGE INCINERATION . . . 3-77
3.5.1. Emissions Estimates from Sewage Sludge Incinerators . . . 3-79
3.5.2. Solid Waste from Sewage Sludge Incinerators . . . 3-83
3.6. TIRE COMBUSTION . . . 3-83
3.7. COMBUSTION OF WASTEWATER SLUDGE AT BLEACHED CHEMICAL PULP MILLS . . . 3-87
3.8. BIOGAS COMBUSTION . . . 3-87

4. COMBUSTION SOURCES OF CDDs/CDFs: POWER/ENERGY GENERATION . . . 4-1
4.1. MOTOR VEHICLE FUEL COMBUSTION . . . 4-1
4.1.1. Tailpipe Emission Studies . . . 4-1
4.1.2. Tunnel Emission Studies . . . 4-20
4.1.3. National Emission Estimates . . . 4-28
4.1.3.1. Activity Information for On-Road Vehicles . . . 4-28
4.1.3.2. Activity Information for Off-Road Uses . . . 4-31
4.1.3.3 Emission Estimates . . . 4-32
4.2. WOOD COMBUSTION . . . 4-38
4.2.1. Flue Emissions from Wood Combustion (Residential) . . . 4-38
4.2.1.1. Emissions Data . . . 4-38
4.2.1.2. Activity Level Information . . . 4-41
4.2.1.3. Emission Estimates . . . 4-44
4.2.2. Stack Emissions from Wood Combustion (Industrial) . . . 4-44
4.2.2.1. Emissions Data . . . 4-44
4.2.2.2. Activity Level Information . . . 4-50
4.2.2.3. Emission Estimates . . . 4-51
4.2.3. Solid Waste from Wood Combustion (Residential and Industrial) . . . 4-52
4.3. OIL COMBUSTION . . . 4-60
4.3.1. Institutional/Commercial and Residential Oil Combustion . . . 4-61
4.3.2. Utility Sector and Industrial Oil Combustion . . . 4-64
4.3.3. Used Oil Combustion . . . 4-67
4.4. COAL COMBUSTION . . . 4-67
4.4.1. Utilities and Industrial Boilers . . . 4-68
4.4.2. Residential Coal Combustion . . . 4-74
4.4.3. Solid Wastes from Coal Combustion . . . 4-77

5. COMBUSTION SOURCES OF CDDs/CDFs: OTHER HIGH-TEMPERATURE SOURCES . . . 5-1
5.1. CEMENT KILNS . . . 5-1
5.1.1. Process Description of Portland Cement Kilns . . . 5-1
5.1.2. Cement Kilns That Burn Hazardous Waste . . . 5-2

CONTENTS (continued)

5.1.3. Air Pollution Control Devices 5-3
5.1.4. CDD/CDF Emissions Data 5-4
5.1.4.1. Emissions Data for 1989 through 1996 5-4
5.1.4.2. Emissions Data for 1999 and 2000 5-7
5.1.4.3. Emission Factor Estimates for Cement Kilns Burning Hazardous Waste 5-7
5.1.4.4. Emission Factor Estimates for Cement Kilns Burning Nonhazardous Waste 5-9
5.1.4.5. Confidence Ratings of Emission Factor Estimates 5-10
5.1.5. Activity Level Information 5-10
5.1.6. National CDD/CDF Emission Estimates 5-14
5.1.6.1. Estimates for Reference Years 1987 and 1995 5-14
5.1.6.2. Estimates for Reference Year 2000 5-15
5.1.7. EPA Regulatory Activities 5-16
5.1.8. Solid Waste from Cement Manufacturing: Cement Kiln Dust 5-16
5.2. LIGHTWEIGHT AGGREGATE KILNS 5-21
5.3. ASPHALT MIXING PLANTS 5-22
5.4. PETROLEUM REFINING CATALYST REGENERATION 5-24
5.5. CIGARETTE SMOKING 5-28
5.6. PYROLYSIS OF BROMINATED FLAME RETARDANTS 5-39
5.7. CARBON REACTIVATION FURNACES 5-39
5.8. KRAFT BLACK LIQUOR RECOVERY BOILERS 5-42
5.9. OTHER IDENTIFIED SOURCES 5-46

6. COMBUSTION SOURCES OF CDDs/CDFs: MINIMALLY CONTROLLED AND UNCONTROLLED COMBUSTION SOURCES 6-1
6.1. COMBUSTION OF LANDFILL GAS 6-1
6.1.1. Emissions Data 6-1
6.1.2. Activity Level Information 6-1
6.1.2.1. Activity Levels for 1987 and 1995 6-3
6.1.2.2. Activity Level for 2000 6-4
6.1.3. Emission Estimates 6-4
6.2. ACCIDENTAL FIRES 6-5
6.2.1. Soot and Ash Studies 6-5
6.2.2. Fume and Smoke Studies 6-7
6.2.3. Data Evaluation 6-8
6.2.3.1. Structural Fires 6-8
6.2.3.1.1. Emissions data 6-8
6.2.3.1.2. Activity level information 6-9
6.2.3.1.3. Emission estimates 6-9
6.2.3.2. Vehicle Fires 6-10
6.3. LANDFILL FIRES 6-11
6.3.1. Emissions Data 6-11

CONTENTS (continued)

6.3.2. Activity Level Information and Emission Estimates 6-12
6.4. FOREST AND BRUSH FIRES 6-12
6.4.1. Emissions Data 6-12
6.4.2. Activity Level Information 6-18
6.4.2.1. Approach for Reference Year 2000 (Office of Air Quality Planning and Standards [OAQPS]) 6-18
6.4.2.2. Approach for Reference Years 1987 and 1995 6-18
6.4.3. Emission Estimates 6-19
6.5. BACKYARD BARREL BURNING 6-20
6.5.1. Emissions Data 6-20
6.5.2. Activity Level Information 6-21
6.5.2.1. Summary of Barrel Burn Surveys 6-23
6.5.2.2. Estimates of Activity Level 6-24
6.5.2.3. Alternative Approach to Estimating Activity Level 6-25
6.5.3. Emission Estimates 6-26
6.5.4. Composition of Ash from Barrel Burning 6-26
6.6. RESIDENTIAL YARD WASTE BURNING 6-26
6.6.1. Emissions Data 6-26
6.6.2. Activity Level Information 6-28
6.6.3. Emission Estimates 6-29
6.7. LAND-CLEARING DEBRIS BURNING 6-30
6.7.1. Emissions Data 6-30
6.7.2. Activity Level Information 6-30
6.7.2.1. Residential Construction 6-30
6.7.2.2. Nonresidential Construction 6-30
6.7.2.3. Roadway Construction 6-31
6.7.2.4. Fuel Loading Factors 6-31
6.7.3. Emission Estimates 6-32
6.8. UNCONTROLLED COMBUSTION OF POLYCHLORINATED BIPHENYLS 6-32
6.9. VOLCANOES 6-33
6.10. FIREWORKS 6-34
6.11. OPEN BURNING AND OPEN DETONATION OF ENERGETIC MATERIALS 6-36

7. METAL SMELTING AND REFINING SOURCES OF CDDs/CDFs 7-1
7.1. PRIMARY NONFERROUS METAL SMELTING/REFINING 7-1
7.1.1. Primary Copper Smelting and Refining 7-1
7.1.2. Primary Magnesium Smelting and Refining 7-4
7.1.3. Primary Nickel Smelting and Refining 7-6
7.1.4. Primary Aluminum Smelting and Refining 7-6
7.1.5. Primary Titanium Smelting and Refining 7-7
7.2. SECONDARY NONFERROUS METAL SMELTING 7-8

CONTENTS (continued)

7.2.1. Secondary Aluminum Smelters 7-8
7.2.2. Secondary Copper Smelters 7-14
7.2.2.1. Emissions Data 7-15
7.2.2.2. Activity Level Information 7-20
7.2.2.3. Emission Estimates 7-20
7.2.3. Secondary Lead Smelters 7-22
7.3. PRIMARY FERROUS METAL SMELTING/REFINING 7-27
7.3.1. Sinter Production 7-27
7.3.2. Coke Production 7-32
7.4. SECONDARY FERROUS METAL SMELTING/REFINING 7-33
7.5. FERROUS FOUNDRIES 7-36
7.6. SCRAP ELECTRIC WIRE RECOVERY 7-40
7.7. DRUM AND BARREL RECLAMATION FURNACES 7-45
7.8. SOLID WASTE FROM PRIMARY/SECONDARY IRON/STEEL MILLS/FOUNDRIES 7-48

8. CHEMICAL MANUFACTURING AND PROCESSING SOURCES 8-1
8.1. BLEACHED CHEMICAL WOOD PULP AND PAPER MILLS 8-1
8.1.1. Estimates of National Emissions in 1987 and 1995 8-8
8.1.2. Estimates of National Emissions in 2000 8-8
8.2. MANUFACTURE OF CHLORINE, CHLORINE DERIVATIVES, AND METAL CHLORIDES 8-9
8.2.1. Manufacture of Chlorine 8-9
8.2.2. Manufacture of Chlorine Derivatives and Metal Chlorides 8-12
8.3. MANUFACTURE OF HALOGENATED ORGANIC CHEMICALS 8-14
8.3.1. Chlorophenols 8-15
8.3.1.1. Regulatory Actions for Chlorophenols 8-16
8.3.2. Chlorobenzenes 8-24
8.3.2.1. Regulatory Actions for Chlorobenzenes 8-26
8.3.3. Chlorobiphenyls 8-27
8.3.4. Ethylene Dichloride/Vinyl Chloride Monomer/Polyvinyl Chloride Manufacturing 8-30
8.3.4.1. Water Releases 8-33
8.3.4.2. Land Releases 8-36
8.3.4.3. Air Releases 8-36
8.3.4.4. Transfers to Secure Landfills 8-38
8.3.4.5. Products 8-41
8.3.5. Other Aliphatic Chlorine Compounds 8-44
8.3.6. Dyes, Pigments, and Printing Inks 8-45
8.3.6.1. Dioxazine Dyes and Pigments 8-45
8.3.6.2. Phthalocyanine Dyes and Printing Inks 8-48
8.3.7. TSCA Dioxin/Furan Test Rule 8-50
8.3.8. Halogenated Pesticides and FIFRA Pesticides Data Call-In 8-52

CONTENTS (continued)

8.4. OTHER CHEMICAL MANUFACTURING AND PROCESSING SOURCES 8-73
8.4.1. Municipal Wastewater Treatment Plants 8-73
8.4.1.1. Sources 8-73
8.4.1.2. Releases to Water 8-77
8.4.1.2.1 Emissions data 8-77
8.4.1.2.2 Activity level information 8-78
8.4.1.2.3 Emission Estimates 8-81
8.4.1.3. Sewage Sludge Land Disposal 8-81
8.4.1.3.1 Emissions data 8-81
8.4.1.3.2 Activity level information 8-88
8.4.1.3.3 Emission estimates 8-89
8.4.2. Drinking Water Treatment Plants 8-91
8.4.3. Soaps and Detergents 8-93
8.4.4. Textile Manufacturing and Dry Cleaning 8-94

9. INDICATIONS OF POSSIBLE NATURAL SOURCES OF CDDs/CDFs 9-1
9.1. BIOLOGICAL SOURCES OF CDDs/CDFs 9-1
9.1.1. Biotransformation of Chlorophenols 9-1
9.1.2. Biotransformation of Higher CDDs/CDFs 9-4
9.1.3. Dioxin-Like Compounds in Animal Manure 9-6
9.2. PHOTOTRANSFORMATION OF CHLOROPHENOLS 9-8
9.2.1. Photolysis of Higher CDDs/CDFs 9-10
9.2.2. Photolysis in Water 9-11
9.2.3. Photolysis on Soil 9-11
9.2.4. Photolysis on Vegetation 9-12
9.2.5. Photolysis in Air 9-13
9.3. CDDs/CDFs IN BALL CLAY 9-14
9.3.1. Initial Discovery of CDD/CDF Contamination of Ball Clay 9-14
9.3.2. Characteristics of Mississippi Embayment Ball Clays 9-15
9.3.3. Levels of Dioxin-Like Compounds in Ball Clay 9-15
9.3.4. Evidence for Ball Clay as a Natural Source 9-16
9.3.5. Environmental Releases of Dioxin-Like Compounds from the Mining and Processing of Ball Clay 9-19

10. SOURCES OF DIOXIN-LIKE POLYCHLORINATED BIPHENYLS (PCBs) 10-1
10.1. GENERAL FINDINGS OF THE EMISSIONS INVENTORY 10-1
10.2. RELEASES OF COMMERCIAL PCBs 10-4
10.2.1. Approved PCB Disposal/Destruction Methods 10-11
10.2.1.1. Approved Incinerators/High-Efficiency Boilers 10-14
10.2.1.2. Approved Chemical Waste Landfills 10-14
10.2.1.3. Other Approved Disposal Methods 10-15
10.2.2. Emission Estimates 10-15

CONTENTS (continued)

10.2.3. Accidental Releases of Still-in-Service PCBs 10-15
10.2.3.1. Leaks and Spills 10-16
10.2.3.2. Accidental Fires 10-18
10.2.4. Municipal Wastewater Treatment 10-19
10.3. CHEMICAL MANUFACTURING AND PROCESSING SOURCES 10-26
10.4. COMBUSTION SOURCES 10-26
10.4.1. Municipal Waste Combustors 10-26
10.4.2. Industrial Wood Combustion 10-27
10.4.3. Medical Waste Incineration 10-29
10.4.4. Tire Combustion 10-30
10.4.5. Cigarette Smoking 10-31
10.4.6. Sewage Sludge Incineration 10-31
10.4.7. Backyard Barrel Burning 10-34
10.4.8. Petroleum Refining Catalyst Regeneration 10-34
10.5. NATURAL SOURCES 10-36
10.5.1. Biotransformation of Other PCBs 10-36
10.5.2. Photochemical Transformation of Other PCBs 10-39
10.6. PAST USE OF COMMERCIAL PCBs 10-41

11. RESERVOIR SOURCES OF CDDs/CDFs AND DIOXIN-LIKE PCBs 11-1
11.1. POTENTIAL RESERVOIRS 11-1
11.2. CHARACTERIZATION OF RESERVOIR SOURCES 11-3
11.2.1. Soil 11-3
11.2.1.1. Potential Mass of Dioxin-Like Compounds Present 11-3
11.2.1.2. Mechanisms Responsible for Releases from Surface Soils 11-9
11.2.1.3. Estimated Annual Releases from Soil to Water 11-12
11.2.1.4. Estimated Annual Releases from Soil to Air 11-14
11.2.2. Water 11-17
11.2.2.1. Potential Mass of Dioxin-Like Compounds Present 11-17
11.2.2.2. Mechanisms Responsible for Supply to and Releases from Water 11-17
11.2.3. Sediment 11-20
11.2.3.1. Potential Mass of Dioxin-Like Compounds Present 11-20
11.2.3.2. Mechanisms Responsible for Supply to and Releases from Sediment 11-20
11.2.3.3. Releases from Sediment to Water 11-21
11.2.4. Biota 11-22
11.2.4.1. Potential Mass of Dioxin-Like Compounds Present 11-22
11.2.4.2. Mechanisms Responsible for Supply to and Releases from Biota 11-22
11.2.4.3. Approaches for Measuring and Estimating Releases from Biota 11-24
11.3. SUMMARY AND CONCLUSIONS 11-26

CONTENTS (continued)

11.3.1. Reservoir Sources 11-26
11.3.2. Implications for Human Exposure 11-27

REFERENCES R-1

LIST OF TABLES

Table 1-1. Nomenclature for dioxin-like compounds 1-2

Table 1-2. Municipal waste combustors[a] 1-4

Table 1-3. Hazardous waste incinerators and cement kilns and lightweight aggregate kilns burning hazardous waste 1-5

Table 1-4. Cement kilns not burning hazardous waste 1-5

Table 1-5. Secondary aluminum smelters 1-6

Table 1-6. Medical waste incinerators 1-6

Table 1-7. Pulp and paper mills 1-6

Table 1-8. The TEF scheme for I-TEQ_{DF} 1-9

Table 1-9. The TEF scheme for dioxin-like PCBs, as determined by the World Health Organization in 1994 1-9

Table 1-10. The TEF scheme for TEQ_{DFP}-WHO_{98} 1-10

Table 1-11. Known and suspected sources of CDDs/CDFs 1-14

Table 1-12. Inventory of contemporary releases (g/yr) of dioxin-like compounds from known sources in the United States for reference years 2000, 1995, and 1987 and preliminary release estimates for 2000 1-17

Table 1-13. Products containing CDDs/CDFs (g TEQ_{DF}-WHO_{98}/yr) 1-23

Table 1-14. I-TEQ_{DF} emission factors used to develop national emission inventory estimates of releases to air 1-32

Table 1-15. TEQ_{DF}-WHO_{98} emission factors used to develop national emission inventory estimates of releases to air 1-34

Table 1-16. Confidence rating scheme for U.S. emission estimates 1-36

Table 1-17. Ranking of sources of dioxin-like compounds based on environmental releases (from high to low) for reference years 2000, 1995, and 1987 1-38

Table 2-1. Concentration of CDDs/CDFs on municipal incinerator fly ash at varying temperatures 2-7

LIST OF TABLES (continued)

Table 2-2. CDDs/CDFs formed from the thermolytic reaction of 690 mg benzene + $FeCl_3$ silica complex 2-12

Table 2-3. *De novo* formation of CDDs/CDFs after heating Mg-Al silicate, 4% charcoal, 7% Cl, 1% $CuCl_2$ in H_2O at 300°C 2-14

Table 3-1. Inventory of municipal waste combustors (MWCs) in 2000 by technology, air pollution control device (APCD), size[a], and annual activity level (kg/yr) 3-14

Table 3-2. Inventory of municipal waste combustors (MWCs) in 1995 by technology, air pollution control device (APCD), and annual activity level (kg/yr) 3-16

Table 3-3. Inventory of municipal waste combustors (MWCs) in 1987 by technology, air pollution control device (APCD), and annual activity level (kg/yr) 3-18

Table 3-4. National average CDD/CDF congener concentrations for large municipal waste combustors (ng/dscm @ 7% O_2) 3-20

Table 3-6. CDD/CDF TEQ emission factors (ng TEQ/kg waste) for municipal solid waste incineration 3-24

Table 3-7a. Annual I-TEQ_{DF} emissions from municipal waste combustors (MWCs) operating in 1995 3-25

Table 3-7b. Annual TEQ_{DF}-WHO_{98} emissions from municipal waste combustors (MWCs) operating in 1995 3-27

Table 3-8a. Annual I-TEQ_{DF} emissions to the air from municipal waste combustors (MWCs) operating in 1987 3-29

Table 3-8b. Annual TEQ_{DF}-WHO_{98} emissions to the air from municipal waste combustors (MWCs) operating in 1987 3-30

Table 3-9. Average and range of CDD/CDF congener groups in fly ash from a municipal incinerator (µg/kg) 3-36

Table 3-10. Comparison of the amount of TEQs generated annually in municipal waste combustor ash 3-38

Table 3-11. Concentration of CDD/CDF congener groups (ng/kg) in fly ash samples from combustion of municipal solid waste in eight Japanese incinerators 3-39

LIST OF TABLES (continued)

Table 3-12. Concentration of CDD/CDF congener groups in fly ash samples from municipal solid waste 3-39

Table 3-13. CDD/CDF concentrations in municipal solid waste ash from a newly constructed municipal waste combustor in Japan 3-40

Table 3-14a. CDD/CDF emission factors for hazardous waste incinerators and boilers tested from 1993 to 1996 3-48

Table 3-14b. CDD/CDF emission factors for hazardous waste incinerators and boilers tested in 2000 3-49

Table 3-15. CDD/CDF emission factors for halogen acid furnaces tested in 2000 3-54

Table 3-16. Estimated breakdown of facilities by air pollution control device (APCD) . . . 3-60

Table 3-17. Summary of annual operating hours for each medical waste incinerator (MWI) type 3-61

Table 3-18. TEQ emissions from medical waste incinerators (MWIs) for reference year 1987 3-62

Table 3-19. TEQ emissions from medical waste incinerators (MWIs) for reference year 1995 3-62

Table 3-20. TEQ emissions from medical waste incinerators (MWIs) for reference year 2000 3-63

Table 3-21. Congener-specific profile for Camellia Memorial Lawn crematorium 3-70

Table 3-22. Congener-specific profile for the Woodlawn Cemetery crematorium 3-71

Table 3-23. Operational data for the Woodlawn Cemetery crematorium, scrubber inlet . . . 3-73

Table 3-24. Congener-specific profile for the Camellia Memorial Lawn crematorium and the Woodlawn Cemetery crematorium 3-74

Table 3-25. Congener-specific profile for the University of Georgia Veterinary School . . . 3-77

Table 3-26. CDD/CDF emission factors for sewage sludge incinerators 3-82

Table 3-27. CDD/CDF air emission factors for a tire combustion facility 3-84

LIST OF TABLES (continued)

Table 3-28. CDD/CDF emission factors for combustion of bleached-kraft mill sludge in wood residue boilers 3-88

Table 3-5. National CDD/CDF TEQ emissions (g/yr) for large and small municipal waste combustors (MWCs) operating in 2000 3-90

Table 4-1. Description and results of vehicle emission testing studies for CDDs and CDFs 4-3

Table 4-2. CDD/CDF congener emission factors (pg/L) for diesel-fueled automobiles 4-5

Table 4-3. CDD/CDF congener emission factors (pg/L) for diesel-fueled trucks 4-7

Table 4-4. CDD/CDF congener emission factors (pg/L) for leaded gasoline-fueled automobiles 4-9

Table 4-5. CDD/CDF congener emission factors (pg/L) for unleaded gasoline-fueled automobiles without catalytic converters 4-11

Table 4-6. CDD/CDF congener emission factors (pg/L) for unleaded gasoline-fueled automobiles with catalytic converters 4-13

Table 4-7. Total dioxin emission concentrations from heavy-duty diesel engines in Germany 4-21

Table 4-8. Levels of 2,3,7,8-chlorine-substituted congeners and total CDDs/CDFs in vehicle exhaust particles (pg/g) for gasoline engines and suspended particulate matter (SPM) 4-22

Table 4-9. Levels of 2,3,7,8-chlorine-substituted congeners and total CDDs/CDFs in vehicle exhaust particles (pg/g) for diesel engines 4-23

Table 4-10. CDD/CDF concentrations (pg/m^3) from European tunnel air studies 4-24

Table 4-11. Baltimore Harbor tunnel study: estimated emission factors (pg/km) for heavy-duty diesel trucks 4-26

Table 4-12. Average CDD/CDF concentration in flue gas while burning wood and crops 4-40

Table 4-13. CDD/CDF concentrations (pg TEQ/kg wood) in emissions from residential wood stoves in Canada 4-42

LIST OF TABLES (continued)

Table 4-14. CDD/CDF mean emission factors (ng/kg wood) for industrial wood combustors 4-45

Table 4-15. NCASI CDD/CDF TEQ concentrations and emissions for wood residue-fired boilers 4-50

Table 4-16. CDD/CDF concentrations (ng/kg) in residential chimney soot from wood stoves and fireplaces 4-53

Table 4-17. CDD/CDF concentrations (ng/kg) in bottom ash from residential wood stoves and fireplaces 4-54

Table 4-18. CDD/CDF concentrations in chimney soot (Bavaria, Germany) 4-56

Table 4-19. CDD/CDF concentrations (ng/kg) in fly ash from wood-working industry . . . 4-57

Table 4-20. CDD/CDF concentrations (ng/kg) in electrostatic precipitator waste ash from wood-fired industrial boiler 4-59

Table 4-21. Estimated CDD/CDF emission factors for oil-fired residential furnaces 4-62

Table 4-22. CDD/CDF emission factors (pg/L oil) for oil-fired utility/industrial boilers . . 4-65

Table 4-23. CDD/CDF concentrations (pg/Nm^3) in stack emissions from U.S. coal-fired power plants 4-70

Table 4-24. Characteristics of U.S. coal-fired power plants tested by the U.S. Department of Energy 4-71

Table 4-25. CDD/CDF emission factors (ng/kg coal) for coal-fired utility/industrial power plants 4-72

Table 4-26. CDD/CDF emission factors (ng/kg coal) for residential coal combustors 4-75

Table 4-27. CDD/CDF concentrations and amounts disposed of in solid wastes from coal-fired utilities 4-79

Table 5-1. CDD/CDF emission factors (ng/kg clinker produced) for cement kilns burning hazardous waste for reference years 1987 and 1995 5-8

Table 5-2. CDD/CDF emission factors (ng/hr) for cement kilns burning hazardous waste for reference year 2000 5-10

LIST OF TABLES (continued)

Table 5-3. CDD/CDF emission factors (ng/kg clinker produced) for cement kilns not burning hazardous waste for reference years 1987, 1995, and 2000 5-12

Table 5-4. National emission estimates for cement kilns for reference years 1987 and 1995 5-15

Table 5-5. National emission estimates for cement kilns for reference year 2000 5-17

Table 5-6. CDD/CDF concentrations (ng/kg) in ash samples from cement kiln electrostatic precipitator and lightweight aggregate (LWA) kiln fabric filter . . 5-20

Table 5-7. CDD/CDF estimates in cement kiln dust (CKD) for reference years 1987, 1995, and 2000 5-21

Table 5-8. Congener-specific emission factors (ng/kg asphalt produced) derived from the testing of air emissions at two hot-mix asphalt plants in the United States 5-24

Table 5-9. CDD/CDF emission factors (ng/barrel)[a] for petroleum catalytic reforming units 5-29

Table 5-10. CDD concentrations in Japanese cigarettes, smoke, and ash 5-32

Table 5-11. CDD/CDF concentrations (pg/cig) in cigarette smoke, normalized to a per-cigarette basis 5-34

Table 5-12. CDD/CDF concentrations (pg/pack) in tobacco cigarette brands from various countries 5-37

Table 5-13. CDD/CDF mean emission factors (ng/kg feed) for black liquor recovery boilers 5-44

Table 5-14. CDD/CDF TEQ emission factors and emission estimates from Kraft recovery furnaces and Kraft lime kilns 5-47

Table 5-15. CDD/CDF concentrations in candle materials and emissions 5-47

Table 6-1. CDD/CDF emission factors for a landfill flare 6-2

Table 6-2 CDD/CDF mean emission factors (ng/kg) for forest fires 6-16

Table 6-3. Forest fire fuel loading factors (tons/acre) 6-19

LIST OF TABLES (continued)

Table 6-4. CDD/CDF average air emission factors (ng/kg waste burned) from barrel burning of household waste 6-22

Table 6-5. CDD/CDF analysis for composite ash samples from barrel burning (ng/kg ash) 6-27

Table 6-6. PCB analysis for composite ash samples from barrel burning (ng/kg ash) 6-28

Table 6-7. CDDs/CDFs in dust fall and ashes from volcanoes 6-34

Table 6-8. Residue of HpCDD/HpCDF and OCDD/OCDF (ng/kg) in paper cartridges and charges of select pyrotechnic products 6-35

Table 7-1. CDD/CDF emission concentrations (pg TEQ/m^3 @ 11% oxygen) for primary copper smelters 7-2

Table 7-2. CDD/CDF emissions data from primary and secondary copper and secondary lead smelters 7-3

Table 7-3. CDD/CDF emission factors (ng/kg scrap feed) for secondary aluminum smelters for 2000 7-11

Table 7-4. CDD/CDF emission factors (ng/kg scrap feed) for secondary aluminum smelters for 1995 and 1987 7-12

Table 7-5. CDD/CDF mean emission factors (ng/kg scrap feed) for secondary copper smelters 7-17

Table 7-6. CDD/CDF emission factors (ng/kg lead produced) for secondary lead smelters 7-25

Table 7-7. Estimated annual TEQ emissions (g TEQ) 7-27

Table 7-8. CDD/CDF emission factors (ng/kg sinter) for sintering plants 7-30

Table 7-9. Operating parameters for U.S. iron ore sintering plants 7-32

Table 7-10. CDD/CDF emission estimates for Canadian coke oven facilities, blast furnace facilities, and electric arc furnaces 7-34

Table 7-11. CDD/CDF emission concentrations and rates for Canadian electric arc furnaces 7-37

LIST OF TABLES (continued)

Table 7-12. CDD/CDF emission factors for a U.S. ferrous foundry 7-39

Table 7-13. Congener-specific profile for ferrous foundries 7-40

Table 7-14. CDD/CDF emission factors for a scrap wire incinerator 7-42

Table 7-15. CDD/CDF concentrations in fly ash and ash/soil at metal recovery sites 7-44

Table 7-16. CDD/CDF emission factors for a drum and barrel reclamation facility 7-46

Table 8-1. CDD/CDF concentrations in pulp and paper mill bleached pulp, wastewater sludge, and wastewater effluent (circa 1988) 8-2

Table 8-2. CDD/CDF concentrations in pulp and paper mill bleached pulp, wastewater sludge, and wastewater effluent (mid-1990s) 8-5

Table 8-3. Summary of bleached chemical pulp and paper mill discharges (g/yr) of 2,3,7,8-TCDD and 2,3,7,8-TCDF 8-7

Table 8-4. CDD/CDF TEQ concentrations and emissions for the paper and pulp industry by source 8-10

Table 8-5. CDD/CDF concentrations (µg/kg) in graphite electrode sludge from chlorine production 8-11

Table 8-6. Releases of dioxin-like compounds in wastewater discharges from chlor-alkali and mixed chemical manufacturing facilities to surface water in reference years 2000 and 1995 8-13

Table 8-7. Congener-specific and TEQ annual releases to air (g/yr) from chlor-alkali and mixed chemical production facilities in 2000 8-14

Table 8-8. CDD/CDF concentrations (µg/kg) in metal chlorides 8-15

Table 8-9. CDD/CDF concentrations (mg/kg) in mono- through tetrachlorophenols 8-17

Table 8-10. CDD/CDF concentrations (historical and current) (µg/kg) in technical-grade pentachlorophenol (PCP) products 8-18

Table 8-11. Historical CDD/CDF concentrations (µg/kg) in pentachlorophenol-Na (PCP-Na) 8-20

LIST OF TABLES (continued)

Table 8-12. Summary of specific dioxin-containing wastes that must comply with land disposal restrictions 8-21

Table 8-13. CDD/CDF concentrations (µg/kg) in chlorobenzenes 8-25

Table 8-14. Concentrations of CDD/CDF congener groups in unused commercial polychlorinated biphenyl (PCB) mixtures (mg/kg) 8-28

Table 8-15. 2,3,7,8-Substituted congener concentrations in unused polychlorinated biphenyl (PCB) mixtures (µg/kg) 8-29

Table 8-16. Reported CDD/CDF concentrations (µg/kg) in wastes from polyvinyl chloride (PVC) manufacture 8-32

Table 8-17. Releases of dioxin-like compounds (g/yr) in wastewater discharges from EDC/VCM/PVC and integrated chlorine chemical manufacturing facilities to surface water in reference years 2000 and 1995 8-34

Table 8-18. Congener-specific releases to land from an EDC/VCM/PVC integrated chemical manufacturing facility[a] in reference years 2000 and 1995 8-37

Table 8-19. Congener-specific and TEQ releases to air (g/yr) from EDC/VCM/PVC integrated chemical manufacturing facilities in reference years 2000 and 1995 8-39

Table 8-20. Congener-specific and TEQ transfers to secure landfills (g/yr)[a] from EDC/VCM/PVC integrated chemical production facilities in 2000 8-40

Table 8-21. CDD/CDF concentrations in products from U.S. EDC/VCM/PVC manufacturers 8-42

Table 8-22. CDD/CDF concentrations (µg/kg) in samples of dioxazine dyes and pigments (Canada) 8-46

Table 8-23. CDD/CDF concentrations (ng/kg) in printing inks (Germany) 8-49

Table 8-24. Chemicals requiring Toxic Substances Control Act Section 4 testing under the dioxin/furan rule 8-51

Table 8-25. Congeners and limits of quantitation (LOQs) for which quantitation is required under the dioxin/furan test rule and pesticide Data Call-In 8-52

Table 8-26. Precursor chemicals subject to reporting requirements under Toxic Substances Control Act Section 8(a) 8-53

LIST OF TABLES (continued)

Table 8-27. Results of analytical testing for dioxins and furans in the chemicals tested to date under Section 4 of the dioxin/furan test rule 8-54

Table 8-28. CDD/CDF concentrations (µg/kg) in chloranil and carbazole violet samples analyzed pursuant to the EPA dioxin/furan test rule 8-55

Table 8-29. Status of first pesticide Data Call-In: pesticides suspected of having the potential to become contaminated with dioxins if synthesized under conditions favoring dioxin formation 8-62

Table 8-30. Status of second pesticide Data Call-In: pesticides suspected of being contaminated with dioxins 8-67

Table 8-31. Summary of analytical data submitted to EPA in response to pesticide Data Call-In(s) 8-71

Table 8-32. Summary of results for CDDs/CDFs in technical 2,4-D and 2,4-D ester herbicides 8-72

Table 8-33. CDD/CDF concentrations (µg/kg) in samples of 2,4-D and pesticide formulations containing 2,4-D 8-74

Table 8-34. Mean CDD/CDF concentrations and range of detection limits (DLs) (pg/L) in effluents from nine U.S. publicly owned treatment works (POTWs) 8-79

Table 8-35. Effluent concentrations (pg/L) of CDDs/CDFs from publicly owned treatment works in Mississippi 8-80

Table 8-36. CDD/CDF concentrations (ng/kg) measured in the 1998/1999 National Sewage Sludge Survey 8-82

Table 8-37. CDD/CDF concentrations (ng/kg) measured in 99 sludges collected from U.S. publicly owned treatment works (POTWs) during 1994 8-84

Table 8-38. Concentrations of CDDs/CDFs (ng/kg dry matter) in sewage sludge from publicly owned treatment works in Mississippi 8-85

Table 8-39. CDD/CDF median concentrations (ng/kg) measured in 1999 from a publicly owned treatment works facility in Ohio 8-86

Table 8-40. CDD/CDF mean concentrations (ng/kg) measured in the 2001 National Sewage Sludge Survey 8-87

LIST OF TABLES (continued)

Table 8-41. Quantity of sewage sludge disposed of and potential dioxin TEQ releases from primary, secondary, and advanced treatment publicly owned treatment works for reference year 1987 8-90

Table 8-42. Quantity of sewage sludge disposed of and potential dioxin TEQ releases from primary, secondary, and advanced treatment publicly owned treatment works for reference year 1995 8-91

Table 8-43. Quantity of sewage sludge disposed of and potential dioxin TEQ releases from primary, secondary, and advanced treatment publicly owned treatment works for reference year 2000 8-92

Table 8-44. Biosolids disposal practices for reference year 2000 8-92

Table 8-45. CDD/CDF concentrations in Swedish liquid soap, tall oil, and tall resin 8-95

Table 9-1. Estimated quantity of animal manure produced in the United States in 2000 . . . 9-7

Table 9-2. CDD and CDF concentrations (ng/kg dry weight) in samples of animal manure in the United Kingdom 9-8

Table 9-3. Concentrations of CDDs (pg/g, dry weight) in eight ball clay samples in the United States 9-16

Table 9-4. Comparison of the mean CDD/CDF congener group concentrations in ball clay with those in urban and rural soils in North America (pg/g, dry weight) 9-17

Table 10-1. Confidence rating classes for 2000 for releases from all known and suspected source categories of dioxin-like PCBs 10-2

Table 10-2. Inventory of contemporary releases of dioxin-like PCBs in the United States for 1987, 1995, and 2000 and preliminary release estimates of dioxin-like PCBs for 2000 (g TEQ_p-WHO_{98}/yr) 10-3

Table 10-3. Weight percent concentrations of dioxin-like PCBs in Aroclors, Clophens, and Kanechlors 10-7

Table 10-4. Disposal requirements for PCBs and PCB items 10-12

Table 10-5. Off-site transfers of PCBs reported in the Toxics Release Inventory (TRI) (1988–2000) 10-16

LIST OF TABLES (continued)

Table 10-6. Releases of PCBs reported in the Toxics Release Inventory (TRI) (1988–2000) 10-17

Table 10-7. Aroclor concentrations (ng/kg) measured in EPA's National Sewage Sludge Survey 10-20

Table 10-8. Dioxin-like PCB concentrations measured in sludges collected from 74 U.S. publicly owned treatment works (POTWs) during 1994 10-21

Table 10-9. Dioxin-like PCB concentrations in sewage sludge collected from U.S. publicly owned treatment works during 1999 10-22

Table 10-10. Quantity of sewage sludge disposed of annually in 1989 by primary, secondary, or advanced treatment publicly owned treatment works (POTWs) and potential dioxin-like PCB TEQ releases 10-23

Table 10-11. Quantity of sewage sludge disposed of annually in 1995 by primary, secondary, or advanced treatment publicly owned treatment works (POTWs) and potential dioxin-like PCB TEQ releases 10-24

Table 10-12. Quantity of sewage sludge disposed of annually in 2000 by primary, secondary, or advanced treatment publicly owned treatment works (POTWs) and potential dioxin-like PCB TEQ releases 10-25

Table 10-13. PCB congener group emission factors for industrial wood combustors[a] 10-28

Table 10-14. PCB congener group emission factors for medical waste incinerators (MWIs) 10-29

Table 10-15. PCB congener group emission factors for a tire combustor[a] 10-30

Table 10-16. Dioxin-like PCB concentrations in cigarette tobacco in brands from various countries (pg/pack) 10-32

Table 10-17. Dioxin-like PCB concentrations in stack gas collected from a U.S. sewage sludge incinerator 10-33

Table 10-18. Dioxin-like PCB emission factors from backyard barrel burning 10-35

Table 10-19. PCB congener group emission factors for a petroleum catalytic reforming unit 10-35

LIST OF TABLES (continued)

Table 10-20. Estimated tropospheric half-lives of dioxin-like PCBs with respect to gas-phase reaction with the OH radical 10-40

Table 10-21. Estimated PCB loads in the global environment as of 1985 10-42

Table 10-22. Estimated domestic sales of aroclors and releases of PCBs, 1957–1974 (metric tons) 10-43

Table 10-23. Estimated U.S. usage of PCBs by use category, 1930–1975 10-44

Table 10-24. Estimated direct releases of Aroclors to the U.S. environment, 1930–1974[a] (metric tons) 10-45

Table 10-25. Estimated releases of dioxin-like PCB TEQs to the U.S. environment, 1930–1977 10-46

Table 11-1. Historical production, sales, and usage of 2,4-dichlorophenoxy-acetic acid (2,4-D) (metric tons) 11-4

Table 11-2. Historical production, sales, and usage of 2,4,5-trichlorophen-oxyacetic acid (2,4,5-T) (metric tons) 11-7

Table 11-3. CDD/CDF concentrations (μg/kg) in recent sample of 2,4,5-trichloro-phenoxyacetic acid (2,4,5-T) 11-10

Table 11-4. PCB 138 fluxes predicted by Harner et al. (1995) 11-16

Table 11-5. Summary of flux calculations for total PCBs in Green Bay 11-19

Table 11-6. Comparison of model-estimated PCB concentrations with observed values 11-22

LIST OF FIGURES

Figure 1-1. Chemical structure of 2,3,7,8-TCDD and related compounds 1-7

Figure 1-2. Estimated CDD/CDF I-TEQ emissions to air from combustion sources in the United States for reference year 1987 1-24

Figure 1-3. Estimated CDD/CDF I-TEQ emissions to air from combustion sources in the United States for reference year 1995 1-25

Figure 1-4. Estimated CDD/CDF I-TEQ emissions to air from combustion sources in the United States for reference year 2000. 1-26

Figure 1-5. Comparison of estimates of annual I-TEQ emissions to air (g I-TEQ/yr) for reference years 1987, 1995, and 2000. 1-27

Figure 1-6. Estimated CDD/CDF WHO-TEQ emissions to air from combustion sources in the United States for reference year 1987 1-28

Figure 1-7. Estimated CDD/CDF WHO-TEQ emissions to air from combustion sources in the United States for reference year 1995. 1-29

Figure 1-8. Estimated CDD/CDF WHO-TEQ emissions to air from combustion sources in the United States for reference year 2000. 1-30

Figure 1-9. Comparison of estimates of annual WHO-TEQ emissions to air (g WHO-TEQ/yr) for reference years 1987, 1995, and 2000. 1-31

Figure 1-10. Congener profiles (as percent distributions to the sum of CDDs and CDFs) of anthropogenic sources of chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans in the United States 1-45

Figure 2-1. Typical mean distribution of CDD and CDF congeners in contemporary municipal solid waste 2-3

Figure 2-2. The *de novo* synthesis of CDDs/CDFs from heating carbon particulate at 300°C at varying retention times 2-15

Figure 2-3. Temperature effects on CDD/CDF formation 2-16

Figure 3-1. Typical mass burn waterwall municipal solid waste combustor 3-3

Figure 3-2. Typical mass burn rotary kiln combustor 3-4

Figure 3-3. Typical modular starved-air combustor with transfer rams 3-5

LIST OF FIGURES (continued)

Figure 3-4. Typical modular excess-air combustor 3-6

Figure 3-5. Typical dedicated refuse-derived fuel-fired spreader stoker boiler 3-7

Figure 3-6. Fluidized-bed refuse-derived fuel furnace 3-8

Figure 3-7. Municipal waste combustor design classes for 1987 3-11

Figure 3-8. Municipal waste combustor design classes for 1995 3-12

Figure 3-9. Municipal waste combustor design classes for 2000 3-13

Figure 3-10. Congener and congener group profiles for air emissions from a mass burn waterwall municipal waste combustor equipped with a dry scrubber and fabric filter 3-32

Figure 3-11. 2,3,7,8-TCDD frequency distribution (negative natural log concentration) . . . 3-33

Figure 3-12. 1,2,3,7,8-PeCDD frequency distribution (negative natural log concentration) . 3-34

Figure 3-13. Congener profile for air emissions from 17 hazardous waste incinerators tested from 1993 through 1996. 3-50

Figure 3-14. Congener and congener group profiles for air emissions from boilers and industrial furnaces burning hazardous waste 3-52

Figure 3-15. Congener and congener group profiles for air emissions from medical waste incinerators without air pollution control devices (nondetects set equal to zero) 3-66

Figure 3-16. Congener and congener group profiles for air emissions from medical waste incinerators equipped with a wet scrubber and fabric filter 3-67

Figure 3-17. Congener and congener group profiles for air emissions from the Camellia Memorial Lawn crematorium and Woodlawn Cemetery crematorium 3-75

Figure 3-18. Congener profile for air emissions from the University of Georgia animal crematorium 3-78

Figure 3-19. Congener and congener group profiles for air emissions from sewage sludge incinerators 3-81

LIST OF FIGURES (continued)

Figure 3-20. Congener and congener group profiles for air emissions from a tire combustor 3-85

Figure 4-1. Congener and congener group profiles for air emissions from diesel-fueled vehicles 4-15

Figure 4-2. Congener and congener group profiles for air emissions from leaded gas-fueled vehicles 4-16

Figure 4-3. Congener and congener group profiles for air emissions from unleaded gas-fueled vehicles 4-17

Figure 4-4. Tunnel air concentrations 4-29

Figure 4-5a. Congener and congener group profiles for air emissions from industrial wood combustors 4-46

Figure 4-5b. Congener and congener group profiles for air emissions from bleached Kraft mill bark combustors 4-47

Figure 4-6. Congener group profile for air emissions from residential oil-fueled furnaces 4-63

Figure 4-7. Congener and congener group profiles for air emissions from industrial oil-fueled boilers 4-66

Figure 4-8. Congener and congener group profiles for air emissions from industrial/utility coal-fueled combustors (nondetects set equal to zero) 4-73

Figure 4-9. Congener group profile for air emissions from residential coal-fueled combustors 4-77

Figure 5-1. Congener profile for air emissions from cement kilns burning hazardous waste for reference years 1987 and 1995 (nondetect set equal to zero) 5-9

Figure 5-2. Congener profile for air emissions from cement kilns burning hazardous waste for reference year 2000. 5-11

Figure 5-3. Congener profile for air emissions from cement kilns burning nonhazardous waste for reference years 1987, 1995, and 2000. 5-13

Figure 5-4. Congener and congener group profiles for air emissions from petroleum catalytic reforming units 5-30

LIST OF FIGURES (continued)

Figure 5-5. CDD profiles for Japanese cigarettes, smoke, and ash 5-33

Figure 5-6. Congener group profiles for mainstream and sidestream cigarette smoke 5-35

Figure 5-8 Congener and congener group profiles for air emissions from Kraft black liquor recovery boilers (nondetect set equal to zero) 5-45

Figure 5-7. Congener group profiles for cigarette tobacco from various countries 5-38

Figure 6-1. Congener profile for landfill flare air emissions 6-3

Figure 6-2. Congener profile for forest fire simulation approach emissions 6-17

Figure 7-1. Congener and congener group profiles for air emissions from secondary aluminum smelters 7-13

Figure 7-2a. Congener group profile for air emissions from a secondary copper smelter . . . 7-18

Figure 7-2b. Congener and congener group profiles for a closed secondary copper smelter 7-19

Figure 7-3. Congener and congener group profiles for air emissions from secondary lead smelters 7-26

Figure 7-4. Congener profiles for air emissions from U.S. iron ore sintering plants 7-31

Figure 7-5. Congener group profile for air emissions from a scrap wire incinerator 7-43

Figure 7-6. Congener group profile for air emissions from a drum incinerator 7-47

Figure 8-1. 104 Mill Study full congener analysis results for pulp (nondetects equal to zero) 8-3

Figure 8-2. 104 Mill Study full congener analysis results for sludge 8-3

Figure 8-3. 104 Mill Study full congener analysis results for effluent 8-4

Figure 8-4. Congener profile for technical-grade PCP (developed from data in last column in Table 8-10) 8-57

Figure 8-5. Congener profile for 2,4-D (salts and esters) (based on mean concentrations reported in Table 8-34) 8-73

LIST OF FIGURES (continued)

Figure 8-6. Congener profiles for sewage sludge (created from data in Table 8-38) 8-88

Figure 11-1. Fluxes among environmental reservoirs 11-2

LIST OF ABBREVIATIONS AND ACRONYMS

AHA	American Hospital Association
AMSA	Association of Metropolitan Sewerage Agencies
APCD	Air pollution control device
BDDs	polybrominated dibenzo-*p*-dioxins
BDFs	polybrominated dibenzofurans
Btu	British thermal unit
$CaCl_2$	calcium chloride
CARB	California Air Resources Board
CBI	Confidential Business Information
CDD	polychlorinated dibenzo-*p*-dioxin
CDF	polychlorinated dibenzofuran
CFR	Code of Federal Regulations
CSF	Confidential Statement of Formula
CKD	cement kiln dust
CO	carbon monoxide
CO_2	carbon dioxide
CuCl	copper (I) chloride
$CuCl_2$	copper (II) chloride
DBF	dibenzofuran
DCBz	dichlorobenzene
DCI	data call-in
DCP	dichlorophenol
DL	detection limit
dscm	dry standard cubic meter
DSI	dry sorbent injection
EDC	ethylene dichloride
EIA	Energy Information Administration
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	electrostatic precipitator
FF	fabric filter
FCEM	field chemical emissions measurement
$FeCl_3$	ferric (iron) chloride

LIST OF ABBREVIATIONS AND ACRONYMS (continued)

FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
GAC	granular activated carbon
GC/ECD	gas chromatography/electron capture detector
GC/MS	gas chromatography/mass spectrometry
HCl	hydrogen chloride
HCBz	hexachlorobenzene
HDD	halogenated dibenzo-*p*-dioxin
HDF	halogenated dibenzofuran
HWI	hazardous waste incinerator
HxCB	hexachlorobiphenyl
IUPAC	International Union of Pure and Applied Chemistry
KCl	potassium chloride
LOQ	limit of quantitation
MB-WW	mass burn waterwall
MCBz	monochlorobenzene
$MgCl_2$	magnesium chloride
MgO	magnesium oxide
MSW	municipal solid waste
MWI	medical waste incinerator
NaCl	sodium chloride
NaOCl	soldium hypochlorite
NCASI	National Council of the Paper Industry for Air and Stream Improvement
$NiCl_2$	nickel chloride
NiO	nickel oxide
Nm^3	standard cubic meter
NMOC	nonmethane organic compound
OAQPS	Office of Air Quality Planning and Standards
O_2	molecular oxygen
OH	hydroxide ion
OPP	Office of Pesticide Programs
ORD	Office of Research and Development
OSW	Office of Solid Waste
Pb	lead

LIST OF ABBREVIATIONS AND ACRONYMS (continued)

PCA	Portland Cement Association
PCB	polychlorinated biphenyl
PCP	pentachlorophenol
PCP-Na	pentachlorophenate
PeCB	pentachlorobiphenyl
PeCBz	pentachlorobenzene
PM	particulate matter
POTW	publicly owned treatment works
ppb	parts per billion
ppm	parts per million
ppmv	parts per million (volume basis)
ppt	parts per trillion
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
RCRA	Resource Conservation and Recovery Act
RDF	refuse-derived fuel
SIC	Standard Industrial Classification
SIP	State Implementation Plan
SNUR	Significant New Use Rule
SO_2	sulfur dioxide
TCBz	trichlorobenzene
TCDD	2,3,7,8-tetrachlorobidenzo-*p*-dioxin
TCDF	2,3,.7,8-tetrachlorobidenzofuran
TeCB	tetrachlorobiphenyl
TeCP	tetrachlorophenol
TEF	toxicity equivalency factor
TEQ	toxicity equivalence
TEQ/yr	toxicity equivalents per year
$TiCl_4$	titanium tetrachloride
TrCB	trichlorobiphenyl
TrCP	trichlorophenol
TRI	Toxics Release Inventory
TSCA	Toxic Substances Control Act

LIST OF ABBREVIATIONS AND ACRONYMS (continued)

2,4-D	2,4-dichlorophenoxyacetic acid
2,4-DB	4-(2,4-dichlorophenoxy) butyric acid
2,4-DCP	2,4-dichlorophenol
2,4-DP	2-(2,4-dichlorophenoxy) propionic acid
2,4,5-T	2,4,5-trichlorophenoxy (phenoxy herbicides)
U.K.	United Kingdom
USDA	U.S. Department of Agriculture
VCM	vinyl chloride monomer
WHO	World Health Organization
WS	wet scrubber

FOREWORD

The purpose of this document is to present an inventory of sources and environmental releases of dioxin-like compounds in the United States. This inventory is associated with three distinct reference years: 1987, 1995, and 2000. The presentation of information in this manner permits the ranking of sources by magnitude of annual release and allows for the evaluation of environmental trends over time.

The term "dioxin-like" includes congeners of polychlorinated dibenzo-*p*-dioxins (CDDs), polychlorinated dibenzofurans (CDFs) having chlorine atoms in the 2,3,7,8 positions on the molecule, and certain coplanar-substituted polychlorinated biphenyls (PCBs). Dioxin-like refers to the fact that these compounds have similar chemical structure and physical-chemical properties and invoke a common toxic response. Because of their hydrophobic nature and resistance towards metabolism, these chemicals persist and bioaccumulate in fatty tissues of animals and humans. Consequently, the principal route of chronic population exposure is through the dietary consumption of animal fats, fish, shellfish, and dairy products. Dioxin-like compounds are persistent in soils and sediments, with environmental half-lives ranging from years to several decades. Understanding the sources and environmental releases of dioxin-like compounds is fundamental to ultimately linking sources with population exposures. It is through such understanding that actions can be taken to reduce human exposures.

The quantitative results of the inventory are expressed in terms of the toxicity equivalence (TEQ) of the mixture of polychlorinated dibenzo-*p*-dioxin (CDD) and polychlorinated dibenzofuran (CDF) compounds present in environmental releases using a procedure sanctioned by the World Health Organization (WHO) in 1998. This TEQ procedure translates the complex mixture of CDDs and CDFs characteristic of environmental releases into an equivalent toxicity concentration of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), the most toxic member of this class of compounds. With this procedure, the quantity of the mixture of CDDs and CDFs present as a release is given the notation grams (g) TEQ_{DF}-WHO_{98}.

This inventory of sources and environmental releases of dioxin-like compounds concludes that, between 1987 and 2000, there was approximately 90% reduction in the release of dioxin-like compounds to the circulating environment of the United States from all known sources combined. Annual emission estimates (TEQ_{DF}-WHO_{98}) of releases of CDDs/CDFs to air, water, and land from reasonably quantifiable sources are approximately 1,422 g in reference year 2000; 3,444 g in reference year 1995; and 13,965 g in reference year 1987. In 1987 and 1995, the leading sources of dioxin emissions to the U.S. environment were municipal waste combustors. The inventory also identifies bleached chlorine pulp and paper mills as a significant source of dioxin to the aquatic environment in 1987 but a minor source in 1995 and 2000. The inventory concludes that

the major source of dioxin in 2000 was the uncontrolled burning of refuse in backyard burn barrels in rural areas of the United States.

The reduction in environmental releases of dioxin-like compounds from 1987 to 2000 is attributable to source-specific regulations, improvements in source technology, advancements in the pollution control technologies specific to controlling dioxin discharges and releases, and the voluntary actions of U.S. industries to reduce or prevent dioxin releases.

Peter W. Preuss, Ph.D.
Director
National Center for Environmental Assessment
Office of Research and Development

PREFACE

This document, *An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States for the Years 1987, 1995, and 2000*, was prepared by the National Center for Environmental Assessment, which is the health risk assessment program in the Office of Research and Development. The document presents estimates of annual releases of dioxin-like compounds specific for each year. It is a detailed compilation and description of all known U.S. sources and their associated activities that cause these compounds to be released into the open and circulating environment, i.e., to air, water, and land. The overall purpose of this report is to document and describe sources in the United States that release dioxin-like compounds into the open environment, quantify annual releases to the environment from known sources in a scientific and transparent manner, and provide a reliable basis for observing trends in environmental releases. To the extent practical, the inventory is a comprehensive analysis of dioxin sources.

This final document reflects a consideration of all comments received on an External Review Draft dated March 2005 (EPA600/P-03/002A) provided by an expert panel at a peer-review workshop held September 13–15, 2005, and comments received during a 60-day public review and comment period (May 6–July 5, 2005).

Over 800 references were reviewed and cited in the preparation of this document. The citations generally reflect publications up to and including the year 2003.

AUTHORS, CONTRIBUTORS, AND REVIEWERS

The National Center for Environmental Assessment (NCEA) was responsible for preparing this document. Major portions of this report were prepared by Versar, Inc. under EPA Contract No. 68-W-99-041. David Cleverly of NCEA served as the EPA Work Assignment Manager, providing overall direction and coordination of the project, as well as author of several chapters.

Authors

David Cleverly
National Center for Environmental Assessment
Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC

Greg Schweer
Office of Pollution Prevention and Toxics
U.S. Environmental Protection Agency
Washington, DC

Ronald Lee
Versar, Inc.
Springfield, VA

Kelly McAloon
Versar, Inc.
Springfield, VA

Charles Peck
Versar, Inc.
Springfield, VA

Marit Espevik Randall
Versar, Inc.
Springfield, VA

Karie Traub Riley
Versar, Inc.
Springfield, VA

Contributors

Frank Behan, Office of Solid Waste, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC

Laurel Driver, Office of Air Quality Planning and Standards, Office of Air and Radiation, U.S. Environmental Protection Agency, Research Triangle Park, NC

Marietta Echeverria, National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Washington, DC

Joseph Ferrario, Environmental Chemistry Laboratory, Office of Pesticide Programs, Office of Prevention, Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Stennis Space Center, MS

Roy Huntley, Office of Air Quality Planning and Standards, Office of Air and Radiation, U.S. Environmental Protection Agency, Research Triangle Park, NC

John Schaum, National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Washington, DC

Walt Stevenson, Office of Air Quality Planning and Standards, Office of Air and Radiation, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dwain Winters, Office of Pollution Prevention and Toxics, Office of Prevention, Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Washington, DC

Reviewers

Internal EPA Review: Internal EPA review occurred from May 2 through June 5, 2003. The key reviewers included the following individuals and offices:

Elmer Akin, EPA Region 4, Atlanta, GA

Don Anderson, Office of Science and Technology, Office of Water, Washington, DC

John D Bachmann, Office of Air Quality Planning and Standards, Research Triangle Park, NC

Angela L. Bandemehr, Office of International Affairs, Washington, DC

Frank Behan, Office of Solid Waste, Washington, DC

AUTHORS, CONTRIBUTORS, AND REVIEWERS (continued)

Tom Braverman, Office of Air Quality Planning and Standards, Research Triangle Park, NC

Laurel Driver, Office of Air Quality Planning and Standards, Research Triangle Park, NC

Dale Evarts, Office of Air Quality Planning and Standards, Research Triangle Park, NC

Brian Gullett, National Risk Management Laboratory, Research Triangle Park, NC

Bob Holloway, Office of Solid Waste, Washington, DC

Roy Huntley, Office of Air Quality Planning and Standards, Research Triangle Park, NC

Phil Lorang, Office of Air Quality Planning and Standards, Research Triangle Park, NC

Ed Ohanian, Office of Water, Washington, DC

Debbie Sisco, Office of Pesticide Programs, Washington, DC

Alan Rubin, Office of Water, Washington, DC

John Schaum, National Center for Environmental Assessment, Washington, DC

Laurie Schuda, National Center for Environmental Assessment, Washington, DC

Joe Somers, Office of Transportation and Air Quality, Ann Arbor, MI

Walt Stevenson, Office of Air Quality Planning and Standards, Research Triangle Park, NC

Dwain Winters, Office of Pollution Prevention and Toxics, Washington, DC

Donn Viviani, Office of Policy, Economics, and Innovation, Washington, DC

External Peer Review: This document has undergone two external peer reviews: the first External Review Draft (EPA/600/P-98/002Aa) published in April 1998 was reviewed by an expert panel at a public meeting held in Alexandria, Virginia, on June 3–4, 1998. The most recent External Review Draft (EPA600/P-03/002A) published in March 2005 was released for public review and comment on May 6, 2005, and was subsequently reviewed at a public meeting held in Arlington, Virginia, on September 13–15, 2005.

1. Peer review meeting September 13-15, 2005

Panel Chair
Heidelore Fiedler, Ph.D., Scientific Affairs Officer, United Nations Environment Programme Chemicals, Chatelaine, Switzerland

Panel Members
Judith A. Abbott, Ph.D., Research Scientist, Bureau of Toxic Substance Assessment, New York State Department of Health, Albany, NY

Gary A. Amendola, Ph.D., President, Amendola Engineering, Westlake, OH

Patrick Dyke, President, PD Consulting, Oxford, United Kingdom

Christopher C. Lutes, Ph.D., Principal Scientist/Associate Vice President, ARCADIS G&M, Inc., Durham, NC

Jozef M. Pacyna, Ph.D., Center for Ecological Economics, Norwegian Institute for Air Research, Kjeller, Norway

2. Peer review meeting June 3–4, 1998

Panel Chair
Valerie Thomas, Ph.D., Research Scientist, Center for Energy and Environmental Studies, Princeton University

Panel Members
Patrick Dyke, President, PD Consulting, Oxford, United Kingdom

Raouf Morcos, Manager, National Office of Pollution Prevention, Environment Canada Quebec, Canada

William Randall Seeker, Ph.D., Senior Vice President, Energy and Environmental Research, Irvine, CA

Chun Yi Wu, Senior Engineer, Air Quality Division, Minnesota Pollution Control Agency, St. Paul, MN

ACKNOWLEDGMENT

The authors would like to acknowledge the contributions of the following individuals: Terri Konoza of NCEA who managed the document production activities and provided editing, proofreading, and word processing support; Patricia von Brook of KBM Group who provided editing support; and Christine Chang of KBM Group who provided word processing support.

EXECUTIVE SUMMARY

This report, *An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States for the Years 1987, 1995, and 2000,* presents estimates of annual releases of dioxin-like compounds specific to each year. It is a detailed compilation and description of all known U.S. sources and their associated activities that cause these compounds to be released into the open and circulating environment, i.e., to air, water, and land. The overall purpose of this report is to document and describe sources in the United States that release dioxin-like compounds into the open environment, quantify annual releases to the environment from known sources in a scientific and transparent manner, and provide a reliable basis for observing trends in environmental releases. To the extent practical, the inventory is a comprehensive analysis of dioxin sources.

The term "dioxin-like" refers to chemical compounds that mimic the chemical and physical properties of dioxin and have similar toxic effects. These include compounds of chlorinated dibenzo-*p*-dioxins (CDDs), chlorinated dibenzofurans (CDFs), and certain coplanar polychlorinated biphenyls (PCBs). The dioxin-like CDDs and CDFs have chlorine atoms in the 2,3,7,8 positions on the molecule. Dioxin-like PCBs contain zero or one chlorine atom in the 2,2',6 or 6' positions. All together there are 7 CDDs, 10 CDFs, and 12 PCBs that are considered to be dioxin like. It should be emphasized that releases of dioxin-like compounds presented in this inventory are, for the most part, for dioxin-like CDDs and CDFs. Sources of dioxin-like PCBs are generally poorly characterized.

Approach

Only sources judged to have a reasonable likelihood for releases of dioxin-like compounds to the air, water, and land of the United States are addressed in this report. The release estimates were derived in one of two ways: (1) dioxin was measured as an actual release from the source (i.e., points of release from the source were sampled and evaluated), or (2) dioxin releases were calculated on the basis of an emission factor and activity level. The emission factor is the amount of dioxin anticipated to be emitted per unit of activity and is derived from measurements made at sources having similar characteristics. The activity level is the amount of material processed, produced, or consumed by the source in the course of a year or, in the case of mobile sources, the number of kilometers driven. It can take several forms, such as kilograms of material processed per year by an industrial facility, vehicle kilometers traveled per year by trucks and automobiles, and liters of wastewater discharged into surface water from industrial sources. The activity level is multiplied by the emission factor to arrive at an estimate of annual dioxin releases from those sources lacking direct measurement of dioxin emissions.

Confidence in the accuracy of both the emission factor and the activity level are rated as low, medium, or high, based on the quality of the data. All the release estimates from sources in the inventory are assigned an overall confidence rating based on the lowest rating assigned to either the emission factor or the activity level. In some cases, the data were not adequate to support even a low confidence rating. These cases were treated in one of two ways. If the data were sufficient to make an approximate, but clearly nonrepresentative, estimate of releases, the estimates were labeled as preliminary and were not included in the national inventory. If limited data suggested that dioxin releases were possible from a source but were not adequate to support even rudimentary calculations of emissions, the source was labeled as unquantifiable. This approach resulted in the classification scheme shown below.

Category A	High Confidence	Included in the national quantitative inventory
Category B	Medium Confidence	
Category C	Low Confidence	
Category D	Preliminary	Not included in the national quantitative inventory
Category E	Unquantifiable	

Throughout this document, environmental release estimates are presented in terms of toxicity equivalence (TEQs). TEQs are derived from a toxicity weighting system that converts all mixture components to a single value normalized to the toxicity of 2,3,7,8-TCDD. This is done for convenience in presenting summary information and to facilitate comparisons across sources. For many situations, however, it is important to use the individual CDD/CDF and PCB congener values rather than TEQs. CDD and CDF congener-specific releases for most sources are given in tables in each chapter. The summary amounts of dioxin-like compounds released to the environment are reported in units of grams (g) TEQ, developed by the World Health Organization (WHO), and are given the abbreviated notation of TEQ_{DF}-WHO_{98} throughout the document.

The major findings of the inventory of sources and environmental releases of dioxin-like compounds in the United States are:

1. In 1987, 1995, and 2000, approximately 13,965; 3,444; and 1,422 g TEQ, respectively, were released into the U.S. environment from all sources. Figure ES-1 graphically displays these releases.

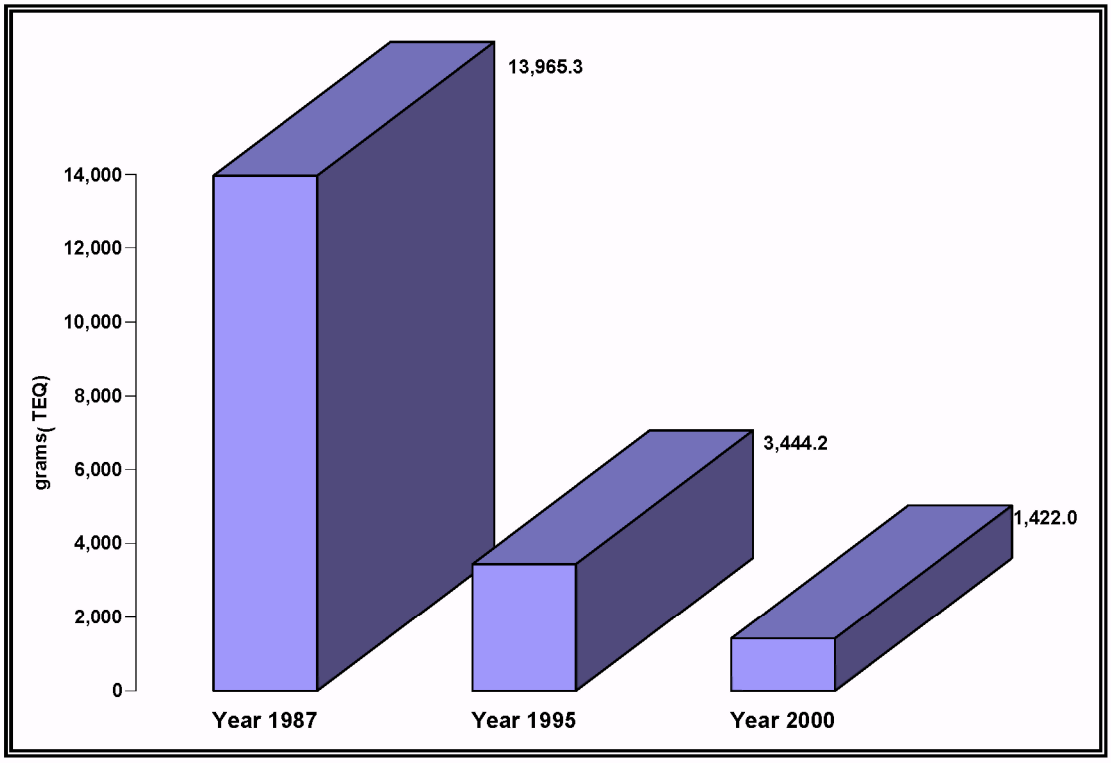


Figure ES-1. Total environmental releases of dioxin-like compounds (g TEQ) from all quantifiable sources during 1987, 1995, and 2000.

2. Environmental releases of dioxin-like compounds decreased by approximately 90% between 1987 and 2000. As shown in Figure ES-1, most of the reductions (75%) occurred between 1987 and 1995. The overall reduction in releases of dioxin-like compounds is attributed to the control of air emissions of these compounds from municipal waste combustors (MWCs), medical waste incinerators, and cement kilns burning hazardous waste and of wastewater discharges of the compounds into surface waters from pulp and paper mills using chlorine. These reductions were achieved through a combination of regulatory activities, improved emission controls, voluntary actions on the part of industry, and the closing of a number of facilities. Table ES-1 shows the reductions made by the largest sources of dioxin-like compound releases. Emission estimates for individual sources that could be quantified, i.e., Categories A, B, and C, are presented in the main text of this report.

3. The leading source of dioxin-like compounds in 2000 was the backyard burning of refuse in barrels (498.5 g TEQ, or 35% of total releases), as shown in Table ES-2, which presents the top 10 sources of releases for 2000, 1995, and 1987. Backyard barrel burning of refuse is an activity that occurs in rural areas of the United States. It is unregulated on a national level, but many states have banned or limited the practice (New Jersey, New York, California, Minnesota, Wisconsin, Massachusetts, and

Table ES-1. Reductions of releases of dioxin-like compounds to the environment in reference years 2000 and 1987 from major sources in the United States

Source category	Releases to:	2000 (g TEQ)	1987 (g TEQ)	Percent reduction
Municipal waste combustion	Air	83.8	8,905.1	>99
Medical waste incineration	Air	378.0	2,570.0	85
Cement kilns burning hazardous waste	Air	18.8	117.8	84
Bleached chemical wood pulp and paper mills	Surface water	1.0	356.0	>99

Florida to name a few). In 1995 and 1987 MWCs were the leading source of releases (1,393.5 g, or 40% of total releases in 1995; 8,905.1 g, or 64% of releases in 1987). However, due to strict regulatory requirements limiting dioxin emissions, MWCs were ranked fourth among the top 10 sources in 2000, with emissions of only 83.8 g, or 6% of total releases. Automobiles burning leaded gasoline were ranked as the eighth leading source of dioxin in 1987. The phase out of lead in gasoline eliminated this source by 2000. Cement kilns burning hazardous waste dropped out of the top 10 sources in 2000, due primarily to voluntary actions of industry combined with national regulatory requirements to reduce dioxin emissions.

4. Environmental releases of dioxin-like compounds in the United States occur from a wide variety of sources but are dominated by releases to the air from combustion sources. Figure ES-2 presents the breakdown of releases to air, water, and land for each reference year.

5. There are potential sources of dioxin-like compounds that were not included in the inventory. Significant amounts of the dioxin-like compounds produced annually in the United States are not considered releases to the open and circulating environment and, therefore, are not included in the national inventory. Examples include dioxin-like compounds generated internal to a process but destroyed before release and waste streams that are disposed of in approved and secure landfills. There are also potential sources for which no information exists to permit any reliable estimates of

Table ES-2. Top 10 sources of dioxin-like compound releases and amounts released (g TEQ) for reference years 2000, 1995, and 1987

Rank	2000 (1,422 g total)		1995 (3,444 g total)		1987 (13,965 g total)	
1	Backyard barrel burning of refuse (air)	498.5	Municipal waste combustion (incineration of refuse) (air)	1,393.5	Municipal waste combustion (incineration of refuse) (air)	8,905.1
2	Medical waste/ pathological incineration (air)	378.0	Backyard barrel burning of refuse (air)	628.0	Medical waste/pathological incineration (air)	2,570.0
3	Municipal wastewater treatment sludge (applied to land and incinerated) (land and air)	89.7	Medical waste/pathological incineration (air)	487.0	Secondary copper smelting (air)	983.0
4	Municipal waste combustion (incineration of refuse) (air)	83.8	Secondary copper smelting (air)	271.0	Backyard barrel burning of refuse (air)	604.0
5	Coal-fired utility boilers (electric generating plants) (air)	69.5	Cement kilns (hazardous waste burning) (air)	156.1	Bleached chemical wood pulp and paper mills (land, water)	370.1
6	Diesel heavy-duty trucks (air)	65.4	Municipal wastewater treatment sludge (applied to land and incinerated) (land and air)	133.3	Cement kilns (hazardous waste burning) (air)	117.8
7	Industrial wood combustion (air)	41.5	Coal-fired utility boilers (electric generating plants) (air)	60.1	Municipal wastewater treatment sludge (applied to land and incinerated) (land and air)	85.0
8	Diesel off-road equipment (includes ships, farm equipment, trains) (air)	33.1	Ethylene dichloride/vinyl chloride production (land, air, water)	35.7	Coal-fired utility boilers (electric generating plants) (air)	50.9
9	Ethylene dichloride/vinyl chloride production (land, air, water)	30.0	Diesel heavy-duty trucks (air)	33.3	Automobiles using leaded gasoline (air)	37.5
10	Sintering plants (air)	27.6	Bleached chemical wood pulp and paper mills (land and water)	30.0	2,4-Dichlorophenoxy acetic acid (2,4-D) (land)	33.4

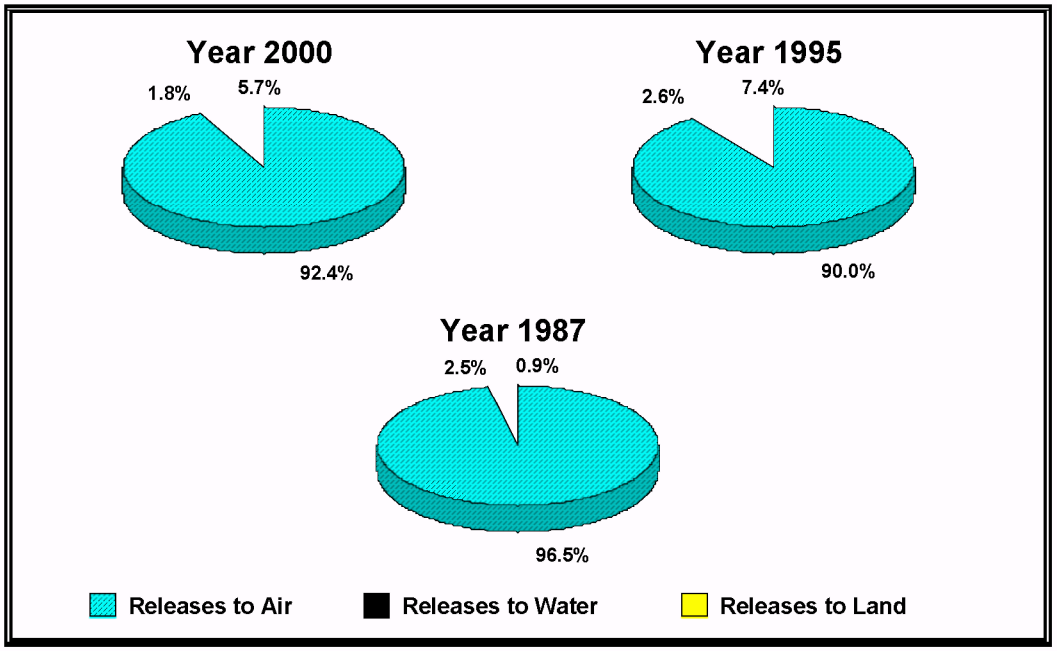


Figure ES-2. Releases of dioxin-like compounds to air, water, and land in 2000, 1995, and 1987.

environmental releases; therefore, these potential sources could not be included in the inventory. EPA has classified these potential sources as Category D sources. Examples include forest and grassland fires and accidental fires at municipal solid waste landfills. Taken together, these sources have the potential to significantly increase the emission estimates in the present inventory.

6. The amount of dioxin-like PCBs released from man-made sources remains poorly characterized. Only a total of 19.5, 78.5, and 51.5 g of PCB TEQ could be quantified for 2000, 1995, and 1987, respectively. To date, only sewage sludge has been adequately characterized as a source of dioxin-like PCB releases.

1. BACKGROUND, APPROACH, AND CONCLUSIONS

1.1. BACKGROUND

This report presents a comprehensive inventory of sources of releases of dioxin-like compounds in the United States for the years 1987, 1995, and 2000. It is a detailed review and description of all known sources and their associated activities that cause these compounds to be released into the "open and circulating environment," i.e., air, water, and land.

The aim of this report is to:

- Document and describe sources that release dioxin-like compounds into the circulating environment of the United States.
- Quantify annual releases to the environment of the United States from known sources in a scientific and transparent manner.
- Provide a reliable basis for time-trends analyses such as observing changes in total releases to the circulating environment from 1987 to 2000. Time-trend analyses provide a quantitative indication of the achievements made (or lack thereof) in reducing environmental releases of dioxin-like compounds from specific sources in the United States.

This is the second dioxin source inventory issued by the U.S. Environmental Protection Agency (EPA, or the Agency). The first one was issued in draft form and covered the years 1987 and 1995 (U.S. EPA, 1998a). The current effort updates this earlier document and adds annual release estimates for 2000.

The intended audience and users of the dioxin inventory include:

- Members of the general public who are interested in learning more about sources of emissions of dioxin-like compounds to the U.S. environment and in obtaining peer-reviewed estimates of releases.
- State and local regulatory agencies that are interested in obtaining reliable and peer-reviewed information on sources and environmental releases of dioxin-like compounds.
- EPA Regional and Program Offices that are responsible for evaluating the need for regulating and/or preventing dioxin releases to the environment.
- Risk assessors in the private and public sectors who need reliable information on sources and releases of dioxin-like compounds to improve quantitative risk assessments of dioxin sources.

- Researchers who are interested in documented and time-specific dioxin source and emissions data to be used in sequential time-trends analyses.

- Private and public stakeholder groups that are interested in obtaining reliable and peer-reviewed information on dioxin sources and releases and in observing time trends in environmental releases of dioxin-like compounds from specific source categories.

A complete listing of the nomenclature used in this report is depicted in Table 1-1.

Table 1-1. Nomenclature for dioxin-like compounds

Term/symbol	Definition
CDD	Chlorinated dibenzo-*p*-dioxin, halogens substituted in any position
CDF	Chlorinated dibenzofuran, halogens substituted in any position
PCB	Polychlorinated biphenyl
M	Symbol for mono (i.e., one halogen substitution)
D	Symbol for di (i.e., two halogen substitution)
Tr	Symbol for tri (i.e., three halogen substitution)
T	Symbol for tetra (i.e., four halogen substitution)
Pe	Symbol for penta (i.e., five halogen substitution)
Hx	Symbol for hexa (i.e., six halogen substitution)
Hp	Symbol for hepta (i.e., seven halogen substitution)
O	Symbol for octa (i.e., eight halogen substitution)
2,3,7,8	Halogen substitutions in the 2,3,7,8 positions
Congener	Any one particular member of the same chemical family (e.g., there are 75 congeners of CDDs).
Congener group	Group of structurally related chemicals that have the same degree of chlorination (e.g., there are eight congener groups of CDDs, monochlorinated [MCDD] through octachlorinated [OCDD]).
Isomer	Substances that belong to the same congener group (e.g., 22 isomers constitute the congener group of TCDDs).
Specific isomer	Denoted by unique chemical notation (e.g., 2,4,8,9-tetrachlorodibenzofuran is referred to as 2,4,8,9-TCDF).

Source: Adapted from U.S. EPA (1989a).

1.1.1. Reference Years

A central part of EPA's dioxin inventory is the organization of estimates of annual releases of dioxin-like compounds into reference years 1987, 1995, and 2000. The selection and use of three reference years provides a basis for comparing environmental releases over time.

The year 1987 was selected as the initial reference year because it was the earliest time when it was feasible to assemble a reasonably comprehensive inventory. Prior to that time, very little data existed on dioxin emissions from stacks or other release points. The first study providing the type of data needed for a national inventory was EPA's National Dioxin Study (U.S. EPA, 1987a). The year 1987 also corresponds roughly with the time when significant advances occurred in emissions measurement techniques and in the development of high-resolution mass spectrometry and gas chromatography, which allowed analytical laboratories to detect low levels of polychlorinated dibenzo-*p*-dioxin (CDD) and polychlorinated dibenzofuran (CDF) congeners in environmental samples. Soon after this time, a number of facilities began upgrades specifically intended to reduce CDD/CDF emissions. Consequently, 1987 emissions are representative of levels of emissions that occurred before the widespread installation of pollution control systems and pollution prevention techniques specifically designed to reduce dioxin releases from man-made sources into the air, land, and water.

EPA selected 1995 as the second reference year because it reflects the completion time of the first set of regulatory activities specifically tailored to reduce dioxin releases from major sources. By 1995, EPA had proposed or promulgated regulations limiting CDD/CDF emissions from municipal waste combustors (MWCs), medical waste incinerators (MWIs), hazardous waste incinerators, cement kilns burning hazardous waste, and pulp and paper mill facilities using bleached chlorine processes.

The year 2000 was chosen as the most current date that could be addressed when this effort began in 2002. Also, it corresponds to a reasonable time interval since 1995 when one could expect to see further changes occurring in releases as a result of continuing regulatory activities, voluntary actions on the part of industry, and facility closures.

1.1.2. Regulatory Summary

Tables 1-2 through 1-7 present a synopsis of EPA emission standards for the control of dioxin releases. As discussed in Section 1.3.2, these regulations (along with other factors) contributed to the reductions in dioxin emissions observed over time.

Table 1-2. Municipal waste combustors[a]

Category[b]	Stack emission limit[c] (ng total CDD/CDF/dscm)	Effective date
New large	13	September 20, 1994[d] June 19, 1996[e]
Existing large With electrostatic precipitators as the APCD With dry scrubber/fabric filters as the APCD	 60 30	 When SIPs are approved[f]
New small	13	June 6, 2001[g]
Existing small With electrostatic precipitators as the APCD With dry scrubber/fabric filters as the APCD	 60 30	 When SIPs are approved[h]

[a]Air emission standards promulgated December 19, 1995.
[b]Large = aggregate capacity ≥225 tons/day; small = aggregate capacity <225 tons/day.
[c]ng total CDD/CDF/dscm = nanogram total Cl_4 - Cl_8 CDDs plus CDFs per dry standard cubic meter of stack gas volume, corrected to 7% O_2.
[d]Began construction on this date.
[e]Modified or upgraded on this date.
[f]When SIPs have been approved by EPA (approx. 3 yr from the final rule or 1998).
[g]For facilities constructed on or before this date.
[h]When SIPs have been approved by EPA (approx. 3 yr from the final rule or 2003).

APCD = Air pollution control device
SIP = State Implementation Plan

1.1.3. Definition of Dioxin-Like Compound

This inventory of sources and environmental releases addresses specific compounds in the following chemical classes: CDDs, CDFs, and polychlorinated biphenyls (PCBs). These subsets of chemicals are defined as "dioxin like." Dioxin-like refers to the fact that these compounds have similar chemical structures and physical-chemical properties, and they invoke a common battery of toxic responses. Because of their hydrophobic nature and resistance towards metabolism, these chemicals persist and bioaccumulate in the fatty tissues of animals and humans. The CDDs include 75 individual compounds; CDFs include 135 compounds. These individual compounds are technically referred to as congeners. Only 7 of the 75 congeners of CDDs, or of brominated dibenzo-*p*-dioxins (BDDs), arethought to have dioxin-like toxicity; they are the ones with chlorine substitutions in—at a minimum—the 2, 3, 7, and 8 positions. Only 10 of the 135 possible congeners of CDFs are thought to have dioxin-like toxicity; they also are the ones with substitutions in the 2, 3, 7, and 8 positions. This suggests that 17 individual CDDs/CDFs exhibit dioxin-like toxicity.

Table 1-3. Hazardous waste incinerators and cement kilns and lightweight aggregate kilns burning hazardous waste[a]

Source	Standards for new facilities[b]	Standards for existing facilities[b]
Hazardous waste incinerators	0.11 ng I-TEQ/dscm for dry APCD and/or waste heat boiler sources 0.20 ng I-TEQ/dscm for all other incinerators	0.20 ng I-TEQ/dscm and temperature control <400°F at the APCD inlet 0.40 ng I-TEQ/dscm when PM control device operated >400°F
Cement kilns burning hazardous waste	0.20 ng I-TEQ/dscm and temperature control <400°F at the APCD inlet 0.40 ng I-TEQ/dscm when PM control device operated >400°F	0.20 ng I-TEQ/dscm and temperature control <400°F at the APCD inlet 0.40 ng I-TEQ/dscm when PM control device operated >400°F
Lightweight aggregate kilns burning hazardous waste	0.20 ng I-TEQ/dscm or rapid quench below 400°F at kiln exit	0.20 ng I-TEQ/dscm or rapid quench below 400°F at kiln exit

[a]Air emission standards promulgated September 30, 1999, and December, 2005.
[b]ng I-TEQ/dscm = nanogram I-TEQ per dry standard cubic meter of stack gas volume, corrected to 7% O_2.

APCD = Air pollution control device (dry = dry scrubber or fabric filter)
PM = Particulate matter

Table 1-4. Cement kilns not burning hazardous waste[a]

Existing cement kilns[b]	New cement kilns[b]
0.20 ng I-TEQ/dscm and temperature control <400°F at the APCD inlet 0.40 ng I-TEQ/dscm when PM control device operated >400°F	0.20 ng I-TEQ/dscm and temperature control <400°F at the APCD inlet 0.40 ng I-TEQ/dscm when PM control device operated >400°F

[a]Air emission standards promulgated June 14, 1999.
[b]ng I-TEQ/dscm = nanogram I-TEQ per dry standard cubic meter of stack gas volume, corrected to 7% O_2.

APCD = Air pollution control device
PM = Particulate matter

There are 209 PCB congeners, of which only 12 are thought to have dioxin-like toxicity; those with four or more lateral chlorine atoms with one or no substitution in the ortho position. These compounds are sometimes referred to as coplanar, meaning that they can assume a flat configuration with rings aligned along the same plane. The physical/chemical properties of each congener vary according to the degree and position of chlorine substitution.

Table 1-5. Secondary aluminum smelters[a]

Process	Emission standard
Sweat furnace	0.8 ng I-TEQ/dscm stack gas corrected to 7% O_2
Thermal chip dryer	2.50 μg I-TEQ per metric ton of scrap charged to the dryer
Scrap dryer/delacquering kiln/decoating kiln	0.25 g I-TEQ per metric ton of scrap charged to the kiln
Scrap dryer/delacquering kiln/decoating kiln equipped with an afterburner	5.0 g I-TEQ per metric ton of scrap charged to the kiln

[a]Air emission standards promulgated March 23, 2000.

Table 1-6. Medical waste incinerators[a]

Category[b]	Standard[c]	When built
New		Constructed after June 20, 1996, or existing units that commenced modification after March 16, 1998.
Small	125 ng total CDD/CDF/dscm or 2.3 ng I-TEQ/dscm	
Medium and large	25 ng total CDD/CDF/dscm or 0.6 ng I-TEQ/dscm	
Existing (all sizes)	125 ng total CDD/CDF/dscm or 2.3 ng I-TEQ/dscm	Constructed on or before June 20, 1996; requires approval of SIPs[d]

[a]Air emission standards promulgated September 15, 1997.
[b]Small = capacity <100 kg/hr; medium = capacity >100 to 227 kg/hr; large = capacity >227 kg/hr.
[c]ng/dscm = nanogram per dry standard cubic meter of stack gas volume, corrected to 7% O_2.
[d]When SIPs have been approved by EPA (approx. 5 yr from the final rule or 2002).

Table 1-7. Pulp and paper mills[a]

Pollutant	Maximum 1-day wastewater discharge
Tetrachlorodibenzo-*p*-dioxin	<5 parts per quadrillion
Tetrachlorodibenzofuran	31.9 picograms per liter

[a]Effluent standards promulgated November 14, 1997.

Generally speaking, this document focuses on the 17 CDDs/CDFs and a few of the coplanar PCBs that are frequently encountered in source characterization or environmental samples.

CDDs and CDFs are tricyclic aromatic compounds that have similar physical and chemical properties. Certain PCBs (the so-called coplanar or mono-ortho coplanar congeners) are also structurally and conformationally similar. The most widely studied of this general class of compounds is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). TCDD, often called simply "dioxin," represents the reference compound for this class of compounds. The structures of TCDD and several related compounds are shown in Figure 1-1. Although sometimes confusing, the term "dioxin" is often also used to refer to the complex mixtures of TCDD and related compounds emitted from sources or found in the environment or in biological samples. It can also be used to refer to the total TCDD "equivalents" found in a sample. This concept of toxicity equivalence is discussed below.

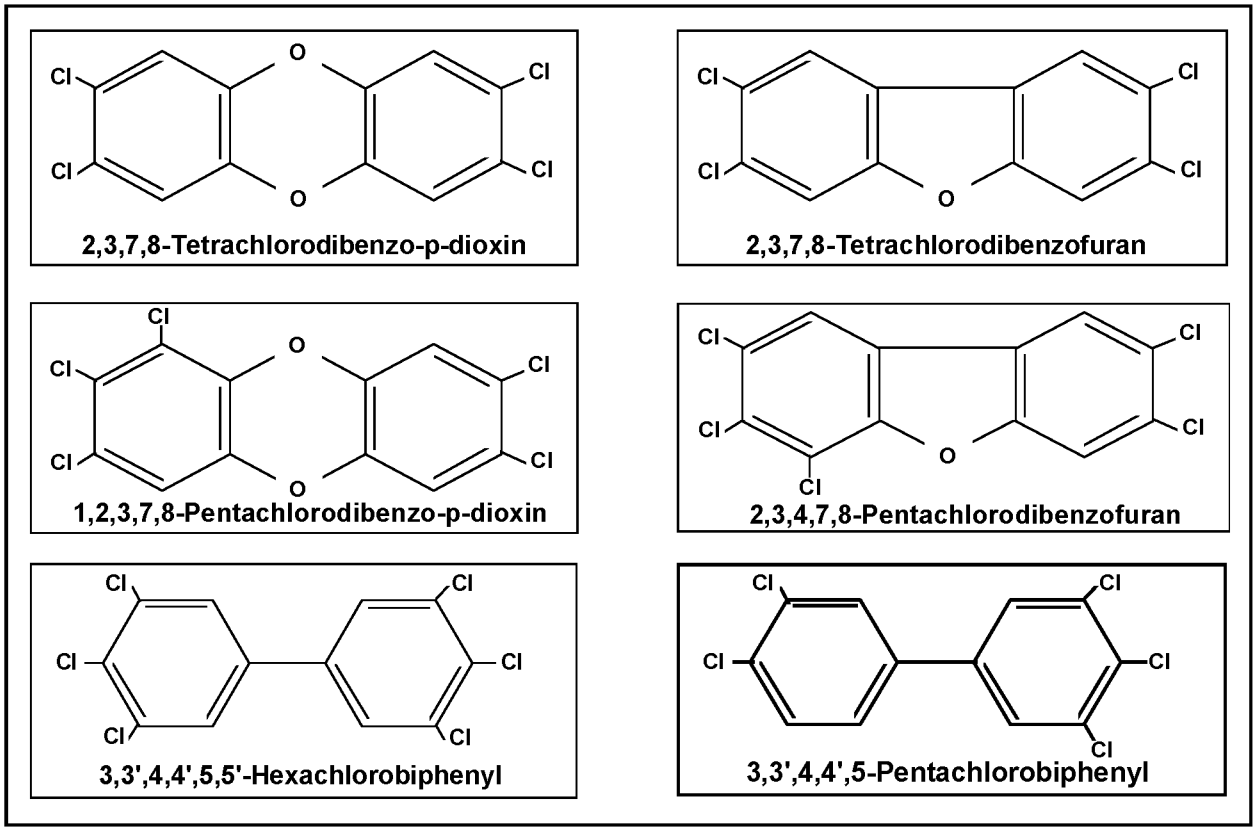


Figure 1-1. Chemical structure of 2,3,7,8-TCDD and related compounds.

1.1.4. Toxicity Equivalence Factors

CDDs, CDFs, and PCBs are commonly found as complex mixtures when detected in environmental media and biological tissues or when measured as environmental releases from specific sources. Humans are likely to be exposed to mixtures of CDDs, CDFs, and dioxin-like PCB congeners that vary by source and pathway, complicating the assessment of human health risk assessment. In order to address this problem, the concept of a "toxicity equivalence" (TEQ) has been considered and discussed by the scientific community, and toxicity equivalence factors (TEFs) have been developed and introduced to facilitate risk assessment of exposure to these chemical mixtures.

On the most basic level, TEFs compare the potential toxicity of each dioxin-like compound in the mixture to the well-studied and well-understood toxicity of TCDD, the most toxic member of the group. The comparison procedure involves assigning individual TEFs to the 2,3,7,8-substituted CDD/CDF congeners and dioxin-like PCBs. To accomplish this, scientists have reviewed the toxicological databases and, with considerations of chemical structure, persistence, and resistance to metabolism, have agreed to ascribe specific "order of magnitude" TEFs for each dioxin-like congener relative to TCDD, which is assigned a TEF of 1. The other congeners have TEF values ranging from 1 to 0.00001.

Thus, these TEFs are the result of scientific judgment of a panel of experts using all of the available data and are selected to account for uncertainties in the available data and to avoid underestimating risk. In this sense, they can be described as "public health-conservative" values. To apply this TEF concept, the TEF of each congener present in a mixture is multiplied by the respective mass concentration, and the products are summed to represent the 2,3,7,8-TCDD TEQ of the mixture (eq 1-1).

$$TEQ \cong \sum i\text{-}n(Congener_i \times TEF_i) + (Congener_j \times TEF_j) + ...(Congener_n \times TEF_n) \qquad (1\text{-}1)$$

The TEF values for CDDs and CDFs were originally adopted by international convention (U.S. EPA, 1989a). These values were further reviewed and/or revised, and TEFs were also developed for PCBs (Ahlborg et al., 1994; Van den Berg et al., 1998). A problem arises in that past and present quantitative exposure and risk assessments may not have clearly identified which of three TEF schemes was used to estimate the TEQ. This document uses a new uniform TEQ nomenclature that clearly distinguishes between the different TEF schemes and identifies the congener groups included in specific TEQ calculations. The nomenclature uses the following abbreviations to designate which TEF scheme was used in the TEQ calculation:

- I-TEQ refers to the international TEF scheme adopted by EPA in 1989 (U.S. EPA, 1989a). See Table 1-8.

- $TEQ\text{-}WHO_{94}$ refers to the 1994 World Health Organization (WHO) extension of the I-TEF scheme to include 13 dioxin-like PCBs (Ahlborg et al., 1994). See Table 1-9.

- $TEQ\text{-}WHO_{98}$ refers to the 1998 WHO update to the previously established TEFs for dioxins, furans, and dioxin-like PCBs (Van den Berg et al., 1998). See Table 1-10.

Table 1-8. The TEF scheme for $I\text{-}TEQ_{DF}$

Dioxin congener	TEF	Furan congener	TEF
2,3,7,8-TCDD	1	2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDD	0.5	1,2,3,7,8-PeCDF	0.05
1,2,3,4,7,8-HxCDD	0.1	2,3,4,7,8-PeCDF	0.5
1,2,3,6,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDD	0.01	1,2,3,7,8,9-HxCDF	0.1
OCDD	0.001	2,3,4,6,7,8-HxCDF	0.1
		1,2,3,4,6,7,8-HpCDF	0.01
		1,2,3,4,7,8,9-HpCDF	0.01
		OCDF	0.001

Table 1-9. The TEF scheme for dioxin-like PCBs, as determined by the World Health Organization in 1994

Chemical structure	IUPAC number	TEF
3,3',4,4'-TCB	PCB-77	0.0005
2,3,3',4,4'-PeCB	PCB-105	0.0001
2,3,4,4',5-PeCB	PCB-114	0.0005
2,3',4,4',5-PeCB	PCB-118	0.0001
2',3,4,4',5-PeCB	PCB-123	0.0001
3,3',4,4',5-PeCB	PCB-126	0.1
2,3,3',4,4',5-HxCB	PCB-156	0.0005
2,3',4,4',5,5'-HxCB	PCB-157	0.0005
3,3',4,4',5,5'-HxCB	PCB-167	0.00001
3,3',4,4',5,5'-HxCB	PCB-169	0.01
2,2',3,3',4,4',5-HpCB	PCB-170	0.0001
2,2',3,4,4',5,5'-HpCB	PCB-180	0.00001
2,3,3',4,4',5,5'-HpCB	PCB-189	0.0001

Table 1-10. The TEF scheme for TEQ_{DFP}-WHO_{98}

Dioxin congener	TEF	Furan congener	TEF
2,3,7,8-TCDD	1	2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDD	1	1,2,3,7,8-PeCDF	0.05
1,2,3,4,7,8-HxCDD	0.1	2,3,4,7,8-PeCDF	0.5
1,2,3,6,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDD	0.01	1,2,3,7,8,9-HxCDF	0.1
OCDD	0.0001	2,3,4,6,7,8-HxCDF	0.1
		1,2,3,4,6,7,8-HpCDF	0.01
		1,2,3,4,7,8,9-HpCDF	0.01
		OCDF	0.0001

Chemical structure	IUPAC number	TEF
3,3',4,4'-TCB	PCB-77	0.0001
3,4,4',5-TCB	PCB-81	0.0001
2,3,3',4,4'-PeCB	PCB-105	0.0001
2,3,4,4',5-PeCB	PCB-114	0.0005
2,3',4,4',5-PeCB	PCB-118	0.0001
2',3,4,4',5-PeCB	PCB-123	0.0001
3,3',4,4',5-PeCB	PCB-126	0.1
2,3,3',4,4',5-HxCB	PCB-156	0.0005
2,3,3',4,4',5'-HxCB	PCB-157	0.0005
2,3',4,4',5,5'-HxCB	PCB-167	0.00001
3,3',4,4',5,5'-HxCB	PCB-169	0.01
2,3,3',4,4',5,5'-HpCB	PCB-189	0.0001

The nomenclature also uses subscripts to indicate which family of compounds is included in any specific TEQ calculation. Under this convention, a subscript D is used to designate dioxins, a subscript F to designate furans, and a subscript P to designate PCBs. As an example, TEQ_{DF}-WHO_{98} would be used to describe a mixture for which only dioxin and furan congeners were determined and where the TEQ was calculated using the WHO_{98} scheme. If PCBs had also been determined, the nomenclature would be TEQ_{DFP}-WHO_{98}. Note that the designations TEQ_{DF}-WHO_{98} and I-TEQ_{DF} are interchangeable, as the TEFs for dioxins and furans are the same in each scheme. Note also that in this document I-TEQ sometimes appears without the D or F subscripts. This indicates that the TEQ calculation includes both dioxins and furans. This document emphasizes the WHO_{98} TEF scheme as the preferred scheme to be used to assign TEQs to complex environmental mixtures.

Throughout this document, environmental release estimates are presented in terms of TEQs. This is done for convenience in presenting summary information and to facilitate comparisons across sources. For purposes of environmental fate modeling, however, it is important to use the individual CDD/CDF and PCB congener values rather than TEQs. This is because the physical/chemical properties of individual CDD/CDF congeners vary and, consequently, the congeners will behave differently in the environment. For example, the relative mix of congeners released from a stack cannot be assumed to remain constant during transport through the atmosphere and deposition to various media. The full congener-specific release rates for most sources are given in an electronic database that will become available as a companion to this document.

1.1.5. Information Sources

In general, the literature used to prepare this report includes documents published in 2003 or earlier. Some 2004 documents are cited, primarily in Chapter 2, which covers formation theory, but a thorough literature review was not extended past 2003.

EPA's Toxics Release Inventory (TRI) began collecting data on PCBs in 1988 and on CDDs/CDFs in 2000 (U.S. EPA, 2003c). These data were considered in this report for purposes of identifying possible sources, but they were not used for making quantitative release estimates because of the following considerations:

- With respect to PCBs, the TRI data are reported as total PCBs rather than on a congener-specific basis. Thus, it is unknown what portion of these releases are dioxin-like PCBs, and TEQs cannot be calculated. In their present format, the PCB TRI data are not readily usable within the structure of this dioxin inventory.

- With respect to CDDs/CDFs, the reporting format under TRI is the sum quantity of the 17 toxic CDDs/CDFs that are emitted in a given year (i.e., the sum of the 2,3,7,8-chlorine-substituted compounds). Neither the releases of the individual CDD/CDF congeners nor the TEQs must be reported; therefore, the dioxin TRI data are not readily usable within the structure of this dioxin inventory.

- The accuracy of the TRI data is unknown because they are self-reported and are not required to be based on measurements.

- The TRI reports lack specific details and descriptions of the reporting industries. This information is needed for the dioxin inventory because the calculation of source-specific emission factors (representative of industrial source categories) strongly depends on closely matching facilities in terms of similarity of process, production, and pollution control.

- The TRI reporting format does not include information on the strengths/weaknesses of the data, and therefore, it would be difficult to evaluate these data in terms of the confidence rating scheme developed for this inventory (presented in Section 1.2.3).

1.2. APPROACH

Only sources judged to have a reasonable likelihood for releases to the circulating environment were addressed in this report. For example:

- CDDs/CDFs and dioxin-like PCBs in air emissions and wastewater discharges are included, whereas those in intermediate products or internal wastestreams are not. For example, the CDDs/CDFs in a wastestream going to an on-site incinerator are not addressed in this report, but any CDDs/CDFs in the stack emissions from the incinerator are included.

- CDDs/CDFs and dioxin-like PCBs in wastestreams applied to land in the form of "land farming" are included, whereas those disposed of in permitted landfills were excluded. Properly designed and operated landfills are considered to achieve long-term isolation from the circulating environment. Land farming, however, involves the application of wastes directly to land, clearly allowing for releases to the circulating environment.

1.2.1. Source Classes

The major identified sources of environmental releases of dioxin-like compounds in the United States are grouped into five broad categories.

Combustion. CDDs/CDFs are formed in most combustion systems (which can include those that incinerate wastes such as municipal solid waste, sewage sludge, medical waste, and hazardous wastes); in other high-temperature sources (such as cement kilns); in poorly or uncontrolled combustion sources (such as forest fires, brush fires, landfill fires, accidental fires, building fires, and open burning of wastes); and during the burning of various fuels (such as coal, wood, and petroleum products).

Metals smelting, refining, and processing. CDDs/CDFs can be formed during various types of primary and secondary metals operations, including iron ore sintering, lead smelting, copper smelting, magnesium and titanium dioxide production, steel production, and scrap metal recovery.

Chemical manufacturing. CDDs/CDFs can be formed as by-products of the manufacture of chlorine-bleached wood pulp, chlorinated phenols (e.g., pentachlorophenol [PCP]), PCBs, chlorobenzenes, phenoxy herbicides (e.g., 2,4-D and 2,4,5-T), and chlorinated aliphatic compounds (e.g., ethylene dichloride, vinyl chloride, polyvinyl chloride).

Natural sources and processes. The evidence for the widespread existence of natural sources of dioxin is quite weak. Recent studies suggest that CDDs/CDFs can form under certain environmental conditions (e.g., composting) from the action of microorganisms on chlorinated phenolic compounds. Similarly, CDDs/CDFs have been reported to form during photolysis of highly chlorinated phenols. Certain clays used in ceramics (e.g., ball clay) are believed to have become contaminated with dioxin as a result of natural processes, but the source of contamination remains unknown. Although it has been suggested that volcanos may be a natural source, there is no reliable evidence that volcanos produce and emit significant amounts of dioxin during eruptions.

Reservoirs. Reservoirs are environmental compartments and materials that have the capacity to store previously formed CDDs/CDFs or dioxin-like PCBs. These compounds are thus sequestered from the open and circulating environment. Potential reservoirs include soils, sediments, and biota as well as some anthropogenic materials, such as PCP treated telephone poles. Dioxin-like compounds in these reservoirs have the potential for redistribution and circulation in the environment through the physical processes of leaching, volatilization, erosion, sedimentation, and deposition. Whenever dioxins are released from their place of storage back into the circulating environment, the reservoir is considered a source of dioxin.

Sources can also be categorized in terms of when releases occur: (1) contemporary formation sources (sources that have essentially simultaneous formation and release) and (2) reservoir sources (materials or places that contain previously formed CDDs/CDFs or dioxin-like PCBs that are re-released to the environment). The contemporary formation sources are discussed in Chapters 2 through 10 and the reservoir sources are discussed in Chapter 11.

Table 1-11 provides a comprehensive list of all known or suspected sources of CDDs/CDFs in the United States. The checkmarks indicate how each source was classified in terms of the following six categories:

1. *Contemporary formation sources with reasonably well-quantified releases* (see Section 1.4.2). These sources are listed in Table 1-11 and release estimates are shown in Table 1-12.

2. *Contemporary formation sources without quantified release estimates*. These sources are listed in Table 1-12.

3. *Reservoir sources with reasonably well-quantified releases*. These sources would have been listed in Table 1-11, but none have yet been identified.

Table 1-11. Known and suspected sources of CDDs/CDFs

Source category	Contemporary formation sources			Reservoir sources		
	Quantifiable (Categories A, B and C)	Preliminary estimate (Category D)	Not quantifiable (Category E)	Quantifiable (Categories A, B and C)	Preliminary estimate (Category D)	Not quantifiable (Category E)
COMBUSTION SOURCES						
Waste incineration						
Municipal waste combustion	✓					
Hazardous waste incineration	✓					
Boilers/industrial furnaces	✓					
Medical waste/pathological incineration	✓					
Crematoria	✓					
Sewage sludge incineration	✓					
Tire combustion	✓					
Pulp and paper mill sludge incinerators	✓					
Biogas combustion		✓				
Power/energy generation						
Vehicle fuel combustion - leaded[a]	✓					
- unleaded	✓					
- diesel	✓					
Wood combustion - residential	✓					
- industrial	✓					
Coal combustion - residential		✓				
- industrial/utility	✓					
Oil combustion - residential		✓				
- industrial/utility	✓					
Other high-temperature sources						
Cement kilns burning hazardous waste	✓					
Cement kilns burning nonhazardous waste	✓					
Asphalt mixing plants		✓				
Petroleum refining catalyst regeneration	✓					
Cigarette combustion	✓					
Carbon reactivation furnaces	✓					
Kraft recovery boilers	✓					
Manufacture of ball clay products			✓			
Glass manufacturing			✓			
Lime kilns			✓			
Rubber manufacturing			✓			

Table 1-11. Known and suspected CDD/CDF sources (continued)

Source category	Contemporary formation sources			Reservoir sources		
	Quantifiable (Categories A, B and C)	Preliminary estimate (Category D)	Not quantifiable (Category E)	Quantifiable (Categories A, B and C)	Preliminary estimate (Category D)	Not quantifiable (Category E)
Minimally controlled or uncontrolled combustion						
Combustion of landfill gas in flares		✓				
Landfill fires		✓				
Accidental fires, structural		✓				
Accidental fires, vehicles		✓				
Forest, brush, and straw fires		✓				
Backyard barrel burning	✓					
Uncontrolled combustion of PCBs			✓			
Burning of candles			✓			
METAL SMELTING/REFINING						
Ferrous metal smelting/refining						
Sintering plants	✓					
Coke production		✓				
Electric arc furnaces		✓				
Ferrous foundries		✓				
Nonferrous metal smelting/refining						
Primary aluminum			✓			
Primary copper	✓					
Primary magnesium		✓				
Primary nickel			✓			
Secondary aluminum	✓					
Secondary copper	✓					
Secondary lead	✓					
Scrap electric wire recovery			✓			
Drum and barrel reclamation	✓					

Table 1-11. Known and suspected CDD/CDF sources (continued)

Source category	Contemporary formation sources			Reservoir sources		
	Quantifiable (Categories A, B and C)	Preliminary estimate (Category D)	Not quantifiable (Category E)	Quantifiable (Categories A, B and C)	Preliminary estimate (Category D)	Not quantifiable (Category E)
CHEMICAL MANUFACTURING (releases to the environment)						
Bleached chemical wood pulp and paper mills	✓					
Mono- through tetrachlorophenols			✓			
Pentachlorophenol			✓			
Chlorobenzenes			✓			
Chlorobiphenyls (leaks/spills)			✓			
Ethylene dichloride/vinyl chloride	✓					
Dioxazine dyes and pigments			✓			
2,4-Dichlorophenoxy acetic acid			✓			
Municipal wastewater treatment		✓				
Tall oil-based liquid soaps			✓			
BIOLOGICAL AND PHOTOCHEMICAL PROCESSES			✓			✓
RESERVOIR SOURCES						
Land					✓	
Air						✓
Water						✓
Sediments						✓
Anthropogenic structures						
PCP-treated wood						✓

[a]Leaded fuel production and the manufacture of motor vehicle engines requiring leaded fuel for highway use are prohibited in the United States. (See Chapter 4, Section 4.1, for details.)

Table 1-12. Inventory of contemporary releases (g/yr) of dioxin-like compounds from known sources in the United States for reference years 2000, 1995, and 1987 and preliminary release estimates for 2000

Source Category	2000 Inventory			1995 Inventory			1987 Inventory			2000 Preliminary indication
	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	Category D rating TEQ_{DF}-WHO_{98}
RELEASES TO AIR										
WASTE INCINERATION										
Municipal waste combustion	83.8	76.3	A	1,393.5	1,101.3	B	8,905.1	7,858.8	B	
Hazardous waste incineration	3.2	3.2	B	5.8	5.7	B	5.0	5.0	B	
Boilers/industrial furnaces	1.8	1.8	C	0.4	0.4	C	0.8	0.8	C	
Halogen acid furnaces	0.3	0.3	C	NA	NA		NA	NA		
Medical waste/pathological incineration	378	357	C	487	459	C	2,570	2,440	C	
Crematoria										
- human	0.3	0.3	C	0.2	0.2	C	0.2	0.1	C	
- animal										<1
Sewage sludge incineration	9.6	9.4	B	14.2	14	B	5.8	5.8	B	
Tire combustion	0.5	0.5	C	0.1	0.1	C	0.1	0.1	C	
Pulp and paper mill sludge incinerators[b]										
Biogas combustion										<1
POWER/ENERGY GENERATION										
Vehicle fuel combustion										
- leaded gasoline[c]				1.6	1.3	C	37.5	31.9	C	
- unleaded gasoline on-road	7	6.7	C	4.7	4.4	C	3.6	3.3	C	
- unleaded gasoline off-road	0.4	0.4	C	NA	NA		NA	NA		
- diesel on-road (Trucks)	65.4	61.7	C	33.3	31.5	C	27.8	26.3	C	
- diesel off-road										
- equipment	22	21	C	12	11	C	9.4	8.8	C	
- railroad	6.8	6.4	C	7	6.6	C	5.8	5.5	C	
- commercial marine vessel	4.3	4	C	4.8	4.5	C	3.8	3.6	C	

Table 1-12. Inventory of contemporary releases (g/yr) of dioxin-like compounds from known sources in the United States for reference years 2000, 1995, and 1987 and preliminary release estimates for 2000 (continued)

Source Category	2000 Inventory			1995 Inventory			1987 Inventory			2000 Preliminary indication
										Category D rating
	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	TEQ_{DF}-WHO_{98}
Wood combustion										
- residential	11.3[d]	11.3[d]	C	15.7[d]	15.7[d]	C	22[d]	22[d]	C	
- industrial	41.5	39.4	C	26.2	24.9	C	26.5	25.2	C	
Coal combustion										
- utility boilers	69.5	70.4	B	60.1	60.9	B	50.9	51.4	B	
- residential[e]										<10[d]
- commercial/industrial										>10[d]
Oil combustion										
- industrial/utility, residual oil	1.7	1.5	C	10.7	9.3	C	17.8	15.5	C	
- industrial/utility, distillate oil	7.3	6.3	C	7.3	6.4	C	8.3	7.2	C	
- institutional/commercial heating, residual oil	0.7	0.6	C	0.8	0.7	C	1.5	1.3	C	
- institutional/commercial heating, distillate oil	2.9	2.5	C	3.1	2.7	C	3.7	3.2	C	
- residential, distillate oil	4.5	3.6	C	5.0	3.9	C	5.4	4.2	C	
OTHER HIGH-TEMPERATURE SOURCES										
Cement kilns burning hazardous waste	18.8	16.6	B	156.1	145.3	C	117.8	109.6	C	
Lightweight aggregate kilns burning hazardous waste	1.9[d]	1.8[d]	C	2.4[d]	2.4[d]	C	3.3[d]	3.3[d]	C	
Cement kilns burning nonhazardous waste	17.2	16.6	C	16.6	15.9	C	12.7	12.3	C	
Asphalt mixing plants										<1[d]
Petroleum refining catalyst regeneration	2.2	2.1	C	2.2	2.1	C	2.2	2.1	C	
Cigarette combustion	0.4	0.4	C	0.8	0.8	C	1	1	C	
Carbon reactivation furnaces	0.1[d]	0.1[d]	C	0.1[d]	0.1[d]	C	0.1[d]	0.1[d]	C	
Kraft recovery boilers	0.8	0.8	B	2.3	2.3	B	2	2	B	

Table 1-12. Inventory of contemporary releases (g/yr) of dioxin-like compounds from known sources in the United States for reference years 2000, 1995, and 1987 and preliminary release estimates for 2000 (continued)

Source Category	2000 Inventory			1995 Inventory			1987 Inventory			2000 Preliminary indication
	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	Category D rating TEQ_{DF}-WHO_{98}
MINIMALLY CONTROLLED OR UNCONTROLLED COMBUSTION[f]										
Combustion of landfill gas										[d]
Landfill fires										>10,000[g]
Accidental fires										
- structural										>10[d]
- vehicles										[d]
Forest and brush fires[h]										≥10
Backyard barrel burning[i]	498.5	472.6	C	628	595	C	604	573	C	≤1,000
Residential yard waste burning[j]										
Land clearing debris burning										≤10
										≤1000
METALLURGICAL PROCESSES										
Ferrous metal smelting/ refining										
- sintering plants	27.6	24.4	A	28	25.1	B	32.7	29.3	C	
- coke production										<10[d]
- electric arc furnaces										<100
- foundries										>10[d]
Nonferrous metal smelting/ refining										
- primary copper	0.3[d]	0.3[d]	B	<0.5[d]	<0.5[d]	B	<0.5[d]	<0.5[d]	B	
- secondary aluminum	8.3	7.8	C	19.5	18.3	C	10.9	10.2	C	
- secondary copper	0.9	0.9	C	271	266	C	983	966	C	
- secondary lead	2.5	2.4	B	1.7	1.6	B	1.3	1.2	B	
- primary magnesium	4.3[d]	4.3[d]	A	4.1[d]	4.1[d]	C	NA	NA		
Drum and barrel reclamation	0.6	0.6	C	0.1	0.1	C	0.1	0.1	C	

Table 1-12. Inventory of contemporary releases (g/yr) of dioxin-like compounds from known sources in the United States for reference years 2000, 1995, and 1987 and preliminary release estimates for 2000 (continued)

Source Category	2000 Inventory			1995 Inventory			1987 Inventory			2000 Preliminary indication
	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	Category D rating TEQ_{DF}-WHO_{98}
CHEMICAL MANUFACTURE/PROCESSING SOURCES										
Ethylene dichloride/vinyl chloride/PVC	5.5[d]	5.5	A	11.2[d]	11.2	A	NA	NA		
Chor-alkali facilities	1.8[d]	1.8[d]	A	1.8 [d]	1.8 [d]	C	NA	NA		
TOTAL RELEASES TO AIR[k]	1,314.5	1,243.6	A, B, C	3,239.9	2,857.1	A, B, C	13,482.6	12,230.7	A, B, C	
RELEASES TO WATER										
CHEMICAL MANUFACTURE/PROCESSING SOURCES										
Bleached chemical wood pulp and paper mills	1.0	1.0	A	28	28	A	356	356	A	
POTW (municipal) wastewater										>10
Ethylene dichloride/vinyl chloride/PVC	23.1[d]	23.9[d]	A	23.1[d]	23.9[d]	C	NA	NA		
Chor-alkali facilities	1.8[d]	1.8[d]	A	1.8[d]	[d] 1.8	C	NA	NA		
TOTAL RELEASES TO WATER[k]	25.9	26.7	A, B, C	52.9	53.7	A, B, C	356	356	A, B, C	
RELEASES TO LAND										
CHEMICAL MANUFACTURING/PROCESSING SOURCES										
Bleached chemical wood pulp and paper mill sludge	0.1	0.1	A	2	2	A	14.1	14.1	A	
Ethylene dichloride/vinyl chloride/PVC	1.4	1.5	A	1.4	1.5	B	NA	NA		
Municipal wastewater treatment sludge	78.2	78.2	A	116.1	156.5	A	76.6	103	A	
Commercially marketed sewage sludge	1.9	1.9	A	3	4	A	2.6	3.5	A	

Table 1-12. Inventory of contemporary releases (g/yr) of dioxin-like compounds from known sources in the United States for reference years 2000, 1995, and 1987 and preliminary release estimates for 2000 (continued)

Source Category	2000 Inventory			1995 Inventory			1987 Inventory			2000 Preliminary indication
	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	TEQ_{DF}-WHO_{98}	I-TEQ	Category rating[a]	Category D rating TEQ_{DF}-WHO_{98}
2,4-Dichlorophenoxy acetic acid	NA	NA		28.9	18.4	A	33.4	21.3	A	
TOTAL RELEASES TO LAND[k]	81.6	81.7	A, B, C	151.4	182.4	A, B, C	126.7	141.9	A, B, C	
OVERALL RELEASES TO OPEN AND CIRCULATING ENVIRONMENT	**1,422.0**	**1,352.0**	**A, B, C**	**3,444.2**	**3,093.2**	**A, B, C**	**13,965.3**	**12728.6**	**A, B, C**	

[a]The most reliable estimates of environmental releases are those sources in categories A, B, and C.
[b]Included in estimate for wood combustion, industrial.
[c]Leaded fuel production and the manufacture of motor vehicle engines requiring leaded fuel for highway use are prohibited in the United States. (See Chapter 4, Section 4.1 for details.)
[d]Estimate based on a TEQ_{DF}-WHO_{98} emissions estimate.
[e]Includes combustion of bituminous/subbituminous coal and anthracite coal.
[f]Refers to conventional pollutant control, not dioxin emissions control. Very few sources listed in this inventory control specifically for CDD/CDF emissions.
[g]Congener-specific emissions data were not available; the Nordic TEQ estimate was used as a surrogate for the I-TEQ_{DF} emissions estimate.
[h]Includes forest wildfires and prescribed burning for forest management.
[i]Term refers to the burning of residential waste in barrels.
[j]Includes burning of brush and leaves.
[k]Total reflects only the total of the estimates made in this report.

Category ratings:

A = Characterization of the source category judged to be **adequate for quantitative estimation** with **high confidence** in the **emission factor** and **high confidence** in **activity level**.

B = Characterization of the source category judged to be **adequate for quantitative estimation** with **medium confidence** in the **emission factor** and at least **medium confidence** in **activity level**.

C = Characterization of the source category judged to be **adequate for quantitative estimation** with **low confidence** in either the **emission factor** and/or the **activity level**.

D = **Preliminary indication** of the potential magnitude of emissions from "Unquantified" (Category D) sources; **based on extremely limited data, judged to be clearly nonrepresentative**. D estimates are not included in the inventory of source emissions, but serve the purpose of highlighting sources in need of more adequate emissions information.

NA = Not available (information is lacking).
POTW = Publicly owned treatment works or sewage treatment plant.

4. *Reservoir sources with preliminary release estimates*. These sources are discussed in Chapter 11.

5. *Reservoir sources without quantified releases*. These sources are discussed in Chapter 11.

Only contemporary formation sources (numbers 1 and 2 above) are considered for inclusion in the national inventory. Reservoir sources are not considered because they are not original releases, but rather the recirculation of past releases. To date, no reliable estimates of releases from the reservoir sources have been made because information is either lacking or is inadequate to allow for estimates to be made.

This document includes discussions on products that contain dioxin-like compounds. Some of these products, such as 2,4-D, are considered to be sources because they are clearly used in ways that result in environmental releases (e.g., they are sprayed onto agricultural lands for weed control). If a release from the product occurs, it is added to the national dioxin inventory. Other products containing dioxin-like compounds, such as vinyl chloride products, do not appear to have environmental releases and are not considered sources. For all CDD-/CDF-containing products, this document summarizes the available information about contamination levels and, where possible, makes estimates of the total amount of CDDs/CDFs produced annually in these products. Estimates of the CDD/CDF TEQ amounts in products are summarized in Table 1-13.

Table 1-13. Products containing CDDs/CDFs (g TEQ_{DF}-WHO_{98}/yr)

Product	2000	1995	1987
Bleached chemical wood pulp	0.58	40	505
Ethylene dichloride/vinyl chloride	0.02	0.02	NA
Chloranil	1.16	64	NA
Pentachlorophenol	4,395	4,800	20,000
2,4 -Dichlorophenoxy acetic acid (2,4-D)[a]	NA	28.9	33.4
TOTAL	4,397	4,933	20,538

[a] Only 2,4-D is considered to be an environmental release.

NA = Information not available

1.2.2. Quantitative Method for Inventory of Sources

Some source types have a high percentage of facilities with measured CDD/CDF releases, such as municipal waste combustion, hazardous waste incineration, and cement kilns that burn hazardous waste (air emissions), and wastewater releases from chlorine-bleached pulp and paper mills. In addition, some source activities have been adequately sampled with respect to levels of

lands and 2,4-D applied to agricultural lands. Other source categories have relatively few tested facilities and/or the activity has not been comprehensively evaluated for dioxin releases. In these cases, EPA relies on the use of emission factors to estimate CDD/CDF releases from the untested sources. This provides a method of extrapolation from tested sources to national estimates of environmental releases. Many of the national emission estimates, therefore, have been developed using this "top-down" approach.

The first step in this approach is to derive from the available emissions monitoring data an emission factor (or series of emission factors) deemed to be representative of the source category (or segments of a source category that differ in, e.g., configuration, fuel type, air pollution control equipment). The emission factor relates mass of CDDs/CDFs or dioxin-like PCBs released into the environment with some measure of activity (e.g., kilograms of material processed per year, vehicle miles traveled per year, liters of wastewater discharged per year). It is developed by averaging the emission factors for the tested facilities or activities within the particular classification of sources. For example, mass burn MWCs equipped with dry scrubbers (DSs) combined with fabric filters (FFs) will have an average emission factor derived from the tested facilities within this source classification. This average emission factor is then multiplied by the measure of activity for the nontested facilities in the class (e.g., total kilograms of material processed by these facilities annually). Finally, emissions are summed for the tested facilities and nontested facilities. In general, this procedure can be represented by the followinge quations:

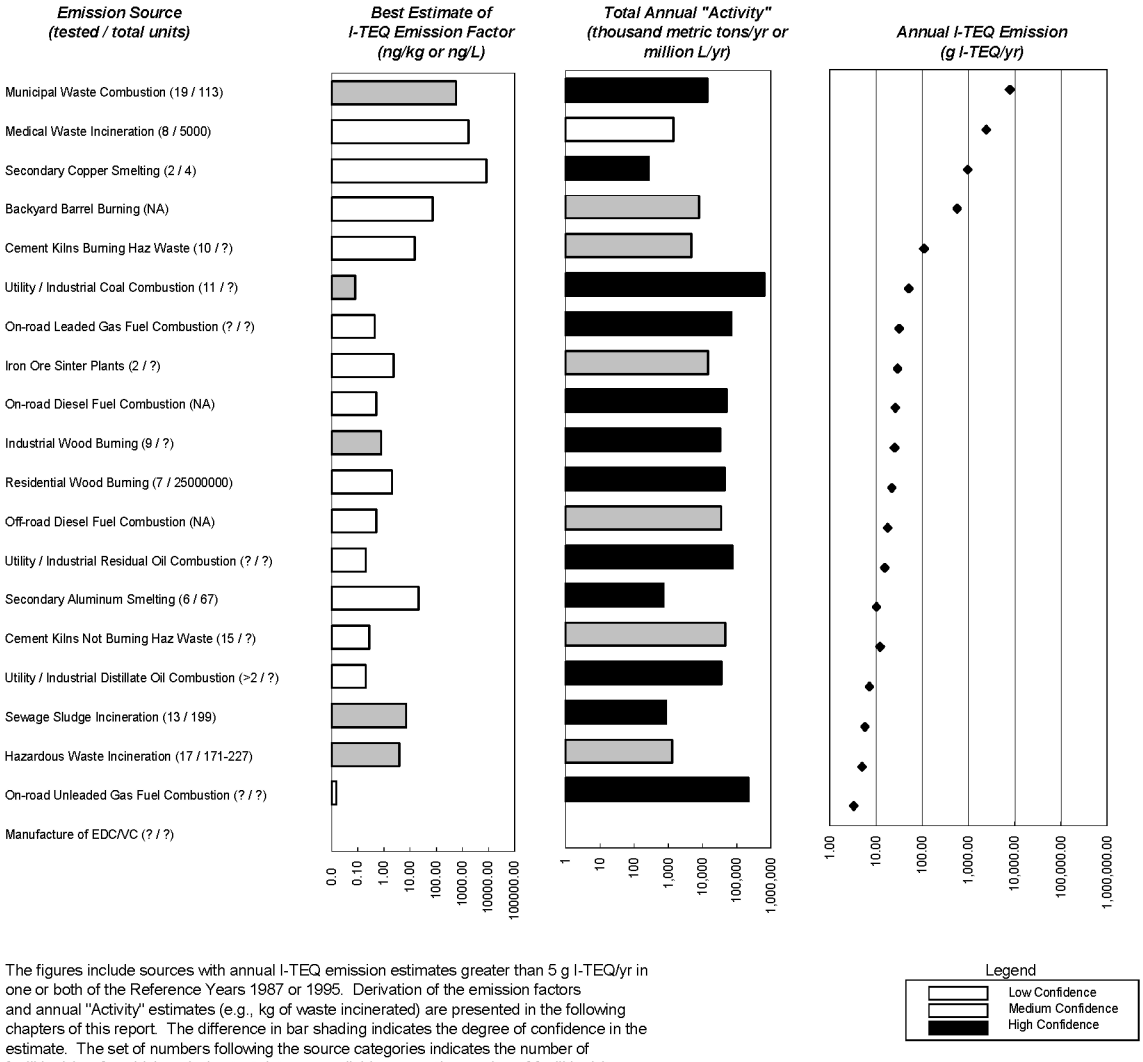
$$E_{total} = \sum E_{tested,\,I} + \sum E_{untested,\,I} \tag{1-2}$$

$$E_{total} = \sum E_{tested,\,I} + \sum (EF_i * A_i)_{untested} \tag{1-3}$$

where:

E_{total} = annual emissions from all facilities (g TEQ/yr)
$E_{tested,\,I}$ = annual emissions from all tested facilities in class I (g TEQ/yr)
$E_{untested,\,I}$ = annual emissions from all untested facilities in class I (g TEQ/yr)
EF_i = mean emission factor for tested facilities in class I (g TEQ/kg)
A_i = activity measure for untested facilities in class I (kg/yr)

Figures 1-2 through 1-4 and 1-6 through 1-8 depict the various source categories and their emission factors, activity levels, and annual emissions for reference years 1987, 1995, and 2000, respectively, in I-TEQ and WHO-TEQ units. Figures 1-5 and 1-9 depict comparisons of the estimated I-TEQ and WHO-TEQ air emissions for these years.



The figures include sources with annual I-TEQ emission estimates greater than 5 g I-TEQ/yr in one or both of the Reference Years 1987 or 1995. Derivation of the emission factors and annual "Activity" estimates (e.g., kg of waste incinerated) are presented in the following chapters of this report. The difference in bar shading indicates the degree of confidence in the estimate. The set of numbers following the source categories indicates the number of facilities/sites for which emission test data are available versus the number of facilities/sites in the category. A question mark (?) indicates that the precise number of facilities/sites could not be estimated.

Figure 1-2. Estimated CDD/CDF I-TEQ emissions to air from combustion sources in the United States for reference year 1987 (municipal solid waste incineration is currently referred to as municipal waste combustion).

Some source categories are made up of facilities that vary widely in terms of design and operating conditions. For these sources, as explained above, an attempt was made to create subcategories that grouped facilities with common features and then to develop separate emission factors for each subcategory. Implicit in this procedure is the assumption that facilities with similar design and operating conditions should have similar CDD/CDF release potential.For most source categories, however, the specific combination of features that contributes mostto

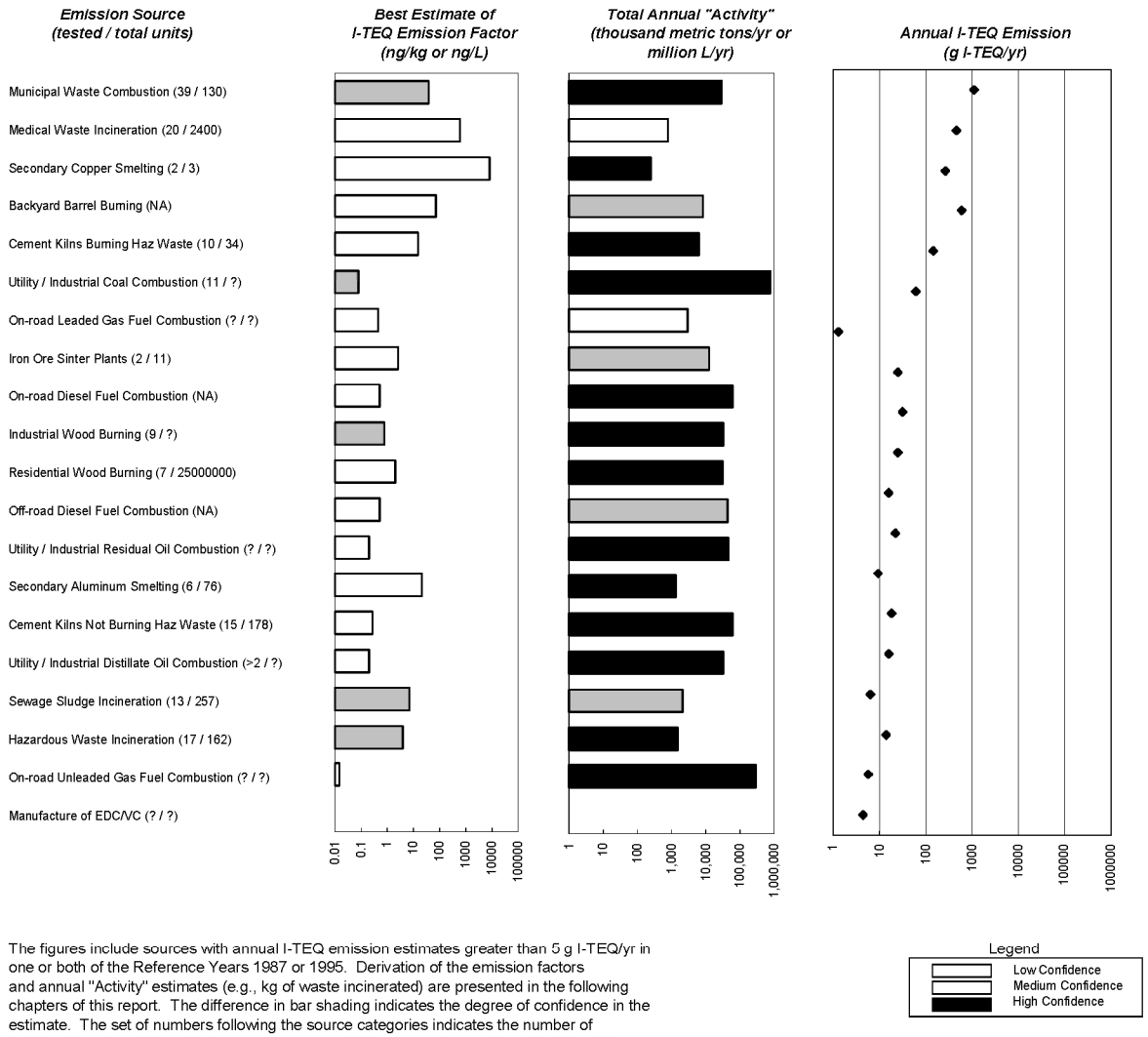
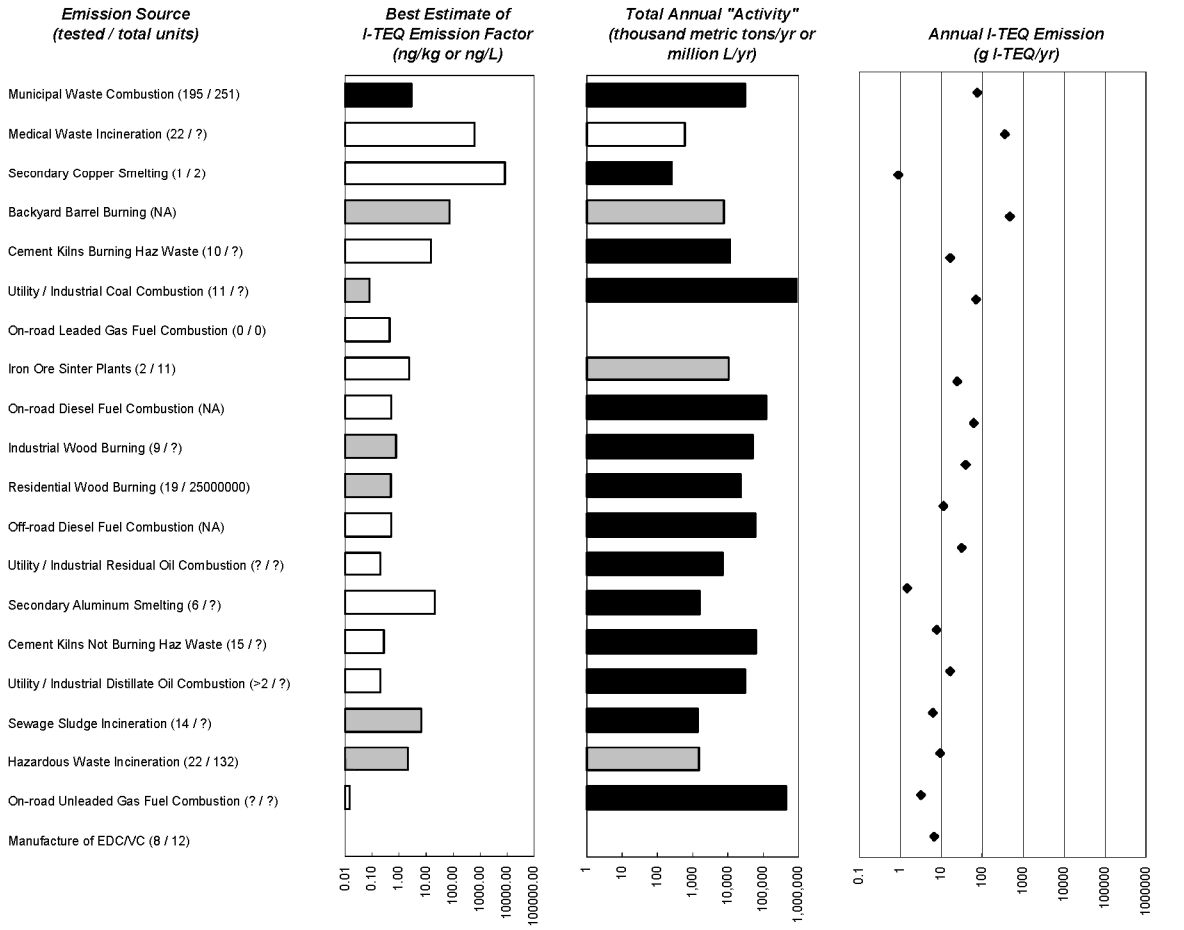


Figure 1-3. Estimated CDD/CDF I-TEQ emissions to air from combustion sources in the United States for reference year 1995 (municipal solid waste incineration is currently referred to as municipal waste combustion).

CDD/CDF or dioxin-like PCB releases is not well understood. Therefore, how to best subcategorize a source category was often problematic. For each subcategorized source category in this document, a discussion is presented about the variability in design and operating conditions, what was known about how these features contributed to CDD/CDF or dioxin-like PCB releases, and the rationale for creating subcategories.



The figures include sources with annual I-TEQ emission estimates greater than 5 g I-TEQ/yr in one or both of the Reference Years 1987 or 1995. Derivation of the emission factors and annual "Activity" estimates (e.g., kg of waste incinerated) are presented in the following chapters of this report. The difference in bar shading indicates the degree of confidence in the estimate. The set of numbers following the source categories indicates the number of facilities/sites for which emission test data are available versus the number of facilities/sites in the category. A question mark (?) indicates that the precise number of facilities/sites could not be estimated.

Figure 1-4. Estimated CDD/CDF I-TEQ emissions to air from combustion sources in the United States for reference year 2000.

The emission factors developed for the inventory are intended to be used for estimating total emissions for a source category rather than emissions from individual facilities. EPA has made uncertainty determinations for each of these emission factors, based, in part, on the assumption that by applying them to a group of facilities, the potential for overestimating or underestimating individual facilities will, to some extent, be self-compensating. This means that in using these emission factors one can place significantly greater confidence in an emission

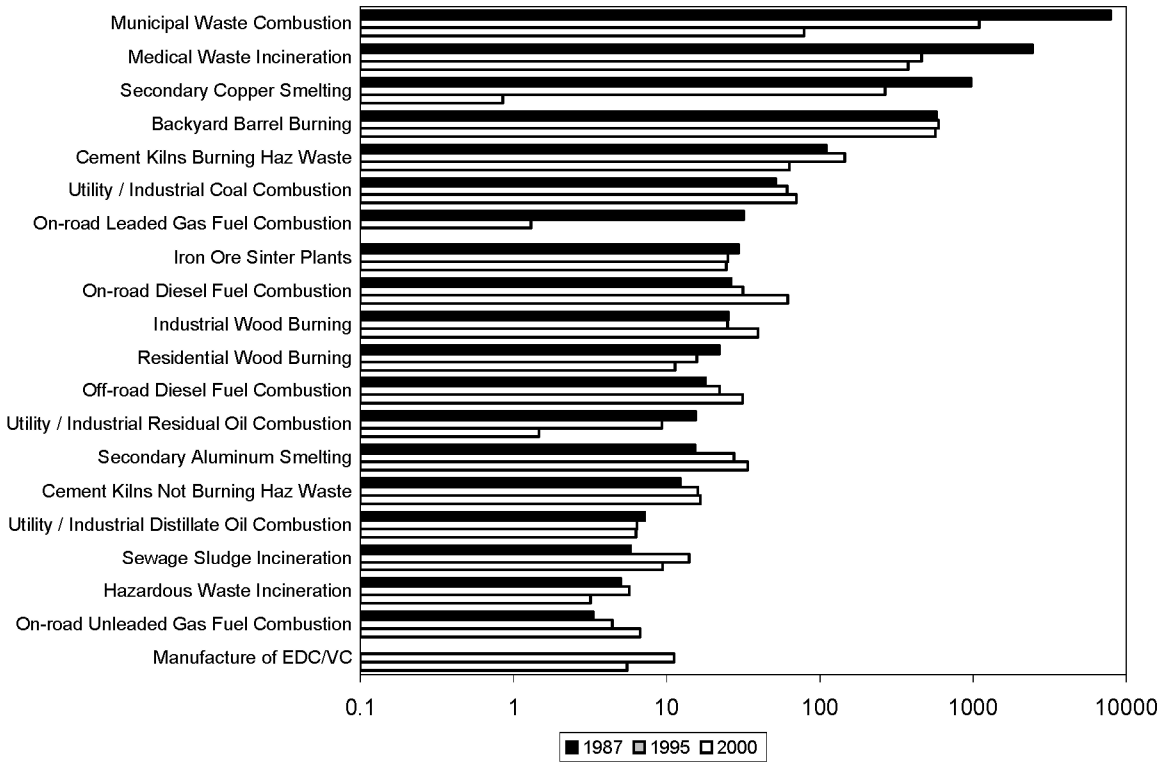
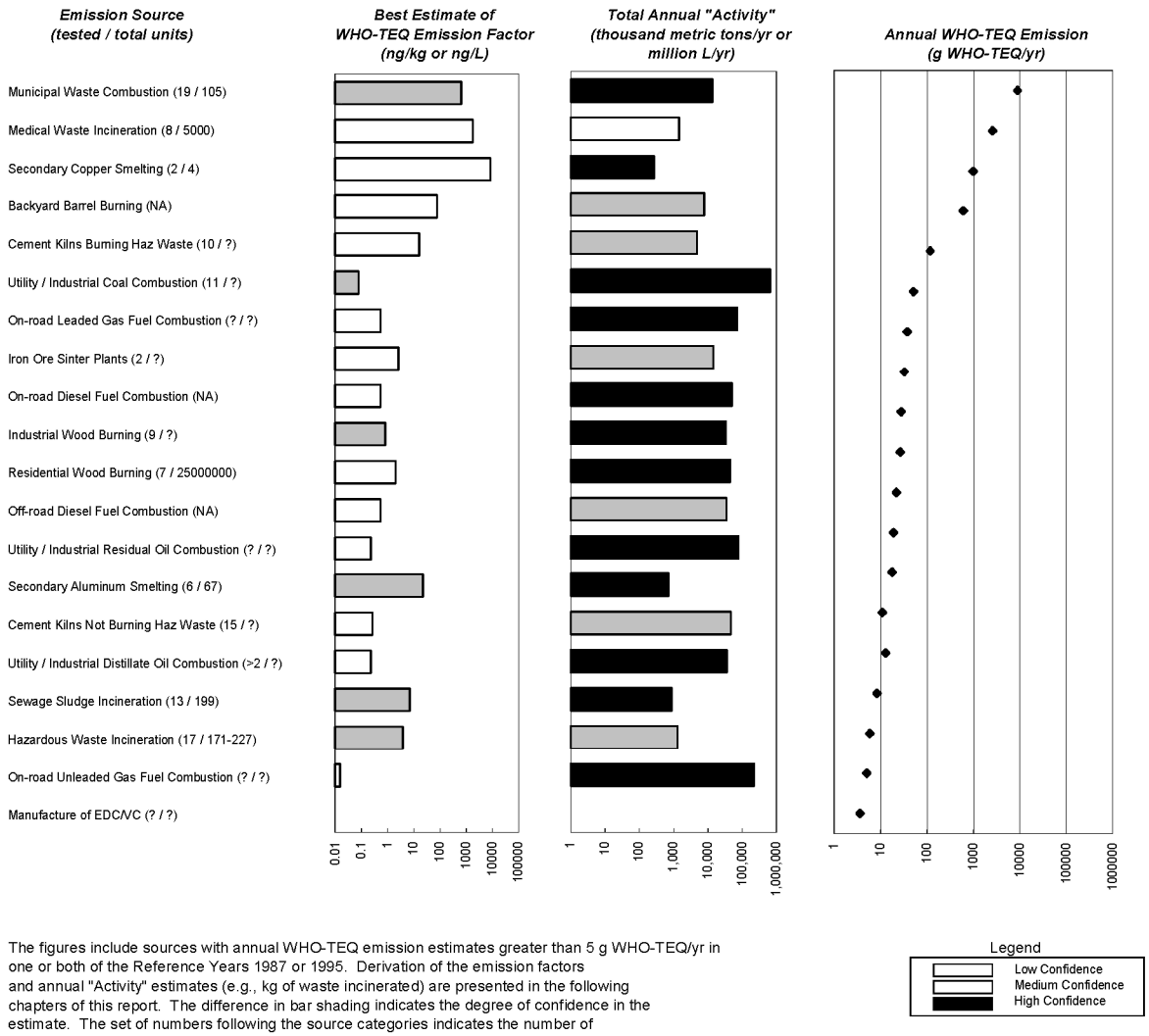


Figure 1-5. Comparison of estimates of annual I-TEQ emissions to air (g I-TEQ/yr) for reference years 1987, 1995, and 2000.

estimate for a class than in an estimate for any individual facility. Given the limited amount of data available for deriving emission factors and the limitations of our understanding about facility-specific conditions that determine formation and control of dioxin-like compounds, the current state of knowledge cannot support the development of emission factors that can be used to accurately estimate emissions on an individual facility-specific basis. The emission factors developed for each of the categories discussed in this national emissions inventory are listed in I-TEQ and TEQ_{DF}-WHO_{98} in Tables 1-14 and 1-15, respectively.

1.2.3. Confidence Ratings

Each source emission calculation required estimates of an emission factor and an activity level. For each emission source, the quantity and quality of the available information for both vary considerably. Consequently, it is important that emission estimates be accompanied by some indicator of the uncertainties associated with their development. For this reason, a



The figures include sources with annual WHO-TEQ emission estimates greater than 5 g WHO-TEQ/yr in one or both of the Reference Years 1987 or 1995. Derivation of the emission factors and annual "Activity" estimates (e.g., kg of waste incinerated) are presented in the following chapters of this report. The difference in bar shading indicates the degree of confidence in the estimate. The set of numbers following the source categories indicates the number of facilities/sites for which emission test data are available versus the number of facilities/sites in the category. A question mark (?) indicates that the precise number of facilities/sites could not be estimated.

Figure 1-6. Estimated CDD/CDF WHO-TEQ emissions to air from combustion sources in the United States for reference year 1987 (municipal solid waste incineration is currently referred to as municipal waste combustion).

qualitative confidence rating scheme was developed as an integral part of the emissions estimate with the following considerations.

Emission factor. The uncertainty in the emission factor estimate depends primarily on how well the tested facilities represent the untested facilities. In general, confidence in the emission factor increases with increases in the number of tested facilities relative to the total number of facilities. Variability in terms of physical design and operating conditions within a

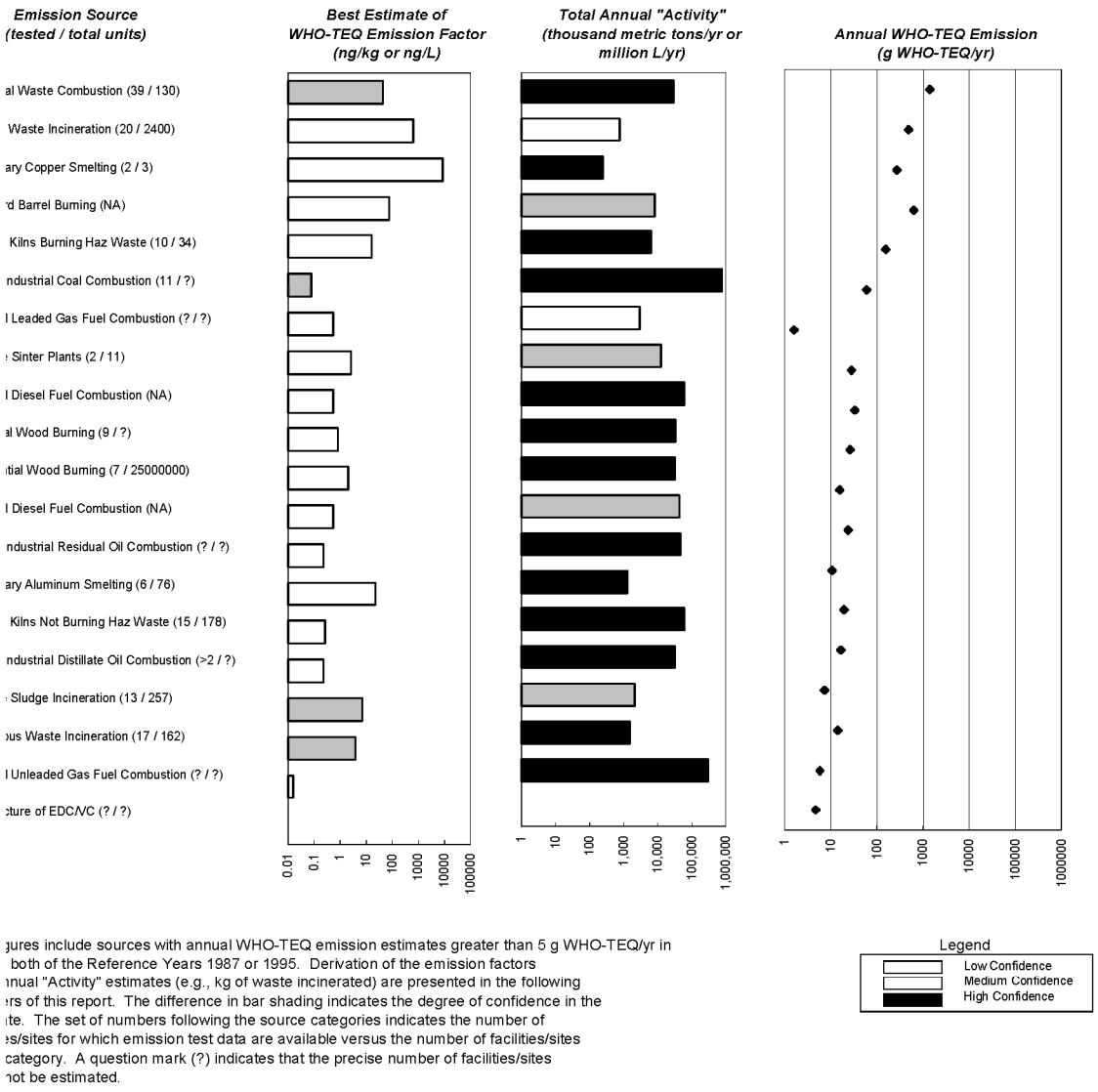
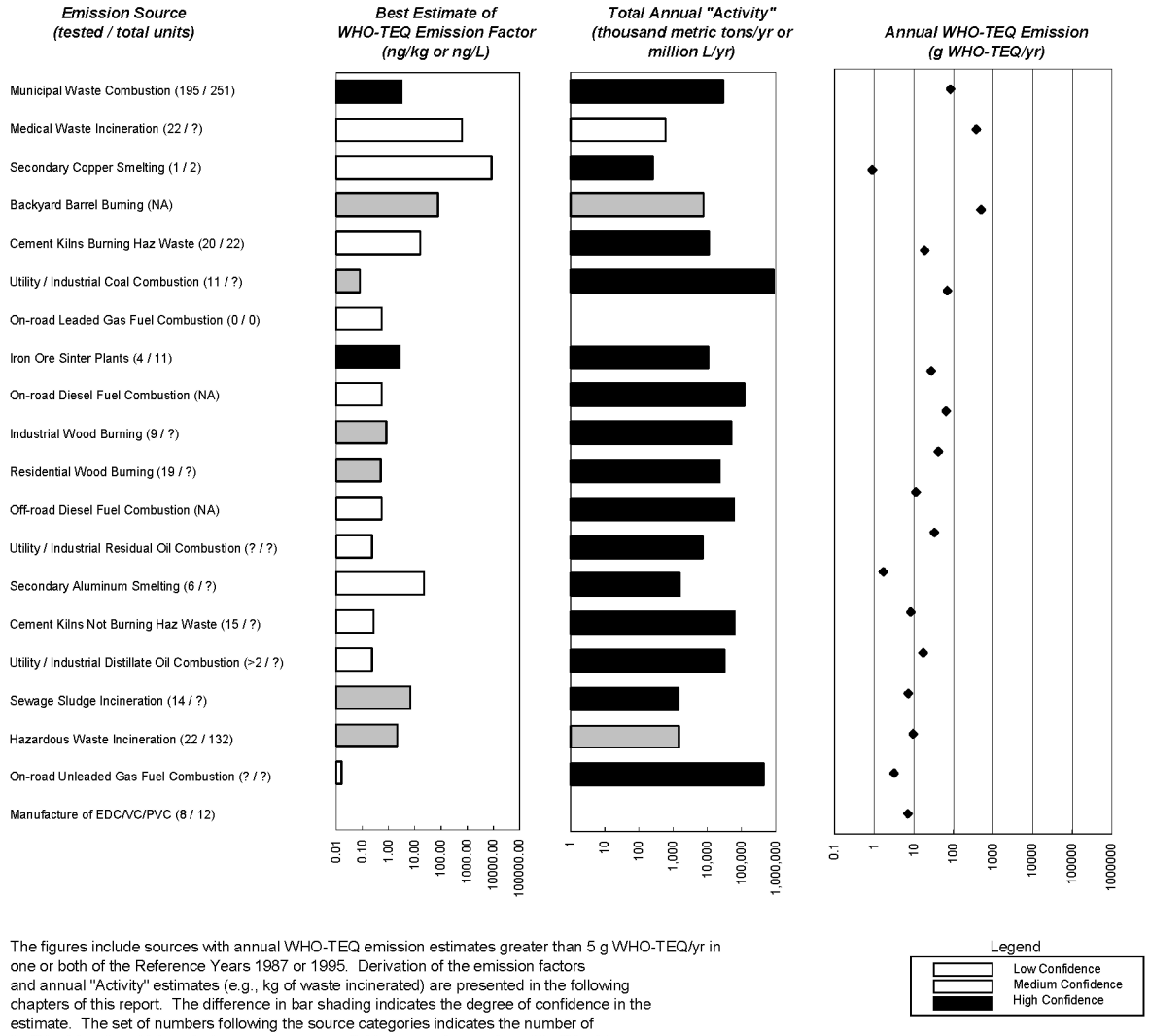


Figure 1-7. Estimated CDD/CDF WHO-TEQ emissions to air from combustion sources in the United States for reference year 1995.

class or subclass must also be considered. The more variability among facilities, the less confidence that a test of any single facility is representative of that class or subclass. The quality of the supporting documentation also affects uncertainty. Whenever possible, original engineering test reports were used. Peer-reviewed reports from the open literature were also used for developing some emission factors. In some cases, however, draft reports that had undergone more limited review were also used. In a few cases, unpublished references (such as personal communication with experts) were used and are clearly noted in the text.



The figures include sources with annual WHO-TEQ emission estimates greater than 5 g WHO-TEQ/yr in one or both of the Reference Years 1987 or 1995. Derivation of the emission factors and annual "Activity" estimates (e.g., kg of waste incinerated) are presented in the following chapters of this report. The difference in bar shading indicates the degree of confidence in the estimate. The set of numbers following the source categories indicates the number of facilities/sites for which emission test data are available versus the number of facilities/sites in the category. A question mark (?) indicates that the precise number of facilities/sites could not be estimated.

Figure 1-8. Estimated CDD/CDF WHO-TEQ emissions to air from combustion sources in the United States for reference year 2000.

Activity level. The uncertainty in the activity level estimate was judged primarily on the basis of the extent of the underlying data. Estimates derived from comprehensive surveys (including most facilities in a source category) were assigned high confidence. As the number of facilities in the survey relative to the total decreased, confidence also decreased. The quality of the supporting documentation also affects uncertainty. Peer-reviewed reports from the open literature (including government and trade association survey data) were considered to be the

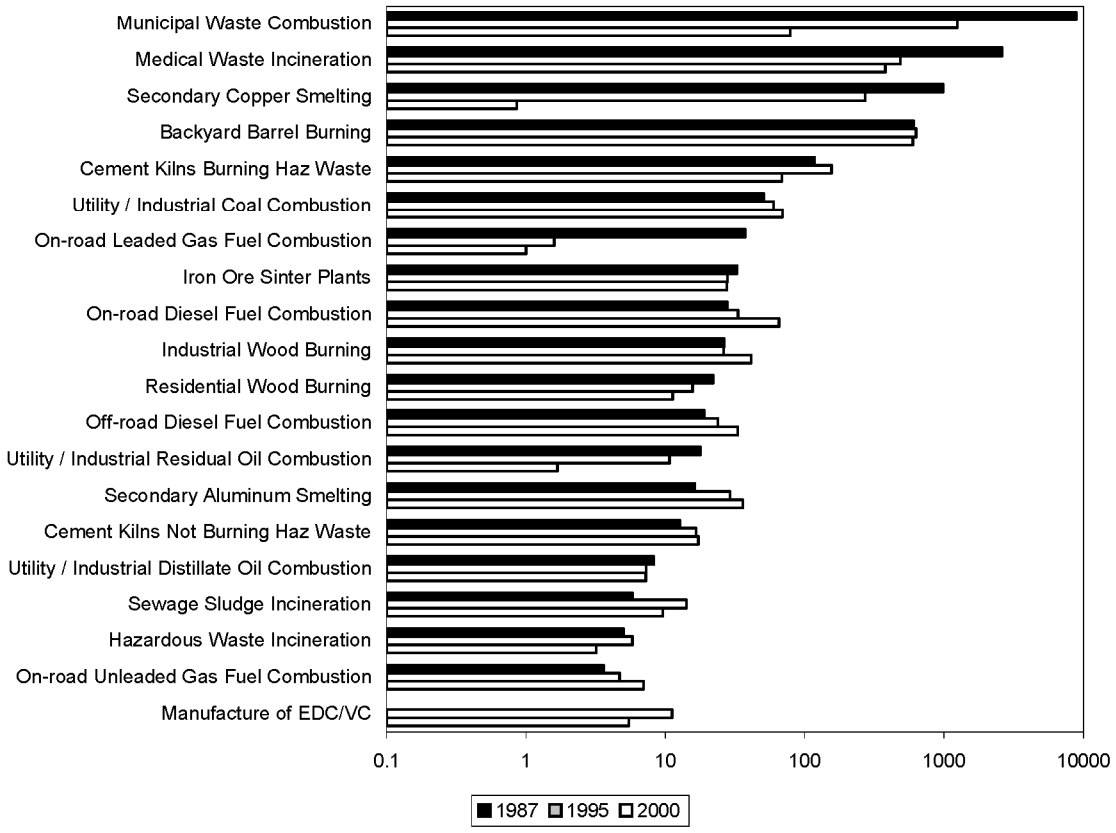


Figure 1-9. Comparison of estimates of annual WHO-TEQ emissions to air (g WHO-TEQ/yr) for reference years 1987, 1995, and 2000.

most reliable. However, as with the emission factor estimates, draft reports that had undergone more limited review were used in some cases, and in a few cases unpublished references such as personal communication with experts were used. These are clearly noted in the text.

1.2.3.1. *Rating Scheme*

The confidence rating scheme shown in Table 1-16 represents the qualitative criteria used to assign a high, medium, or low confidence rating to emission factors and activity levels for those source categories for which emission estimates could be reliably quantified. The overall confidence rating assigned to an emissions estimate was determined by the confidence ratings assigned to the corresponding activity level and emission factor. If the lowest rating assigned to either the activity level or the emission factor is "high," then the category rating assigned to the emission estimate is high (Category A). If the lowest rating assigned to either the activity level

Table 1-14. I-TEQ$_{DF}$ emission factors used to develop national emission inventory estimates of releases to air

Source category	I-TEQ$_{DF}$ emission factor			Emission factor unit
	2000	1995	1987	
WASTE INCINERATION				
Municipal waste combustion	2.82	38.2[a]	[a]	ng TEQ/kg waste combusted
Hazardous waste incineration	2.12	3.83	3.83	ng TEQ/kg waste combusted
Boilers/industrial furnaces	1.21	0.64	573 0.64	ng TEQ/kg waste combusted
Halogen acid furnaces	0.803			ng TEQ/kg waste feed
Medical waste/pathological incineration	[a]	[a]	[a]	ng TEQ/kg waste combusted
Crematoria - human		17,000		ng TEQ/body
- animal	630 410 0.11	598	1,706 17,000	ng TEQ/kg animal
Sewage sludge incineration	6.65	6.94	6.94	ng TEQ/kg dry sludge combusted
Tire combustion	0.282	0.282	0.282	ng TEQ/kg tires combusted
Pulp and paper mill sludge incinerators[b]				
POWER/ENERGY GENERATION				
Vehicle fuel combustion - leaded[c]	NA	45	45	pg TEQ/km driven
- unleaded	1.5	1.5	1.5	pg TEQ/km driven
- diesel	172	172	172	pg TEQ/km driven
Wood combustion - residential	0.5	2	2	ng TEQ/kg wood combusted
- industrial	0.56–13.2[d]	0.56–13.2[d]	0.56–13.2[d]	ng TEQ/kg wood combusted
Coal combustion - utility	0.079	0.079	0.079	ng TEQ/kg coal combusted
Oil combustion - industrial/utility	0.2	0.2	0.2	ng TEQ/L oil combusted
OTHER HIGH-TEMPERATURE SOURCES				
Cement kilns burning hazardous waste	1.444	1.04–28.58[e]	1.04–28.58[e]	ng TEQ/kg clinker produced
Lightweight aggregate kilns	2.06			ng TEQ/ kg waste feed
Cement kilns not burning hazardous waste	0.27	0.27	0.27	ng TEQ/kg clinker produced
Petroleum refining catalyst regeneration	1.52	1.52	1.52	ng TEQ/barrel reformer feed
Cigarette combustion	0.00043–0.0029	0.00043–0.0029	0.00043–0.0029	ng TEQ/cigarette
Carbon reactivation furnaces	1.2	1.2	1.2	ng TEQ/kg of reactivated carbon
Kraft recovery boilers	0.029	0.029	0.029	ng TEQ/kg solids combusted

Table 1-14. I-TEQ$_{DF}$ emission factors used to develop national emission inventory estimates of releases to air (continued)

Source category	I-TEQ$_{DF}$ emission factor			Emission factor unit
	2000	1995	1987	
MINIMALLY CONTROLLED OR UNCONTROLLED COMBUSTION				
Backyard barrel burning[f]	72.8	72.8	72.8	ng TEQ/kg waste combusted
METALLURGICAL PROCESSES				
Ferrous metal smelting/refining - sintering plants	0.55–4.14	0.55–4.14	0.55–4.14	ng TEQ/kg sinter
Nonferrous metal smelting/refining				
- primary copper	<0.31	<0.31	<0.31	ng TEQ/kg copper produced
- secondary aluminum smelting	4.9	4.9	4.9	ng TEQ/kg scrap feed
- secondary copper smelting[g]				ng TEQ/kg scrap consumed
- secondary lead smelters	0.05–8.31	0.05–8.31	0.05–8.31	ng TEQ/kg lead produced
Drum and barrel reclamation	16.5	16.5	16.5	ng TEQ/drum
CHEMICAL MANUFACTURING/PROCESSING SOURCES				
Ethylene dichloride/vinyl chloride		0.95[a]		ng TEQ/kg EDC produced

[a]Different emission factors were derived for various subcategories within this industry; the value listed is a weighted average.
[b]Included in total for wood combustion, industrial.
[c]Leaded fuel production and the manufacture of motor vehicle engines requiring leaded fuel for highway use are prohibited in the United States. (See Chapter 4, Section 4.1, for details.)
[d]Emission factor of 0.56 ng I-TEQ$_{DF}$/kg used for nonsalt-laden wood; emission factor of 13.2 ng I-TEQ$_{DF}$/kg used for salt-laden wood.
[e]Emission factor of 1.04 ng I-TEQ$_{DF}$/kg used for kilns with air pollution control device (APCD) inlet temperatures less than 232°C; emission factor of 28.58 ng I-TEQ$_{DF}$/kg used for kilns with APCD inlet temperatures greater than 232°C.
[f]Includes the burning of brush and leaf residential yard waste.
[g]Facility-specific emission factors were used ranging from 3.6 to 16,600 ng I-TEQ$_{DF}$/kg scrap consumed.

Table 1-15. TEQ_{DF}-WHO_{98} emission factors used to develop national emission inventory estimates of releases to air

Emission source category	TEQ_{DF}-WHO_{98} emission factor			Emission factor unit
	2000	1995	1987	
WASTE INCINERATION				
Municipal waste combustion	3.10	[a]	[a]	ng TEQ/kg waste combusted
Hazardous waste incineration	2.13	3.88	3.88	ng TEQ/kg waste combusted
Boilers/industrial furnaces	1.21	43.4 0.65	644 0.65	ng TEQ/kg waste combusted
Halogen acid furnaces	0.836			ng TEQ/kg waste feed
Medical waste/pathological incineration	[a]	[a]	[a]	ng TEQ/kg waste combusted
Crematoria - human[b]	630 434	17,000 633	1,811 17,000	ng TEQ/body
- animal	0.12			ng TEQ/kg animal
Sewage sludge incineration	6.74	7.04	7.04	ng TEQ/kg dry sludge combusted
Tire combustion	0.281	0.281	0.281	ng TEQ/kg tires combusted
Pulp and paper mill sludge incinerators[c]				
POWER/ENERGY GENERATION				
Vehicle fuel combustion - leaded[d]	NA	53	53	pg TEQ/km driven
- unleaded	1.6	1.6	1.6	pg TEQ/km driven
- diesel	182	182	182	pg TEQ/km driven
Wood combustion - residential	[b]	[b]	[b]	ng TEQ/kg wood combusted
- industrial[e]	0.6–13.2	0.6–13.2	0.6–13.2	ng TEQ/kg wood combusted
Coal combustion - utility	0.5 0.78	2 0.078	2 0.078	ng TEQ/kg coal combusted
Oil combustion - industrial/utility	0.23	0.23	0.23	ng TEQ/L oil combusted
OTHER HIGH-TEMPERATURE SOURCES				
Cement kilns burning hazardous waste	1.635	1.11–30.7[f]	1.11–30.7[f]	ng TEQ/kg clinker produced
Lightweight aggregate kilns	1.99			ng TEQ/ kg waste feed
Cement kilns not burning hazardous waste	0.26	0.26	0.26	ng TEQ/kg clinker produced
Petroleum refining catalyst regeneration	1.59	1.59	1.59	ng TEQ/barrel reformer feed
Cigarette combustion	0.00044–0.003	0.00044–0.003	0.00044–0.003	ng TEQ/cigarette
Carbon reactivation furnaces	1.2[b]	1.2[b]	1.2[b]	ng TEQ/kg of reactivated carbon
Kraft recovery boilers	0.028	0.028	0.028	ng TEQ/kg solids combusted

Table 1-15. TEQ_{DF}-WHO_{98} emission factors used to develop national emission inventory estimates of releases to air (continued)

Emission source category	TEQ_{DF}-WHO_{98} emission factor			Emission factor unit
	2000	1995	1987	
MINIMALLY CONTROLLED OR UNCONTROLLED COMBUSTION				
Backyard barrel burning[g]	76.8[b]	76.8[b]	76.8[b]	ng TEQ/kg waste combusted
METALLURGICAL PROCESSES				
Ferrous metal smelting/refining - sintering plants	0.62–4.61	0.62–4.61	0.62–4.61	ng TEQ/kg sinter
Nonferrous metal smelting/refining				
- primary copper[b]	<0.31	<0.31	<0.31	ng TEQ/kg copper produced
- secondary aluminum smelting	5.2	5.2	5.2	ng TEQ/kg scrap feed
- secondary copper smelting[h]				ng TEQ/kg scrap consumed
- secondary lead smelters	0.05–8.81	0.05–8.81	0.05–8.81	ng TEQ/kg lead produced
Drum and barrel reclamation	17.5	17.5	17.5	ng TEQ/drum
CHEMICAL MANUFACTURING/PROCESSING SOURCES				
Ethylene dichloride/vinyl chloride		0.95[a, b]		ng TEQ/kg EDC produced

[a]Different emission factors were derived for various subcategories within this industry; the value listed is a weighted average.
[b]Congener-specific data were not available; the TEQ_{DF} emission factor was used as a surrogate for the TEQ_{DF}-WHO_{98} emission factor.
[c]Included in total for wood combustion, industrial.
[d]Leaded fuel production and the manufacture of motor vehicle engines requiring leaded fuel for highway use are prohibited in the United States. (See Chapter 4, Section 4.1, for details).
[e]Emission factor of 0.6 ng I-TEQ_{DF}/kg used for non-salt-laden wood; emission factor of 13.2 ng I-TEQ_{DF}/kg used for salt-laden wood.
[f]Emission factor of 1.11 ng I-TEQ_{DF}/kg used for kilns with air pollution control device (APCD) inlet temperatures less than 232°C; emission factor of 28.58 ng I-TEQ_{DF}/kg used for kilns with APCD inlet temperatures greater than 232°C.
[g]This term refers to the burning of residential waste in barrels.
[h]Facility-specific emission factors were used ranging from 3.6 to 16,600 ng TEQ_{DF}-WHO_{98}/kg scrap consumed.

Table 1-16. Confidence rating scheme for U.S. emission estimates

Confidence rating	Activity level estimate	Emission factor estimate
Categories/media for which releases can be reasonably quantified		
High	Derived from comprehensive survey	Derived from comprehensive survey
Medium	Based on estimates of average plant activity level and number of plants or limited survey	Derived from testing at a limited but reasonable number of facilities believed to be representative of source category
Low	Based on data judged possibly nonrepresentative	Derived from testing at only a few, possibly nonrepresentative facilities or from similar source categories
Categories/media for which releases cannot be reasonably quantified		
Preliminary estimate	Based on extremely limited data, judged to be clearly nonrepresentative	Based on extremely limited data, judged to be clearly nonrepresentative
Not quantified	No data available	(1) Argument based on theory but no data, or (2) Data available indicating formation but not in a form that allows developing an emission factor

or the emission factor term is "medium," then the category rating assigned to the emission estimate is medium (Category B). If the lowest rating assigned to either the activity level or the emission factor is "low," then the category rating assigned to the emission estimate is low (Category C). It is emphasized that this confidence rating scheme should not be interpreted as a statistical measure, but rather as subjective judgment of the relative uncertainty among sources.

For many source categories, either emission factor information or activity level information was inadequate to support development of reliable quantitative release estimates for one or more media. For some of these source categories, sufficient information was available to make preliminary estimates of emissions of CDDs/CDFs or dioxin-like PCBs; however, the confidence in the activity level estimates or emission factor estimates was so low that they could not be included in the sum of quantified emissions from sources with confidence ratings of A, B, and C. These preliminary estimates were given an overall confidence rating of D. The preliminary release estimates for sources with a confidence rating of D are given in the right-most column of Table 1-12. Because these are order-of-magnitude estimates, they are made for 2000 only. As preliminary estimates of source magnitude, they can be used to help prioritize

future research and data collection. The actual magnitude of emissions from these sources could be significantly lower or higher than these preliminary estimates. Although EPA has chosen not to include them in the more thoroughly characterized emissions of the national inventory, some of these poorly characterized sources have the potential of being major contributors of releases to the environment. It is important to present these estimates because they may help determine priorities for future data collection efforts. As the uncertainty around these sources is reduced, they will be included in future inventory calculations.

For other sources, some information exists that suggests that they may release dioxin-like compounds; however, the available data were judged to be insufficient for developing any quantitative emissions estimate. These source categories were assigned a confidence rating of E and also were not included in the national inventory (see the "Not quantifiable" column in Table 1-11).

1.3. CONCLUSIONS

1.3.1. Total Environmental Releases

Nationwide emission estimates of grams I-TEQ_{DF} and TEQ_{DF}-WHO_{98} released to the open and circulating environment of the United States are presented in Table 1-12. For the year 2000, EPA draws the following conclusions:

- The total releases in the inventory (Categories A, B, and C) were 1,422 g TEQ_{DF}-WHO_{98}/yr. These were dominated by releases to the air (92%). Most of the air releases were from combustion sources. Table 1-17 presents a ranking of sources for 2000, 1995, and 1987 based on the magnitude of environmental release. The top three sources were backyard barrel burning of refuse (498.5 g, 32% of total), MWIs (378 g, 27%), and the incineration and land application of municipal wastewater treatment sludge (89.7 g, 5%).

- There is a significant potential for release of dioxin-like compounds from Category D sources. However, these sources a currently poorly characterized. The most important Category D sources are forest fires and accidental fires at MSW landfills. Research is recommended to confirm emissions from these sources and to provide a more accurate assessment of releases.

- A total of 18 contemporary formation sources were classified as Category E. Information suggests these may be sources of dioxin-like compounds, but it is insufficient to make a national estimate of releases. Additional research on these sources is recommended in order to adequately identify them as actual sources and to provide data for estimating releases.

Table 1-17. Ranking of sources of dioxin-like compounds based on environmental releases (from high to low) for reference years 2000, 1995, and 1987

2000			1995			1987		
Source (released to)	**Releases (grams)**	**Percent of total**	**Source (released to)**	**Releases (grams)**	**Percent of total**	**Source (released to)**	**Releases (grams)**	**Percent of total**
Backyard barrel burning of refuse (air)	498.5	35.1	Municipal waste combustion (air)	1,393.5	40.5	Municipal waste combustion (air)	8,905.1	63.8
Medical waste/pathological incineration (air)	378.0	26.6	Backyard barrel burning of refuse (air)	628.0	18.2	Medical waste/ pathological incineration (air)	2,570.0	18.4
Municipal wastewater treatment sludge, land application and incineration (land, air)	89.7	6.3	Medical waste/pathological incineration (air)	487.0	14.1	Secondary copper smelters (air)	983.0	7.0
Municipal waste combustion (air)	83.8	5.9	Secondary copper smelters (air)	271.0	7.9	Backyard barrel burning of refuse (air)	604.0	4.3
Coal fired-utility boilers (air)	69.5	4.9	Cement kilns burning hazardous waste (air)	156.1	4.5	Bleached chemical wood pulp and paper mills (land, water)	370.1	2.7
Diesel heavy-duty trucks (air)	65.4	4.6	Municipal wastewater treatment sludge, land application and incineration (land and air)	133.3	3.9	Cement kilns burning hazardous waste (air)	117.8	0.8
Industrial wood combustion (air)	41.5	2.9	Coal fired-utility boilers (air)	60.1	1.7	Municipal wastewater treatment sludge, land application and incineration (air, land)	85.0	0.6
Diesel off-road equipment, ships, trains, tractors (air)	33.1	2.3	Ethylene dichloride/vinyl chloride production (land, air, water)	35.7	1.0	Coal fired-utility boilers (air)	50.9	0.4

Table 1-17. Ranking of sources of dioxin-like compounds based on environmental releases (from high to low) for reference years 2000, 1995, and 1987 (continued)

2000			1995			1987		
Source (released to)	Releases (grams)	Percent of total	Source (released to)	Releases (grams)	Percent of total	Source (released to)	Releases (grams)	Percent of total
Ethylene dichloride/ vinyl chloride production (water, land, air)	30.0	2.1	Diesel heavy-duty trucks (air)	33.3	1.0	Automobiles using leaded gasoline (air)	37.5	0.3
Sintering plants (air)	27.6	1.9	Bleached chemical wood pulp and paper mills (land, water)	30.0	0.9	2,4-Dichlorophenoxy acetic acid (land)	33.4	0.2
Cement kilns burning hazardous waste (air)	18.8	1.3	2,4-Dichlorophenoxy acetic acid (land)	28.9	0.8	Sintering plants (air)	32.7	0.2
Cement kilns burning nonhazardous waste (air)	17.2	1.2	Sintering plants (air)	28.0	0.8	Diesel heavy-duty trucks (air)	27.8	0.2
Residential wood combustion (air)	11.3	0.8	Industrial wood combustion (air)	26.2	0.8	Industrial wood combustion (air)	26.5	0.2
Secondary aluminum smelting (air)	8.3	0.6	Diesel off-road equipment: ships, trains, tractors (air)	23.8	0.7	Residential wood combustion (air)	22.0	0.2
Industrial/utility oil combustion, distillate oil (air)	7.3	0.5	Secondary aluminum smelters (air)	19.5	0.6	Diesel off-road equipment: ships, trains, tractors (air)	19.0	0.2
Automobiles using unleaded gasoline (air)	7.0	0.5	Cement kilns burning nonhazardous waste (air)	16.6	0.5	Industrial/utility oil combustion, residual oil (air)	17.8	0.1
Residential heating, distillate oil (air)	4.5	0.3	Residential wood combustion (air)	15.7	0.5	Cement kilns burning nonhazardous waste (air)	12.7	0.1
Primary magnesium production (air)	4.3	0.3	Industrial/utility oil combustion, residual oil (air)	10.7	0.3	Secondary aluminum smelting (air)	10.9	0.1

Table 1-17. Ranking of sources of dioxin-like compounds based on environmental releases (from high to low) for reference years 2000, 1995, and 1987 (continued)

2000			1995			1987		
Source (released to)	Releases (grams)	Percent of total	Source (released to)	Releases (grams)	Percent of total	Source (released to)	Releases (grams)	Percent of total
Chlor alkali facilities (air, water)	3.6	0.3	Industrial/utility oil combustion, distillate oil (air)	7.3	0.2	Industrial/utility oil combustion, distillate oil (air)	8.3	0.1
Hazardous waste incineration (air)	3.2	0.2	Hazardous waste incineration (air)	5.8	0.2	Residential heating, distillate oil (air)	5.4	0.1
Institutional/commercial heating, distillate oil (air)	2.9	0.2	Residential heating, distillate oil (air)	5.0	0.1	Hazardous waste incineration (air)	5.0	0.04
Secondary lead smelting (air)	2.5	0.2	Automobiles using unleaded gasoline (air)	4.7	0.1	Institutional/commercial heating, distillate oil (air)	3.7	0.03
Petroleum refining catalyst regeneration (air)	2.2	0.2	Primary magnesium production (air)	4.1	0.1	Automobiles using unleaded gasoline (air)	3.6	0.03
Lightweight aggregate kilns burning hazardous waste (air)	1.9	0.1	Chlor-alkali facilities (air, water)	3.6	0.1	Lightweight aggregate kilns burning hazardous waste (air)	3.3	0.02
Boilers/industrial furnaces (air)	1.8	0.1	Institutional/commercial heating, distillate oil (air)	3.1	0.1	Petroleum refining catalyst regeneration (air)	2.2	0.02
Industrial/utility oil combustion, residual oil (air)	1.7	0.1	Lightweight aggregate kilns burning hazardous waste (air)	2.4	0.1	Kraft recovery boilers (air)	2.0	0.01
Bleached chemical wood pulp and paper mills (land, water)	1.1	0.1	Kraft recovery boilers (air)	2.3	0.1	Industrial/utility oil combustion, residual oil (air)	1.5	0.01
Secondary copper smelting (air)	0.9	0.1	Petroleum refining catalyst regeneration (air)	2.2	0.1	Secondary lead smelting (air)	1.3	0.01

Table 1-17. Ranking of sources of dioxin-like compounds based on environmental releases (from high to low) for reference years 2000, 1995, and 1987 (continued)

2000			1995			1987		
Source (released to)	Releases (grams)	Percent of total	Source (released to)	Releases (grams)	Percent of total	Source (released to)	Releases (grams)	Percent of total
Kraft recovery boilers (air)	0.8	0.1	Secondary lead smelting (air)	1.7	0.05	Cigarette combustion (air)	1.0	0.01
Institutional/commercial heating, residual oil (air)	0.7	0.05	Automobiles using leaded gasoline (air)	1.6	0.05	Boilers/industrial furnaces (air)	0.8	0.01
Drum and barrel reclamation (air)	0.6	0.04	Industrial/utility oil combustion, residual oil (air)	0.8	0.02	Primary copper smelting (air)	0.5	<0.01
Tire incineration (air)	0.5	0.04	Cigarette combustion (air)	0.8	0.02	Crematoria, human (air)	0.2	<0.01
Cigarette combustion (air)	0.4	0.03	Primary copper smelting (air)	0.5	0.01	Carbon reactivation furnaces (air)	0.1	<0.01
Unleaded gasoline off-road equipment (air)	0.4	0.03	Boilers/industrial furnaces (air)	0.4	0.01	Tire incineration (air)	0.1	<0.01
Halogen acid furnaces (air)	0.3	0.02	Crematoria, human (air)	0.2	0.01	Drum and barrel reclamation (air)	0.1	<0.01
Primary copper smelting (air)	0.3	0.02	Tire incineration (air)	0.1	<0.01			
Crematoria, human (air)	0.3	0.02	Carbon reactivation furnaces (air)	0.1	<0.01			
Carbon reactivation furnaces (air)	0.1	0.01	Drum and barrel reclamation (air)	0.1	<0.01			
Automobiles using leaded gasoline (air)	0	0.00						
TOTAL	1,422.0	100		3,444.2	100		13,965.3	100

- Releases from reservoir sources could significantly add to the inventory. However, environmental reservoirs as sources of the redistribution of previously formed dioxins into the open and circulating environment are currently poorly understood and poorly characterized. This report suggests that urban runoff to surface water and rural soil erosion to surface water can be significant reservoir sources. Releases from reservoirs (air, sediment, water, and biota) could not be reliably quantified, given the lack of information in this area.

- The amount of dioxin-like PCBs released from man-made sources remains poorly characterized. Only a total of 19.5, 78.5, and 51.5 g of PCB TEQ could be quantified for the years 2000, 1995, and 1987, respectively. To date, only sewage sludge has been adequately characterized in terms of the amount of dioxin-like PCBs that may be released from a source.

1.3.2. Time Trends

A significant reduction in total CDD/CDF environmental releases has occurred since 1987. EPA's best estimates of releases of CDDs/CDFs to air, water, and land from reasonably quantifiable sources (Categories A, B, and C) are approximately 1,422 g TEQ_{DF}-WHO_{98} in reference year 2000; 3,444.2 g in reference year 1995; and 13,965.3 g in reference year 1987. From 1987 to 2000 there was an approximately 90% reduction in releases to all media. Most of the reduction in dioxin releases (75%) occurred between 1987 and 1995.

In 1987 and 1995, municipal waste combustion was the leading source of dioxin emissions to the U.S. environment; however, because of reductions in dioxin emissions from MWCs, it dropped to the fourth ranked source in 2000. Burning of domestic refuse in backyard burn barrels remained fairly constant over the years, but in 2000 it emerged as the largest source of dioxin emissions.

Reductions in environmental releases of dioxin-like compounds are attributed primarily to reductions in air emissions from MWCs, MWIs, and cement kilns burning hazardous waste, and in wastewater discharged into surface waters from pulp and paper mills using chlorine. These reductions have occurred from a combination of regulatory activities (see Section 1.1.2), improved emission controls, improved industrial technologies, voluntary actions on the part of industry, and the closing of a number of antiquated facilities.

1.3.3. Sources Not Included in the Inventory

Significant amounts of the dioxin-like compounds produced annually in the United States are not considered releases to the open and circulating environment and are not included in the national inventory. Examples include dioxin-like compounds generated internal to a process but destroyed before release and waste streams that are disposed of in approved landfills.

The only product judged to have the potential for environmental release—and therefore considered for the inventory—was the herbicide 2,4-D. Release estimates are provided for 1987 and 1995. Since 1995, the chemical manufacturers of 2,4-D have been undertaking voluntary actions to significantly reduce the dioxin content of the product. No information is available on the extent of these reductions and, therefore, no release estimate could be made for 2000. Regarding other products, data are presented on the amounts of CDDs/CDFs contained in bleached pulp, ethylene dichloride/vinyl chloride, PCP-treated wood, and dioxazine dyes and pigments. None of these products, however, was considered to have release potential; they were not included in the inventory.

A number of contemporary formation sources were classified as D or E and therefore were not included in the inventory. The largest contemporary formation Category D sources are forest fires and accidental fires at MSW landfills. Taken together, these sources have the potential to significantly increase the present inventory if preliminary release estimates are confirmed.

The possibility remains that truly undiscovered sources exist. Many of the sources that are well-accepted today were discovered only in the past 20 years. For example, CDDs/CDFs in stack emissions from MWCs were not detected until the late 1970s; CDDs/CDFs in the wastewater effluent from bleached pulp and paper mills were found unexpectedly in the mid-1980s; iron ore was not recognized as a source until the early 1990s.

1.3.4. Formation Theory

Current theory proposes that CDDs/CDFs are formed within the cool-down region of combustion processes, either *de novo* or from dioxin precursors. *De novo* synthesis involves solid-phase reactions with carbon, chlorine, and oxygen on combustion-generated particles promoted by copper chloride as a catalyst. A less efficient but plausible formation process is the gas-phase formation from precursors catalyzed by the presence of a transition metal such as copper chloride. The ideal temperatures for *de novo* dioxin formation are between 200 and 400°C. Reducing temperatures to below 200°C, especially at the air pollution control device, will minimize dioxin formation and releases from combustion sources. Chlorine sources present in feeds are necessary for dioxin formation. Experiments suggest that a chlorine content of 1% in the feed/fuel is the threshold for a direct relationship to dioxin formation from combustion sources, i.e., a chlorine content $\geq 1\%$ is strongly correlated to the amount of dioxin formed, but a chlorine content $<1\%$ is not. However, in well-designed, well-controlled, and well-operated full-scale combustion systems there does not appear to be a direct relationship between the amount of chlorine present in the waste and the amount of dioxin emissions from the stack.

Controversy exists regarding the role of PVC in the formation of CDDs/CDFs during municipal waste combustion. Experimental evidence suggests that PVC combustion generates hydrogen chloride gas (HCl) and dioxin precursors such as chlorobenzenes and chlorophenols, both of which may contribute to dioxin formation. HCl is a progenitor of chlorine radicals that then participate in the dioxin formation chemistry. Precursors are foundation molecules to dioxin formation. If PVC is the only source of chlorine and dioxin precursors during the combustion of MSW, then the removal of PVC may reduce the amount of dioxin formed and emitted. However, the complex mixture of materials in MSW provides sufficient chlorine for *de novo* synthesis, and dioxin precursors are formed as products of the incomplete combustion of the waste constituents. Therefore, the elimination of PVC from the waste prior to combustion would not necessarily eliminate the formation and emissions of CDDs/CDFs from municipal waste combustion.

Current information strongly suggests that releases of CDDs/CDFs to the U.S. environment occur principally from anthropogenic activities. However, scientific studies have identified the possibility of natural formation of some CDDs/CDFs (e.g., in ball clay).

1.3.5. Congener Profiles of CDD/CDF Sources

This document presents congener profiles for a number of sources, as shown in Figure 1-10. These profiles show the relative amounts of CDD/CDF congeners in environmental releases. These profiles can be useful for (1) identifying source contributions to near-field air measurements of CDDs/CDFs, (2) comparing sources, and (3) providing insights into the formation of CDDs/CDFs in the releases. There are numerous procedures for deriving a congener profile, and there is no single agreed-upon convention (Cleverly et al., 1997; Lorber et al., 1996; Hagenmaier et al., 1994).

For this report, congener profiles were developed primarily by calculating the ratio of specific 2,3,7,8-substituted CDDs/CDFs in the emissions or product to the total (Cl_4 - Cl_8) CDDs/CDFs. With respect to combustion sources, the profiles were derived by dividing the congener-specific emission factors by the total (Cl_4 - Cl_8) CDD/CDF emission factor for each tested facility and then averaging the congener profiles developed for all tested facilities within the combustor type. For chemical processes and commercial chemicals, CDD/CDF profiles were typically generated by dividing average congener concentrations (ppt) in the chemical by the total CDDs/CDFs present. Profiles for select source categories are presented in Figure 1-10.

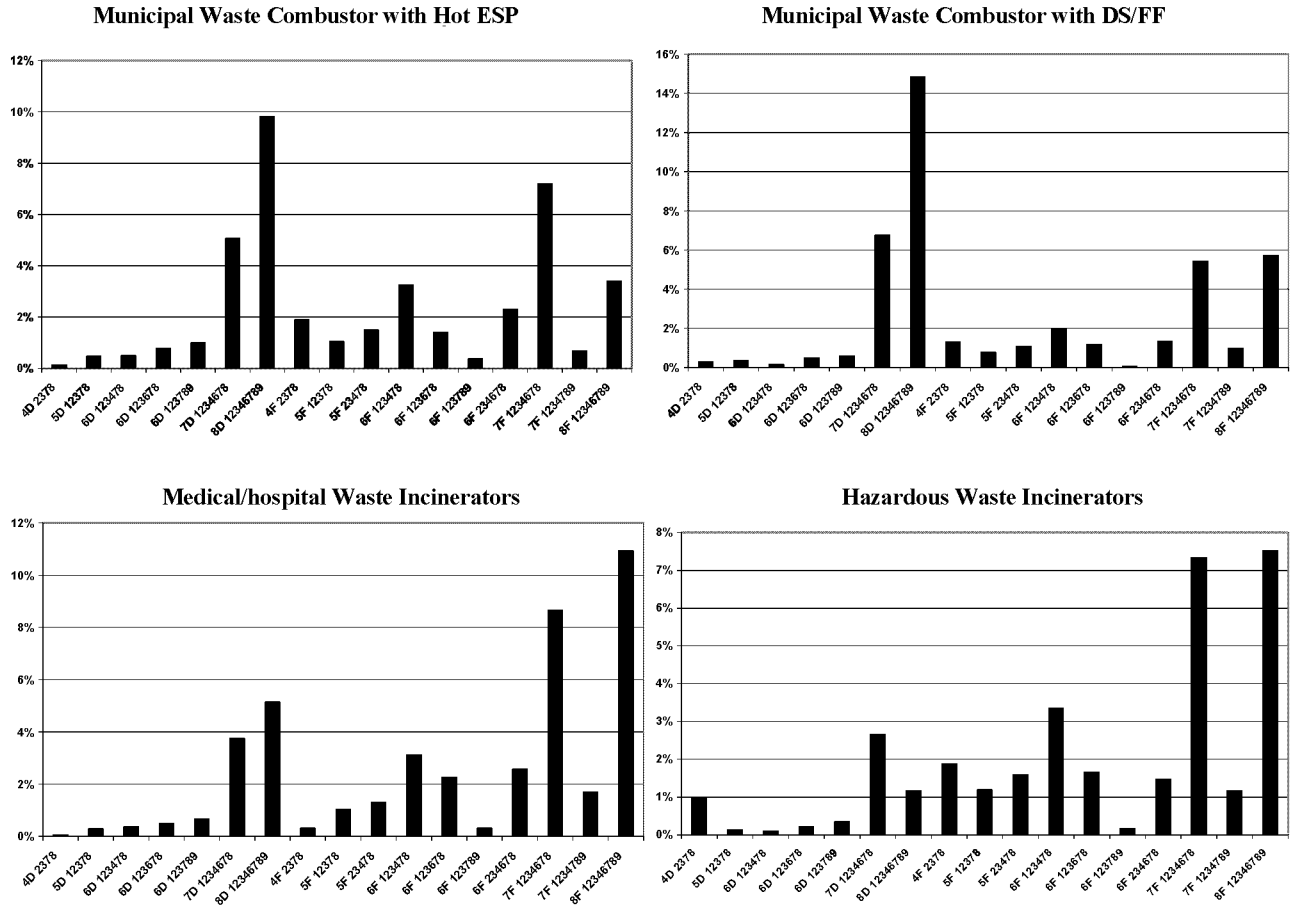


Figure 1-10. Congener profiles (as percent distributions to the sum of CDDs and CDFs) of anthropogenic sources of chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans in the United States.

On the basis of inspection and comparisons of the average CDD/CDF congener profiles across combustion and noncombustion sources, the following observations were made (Cleverly et al., 1997) (these generalizations are derived from this data set, and their application beyond these data is uncertain):

- It appears that combustion sources emit all 2,3,7,8-substituted CDDs/CDFs, although in varying percentages of total CDDs/CDFs.

- In combustion source emissions, 2,3,7,8-TCDD is usually 0.1 to 1% of total CDDs/CDFs. The exception is stack emissions from industrial oil-fired boilers, where the available but limited data indicate that 2,3,7,8-TCDD constitutes an average of 7% of total CDD/CDF emissions.

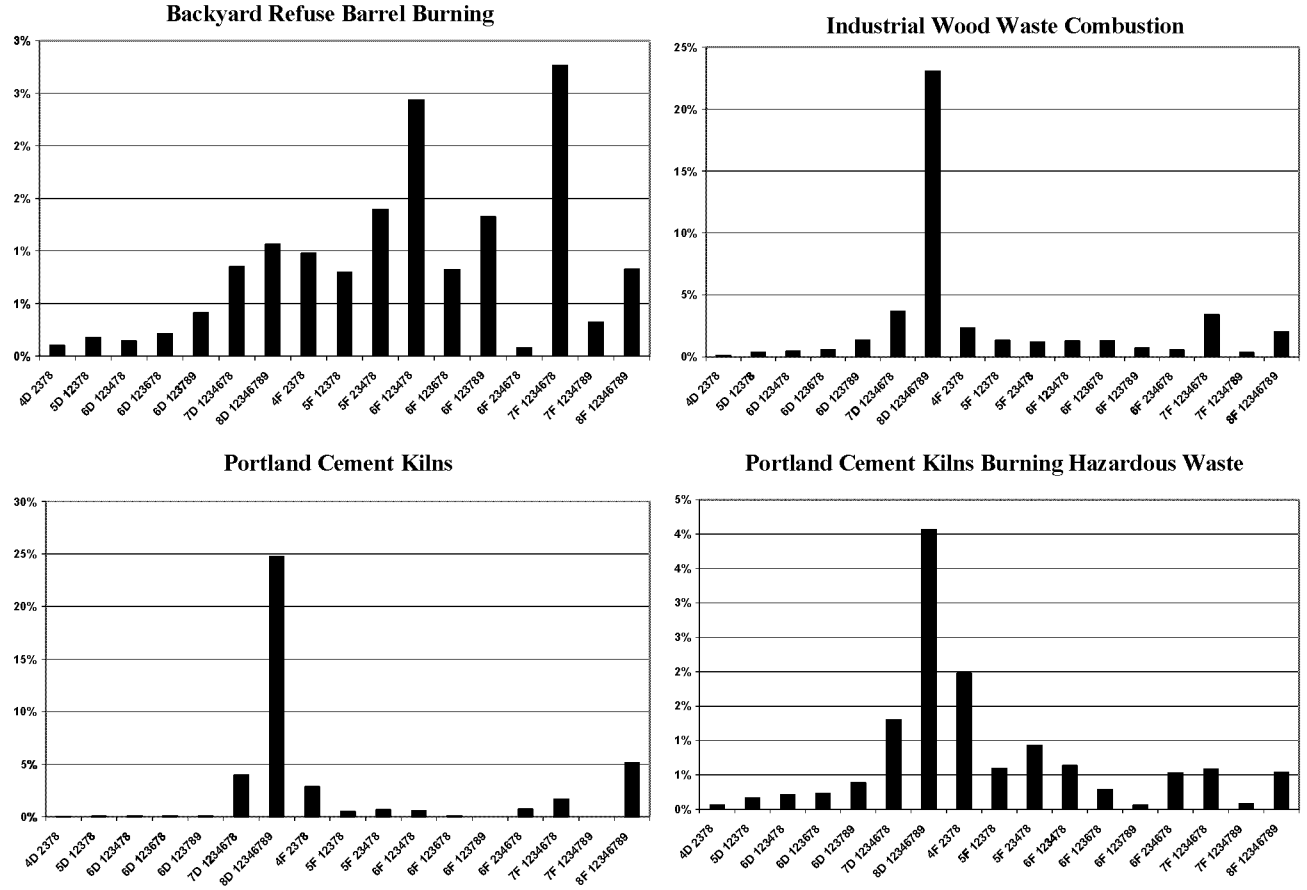


Figure 1-10. Congener profiles (as percent distributions to the sum of CDDs and CDFs) of anthropogenic sources of chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans in the United States (continued).

- It cannot be concluded that OCDD is the dominant congener for all combustion-generated emissions of CDDs/CDFs. OCDD dominates total emissions from mass-burn MWCs that have DSs and FFs for dioxin control, industrial oil-fired boilers, industrial wood-fired boilers, unleaded gasoline combustion, diesel fuel combustion in trucks, and sewage sludge incinerators. The dominant congeners for other combustion sources are 1,2,3,4,6,7,8-HpCDF in emissions from mass-burn MWCs equipped with hot-sided electrostatic precipitators (ESPs), hazardous waste incineration, and secondary aluminum smelters and 2,4-D salts and esters; OCDF in emissions from medical waste incineration and industrial/utility coal-fired boilers; 2,3,4,7,8-PeCDF in cement kilns burning hazardous waste; and 2,3,7,8-TCDF in cement kilns not burning hazardous waste.

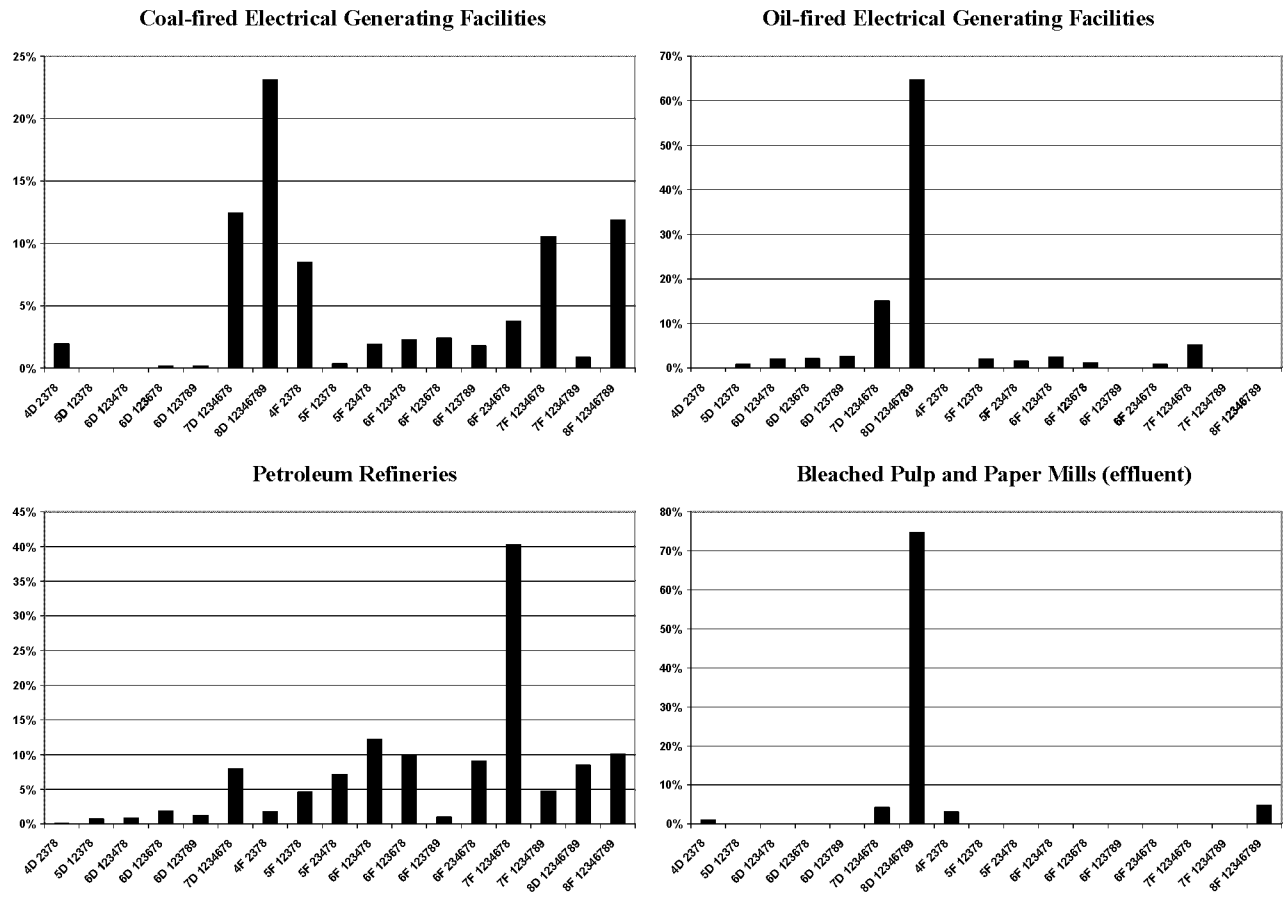


Figure 1-10. Congener profiles (as percent distributions to the sum of CDDs and CDFs) of anthropogenic sources of chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans in the United States (continued).

Evidence for a shift in the congener patterns potentially caused by the application of different air pollution control systems within a combustion source type can be seen in the case of mass-burn MWCs. For mass-burn MWCs equipped with hot-sided ESPs, the most prevalent CDD/CDF congeners are 1,2,3,4,6,7,8-HxCDF; OCDD; 1,2,3,4,6,7,8-HpCDD/1,2,3,4,7,8-HxCDF; 2,3,4,6,7,8-HxCDF/OCDF; 1,2,3,6,7,8-HxCDF. The most prevalent congeners emitted from MWCs equipped with DS/FF are OCDD; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,8-HpCDF; OCDF; and 2,3,7,8-TCDF/1,2,3,4,7,8-HxCDD; 2,3,4,6,7,8-HxCDF.

- There is evidence of marked differences in the distribution of CDD/CDF congeners between cement kilns that burn hazardous waste and those that do not. When not burning hazardous waste as supplemental fuel, the dominant congeners appear to be 2,3,7,8-TCDF; OCDD; 1,2,3,4,6,7,8-HpCDD, and OCDF. When burning hazardous waste, the dominant congeners are 2,3,7,8-PeCDF; 2,3,7,8-TCDF; 1,2,3,4,7,8-

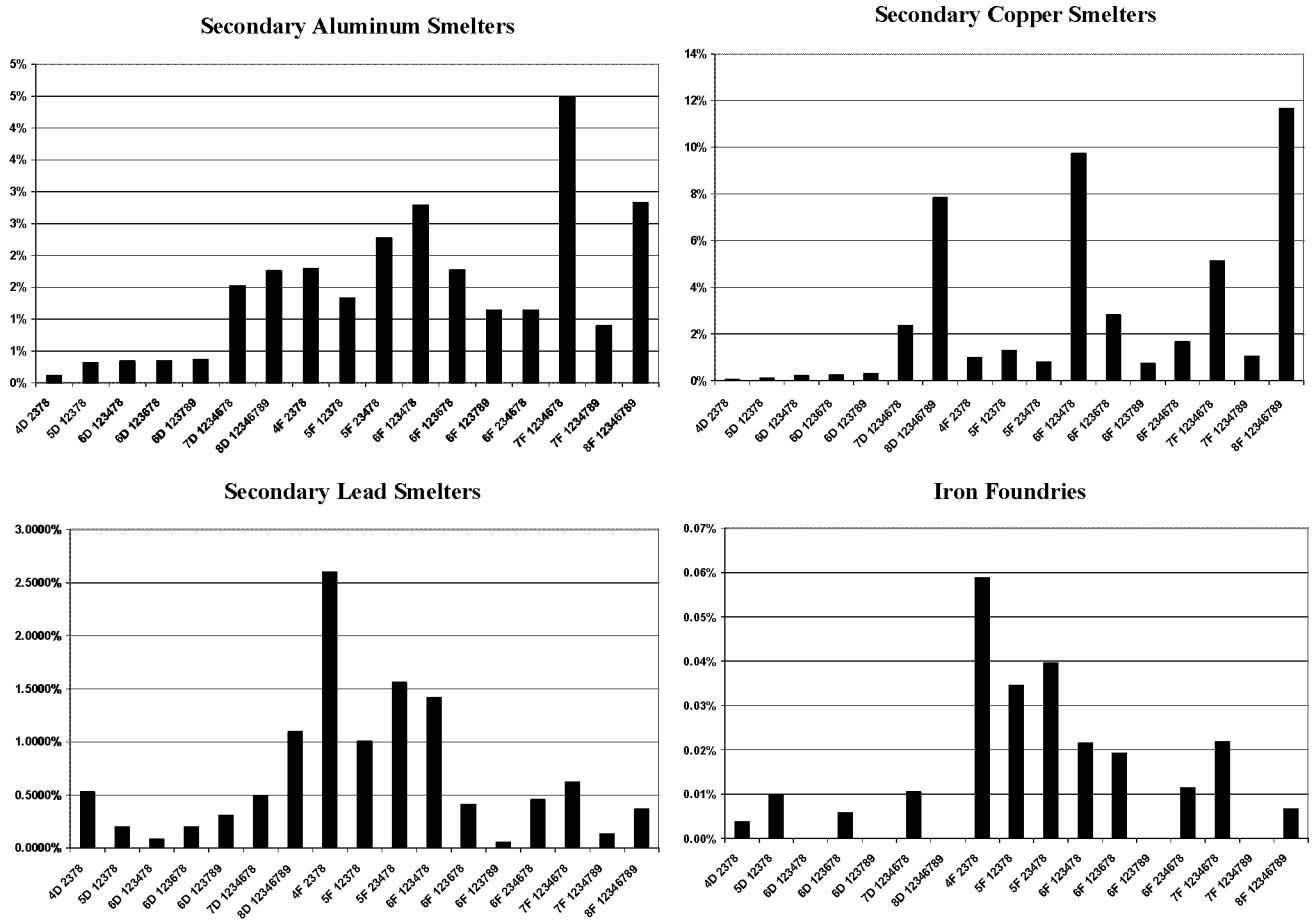


Figure 1-10. Congener profiles (as percent distributions to the sum of CDDs and CDFs) of anthropogenic sources of chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans in the United States (continued).

xCDF; and 1,2,3,4,6,7,8-HpCDD. When burning hazardous waste, OCDD and OCDF are minor constituents of stack emissions.

- The congener profile of 2,4-D salts and esters seems to mimic a combustion source profile in the number of congeners represented and in the minimal amount of 2,3,7,8-TCDD relative to all 2,3,7,8-substituted congeners. A major difference is the prevalence of 1,2,3,7,8-PeCDD in 2,4-D (14%), which is not seen in any other combustion or noncombustion source presented here.

- There are similarities in the congener profiles of PCP, diesel truck emissions, unleaded gasoline vehicle emissions, and emissions from industrial wood combustors. In these sources, OCDD dominates total emissions, but the relative ratio of 1,2,3,4,6,7,8-HpCDD to OCDD is also quite similar.

- The congener profiles for diesel truck exhaust and those for air measurements from a tunnel study of diesel traffic are quite similar.

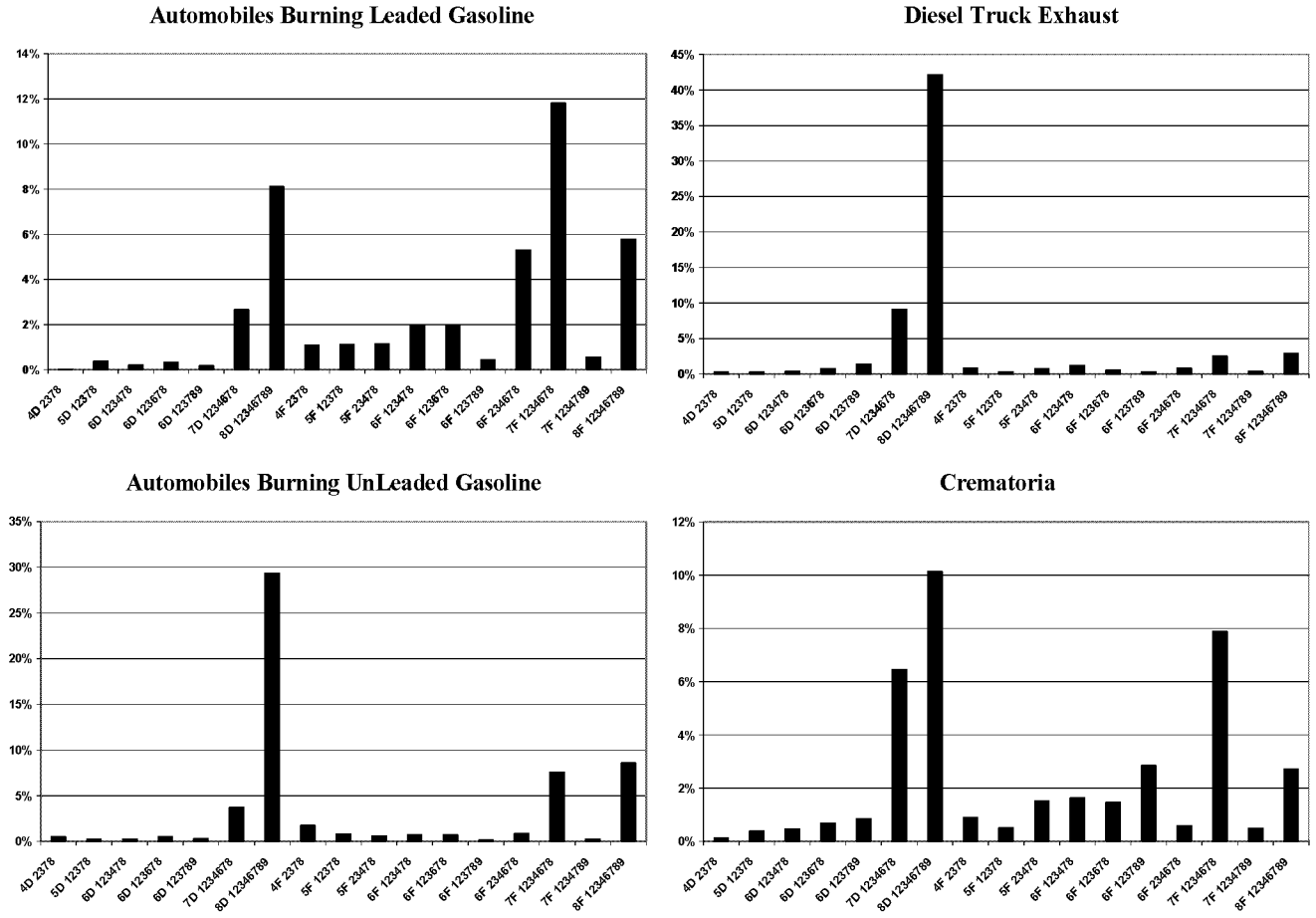


Figure 1-10. Congener profiles (as percent distributions to the sum of CDDs and CDFs) of anthropogenic sources of chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans in the United States (continued).

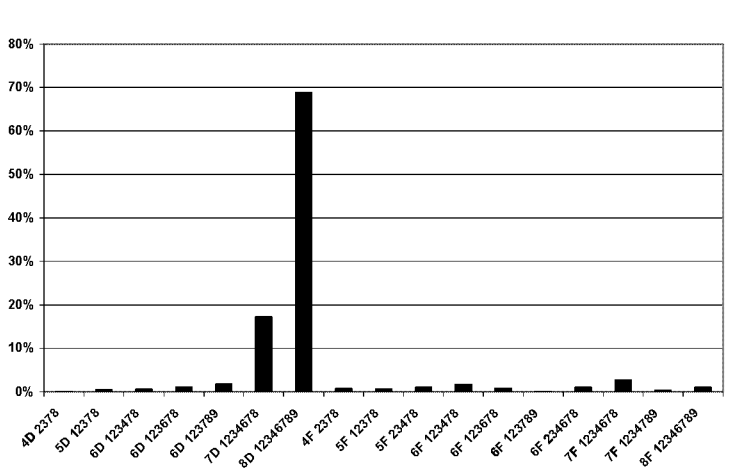


Figure 1-10. Congener profiles (as percent distributions to the sum of CDDs and CDFs) of anthropogenic sources of chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans in the United States (continued).

2. MECHANISMS OF FORMATION OF DIOXIN-LIKE COMPOUNDS DURING COMBUSTION OF ORGANIC MATERIALS

More than a decade of combustion research has contributed to a general understanding of the central molecular mechanisms that form CDDs/CDFs emitted from combustion sources. Current understanding of the conditions necessary to form CDDs/CDFs were derived primarily from studies of full-scale municipal waste combustors (MWCs), augmented with observations involving the experimental combustion of synthetic fuels and feeds in the laboratory. However, the formation mechanisms elucidated by these studies are generally relevant to most combustion systems in which organic material is burned with chlorine.

Intensive studies have examined MWCs from the perspective of identifying the specific formation mechanism(s) that occurs within the system. This knowledge may lead to methods that prevent the formation of CDDs/CDFs and their release into the environment. Although much has been learned from such studies, a method that completely prevents CDDs/CDFs from forming during the combustion of certain organic materials in the presence of a source of chlorine and oxygen is still unknown. The wide variability of organic materials incinerated and thermally processed by a wide range of combustion technologies that have varying temperatures, residence times, and oxygen requirements adds to this complex problem. However, central chemical events involved in the formation of CDDs/CDFs can be identified by evaluating emission test results from MWCs in combination with results from laboratory experiments.

CDD/CDF emissions from combustion sources can potentially be explained by three principal mechanisms that should not be regarded as being mutually exclusive. In the first mechanism (referred to as "pass through"), CDDs/CDFs are present as contaminants in the combusted organic material; they pass through the furnace and are emitted unaltered. This mechanism is discussed in Section 2.1. In the second mechanism (referred to as "precursor"), CDDs/CDFs ultimately form from the thermal breakdown and molecular rearrangement of precursor ring compounds, which are defined as chlorinated aromatic hydrocarbons that have a structural resemblance to the CDD/CDF molecules. Ringed precursors that emanate from the combustion zone are a result of the incomplete oxidation of the constituents of the feed (i.e., products of incomplete combustion). The precursor mechanism is discussed in Section 2.2. The third mechanism (referred to as "*de novo* synthesis") is similar to the precursor mechanism and is described in Section 2.3. *De novo* synthesis describes a pathway of CDD/CDF formation from heterogeneous reactions on fly ash (particulate matter[PM]) involving carbon, oxygen, hydrogen, chlorine, and a transition metal catalyst. With these reactions, intermediate compounds that have an aromatic ring structure are formed.

Studies in this area suggest that aliphatic compounds, which arise as products of incomplete combustion, may play a critical role in initially forming simple ring molecules, which later evolve into complex aromatic precursors. CDDs/CDFs are then formed from the intermediate compounds. In both the second and the third mechanism, formation occurs outside the furnace, in the so-called post-combustion zone. Particulate-bound carbon is suggested as the primary reagent in the *de novo* synthesis pathway.

Section 2.4 presents an overview of studies that have investigated the role that chlorine plays in forming CDDs/CDFs. Although chlorine is an essential component for the formation of CDDs/CDFs in combustion systems, the empirical evidence indicates that for commercial-scale incinerators, chlorine levels in feed are not the dominant controlling factor for rates of CDD/CDF stack emissions. There are complexities related to the combustion process itself, and some types of air pollution control equipment tend to mask any direct association. Therefore, the chlorine content of fuel and feeds to a combustion source is not a good indicator of levels of CDDs/CDFs emitted from the stack of that source.

Section 2.6 discusses the generation and formation of coplanar polychlorinated biphenyls (PCBs). The presence of coplanar PCBs in stack emissions from combustors is an area in need of further research. Evidence to date suggests that PCB emissions are mostly attributable to PCB contamination in waste feeds and that emissions are related to the first mechanism described above. However, newly published research has also indicated that it is possible that PCBs form in much the same way as described in the second and third mechanisms identified in the formation of CDDs/CDFs within the post-combustion zone.

Section 2.7 provides a closing summary of the three principal formation mechanisms and the role of chlorine. From the discussions in this chapter, it should be evident that no clear distinction exists between the precursor and the *de novo* synthesis mechanisms of CDD/CDF formation. Both formation pathways depend on the evolution of precursors within combustion gases, the interaction of reactive fly ashes, a generally oxidative environment, the presence of a transition metal catalyst, the presence of gaseous chlorine, and a favorable range of temperatures. The temperature of the combustion gases (i.e., flue gases) is perhaps the single most important factor in forming dioxin-like compounds. Temperatures between 200 and 450°C are most conducive to the formation of CDDs/CDFs, with maximum formation occurring at around 350°C. If the temperature falls outside this range, the amount of CDDs/CDFs formed is minimized.

2.1. MECHANISM 1 (PASS THROUGH): CDD/CDF CONTAMINATION IN FUEL AS A SOURCE OF COMBUSTION STACK EMISSIONS

The first mechanism involved in stack emissions of CDDs/CDFs is the incomplete destruction of CDD/CDF contaminants present in the fuel or feeds delivered to the combustion chamber. Not all of these molecules are destroyed by the combustion system, thus allowing trace amounts to be emitted from the stack. Most work in this area has involved the study of incineration of municipal solid waste (MSW), where CDDs/CDFs were analytically measured in the raw refuse fed into the incinerator. CDDs/CDFs are ubiquitous in the environment (air, water, and soil) and in foods and paper; therefore, they clearly are present in municipal waste (Tosine et al., 1983; Ozvacic, 1985; Clement et al., 1988; Federal Register, 1991a; Abad et al., 2002).

Abad et al. (2002) provided contemporary measurements of CDDs/CDFs in raw MSW. Twenty-two samples were collected and analyzed for CDDs/CDFs over a 1-year period, from September 1998 through September 1999. The congeners that dominated the total mass of CDDs/CDFs were OCDD and 1,2,3,4,7,8,9-HpCDD. Figure 2-1 displays the mean CDD and CDF congener distribution from this study. Abad et al. found that the I-TEQ concentration in the MSW was highly variable and ranged from 1.55 to 45.16 ng I-TEQ/kg MSW.

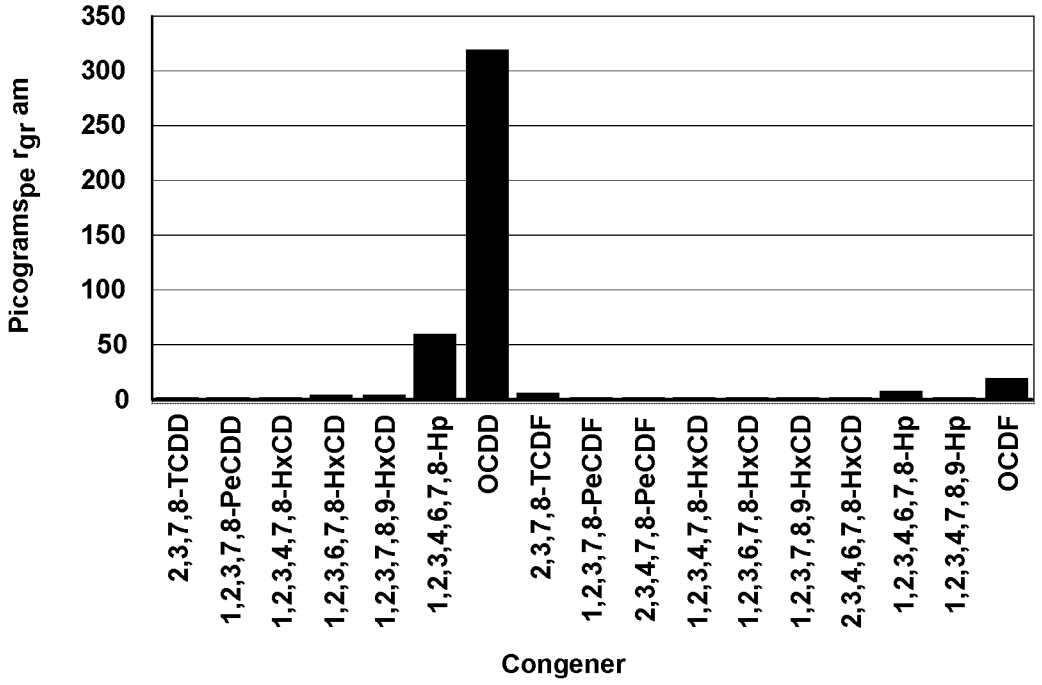


Figure 2-1. Typical mean distribution of CDD and CDF congeners in contemporary municipal solid waste.

Source: Adapted from Abad et al. (2002).

A number of studies have provided evidence that most of the CDDs/CDFs present in MSW are destroyed during combustion (Abad et al., 2002; Clement et al., 1988; Commoner et al., 1984, 1985, 1987; Hay et al., 1986; Environment Canada, 1985). These studies involved a mass balance of the input versus output of CDDs/CDFs at two operational MWCs. The mass of CDDs/CDFs outside the incinerator furnace was found to be much greater than the mass of CDDs/CDFs in the raw MSW fed into the incinerator, and the profiles of the distributions of CDD/CDF congeners were strikingly different. Primarily, the more highly chlorinated congeners were detected as contaminants in the waste, whereas the total array of tetra- through octa-CDDs/CDFs could be detected in the stack gases. Moreover, the ratio of the total CDD concentration to the total CDF concentration in the MSW was greater than 1, whereas in typical incinerator stack emissions this ratio is less than 1 (meaning more dibenzofurans than dioxins are emitted). From such evidence it can be concluded that CDDs/CDFs are being synthesized after the contaminated feed has been combusted (Abad et al., 2002). It is also expected that the conditions of thermal stress imposed by high temperatures reached in typical combustion would destroy and reduce the CDDs/CDFs present as contaminants in the waste feed to levels that are 0.0001 to 10% of the initial concentration, depending on the performance of the combustion source and the level of combustion efficiency. Stehl et al. (1973) demonstrated that the moderate temperature of 800°C enhances the decomposition of CDDs at a rate of about 99.95%, but lower temperatures result in a higher survival rate.

Theoretical modeling has shown that unimolecular destruction of CDDs/CDFs at 99.99% can occur at the following temperatures and retention times within the combustion zone: 977°C with a retention time of 1 sec, 1,000°C at a retention time of 0.5 sec, 1,227°C at a retention time of 4 msec, and 1,727°C at a retention time of 5 μsec (Schaub and Tsang, 1983). Thus, CDDs/CDFs would have to be in concentrations of parts per million in the feed in the combustor to be found in the parts-per-billion or parts-per-trillion level in the stack gas emissions (Shaub and Tsang, 1983). However, it cannot be ruled out that CDDs/CDFs in the waste or fuel may contribute (up to some percentage) to the overall concentration leaving the stack. The only other possible explanation for CDD/CDF emissions from high-temperature combustion of organic material is formation outside and downstream of the furnace.

The above studies point to formation mechanisms other than simple pass through of noncombusted feed contamination. These formation mechanisms are discussed and reviewed in the following sections.

2.2. MECHANISM 2 (PRECURSOR): FORMATION OF CDDs/CDFs FROM PRECURSOR COMPOUNDS

The second mechanism involves the formation of CDDs/CDFs from aromatic precursor compounds in the presence of a chlorine donor. This mechanism has been elucidated by

laboratory experiments involving the combustion of known precursors in quartz ampules under starved-air conditions and in experiments that investigated the role of combustion fly ash in promoting the formation of CDDs/CDFs from precursor compounds. The general reaction in this formation pathway is an interaction between an aromatic precursor compound and chlorine promoted by a transition metal catalyst on a reactive fly ash surface (Stanmore, 2004; Dickson and Karasek, 1987; Liberti and Brocco, 1982). Examples of well-studied precursor compounds include chlorobenzenes, chlorophenols, phenol, and benzene (Esposito et al., 1980). Gaseous hydrogen chloride (HCl), free chlorine (Cl_2), and chlorine radicals ($Cl\cdot$) are the chlorinating agents within the combustion gases. CDD/CDF formation results from heterogeneous gas-phase reactions involving chlorinated precursor compounds and a source of chlorine. Chlorophenol and chlorobenzene compounds have been measured in flue gases from MWCs (Dickson and Karasek, 1987).

Precursors are carried from the furnace to the flue duct as products of incomplete combustion. These compounds can adsorb on the surface of combustion fly ash or entrain in the gas phase within the flue gases. Thus, there are two formation pathways from precursor compounds: heterogeneous solid-phase reactions and homogeneous gas-phase reactions. In the post-combustion region outside the furnace, heterogeneous reactions on the surface of reactive fly ash can ensue to form CDDs/CDFs from the precursor compounds. This occurs at the cool-down temperatures of 200 to 400°C. The heterogeneous gas-phase reactions occur from the breakdown and molecular rearrangement of precursor compounds followed by condensation and chlorination at the higher temperatures of 500 to 800°C. Both reaction pathways are catalyzed by copper chloride ($CuCl_2$) or another transition metal.

Laboratory experiments involving the controlled combustion of precursor compounds have caused the breakdown of the precursor reagent and the subsequent appearance of CDDs/CDFs as products of the reaction. For example, Jansson et al. (1977) produced CDDs through the pyrolysis of wood chips treated with tri-, tetra-, and pentachlorophenol (PCP) in a bench-scale furnace operated at 500 to 600°C. Stehl and Lamparski (1977) combusted grass and paper treated with the herbicide 2,4,5-trichlorophenoxyacetic acid in a bench-scale furnace at 600 to 800°C and generated ppm_v levels of TCDD. Ahling and Lindskog (1982) reported CDD formation during the combustion of tri- and tetrachlorophenol formulations at temperatures of 500 to 600°C. Decreases in oxygen during combustion generally increased the CDD yield.

Ahling and Lindskog (1982) noted that adding copper salts to the tetrachlorophenol formulation significantly enhanced the yield of CDDs. This may have been an early indication of copper's role in catalyzing the condensation of chlorophenol to dioxin. Combustion of PCP resulted in low yields of CDDs. However, when PCP was burned with an insufficient supply of oxygen in the presence of copper, the investigators noted the formation of tetra- through

octachlorinated congeners. Buser (1979) generated CDDs/CDFs on the order of 0.001 to 0.08% (by weight) by heating tri-, tetra-, and pentachlorobenzenes at 620°C in quartz ampules in the presence of oxygen. It was noted that chlorophenols formed as combustion by-products; Buser speculated that these chlorophenols were acting as reaction intermediates in the formation of CDDs/CDFs.

The second condition postulated to regulate the synthesis of CDDs/CDFs from the aromatic precursor compound is the adsorption and interaction with the reactive surface of combustion-generated fly ash (PM) entrained in the combustion plasma and the presence of a transition metal catalyst (Stanmore, 2004; Dickson et al., 1992; Bruce et al., 1991; Cleverly et al., 1991; Gullet et al., 1990a; Commoner et al., 1987; Dickson and Karasek, 1987; Vogg et al., 1987). These are heterogeneous solid-phase reactions that occur at temperatures below 450°C. The molecular precursor leaves the gas phase and condenses onto the fly ash particle. This condition, which places greater emphasis on heterogeneous surface reactions and less emphasis on homogeneous gas-phase reactions, was first postulated by Shaub and Tsang (1983) using thermal-kinetic models based on the temperature of the heat of formation, adsorption, and desorption. Shaub and Tsang modeled CDD production from chlorophenols and concluded that solid-phase formation of CDDs/CDFs was of greater importance than gas-phase formation within an incineration system.

The temperature of the combustion gases is a critical factor in the formation of CDDs/CDFs from aromatic precursor compounds (Weber and Hagenmaier, 1999; Fangmark et al., 1994; Vogg et al., 1987, 1992; Oberg et al.,1989). Vogg et al. (1987) found that formation probably occurs outside of and downstream from the combustion zone of a furnace, in regions where the temperature of the combustion offgases has cooled within a range of 200 to 450°C.

After carefully removing organic contaminants from MWC fly ash, Vogg et al. (1987) added known concentrations of isotopically labeled CDDs/CDFs to the matrix. The MWC fly ash was then heated for 2 hr in a laboratory furnace at varying temperatures. The treated fly ash was exposed to temperatures increasing in 50°C increments within a temperature range of 150 to 500°C. Table 2-1 summarizes these data. Because the relative concentration of CDDs/CDFs increased while exposed to varying temperatures, it was concluded that the temperature of the combustion gas is crucial to promoting the formation of CDDs/CDFs on the surface of fly ash. Within a temperature range of 200 to 450°C, the concentration of CDDs/CDFs increases to some maxima; outside this range, the concentration diminishes.

Table 2-1. Concentration of CDDs/CDFs on municipal incinerator fly ash at varying temperatures

Congener	CDD/CDF concentration on fly ash (ng/g) by temperature				
	200°C	250°C	300°C	350°C	400°C
CDD					
Tetra	15	26	188	220	50
Penta	40	110	517	590	135
Hexa	65	217	1,029	550	110
Hepta	100	208	1,103	430	60
Octa	90	147	483	200	15
CDF					
Tetra	122	560	1,379	1,185	530
Penta	129	367	1,256	1,010	687
Hexa	61	236	944	680	260
Hepta	48	195	689	428	112
Octa	12	74	171	72	12

Source: Adapted from Vogg et al. (1987).

The region of cooler gas temperature is often referred to as the "post-combustion region." This region extends from near the exit of the furnace to the point of release of the combustion gases at stack tip. The heat loss may be inherent in the conduction and transfer through the combustion gas metal ducting system or related to the adsorption/exchange of heat to water in boiler tubes.

Fangmark et al. (1994) found that CDDs/CDFs exhibit a similar dependence at a temperature range of 260 to 430°C, with maximum formation occurring around 340°C. Using a pilot-scale combustor, Behrooz and Altwicker (1996) found that the formation of CDDs/CDFs from the precursor 1,2-dichlorobenzene rapidly occurred within the post-combustion region in a temperature range of 390 to 400°C, with residence times of only 4 to 5 sec. On the other hand, CDD/CDF formation from 1,2-dichlorophenol seemed to require higher temperatures.

Oberg et al. (1989) examined the role of temperature in the formation kinetics using a full-scale hazardous waste incinerator (HWI) operating in Sweden. The investigators observed that maximum CDD/CDF formation transpired in the boiler used to extract heat for cogeneration of energy. In this study, significant increases in total concentration of I-TEQ_{DF} occurred between 280 and 400°C, and concentrations declined at temperatures above 400°C. Weber and Hagenmaier (1999) showed that in gas-phase reactions, chlorophenols react in the presence of

oxygen at temperatures above 340°C to form CDDs/CDFs. Phenoxyradicals were formed, which in turn caused the formation of CDDs. Polychlorinated dihydroxybiphenyls were identified as reaction intermediates in the gas-phase dimerization of chlorophenols, and these intermediates could form CDFs.

Konduri and Altwicker (1994) proposed that rate-limiting factors were the nature and the concentrations of the precursors, the reactivity and availability of the fly ash surface, and the residence time in the post-combustion zone. Dickson and Karasek (1987) investigated fly ash reactivity with $^{13}C_6$-chlorophenol compounds. Several samples of fly ash from MWCs and copper smelters and a variety of combustion fuels were heated at 300°C in quartz tubes under conditions known to catalyze the conversion of chlorophenols to CDDs/CDFs. The MSW fly ash included a sample from a poorly operated mass burn refractory incinerator and a sample from a well-operated fluidized-bed combustor. The MWC fly ash proved to be the most active catalytic medium, despite similarities among the samples with respect to specific surface area and average pore diameter. The fly ash from the refractory MWC generated about seven times more mass of dioxin-like compounds than did the fluidized-bed MWC. In the MSW fly ashes, all CDD/CDF congener groups were formed from labeled chlorophenols; however, only trace amounts of heptachloro- and octachlorodioxin were formed with the copper smelter/refiner. X-ray photoelectron spectroscopy revealed the presence of chlorine adsorbed to the surface of the MWC fly ash but an absence of chlorine sorbed to the copper smelter fly ash.

CDD congener groups have been postulated to form from the labeled PCP precursors by (1) first forming octachlorodioxin by the condensation of two PCP molecules, and (2) forming other less-chlorinated dioxins through dechlorination of the more highly chlorinated isomers. These steps seemed to proceed by an increased reactivity of the chemisorbed precursor molecule caused by the removal of one or more hydrogen or chlorine atoms along the ring structure (Dickson and Karasek, 1987), an observation consistent with the kinetic model of Shaub and Tsang (1983).

In related experiments, Dickson and Karasek (1987) more specifically reported on forming CDDs/CDFs from condensation reactions of chlorophenols on the surface of MWC fly ash heated in a bench-scale furnace. Their experiment was designed to mimic conditions of MSW incineration, to identify the step-wise chemical reactions involved in converting a precursor compound into dioxin, and to determine whether MWC fly ash could promote these reactions. MWC fly ash was obtained from facilities in Canada and Japan. The fly ash was rinsed with solvent to remove any organic constituents prior to initiating the experiment. Twenty grams of fly ash were introduced into a bench-scale furnace (consisting of a simple flow-tube combustion apparatus) and heated at 340°C overnight to desorb any remaining organic compounds from the matrix. $^{13}C_{12}$-labeled PCP and two trichlorophenol isotopes ($^{13}C_{12}$-2,3,5-

trichlorophenol and 3,4,5-trichlorophenol) were added to the surface of the clean fly ash matrix and placed in the oven for 1 hr at 300°C. Pure inert nitrogen gas (flow rate of 10 mL/min) was passed through the flow tube and a constant temperature was maintained.

Tetra- through octa-CDDs were formed from the labeled PCP experiment; more than 100 μg/g of total CDDs were produced. The congener pattern was similar to that found in MWC emissions. The 2,3,5-trichlorophenol experiment primarily produced HxCDDs and very small amounts of tetra- through octa-CDDs. The 3,4,5-trichlorophenol experiment mainly produced OCDD and 1,2,3,4,6,7,8-HpCDD.

Dickson and Karasek (1987) proposed that CDDs on fly ash surfaces may result from chlorophenol undergoing molecular rearrangement or isomerization as a result of dechlorination, dehydrogenation, and transchlorination before condensation occurs. These reactions were proposed as controlling the types and amounts of CDDs that are ultimately formed. Born et al. (1993) conducted experiments on the oxidation of chlorophenols with fly ash in a quartz tube reactor heated to about 300°C. The MWC fly ash mediated the oxidation of chlorophenols to produce carbon dioxide (CO_2) and carbon monoxide (CO) as major products and polychlorinated benzenes, monobenzofurans, and nonhalogenated dibenzo-*p*-dioxins as trace species. Formation of these trace aromatic species occurred after residence times of only 7 to 8 sec, which was consistent with the later experimental result of Behrooz and Altwicker (1995), which showed the potential for rapid formation from a precursor.

Milligan and Altwicker (1996) fitted experimental flow-tube reactor data to classical catalytic reaction models to empirically explain the interaction of 2,3,4,6-tetrachlorophenol (as a model precursor) with reactive MWC fly ash during MSW incineration. The precursor was found to be highly adsorptive on the surface of fly ash, with a first-order dependence on gas-phase precursor concentration to CDD formation. The investigators concluded that chlorophenol's dependence on gas-phase concentration to form CDDs on fly ash reflects the highly heterogeneous nature of the fly ash surface. Moreover, the estimated 6×10^{18} adsorption sites per gram of fly ash suggested the presence of highly energetic sites, which may be important in the surface-catalyzed reactions forming CDDs. An interesting observation by Milligan and Altwicker was that precursor molecules appeared to compete with oxygen molecules for the reactive sites; therefore, chlorophenols are expected to adsorb less readily to the fly ash surface in the presence of oxygen.

Experimental evidence suggests that condensation to CDD of chlorophenol compounds via isomerization and the Smiles rearrangement on reactive MWC fly ash surfaces is a proven pathway for the formation of dioxins from a precursor compound (Addink and Olie, 1995). However, no detailed mechanisms have been presented for CDD/CDF formation from other precursors such as chlorobenzenes under conditions simulating incineration.

A condition in the synthesis of CDDs/CDFs from aromatic precursor compounds is that the presence of a transition metal catalyst promotes the chemical reaction on the surface of fly ash. $CuCl_2$ is a strong catalyst for promoting surface reactions on PM to convert aromatic precursor compounds to CDDs/CDFs (Vogg et al., 1987). $CuCl_2$ promotes ring condensation reactions (of the chlorophenols) on fly ash to form CDDs/CDFs (Addink and Olie, 1995) via the Ullman reaction (Born et al., 1993). In the Ullman reaction, copper catalyzes the formation of diphenyl ethers by the reaction of halogenated benzenes with alkali metal phenolates (Born et al., 1993), with copper participating in a nucleophilic aromatic substitution reaction. Thus, Born et al. proposed a similar mechanism in catalyzing the formation of dioxin-like compounds. Using the Ullman reaction as a model, the authors proposed that the copper-catalyzed condensation of two ortho-substituted chlorophenol molecules form chlorine-free dibenzo-*p*-dioxins.

Vogg et al. (1987) proposed an oxidation reaction pathway, giving rise to the formation of CDDs/CDFs in the post-furnace regions of the incinerator in the following order: (1) HCl is thermolytically derived as a product of the combustion of heterogeneous fuels containing abundant chlorinated organic chemicals and chlorides; (2) oxidation of HCl, with $CuCl_2$ as a catalyst, yields free gaseous chlorine via the Deacon reaction; (3) phenolic compounds (present from combustion of lignin in the waste or other sources) entrained in the combustion plasma are substituted on the ring structure by contact with the Cl_2; and (4) a chlorinated precursor to dioxin (e.g., chlorophenol) is further oxidized (with $CuCl_2$ as a catalyst) to yield CDDs/CDFs and chlorine.

Gullett et al. (1990a, b, 1991a, b, 1992) studied the formation mechanisms through extensive combustion research at EPA and verified the observations of Vogg et al. (1987). It was proven that CDDs/CDFs could ultimately be produced from low-temperature (i.e., 350°C) reactions between chlorine (Cl) and a phenolic precursor combining to form a chlorinated precursor, followed by oxidation of the chlorinated precursors (catalyzed by a copper catalyst such as $CuCl_2$), as shown below.

1. The initial step in dioxin formation is the formation of chlorine from HCl in the presence of oxygen (the Deacon reaction), as follows (Bruce et al., 1991; Vogg et al., 1987):

$$2HCl + \tfrac{1}{2} O_2 \xrightarrow{\text{Heat}} H_2O + Cl_2$$

2. Phenolic compounds adsorbed on the surface of fly ash are chlorinated to form the dioxin precursor, and the dioxin is formed as a product of the breakdown and molecular

rearrangement of the precursor. The reaction is promoted by $CuCl_2$ acting as a catalyst (Vogg et al., 1987; Dickson and Karasek, 1987; Gullett et al., 1992):

(a) phenol + Cl_2 ————> chlorophenol (dioxin precursor)

$$\text{(b) 2-chlorophenol} + \tfrac{1}{2}\,O_2 \xrightarrow{CuCl_2} \text{dioxin} + Cl_2$$

Eklund et al. (1986) observed the high-temperature formation of a large variety of chlorinated toxic compounds, including CDDs/CDFs, from precursors during a simple experiment in which phenol was oxidized with HCl at 550°C. One milligram of phenol was placed in a quartz tube reactor with an aqueous solution (10 μL) of HCl and heated at a temperature of 550°C for 5 min. Trichlorobenzene, dichlorophenol, dichlorobenzofuran, tetrachlorobenzene, trichlorophenol, and tetrachlorophenol were identified as major products formed. Monochlorobenzene, chlorophenol, dichlorobenzene, tetrachloropropene, pentachloropropene, trichlorobenzofuran, TCDF, TrCDD, TCDD, HxCDD, HxCDF, pentachlorobenzene, pentachlorobiphenyl, and pentachlorodihydroxycylohexane were observed as minor products. Trace species formed included MCDF, PeCDF, PeCDD, OCDF, and OCDD.

Eklund et al. (1986) hypothesized that chlorinated organic compounds can be produced from phenols, acids, and any chlorine source in the hot post-combustion region (just beyond the exit to the furnace). The reaction was seen as very sensitive to HCl concentration. No chlorinated compounds could be detected when HCl concentrations were $<10^{-3}$ mol.

Nestrick et al. (1987) reported that the thermolytic reaction between benzene (an unsubstituted precursor) and iron (III) chloride on a silicate surface yielded CDDs/CDFs at temperatures ≥150°C. The experimental protocol introduced 100 to 700 mg benzene and $^{13}C_6$-benzene into a macroreactor system consisting of a benzene volatilization chamber connected to a glass tube furnace. The investigators noted the relevance of this experiment to generalizations about combustion processes because benzene is the usual combustion by-product of organic fuels. Inert nitrogen gas carried the benzene vapor to the furnace area. The exit from the glass tubing to the furnace was plugged with glass wool, and silica gel was introduced from the entrance end to give a bed depth of 7 cm to which ferric trichloride ($FeCl_3$) was added to form an $FeCl_3$/silica reagent. The thermolytic reaction took place in a temperature range of 150 to 400°C at a residence time of 20 min. Although di- through octa-CDDs/CDFs were formed by this reaction at all temperatures studied, the percent yields were extremely small. Table 2-2 summarizes these data.

Table 2-2. CDDs/CDFs formed from the thermolytic reaction of 690 mg benzene + $FeCl_3$ silica complex

Congener	Mass produced (ng)	Number of mols produced	Percent yield[a]
DiCDD	4.9	0.019	4.3 e-7
TrCDD	54.0	0.019	4.3 e-6
TCDD	130.0	0.400	9.0 e-6
PeCDD	220.0	0.620	1.4 e-5
HxCDD	170.0	0.440	9.9 e-6
HpCDD	98.0	0.230	5.2 e-6
OCDD	20.0	0.040	9.0 e-7
Total CDDs	696.9	1.940	4.4 e-5
DiCDF	990	4.2	9.5 e-5
TriCDF	7,800	29.0	6.6 e-4
TCDF	12,000	39.0	8.8 e-4
PeCDF	20,000	59.0	1.3 e-3
HxCDF	33,000	88.0	2.0 e-3
HpCDF	40,000	98.0	1.1 e-3
OCDF	74,000	167.0	3.8 e-3
Total CDFs	187,000	484.2	1.1 e-2

[a] Number of mols of CDD or CDF/mols benzene x 100.

$FeCl_3$ = ferric chloride

Source: Nestrick et al. (1987).

2.3. MECHANISM 3 (*DE NOVO* SYNTHESIS): SYNTHESIS OF CDDs/CDFs DURING COMBUSTION OF ORGANIC MATERIALS

The third mechanism promotes CDD/CDF formation in combustion processes from the oxidation of carbon particulate catalyzed by a transition metal in the presence of chlorine. As in the precursor mechanism (mechanism 2), synthesis is believed to occur in regions outside of the furnace zone of the combustion process, where the combustion gases have cooled to a range of temperatures considered favorable to formation chemistry. A key component to *de novo* synthesis is the production of intermediate compounds (either halogenated or nonhalogenated) that are precursors to CDD/CDF formation. Research in this area has produced CDDs/CDFs directly by heating carbonaceous fly ash in the presence of a transition metal catalyst without the apparent generation of reactive intermediates. Thus, the specific steps involved in the *de novo* process have not been fully and succinctly delineated. However, laboratory experimentation has proven that MWC fly ash itself is a reactive substrate, and the matrix can actually catalyze the *de*

novo formation chemistry. Typically, fly ash is composed of an alumina-silicate construct, with 5 to 10% concentrations of silicon, chlorine (as inorganic chlorides), sulfur, and potassium (NATO, 1988). Twenty percent of the weight of fly ash particles is carbon, and the particles have specific surface areas in the range of 200 to 400 m^2/kg (NATO, 1988).

The *de novo* synthesis essentially is the oxidative breakdown of macromolecular carbon structures, and CDDs/CDFs are formed partially from the aromatic carbon-oxygen functional groups embedded in the carbon skeleton (Huang et al., 1999). The distinguishing feature of the *de novo* synthesis over the precursor synthesis is the oxidation of carbon in particulate at the start of the process to yield precursor compounds. In mechanism 2, the precursor compound is the starting molecule of the condensation reactions forming CDDs/CDFs (Dickson et al., 1992). By this distinction, however, one could argue that mechanism 3 is really an augmentation of mechanism 2 because the production of CDDs/CDFs may still require the formation of a CDD/CDF precursor as an intermediate species. Nevertheless, a distinction is presented here to describe additional pathways suggested for the thermal formation of these compounds.

To delineate the *de novo* synthesis of CDDs/CDFs, Stieglitz et al. (1989) conducted experiments that involved heating particulate carbon containing adsorbed mixtures of magnesium-aluminum (Mg-Al) silicate in the presence of $CuCl_2$ (as a catalyst to the reaction). The authors described heating mixtures of Mg-Al silicate with activated charcoal (4% by weight), chloride as potassium chloride (7% by weight), and $CuCl_2$ (1% in water) in a quartz flow tube reactor at 300°C. The retention time was varied at 15 min, 30 min, and 1, 2, and 4 hr to obtain differences in the amounts of CDDs/CDFs that could be formed. The results are summarized in Table 2-3. In addition to the CDDs/CDFs formed as primary products of the *de novo* synthesis, the investigators observed precursors formed at the varying retention times during the experiment. In particular, similar yields of tri- through hexachlorobenzenes, tri- through heptachloronaphthalenes, and tetra- through heptachlorobiphenyls were quantified; this was seen as highly suggestive of the role these compounds may play as intermediates in the continued formation of CDDs/CDFs.

Stieglitz et al. (1989) made the following observations:

- The *de novo* synthesis of CDDs/CDFs via the oxidation of carbonaceous PM occurred at a temperature of 300°C. Additionally, the experiment yielded parts-per-billion to parts-per-million concentrations of chlorinated benzenes, chlorinated biphenyls, and chlorinated naphthalenes through a similar mechanism. When potassium bromide was substituted for potassium chloride as a source of halogen for the organic compounds in the reaction, polybrominated dibenzo-*p*-dioxins and dibenzofurans formed as reaction products.

Table 2-3. *De novo* formation of CDDs/CDFs after heating Mg-Al silicate, 4% charcoal, 7% Cl, 1% $CuCl_2$ in H_2O at 300°C

Congener	Concentration of CDD/CDF (ng/g) by reaction time (hr)				
	0.25	0.5	1	2	4
TCDD	2	4	14	30	100
PeCDD	110	120	250	490	820
HxCDD	730	780	1,600	2,200	3,800
HpCDD	1,700	1,840	3,500	4,100	6,300
OCDD	800	1,000	2,000	2,250	6,000
Total CDDs	3,342	3,744	7,364	9,070	17,020
TCDF	240	280	670	1,170	1,960
PeCDF	1,360	1,670	3,720	5,550	8,300
HxCDF	2,500	3,350	6,240	8,900	14,000
HpCDF	3,000	3,600	5,500	6,700	9,800
OCDF	1,260	1,450	1,840	1,840	4,330
Total CDFs	8,360	10,350	17,970	24,160	38,390

Cl = chlorine
$CuCl_2$ = copper chloride
Mg-Al = magnesium-aluminum

Source: Stieglitz et al. (1989).

- The transition metal compound $CuCl_2$ catalyzed the *de novo* synthesis of CDDs/CDFs on the surface of particulate carbon in the presence of oxygen, yielding CO_2 and chlorinated/brominated aromatic compounds.

- Particulate carbon, which is characteristic of combustion processes, may act as the source for the direct formation of CDDs/CDFs as well as other chlorinated organics.

Stieglitz et al. (1991) investigated the role that particulate carbon plays in the *de novo* formation of CDDs/CDFs from fly ash containing appreciable quantities of organic chlorine. The investigators found that the fly ash contained 900 ng/g of bound organic chlorine, of which only 1% was extractable. Heating the fly ash at 300 to 400°C for several hours caused the carbon to oxidize, leading to a reduction in the total organic chlorine in the matrix and a corresponding increase in the total extractable organic chlorine (5% extractable total organic chlorine at 300°C and 25 to 30% at 400°C). From this, the authors concluded that the oxidation and degradation of carbon in fly ash are the sources of the formation of CDDs/CDFs; therefore, they are essential in the *de novo* synthesis of these compounds.

Addink et al. (1991) conducted a series of experiments to observe the *de novo* synthesis of CDDs/CDFs in a carbon fly ash system. In this experiment, 4 g of carbon-free MWC fly ash were combined with 0.1 g of activated carbon and placed into a glass tube between two glass wool plugs. The glass tube was then placed into a furnace at specific temperatures ranging from 200 to 400°C. This protocol was repeated for a series of retention times and temperatures. The investigators observed that CDD/CDF formation was optimized at 300°C and at the furnace retention times of 4 to 6 hr. Figure 2-2 displays the relationship between retention time and temperature in CDD/CDF production from the heating of carbon particulate.

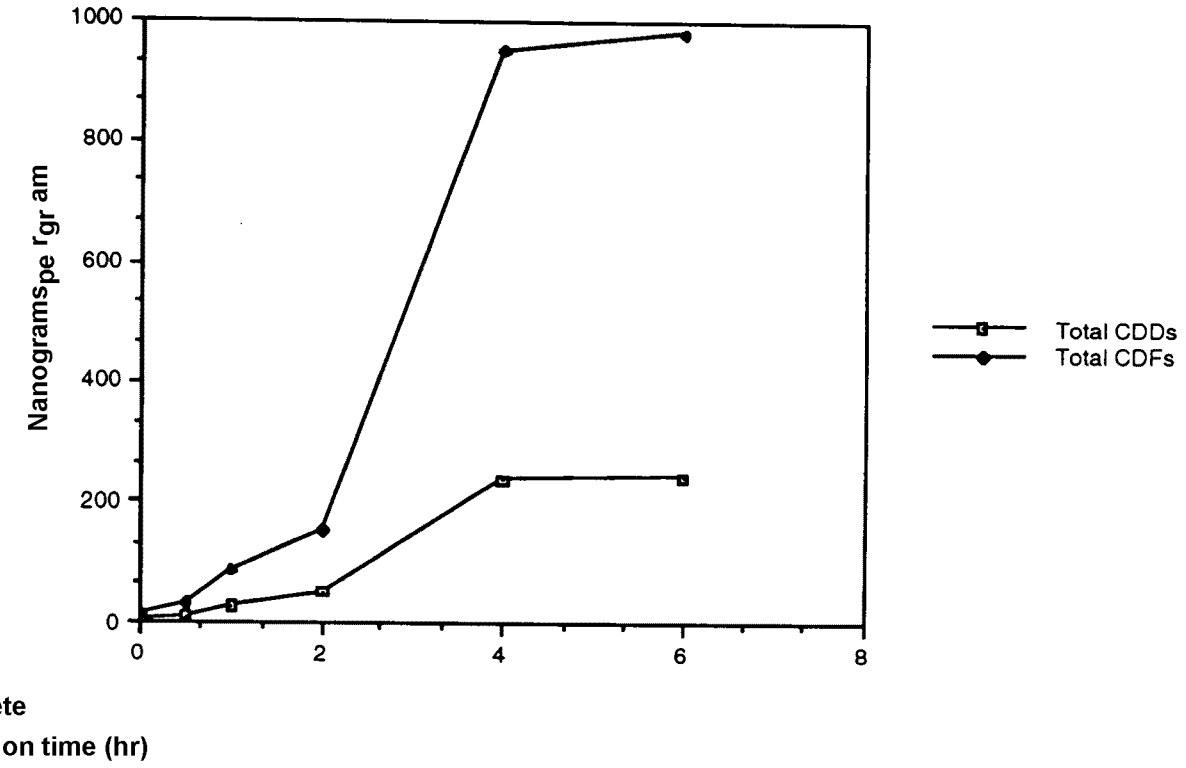


Figure 2-2. The *de novo* synthesis of CDDs/CDFs from heating carbon particulate at 300°C at varying retention times.

Source: Addink et al. (1991).

Addink et al. (1991) also investigated the relationship between furnace temperature and CDD/CDF production from the heating of carbonaceous fly ash. Figure 2-3 displays this relationship. In general, the concentration began to increase at 250°C and crested at 350°C, with a sharp decrease in concentration above 350°C. The authors also noted a relationship between

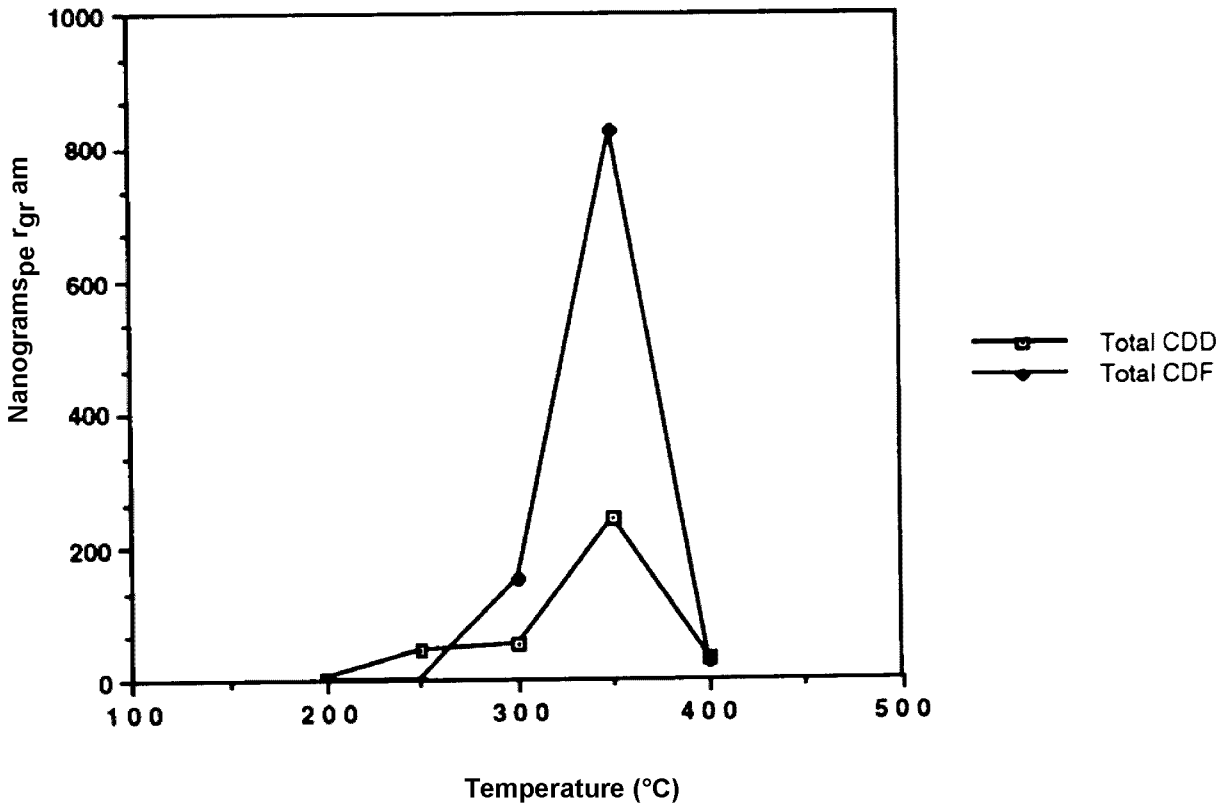


Figure 2-3. Temperature effects on CDD/CDF formation.

Source: Addink et al. (1991).

temperature and the CDD/CDF congener profile: at 300 to 350°C, the less-chlorinated tetra- and penta-CDD/CDF congeners increased in concentration, whereas hexa-, hepta-, and octa-CDD/CDF congeners either remained the same or decreased in concentration. The congener profile of the original MWC fly ash (not subject to *de novo* experimentation) was investigated with respect to changes caused by either temperature or residence time in the furnace. No significant changes occurred, leading the authors to propose an interesting hypothesis for further testing: after formation of CDDs/CDFs occurs on the surface of fly ash, the congener profile remains fixed and insensitive to changes in temperature or residence time, indicating that some form of equilibrium is reached in the formation kinetics.

Gullett and Lemieux (1994) used a pilot-scale combustor to study the effect of varying combustion gas composition, temperature, residence time, quench rate, and sorbent ($Ca[OH]_2$) injection on CDD/CDF formation. The fly ash loading was simulated by injecting fly ash collected from a full-scale MWC. Sampling and analysis indicated that CDDs/CDFs formed on the injected fly ash at levels representative of those observed at full-scale MWCs. A statistical

analysis of the results showed that, although the effect of combustor operating parameters on CDD/CDF formation is interactive and very complicated, substantial reduction in CDD/CDF formation can be realized with high-temperature sorbent injection to reduce HCl or Cl_2 concentrations, control excess air (which also affects the ratio of CDDs to CDFs formed), and increase quench rate.

Milligan and Altwicker (1995) found that increases in the carbon gasification rate caused increases in the amounts of CDDs/CDFs formed and gave further evidence linking the oxidation of carbon to the formation of CDDs/CDFs. Neither the gas-phase CO_2 or CO (products of carbon oxidation) act as precursors to chlorobenzenes or CDDs/CDFs from reactions with carbon particulate (Milligan and Altwicker, 1995). Activated carbon, with its high surface area and excellent adsorptive characteristics, also has the highest gasification rate of all residual carbon (Addink and Olie, 1995).

Experimental evidence suggests the following factors for the *de novo* synthesis of CDDs/CDFs from carbon: (a) carbon consisting of imperfect and degenerated layers of graphite, (b) the presence of oxygen, (c) the presence of chlorine, (d) catylization of the reactions by $CuCl_2$ or some other transition metal, and (e) temperatures in the range of 200 to 350°C (Huang and Buekens, 1995). The oxidation of carbon in fly ash is apparently inhibited at temperatures below 200°C, thus indicating the lower temperature limit for the thermal inertization of *de novo* synthesis (Lasagni et al., 2000).

Lasagni et al. (2000) determined that at a temperature of 250°C, the primary product of the gasification of carbon in fly ash is CO_2, but in a temperature range of 250 to 325°C, organic compounds are formed as products of the oxidation of the carbon. Addink and Olie (1995) raised the possibility that the molecular backbone of CDDs/CDFs may be present in carbon. If this is the case, the generation of dioxins and furans from the oxidation of carbon would not require the formation of intermediate aromatic ring structures. More work is needed to confirm these possibilities.

The *de novo* synthesis of CDDs/CDFs also involves the possibility that aromatic precursors are formed within the post-combustion zone in the following manner: (1) fuel molecules are broken down into smaller molecular species (e.g., C_1 and C_2 molecules) during primary combustion, and (2) these simple molecules recombine in the post-combustion zone to form larger-molecular aromatic species (i.e., chlorobenzenes and chlorophenols) (Altwicker et al., 1993). Thus, small molecular products that evolve in the hot zone of the furnace as a consequence of incomplete fuel or feed material combustion may be important foundation molecules to the subsequent formation of precursor compounds in the cooler, post-combustion region.

Eklund et al. (1988) reported formation of a wide range of chlorinated organic compounds, including CDDs, CDFs, and PCBs, from the oxidation of methane with HCl at temperatures of 400 to 950°C in a quartz flow tube reactor. No active catalysts or reactive fly ashes were added to the combustion system. From these experimental results, the authors hypothesized that chlorocarbons, including CDDs/CDFs, are formed at high temperatures via a series of reversible reactions starting with chloromethyl radicals. The chloromethyl radicals can be formed from the reaction of methyl radicals and HCl in a sooting flame. Methane is chlorinated by HCl in the presence of oxygen at high temperatures, forming chlorinated methanes, which react with methyl radicals at higher temperatures (e.g., 800°C) to form aromatic compounds. In an oxidative atmosphere, chlorinated phenols are formed, but alkanes and alkenes are the primary products. The chlorinated phenols then act as precursors for the subsequent formation of CDDs/CDFs.

Aliphatic compounds are common products of incomplete combustion, and they may be critical to the formation of simple ring structures in the post-combustion zone (Weber et al., 1999; Sidhu, 1999; Froese and Hutzinger, 1996a, b; Jarmohamed and Mulder, 1994). The aromatic precursor compounds may be formed in a potentially rich reaction environment of aliphatic compounds, reactive fly ash particles, HCl, and oxygen. Sidhu (1999) noted that combustion of acetylene on carbon (a common combustion effluent) in the presence of gaseous HCl and $CuCl_2$ (as a catalyst) at 300°C led to the formation of intermediate precursors and, subsequently, CDDs/CDFs.

Propene oxidized at 350 to 550°C when in contact with reactive MWC fly ash in a flow tube reactor formed a wide range of chlorinated aromatic compounds when the resulting combustion gases were mixed with HCl (Jarmohamed and Mulder, 1994). Although the conversion was low (1 to 3%), the oxidation of propene on fly ash in the presence of HCl can yield chlorinated benzenes and monobenzofurans. Incorporating an oxygen atom into the monobenzofuran structure then leads to the formation of monodibenzofuran. The HCl contributes chlorine to the aromatic ring through the Deacon reaction, and cyclization on the fly ash surface can yield cyclohexadienyl-substituted benzenes, which in turn can be further oxidized into CDFs.

Froese and Hutzinger (1996a) investigated the heterogeneous combustion reactions of the nonchlorinated C_2 aliphatics. Acetylene, as a model aliphatic compound, was allowed to react with precleaned MWC fly ash in a tube flow reactor at approximately 600°C. Metal oxides (silicon dioxide [SiO_2], iron oxide [Fe_2O_3], and copper oxide [CuO])—rather than the metal chlorides used in other precursor experiments—were added separately as catalysts. The reactants were put into contact with HCl vapor, which was introduced at a constant flow rate. The

acetylene flow was set at 1.1 mL/min and constantly fell to near 0.9 mL/min over 30 min. Regulated air flow maintained homeostatic oxidation conditions.

Chlorobenzenes and chlorophenols were formed, with isomer patterns generally resembling isomer patterns of chlorobenzene and chlorophenol emissions from MWCs. CuO was seen as catalyzing condensation and chlorination reactions under heterogeneous conditions to form the chlorinated CDD/CDF precursor compounds. Other more volatile compounds formed were short-chain aliphatic products, such as chloromethane, dichloromethane, and chloro- and dichloroacetylene. Chlorobenzene congeners were not the major products formed; perchlorinated aliphatic compounds dominated as gas-phase reaction products.

Froese and Hutzinger (1997) noted that perchlorinated aliphatic compounds (e.g., hexachloropropene, hexachloro-1,3-butadiene, and hexachlorocyclopentadiene) are important intermediates in aromatic ring formation; they concluded that the catalytic reaction of C_2 aliphatic compounds at 600°C dramatically contributes to the formation of chlorinated and nonchlorinated aromatic compounds during combustion. Thus, aliphatic compounds can form CDD/CDF precursor compounds. Variable temperature effects were observed in the formation of CDDs/CDFs in the same reactions. Maximal OCDD formation occurred at 400°C, and the tetra through hepta homologue groups were maximally formed at 600°C. For CDFs, production of more highly chlorinated homologues occurred at 400°C, and the formation of TCDFs occurred at 500°C. Froese and Hutzinger (1996a) noted a 100-fold increase in TCDF formation at 500°C when compared with formation at 400°C. An explanation for this increase is that the higher temperature maximized the formation of the CDD/CDF precursor (chlorophenol) from the aliphatic starting compound.

Froese and Hutzinger (1996b) produced polychlorinated benzene and phenol compounds at a temperature range of 300 to 600°C, caused by the heterogeneous combustion reactions of ethylene and ethane over fly ash in the presence of HCl, oxygen, and a metal catalyst. No chlorobenzene congener precursors were formed from ethylene and ethane at 300°C; however, the formation rate increased with temperature until a maximum production was achieved at 600°C. No definitive temperature dependence was observed for the formation of chlorophenols from the aliphatic starting compounds. However, at 500°C, 2,4,6-trichlorophenol dominated the reaction products; at 300°C, PCP was initially produced.

Froese and Hutzinger (1996b) also investigated the effects of elemental catalysts on potentiating the heterogeneous combustion reactions by measuring the amount of chlorobenzene and chlorophenol product formed from the reactions of ethylene/HCl over each catalyst at 600°C. The reaction with SiO_2 did not have a catalytic effect. Aluminum oxide (Al_2O_3) catalytic action showed high intensity for the dichlorobenzene isomers and decreasing intensity for the higher-chlorinated isomers. Comparison of the amount of dichlorobenzene product formed

indicated that an equal quantity was produced with either Al_2O_3 or fly ash; however, Al_2O_3 formed four to five times more product than did the CuO catalyst. For tri- to hexachlorobenzene congeners, MWC fly ash reactions produced 5 to 10 times more product than did the metal catalysts. However, the presence of the CuO catalyst in these reactions produced a chlorobenzene congener pattern comparable to that of the fly ash reactions. With regard to chlorophenol production, Al_2O_3 also produced a unique dichlorophenol pattern, suggesting that Al_2O_3 has a unique catalytic effect in the high-temperature reactions of C_2 aliphatic compounds.

Reactions with CuO produced additional products, including chlorinated methyl compounds, chlorinated C_2 aliphatics, and perchlorinated C_3–C_5 alkyl compounds. Froese and Hutzinger noted that these perchlorinated alkyl groups, formed by reacting ethylene and ethane over fly ash in the presence of the CuO catalyst, were key intermediate compounds to the formation of first aromatic rings in typical combustion systems. This emphasizes the importance of copper's catalytic effects in a combustion fly ash system. Al_2O_3 catalyzed reactions produced nonchlorinated naphthalene and alkylbiphenyl compounds. Furthermore, the organic chlorine in aliphatic compounds may also act as a direct source of chlorine for the formation of CDDs/CDFs in a carbon fly ash system (Weber et al., 1999).

In an earlier experiment using a similar flow tube apparatus, Froese and Hutzinger (1994) formed chlorinated benzenes and phenols in fly ash catalyzed reactions with trichloroethylene at temperatures of 400 to 500°C. In this case, metal oxides (CuO, FeO_3, and Al_2O_3) were used as catalysts, but no HCl was added for oxychlorination of product compounds. Under combustion conditions, temperature-dependent formation of chlorinated aromatics occurred from the trichloroethylene starting compound. Reaction with fly ash at 600°C formed hexachlorobenzene in concentrations that were about 1,000 times greater than those at 400 and 500°C, with similar results for chlorophenols. The authors hypothesized that key aromatic precursors for CDDs/CDFs are formed in the higher-temperature region of a post-combustion zone (about 600°C) and are then carried to the cooler post-combustion region (about 300°C), where the precursors form CDDs/CDFs.

2.4. THE ROLE OF CHLORINE IN THE FORMATION OF CDDs/CDFs IN COMBUSTION SYSTEMS

The formation of CDDs/CDFs in the post-combustion region of combustion systems via either the precursor or *de novo* synthesis mechanisms requires the availability of a source of chlorine (Luijk et al., 1994; Addink et al., 1995; Stanmore, 2004; Wikstrom et al., 2003). Chlorine concentration in this region is somehow related to the chlorine content of combustion fuels and feed materials in incineration/combustion systems because there can be no other source. The main question regarding the role of chlorine in forming CDDs/CDFs is whether a positive

and direct correlation exists between the amount of chlorine in feeds and the amount of CDDs/CDFs formed and emitted from the stack of a combustion system. If a direct relationship appears to exist, then reductions in the chlorine content of fuels/feeds prior to combustion should result in a corresponding reduction in the concentrations of CDDs/CDFs formed after combustion. If the oxychlorination reactions require a number of steps, then the relationship between chlorine in uncombusted fuels and CDDs/CDFs formed after combustion may not be linear, although it may still be dependent in some nonlinear association. The main question can best be addressed by examining both formation mechanisms revealed in laboratory-scale combustion experiments and correlations between chlorine inputs with CDD/CDF outputs in commercial-scale combustors.

2.4.1. Review of Laboratory-Scale Studies

A wide body of experimental evidence has elucidated the direct and indirect associations between chlorine in feeds and fuels and the potential formation of CDDs/CDFs during combustion. The *de novo* synthesis of CDDs/CDFs requires two basic reactions: (1) the transfer of chlorine to residual carbon particulate, with subsequent formation of carbon-chlorine bonds, and (2) the oxidation of this macromolecular complex to yield CO_2 and volatile and semivolatile organic compounds as side products (Weber et al., 1999). Transition metal compounds such as $CuCl_2$ catalyze these reactions. Gaseous HCl, Cl_2, and $Cl\cdot$ are the most abundant sources of chlorine available for participation in the formation of CDDs/CDFs, and they are initially formed as a combustion by-product from the inorganic and organic chlorine contained in the fuel (Wikstrom et al., 2003; Rigo, 1998; Addink et al., 1995; Rigo et al., 1995; Halonen et al., 1994; Luijk et al., 1994; Altwicker et al., 1993; Wagner and Green, 1993; Dickson et al., 1992; Bruce et al., 1991; Gullet et al., 1990b; Commoner et al., 1987; Vogg et al., 1987).

MSW contains approximately 0.45 to 0.90% (w/w) chlorine (Domalski et al., 1986). The most predominant chlorine species formed from MSW combustion is gaseous HCl, which averages between 400 and 600 ppm in the combustion gas (Wikstrom et al., 2003; U.S. EPA, 1987a). Chlorine is initially released from the chlorine in the MSW and is rapidly transformed to HCl by the abstraction of hydrogen from reaction with hydrocarbons present in the fuel (Wikstrom et al., 2003). HCl may oxidize to yield Cl_2 gas by the Deacon reaction, and the Cl_2 directly chlorinates a CDD/CDF precursor along the aromatic ring structure. Further oxidation of the chlorinated precursor in the presence of a transition metal catalyst (of which $CuCl_2$ was found to be the most active) yields CDDs/CDFs (Altwicker et al., 1993). Increasing the yield of chlorine in vapor phase from HCl oxidation generally increases the rate of CDD/CDF formation. Formation kinetics are most favored at temperatures ranging from 200 to 450°C. However HCl

is considered a weak chlorinating agent because of the tenacity of the hydrogen-to-carbon bond of aromatic compounds (Wikstrom et al., 2003).

Chlorine production from gaseous HCl can be reduced either by limiting initial HCl concentration or by shortening the residence time (Bruce et al., 1991; Gullett et al., 1990b; Commoner et al., 1987). Bruce et al. (1991) observed a general increase in CDD/CDF formation with increases in the vapor-phase concentration of chlorine and verified a dependence of the formation of CDDs/CDFs in the post-combustion zone on the concentration and availability of gaseous chlorine. This latter finding is in agreement with the results of a simple experiment by Eklund et al. (1986) in which unsubstituted phenol was mixed with HCl at 550°C in a quartz tube reactor. A wide range of toxic chlorinated hydrocarbons were formed, including CDDs/CDFs. Eklund et al. (1988) also found a dependence of the amounts of chlorinated phenol product formed from the nonchlorinated starting material on the increased amount of HCl introduced into the reaction. Under the conditions of this experiment, no chlorinated compounds were formed at an HCl concentration of less than 10^{-3} mol, and maximum chlorophenol concentration occurred at around 10^{8} mol.

Born et al. (1993) also observed that increasing levels of HCl gave rise to increasing rates of oxychlorination of precursors, with increasing chances for the post-combustion formation of CDDs/CDFs. However, Addink et al. (1995) observed that an HCl atmosphere and/or chlorine produced approximately equal quantities of CDDs/CDFs during the *de novo* synthesis from oxidation of particulate carbon. Such results suggest that chlorine production via the Deacon reaction in the *de novo* synthesis may not be the only chlorination pathway, and they may indicate that the HCl molecule can be a direct chlorinating agent. In addition, some chlorine is expected to be formed from the oxidation of metal chlorides (e.g., $CuCl_2$), but Cl_2 formation from the Deacon reaction is greater because of the continuous supply of HCl delivered from the combustion chamber (Bruce et al., 1991). In this case, a first-order dependence of HCl to Cl_2 is observed.

However, Wikstrom et al. (2003) reported on the importance of chlorine species on the *de novo* formation of CDDs/CDFs. HCl can react with oxidizing radicals (e.g., hydroxyl radical, or OH) to produce Cl·. Cl· are highly reactive and can replace hydrogen atoms with chlorine atoms in the H-C bond of the aromatic structure. Thus, HCl is most likely an indirect chlorinating agent via the formation of Cl·.

Experimentally, about 18% of the total chlorine content in fuels can be thermally converted to Cl· in the post-combustion region (Procaccini et al., 2003). Although HCl is the primary chlorine-containing product formed from the combustion of chlorine-rich fuels, it may not be the major chlorinating agent in the formation of chloro-organics in the cooled-down region of the combustor. The experiments by Procaccini et al. (2003) indicate that the major role

of HCl in the formation of chloro-organic compounds at cooler temperatures may be that of a chemical progenitor of Cl·. HCl reacts with the oxidizing radicals OH and O that are abundantly present in combustion off-gases to reform Cl·. Cl· readily abstract hydrogen atoms from the H-C bond of aromatic compounds formed as combustion by-products of organic fuels. By this means, unsubstituted aromatic compounds, e.g., benzene, undergo oxy-chlorination reactions with the Cl· to form chlorobenzenes and chlorophenols. These products are well-defined precursor compounds for the synthesis of CDDs/CDFs.

Wagner and Green (1993) investigated the correlation of chlorine content in feed to stack emissions of chlorinated organic compounds in a pilot-scale incinerator using HCl flue gas measurements as a surrogate for fuel-bound organic chlorine. In addition to MSW as a fuel, variable amounts of polyvinyl chloride (PVC) resin were added during 6 of 18 stack test runs. The resulting data were regressed to determine the coefficient of correlation between HCl measurements and total chlorobenzene compound emission measurements. In nearly all of the regression analyses performed, the relationship between HCl emissions and emissions of chlorinated organic compounds was positive and well defined. In addition, the investigators found a direct dependence of HCl emission levels on the level of PVC in the waste, with generally increasing amounts of HCl formed as increasing amounts of PVC were added. From these experiments, they concluded that decreased levels of organically bound chlorine in the waste incinerated led to decreased levels of chlorinated organic compounds in stack emissions.

Kanters and Louw (1994) investigated a possible relationship between chlorine content in waste feed and chlorophenol emissions in a bench-scale thermal reactor. MSW incineration with a higher content of chlorine in the feed caused higher emissions of chlorophenols via the *de novo* synthesis pathway. The investigators lowered the chlorine content of the prototype MWC by replacing chlorine-containing fractions with cellulose. They observed appreciable decreases in the amounts of chlorophenol formed from combustion, and concluded that reductions in the chlorine content of waste feeds or elimination of PVC prior to municipal waste combustion should result in a corresponding reduction in chlorophenol and CDD/CDF emissions.

In a similar experiment, Wikstrom et al. (1996) investigated the influence of chlorine in feed materials on the formation of CDDs/CDFs and benzenes in a laboratory-scale fluidized-bed reactor. Seven artificial fuels (composed of 34% paper, 30% wheat flour, 14% saw dust, 7% polyethylene (PE), and 2% metals), to which varying amounts of organic chlorine and inorganic chlorine ($CaCl_2 \cdot 6H_2O$) were added, were combusted. The chlorine content of these fuels varied from 0.12 to 2%. All combustion was performed with a high degree of combustion efficiency (99.999%) to avoid the formation of polyvinylidene chloride and naphthalenes as products of incomplete combustion of pure PVC. With the combustion conditions held constant, only the

chlorine content of the fuel was varied. Flue gases were sampled for CDDs/CDFs and chlorobenzenes.

In these experiments, concentrations of PCB isomers were approximately 1,000-fold higher than CDDs/CDFs (expressed as concentration of I-TEQ_{DF}). Moreover, a correlation was found between I-TEQ_{DF} and PCB levels in the flue gases and the chlorine content of the fuel. A fivefold increase in both I-TEQ_{DF} and PCB concentrations was observed in the flue gases from combustion of fuels containing 0.5 and 1.7% total chlorine. Furthermore, no differences were observed in the amount of chlorinated product produced or when the source of chlorine in the fuel was organic or inorganic. No correlation was observed between total CDD/CDF and PCB formation and total chlorine in the feed when chlorine levels in feed were 0.5% or lower. The highest amounts of CDDs/CDFs and PCBs were formed from the fuel with the highest total chlorine content (1.7%).

Under the conditions of this experiment, Wikstrom et al. (1996) observed that a chlorine fuel content of 1% was a threshold for formation of excess CDDs/CDFs and PCBs during combustion. The authors noted that MSW in Sweden contained about 0.7% chlorine, of which approximately 40% was organic chlorine. They concluded that MSW was below the observed threshold value of 1% chlorine content associated with a general increase in CDD/CDF and PCB formation in the post-combustion region. They also stated that their study did not support the hypothesis that elimination of only PVC from waste prior to combustion will cause a significant reduction in CDD/CDF emissions if the combustion process is well controlled (high combustion efficiency). Wang et al. (2003) verified the existence of a theoretical chlorine-in-fuel threshold when they demonstrated *de novo* synthesis when combusting fuels with 0.8 to 1.1% chlorine.

A primary by-product of PVC combustion is HCl. Paciorek et al. (1974) thermally degraded pure PVC resin at 400°C and produced 550 mg/g HCl vapor as a primary thermolysis product, which was observed as being 94% of the theoretical amount, based on the percent weight of chlorine on the molecule. Ahling et al. (1978) concluded that HCl can act as a chlorine donor to ultimately yield chlorinated aromatic hydrocarbons from the thermolytic degradation of pure PVC and that these yields are a function of transit time, percent oxygen, and temperature. They observed data from 11 separate experiments conducted with temperatures ranging from 570 to 1,130°C. These data indicated that significant quantities of various isomers of dichloro-, trichloro-, tetrachloro-, and hexachlorobenzenes could be produced. Choudhry and Hutzinger (1983) proposed that the radical species Cl· and H· generated in the incineration process may attack the chlorinated benzenes and abstract hydrogen atoms to produce orthochlorine-substituted chlorophenol radicals. These intermediate radical species then react with molecular oxygen to yield ortho-substituted chlorophenols. As a final step, the ortho-substituted chlorophenols act as ideal precursors to yield CDDs/CDFs with heat and oxygen. The chlorine in aliphatic

compounds has been observed as both yielding high amounts of HCl during combustion and acting as a direct chlorine source for the *de novo* synthesis of CDDs/CDFs (Weber et al., 1999).

Kim et al. (2004) determined that the combustion of pure PVC yielded appreciable amounts of polycyclic aromatic hydrocarbons (PAHs), PCBs, chlorobenzenes, and chlorophenols. They suggested that the gas-phase production of PCBs and chlorobenzenes contributed to the gas-phase formation of CDDs/CDFs through the precursor mechanism. Chlorophenols, however, contributed to the *de novo* formation. Kim et al. (2004) reported that the *de novo* synthesis of CDDs/CDFs from chlorophenols was approximately 100 times greater than their formation from PCB and chlorobenzene precursors.

Katami et al. (2002) found a clear correlation between dioxin formation and the chlorine content of mixed plastics combusted in a laboratory-scale incinerator. PVC, PE, polystyrene (PS), polyethylene terephthalate (PET), and their various mixtures were burned at temperatures greater than 600°C. Average CO concentrations in the exhaust gases were varied from 2 to 880 ppm as a general indication of the quality of the fire in the combustion chamber. When incinerated, each type of plastic formed CDDs/CDFs in the exhaust gases. Of the total CDDs formed, HxCDD and TCDD formed in the greatest amounts when PE was combusted. Mono-CDF was the most abundant CDF formed from PE combustion. Mono-ortho coplanar PCBs were preferentially formed over nonortho-PCBs. The combustion of PS caused TCDD to be formed in the greatest abundance of all possible CDDs, whereas TCDF was the most abundant dibenzofuran. Mono-ortho PCBs formed more than nonortho coplanar PCBs when PS was combusted. The combustion of PET mostly formed MCDD and MCDF among the CDDs/CDFs formed.

When PVC was combusted with the conditions of high temperature and low CO (good combustion), a total of 53.5 ng/g of total CDD was formed, with the HxCDD predominating. In addition, good combustion conditions formed a total of 771 ng/g of CDFs, with Cl_2 and Cl_3 CDF congeners dominating. When PVC was combusted with the conditions of low temperature and high CO (poor combustion), the total CDDs and CDFs formed increased significantly to 429 ng/g and 8,492 ng/g, respectively. TrCDD and DiCDF dominated the congener distributions, suggesting that poor combustion of PVC tends to form high levels of lower-chlorinated CDDs/CDFs. The investigators observed that maintaining good combustion tended to minimize the formation of CDDs/CDFs from the combustion of chlorinated plastics.

Shibata et al. (2003) reported on the formation of CDDs/CDFs from the combustion of PVC in quartz ampules. Synthesis of CDDs/CDFs proceeded *de novo* in a temperature range of 200 to 400°C, with the reaction catalyzed by CuO. Maximum formation occurred at 300°C. HpCDDs and OCDD were the dominant CDDs observed in the flue gases, whereas TCDFs,

PeCDFs, and HxCDFs dominated the CDFs. The ratio of CDFs to CDDs from PVC combustion was greater than 1, which is typical of MSW combustion (Shabata et al., 2003).

Addink and Altwicker (1999) reported on the role of the inorganic chloride ion in the formation of CDDs/CDFs using the labeled compound $Na^{37}Cl$. The inorganic chloride ion forms carbon-chlorine bonds on soot particles during combustion. The chlorine in the soot can be directly inserted into a CDD/CDF molecule during formation, or it can exchange with the chloride ions in the transitional metal catalyst, which promotes CDD/CDF formation. Thus, the inorganic chlorine ion participates as a chlorine donor to CDD/CDF formation.

De Fre and Rymen (1989) reported on the formation of CDDs/CDFs from hydrocarbon combustion in a domestic gas/oil burner in the presence of 15 and 300 ppm concentrations of HCl. More than 100 chlorinated organic compounds were detected in the flue gases whenever HCl was injected into the system. The investigators observed formation of CDDs and CDFs in all experiments where HCl was injected in a hydrocarbon flame. In this case, CDFs were always more abundant than CDDs. It was concluded that the relationship between the HCl concentration and the emitted concentration of CDDs/CDFs under fixed combustion conditions appeared to be exponential for a wide range of temperatures (240 to 900°C).

2.4.2. Review of Full-Scale Combustion Systems

The review of experimental data clearly indicates an association between chlorine content of feed/fuels and the potential synthesis of CDDs/CDFs. Paradoxically, the review of full-scale operating incineration processes does not yield such unequivocal results, indicating that complex kinetic events make strong associations difficult in full-scale systems. The following is a review of studies of the association between chlorine in feeds and stack releases of CDDs/CDFs in full-scale incineration systems.

In the stack testing of a variety of industrial stationary combustion sources during the National Dioxin Study in 1987, EPA made a series of qualitative observations about the relationship between total chlorine present in the fuel/waste and the magnitude of emissions of CDDs/CDFs from the stack of the tested full-scale combustion facilities (U.S. EPA, 1987a). In general, combustion units with the highest CDD emission concentrations had greater quantities of chlorine in the fuel; conversely, sites with the lowest CDD emission concentrations contained only trace quantities of chlorine in the feed. The typical chlorine content of various combustion fuels was reported by Lustenhouwer et al. (1980) as coal, 1,300 μg/g; MSW, 2,500 μg/g; leaded gasoline, 300 to 1,600 μg/g; and unleaded gasoline, 1 to 6 μg/g.

Thomas and Spiro (1995) also analyzed the relationship between CDD/CDF emissions from combustion and the chlorine content of feed materials. Thomas and Spiro (1996) plotted average CDD/CDF emission factors for a variety of combustion systems and processes (black

liquor boilers, unleaded gasoline combustion, leaded gasoline combustion, wire incineration, cigarette combustion, sewage sludge incineration, MWC, PCP-treated wood combustion, hazardous waste incineration, and hospital waste incineration) against the average chlorine concentration of the combusted material. The plot showed that average CDD/CDF emissions of combustion source categories tended to increase with the average chlorine content of the combusted fuel. This analysis indicated that combustion sources with relatively high combustion efficiency and adequate air pollution controls tended to have emissions two orders of magnitude lower than those of poorly operated sources. This suggests that the magnitude of CDD/CDF emissions is strongly dependent on chlorine concentration in fuels in the context of the more poorly controlled and operated combustion sources, and the association becomes less apparent in the well-controlled facilities operating with good combustion practices. The slope of the log-log plot was between 1 and 2 for the poorly controlled and operated facilities, indicating that the relationship between chlorine content and CDD/CDF emissions was more than proportional.

Costner (1998) reported finding a positive correlation between chlorine content of feed material and CDD/CDF emissions at a full-scale hospital waste incinerator. Costner concluded that emissions at this facility were dependent on chlorine input at a concentration as low as 0.031% and that there was no evidence of a threshold in the relationship between chlorine in feed and CDD/CDF emissions.

Rigo et al. (1995) summarized the results of a study commissioned by the American Society of Mechanical Engineers (ASME, 1995). The study was a statistical evaluation of the relationship between HCl concentration in flue gases and various combustion systems (MWCs, hospital waste incinerators, HWIs, biomass combustors, laboratory combustors, and bench-scale combustors) and stack emissions of total CDDs/CDFs. In this study, HCl was used as a surrogate for total chlorine content in the fuel. The data analysis was sufficient for 92 facilities in the database that showed both HCl and CDD/CDF emissions. Of the 92 facilities, 72 did not show a statistically significant relationship between chlorine input and CDD/CDF output in emissions streams, 2 showed increasing CDD/CDF concentrations with increasing chlorine, and 8 showed decreasing CDD/CDF concentrations with increasing chlorine. ASME (1995) reports the following conclusion:

> The failure to find simultaneous increases in most cases and finding inverse relationships in a few indicates that any effect chlorine has on CDD/CDF emissions is smaller than the variability of other causative factors. Whatever effect chlorine has on CDD/CDF emissions in commercial-scale systems is masked by the effect of APCS (air pollution control systems) temperature, ash chemistry, combustion conditions, measurement imprecision, and localized flow stratification.

Liberson and Belanger (1995) reported the results of an analysis of the formation and emission of CDDs/CDFs as a function of total chlorine in combustion feed materials at a rotary kiln HWI. The data were generated from multiple test series conducted over a 13-month period at the HWI while operating a carbon injection system specifically designed to control and reduce CDD/CDF stack emissions. The chlorine feed rates ranged from 0 to 3,300 lb/hr, and the CDD/CDF emission rates ranged from 0.7 to 39 ng/dscm. The authors noted that multiple series of CDD/CDF control systems were used on this HWI (a high-temperature secondary combustion chamber, a spray dryer-evaporative quench that further cools the combustion gases, activated carbon injection to adsorb semivolatile organics, and a cool-side electrostatic precipitator followed by an acid gas scrubber to collect HCl and Cl_2). From analyses of the data, the authors concluded that no correlation exists between CDD/CDF emissions and chlorine feed in a modern MWC using carbon injection for CDD/CDF control.

More recently, Wang et al. (2003) investigated the association between chlorine content of waste feeds and CDD/CDF emissions from full-scale combustion systems. Previously, Wikstrom et al. (1996) had discerned a chlorine content in feeds of 1% as being a threshold concentration for the formation of CDDs/CDFs, i.e., an association with the magnitude of CDDs/CDFs formed occurred only when chlorine content in the feed was $\geq 1\%$. Wang et al. confirmed the apparent existence of a chlorine threshold for emissions of total CDDs/CDFs after statistically reviewing input of chlorine in feed versus output of CDDs/CDFs in emissions at two tested medical incinerators and two tested MWCs. Additionally, the authors examined second-hand data from 13 other dioxin sources obtained from the literature and found that the formation of CDFs was greater than the formation of CDDs when the chlorine content of the waste feed exceeded the threshold. However, when the chlorine content was below the approximate 1% threshold, the formation of CDDs was greater than the formation of CDFs. The authors proposed that chlorine content below the threshold formed chlorinated precursors to CDDs rather than forming the dibenzofuran molecule. Chlorine content above the threshold contributed to deterioration of combustion conditions, causing the formation of PAHs, which, in turn, contributed to the formation of CDFs.

2.5. POTENTIAL PREVENTION OF CDD/CDF FORMATION IN COMBUSTION SYSTEMS

Given what is currently understood about oxychlorination reactions in the synthesis of CDDs/CDFs, researchers have identified certain interventions that could be taken to reduce or impede formation in combustion systems. Raghunathan and Gullett (1996) demonstrated in a pilot-scale incinerator that sulfur compounds can combine with the metal catalyst necessary to stimulate the Deacon reaction of HCl and oxygen to yield Cl_2, thereby neutralizing the catalyzing

agent and reducing the formation of CDDs/CDFs. The Deacon reaction, which forms Cl_2 in the combustion plasma, is seen as occurring only in the presence of a catalyst. Thus, the sulfur dioxide (SO_2) molecule (formed when sulfur in the fuel combines with oxygen) can inhibit the catalytic activity of the fly ash by either combining with a metal-based Deacon catalyst in the fly ash or depleting the Cl_2 formed. The authors observed that the principal action of sulfur in inhibiting the formation of CDDs/CDFs in combustion systems is through SO_2 depletion of Cl_2, as follows:

$$Cl_2 + SO_2 + H_2O \leftrightarrow 2HCl + SO_2$$

The relevance of this finding is that the co-combustion of MSW with coal (that contains sulfur) should lead to dramatic reductions in the amount of CDDs/CDFs formed and emitted, and it may explain why, in the United States, coal combustion at power plants results in CDD/CDF emission rates more than a magnitude lower than those at MWCs.

Naikwadi and Karasek (1989) investigated the addition of calcium oxide (CaO) and triethylamine (TEA) to the flue gases of a combustion system as an inhibitor of the catalytic activity of fly ash. They placed 500 μg ^{13}C-labeled PCP (a dioxin precursor) in a combustion flow tube and allowed it to react with organic-extracted MWC fly ash at 300°C under an air stream. Under these conditions, CDDs/CDFs were formed at concentrations ranging from 1,660 to 2,200 ng/100 μg ^{13}C-PCP. The experimental method was then modified by mixing reactive MWC fly ash with either CaO or TEA. The results showed that the amount of CDDs/CDFs formed could be reduced by an order of magnitude from the reaction of PCP with fly ash and the addition of TEA as an inhibitor. When CaO was mixed with fly ash, the amount of CDDs/CDFs formed decreased more than 20-fold.

2.6. THEORY ON THE EMISSION OF PCBs

Air emissions of PCBs from MSW incineration is less well studied. Probably the formation mechanisms that apply to CDDs/CDFs would also apply to PCBs. Mechanism 1 (pass through) is implicit in the Toxic Substances Control Act rule, which requires 99.9999% destruction in HWIs. When this occurs, 0.0001% of the initial amount of PCBs fed into the HWI may be emitted from the stack. This may indicate that some small fraction of the PCBs present in the fuel fed into an incineration process may result in PCB emissions from the stack of the process.

PCBs have been measured as contaminants in raw refuse prior to incineration in an MWC (Choudhry and Hutzinger, 1983; Federal Register, 1991a). Using this information, it is possible to test mechanism 1 for CDD/CDF emissions: that the PCB contamination present in the fuel is

mainly responsible for emissions from the stack. The mass balance of total PCBs, beginning with measurement in the raw refuse and ending with measurement at the stack of a refuse-derived fuel (RDF) MWC (Federal Register, 1991a), can be used to calculate the destruction rated efficiency (DRE) of incineration of the PCB-contaminated MSW. Using results from test number 11 at the RDF facility (Federal Register, 1991a), a computation of DRE can be made using the following equation (Brunner, 1984):

$$DRE = \frac{W_I - W_O}{W_I} \times 100\%$$

where:

W_I = mass rate of contaminant fed into the incinerator system

W_O = mass rate of contaminant exiting the incinerator system

In test 11, 811 ng total PCB/g refuse were measured in the MSW fed into the incineration system and 9.52 ng/g were measured at the inlet to the pollution control device (i.e., outside the furnace region but preceding emission control). From these measurements, a DRE of 98.8% can be calculated. Therefore, it appears that PCB contamination in the raw MSW fed into this particular incinerator may have accounted for the PCB emissions from the stack of the MWC.

PCBs can be thermolytically converted into CDFs (Choudhry and Hutzinger, 1983; U.S. EPA, 1984). This process occurs at temperatures somewhat lower than those typically measured inside the firebox of an MWC. Laboratory experiments conducted by EPA indicate that the optimum conditions for CDF formation from PCBs are near a temperature of 675°C in the presence of 8% oxygen and a residence time of 0.8 sec (U.S. EPA, 1984). This resulted in a 3 to 4% efficiency of conversion of PCBs into CDFs. Because 1 to 2% of the PCBs present in the raw refuse may survive the thermal stress imposed in the combustion zone of the incinerator (Federal Register, 1991a), it is reasonable to presume that PCBs in the MSW may contribute to the total mass of CDF emissions released from the stack of the incinerator.

Although it appears that contamination of waste feed with PCBs may be an important factor in detecting PCBs in stack emissions from combustion processes, recent research has indicated that these compounds may also be formed in the post-combustion region, either from *de novo* synthesis or from precursor compounds. Zheng et al. (1999) observed the formation of PCBs in the post-combustion region from the pyrolysis of chlorobenzenes using a laboratory-scale furnace. The investigators observed that PCBs were optimally formed from less-chlorinated chlorobenzenes (e.g., 1,3-dichlorobenzene) catalyzed by $CuCl_2$. In this experiment, maximum PCB production occurred at a temperature of 350°C. Wikstrom et al. (1998) reported

secondary formation of PCBs in the post-combustion region similar to the *de novo* synthesis of CDDs/CDFs, albeit PCBs were formed in only small amounts relative to CDDs/CDFs.

Fangmark et al. (1994) postulated that formation of PCBs and CDDs/CDFs in the post-combustion region may occur through the same mechanisms. On the other hand, Blumenstock et al. (1998) produced results in a pilot-scale furnace that were inconsistent with the *de novo* formation of CDDs/CDFs in the post-combustion region (i.e., PCBs seemed to be optimally formed at high temperatures in oxygen-deficient atmospheres). Shin and Chang (1999) noted a positive correlation between PCB concentrations on MSW incineration fly ash and fly ash concentrations of CDDs/CDFs, suggesting that high PCB levels in fly ash may be a contributory cause of the post-combustion formation of CDDs/CDFs (i.e., PCBs are precursors to CDDs/CDFs). Nito et al. (1997) noted the formation of CDDs/CDFs from the pyrolysis of PCBs in a fluidized-bed system, indicating that PCBs in feeds may account for CDFs formed in MSW incineration. More combustion-related research needs to be conducted to firmly establish whether PCB contamination in feeds or post-combustion formation (or both) may explain the presence of PCBs in combustion flue gases.

2.7. SUMMARY AND CONCLUSIONS

2.7.1. Mechanisms of Formation of Dioxin-Like Compounds

There are three primary mechanisms for CDD/CDF emissions from combustion sources.

Mechanism 1 (pass through). This mechanism involves CDDs/CDFs contained in the feed passing through the combustor intact and being subsequently released into the environment. For most systems, this is not thought to be a major contributor to CDD/CDF emissions for three reasons. First, for commercial systems with good combustion controls, the temperatures and residence times should result in the destruction of most CDDs/CDFs in the feed. Second, mass balance studies of a number of combustion systems show that more CDDs/CDFs can be detected in the cool-down region downstream of the furnace than in the feed. Third, the CDD/CDF congener profile in the feed differs from the congener profile in the stack emissions. Consequently, synthesis appears to be a more important mechanism than is pass through. The concentration of CDDs/CDFs in the flue gases of any particular combustion system will ultimately be derived as a result of the balance between reactions leading to formation and reactions leading to destruction of these compounds.

Mechanism 2 (precursor). This mechanism involves the formation of CDDs/CDFs from the thermal breakdown and molecular rearrangement of aromatic precursors either originating in the feed or forming as a product of incomplete combustion. Actual synthesis of CDDs/CDFs occurs in the post-combustor environment. Gaseous benzene is the most abundant aromatic compound associated with products of incomplete combustion of waste. Benzene

reacts with Cl· within the combustion gas plasma, causing aromatic H abstraction and the subsequent formation of chlorobenzenes and chlorophenols. Homogeneous gas-phase formation of CDDs/CDFs occurs from these precursor compounds at temperatures >500°C, catalyzed by the presence of copper compounds. In addition, the CDDs/CDFs can form from gas-phase precursors as heterogeneous, catalytic reactions with reactive fly ash surfaces. This reaction has been observed to be catalyzed by the presence of a transition metal sorbed to the fly ash. The most potent catalyst is $CuCl_2$. Relatively low temperatures—in the range of 200 to 450°C—have been identified as a necessary condition for these heterogeneous reactions to occur, with either lower or higher temperatures inhibiting the process. Because these reactions involve homogeneous gas-phase and heterogeneous solid-phase chemistry, the rate of emissions is less dependent on reactant concentration than on conditions that are favorable to formation, such as temperature, retention time, source and species of chlorine, and the presence of a catalyst.

Mechanism 3 (*de novo* synthesis). This mechanism involves the heterogeneous solid-phase formation of CDDs/CDFs in the post-combustion environment on the surface of fly ash. Such heterogeneous chemistry occurs in two ways: (1) directly from the oxidation of carbon within the fly ash and subsequent reactions with organic and inorganic chlorine, and (2) the oxidative breakdown of macromolecular carbon structures (e.g., graphite) and oxychlorination reactions of aromatic precursors (such as chlorobenzenes and chlorophenols) on fly ash surfaces, leading to CDD/CDF formation. In either case, formation kinetics is most favored at temperatures in the range of 200 to 450°C and is promoted by the catalytic properties of either the fly ash or the presence of a transition metal compound.

Mechanisms 2 and 3 can occur simultaneously, share a number of common reaction pathways, and occur in the same physical environment, and they are controlled by many of the same physical conditions. In well-designed and well-operated combustion systems, the precursor species needed for mechanism 2 are reduced; consequently *de novo* synthesis (mechanism 3) can become the dominant pathway for formation. In systems with incomplete combustion, it is difficult to sort out the relative contribution of these two mechanisms to total emissions. Both mechanisms, however, can be curtailed if steps are taken to minimize the physical conditions needed to support formation (i.e., time, temperature, and reactive surface).

The combustion formation chemistry of PCBs is less well studied than that of CDDs/CDFs, but it is reasonable to assume that these same three mechanisms would apply. For waste incineration, PCBs can exist in significantly higher concentrations in the feed than do CDDs/CDFs. Consequently, mechanism 1 may play a more prominent role in the origin of PCB emissions than of CDD/CDF emissions.

2.7.2. Role of Chlorine

From the various analyses on the role and relationship of chlorine to CDD/CDF formation and emissions, the following observations and conclusions are made.

1. Although chlorine is an essential component in the formation of CDDs/CDFs in combustion systems, the empirical evidence indicates that, for commercial-scale incinerators, chlorine levels in feed are not the dominant controlling factor for the amount of CDDs/CDFs released in stack emissions. Important factors that can affect the rate of CDD/CDF formation include overall combustion efficiency, post-combustion flue gas temperatures and residence times, and the types and designs of air pollution control devices employed on combustion systems. Data from bench-, pilot-, and commercial-scale combustors indicate that CDD/CDF formation can occur by three principal mechanisms. Some of these data, primarily from bench- and pilot-scale combustors, have shown direct correlation between chlorine content in fuels and rates of CDD/CDF formation. Other data, primarily from commercial-scale combustors, show a weaker relationship between the presence of chlorine in feed and fuels and rates of CDD/CDF released from the stacks of combustion systems. The conclusion that the amount of chlorine in feed is not a strong determinant of the magnitude of CDD/CDF stack emissions applies to the overall population of commercial-scale combustors. For any individual commercial-scale combustor, circumstances may exist in which changes in chlorine content in feed could affect CDD/CDF emissions. For uncontrolled combustion, such as open burning of household waste, chlorine content of wastes may play a more significant role in levels of CDD/CDF emissions than the one observed in commercial-scale combustors.

2. Both organic and inorganic forms of chlorine in combustion fuels yield abundant gaseous HCl in the post-combustion region. It has been shown that Cl· are the most potent chlorinating agent in the formation of chloro-organic compounds from combustion. HCl may be the dominant chemical progenitor of Cl· participating in oxychlorination reactions to CDD/CDF synthesis. Formation of Cl· from HCl occurs in the cool-down zone via the oxidation of HCl in the presence of a transition metal catalyst (the Deacon reaction). Although the preponderance of scientific evidence suggests that this is an important pathway for producing chlorinated compounds in emissions, it is still unclear whether HCl can also directly chlorinate aromatics or whether it must first be oxidized to yield Cl_2.

3. Laboratory-scale experiments have examined correlations between chlorine content of feeds and total CDDs/CDFs formed in combustion systems. These experiments suggest that for feeds containing <1% chlorine, the amount of CDDs/CDFs formed is independent of the chlorine

content of the feed. For feeds with a chlorine content >1%, a direct correlation was observed. The existence of an apparent threshold to the chlorine content of waste has been verified in full-scale combustion systems. It has not been determined, however, whether these relationships are relevant to poorly controlled combustion of wastes and biomass, such as backyard barrel burning, landfill fires, and agricultural burning.

4. The combustion of PVC can contribute to the formation of CDDs/CDFs in two ways. First, gaseous HCl is a primary product formed from the combustion of PVC. We have seen that HCl is a major contributor of Cl· necessary for the formation of CDDs/CDFs. Thus, PVC indirectly contributes to dioxin synthesis. Second, the combustion of PVC directly forms benzene, which is followed by oxychlorination reactions that further form chlorinated benzenes and chlorinated phenols; these compounds then act as precursors to CDD/CDF formation.

5. The most critical factors associated with minimizing CDD/CDF formation in combustion systems are (a) achieving nearly complete combustion of the feed through the application of good combustion practice (i.e., time, temperature, and turbulence), and (b) ensuring that combustion gases are quenched to below the temperature range for heterogeneous solid-phase formation chemistry in the post-combustion region of the system, i.e., reducing the temperature to below 200°C.

2.7.3. General Conclusion

Although the formation chemistry of CDDs/CDFs is more complicated and less understood than the relatively simple constructs described in this review, the current weight of evidence suggests that the formation mechanisms outlined above describe the principal pathways of most CDD/CDF formation and emission from combustion sources.

3. COMBUSTION SOURCES OF CDDs/CDFs: WASTE INCINERATION

Incineration is the destruction of solid, liquid, or gaseous wastes through the application of heat within a controlled combustion system. The purposes of incineration are to reduce the volume of waste that needs land disposal and to reduce the toxicity of the waste. In keeping with this definition, incinerator systems can be classified by the types of wastes incinerated: municipal solid waste (MSW) incineration (commonly referred to as municipal waste combustion), medical and pathological waste incineration, hazardous waste incineration, sewage sludge incineration, tire incineration, and biogas flaring. Each of these types of incineration is discussed in this chapter. The purpose of this chapter is to characterize and describe waste incineration technologies in the United States and to derive estimates of annual releases of CDDs and CDFs into the atmosphere from waste incineration facilities for reference years 1987, 1995, and 2000.

As discussed in Chapter 2, combustion research has developed three theories on the mechanisms involved in the emission of CDDs/CDFs from combustion systems: (1) CDDs/CDFs can be introduced into the combustor with the feed and pass through the system unchanged (pass through mechanism), (2) CDDs/CDFs can be formed during combustion (precursor mechanism), and/or (3) CDDs/CDFs can be formed via chemical reactions in the post-combustion portion of the system (*de novo* synthesis). Total CDD/CDF emissions are likely to be the net result of all three mechanisms; however, the relative importance of each mechanism is often uncertain.

To the extent practical with the available data, the combustors in each source category were divided into classes according to similarity of emission factors. This classification effort attempted to reflect the emission mechanisms described above. The emission mechanisms suggest that the aspects of combustor design and operation that could affect CDD/CDF emissions are (a) furnace design, (b) composition of the waste feed, (c) temperature in the post-combustion region of the system, and (d) the type of air pollution control device (APCD) used to remove contaminants from the flue gases. Therefore, incineration systems that are similar in terms of these factors should have similar CDD/CDF emissions. Accordingly, this chapter proposes classification schemes that divide combustors into a variety of design classes based on these factors. Design class, as used here, refers to the combination of furnace type and accompanying APCD.

3.1. MUNICIPAL WASTE COMBUSTION

As noted above, emissions can be related to several factors, including furnace design, composition of the waste feed, temperature in the post-combustion region of the system, and

type of APCD used to remove contaminants from the flue gases. This section proposes a classification scheme that divides municipal waste combustors (MWCs) into a variety of design classes based on those factors. Because different APCDs are operated at different temperatures, operating temperature is used to define some design classes. To account for the influence of the waste feed, the proposed classification system distinguishes between refuse-derived fuel (RDF) and normal MSW. This section begins with a description of the MWC technology and then proposes the design classification scheme. Using this scheme, the municipal waste combustion industry is characterized for the reference years 1987, 1995, and 2000. Finally, the procedures for estimating emissions are explained and the results summarized.

3.1.1. Description of Municipal Waste Combustion Technologies

For the purposes of this report, municipal waste combustion furnace types are divided into three major categories: mass burn, modular, and RDF. Mass burn and RDF technologies dominate the large MWC category and modular technology dominates the small MWC category. Each of these furnace types is described below, followed by a description of the APCDs used with the system.

3.1.1.1. *Furnace Types*

Mass burn. This furnace type was so named because it burned MSW as received (i.e., no preprocessing of the waste was conducted other than removal of items too large to go through the feed system). Today, a number of other furnace types also burn unprocessed waste, as described below. Mass burn furnaces are distinguished from the other types because they burn the waste in a single stationary chamber. In a typical mass burn facility, MSW is placed on a grate that moves through the combustor. Three subcategories of mass burn technologies are described below.

- Mass burn refractory-walled systems represent an older class of MWCs (generally built in the late 1970s to early 1980s) that were designed only to reduce the volume of waste disposed of by 70 to 90%. These facilities usually lack boilers to recover the combustion heat for energy purposes. In the mass burn refractory-walled design, the MSW is delivered to the combustion chamber by a traveling grate or a ram feeding system. Combustion air in excess of stoichiometric amounts (i.e., more oxygen is supplied than is needed for complete combustion) is supplied both below and above the grate. As of 2000, few mass burn refractory-walled MWCs remain; almost all have closed or been dismantled.

- Mass burn waterwall (MB-WW) facilities represent enhanced combustion efficiency, as compared with mass burn refractory-walled incinerators. Although it achieves similar volume reductions, the MB-WW incinerator design provides a more efficient delivery of combustion air, resulting in higher sustained temperatures. Figure 3-1 is a

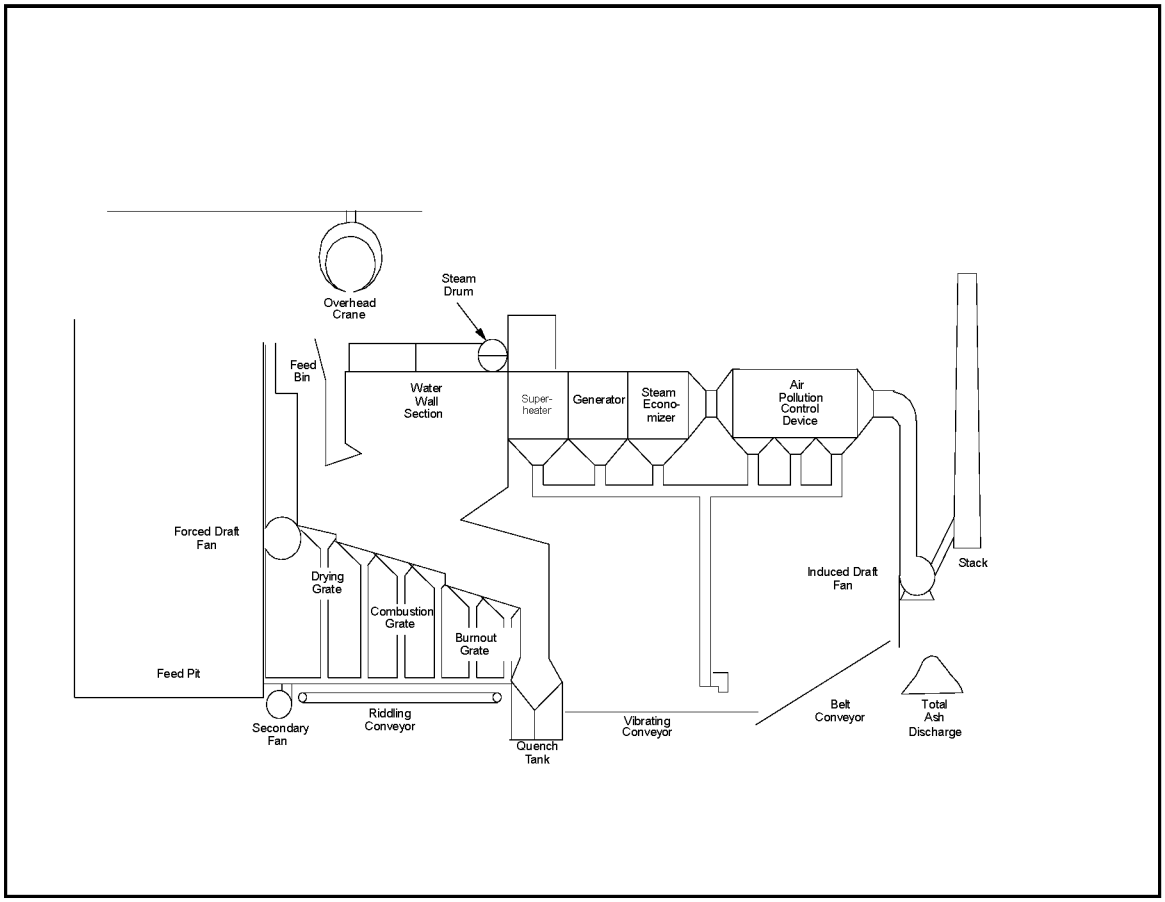


Figure 3-1. Typical mass burn waterwall municipal solid waste combustor.

Source: U.S. EPA (1997a).

schematic of a typical MB-WW MWC. The term "waterwall" refers to a series of steel tubes that run vertically along the walls of the furnace and contain water. Heat from combustion produces steam, which is then used to drive an electrical turbine generator or for other industrial needs. This transfer of energy is called energy recovery. MB-WW incinerators are the dominant form of incinerator found at large municipal waste combustion facilities.

- Mass burn rotary kilns use a water-cooled rotary combustor that consists of a rotating combustion barrel configuration mounted at a 15- to 20-degree angle of decline. The refuse is charged at the top of the rotating kiln by a hydraulic ram (Donnelly, 1992). Preheated combustion air is delivered to the kiln through various portals. The slow rotation of the kiln (10 to 20 rotations/hr) causes the MSW to tumble, thereby exposing more surface area for complete burnout of the waste. These systems are also equipped with boilers for energy recovery. Figure 3-2 is a schematic of a typical rotary kiln combustor.

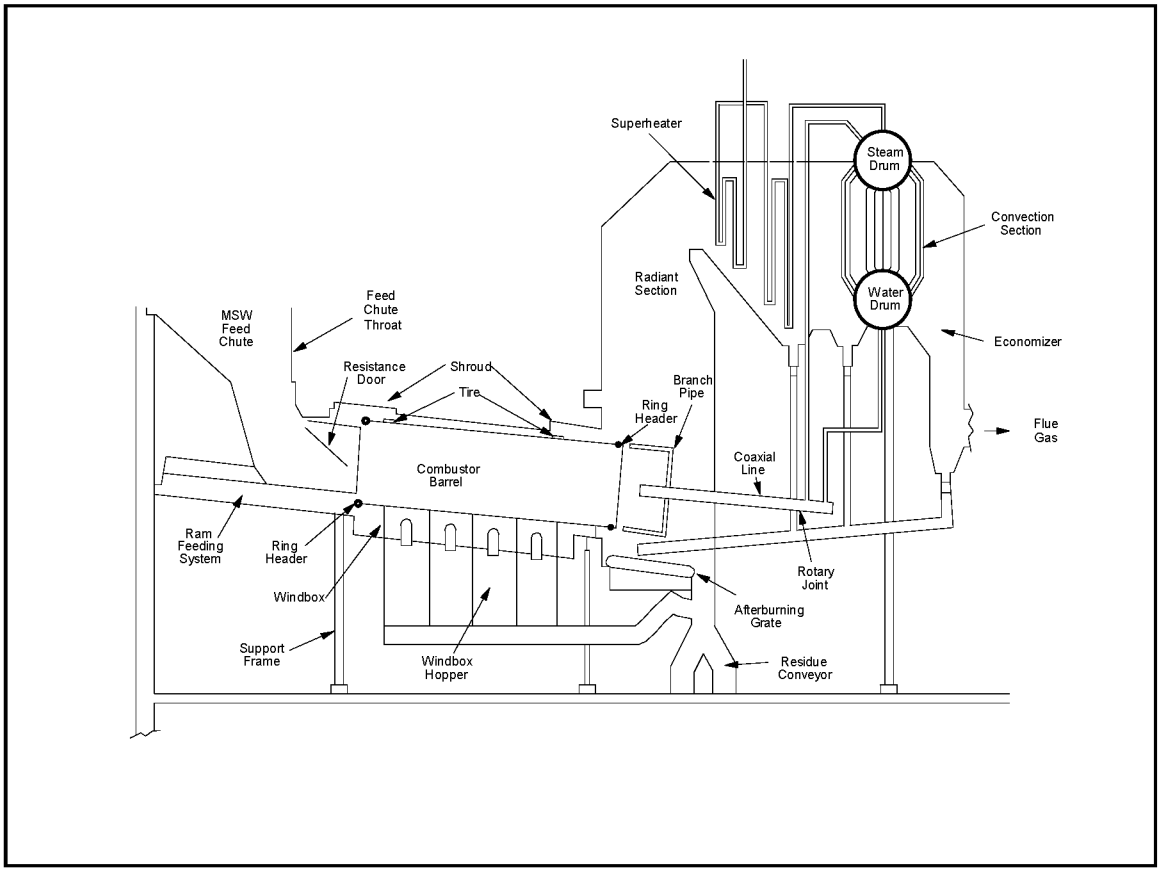


Figure 3-2. Typical mass burn rotary kiln combustor.

Source: U.S. EPA (1997a).

Modular. This is a second general type of municipal waste combustion furnace used in the United States. As with the mass burn type, modular incinerators burn waste without preprocessing. Modular MWCs consist of two vertically mounted combustion chambers (a primary and a secondary chamber). In 1995, the combustion capacity of modular combustors ranged from 4 to 270 metric tons per day, i.e., they are predominately small MWCs. The two major types of modular systems, excess air and starved air, are described below.

- The modular excess-air system consists of a primary and a secondary combustion chamber, both of which operate with air levels in excess of stoichiometric requirements (i.e., 100 to 250% excess air). Figure 3-3 illustrates a typical modular starved-air MWC.

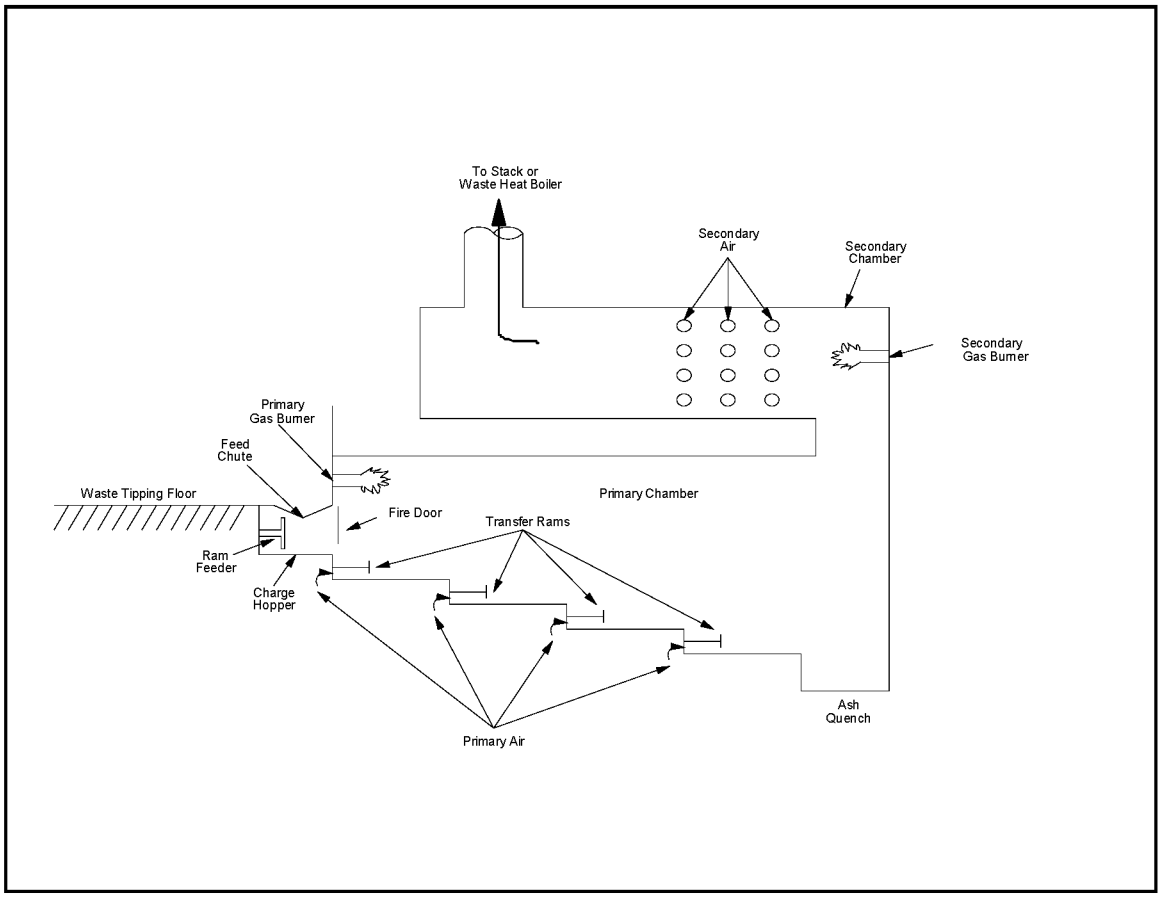


Figure 3-3. Typical modular starved-air combustor with transfer rams.

Source: U.S. EPA (1997a).

- In the starved (or controlled) air type of modular system, air is supplied to the primary chamber at substoichiometric levels. The products of incomplete combustion entrain in the combustion gases that are formed in the primary combustion chamber and then pass into a secondary combustion chamber. Excess air is added to the secondary chamber, and combustion is completed by elevated temperatures sustained with auxiliary fuel (usually natural gas). The high, uniform temperature of the secondary chamber, combined with the turbulent mixing of the combustion gases, results in low levels of particulate matter (PM) and organic contaminants being formed and emitted. Therefore, many existing modular units lack post-combustion APCDs. Figure 3-4 is a schematic view of a modular excess-air MWC.

Refuse-derived fuel (RDF). The third major type of MWC furnace technology is designed to combust RDF; this technology is generally used at very large MWC facilities. RDF is a general term that describes MSW from which relatively noncombustible items are removed,

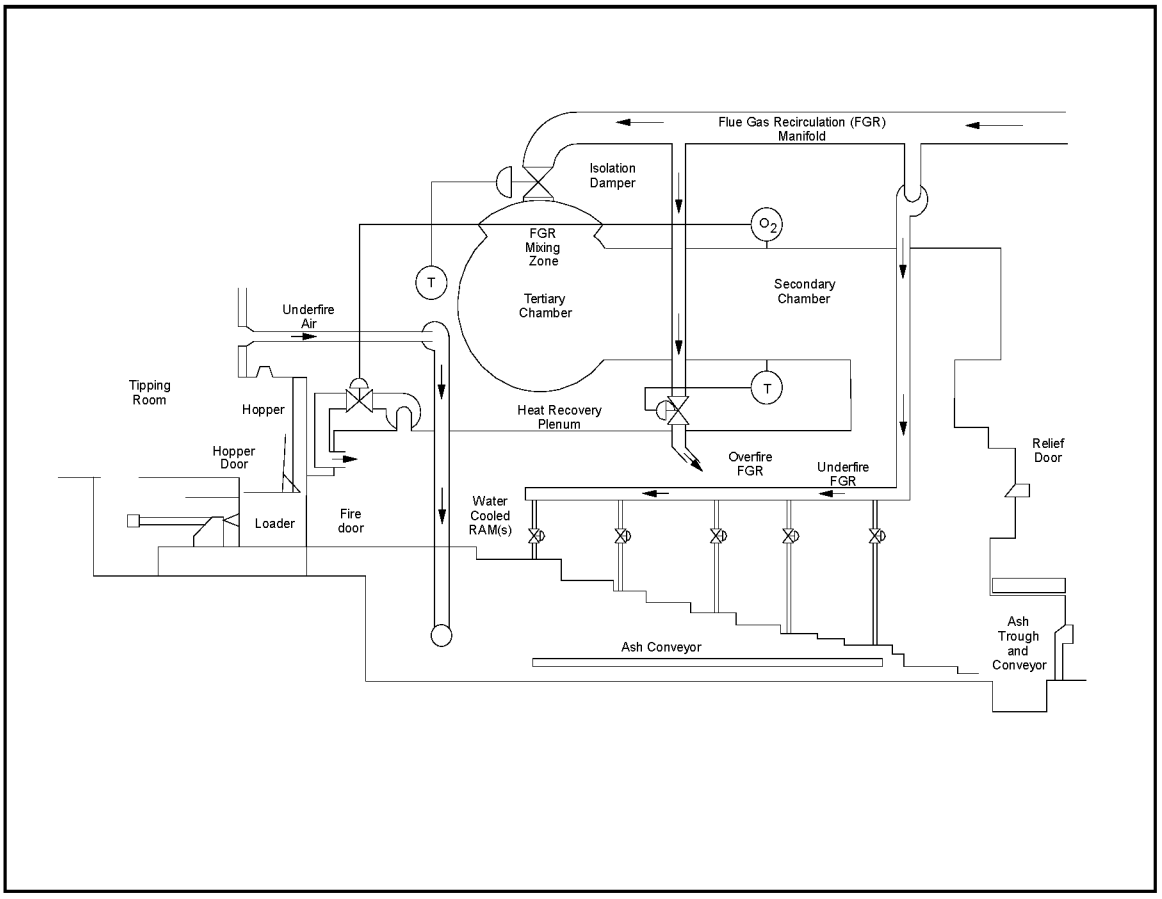


Figure 3-4. Typical modular excess-air combustor.

Source: U.S. EPA (1997a).

thereby enhancing the combustibility of the waste. RDF is commonly prepared by shredding, sorting, and separating out metals to create a dense MSW fuel in a pelletized form having a uniform size. Three types of RDF systems are described below.

- The dedicated RDF system burns RDF exclusively. Figure 3-5 shows a typical dedicated RDF furnace using a spreader-stoker boiler. Pelletized RDF is fed into the combustor through a feed chute using air-swept distributors; this allows a portion of the feed to burn in suspension and the remainder to burn out after falling on a horizontal traveling grate. The traveling grate moves from the rear to the front of the furnace, and distributor settings are adjusted so that most of the waste lands on the rear two-thirds of the grate. This allows more time to complete combustion on the grate. Underfire and overfire air are introduced to enhance combustion, and these incinerators typically operate at 80 to 100% excess air. Waterwall tubes, a

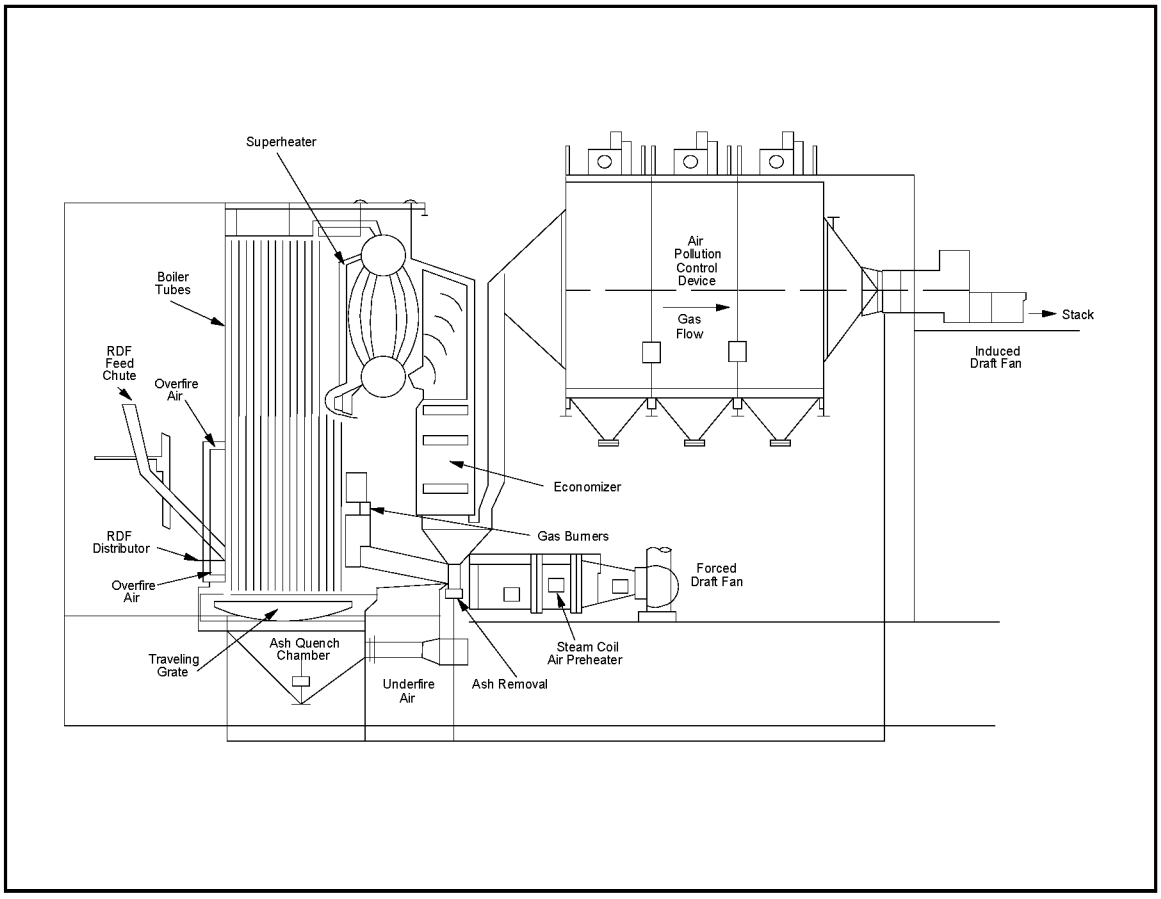


Figure 3-5. Typical dedicated refuse-derived fuel-fired spreader stoker boiler.

Source: U.S. EPA (1997a).

superheater, and an economizer are used to recover heat for production of steam or electricity. The 1995 inventory indicated that dedicated RDF facilities range from 227 to 2,720 metric tons per day total combustion capacity.

- Cofired RDF furnaces burn either RDF or normal MSW along with another fuel.

  The fluidized-bed RDF furnace burns the waste in a turbulent and semisuspended bed of sand. The MSW may be fed into the incinerator either as unprocessed waste or as a form of RDF. The RDF may be injected into or above the bed through ports in the combustor wall. The sand bed is suspended during combustion by introducing underfire air at a high velocity, hence the term "fluidized." Overfire air at 100% of stoichiometric requirements is injected above the sand suspension. Waste-fired fluidized-bed RDF furnaces typically operate at 30 to 100% excess air levels and at

bed temperatures around 815°C. A typical fluidized-bed RDF furnace is represented in Figure 3-6. The technology has two basic designs: a bubbling-bed incineration unit and a circulating-bed incineration unit. The 1995 inventory indicated that fluidized-bed MWCs have capacities ranging from 184 to 920 metric tons per day. These systems are usually equipped with boilers to produce steam.

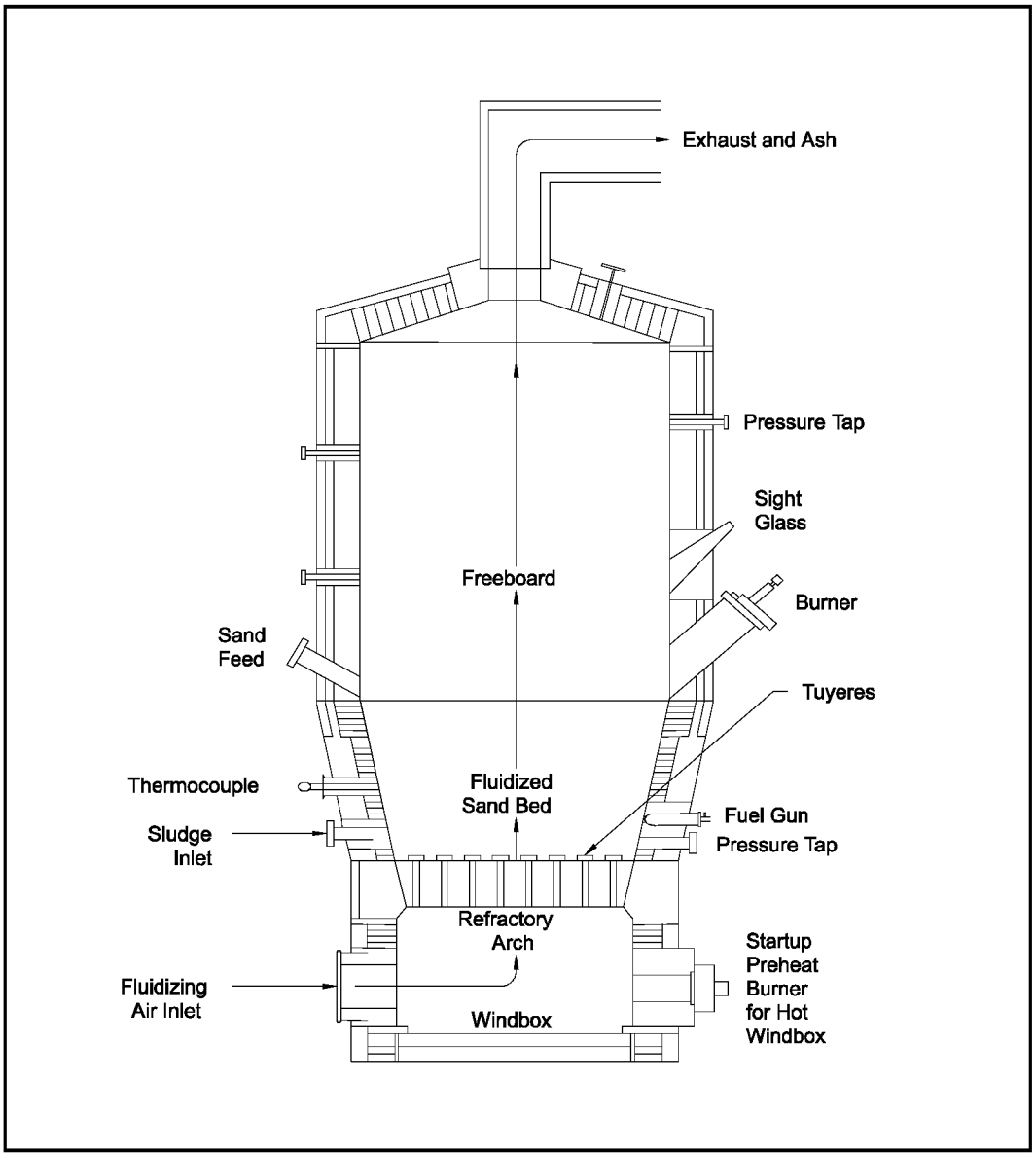


Figure 3-6. Fluidized-bed refuse-derived fuel furnace.

Source: U.S. EPA (1997a).

3.1.1.2. *Air Pollution Control Devices*

MWCs are commonly equipped with one or more post-combustion APCDs to remove various pollutants such as PM, heavy metals, acid gases, and organic contaminants prior to release from the stack (U.S. EPA, 1992a). Types of APCDs include

- Electrostatic precipitator
- Fabric filter
- Spray dry scrubbing system
- Dry sorbent injection
- Wet scrubber

Electrostatic precipitator (ESP). The ESP is generally used to collect and control PM that evolves during MSW combustion by introducing a strong electrical field into the flue gas stream; this in turn charges the particles entrained in the combustion gases (Donnelly, 1992). Large collection plates receive an opposite charge to attract and collect the particles. CDD/CDF formation can occur within the ESP at temperatures in the range of 150°C to about 350°C. As temperatures at the inlet to the ESP increase from 150 to 300°C, CDD/CDF concentrations have been observed to increase by approximately a factor of 2 for each 30°C increase in temperature (U.S. EPA, 1994a). As the temperature increases beyond 300°C, formation rates decline.

Although ESPs in this temperature range efficiently remove most particulates and the associated CDDs/CDFs, the CDD/CDF formation that does occur can result in a net increase in CDD/CDF emissions. This temperature-related formation of CDDs/CDFs within the ESP can be applied, for purposes of this report, to distinguish cold-sided ESPs, which operate at or below 230°C, from hot-sided ESPs, which operate at an inlet temperature greater than 230°C. Most ESPs have been replaced with better-performing and lower-cost fabric filter technology.

Fabric filter (FF). FFs are also PM control devices that remove dioxins associated with particles and any vapors that adsorb to the particles. The filters are usually 6- to 8-inch-diameter bags, 30 feet long, made from woven fiberglass material, and arranged in series. An induction fan forces the combustion gases through the tightly woven fabric. The porosity of the fabric allows the bags to act as filter media and retain a broad range of particle sizes (down to less than 1 μm in diameter). The FF is sensitive to acid gas; therefore, it is usually operated in combination with spray dryer (SD) adsorption of acid gases.

Spray dry scrubbing system (SDSS). Spray dry scrubbing, also called SD adsorption, involves the removal of both acid gas and PM from the post-combustion gases. By themselves, the units probably have little effect on dioxin emissions. In a typical SDSS, hot combustion gases enter a scrubber reactor vessel. An atomized hydrated lime slurry (water plus lime) is injected into the reactor at a controlled velocity (Donnelly, 1992). The slurry rapidly mixes with

the combustion gases within the reactor. The water in the slurry quickly evaporates, and the heat of evaporation causes the combustion gas temperature to rapidly decrease. The neutralizing capacity of hydrated lime reduces the acid gas constituents of the combustion gas (e.g., HCl and SO_2) by greater than 70%. A dry product consisting of PM and hydrated lime settles to the bottom of the reactor vessel.

SDSS technology is used in combination with ESPs or FFs. SDSSs reduce ESP inlet temperatures to make a cold-sided ESP. In addition to acid gas, particulate, and metals control, SDSSs with FFs or ESPs achieve greater than 90% dioxin control (U.S. EPA, 1992a), and they typically achieve greater than 90% SO_2 and HCl control.

Dry sorbent injection (DSI). DSI is used to reduce acid gas emissions. As with SDSSs, these units by themselves probably have little effect on dioxin emissions. In this system, dry hydrated lime or soda ash is injected directly into the combustion chamber or into the flue duct of the hot post-combustion gases. In either case, the reagent reacts with and neutralizes the acid gas constituents (Donnelly, 1992).

Wet scrubber (WS). WS devices are designed for acid gas removal and are more common to MWC facilities in Europe than in the United States. They should help reduce emissions of dioxin in both vapor and particle forms. The devices consist of two-stage scrubbers. The first stage removes HCl, and the second stage removes SO_2 (Donnelly, 1992). Water is used to remove HCl, and caustic or hydrated lime is added to remove SO_2 from the combustion gases.

Other types of APCDs. In addition to the APCDs described above, some less common types are also used in some MWCs. An example is activated carbon injection (CI) technology. Activated carbon is injected into the flue gas prior to the gas reaching SDSSs with FFs (or an ESP). Dioxin (and mercury) are absorbed onto the activated carbon, which is then captured by the FFs or ESP. CI technology improves dioxin control technologies by an additional 75% and is commonly referred to as flue gas polishing. Many APCDs have been retrofitted to include CI, including more than 120 large MWCs.

3.1.1.3. *Classification Scheme*

Based on the array of municipal waste combustion technologies described above, a classification system for deriving CDD/CDF emission estimates was developed. Assuming that facilities with common design and operating characteristics have a similar potential for CDD/CDF emissions, the MWCs operating in 1987 and 1995 were divided into categories according to the eight furnace types and six APCDs described above. This resulted in 17 design classes in 1987 and 40 design classes in 1995. Because fewer types of APCDs were used in 1987

than in 1995, fewer design classes are needed for estimating emissions. The MWCs operating in 2000 were divided into three furnace types and 12 APCDs, resulting in 36 design classes. Design classes for all three reference years are summarized in Figures 3-7 through 3-9.

3.1.2. Characterization of MWCs in Reference Years 2000, 1995, and 1987

Table 3-1 lists, by design/APCD type, the number of facilities and activity level (kg MSW incinerated/yr) for MWCs in reference year 2000. Similar inventories are provided for reference years 1995 and 1987 in Tables 3-2 and 3-3, respectively. This information was derived from five reports: U.S. EPA (1987b), SAIC (1994), Taylor and Zannes (1996), Solid Waste Technologies (1994), and a memorandum dated March 27, 2003, from Jason Huckaby, ERG, to Walt Stevenson, U.S. EPA. In general, the information was collected via telephone interviews with the plant operators.

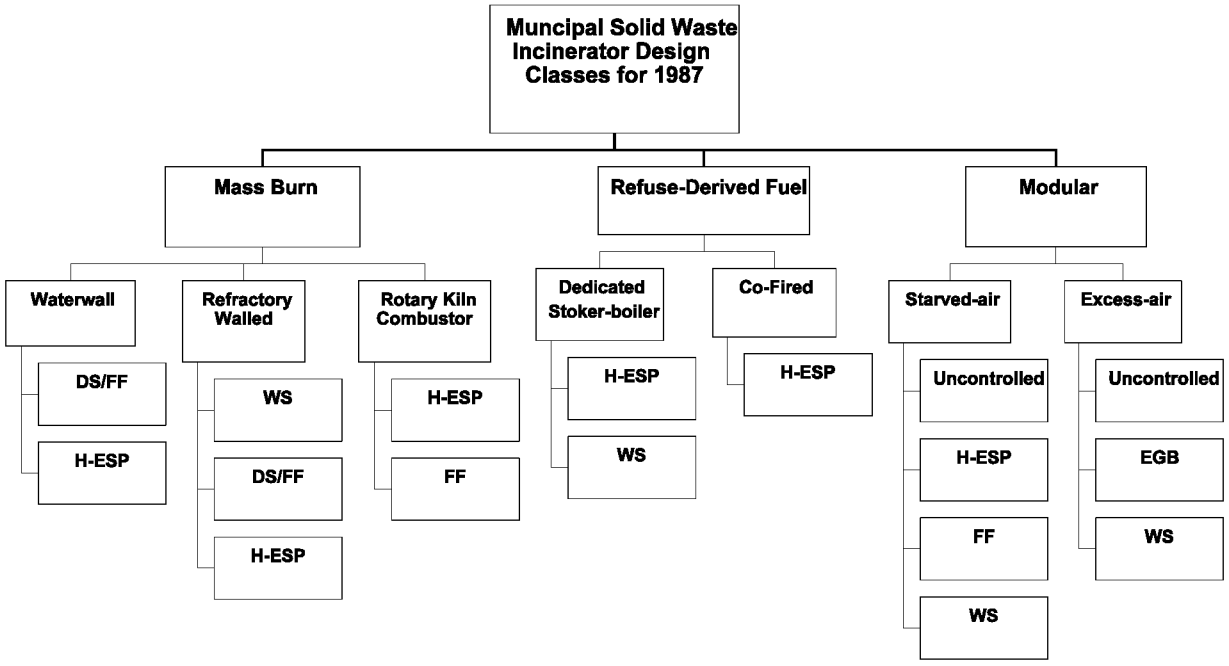


Figure 3-7. Municipal waste combustor design classes for 1987.

DS/FF = Dry scrubber combined with a fabric filter
EGB = Electro gravel bed
FF = Fabric filter
H-ESP = Hot-sided electrostatic precipitator (temperature at control device is >230°C)
WS = Wet scrubber

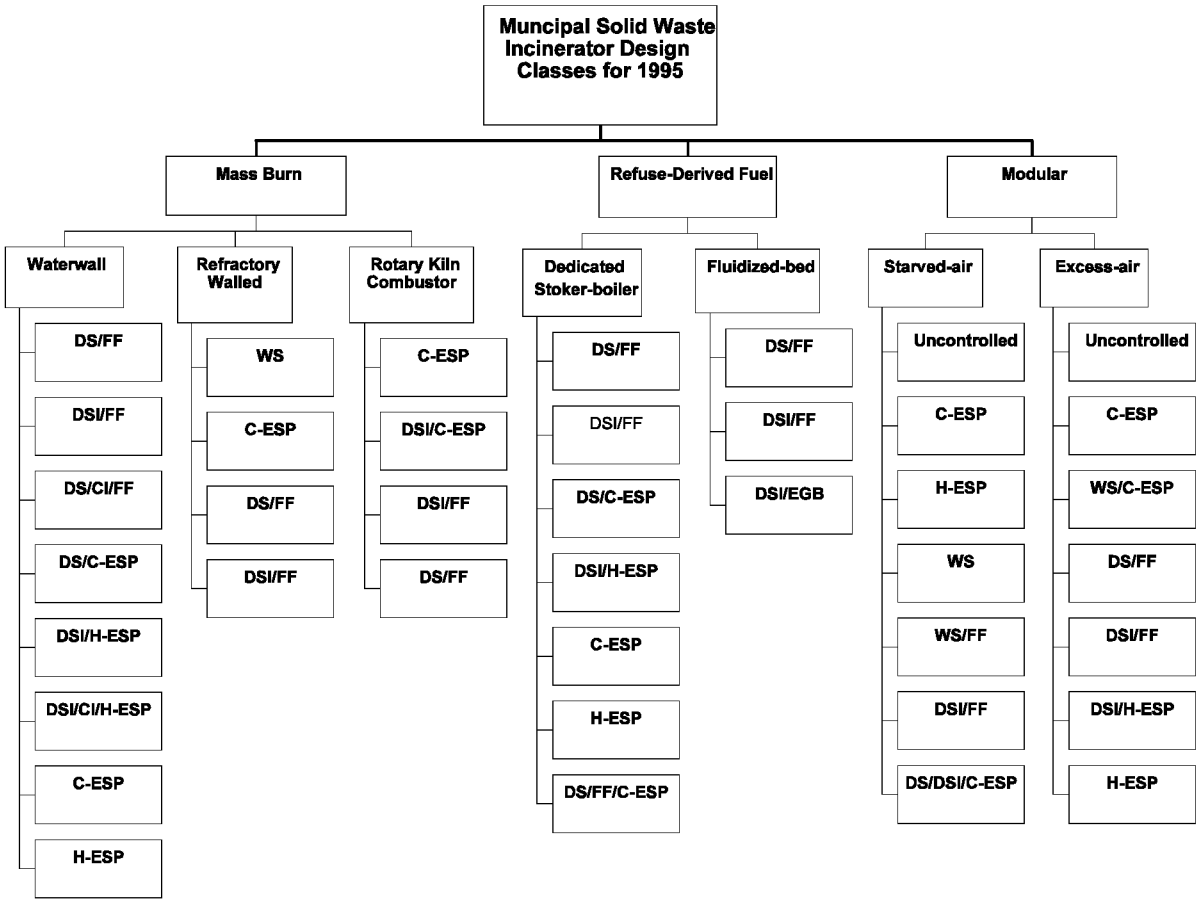


Figure 3-8. Municipal waste combustor design classes for 1995.

C-ESP = Cold-sided electrostatic precipitator (temperature at control device is <230°C)
DS/CI/FF = Dry scrubber with carbon injection and fabric filter
DS/FF = Dry scrubber combined with a fabric filter
DSI/FF = Dry sorbent injection coupled with a fabric filter
EGB = Electro gravel bed
H-ESP = Hot-sided electrostatic precipitator (temperature at control device is >230°C)
WS = Wet scrubber

Using Tables 3-1, 3-2, and 3-3, a number of comparisons can be made between the reference years:

- The number of facilities stayed about the same (105 in 1987, 130 in 1995, and 104 in 2000), but the amount of MSW incinerated more than doubled from 1987 to 1995 (from 13.4 billion kg in 1987 to 29 billion kg in 1995); it remained constant from 1995 to 2000 (30.6 billion kg in 2000).

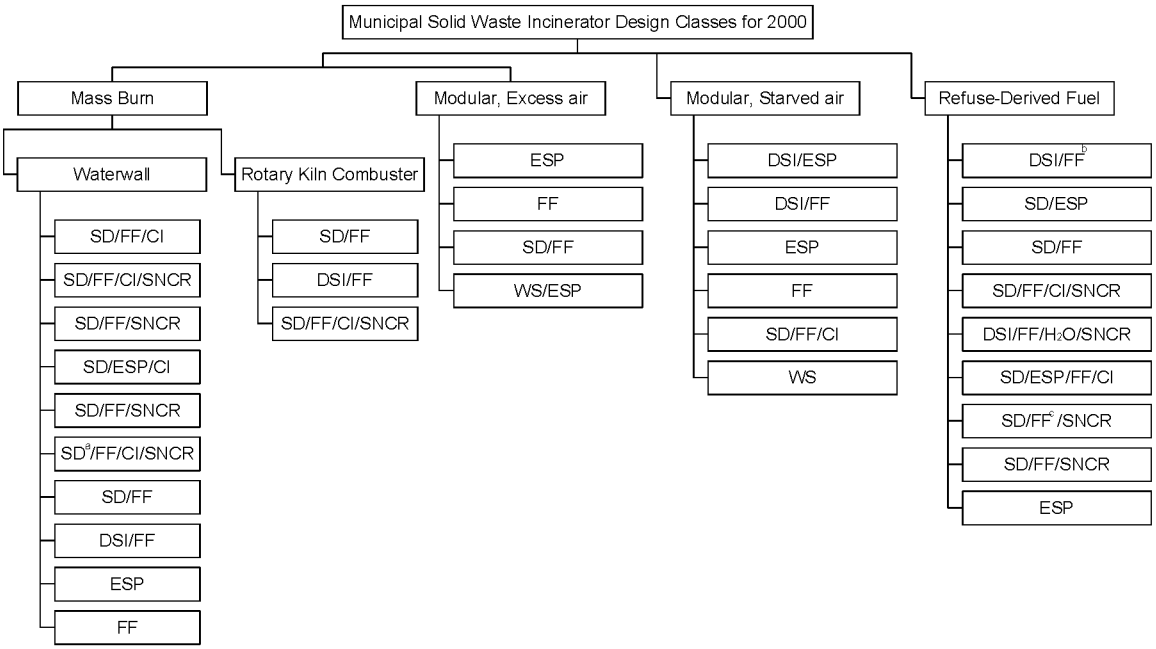


Figure 3-9. Municipal waste combustor design classes for 2000.

[a]Also equipped with furnace dry sorbent injection system.
[b]Also equipped with flue gas cooling (280–290°F).
[c]Also equipped with compact hybrid particulate collector system.

CI = Carbon injection
DSI = Dry sorbent injection
ESP = Electrostatic precipitator
FF = Fabric filter
H_2O = Water scrubber
SD = Spray dryer
SNCR = Selective noncatalytic reduction
WS = Wet scrubber

- In terms of number of facilities, the dominant furnace technology shifted from modular in 1987 (49 units and 1.1 billion kg) to MB-WW facilities in 1995 (57 units and 16.8 billion kg) and 2000 (140 units and 19 billion kg).

- The dominant APCD technology shifted from hot-sided ESPs in 1987 (46 units and 11 billion kg) to SDs with FFs (SDs/FFs) in 1995 (41 units and 12.8 billion kg) and SDs/FFs with CI and selective noncatalytic reduction (88 units and 4.6 billion kg), and SDs/FFs (27 units and 3.1 billion kg) in 2000.

- The use of hot-sided ESPs dropped from 46 facilities in 1987 (11 billion kg) to 12 facilities in 1995 (1.3 billion kg). No hot-sided ESPs were used in 2000.

- The number of uncontrolled facilities dropped from 38 in 1987 (0.6 billion kg) to 10 in 1995 (0.2 billion kg) and 6 in 2000 (0.08 billion kg).

Table 3-1. Inventory of municipal waste combustors (MWCs) in 2000 by technology, air pollution control device (APCD), size[a], and annual activity level (kg/yr)

APCD[b]	MWC type																			
	MB/RC		MB		MB/WW/RC		MB/REF		MB/WW		MOD/EA		MOD/SA		FB/RDF		RDF		TOTAL	
	Size (N)	Activity level	Size (N)	Activity level	Size (N)	Activity level	Size (N)	Activity level	Size (N)	Activity level	Size (N)	Activity level	Size (N)	Activity level	Size (N)	Activity level	Size (N)	Activity level	Size (N)	Activity level
DSI/FF[c]	S(4)	2.78e+08							S(2)	6.27e+07	S(3)	1.13e+08	S(3)	4.7e+07	S(2)	9.41e+07			S(14)	5.95e+08
DSI/ESP							S(2)	1.25e+08					S(7)	1.49e+08					S(9)	2.75e+08
DSI/FF/ H_2O/SNCR																	L(2)	4.44e+07	L(2)	4.44e+07
ESP	S(4)	2.61e+08							S(6)	2.79e+08	S(6)	9.22e+07	S(8)	1.14e+08			S(2)	1.56e+08	S(26)	9.10e+08
FF					S(1)	1.76e+07							S(2)	3.14e+07					S(3)	4.90e+07
WS													S(4)	5.46e+07					S(4)	5.46e+07
WS/ESP											S(3)	1.13e+08							S(3)	1.13e+08
SD[d]/FF/CI/ SNCR	L(3)	3.97e+08							L(75)	1.34e+10							L(4)	6.68e+08	L(82)	1.45e+10
SD/ESP																	L(4)	1.08e+09	L(4)	1.08e+06
SD/ESP/CI									L(4)	3.74e+08									L(4)	3.74e+08
SD/ESP/ CI/SNCR									L(15)	2.79e+09									L(15)	2.79e+09
SD/ESP/ FF[e]/CI																	L(2)	7.41e+08	L(2)	7.41e+08
SD/FF	L(6)	1.11e+09	S(2)	6.27e+07					S(4)	1.25e+08	S(3)	1.32e+08					L(12)	1.69e+09	S(9) L(18)	3.20e+08 2.80e+09
SD/FF[e]/ SNCR									L(13)	2.99e+09							L(8)	1.57e+09	L(21)	4.56e+09
SD/FF/CI									S(2) L(5)	1.25e+08 9.51e+08			S(4)	6.27e+07					S(6) L(5)	1.88e+08 9.51e+08
Unc									S(2)	3.14e+07			S(4)	5.17e+07					S(6)	8.31e+07
TOTAL	L(9) S(8)	1.51e+09 4.94e+08	S(2)	6.27e+07	S(1)	1.76e+07	S(2)	1.25e+08	L(124) S(16)	2.05e+10 6.24e+08	S(15)	4.50e+08	S(31)	5.10e+08	S(2)	9.41e+07	L(34) S(2)	5.97e+09 1.56e+08	L(167) S(79)	2.80e+10 2.60e+09

Table 3-1. Inventory of municipal waste combustors (MWCs) in 2000 by technology, air pollution control device (APCD), size[a], and annual activity level (kg/yr) (continued)

[a]For size, S = small; L = large.
[b]Slash(es) indicates devices used in conjunction.
[c]Also equipped with flue gas cooling (138 to 143°C).
[d]Also equipped with furnace dry sorbent injection system.
[e]Also equipped with compact hybrid particulate collector system.

APCD:
CI = Carbon injection
DSI = Dry sorbent injection
ESP = Electrostatic precipitator
FF = Fabric filter
H_2O = Water scrubber
SD = Spray dryer
SNCR = Selective noncatalytic reduction
Unc = Uncontrolled
WS = Wet scrubber

MWC type:
FB/RDF = Fluidized-bed refuse-derived fuel
MB = Mass burn
MB/RC = Mass burn rotary kiln
MB/REF = Mass burn refractory walled
MB/WW/RC = Mass burn waterwalled/refractory walled
MOD/EA = Modular excess air
RDF = Refuse-derived fuel

Table 3-2. Inventory of municipal waste combustors (MWCs) in 1995 by technology, air pollution control device (APCD), and annual activity level (kg/yr)

APCD[a]	MWC type															
	MB/RC		MB/REF		MB/WW		FB/RDF		RDF/ded		MOD/SA		MOD/EA		TOTAL	
	N	Activity level	N	Activity level	N	Activity level	N	Activity level	N	Activity level	N	Activity level	N	Activity level	N	Activity level
Unc											9	1.87e+08	1	1.41e+07	10	2.01e+08
H-ESP					6	1.04e+09			1	4.22e+07	4	1.82e+08	1	1.97e+07	12	1.28e+09
C-ESP	2	2.00e+08	1	1.69e+08	8	2.81e+09			4	1.81e+09	4	1.25e+08	3	8.28e+07	22	5.20e+09
DSI/H-ESP					1	4.22e+08			1	2.00e+08			1	1.41e+07	3	6.36e+08
DS/FF	2	1.14e+09	2	2.68e+08	28	8.57e+09	1	1.69e+08	7	2.51e+09			1	1.18e+08	41	1.28e+10
DS/CI/FF					3	1.17e+09									3	1.17e+09
DS/FF/C-ESP									1	5.63e+08					1	5.63e+08
WS/FF											1	2.82e+07			1	2.82e+07
WS/C-ESP													1	6.76e+07	1	6.76e+07
DS/C-ESP			1	4.22e+08	8	2.31e+09			4	1.75e+09					13	4.48e+09
DS/DSI/C-ESP											1	7.60e+07			1	7.60e+07
DSI/CI/H-ESP					1	2.75e+08									1	2.75e+08
DSI/C-ESP	6	5.07e+08													6	5.07e+08
DSI/FF	2	2.59e+08	1	1.13e+08	2	1.97e+08	1	8.45e+07	1	4.22e+08	1	3.42e+07	1	1.01e+08	9	1.21e+09
DSI/EGB							1	1.13e+08							1	1.13e+08
WS			2	2.04e+08							3	4.90e+07			5	6.94e+08
TOTAL	12	2.10e+09	7	1.18e+09	57	1.68e+10	3	3.67e+08	19	7.30e+09	23	6.81e+07	9	4.17e+08	130	2.93e+10

Table 3-2. Inventory of municipal waste combustors (MWCs) in 1995 by technology, air pollution control device (APCD), and annual activity level (kg/yr) (continued)

[a]Slash(es) indicates devices used in conjunction.

APCD:
- C-ESP = Cold-sided electrostatic precipitator
- CI = Carbon injection
- DS = Dry scrubber
- DSI = Dry sorbent injection
- EGB = Electro gravel bed
- FF = Fabric filter
- H-ESP = Hot-sided electrostatic precipitator
- SD = Spray dryer
- Unc = Uncontrolled
- WS = Wet scrubber

MWC type:
- FB/RDF = Fluidized-bed refuse-derived fuel
- MB/RC = Mass burn rotary kiln
- MB/REF = Mass burn refractory walled
- MB/WW = Mass burn waterwalled
- MOD/EA = Modular excess air
- MOD/SA = Modular starved air
- RDF/ded = Refuse-derived fuel/dedicated

Table 3-3. Inventory of municipal waste combustors (MWCs) in 1987 by technology, air pollution control device (APCD), and annual activity level (kg/yr)

APCD[a]	MWC type															
	MB/RC		MB/REF		MB/WW		RDF/ded		RDF/cofired		MOD/SA		MOD/EA		TOTAL	
	N	Activity level	N	Activity level	N	Activity level	N	Activity level	N	Activity level	N	Activity level	N	Activity level	N	Activity level
Unc											36	5.73e+08	2	4.17e+07	38	6.15e+08
H- ESP	3	3.94e+08	12	2.00e+09	19	5.20e+09	7	3.01e+09	3	2.53e+08	2	1.17e+08			46	1.10e+10
DS/FF			1	1.41e+07	1	1.55e+08									2	1.69e+08
FF	1	1.58e+07									3	1.43e+08			4	1.59e+08
EGB													1	6.76e+07	1	6.76e+07
WS			7	9.01e+08			2	3.38e+08			4	5.30e+07	1	1.27e+08	14	1.42e+09
TOTAL	4	4.10e+08	20	2.92e+09	20	5.36e+09	9	3.35e+09	3	2.53e+08	45	8.9e+08	4	2.36e+08	105	1.34e+10

[a]Slash indicates devices used in conjunction.

APCD:
DS = Dry scrubber
EGB = Electro gravel bed
FF = Fabric filter
H-ESP = Hot-sided electrostatic precipitator
Unc = Uncontrolled
WS = Wet scrubber

MWC type:
MB/RC = Mass burn rotary kiln
MB/REF = Mass burn refractory walled
MB/WW = Mass burn waterwalled
MOD/EA = Modular excess air
MOD/SA = Modular starved air
RDF/cofired = Refuse-derived fuel/cofired
RDF/ded = Refuse-derived fuel/dedicated

3.1.3. Estimation of CDD/CDF Emissions from MWCs

Compared with other CDD/CDF source categories, MWCs have been more extensively evaluated for CDD/CDF emissions. In 2000, due to new regulations, EPA's Office of Air Quality Planning and Standards (OAQPS) obtained emission test reports for all large MWCs.

3.1.3.1. *Estimating CDD/CDF Emissions from MWCs in Reference Year 2000*

EPA regulates dioxin emissions from MWCs on the basis of whether a facility is large or small (see Section 3.1.7). Large facilities are those with a total design combustion capacity >250 tons/day; small facilities are those with a combustion capacity <250 tons/day). Combustion capacity is determined on the basis of a single incineration unit. Facilities may comprise more than one incinerator unit. In 2000, all large MWC facilities were source tested for stack emissions of dioxin, as required by EPA regulations. Therefore, actual emissions from large facilities were used to represent facility-specific dioxin emissions in 2000. More than 70% of the small MWCs have been tested for dioxin emissions, and the available data were used to represent facility-specific dioxin emissions in 2000. For small MWCs that were not source tested, dioxin emissions were estimated on the basis of emission factors.

Using the test reports, concentrations and emissions were calculated for each of the 17 named dioxin/furan congeners and the remainder of the congener groups (homologues), making up total dioxin/furan emissions (for 27 congeners/groups) for each of the MWC units (Memorandum dated March 27, 2003, from Jason Huckaby, ERG, to Walt Stevenson, U.S. EPA). The calculations were based on the individual CDD/CDF congener/group concentrations for the MWC, the flue gas flow rate and MWC steam generation rate during the test, and the annual steam generation at the MWC. Table 3-4 presents the average CDD/CDF congener-specific stack gas concentrations used to derive the emission factors for the nontested facilities. Table 3-4 shows concentrations for three detection limit (DL) assumptions: (1) a value of zero for concentrations below the DL, (2) a value of one-half the DL for concentrations below the DL, and (3) a value of the DL for concentrations below the DL.

Table 3-5 shows facility-specific dioxin emissions for all MWCs operating in 2000 (because of its size, Table 3-5 is placed at the end of this chapter). Note that the facilities are divided into large and small MWCs. In total, 83.8 g TEQ_{DF}-WHO_{98} (76.3 g I-TEQ) were emitted from all 104 MWCs in 2000. Of this total amount, 13.8 g TEQ_{DF}-WHO_{98} (12.7 g I-TEQ) were emitted from large MWCs and 69.9 g TEQ_{DF}-WHO_{98} (63.6 g I-TEQ) were emitted from small MWCs. Although 91% of the MSW combusted in 2000 was incinerated in large MWCs, the large MWCs accounted for only 17% of total dioxin emissions.

Table 3-4. National average CDD/CDF congener concentrations for large municipal waste combustors (ng/dscm @ 7% O_2)

Congener	Nondetect set to zero[a]	Nondetect set to ½ detection limit[a]	Nondetect set to detection limit[a]
TrCDD	0.031	0.031	0.031
2,3,7,8-TCDD	0.005	0.006	0.006
1,2,3,7,8-PeCDD	0.016	0.016	0.017
1,2,3,4,7,8-HxCDD	0.016	0.016	0.016
1,2,3,6,7,8-HxCDD	0.037	0.036	0.037
1,2,3,7,8,9-HxCDD	0.032	0.032	0.032
1,2,3,4,6,7,8-HpCDD	0.219	0.219	0.219
OCDD	0.345	0.345	0.345
Other TCDDs	0.232	0.239	0.246
Other PeCDDs	0.323	0.334	0.344
Other HxCDDs	0.494	0.502	0.510
Other HpCDDs	0.220	0.220	0.220
TrCDF	0.037	0.037	0.037
2,3,7,8-TCDF	0.072	0.072	0.073
1,2,3,7,8-PeCDF	0.050	0.051	0.052
2,3,4,7,8-PeCDF	0.069	0.069	0.069
1,2,3,4,7,8-HxCDF	0.082	0.083	0.083
1,2,3,6,7,8-HxCDF	0.059	0.059	0.060
1,2,3,7,8,9-HxCDF	0.013	0.013	0.014
2,3,4,6,7,8-HxCDF	0.066	0.066	0.067
1,2,3,4,6,7,8-HpCDF	0.156	0.157	0.159
1,2,3,4,7,8,9-HpCDF	0.024	0.024	0.024
OCDF	0.090	0.092	0.094
Other TCDF	1.081	1.083	1.085
Other PeCDF	0.747	0.758	0.770
Other HxCDF	0.326	0.329	0.332
Other HpCDF	0.079	0.079	0.079
TOTAL	4.92	4.97	5.02

[a]Values incorporating use of the detection limit when the laboratory report indicated "not detected" for individual CDD/CDF congeners.

Source: Memorandum dated March 27, 2003, from Jason Huckaby, ERG, to Walt Stevenson, U.S. EPA.

3.1.3.2. *Estimating CDD/CDF Emissions from MWCs in Reference Years 1995 and 1987*

Within the context of this report, adequate emissions testing for CDDs/CDFs was available for 11 of the 113 facilities in the 1987 inventory and 27 of the 130 facilities in the 1995 inventory. Nationwide CDD/CDF air emissions from MWCs for reference years 1987 and 1995 were estimated using the three-step process described below.

Step 1. Estimation of emissions from all stack-tested facilities. The EPA stack testing method (EPA Method 23) produces a measurement of CDDs/CDFs in units of mass concentration of CDD/CDF (nanograms per dry standard cubic meter [ng/dscm] of combustion gas) at standard temperature and pressure (20°C and 1 atmosphere [atm]) and adjusted to a measurement of 7% oxygen in the flue gas (U.S. EPA, 1995a). This concentration is assumed to represent conditions at the point of release from the stack into the air. Equation 3-1 was used to derive annual emission estimates for each tested facility:

$$E_{TEQ} = \frac{C \times V \times CF \times H}{10^9\ ng/g} \qquad (3\text{-}1)$$

where:

E_{TEQ} = annual TEQ emissions (g/yr)

C = combustion flue gas TEQ concentration (ng/dscm) (20°C, 1 atm; adjusted to 7% O_2)

V = volumetric flow rate of combustion flue gas (dscm/hr) (20°C, 1 atm; adjusted to 7% O_2)

CF = capacity factor; fraction of time that the MWC operates (0.85)

H = total hours in a year (8,760 hr)

After calculating annual emissions for each tested facility, the emissions were summed across all tested facilities for each reference year. (Many of the emission tests do not correspond exactly to these two years. In these cases, the equipment conditions present at the time of the test were compared with those during the reference year to determine their applicability.)

Step 2. Estimation of emissions from all nonstack-tested facilities. This step involves multiplying the emission factor and the annual activity level for each MWC design class and then summing across classes. The activity levels for reference years 1995 and 1987 are summarized in Tables 3-2 and 3-3, respectively. The emission factors were derived by averaging the emission factors across each tested facility in a design class. The emission factor for each facility was calculated using the following equation:

$$EF_{MWC} = \frac{C \times F_v}{I_w} \qquad (3\text{-}2)$$

where:

EF_{MWC} = emission factor; average ng TEQ/kg of waste burned

C = TEQ or CDD/CDF concentration in flue gases (ng TEQ/dscm) (20°C, 1 atm; adjusted to 7% O_2)

F_v = volumetric flue gas flow rate (dscm/hr) (20°C, 1 atm; adjusted to 7% O_2)

I_w = average waste incineration rate (kg/hr)

Using an MB-WW MWC equipped with a cold-sided ESP as an example, and given:

C = 10 ng TEQ/dscm (20°C, 1 atm; adjusted to 7% O_2)

F_v = 40,000 dscm/hr (20°C, 1 atm; adjusted to 7% O_2)

I_w = 10,000 kg MSW/hr, then

$$EF_{MB\text{-}WW} = \frac{10\ ng}{dscm} \times \frac{40{,}000\ dscm}{hr} \times \frac{hr}{10{,}000\ kg}$$

$$= \frac{40\ ng\ TEQ}{kg\ MSW\ burned}$$

EPA was not able to obtain engineering test reports of CDD/CDF emissions for a number of design classes. In these cases, the above procedure could not be used to derive emission factors. Instead, the emission factors of the tested design class that was judged most similar in terms of dioxin control was assumed to apply to the untested class. The following logic was used to make this decision:

1. The tested APCDs for the furnace type of the untested class were reviewed to see whether any operated at a similar temperature.

2. If any operated at similar temperatures, the one with the most similar technology was assumed to apply.

3. If none operated at a similar temperature, then the most similar furnace type with the same control device was assumed to apply.

Table 3-6 lists all design categories with no tested facilities and shows the class with tested facilities that was judged to be most similar. The emission factors for each design class are the same for both reference years because the emission factor is determined only by the design and operating conditions and is independent of the year of the test.

Step 3. Summation of emissions from tested and untested facilities. This step involves summing emissions from all tested and untested facilities. This process is shown in Tables 3-7a and 3-7b and 3-8a and 3-8b for the reference years 1995 and 1987, respectively. The tables are organized by design class and show the emission estimates for the tested and untested facilities separately. The calculation of emissions from untested facilities is broken out to show the activity level and emission factor for each design class.

3.1.4. Summary of CDD/CDF (TEQ) Emissions from MWCs for 2000, 1995, and 1987

The activity level estimates (i.e., the amount of MSW that is annually combusted by the various municipal waste combustion technologies) are given a high confidence rating for 1987 (13.4 billion kg of waste), 1995 (29.3 billion kg of waste), and 2000 (30.6 billion kg of waste). For all three years, independent sources conducted comprehensive surveys of activity levels for virtually all facilities (U.S. EPA, 1987b; Solid Waste Technologies, 1994; SAIC, 1994; Taylor and Zannes, 1996; Memorandum dated March 27, 2003, from Jason Huckaby, ERG, to Walt Stevenson, U.S. EPA).

The emission factor estimates are given a high confidence rating for 2000 and a medium confidence rating for both 1995 and 1987. A large number of MWC facilities were tested in 2000, whereas a moderate fraction of the facilities were tested in 1995 and 1987: 27 of 130 facilities (21%) in 1995 and 11 of 104 facilities in 1987 (10%). The tested facilities represented 27 and 21% of the total activity level of operating MWCs in 1995 and 1987, respectively. These tests represent most of the design categories identified in this report. The emission factors were developed from emission tests that followed standard EPA protocols, used strict QA/QC procedures, and were well documented in engineering reports. Because all tests were conducted under normal operating conditions, some uncertainty exists about the magnitude of emissions that may have occurred during other conditions (e.g., upset conditions, start up, and shut down). In summary, this report estimates the following dioxin releases to air from MWCs operating in 2000, 1995 and 1987.

Table 3-6. CDD/CDF TEQ emission factors (ng TEQ/kg waste) for municipal solid waste incineration

Incinerator design	Air pollution control device (APCD)[a]	Average I-TEQ_{DF} emission factor	Average TEQ_{DF}-WHO_{98} emission factor	Basis and rationale
MOD/SA	C-ESP	16.2	17	Based on MOD/EA; C-ESP, similar furnace (modular design) and same APCD
	DS/DSI/ C-ESP	16.2	17	Based on MOD/EA; C-ESP, similar furnace (modular design) and similar emission control
	DSI/FF	0.025	0.024	Based on direct tests
	FF	16.2	17	Based on MOD/EA; C-ESP, similar furnace (modular design) and similar emission control
	H-ESP	79	85.7	Based on direct tests
	UNC	0.025	0.024	Based on MOD/SA; DSI/FF, same furnace and most similar expected emissions
	WS	16.2	17	Based on MOD/EA; C-ESP, similar furnace (modular design) and similar APCD temperature
	WS/FF	16.2	17	Based on MOD/EA; C-ESP, similar furnace (modular design) and similar APCD temperature
MOD/EA	C-ESP	16.2	17	Based on direct tests
	DS/FF	16.2	17	Based on MOD/EA; C-ESP, same furnace and similar temperature in APCD; may overestimate emissions
	DSI/FF	0.025	0.024	Based on MOD/SA; DSI/FF, similar (modular design) furnace and same APCD
	DSI/H-ESP	118	119	Based on MOD/EA; H-ESP, same furnace and similar emissions
	EGB	0.025	0.024	Based on MOD/SA; DSI/FF, same furnace and most similar expected emissions
	H-ESP	118	119	Based on direct tests
	Unc	0.025	0.024	Based on MOD/SA; DSI/FF, same furnace and most similar expected emissions
	WS	16.2	17	Based on MOD/EA; C-ESP, same furnace and similar APCD temperature
	WS/C-ESP	16.2	17	Based on MOD/EA; C-ESP, same furnace and similar APCD
FB/RDF	DS/FF	0.63	0.72	Based on MB/WW; DS/FF similar furnace and same APCD
	DSI/EGB	0.63	0.72	Based on MB/WW; DS/FF similar furnace; may underestimate emissions
	DSI/FF	0.63	0.72	Based on MB/WW; DS/FF similar furnace; may underestimate emissions

[a]Slash indicates devices used in conjunction.

APCD:
C-ESP = Cold-sided electrostatic precipitator
DS = Dry scrubber
DSI = Dry sorbent injection
EGB = Electro gravel bed
FF = Fabric filter
H-ESP = Hot-sided electrostatic precipitator
Unc = Uncontrolled
WS = Wet scrubber

MWC type:
FB/RDF = Fluidized-bed refuse-derived fuel
MB/WW = Mass burn waterwalled
MOD/EA = Modular excess air
MOD/SA = Modular starved air

Table 3-7a. Annual I-TEQ$_{DF}$ emissions from municipal waste combustors (MWCs) operating in 1995

MWC type	Air pollution control device (APCD)[a]	I-TEQ$_{DF}$ emissions from tested facilities (g TEQ/yr)	Average I-TEQ$_{DF}$ emission factor (ng/kg)	Activity level nontested facilities (kg/yr)	I-TEQ$_{DF}$ emissions from nontested facilities (g TEQ/yr)	Total I-TEQ$_{DF}$ emissions from all facilities (g TEQ/yr)
MB/WW	C-ESP	0	6.1	2.81e+09	17.1	17.1
	DS/C-ESP	2.1	6.1	1.88e+09	11.5	13.6
	DS/CI/FF	0.64	1.5	7.44e+08	1.1	1.7
	DS/FF	2	0.63	5.98e+09	3.8	5.8
	DSI/CI/H-ESP	2.1	–	0	0.0	2.1
	DSI/FF	0.3	–	0	0.0	0.3
	DSI/H-ESP	0	7.74	4.22e+08	3.3	3.3
	H-ESP	163	473	1.79e+08	84.7	247.6
	Subtotal	170.1		1.20e+10	121.4	291.5
MB/REF	C-ESP	39.8	–	0	0	39.8
	DS/C-ESP	21.6	–	0	0	21.6
	DS/FF	0	0.63	2.68e+08	0.2	0.2
	DSI/FF	0	1.91	1.13e+08	0.2	0.2
	WS	0	236	2.04e+08	48.1	48.1
	Subtotal	61.4		5.85e+08	48.5	109.9
MB/RC	C-ESP	0	47.0	2.00e+08	9.4	9.4
	DS/FF	0.25	0.65	7.57e+08	0.5	0.8
	DSI/C-ESP	0	47.0	5.07e+08	23.8	23.8
	DSI/FF	5.3	47.0	1.46e+08	6.9	12.2
	Subtotal	5.6		1.61e+09	40.6	46.2
RDF/ded	C-ESP	32.5	231	1.67e+09	385.8	418.3
	DS/C-ESP	0.3	0.53	1.14e+09	0.6	0.9
	DS/FF	0.1	0.24	1.58e+09	0.4	0.5
	DSI/FF	0	231	4.22e+08	97.5	97.5
	DSI/H-ESP	0	231	2.00e+08	46.2	46.2
	H-ESP	0	1,492	4.22e+07	63.0	63
	DS/FF/C-ESP	0	0.24	5.63e+08	0.1	0.1
	Subtotal	32.9		5.62e+09	593.5	626.4
MOD/SA	C-ESP	0	16.2	1.25e+08	2.0	2
	DSI/FF	0	–	0	0.0	0
	H-ESP	8	79	8.03e+07	6.3	14.3
	Unc	0	0.025	1.87e+08	0.0	0.005
	WS	0	16.2	4.90e+07	0.8	0.8
	WS/FF	0	16.2	2.82e+07	0.5	0.5
	DS/DSI/C-ESP	0	16.2	7.60e+07	1.2	1.2
	Subtotal	8		5.46e+08	10.9	18.9

Table 3-7a. Annual I-TEQ$_{DF}$ emissions from municipal waste combustors (MWCs) operating in 1995 (continued)

MWC type	Air pollution control device (APCD)[a]	I-TEQ$_{DF}$ emissions from tested facilities (g TEQ/yr)	Average I-TEQ$_{DF}$ emission factor (ng/kg)	Activity level nontested facilities (kg/yr)	I-TEQ$_{DF}$ emissions from nontested facilities (g TEQ/yr)	Total I-TEQ$_{DF}$ emissions from all facilities (g TEQ/yr)
MOD/EA	C-ESP	0.1	16.2	6.25e+07	1	1.1
	DS/FF	0	16.2	1.18e+08	1.9	1.9
	DSI/FF	0	0.025	1.01e+08	0.003	0.003
	DSI/H-ESP	0	118	1.41e+07	1.7	1.7
	H-ESP	2.3	[b]	0	0	2.3
	Unc	0	0.025	1.41e+07	0.0003	0.0003
	WS/C-ESP	0	16.2	6.76e+07	1.1	1.1
	Subtotal	2.4		3.77e+08	5.7	8.1
FB/RDF	DS/FF	0	0.63	1.69e+08	0.1	0.1
	DSI/EGB	0	0.63	1.13e+08	0.1	0.1
	DSI/FF	0	0.63	8.45e+07	0.1	0.1
	Subtotal	0		3.67e+08	0.3	0.3
TOTAL		280.4		2.11e+10	820.9	1,101.3

[a]Slash indicates devices used in conjunction.
[b]Value could not be calculated.

– = Emissions not developed

APCD:
- C-ESP = Cold-sided electrostatic precipitator
- CI = Carbon injection
- DS = Dry scrubber
- DSI = Dry sorbent injection
- EGB = Electro gravel bed
- FF = Fabric filter
- H-ESP = Hot-sided electrostatic precipitator
- Unc = Uncontrolled
- WS = Wet scrubber

MWC type:
- FB/RDF = Fluidized-bed refuse-derived fuel
- MB/RC = Mass burn rotary kiln
- MB/REF = Mass burn refractory walled
- MB/WW = Mass burn waterwalled
- MOD/EA = Modular excess air
- MOD/SA = Modular starved air
- RDF/ded = Refuse-derived fuel/dedicated

Table 3-7b. Annual TEQ_{DF}-WHO_{98} emissions from municipal waste combustors (MWCs) operating in 1995

MWC type	Air pollution control device (APCD)[a]	TEQ_{DF}-WHO_{98} emissions from tested facilities (g TEQ/yr)	Average TEQ_{DF}-WHO_{98} emission factor (ng/kg)	Activity level nontested facilities (kg/yr)	TEQ_{DF}-WHO_{98} emissions from nontested facilities (g TEQ/yr)	Total TEQ_{DF}-WHO_{98} emissions from all facilities (g TEQ/yr)
MB/WW	C-ESP	0	6.54	2.81e+09	18.4	18.4
	DS/C-ESP	2.24	6.54	1.88e+09	12.3	14.54
	DS/CI/FF	0.68	1.61	7.44e+08	1.2	1.88
	DS/FF	2.1	0.72	5.98e+09	4.3	6.4
	DSI/CI/H-ESP	2.26	–	0.0	0.0	2.26
	DSI/FF	0.3	–	0.0	0.0	0.3
	DSI/H-ESP	0	8.22	4.22e+08	3.5	3.5
	H-ESP	183	535.0	1.79e+08	95.8	278.8
	Subtotal	190.6		1.20e+10	135.4	326.0
MB/REF	C-ESP	43	–	0.0	0.0	43.0
	DS/C-ESP	22.5	–	0.0	0.0	22.5
	DS/FF	0	0.72	2.68e+08	0.2	0.2
	DSI/FF	0	2.07	1.13e+08	0.2	0.2
	WS	0	254.0	2.04e+08	51.8	51.8
	Subtotal	65.5		5.85e+08	52.2	117.7
MB/RC	C-ESP	0	93.1	2.00e+08	18.6	18.6
	DS/FF	0.265	0.68	7.57e+08	0.5	0.8
	DSI/C-ESP	0	93.1	5.07e+08	47.2	47.2
	DSI/FF	10.5	93.1	1.46e+08	13.6	24.1
	Subtotal	10.8		1.61e+09	79.9	90.7
RDF/ded	C-ESP	35.6	253.0	1.67e+09	422.5	458.1
	DS/C-ESP	0.34	0.56	1.14e+09	0.6	1.0
	DS/FF	0.1	0.26	1.58e+09	0.4	0.5
	DSI/FF	0	253.0	4.22e+08	106.8	106.8
	DSI/H-ESP	0	253.0	2.00e+08	50.6	50.6
	H-ESP	0	1,679.0	4.22e+07	70.9	70.9
	DS/FF/C-ESP	0	253.0	5.63e+08	142.4	142.4
	Subtotal	36		5.62e+09	794.2	830.2
MOD/SA	C-ESP	0	17.0	1.25e+08	2.1	2.1
	DSI/FF	0.0008	–	0.0	0.0	0.001
	H-ESP	8.69	85.7	8.03e+07	6.9	15.6
	Unc	0	0.024	1.87e+08	0.0	0.005
	WS	0	17.0	4.90e+07	0.8	0.8
	WS/FF	0	17.0	2.82e+07	0.5	0.5
	DS/DSI/C-ESP	0	17.0	7.60e+07	1.3	1.3
	Subtotal	8.7		5.46e+08	11.6	20.3

Table 3-7b. Annual TEQ_{DF}-WHO_{98} emissions from municipal waste combustors (MWCs) operating in 1995 (continued)

MWC type	Air pollution control device (APCD)[a]	TEQ_{DF}-WHO_{98} emissions from tested facilities (g TEQ/yr)	Average TEQ_{DF}-WHO_{98} emission factor (ng/kg)	Activity level nontested facilities (kg/yr)	TEQ_{DF}-WHO_{98} emissions from nontested facilities (g TEQ/yr)	Total TEQ_{DF}-WHO_{98} emissions from all facilities (g TEQ/yr)
MOD/EA	C-ESP	0.068	17.0	6.25e+07	1.06	1.1
	DS/FF	0	17.0	1.18e+08	2.01	2.0
	DSI/FF	0	0.024	1.01e+08	0.002	0.002
	DSI/H-ESP	0	119.0	1.41e+07	1.68	1.7
	H-ESP	2.35	–	0.0	0.0	2.4
	Unc	0	0.024	1.41e+07	0.003	0.003
	WS/C-ESP	0	17.0	6.76e+07	1.15	1.2
	Subtotal	2.4		3.77e+08	5.9	8.3
FB/RDF	DS/FF	0	0.72	1.69e+08	0.114	0.1
	DSI/EGB	0	0.72	1.13e+08	0.076	0.1
	DSI/FF	0	0.72	8.45e+07	0.057	0.1
	Subtotal	0		3.67e+08	0.3	0.3
TOTAL		314		2.11e+10	1,079.5	1,393.5

[a]Slash indicates devices used in conjunction.

– = Emissions not developed

APCD:
- C-ESP = Cold-sided electrostatic precipitator
- CI = Carbon injection
- DS = Dry scrubber
- DSI = Dry sorbent injection
- EGB = Electro gravel bed
- FF = Fabric filter
- H-ESP = Hot-sided electrostatic precipitator
- Unc = Uncontrolled
- WS = Wet scrubber

MWC type:
- FB/RDF = Fluidized-bed refuse-derived fuel
- MB/RC = Mass burn rotary kiln
- MB/REF = Mass burn refractory walled
- MB/WW = Mass burn waterwalled
- MOD/EA = Modular excess air
- MOD/SA = Modular starved air
- RDF/ded = Refuse-derived fuel/dedicated

Table 3-8a. Annual I-TEQ$_{DF}$ emissions to the air from municipal waste combustors (MWCs) operating in 1987

MWC type	Air pollution control device (APCD)[a]	I-TEQ$_{DF}$ emissions from tested facilities (g TEQ/yr)	Average I-TEQ$_{DF}$ emission factor (ng/kg)	Activity level nontested facilities (kg/yr)	I-TEQ$_{DF}$ emissions from nontested facilities (g TEQ/yr)	Total I-TEQ$_{DF}$ emissions from all facilities (g TEQ/yr)
MB/WW	DS/FF	0.0373	–	1.55e+08	0.0	0.0373
	H-ESP	433.0	473.0	3.27e+09	1,546.7	1,979.7
	Subtotal	433.0		3.43e+09	1,546.7	1,979.7
MB/REF	DS/FF	0.0	0.63	1.41e+08	0.09	0.09
	H-ESP	0.0	473.0	2.00e+09	946.0	946.0
	WS	0.0	236.0	9.01e+08	212.6	212.6
	Subtotal	0.0		3.04e+09	1,158.7	1,158.7
MB/RC	FF	0.0	47.0	1.58e+07	0.7	0.7
	H-ESP	48.2	285.0	2.25e+08	64.1	112.3
	Subtotal	48.2		2.41e+08	64.8	113.0
RDF/ded	H-ESP	840.0	1,492.0	2.45e+09	3,655.4	4,495.4
	WS	0.0	231.0	3.38e+08	78.1	78.1
	Subtotal	840.0		2.79e+09	3,733.5	4,573.5
RDF/cofired	H-ESP	0.0	231.0	2.53e+08	58.4	58.4
MOD/SA	FF	0.0	16.2	1.43e+08	2.3	2.3
	H-ESP	0.0643	79.0	3.61e+08	28.5	28.6
	Unc	0.0	0.025	5.73e+08	0.01	0.01
	WS	0.0	16.2	5.30e+07	0.86	0.86
	Subtotal	0.0643		1.13e+09	31.7	31.8
MOD/EA	EGB	0.0	0.025	6.76e+07	0.002	0.002
	Unc	0.0	0.025	4.17e+07	0.001	0.001
	WS	0.0	16.2	1.27e+08	2.057	2.057
	Subtotal	0.0		2.36e+08	2.1	2.1
TOTAL		1,321.3		1.11e+10	6,537.5	7,858.8

[a]Slash indicates devices used in conjunction.

APCD:
- DS = Dry scrubber
- EGB = Electro gravel bed
- FF = Fabric filter
- H-ESP = Hot-sided electrostatic precipitator
- Unc = Uncontrolled
- WS = Wet scrubber

MWC type:
- MB/RC = Mass burn rotary kiln
- MB/REF = Mass burn refractory walled
- MB/WW = Mass burn waterwalled
- MOD/EA = Modular excess air
- MOD/SA = Modular starved air
- RDF/cofired = Refuse-derived fuel/cofired
- RDF/ded = Refuse-derived fuel/dedicated

Table 3-8b. Annual TEQ_{DF}-WHO_{98} emissions to the air from municipal waste combustors (MWCs) operating in 1987

MWC type	Air pollution control device (APCD)[a]	TEQ_{DF}-WHO_{98} emissions from tested facilities (g TEQ/yr)	Average TEQ_{DF}-WHO_{98} emission factor (ng/kg)	Activity level nontested facilities (kg/yr)	TEQ_{DF}-WHO_{98} emissions from nontested facilities (g TEQ/yr)	Total TEQ_{DF}-WHO_{98} emissions from all facilities (g TEQ/yr)
MB/WW	DS/FF	0.039	–	0	0.0	0.039
	H-ESP	485.0	535.0	3.27e+09	1,749.5	2,234.5
	Subtotal	485.0			1,749.5	2,234.5
MB/REF	DS/FF	0.0	0.72	1.41e+08	0.1	0.1
	H-ESP	0.0	535.0	2.00e+09	1,070.0	1,070.0
	WS	0.0	254.0	9.01e+08	228.9	228.9
	Subtotal	0.0			1,299.0	1,299.0
MB/RC	FF	0.0	93.1	1.58e+07	1.47	1.47
	H-ESP	53.4	316.0	2.25e+08	71.1	124.5
	Subtotal	53.4			72.6	126.0
RDF/ded	H-ESP	946.0	1,679.0	2.45e+09	4,113.6	5,059.6
	WS	0.0	253.0	3.38e+08	85.5	85.5
	Subtotal	946.0			4,199.1	5,145.1
RDF/cofired	H-ESP	0.0	253.0	2.53e+08	64.0	64.0
MOD/SA	FF	0.0	17.0	1.43e+08	2.4	2.4
	H-ESP	0.068	85.7	3.61e+08	30.9	31.0
	Unc	0.0	0.024	5.73e+08	0.01	0.01
	WS	0.0	17.0	5.30e+07	0.9	0.9
	Subtotal	0.068			34.2	34.3
MOD/EA	EGB	0.0	0.024	6.76e+07	0.0016	0.0016
	Unc	0.0	0.024	4.17e+07	0.001	0.001
	WS	0.0	17.0	1.27e+08	2.16	2.16
	Subtotal	0.0			2.2	2.2
TOTAL		1,484.5		3.04e+09	7,420.6	8,905.1

[a]Slash indicates devices used in conjunction.

APCD:
- DS = Dry scrubber
- EGB = Electro gravel bed
- FF = Fabric filter
- H-ESP = Hot-sided electrostatic precipitator
- Unc = Uncontrolled
- WS = Wet scrubber

MWC type:
- MB/RC = Mass burn rotary kiln
- MB/REF = Mass burn refractory walled
- MB/WW = Mass burn waterwalled
- MOD/EA = Modular excess air
- MOD/SA = Modular starved air
- RDF/cofired = Refuse-derived fuel/cofired
- RDF/ded = Refuse-derived fuel/dedicated

Reference year	g TEQ_{DF}-WHO_{98}	g I-TEQ	Confidence rating
2000	83.8	76.3	A
1995	1,393.5	1,101.3	B
1987	8,905.1	7,858.8	B

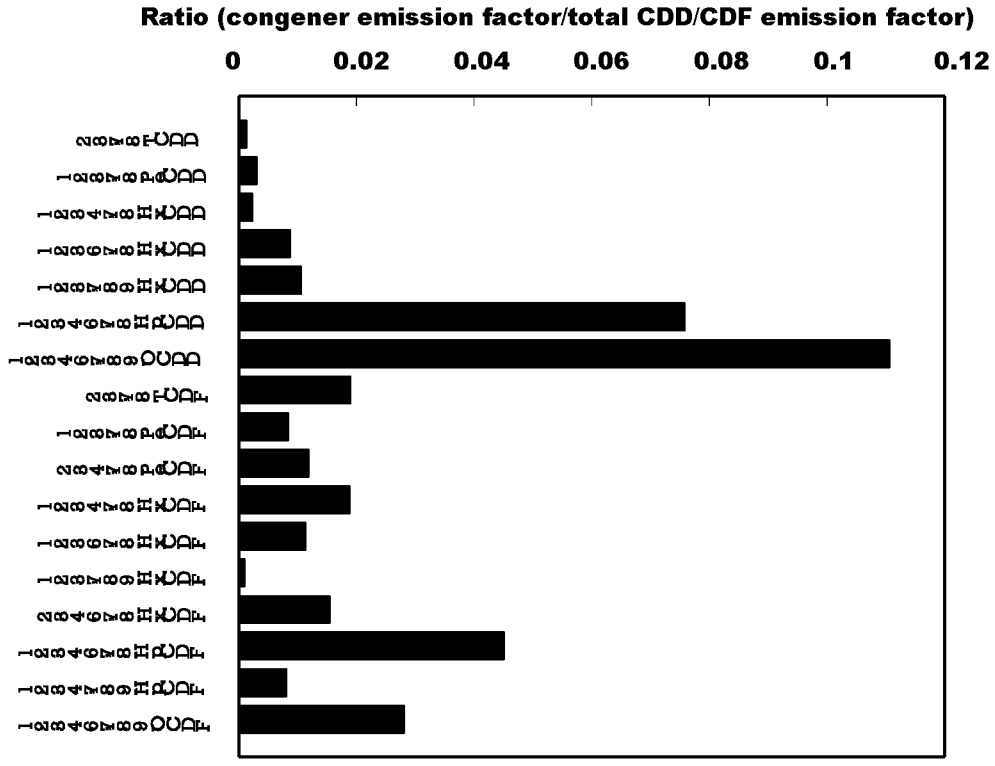
As noted, a high confidence rating (A) is assigned to the estimate of dioxin emissions from MWCs in 2000 because a large number of facilities were tested, providing a highly certain and representative emissions estimate. Table 3-5 displays the CDD/CDF TEQ emissions by each MWC facility operating in 2000. Moreover, the activity level of MWCs in 2000 is known and is very representative of this source. A confidence rating B is assigned to the overall dioxin air releases for years 1995 and 1987. Although the activity level for those years is known and is considered very representative, fewer facilities were stack tested in those years relative to the total number of MWCs in operation. Therefore, there was a reliance on the use of emission factors to estimate releases in 1995 and 1987. However, estimates for these years are considered representative of MWCs operating in those years.

3.1.5. Congener Profiles of Municipal Waste Combustion Facilities

The air emissions from MWCs contain a mixture of CDD and CDF congeners. These mixtures can be translated into what are called "congener profiles," which represent the distribution of total CDDs and total CDFs present in the mixture. A congener profile may serve as a signature of the types of CDDs/CDFs associated with a particular MWC technology and APCD. Figure 3-10 is a congener profile of an MB-WW MWC equipped with an SDSS and an FF (the most common type of MWC and APCD design in use today). This congener profile indicates that OCDD dominates CDD/CDF emissions and that every toxic CDD/CDF congener is detected in the emissions. Figures 3-11 and 3-12 present 2,3,7,8-TCDD frequency distribution and 1,2,3,7,8-PeCDD frequency distribution, respectively. According to a memorandum dated March 27, 2003, from Jason Huckaby, ERG, to Walt Stevenson, U.S. EPA, the distribution of these two congeners varies little from MWC to MWC. Although these two congeners represent less than 1% of total dioxin/furan emissions, they contribute approximately 13 to 23% of the I-TEQ_{DF} emissions, depending on which TEF system is used.

3.1.6. Estimated CDDs/CDFs in MWC Ash

Ash from MWCs is required to be disposed of in permitted landfills from which releases to the general environment are controlled. For background purposes, however, some information is presented below about the quantities of CDDs/CDFs in ash from MWCs.



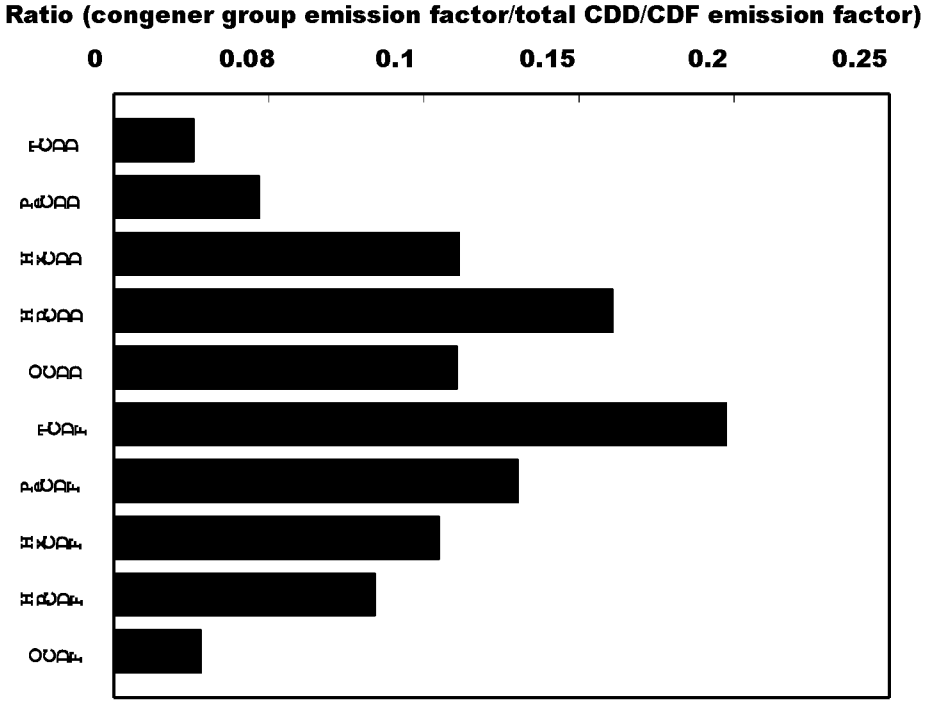


Figure 3-10. Congener and congener group profiles for air emissions from a mass burn waterwall municipal waste combustor equipped with a dry scrubber and fabric filter.

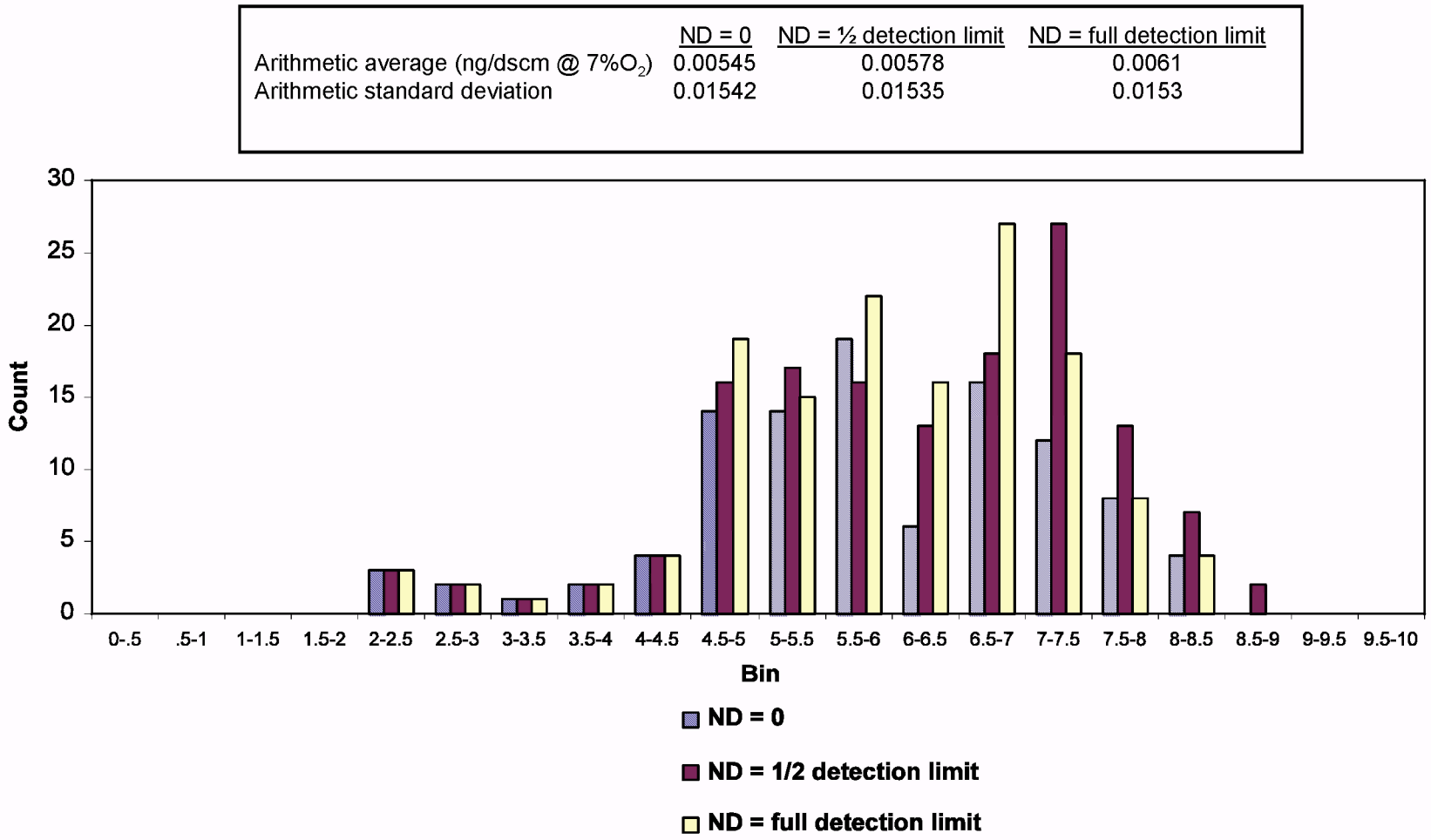


Figure 3-11. 2,3,7,8-TCDD frequency distribution (negative natural log concentration).

	ND = 0	ND = ½ detection limit	ND = full detection limit
Arithmetic average (ng/dscm @ 7%O_2)	0.01589	0.0163	0.01669
Arithmetic standard deviation	0.03375	0.03364	0.0336

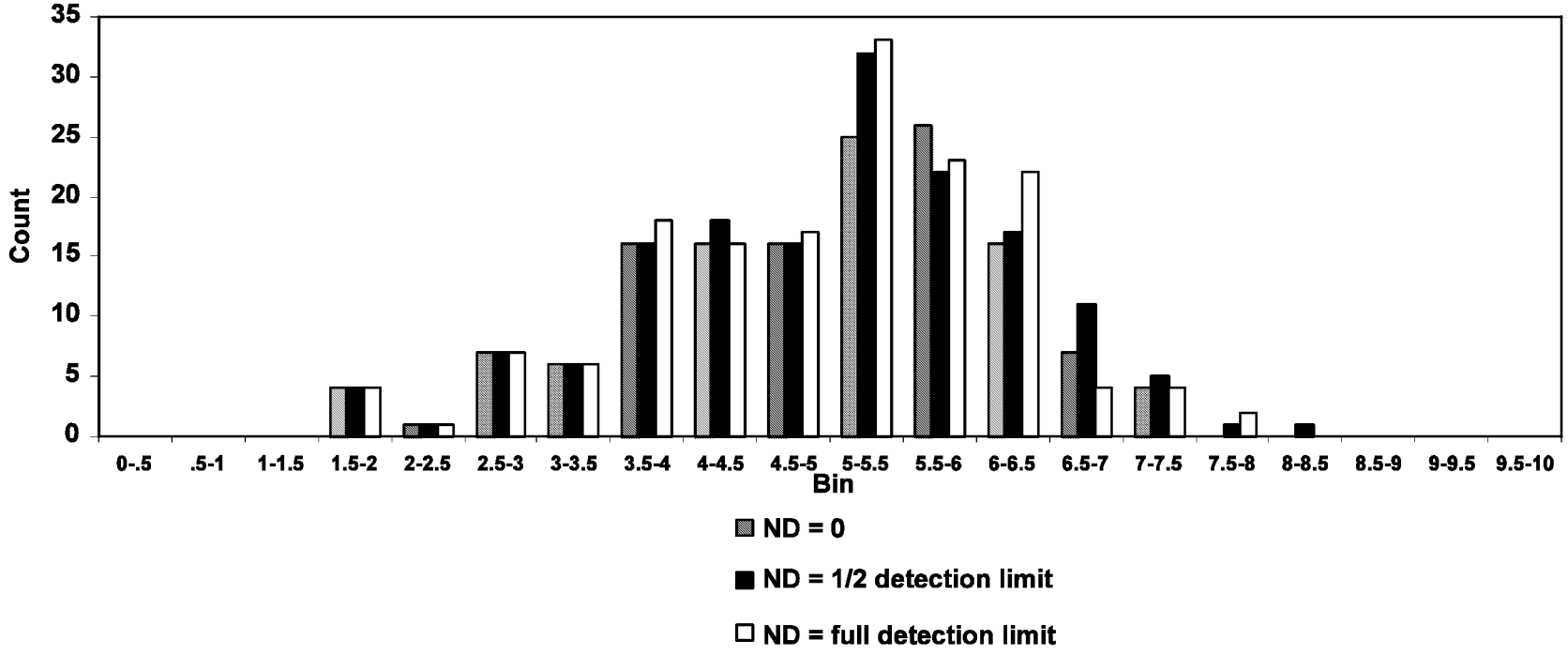


Figure 3-12. 1,2,3,7,8-PeCDD frequency distribution (negative natural log concentration).

An estimated 7 million metric tons of total ash (bottom ash plus fly ash) were generated by MWCs in 1992 (telephone conversation between J. Loundsberry, U.S. EPA Office of Solid Waste, and L. Brown, Versar, Inc., February 24, 1993). EPA indicated that 2 to 5 million metric tons of total ash were produced annually in the late 1980s from MWCs, with fly ash comprising 5 to 15% of the total (U.S. EPA, 1991a) .

EPA reported the results of analyses of MWC ash samples for CDDs/CDFs (U.S. EPA, 1990a). Ashes from five state-of-the-art facilities located in different regions of the United States were analyzed for all 2,3,7,8-substituted CDDs/CDFs. The TEQ levels in the ash (fly ash mixed with bottom ash) ranged from 106 to 466 ng I-TEQ_{DF}/kg, with a mean value of 258 ng I-TEQ_{DF}/kg. CDD/CDF levels are generally much higher in fly ash than in bottom ash. For example, Fiedler and Hutzinger (1992) reported levels of 13,000 ng I-TEQ_{DF}/kg in fly ash.

In another study (Washington State Department of Ecology, 1998), CDD/CDF congener data were reported for ash and other solid residuals from three municipal incinerators (Fort Lewis, Bellingham [municipal plus medical wastes], and Spokane). The data were compiled and evaluated to determine a total I-TEQ concentration and loading. Nondetect values were included as either zero or one-half the DL or at the DL. The results were as follows, assuming that nondetect values were at zero concentration:

Location	Type of Residual	I-TEQ (µg/kg)	I-TEQ (mg/day)
Ft. Lewis	Bottom ash	0.0	0.0
	Fly ash	4.98	0.76
Bellingham	Mixed ash (average of three tests)	0.038	1.14
Spokane	Mixed ash	0.163	38.0
	Fly ash	0.510	24.3
	Bottom ash	0.0001	0.02

In Shane et al. (1990), ash from five municipal incinerators was analyzed for a number of constituents, including CDDs (but not CDFs) and PCBs. For dioxins, three of the incinerators were at nondetectable levels (DL of 1 µg/kg). The other two incinerators had detectable levels of five CDD congener groups (no analyses were reported for individual congeners), and the averages for the two units were 26, 59, 53, 25, and 12 µg/kg for TCDD, PeCDD, HxCDD, HpCDD, and OCDD, respectively. These levels were much higher that those reported by EPA (U.S. EPA, 1990a).

For PCBs, the five sets of ashes were analyzed for 10 congener groups. All groups were detected for one of the incinerators. However, the other four incinerators contained little or no

octa, nona, or deca congeners. The average PCB concentration (all congener groups) for the five incinerators was 216 µg/kg, with a range of 99 to 322 µg/kg.

No generation rates of the ashes were given (Shane et al., 1990); therefore, the measured concentrations cannot be readily converted to quantities of CDDs or PCBs. The ashes from each of the five incinerators were disposed of in various ways. For two of the incinerators, the ash was sent to metal recovery and also landfilled. For a third, the fly ash was sold. For a fourth, the ashes were landfilled only. For the fifth, the ashes were used in road building and also landfilled. For those incinerators with more than one ash disposition, no breakdown was given of how much went to each location. Fifteen other incinerators were discussed in Shane et al. (1990). Thirteen of them disposed of their ash exclusively in landfills, and the other two partially disposed of their ash in landfills.

Table 7 in Clement et al. (1988) presents 13 data sets for CDD/CDF congener groups for municipal incinerator ash. The average data for each congener group and the ranges of each group are given in Table 3-9. No data were presented for individual congeners or for ash quantities.

Table 3-9. Average and range of CDD/CDF congener groups in fly ash from a municipal incinerator (µg/kg)

Congener group	Average concentration	Concentration range
TCDD	3.7	1.6–12
PeCDD	6.4	2–25
HxCDD	9.1	1.5–42
HpCDD	2.3	0.5–9.2
OCDD	1.5	0.2–6
TOTAL CDDs	23.0	6.2–94
TCDF	12.0	5.1–36
PeCDF	17.0	8.3–40
HxCDF	14.0	3.9–40
HpCDF	2.9	0.8–9.2
OCDF	1.2	ND–2.1
TOTAL CDFs	47.1	22–110

Source: Clement et al. (1988).

Ash from three incinerators (one in North America, one in Europe, and one in Japan) had mean CDD concentrations of 363, 588, and 2.6 μg/kg, respectively (Table 3-3 in U.S. EPA, 1987a). The values ranged from less than 0.5 to 3.537 μg/kg. For CDFs, the respective mean concentrations for the first two incinerators were 923 and 288 μg/kg. Data for the third incinerator were not reported. The CDF range for the two incinerators was from less than 0.5 to 1,770 μg/kg. No data were given for individual congeners or for quantities of ashes.

In Table 1 in Lahl et al. (1991), data are presented for concentrations of total CDDs and total CDFs in the ash from an ESP from a municipal incinerator. Total CDDs were 140.46 μg/kg in the summer samples and 86 μg/kg in the winter samples. Total CDFs were 54.97 μg/kg in the summer samples and 73.85 μg/kg in the winter samples. No data were given for individual congeners, nor was there information about the quantity of precipitator ash generated. It was assumed that the data were not for TEQs.

A wire reclamation incinerator was reported to have 0.41 μg/kg of CDDs and 11.6 μg/kg of CDFs in fly ash from its stack emissions (Table 3-11 in U.S. EPA, 1987a). For the same incinerator, the furnace ash concentrations were reported as 0.58 μg/kg CDDs and 0.73 μg/kg CDFs. Again, no data were given for individual congeners or for quantities of the ashes.

Data from the aforementioned sources are compiled in Table 3-10 of this document for comparison purposes. Annual TEQ amounts were estimated by multiplying the mean TEQ total ash concentration by the estimated amount of MWC ash generated annually (approximately 7 million metric tons in 1995 and 5 million metric tons in 1987). Where possible, ash quantities were broken down into fly ash or bottom ash. Fly ash was assumed to be 10% of the total ash, and bottom ash was assumed to be 90% of the total ash.

Imagawa and Lee (2001) analyzed samples collected from eight Japanese MSW incinerators to determine dioxin levels in the fly ash (Table 3-11). Specific congener data were not available, so TEQ calculations could not be performed.

Kobylecki et al. (2001) analyzed the reduction of dioxins in fly ash by pelletizing the ash and reburning the pellets in a laboratory-scale bubbling fluidized-bed furnace. Fly ash for the test input material was collected from a fly ash filter vessel during 4 days of MWC operation. The concentrations of the dioxin collected and composited congeners are shown in Table 3-12. The total TEQ value derived by Kobylecki was 862 ng I-TEQ_{DF}/kg of fly ash.

Sakai et al. (2001) analyzed the levels of dioxins and PCBs in fly ash and bottom ash from a newly constructed MWC in Japan (Table 3-13). TEQ values derived from the data give a total of 423 ng I-TEQ_{DF}/kg for fly ash and 10.5 ng I-TEQ_{DF}/kg for bottom ash for dioxins and 31.6 ng I-TEQ_{DF}/kg for fly ash and 0.85 ng I-TEQ_{DF}/kg for bottom ash for PCBs.

Table 3-10. Comparison of the amount of TEQs generated annually in municipal waste combustor ash

Data source	Type of ash	Mean total CDD/CDF concentration (ng/kg)	Mean I-TEQ_{DF} (ng/kg)	Annual TEQ amount 1995 value[a] (g I-TEQ_{DF}/yr)	Annual TEQ amount 1987 value[a] (g I-TEQ_{DF}/yr)
U.S. EPA (1990a)	Mixed	12,383	258	1,806	1,290
Washington State Department of Ecology (1998)					
Ft. Lewis	Bottom	0	0	0	0
	Fly	71,280	4,980	3,486	2,490
Bellingham	Mixed	1,884	38	266	190
Spokane	Mixed	1,414	163	1,141	815
	Fly	10,320	510	357	255
	Bottom	100	0.1	1	0.05
Shane et al. (1990)	Fly	175,000	–	–	–
Clement et al. (1988)	Fly	70,000	–	–	–
U.S. EPA (1987a)					
North America	Fly	1,286,000	–	–	–
Europe	Fly	876,000	–	–	–
Japan	Fly	2,600	–	–	–
Wire reclamation	Fly	12,010	–	–	–
	Bottom	1,310	–	–	
Lahl et al. (1991)	Mixed	177,640	–	–	–

[a]In calculating the annual TEQ amounts, fly ash and bottom ash were considered to be 10% and 90% of the total ash, respectively.

– = Value could not be calculated

Each of the five facilities sampled by EPA had companion ash disposal facilities equipped with leachate collection systems or some means of collecting leachate samples (U.S. EPA, 1990a). Leachate samples were collected and analyzed for each of these systems. Detectable levels were found in the leachate at only one facility (3 ng I-TEQ_{DF}/L); the only detectable congeners were HpCDDs, OCDD, and HpCDFs.

Table 3-11. Concentration of CDD/CDF congener groups (ng/kg) in fly ash samples from combustion of municipal solid waste in eight Japanese incinerators[a]

Congener group	Stoker incinerators				Fluidized-bed incinerators			
	B	C	D	E	F	I	J	L
TCDD	5,000	200,000	80,000	75,000	6,000	10,000	10,000	5,000
PeCDD	20,000	340,000	200,000	105,000	10,000	28,000	37,000	10,000
HxCDD	45,000	440,000	250,000	90,000	12,000	41,000	100,000	30,000
HpCDD	70,000	340,000	230,000	37,000	8,000	40,000	200,000	40,000
OCDD	125,000	110,000	160,000	15,000	7,000	25,000	187,000	50,000
TCDF	25,000	210,000	330,000	50,000	13,000	18,000	50,000	70,000
PeCDF	50,000	410,000	320,000	45,000	14,000	32,000	125,000	120,000
HxCDF	65,000	400,000	300,000	22,000	21,000	34,000	210,000	200,000
HpCDF	75,000	230,000	200,000	10,000	17,000	33,000	225,000	270,000
OCDF	40,000	20,000	40,000	1,000	10,000	13,000	150,000	120,000

[a] Incinerators are designated by letters because they remained anonymous.

Source: Imagawa and Lee (2001) (numbers estimated from Figure 2 of report).

Table 3-12. Concentration of CDD/CDF congener groups in fly ash samples from municipal solid waste

Congener group	Concentration (ng/kg)	TEQ (ng/kg)
TCDD	8,000	15
PeCDD	9,000	45
HxCDD	40,000	100
HpCDD	10,800	50
OCDD	8,000	1
TCDF	8,000	10
PeCDF	10,000	300
HxCDF	9,500	300
HpCDF	8,500	40
OCDF	8,000	1
TOTAL	119,800	862

Source: Kobylecki et al. (2001) (estimated from values in Figure 4 of "Before Incineration").

Table 3-13. CDD/CDF concentrations in municipal solid waste ash from a newly constructed municipal waste combustor in Japan

Congener	Concentration (ng/kg)		I-TEQs (ng/kg)	
	Fly ash	Bottom ash	Fly ash	Bottom ash
2,3,7,8-TCDD	19	1.6	19.0	1.6
1,2,3,7,8-PeCD	78	3.1	39.0	1.65
1,2,3,4,7,8-HxCDD	92	2.6	9.2	0.26
1,2,3,6,7,8-HxCDD	210	5.6	21.0	0.56
1,2,3,7,8,9-HxCDD	130	3.6	13.0	0.36
1,2,3,4,6,7,8-HpCDD	1,300	33.0	13.0	0.33
OCDD	2,800	110.0	2.8	0.11
2,3,7,8-TCDF	150	4.8	15.0	0.48
1,2,3,7,8-PeCDF	290	5.3	14.5	0.265
2,3,4,7,8-PeCDF	320	5.9	160.0	2.95
1,2,3,4,7,8-HxCDF	310	4.4	31.0	0.44
1,2,3,6,7,8-HxCDF	310	4.9	31.0	0.49
1,2,3,7,8,9-HxCDF	21	0.36	2.1	0.036
2,3,4,6,7,8-HxCDF	400	6.7	40.0	0.67
1,2,3,4,6,7,8-HpCDF	1,100	23.0	11.0	0.23
1,2,3,4,7,8,9-HpCDF	110	1.6	1.1	0.016
OCDF	320	9.3	0.32	0.0093
TOTAL	7,960	226.0	423.0	10.5

Source: Sakai et al. (2001).

3.1.7. Recent EPA Regulatory Activities

As part of the 1990 Clean Air Act mandates, EPA promulgated CDD/CDF emission standards for all existing and new MWC units at facilities with aggregate combustion capacities greater than 35 metric tons per day (Federal Register, 1995a). These standards, established under Section 129 of the Clean Air Act, required facilities to use "maximum achievable control technology" (MACT) at MWC units and emission control retrofit for large MWC units (units with capacities greater than 225 metric tons per day) by December 2000. In response to a court remand, the regulations were subsequently amended to remove small MWC units (units with capacities ranging from 35 to 225 metric tons per day) (Federal Register, 1995a).

The specific emission standards for large MWCs (expressed as ng/dscm of total CDD/CDF, based on standard dry gas corrected to 7% oxygen) are a function of the size, APCD configuration, and age of the facility, as listed below.

1995 emission standards (ng total CDD/CDF/dscm)	Facility age, size, and APCD
60	Existing; >225 metric tons/day; ESP-based APCD
30	Existing; >225 metric tons/day; non-ESP-based APCD
13	New; >225 metric tons/day

EPA reestablished emission standards for small MWCs in December 2000. These standards contain two dioxin emission limits: one for small MWCs at plants with an aggregate capacity greater than 250 tons/day (Class I MWCs) and another for small MWCs at plants with an aggregate capacity less than 250 tons/day (Class II MWCs). The limits for the Class I MWCs were the same as the 1995 limits for large MWCs. The limit for the smaller Class II MWCs is 125 ng/dscm. These small MWCs were on schedule to comply with the standards by December 2005. Small MWC emissions were estimated to be 63 g/yr I-TEQ in 2000 and should be less than 2 g/yr in 2005, when all control retrofits are completed (Federal Register, 2003).

3.2. HAZARDOUS WASTE INCINERATION

Hazardous waste incineration is the controlled pyrolysis and/or oxidation of potentially dangerous liquid, gaseous, and solid waste. It is one of the technologies used to manage hazardous waste under the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, or Superfund).

Hazardous wastes are burned in a variety of situations and are covered in a number of different sections in this report.

- Much hazardous waste is burned in facilities dedicated to burning this type of waste. Most of these dedicated facilities are located on-site at chemical manufacturing facilities and burn only the waste associated with their on-site industrial operations. Hazardous waste is also burned at dedicated facilities located off-site. These facilities accept waste from multiple sources. On- and off-site hazardous waste burning facilities are addressed in Sections 3.2.1 through 3.2.4.

- Hazardous waste is also burned in industrial boilers and furnaces that are permitted to burn the waste as supplemental fuel. These facilities have significantly different furnace designs and operations than those of dedicated hazardous waste incinerators (HWIs). They are discussed in Section 3.2.6.

- Hazardous waste is also burned in halogen acid furnaces (HAFs), in which halogen acids (such as HCl) may be produced from halogenated secondary materials. These facilities are discussed in Section 3.2.7.

- A number of cement kilns and lightweight aggregate kilns are also permitted to burn hazardous waste as auxiliary fuel. These are discussed separately in Section 5.1.

- Mobile HWIs are typically used for site cleanup at Superfund sites. These units can be transported from one location to another and operate for a limited duration at any given location. Because these facilities are transitory, they are not included in this inventory at this time.

The following sections review the types of hazardous waste incineration technologies commonly in use in the United States and present the CDD/CDF emission estimates from all facilities operating in 1987, 1995, and 2000.

3.2.1. Furnace Designs for HWIs

The four principal furnace designs employed for the combustion of hazardous waste in the United States are rotary kiln, liquid injection, fixed-hearth, and fluidized-bed (Dempsey and Oppelt, 1993). The majority of commercial operations use rotary kiln incinerators. On-site (noncommercial) hazardous waste incineration technologies use an equal mix of rotary kiln and liquid injection furnaces, along with some fixed-hearth and fluidized-bed operations (U.S. EPA, 1996a). These HWI technologies are discussed below.

Rotary kiln. Rotary kiln incinerators consist of a rotary kiln coupled with a high-temperature afterburner. Because rotary kilns are excess-air units designed to combust hazardous waste in any physical form (i.e., liquid, semisolid, or solid), they are the most common type of HWI used by commercial off-site operators. The rotary kiln is a horizontal cylinder lined with refractory material. Rotation of the cylinder on a slight slope provides for gravitational transport of the hazardous waste through the kiln (Buonicore, 1992a). The tumbling action of the rotating kiln causes mixing and exposure of the waste to the heat of combustion, thereby enhancing burnout.

Solid and semisolid wastes are loaded into the top of the kiln by an auger or rotating screw. Fluid and pumpable sludges and wastes are typically introduced into the kiln through a water-cooled tube. Liquid hazardous waste is fed directly into the kiln through a burner nozzle. Auxiliary fuel (natural gas or oil) is burned in the kiln chamber at startup to reach elevated temperatures. The typical heating value of hazardous waste (8,000 British thermal units [Btu]/kg) is sufficient to sustain combustion without auxiliary fuel (U.S. EPA, 1996a). The combustion gases emanating from the kiln are passed through a high-temperature afterburner chamber to more completely destroy organic pollutants entrained in the flue gases. Rotary kilns can be designed to operate at temperatures as high as 2,580°C, but they more commonly operate at about 1,100°C.

Liquid injection. Liquid injection incinerators are designed to burn liquid hazardous waste. These wastes must be sufficiently fluid to pass through an atomizer for injection as droplets into the combustion chamber. The incinerator consists of a refractory-lined steel cylinder mounted in either a horizontal or a vertical alignment. The combustion chamber is equipped with one or more waste burners. Because of the rather large surface area of the atomized droplets of liquid hazardous waste, the droplets quickly vaporize. The moisture evaporates, leaving a highly combustible mix of waste fumes and combustion air (U.S. EPA, 1996a). Secondary air is added to the combustion chamber to complete the oxidation of the fume and air mixture.

Fixed-hearth. Fixed-hearth incinerators are starved-air or pyrolytic incinerators. Waste is ram-fed into the primary chamber and incinerated at about 50 to 80% of stoichiometric requirements. The resulting smoke and pyrolytic combustion products are then passed through a secondary combustion chamber where relatively high temperatures are maintained by the combustion of auxiliary fuel. Oxygen is introduced into the secondary chamber to promote complete thermal oxidation of the organic molecules entrained in the gases. Other types of hearths include roller hearths and rotary hearths. Roller hearths use a conveyor system to move waste from the kiln entrance to the exit. In rotary hearths, waste enters and exits through the same gate, and the hearth rotates inside a circular tunnel kiln.

Fluidized-bed. The fluidized-bed incinerator is similar in design to the incinerators used in MSW incineration (see Section 3.1). In fluidized-bed HWIs, a layer of sand is placed on the bottom of the combustion chamber. The bed is preheated by underfire auxiliary fuel at startup. The hot gases channel through the sand at relatively high velocity, and the turbulent mixing of combustion gases and combustion air causes the sand to become suspended (Buonicore, 1992a) and take on the appearance of a fluid medium; hence the term "fluidized-bed" combustor. The incinerator is operated at temperatures below the melting point of the bed material (typical temperatures are within a range of 650 to 940°C). A constraint on the types of waste burned is that the solid waste particles must be capable of being suspended within a furnace. When the liquid or solid waste is combusted in the fluid medium, the exothermic reaction causes heat to be released into the upper portion of the combustion chamber. The upper portion typically has much larger volume than the lower portion, and temperatures can reach 1,000°C (Buonicore, 1992a). This high temperature is sufficient to combust volatilized pollutants emanating from the combustion bed.

3.2.2. APCDs for HWIs

Most HWIs use APCDs to remove undesirable components from the flue gases that evolve during the combustion of the hazardous waste. These unwanted pollutants include suspended ash particles (PM), acid gases, metals, and organic pollutants. The APCD controls collect these pollutants and reduce the amount discharged from the incinerator stack to the atmosphere. The levels and types of these combustion byproducts are highly site specific, depending on factors such as waste composition and incinerator system design and operating parameters (e.g., temperature and exhaust gas velocity). The APCD typically comprises a series of different devices that work together to clean the combustion exhaust flue gas. Unit operations usually include exhaust gas cooling followed by PM and acid gas control.

Exhaust gas cooling may be achieved by using a waste heat boiler or heat exchanger, mixing with cool ambient air, or injecting a water spray into the exhaust gas. A variety of types of APCDs are used to remove PM and acid gases. Such devices include WSs (such as venturi, packed bed, and ionizing systems), ESPs, and FFs (sometimes used in combination with dry acid gas scrubbing). In general, the control systems can be grouped into the following three categories: wet, dry, and hybrid wet/dry systems. The controls for acid gases (either dry or wet systems) cause temperatures to be reduced before the gases reach the control device. This impedes the formation of CDDs/CDFs in the post-combustion area of the typical HWI. It is not unusual for stack concentrations of CDDs/CDFs at a particular HWI to be in the range of 1 to 100 ng/dscm (Helble, 1993), which is low when compared with concentrations from other waste incineration systems. However, the range of total CDD/CDF flue gas concentrations measured in the stack emissions of HWIs during trial burns across the class of HWI facilities spans four orders of magnitude, ranging from 0.1 to 1,600 ng/dscm (Helble).

The three categories of APCD systems are described below:

- **Wet system.** A WS is used for both particulate and acid gas control. Typically, a venturi scrubber and a packed-bed scrubber are used in a back-to-back arrangement. Ionizing WSs, wet ESPs, and innovative venturi-type scrubbers may be used for more efficient particulate control. WSs generate a wet effluent liquid wastestream (scrubber blowdown). They are relatively inefficient at fine particulate control when compared with dry control techniques, and they have equipment corrosion concerns. However, WSs provide efficient control of acid gases and have lower operating temperatures (compared with dry systems), which may help control the emissions of volatile metals and organic pollutants.

- **Dry system.** In SDSSs, an FF or ESP is used for particulate control, frequently in combination with dry scrubbing for acid gas control. Compared with WSs, SDSSs are inefficient in controlling acid gases.

- **Hybrid system.** In hybrid systems, a dry technique (ESP or FF) is used for particulate control, followed by a wet technique (WS) for acid gas control. Hybrid systems have the advantages of both wet and dry systems (lower operating temperature for capture of volatile metals, efficient collection of fine particulates, efficient capture of acid gases) while avoiding many of the disadvantages. In some hybrid systems, known as "zero discharge systems," the WS liquid is used in the dry scrubbing operation, thus minimizing the amount of liquid byproduct waste.

Facilities that do not use any APCDs fall under a separate and unique category. These are primarily liquid waste injection facilities, which burn wastes with low ash and low chlorine content; therefore, they are low emitters of PM and acid gases.

3.2.3. Estimation of CDD/CDF Emission Factors for HWIs

To estimate emission factors, EPA's Office of Research and Development (ORD) generally subdivides the combustors in each source category into design classes judged to have similar potential for CDD/CDF emissions. However, as explained below, dedicated HWIs have not been subdivided.

Total CDD/CDF emissions are likely the net result of all three of the mechanisms described above (pass through, precursor, and *de novo* synthesis); however, the relative importance of each mechanism can vary among source categories. In the case of HWIs, the third mechanism (post-combustion formation) is likely to dominate, because HWIs are typically operated at high temperatures and with long residence times, and most have sophisticated real-time monitoring and controls to manage the combustion process. Therefore, any CDDs/CDFs present in the feed or formed during combustion are likely to be destroyed before exiting the combustion chamber. Consequently, for purposes of generating emission factors, it was decided not to subdivide this class on the basis of furnace type.

Emissions resulting from the post-combustion formation of CDDs/CDFs in HWIs can be minimized using a variety of technologies:

- **Rapid flue gas quenching.** The use of wet and dry scrubbing devices to remove acid gases usually results in the rapid reduction of flue gas temperatures at the inlet to the APCD. If the temperature is reduced below 200°C, the low-temperature catalytic formation of CDDs/CDFs is substantially retarded.

- **Use of PM APCDs.** PM control devices can effectively capture condensed and adsorbed CDDs/CDFs that are associated with the entrained PM (in particular, those adsorbed on unburned carbon-containing particulates).

- **Use of activated carbon.** Activated CI is used at some HWIs to collect (sorb) CDDs/CDFs from the flue gas. This may be achieved using carbon beds or by injecting carbon and collecting it in a downstream PM APCD.

All of these approaches appear to be very effective in controlling dioxin emissions at dedicated HWIs; emissions data are insufficient to generalize about any minor differences. Consequently, for purposes of generating emission factors, ORD decided not to subdivide this class on the basis of APCD type.

EPA's Office of Solid Waste (OSW) compiled a database summarizing the results of stack testing for CDDs/CDFs at a number of HWIs between 1993 and 2000 (U.S. EPA, 2002b). The CDD/CDF emission factors for HWIs in 1995 are based on data from 17 HWIs tested between 1993 and 1996; emissions of HWIs in 2000 are based on data from 22 HWIs tested in 2000. The furnaces at the 22 HWI facilities tested in 2000 were 11 rotary kiln incinerators, 6 liquid injection incinerators, 2 rotary hearth units, 1 fluidized-bed incinerator, and 1 roller hearth.

Rather than classifying the dedicated HWI designs to derive an emission factor, ORD decided to derive the emission factor as an average across all tested facilities. First, an average emission factor was calculated using eq 3-3.

$$EF_{HWI} = \frac{C \times F_v}{I_w} \tag{3-3}$$

where:

EF_{HWI} = emission factor (average ng TEQ per kg of waste burned)

C = TEQ or CDD/CDF concentration in flue gases (ng TEQ/dscm) (20°C, 1 atm; adjusted to 7% O_2)

F_v = volumetric flue gas flow rate (dscm/hr) (20°C, 1 atm; adjusted to 7% O_2)

I_w = average waste incineration rate (kg/hr)

Although 22 HWIs were tested in 2000, the OSW database contained values for flue gas flow rates for only 12 of these incinerators. Therefore, only 12 HWIs could be used to develop an emission factor. After developing an average emission factor for each HWI, the overall average congener-specific emission factor was derived using eq 3-4.

$$EF_{avgHWI_{n=1-17}} = (EF_{HWI_1} + EF_{HWI_2} + EF_{HWI_3} + \ldots\ldots + EF_{HWI_{17}}) / N \tag{3-4}$$

where:

EF_{avgHWI} = average emission factor for the tested HWIs (ng/kg)

N = number of tested facilities

Tables 3-14a and 3-14b present the average emission factors developed for specific congeners, total CDDs and total CDFs, and TEQs for the HWIs tested from 1993 to 1996 and in 2000, respectively. The average congener emission profile for the 17 HWIs tested from 1993 to 1996 are presented in Figure 3-13. The average emission factor for the 17 HWIs was 3.88 ng TEQ_{DF}-WHO_{98}/kg (3.83 ng I-TEQ_{DF}/kg) of waste feed (assuming nondetect values were zero). The average emission factor for the 22 HWIs tested in 2000 was 2.13 ng TEQ_{DF}-WHO_{98}/kg (2.12 ng I-TEQ_{DF}/kg) of waste feed (assuming nondetect values were zero). The emission factor developed for reference year 1995 was used as a surrogate for reference year 1987.

3.2.4. Emission Estimates for HWIs

Although emissions data were available for 10% of the HWIs operating in 1995 and 17% of the HWIs operating in 2000 in the United States (i.e., 22 of the 132 HWIs operating in 2000 have been tested), the emission factor estimates are assigned a medium confidence rating because of uncertainties resulting from the following:

- **Variability of the waste feeds.** The physical and chemical composition of the waste can vary from facility to facility and even within a facility. Consequently, CDD/CDF emissions measured for one feed may not be representative of those of other feeds.

- **Trial burns.** Much of the CDD/CDF emissions data were collected during trial burns, which are required as part of the RCRA permitting process and are used to establish the destruction rate efficiency of principal hazardous organic constituents in the waste. During trial burns, a prototype waste is burned that is intended to maximize the difficulty in achieving good combustion. For example, chlorine, metals, and organics may be added to the waste. The HWI may also be operated outside normal operating conditions. The temperature of both the furnace and the APCD may vary by a wide margin (high and low temperatures), and the waste feed system may be increased to maximum design load. Accordingly, it is uncertain how representative the CDD/CDF emissions measured during the trial burn will be of emissions during normal operating conditions.

Dempsey and Oppelt (1993) estimated that up to 1.3 million metric tons of hazardous waste were combusted in HWIs during 1987. A confidence rating of medium is assigned to this estimate. EPA estimated that 1.5 million metric tons of hazardous waste were combusted in HWIs each year in the early 1990s (Federal Register, 1996a). The activity level estimate for

Table 3-14a. CDD/CDF emission factors for hazardous waste incinerators and boilers tested from 1993 to 1996

Congener	Incinerator average mean emission factor (17 facilities) (ng/kg feed)		Hot-sided ESP boilers mean emission factor (2 facilities) (ng/kg feed)	
	Nondetect set to ½ detection limit	Nondetect set to zero	Nondetect set to ½ detection limit	Nondetect set to zero
2,3,7,8-TCDD	0.44	0.14	0.1	0.0
1,2,3,7,8-PeCDD	0.18	0.14	0.11	0.04
1,2,3,4,7,8-HxCDD	0.22	0.18	0.15	0.08
1,2,3,6,7,8-HxCDD	0.32	0.28	0.2	0.18
1,2,3,7,8,9-HxCDD	0.49	0.48	0.22	0.2
1,2,3,4,6,7,8-HpCDD	1.77	1.74	1.17	1.17
OCDD	4.13	3.74	5.24	5.24
2,3,7,8-TCDF	2.96	2.69	0.81	0.81
1,2,3,7,8-PeCDF	2.36	2.33	0.38	0.38
2,3,4,7,8-PeCDF	2.56	2.51	0.52	0.52
1,2,3,4,7,8-HxCDF	9.71	9.71	0.83	0.83
1,2,3,6,7,8-HxCDF	3.95	3.95	0.37	0.37
1,2,3,7,8,9-HxCDF	0.31	0.29	0.08	0.02
2,3,4,6,7,8-HxCDF	2.7	2.7	0.56	0.56
1,2,3,4,6,7,8-HpCDF	16.87	16.68	1.04	0.93
1,2,3,4,7,8,9-HpCDF	1.74	1.71	0.18	0.16
OCDF	13.79	13.46	0.7	0.7
Total I-TEQ_{DF}	4.22	3.83	0.78	0.64
Total TEQ_{DF}-WHO_{98}	4.29	3.88	0.83	0.65
Total CDD/CDF	153	153	28.83	28.39

ESP = Electrostatic precipitator

Table 3-14b. CDD/CDF emission factors for hazardous waste incinerators and boilers tested in 2000

Congener/congener group	Incinerator average mean emission factor (12 facilities) (ng/kg feed)[a]		Hot-sided ESP boilers mean emission factor (1 facility) (ng/kg feed)[a]	
	Nondetect set to ½ detection limit	Nondetect set to zero	Nondetect set to ½ detection limit	Nondetect set to zero
2,3,7,8-TCDD	0.0615	0.036	0.0346	0.0
1,2,3,7,8-PeCDD	0.6141	0.0907	0.0488	0.0
1,2,3,4,7,8-HxCDD	0.2347	0.1395	0.1149	0.0789
1,2,3,6,7,8-HxCDD	0.5408	0.4351	0.1715	0.1228
1,2,3,7,8,9-HxCDD	0.3037	0.2178	0.3361	0.231
1,2,3,4,6,7,8-HpCDD	2.729	2.699	1.406	1.4055
OCDD	5.211	5.17	1.554	1.5541
2,3,7,8-TCDF	0.6931	0.6399	0.9531	0.9531
1,2,3,7,8-PeCDF	0.9406	0.8375	0.4599	0.3862
2,3,4,7,8-PeCDF	0.88	0.735	0.8836	0.8836
1,2,3,4,7,8-HxCDF	4.085	4.045	3.611	3.6108
1,2,3,6,7,8-HxCDF	3.031	3.001	0.69	0.561
1,2,3,7,8,9-HxCDF	2.667	2.637	0.038	0.0
2,3,4,6,7,8-HxCDF	1.218	1.121	1.3272	1.3272
1,2,3,4,6,7,8-HpCDF	28.74	28.71	4.6345	4.6345
1,2,3,4,7,8,9-HpCDF	5.056	5.021	0.1895	0.1257
OCDF	36.270	36.23	0.7841	0.7841
Total I-TEQ_{DF}	2.54	2.119	1.313	1.214
Total TEQ_{DF}-WHO_{98}	2.809	2.127	1.335	
Total CDD/CDF	195.70	194.10	17.24	16.66

[a]Values incorporating use of the detection limit when the laboratory report indicated "not detected" for individual CDD/CDF congeners.

ESP = Electrostatic precipitator
NR = Not reported

Source: U.S. EPA (2002a).

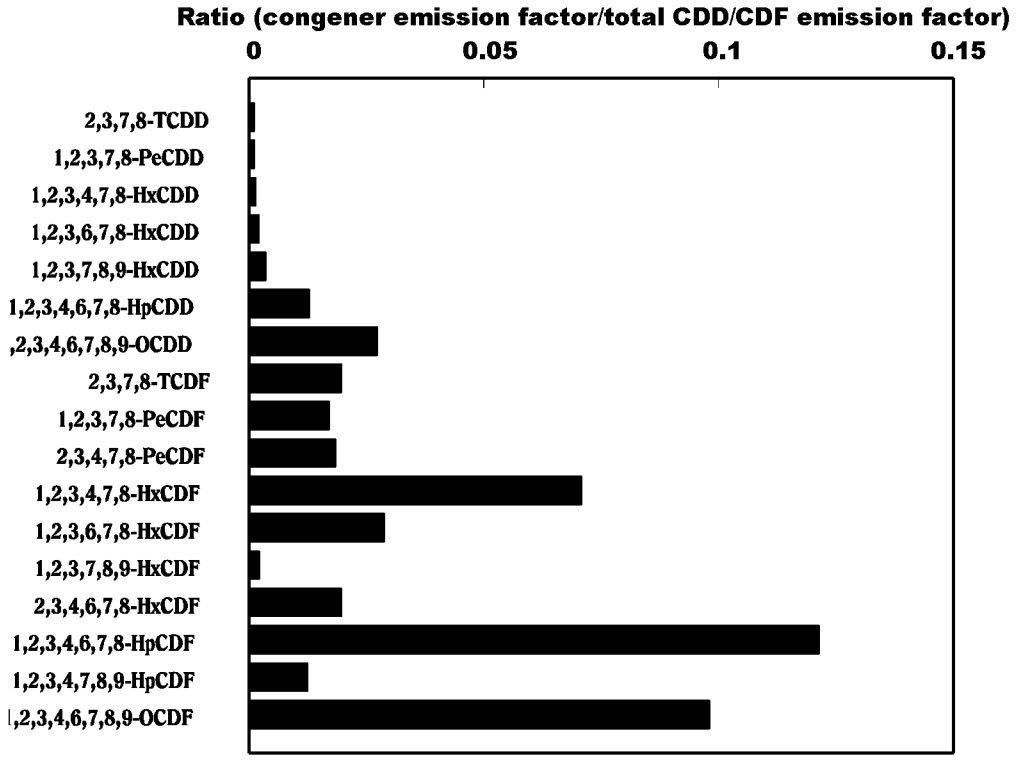


Figure 3-13. Congener profile for air emissions from 17 hazardous waste incinerators tested from 1993 through 1996.

1995 is assigned a high confidence rating because it is based on a review by EPA of the various studies and surveys conducted in the 1990s to assess the quantity and types of hazardous wastes being managed by various treatment, storage, and disposal facilities. Because of a lack of data regarding the amount of waste burned in 2000, the 1995 estimate (1.5 million metric tons) was also used for determining TEQ emissions for 2000.

The annual TEQ emissions for reference years 1987, 1995, and 2000 were estimated using eq 3-5.

$$E_{HWI} = EF_{HWI} \times A_{HWI} \tag{3-5}$$

where:

E_{HWI} = annual emissions from all HWIs, tested and nontested (g TEQ/yr)

EF_{HWI} = mean emission factor for HWIs (ng TEQ/kg of waste burned)

A_{HWI} = annual activity level of all operating HWIs (million metric tons/yr)

Applying the average TEQ emission factor for dedicated HWIs (3.88 ng TEQ_{DF}-WHO_{98}/kg waste [3.83 ng I-TEQ_{DF}/kg waste]) to these production estimates yields estimated emissions of 5 g TEQ (TEQ_{DF}-WHO_{98} or I-TEQ_{DF}) in 1987 and 5.8 g TEQ_{DF}-WHO_{98} (5.7 g I-TEQ_{DF}) in 1995. For 2000, applying the average TEQ emission factors for dedicated HWIs (2.13 ng TEQ_{DF}-WHO_{98}/kg waste [2.12 ng I-TEQ_{DF}/kg waste]) to a production estimate of 1.5 million metric tons yields estimated emissions of 3.2 g TEQ_{DF}-WHO_{98} (3.18 g I-TEQ_{DF}). Medium confidence rating is assigned to these estimates because the emission factor was given a medium confidence rating.

3.2.5. Recent EPA Regulatory Activities

CDD/CDF emissions from HWIs are regulated by EPA (Federal Register, 1999a, 2004). The regulations are specific to the I-TEQ concentration in the combustion gases leaving the stack. Existing HWIs equipped with waste heat boilers and dry scrubbers (as APCDs) cannot emit more than 0.28 ng I-TEQ/dscm. All other existing HWIs are limited to 0.4 ng I-TEQ/dscm of stack gas. Regulatory requirements are more strict for newly built HWIs: those equipped with waste heat boilers and dry scrubbers (as APCDs) cannot emit more than 0.11 ng I-TEQ/dscm, and all others are limited to 0.2 ng I-TEQ/dscm of stack gas.

3.2.6. Industrial Boilers and Furnaces Burning Hazardous Waste

In 1991, EPA established rules that allow the combustion of some liquid hazardous waste in industrial boilers and furnaces (Federal Register, 1991b). These facilities typically burn oil or coal for the primary purpose of generating electricity. Liquid hazardous waste can be burned only as supplemental (auxiliary) fuel, and the rule limits use to no more than 5% of the primary fuels. These facilities typically use an atomizer to inject the waste as droplets into the combustion chamber. They are equipped with particulate and acid gas emission controls and in general are sophisticated, well-controlled facilities that achieve good combustion.

The national OSW database contains congener-specific emission concentrations for two boilers burning liquid hazardous waste as supplemental fuel tested from 1993 to 1996. The average congener and congener group emission profiles for the industrial boiler data set are presented in Figure 3-14. The database also contains congener-specific emission concentrations for four boilers tested in 2000. Of the boilers tested in 2000, sufficient data to calculate average TEQ emissions were available for only one boiler. The average congener and TEQ emission factors are presented in Tables 3-14a and 3-14b. The limited set of emissions data prevented subdividing this class to derive an emission factor. The equation used to derive the emission factor is the same as eq 3-4. The TEQ emission factors for the industrial boiler are 0.65 ng

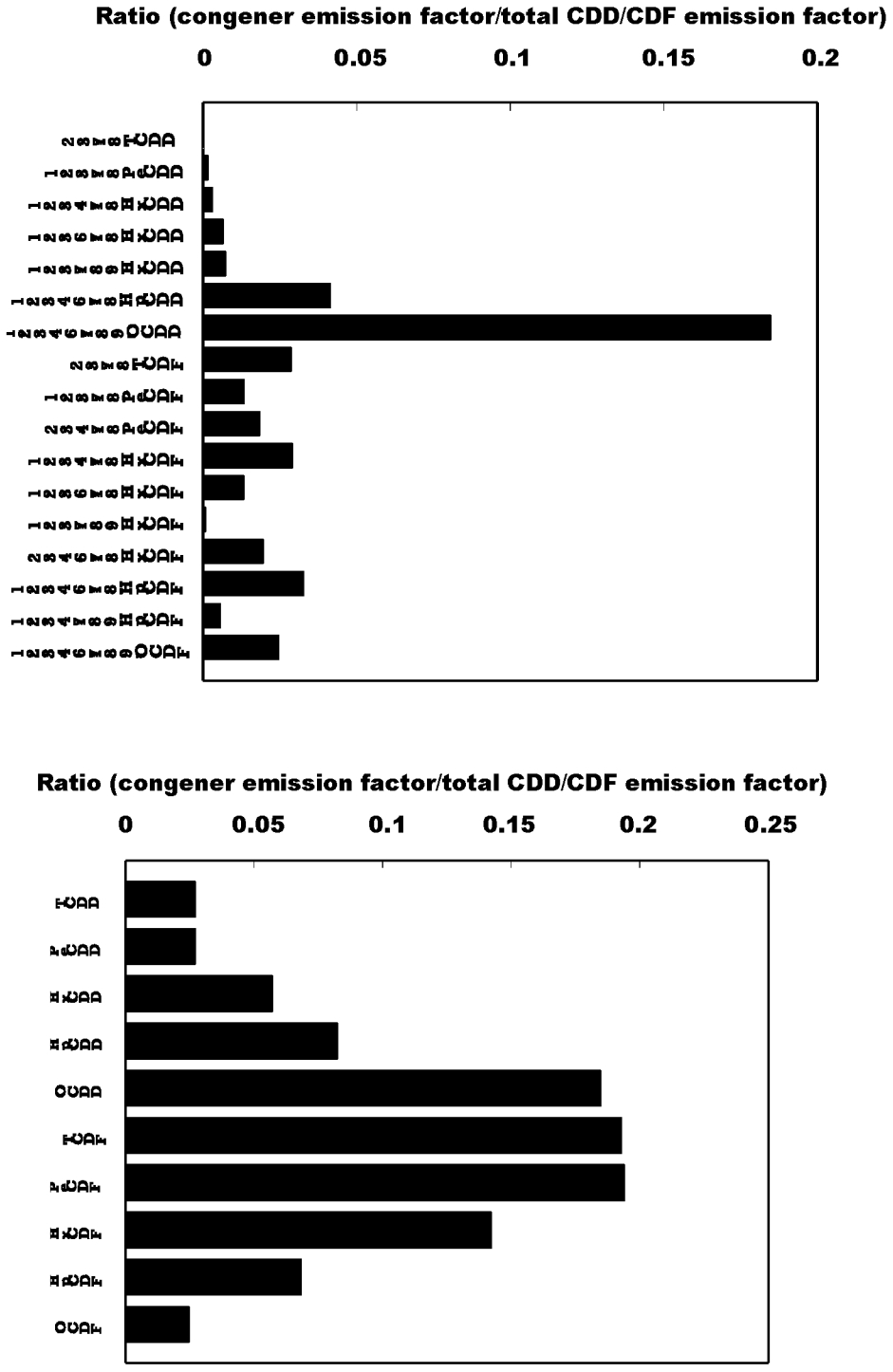


Figure 3-14. Congener and congener group profiles for air emissions from boilers and industrial furnaces burning hazardous waste.

TEQ_{DF}-WHO_{98}/kg (0.64 ng I-TEQ_{DF}/kg) of waste feed for 1993 to 1996 and 1.212 ng TEQ_{DF}-WHO_{98}/kg (1.214 ng I-TEQ_{DF}/kg) of waste feed for 2000. These emission factors are assigned a low confidence rating because they reflect testing at only 2 of 136 hazardous waste boilers and furnaces operating from 1993 to 1996 and only 1 of the 114 hazardous waste boilers and furnaces operating in 2000.

Dempsey and Oppelt (1993) estimated that approximately 1.2 billion kg of hazardous waste were combusted in industrial boilers/furnaces in 1987. EPA estimated that in each year in the early 1990s approximately 0.6 billion kg of hazardous waste were combusted in industrial boilers/furnaces (Federal Register, 1996a). It is possible that cement kilns and light-weight aggregate kilns burning hazardous waste were included in the estimate by Dempsey and Oppelt for 1987; the estimate for 1995 does not appear to include these hazardous waste-burning kilns. A confidence rating of low is assigned to the estimated activity level for 1987, which was largely based on a review of state permits (Dempsey and Oppelt, 1993). The activity level estimate for 1995 is assigned a medium confidence rating because it was based on a review by EPA of the various studies and surveys conducted in the 1990s to assess the quantity and types of hazardous wastes being managed by various treatment, storage, and disposal facilities. Because of a lack of data regarding the amount of waste burned in 2000, the 1995 estimate (1.5 million metric tons) was used as a surrogate for 2000.

Equation 3-5, which was used to calculate annual TEQ emissions for dedicated HWIs, was also used to calculate annual TEQ emissions for industrial boilers/furnaces. Multiplying the average TEQ emission factors by the total estimated kg of liquid hazardous waste burned in 1987, 1995, and 2000 yields annual emissions in g-TEQ/yr. From this procedure, the emissions from all industrial boilers/furnaces burning hazardous waste as supplemental fuel are estimated as 0.78 g TEQ_{DF}-WHO_{98} (0.77 g I-TEQ_{DF}) in 1987, 0.39 g TEQ_{DF}-WHO_{98} (0.38 g I-TEQ_{DF}) in 1995, and 1.82 g TEQ (TEQ_{DF}-WHO_{98} or I-TEQ_{DF}) in 2000. Because of the low confidence rating for the emission factor, the overall confidence rating is low for the emission estimates for all three reference years.

3.2.7. Halogen Acid Furnaces Burning Hazardous Waste

Hazardous waste can be used in the production of halogen acids using an HAF. According to EPA rules, products that qualify as hazardous waste, as defined in 40 CFR 261.2 must be regulated as such, even if the products are used in the production of halogen acids using an HAF (Federal Register, 1991c).

The national OSW database contains congener-specific emission concentrations for two HAFs burning liquid hazardous waste as supplemental fuel tested in 2000. Data from these two facilities were used to calculate an emission factor for HAFs. The average congener and TEQ

emission factors are presented in Table 3-15. The equation used to derive the emission factor is the same as eq 3-4. The average TEQ emission factor for HAFs is 0.836 ng TEQ_{DF}-WHO_{98}/kg (0.803 ng I-TEQ_{DF}/kg) of waste feed for reference year 2000. This emission factor is assigned a low confidence rating because it reflects testing at only 12.5% of all HAFs operating in 2000 (2 out of 16).

Table 3-15. CDD/CDF emission factors for halogen acid furnaces tested in 2000

Congener/congener group	Incinerator average mean emission factor (12 facilities) (ng/kg feed)	
	Nondetect set to ½ detection limit	Nondetect set to zero
2,3,7,8-TCDD	0.0274	0.0208
1,2,3,7,8-PeCDD	0.1164	0.112
1,2,3,4,7,8-HxCDD	0.0979	0.0913
1,2,3,6,7,8-HxCDD	0.1663	0.1594
1,2,3,7,8,9-HxCDD	0.1686	0.1293
1,2,3,4,6,7,8-HpCDD	0.9868	0.9868
OCDD	1.4944	1.4944
2,3,7,8-TCDF	0.3821	0.3821
1,2,3,7,8-PeCDF	0.583	0.583
2,3,4,7,8-PeCDF	0.5689	0.5689
1,2,3,4,7,8-HxCDF	1.1244	1.1244
1,2,3,6,7,8-HxCDF	0.7172	0.7172
1,2,3,7,8,9-HxCDF	0.4412	0.4412
2,3,4,6,7,8-HxCDF	0.2685	0.2685
1,2,3,4,6,7,8-HpCDF	3.4914	3.4914
1,2,3,4,7,8,9-HpCDF	1.0429	1.0429
OCDF	25.015	25.015
Total I-TEQ_{DF}	0.8176	0.8034
Total TEQ_{DF}-WHO_{98}	0.8519	0.8356
Total CDD/CDF	62.4773	62.4607

Source: U.S. EPA (2002a).

The amount of hazardous waste combusted using HAFs in 2000 was conservatively estimated to be 375,600 metric tons. This estimate is based on data provided by OSW that described activity levels for each individual HAF in 2000. Activity data were available for 14 of the 16 facilities. By assuming that plants operate continuously throughout the year, that they are always running at 80% of maximum capacity, and that the activity levels represent the maximum capacity, a conservative estimate for the annual quantity burned per HAF was derived (23,480

kg/yr). This quantity multiplied by the total universe of 16 facilities yields the final estimate of 375,600 metric tons. This was assigned a low confidence rating because the data was possibly nonrepresentative.

Equation 3-5, which was used to calculate annual TEQ emissions from dedicated HWIs, was also used to calculate annual TEQ emissions from HAFs. Multiplying the average TEQ emission factors by the total estimated kilograms of liquid hazardous waste burned in 2000 yields annual emissions in g I-TEQ_{DF}. From this procedure, the emissions from all industrial boilers/furnaces burning hazardous waste as supplemental fuel are estimated as 0.31 g TEQ_{DF}-WHO_{98} (0.3 g I-TEQ_{DF}). Because of the low confidence rating for the emission factor, the overall confidence rating is low for the emission estimates.

3.2.8. Solid Waste from Hazardous Waste Combustion

U.S. EPA (1987a) contains limited data on ash generated from hazardous waste incineration. The study indicates that the mean concentrations of CDDs and CDFs from an HWI with an afterburner were 538 μg/kg and 2,853 μg/kg, respectively (Table 3-8 in U.S. EPA, 1987a). Specific data for congeners and for ash quantities were not provided.

3.3. MEDICAL WASTE INCINERATION

Medical waste incineration is the controlled burning of solid wastes generated primarily by hospitals, veterinary facilities, and medical research facilities. EPA defines medical waste as any solid waste generated in the treatment, diagnosis, or immunization of humans or animals or research pertaining thereto or in the production or testing of biologicals (Federal Register, 1997a). The primary purposes of medical waste incineration are to reduce the volume and mass of waste in need of land disposal and to sterilize the infectious materials. The following sections review the basic types of medical waste incinerator (MWI) designs used to incinerate medical waste and the distribution of APCDs used on MWIs and summarize the derivation of dioxin TEQ emission factors for MWIs and the national dioxin TEQ emission estimates for reference years 1987, 1995, and 2000.

3.3.1. Design Types of MWIs Operating in the United States

For purposes of this document, EPA has classified MWIs into three broad technology categories: modular furnaces using controlled air, modular furnaces using excess air, and rotary kilns. Of the MWIs in use today, the vast majority are believed to be modular furnaces using controlled air. EPA has estimated that 97% are modular furnaces using controlled air, 2% are modular furnaces using excess air, and 1% are rotary kiln combustors (U.S. EPA, 1997a).

Modular furnaces using controlled air. Modular furnaces have two separate combustion chambers mounted in series (one on top of the other). The lower chamber is where the primary combustion of the medical waste occurs. Medical waste is ram-fed into the primary chamber and underfire air is delivered beneath the incinerator hearth to sustain good burning of the waste. The primary combustion chamber is operated at below stoichiometric levels, hence the terms "controlled air" or "starved air." With substoichiometric conditions, combustion occurs at relatively low temperatures (760 to 985°C). Under the conditions of low oxygen and low temperatures, partial pyrolysis of the waste occurs and volatile compounds are released.

The combustion gases pass into a second chamber. Auxiliary fuel (such as natural gas) is burned to sustain elevated temperatures (985 to 1,095°C) in this secondary chamber. The net effect of exposing the combustion gases to an elevated temperature is more complete destruction of the organic contaminants entrained in the combustion gases emanating from the primary combustion chamber. Combustion air at 100 to 300% in excess of stoichiometric requirements is usually added to the secondary chamber. Gases exiting the secondary chamber are directed to an incinerator stack (U.S. EPA, 1991b, 1997a; Buonicore, 1992b). Because of its low cost and good combustion performance, this design has been the most popular choice for MWIs and has accounted for more than 95% of systems installed over the past two decades (U.S. EPA, 1990b, 1991b; Buonicore, 1992b).

Modular furnaces using excess air. These systems use the same modular furnace configuration as described above for the controlled-air systems. The difference is that the primary combustion chamber is operated at air levels of 100 to 300% in excess of stoichiometric requirements, hence the name "excess air." A secondary chamber is located on top of the primary unit. Auxiliary fuel is added to sustain high temperatures in an excess-air environment. Excess-air MWIs typically have smaller capacity than do controlled-air units, and they are usually batch-fed operations. This means that the medical waste is ram-fed into the unit and allowed to burn completely before another batch of medical waste is added to the primary combustion chamber. Figure 3-4 shows a schematic of a typical modular furnace using excess air.

Rotary kiln. In terms of design and operational features, the rotary kiln technology used in medical waste incineration is similar to that employed in both municipal and hazardous waste incineration (see description in Section 3.1). Because of their relatively high capital and operating costs, few rotary kiln incinerators are in operation for medical waste treatment (U.S. EPA, 1990b, 1991b; Buonicore, 1992b).

MWIs can be operated in three modes: batch, intermittent, and continuous. Batch incinerators burn a single load of waste, typically only once per day. Waste is loaded and ashes are removed manually. Intermittent incinerators, which are loaded continuously and frequently

with small waste batches, operate less than 24 hr/day, usually on a shift basis. Either manual or automated charging systems can be used, but the incinerator must be shut down for ash removal. Continuous incinerators are operated 24 hr/day and use automatic charging systems to charge waste into the unit in small, frequent batches. All continuous incinerators operate using a mechanism to automatically remove the ash from the incinerator (U.S. EPA, 1990b, 1991b).

3.3.2. Characterization of MWIs for Reference Years 1987, 1995, and 2000

Medical waste incineration remains a poorly characterized industry in the United States in terms of knowing the exact number of facilities in operation over time, the types of APCDs installed on these units, and the aggregate volume and weight of medical waste that is combusted in any given year (U.S. EPA, 1997a). The primary reason for this lack of information is that permits were not generally required for the control of pollutant stack emissions from MWIs until the early 1990s, when state regulatory agencies began setting limits on emissions of PM and other contaminants (Federal Register, 1997a). Prior to that, only opacity was controlled.

The information available to characterize MWIs from 1987 and 1995 comes from national telephone surveys, stack emission permits, and data gathered by EPA during public hearings (Federal Register, 1997a). For 2000, information was also provided by a memorandum on emissions from MWIs (Strong and Hanks, 1999) and a limited telephone survey (McAloon, 2003). Strong and Hanks provided information on MWIs in the United States, including the APCD being used by each facility. A telephone survey was conducted with the state agencies in each of these six states to obtain the number of MWIs that were operating in 2000. EPA was able to obtain an updated list from four of the six states, which are shown below, along with the dates they were contacted, the number of MWIs operating in 1999, the updated number of MWIs for that state in 2000, and the percent of facilities closed over this time period for each state.

		No. of MWIs		Percentage of facilities
State	Date contacted	1999	2000	closed from 1999 to 2000
Illinois	Jan. 16, 2003	97	13	86.6
Louisiana	Jan. 16, 2003	92	24	73.91
Maryland	Dec. 2, 2002	36	30	16.67
Michigan	Nov. 26, 2002	228	45	80.26

The geometric mean of the closure percentages for the four states was determined to be 54.09 and the arithmetic mean was 64.36. Maryland had the lowest closure percent from 1999 to 2000; however, through discussions with representatives of Maryland state agencies, it was

determined that close to 70% of the facilities operating in 1999 would be shut down as of 2003. It was therefore assumed that the average closure percent of 64.36 was a fairly good estimate for all states. This average was applied to the total number of facilities operating in 1999 from the Strong and Hanks (1999) memorandum to estimate the number of facilities operating in 2000.

The information obtained from these sources suggests the following:

- The number of MWIs in operation for each reference year was approximately 5,000 in 1987 (U.S. EPA, 1987c), 2,375 in 1995 (Federal Register, 1997a), and 1,065 in 2000 (Strong and Hanks, 1999; McAloon, 2003).

- The amount of medical waste combusted annually in the United States was approximately 1.43 billion kg in 1987 (U.S. EPA, 1987c) and 0.77 billion kg in 1995 (Federal Register, 1997a).

These estimates indicate that between 1987 and 1995 the total number of operating MWIs and the total amount of waste combusted decreased by more than 50%. From 1995 to 2000, the total number of operating MWIs decreased by approximately 55%. A variety of factors probably contributed to the reduction in the number of operating facilities, including federal and state regulations and air pollution control requirements. In 1997, EPA adopted emission guidelines for existing MWIs (incinerators constructed on or before June 20, 1996) and New Source Performance Standards for new MWIs (incinerators constructed after June 20, 1996). The Clean Air Act requires that states implement the emission guidelines according to a state plan and that they submit the state plan to EPA within one year of EPA's promulgation of the guidelines (i.e., by September 15, 1998). The compliance schedule, however, allows up to three years from EPA approval of the state plan for MWIs to comply, provided the plan includes enforceable increments of progress. All MWIs were required to be in compliance within three years of approval of their state plan or by September 15, 2002, whichever was earlier.

Compliance is stated to be either completion of retrofit of air pollution controls or shutdown of the facility. As a result, many facilities have closed down and hospitals have switched to less expensive medical waste treatment technologies, such as autoclaving (Federal Register, 1997a). Autoclaving, or steam sterilization, is one of the most common waste management practices used today. This process involves placing bags of infectious waste into a sealed chamber, sometimes pressurized, and then heating it by direct contact with steam to sterilize the waste.

The actual controls used on MWIs on a facility-by-facility basis in 1987 are unknown, and EPA generally assumes that MWIs were mostly uncontrolled (U.S. EPA, 1987c). However, the modular design does cause some destruction of organic pollutants within the secondary

combustion chamber. Residence time within the secondary chamber is key to inducing the thermal destruction of the organic compounds. Residence time is the time that the organic compounds entrained within the flue gases are exposed to elevated temperatures in the secondary chamber. EPA has demonstrated with full-scale MWIs that increasing residence time from 1/4 sec to 2 sec in the secondary chamber can reduce organic pollutant emissions, including CDDs/CDFs, by up to 90% (Federal Register, 1997a). In this regard, residence time can be viewed as a method of air pollution control.

EPA estimates that about two-thirds of the medical waste burned in MWIs in 1995 went to facilities that had some method of air pollution control (Federal Register, 1997a).The types of APCDs installed and the methods used on MWIs include DSI, FFs, ESPs, WSs, and FFs combined with packed-bed scrubbers (composed of granular activated carbon). Some organic constituents in the flue gases can be adsorbed by the packed bed. Within the uncontrolled class of MWIs, about 12% of the waste was combusted in facilities with design capacities of less than 200 lb/hr, with the majority of waste burned at facilities with capacities greater than 200 lb/hr. In controlled facilities, an estimated 70% of the aggregate activity level is associated with facilities equipped with either WSs, FFs, or ESPs; 29.9% is associated with facilities that use DSI combined with FFs; and less than 1% is associated with facilities that have an FF/packed-bed APCD (AHA, 1995; Federal Register, 1997a).

Strong and Hanks (1999) provided information on the types of APCDs used by facilities operating in 1999. Ten types were included in the memorandum, which included residence time as a type of control technology. The 10 types were 1/4-sec combustion, 1-sec combustion, 2-sec combustion, low-efficiency WS, moderate-efficiency WS, high-efficiency WS, dry lime inject-FF, dry lime inject-FF with CI, WS/dry lime inject-FF, and SD/FF with CI. Table 3-16 provides an estimated breakdown of these APCDs.

3.3.3. Estimation of CDD/CDF Emissions from MWIs

Emission tests reported for 22 MWIs (about 3% of the existing facilities operating in 2000) were collected for use in this document; emission levels of dioxin-like compounds at most facilities are unmeasured. Because so few facilities have been evaluated, the estimation of annual air emissions of CDDs/CDFs from MWIs is quite dependent on extrapolations, engineering judgment, and assumptions. In addition, the information about the activity levels of these facilities is also quite limited.

The analysis divided MWIs into three design types on the basis of mode of daily operation: batch, intermittent, or continuous. This was done using the information from the inventory on design-rated annual incineration capacity of each facility. The smaller capacity

Table 3-16. Estimated breakdown of facilities by air pollution control device (APCD)

APCD	Number of facilities	Percent of total
1/4-sec combustion	229	17.5
1-sec combustion	259	19.8
2-sec combustion	455	34.8
Low-efficiency wet scrubber	208	15.9
Moderate-efficiency wet scrubber	75	5.7
High-efficiency wet scrubber	16	1.2
Dry lime inject fabric filter	44	3.4
Dry lime inject fabric filter with carbon injection	7	0.5
Wet scrubber/dry lime inject fabric filter	14	1.1
Spray dryer fabric filter with carbon injection	1	0.1

Source: Strong and Hanks (1999).

units were assumed to be batch operations, and the others were classified as either intermittent or continuous, assuming a ratio of 3 to 1.

The activity level of each facility was estimated by multiplying the design-rated annual incineration capacity of the MWI (kg/hr) by the hours of operation (hr/yr). The annual hours of operation were determined by assuming a capacity factor (defined as the fraction of time that a unit operates over the year) for each design type of MWI (Randall, 1995). Table 3-17 is a summary of the estimated annual operating hours for each MWI design type.

In estimating dioxin emissions, the MWIs were divided into two classes: those having APCDs (controlled) and those lacking any APCD (uncontrolled). These two classes of MWIs are discussed below.

For 1987, it is assumed that every MWI was uncontrolled. An EPA study of MWIs conducted at that time indicated that MWIs operating in 1987 did not need controls because they were not subject to state or federal limits on either PM or organic pollutant emissions (U.S. EPA, 1987c). The activity level estimates were derived from data presented in that 1987 study. This approach resulted in the following activity level assumptions for 1987: (a) 15% of the activity level (0.22 billion kg) was incinerated annually by MWIs with capacities less than or equal to 200 lb/hr, and (b) 85% of the activity level (1.21 billion kg) was incinerated annually by facilities with capacities greater than 200 lb/hr (see Table 3-18). For 1995, the activity levels were then summed across facilities for each APCD subclass (see Table 3-19).

Table 3-17. Summary of annual operating hours for each medical waste incinerator (MWI) type

MWI type	Capacity range (lb/hr)	Annual charging hours (hr/yr)	Maximum annual charging hours (hr/yr)	Capacity factor
Continuous commercial	>1,000	7,776	8,760	0.89
Continuous onsite	501–1,000 >1,000	1,826 2,174	5,475	0.33 0.40
Intermittent	≤500	1,250	4,380	0.29
Batch	Case by case	Case by case		Case by case

Source: U.S. EPA (1990c).

In 1997, the amount of waste combusted by MWIs was estimated to be 0.8 million tons/yr (0.7 billion kg/yr) (NRC, 2000). This number represents a 9% decrease from 1995. If we assume that this decrease occurred every two years from 1997 to 2000, the estimated amount of waste combusted by MWIs for 2000 would be 0.6 billion kg/yr. This is a conservative estimate, considering the large number of facilities that have shut down or switched to less expensive medical waste treatment technologies. For 2000 activity level estimates, the same distributions among APCD classes were assumed as for 1995. These activity level estimates are presented in Table 3-20. For all years, these activity levels were assigned a rating of low confidence because the data were judged to be possibly nonrepresentative.

The stack test results showing the air emissions of dioxin from 24 MWIs were obtained and used to calculate 1987 and 1995 emission estimates. After reviewing these test reports, EPA determined that 20 met the criteria for acceptability (see Section 3.1.3). In some cases, CDD/CDF congener-specific data were not reported or values were missing. In other cases, the protocols used in the laboratory analysis were not described; therefore, no determination of the adequacy of the laboratory methods could be made. For 2000, two additional test reports from facilities operating in that year were obtained and were included with the previously obtained test reports in order to calculate updated emission estimates. Each test report was included in its respective MWI subclass according to its APCD and was also included in the overall emission estimate.

Table 3-18. TEQ emissions from medical waste incinerators (MWIs) for reference year 1987

MWI class[a]	No. of tested facilities	Activity level (kg/yr)	Total CDD/ CDF emission factor[b] (g/kg)	I-TEQ_{DF} emission factor (g/kg)	TEQ_{DF}-WHO_{98} emission factor (g/kg)	Annual CDD/ CDF emissions (g/yr)	Annual I-TEQ_{DF} emissions (g/yr)	Annual WHO_{98}-TEQ_{DF} emissions (g/yr)
≤200 lb/hr	3	2.19e+08	9.25e-05	1.86e-06	1.98e-06	2.02e+04	4.08e+02	4.34e+02
>200 lb/hr	5	1.21e+09	6.05e-05	1.68e-06	1.78e-06	7.32e+04	2.03e+03	2.14e+03
TOTAL	8	1.43e+09				9.34e+04	2.44e+03	2.57e+03

Table 3-19. TEQ emissions from medical waste incinerators (MWIs) for reference year 1995

MWI class (air pollution control device [APCD])	MWI subclass (capacity or APCD[a])	No. of tested facilities	Total CDD/CDF emission factor (ng/kg)	I-TEQ_{DF} emission factor (ng/kg)	TEQ_{DF}-WHO_{98} emission factor (ng/kg)	Activity level (kg/yr)	Annual CDD/CDF emissions (g/yr)	Annual I-TEQ_{DF} emissions (g/yr)	Annual TEQ_{DF}-WHO_{98} emissions (g/yr)
Uncontrolled	≤200 lb/hr	3	9.25e+04	1.86e+03	1.98e+03	3.06e+07	2.83e+03	5.71e+01	6.06e+01
	>200 lb/hr	5	6.05e+04	1.80e+03	1.78e+03	2.23e+08	1.35e+04	3.75e+02	3.97E+02
Controlled	WS/FF/ESP	9	4.67e+04	7.22e+01	6.63e+01	3.71e+08	1.73e+03	2.68e+01	2.76E+01
	DSI/FF	2	2.85e+02	6.78	4.61	1.46e+08	4.16e+01	9.90e-01	1.00E+00
	FF/PBS	1	1.11e+05	1.35e+03	1.49e+03	6.99e+05	7.76e+01	9.44e-01	1.04e+00
TOTAL						7.71e+08	1.82e+04	4.59e+02	4.87E+02

[a]Slash(es) indicates devices used in conjunction.

APCD (air pollution control device):
DSI = Dry sorbent injection
ESP = Electrostatic precipitator
FF = Fabric filter
PBS = Packed-bed scrubber
WS = Wet scrubber

Table 3-20. TEQ emissions from medical waste incinerators (MWIs) for reference year 2000

MWI class (air pollution control device [APCD])	MWI subclass (capacity or APCD[a])	No. of tested facilities	Total CDD/CDF emission factor (ng/kg)	I-TEQ_{DF} emission factor (ng/kg)	TEQ_{DF}-WHO_{98} emission factor (ng/kg)	Activity level (kg/yr)	Annual CDD/CDF emissions (g/yr)	Annual I-TEQ_{DF} emissions (g/yr)	Annual TEQ_{DF}-WHO_{98} emissions (g/yr)
Uncontrolled	≤200 lb/hr	3	9.25e+04	1.86e+03	1.98e+03	2.40e+07	2.22e+03	4.46e+01	4.75e+01
	>200 lb/hr	5	6.05e+04	1.68e+03	1.78e+03	1.74e+08	1.05e+04	3.13e+02	3.10e+02
Controlled	WS/FF/ESP	9	4.67e+04	6.44e+01	6.63e+01	2.88e+08	1.34e+04	2.08e+01	1.91e+01
	DSI/FF	2	2.85e+02	4.56	4.61	1.14e+08	3.25e+01	7.73e–01	5.26e–01
	FF/PBS	1	1.11e+05	1.35e+03	1.49e+03	5.40e+05	5.99e+03	7.29e+01	8.05e+01
TOTAL						6.01e+08	3.22e+04	3.57e+02	3.78e+02

[a]Slash(es) indicates devices used in conjunction.

APCD:
DSI = Dry sorbent injection
ESP = Electrostatic precipitator
FF = Fabric filter
PBS = Packed-bed scrubber
WS = Wet scrubber

The EPA stack testing method (EPA Method 23) produces a measurement of CDDs/CDFs in units of mass concentration (ng/dscm) at standard temperature and pressure and 1 atm and adjusted to a measurement of 7% oxygen in the flue gas (U.S. EPA, 1995a). This concentration is assumed to represent conditions at the point of release from the stack into the air and to be representative of routine emissions. The emission factors were derived by averaging the emission factors across each tested facility in a design class. The emission factor for each tested MWI was calculated using the following equation:

$$EF_{MWI} = \frac{C \times F_v}{I_w} \quad (3\text{-}8)$$

where:

EF_{MWI} = emission factor per MWI (average ng TEQ per kg medical waste burned)

C = average TEQ concentration in flue gases of tested MWIs (ng TEQ/dscm) (20°C, 1 atm; adjusted to 7% O_2)

F_v = average volumetric flue gas flow rate (dscm/hr) (20°C, 1 atm; adjusted to 7% O_2)

I_w = average medical waste incineration rate of the tested MWI (kg/hr)

3.3.4. Summary of CDD/CDF Emissions from MWIs

Annual dioxin emissions were estimated by multiplying the emission factor and activity level developed for each design class and then summing the calculated emissions for all classes. Tables 3-18, 3-19, and 3-20 summarize the resulting national TEQ air emissions for reference years 1987, 1995, and 2000, respectively. These tables also indicate the activity level and the TEQ emission factor used in estimating annual TEQ emissions.

In estimating annual TEQ emissions for each reference year, a low confidence rating was assigned to the estimate of the activity level, primarily because very limited information is available on a facility-level basis for characterizing MWIs in terms of the frequency and duration of operation, the actual waste volume handled, and the level of pollution control. The 1987 inventory of facilities was based on very limited information. Although the 1995 OAQPS inventory was more comprehensive than the 1987 inventory, it was still based on a fairly limited survey of operating facilities (approximately 6%). The 2000 inventory included only two additional facilities and estimated an activity level based on a 1997 value and the distribution among APCDs from the 1995 estimates.

The emission factor estimates were given a low confidence rating because the reports of only 20 tested MWI facilities could be used to derive emission factors representing the 2,375 facilities operating in 1995 (i.e., less than 1% of the estimated number of operating facilities) and only two additional test reports were obtained for 2000. Even fewer tested facilities could be

used to represent the larger number of facilities operating in 1987 (8 tested facilities were used to represent 5,000 facilities). The limited emission tests available cover all design categories used here to develop emission factors. However, because of the large number of facilities in each of these classes, it is very uncertain whether the few tested facilities in each class capture the true variability in emissions.

Table 3-20 shows the 2000 emissions estimate as being 378 g TEQ_{DF}-WHO_{98} (357 g I-TEQ_{DF}). The TEQ emissions are estimated to have been 487 g TEQ_{DF}-WHO_{98} (459 g I-TEQ_{DF}) in 1995 (Table 3-19) and 2,590 g TEQ_{DF}-WHO_{98} (2,440 g I-TEQ_{DF}) in 1987 (Table 3-18). Because the activity level and emission factors had low confidence ratings, the emission estimates for all years were assigned a low confidence rating, i.e., a Category C. Figures 3-15 and 3-16 display the congener and congener group profiles of MWIs without APCDs and those equipped with WSs and FFs, respectively.

3.3.5. Recent EPA Regulatory Activities

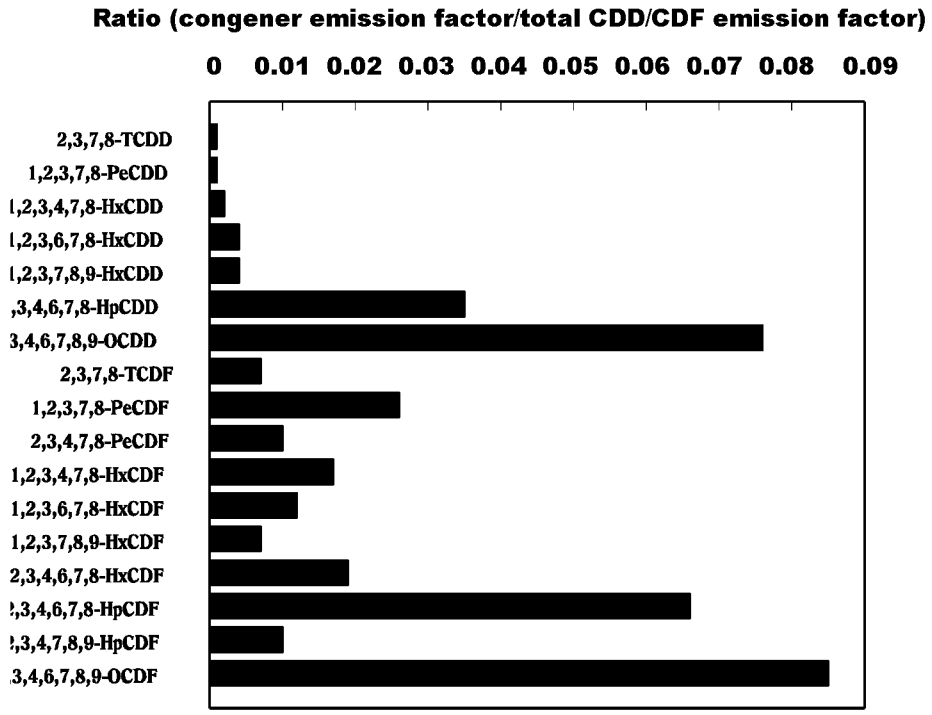
In September 1997, EPA promulgated final regulations under the Clean Air Act Amendments limiting CDD/CDF stack emissions from MWIs (Federal Register, 1997a). These emission limits are specific to the sum of CDD and CDF emissions (the sum of tetra- through octa-CDDs and CDFs). For either new or existing MWIs that were operational before or after June 20, 1996, EPA limits the total CDD/CDF concentration in the stack gases to 2.3 ng/dscm. This would require the application of WSs, DSI of activated carbon combined with FFs and/or SDs/FFs. EPA expects that many facilities that currently operate on-site incinerators will switch to less expensive methods of treatment and disposal of medical and infectious waste when faced with the compliance costs associated with the emission standards for MWIs. EPA projects that, following full compliance with these standards, annual emissions from MWIs will be 5 to 7 g I-TEQ_{DF}/yr.

3.4. CREMATORIA

3.4.1. Human Crematoria

3.4.1.1 *Emissions Data*

Bremmer et al. (1994) measured CDD/CDF emissions at two crematoria in the Netherlands. The first, a "cold"-type furnace with direct, uncooled emissions, was calculated to yield 2,400 ng I-TEQ_{DF} per body. In the cold-type furnaces, the coffin is placed inside at a temperature of about 300°C. The temperature of the chamber is then increased to 800 to 900°C using a burner and kept there for 2 to 2.5 hr. The second furnace, a "warm" type in which flue gases are cooled to 220°C prior to discharge, was calculated to yield 4,900 ng I-TEQ_{DF} per body. In the warm-type furnace, the coffin is placed in a chamber preheated to 800°C or higher for 1.2 to 1.5 hr. The chamber exhausts from both furnace types were incinerated in an afterburner at a



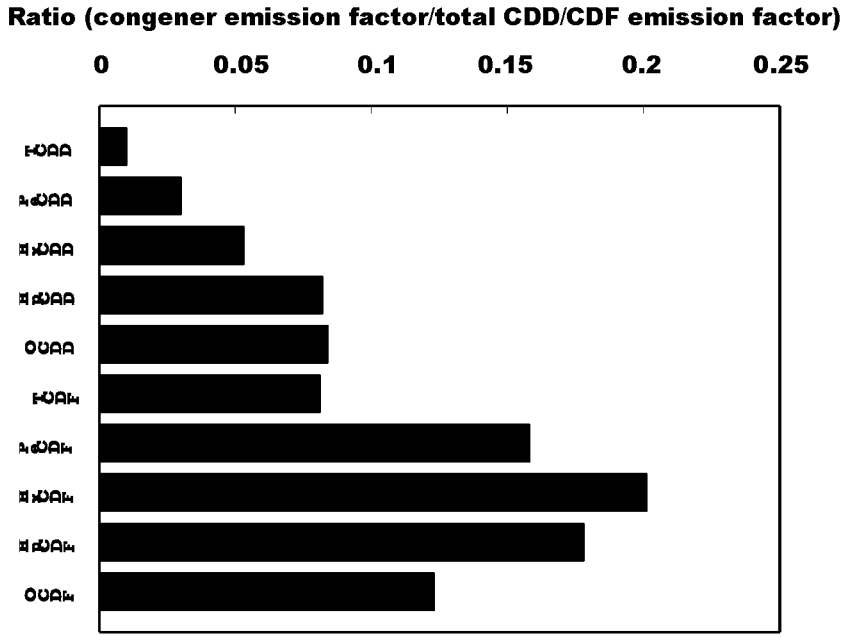
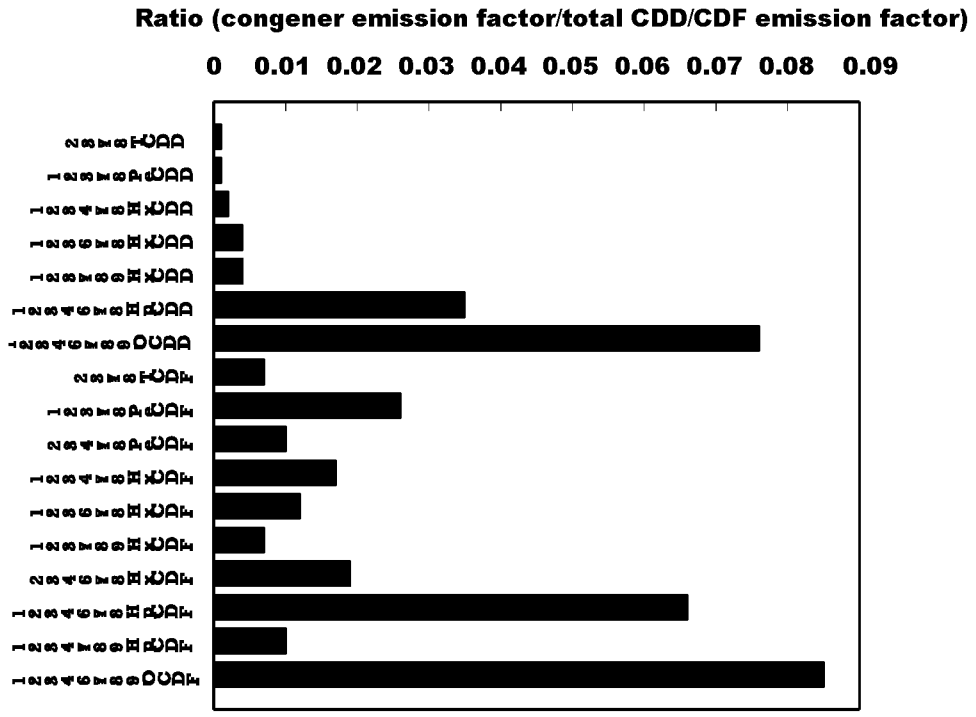


Figure 3-15. Congener and congener group profiles for air emissions from medical waste incinerators without air pollution control devices (nondetects set equal to zero).



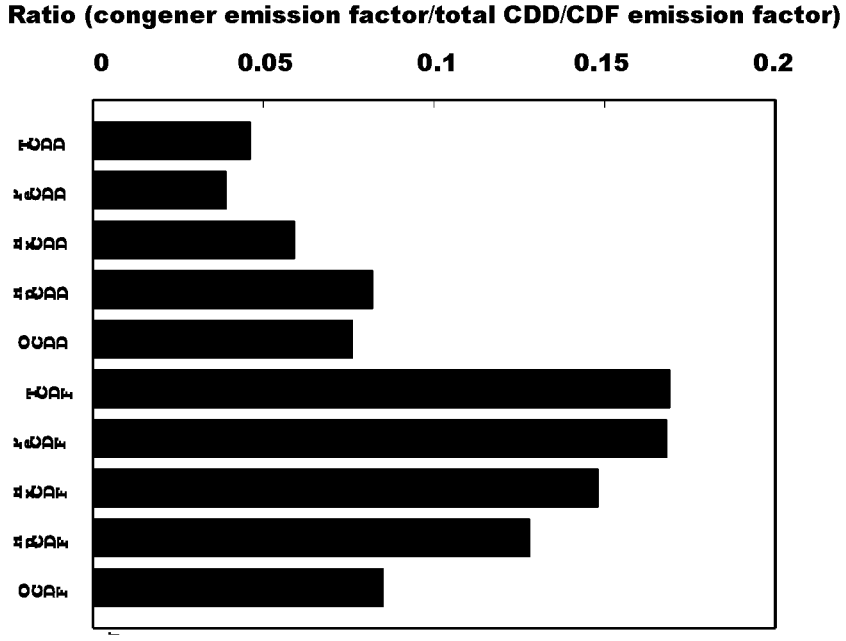


Figure 3-16. Congener and congener group profiles for air emissions from medical waste incinerators equipped with a wet scrubber and fabric filter.

temperature of about 850°C. The higher emission rate for the warm-type furnace was attributed by the authors to the formation of CDDs/CDFs during the intentional cooling of the flue gases to 220°C.

Jager et al. (1992) (as reported in Bremmer et al., 1994) measured an emission rate of 28,000 ng I-TEQ_{DF} per body for a crematorium in Berlin, Germany. No operating process information was provided by Bremmer et al. for the facility.

Mitchell and Loader (1993) reported even higher emission factors for two crematoria in the United Kingdom. The first facility tested was manually operated and had primary and secondary combustion chambers preheated to 650°C and a residence time of 1 sec in the secondary combustion chamber. The second tested facility was computer controlled and had primary and secondary combustion chambers heated to 850°C and a residence time of 2 sec in the secondary combustion chamber. The measured stack gas TEQ concentrations ranged from 42 to 71.3 ng I-TEQ_{DF}/m^3 (at 11% oxygen) at the first facility and from 25.4 to 45.5 ng I-TEQ_{DF}/m^3 (at 11% oxygen) at the second facility. Emission factors based on these test results and gas generation rates reported by Bremmer et al. (1994) were calculated to range from 70,000 to 80,000 ng I-TEQ_{DF}/body (HMIP, 1995).

Takeda et al. (1998) measured CDD/CDF emissions at 10 crematoria in Japan. Although there are more than 1,600 crematoria in Japan, the 10 tested facilities handle 4% of the cremations carried out in Japan annually. A wide range of CDD/CDF emissions were observed. When nondetect values were treated as zero, the emission factor range was 42 to 62,000 ng I-TEQ_{DF}/body (mean of 9,200 ng I-TEQ_{DF}/body). When nondetect values were treated as one-half the DL, the range was 450 to 63,000 ng I-TEQ_{DF}/body (mean of 11,000 ng I-TEQ_{DF}/body).

To obtain more data on CDD/CDF emissions from crematoria in Japan, Takeda et al. (2001) measured CDD/CDF emissions at 17 additional crematoria. In that study, all the crematoria except one had secondary combustion chambers. Additionally, one crematorium had a secondary combustion chamber but did not use it. One to four main chambers were connected to the secondary chambers, and the temperature of the main chambers ranged from approximately 650 to 1,150°C. In most cases, only one body was cremated at time. However, between two and four bodies were cremated at four sampling events. A coffin and any accompanying materials were combusted along with the body. Emission factors ranged from 120 to 24,000 ng I-TEQ_{DF}/body. In general, as the average temperature in the main combustion chamber increased, CDD/CDF emissions decreased. However, the crematorium that had a secondary combustion chamber but did not use it had both high temperatures in the main combustion chamber and high CDD/CDF emissions. Additionally, with the rise of the average temperature in the secondary combustion chamber of the eight crematoria without dust collectors, CDD/CDF emissions decreased. For crematoria with dust collectors, the relationship

between the average temperature in the secondary combustion chamber and CDD/CDF emissions was not clear.

EPA obtained test data from two crematoria for humans operating in the United States, one at Camellia Memorial Lawn in California (CARB, 1990a) and one at Woodlawn Cemetery in New York (U.S. EPA, 1999a). Additionally, EPA obtained test data from one crematorium for animals operating in the United States: University of Georgia Veterinary School (U.S. EPA, 2000a); however, it is not appropriate to use the emission factors from this facility to characterize emissions associated with human cremation.

Testing at the Camellia Memorial Lawn crematorium, which is classified as a warm-type facility using the criteria of Bremmer et al. (1994), was conducted in 1990 (CARB, 1990a). The combusted material at this facility consisted of the body, as well as 4 lb of cardboard, up to 6 lb of wood, and an unquantified amount of unspecified plastic wrapping. The three emissions tests conducted at this facility, which operates using an afterburner, yielded an average emission factor of 543 ng TEQ_{DF}-WHO_{98}/body (501 ng I-TEQ_{DF}/body). Table 3-21 presents the congener-specific emission factors for this facility.

Testing at Woodlawn Cemetery, which has a crematorium with a primary combustion chamber, a secondary combustion chamber, and a scrubber APCD, was conducted in 1995. Tests were run at three secondary combustion chamber temperatures: 675, 870, and 980°C (U.S. EPA, 1999a). The combusted material consisted of the body, as well as a 10- to 100-lb casket constructed of fiberboard, particle board, or wood and various body wrappings and articles such as a plastic sheet, a cloth sheet, or clothes. For this facility, average emission factors of 362 and 709 ng TEQ_{DF}-WHO_{98}/body cremated (348 and 638 ng I-TEQ_{DF}/body cremated) were calculated, based on emissions collected at the scrubber inlet and outlet, respectively. The congener-specific emission factors for this facility are shown in Table 3-22.

In 1995, 1,155 crematoria were reported to be operating in the United States; this number had decreased to approximately 1,060 by 2000. To determine whether the emissions data collected at the Woodlawn Cemetery facility are representative of a typical crematorium operating in the United States, representatives from the Cremation Association of North America (CANA) were contacted to identify the typical operating conditions at U.S. crematoria. According to the CANA representatives, all crematoria operating in the United States have primary and secondary combustion chambers. Additionally, crematoria with operating conditions that indicate the presence of an afterburner are considered to contain secondary combustion chambers. The primary and secondary combustion chambers at U.S. crematoria typically operate at between 675 and 870°C, but many operate at 980°C, as required by their respective states.

Table 3-21. Congener-specific profile for Camellia Memorial Lawn crematorium

Congener/congener group	Mean facility emission factor (ng/body)	
	Assuming nondetect set to zero	Assuming nondetect set to ½ detection limit
2,3,7,8-TCDD	28.9	28.9
1,2,3,7,8-PeCDD	89.6	89.6
1,2,3,4,7,8-HxCDD	108	108
1,2,3,6,7,8-HxCDD	157	157
1,2,3,7,8,9-HxCDD	197	197
1,2,3,4,6,7,8-HpCDD	1,484	1,484
OCDD	2,331	2,331
2,3,7,8-TCDF	206	206
1,2,3,7,8-PeCDF	108	117
2,3,4,7,8-PeCDF	339	349
1,2,3,4,7,8-HxCDF	374	374
1,2,3,6,7,8-HxCDF	338	338
1,2,3,7,8,9-HxCDF	657	657
2,3,4,6,7,8-HxCDF	135	135
1,2,3,4,6,7,8-HpCDF	1,689	1,813
1,2,3,4,7,8,9-HpCDF	104	112
OCDF	624	624
Total 2,3,7,8-CDD	4,396	4,396
Total 2,3,7,8-CDF	4,574	4,725
Total I-TEQ_{DF}	501.8	508.6
Total TEQ_{DF}-WHO_{98}	544.1	550.9
Total TCDD	554	554
Total PeCDD	860	860
Total HxCDD	2,224	2,224
Total HpCDD	3,180	3,180
Total OCDD	2,331	2,331
Total TCDF	4,335	4,335
Total PeCDF	2,563	2,563
Total HxCDF	4,306	4,306
Total HpCDF	2,030	2,154
Total OCDF	624	624
Total CDD/CDF	23,007	23,131

Source: CARB (1990a).

Table 3-22. Congener-specific profile for the Woodlawn Cemetery crematorium

Congener	Mean emission factor, scrubber inlet (ng/body)		Mean emission factor, scrubber outlet (ng/body)	
	Nondetect set to zero	Nondetect set to ½ detection limit	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	11	12	39	45
1,2,3,7,8-PeCD	31	44	168	364
1,2,3,4,7,8-HxCDD	74	74	239	258
1,2,3,6,7,8-HxCDD	115	115	565	603
1,2,3,7,8,9-HxCDD	83	83	524	553
1,2,3,4,6,7,8-HpCDD	724	724	1,253	1,302
OCDD	1,120	1,120	10,698	1,154
2,3,7,8-TCDF	106	106	256	279
1,2,3,7,8-PeCDF	116	116	150	170
2,3,4,7,8-PeCDF	285	285	409	463
1,2,3,4,7,8-HxCDF	263	264	252	280
1,2,3,6,7,8-HxCDF	278	278	253	282
1,2,3,7,8,9-HxCDF	146	146	139	148
2,3,4,6,7,8-HxCDF	466	466	429	474
1,2,3,4,6,7,8-HpCDF	962	963	872	948
1,2,3,4,7,8,9-HpCDF	165	165	142	148
OCDF	435	435	3,499	363
Total I-TEQ_{DF}	348	356	638	780
Total TEQ_{DF}-WHO_{98}	362	376	709	961

Source: U.S. EPA (1999a).

Only one or two facilities in the United States incorporate the use of an APCD, such as a scrubber. Therefore, the inlet dioxin emission factors rather than the outlet dioxin emission factors at the Woodlawn crematorium would be representative of a typical crematorium operating in the United States (telephone conversation between Allen Krobath, CANA, and K. Riley, Versar, Inc., February 12, 2003, and telephone conversation between Dale Walter, Matthews Cremation, and K. Riley, Versar Inc., February 13, 2003).

In the previous inventory, an average emission factor of 17,000 ng I-TEQ_{DF}/body (assuming nondetect values were zero) was developed, based on emission factors measured for 16 of the tested facilities, including the one at Camellia Memorial Lawn (CARB, 1990a), the 10 Japanese facilities (Takeda et al., 1998), the two Dutch facilities (Bremmer et al., 1994), the one German facility (Jager et al., 1992), and the two British facilities (Mitchell and Loader, 1993). The more recent data provided by Takeda et al. (2001) for the 17 Japanese facilities support the emission factor of 17,000 ng I-TEQ_{DF}/body. However, an average emission factor developed

using the data reported for the two U.S. crematoria (i.e., the outlet values for the Camellia Memorial Lawn facility and the inlet values for the Woodlawn Cemetery facility) is 453 ng TEQ_{DF}-WHO_{98}/body (425 I-TEQ_{DF}/body cremated), assuming nondetect values were zero. These values are two orders of magnitude less than the overall average calculated above. An examination of the differences in U.S. and foreign operating practices may provide a rationale for the large discrepancies.

Bremmer et al. (1994) reported an emission factor of 2,400 ng I-TEQ_{DF}/body for a Dutch facility with a cold-type furnace and an emission factor of 4,900 ng I-TEQ_{DF}/body for another Dutch facility with a warm-type furnace where flue gases were cooled to 220°C. Neither of the U.S. facilities are considered to have cold-type furnaces. Additionally, the flue gases at the Camellia Memorial Lawn crematorium were not cooled prior to exiting the furnace. At the Woodlawn Cemetery facility, the flue gases were cooled from 681 to 860°C prior to entering the scrubber to 271 to 354°C by the time they exited the scrubber and the furnace. The emissions were higher at the scrubber outlet than at the inlet (961 vs. 325 ng TEQ_{DF}-WHO_{98}/body [780 vs. 319 I-TEF/body]); however, the emissions were not of the same magnitude as those reported by Bremmer for the warm-type facility (4,900 ng I-TEQ_{DF}/body). The Jager et al. (1992) report did not include operating process information; therefore, the German facility could not be compared with the U.S. facilities. Additionally, the emission values derived from the Mitchell and Loader (1993) emission concentrations were calculated using gas generation rates from the Bremmer et al. report and, as such, may not be indicative of crematoria in the United States.

In the Takeda et al. (1998, 2001) reports, the burn time for the cremations varied from 47 to 117 min. The average burn time in the U.S. studies was 120 min. This shorter burn time may not be optimal for dioxin reduction, resulting in higher dioxin emissions. Also, the secondary combustion chamber temperatures ranged from 250 to 950°C in the Takeda studies, again resulting in higher emission rates. In fact, in Takeda et al. (2001) two of the three runs that had the highest TEQ concentrations per body came from a crematorium that did not use a secondary combustion chamber. Of the 31 crematoria sampled in Takeda et al. (2001), 26 had lower than 5,000 ng I-TEQ_{DF}/body.

Because the Woodlawn facility is unique in that it incorporates an APCD, the sample data for the air stream entering the scrubber versus the stream exiting the scrubber should be analyzed. A comparison of the dioxin concentrations of these air streams shows a significant increase in dioxin concentrations in the stream exiting the scrubber. This increase can be attributed to the decrease in temperature that occurred in the scrubber. Upon exiting the scrubber, the flue gas temperatures were in the range of 271 to 354°C, compared with temperatures of between 681 and 860°C at the scrubber inlet. As discussed in Section 2, these exit flue gas temperatures lie in the

optimum temperature range for dioxin formation; therefore, an increase in dioxin concentrations would be expected.

An analysis of scrubber inlet dioxin data indicates that the average dioxin concentrations increased with temperature (189, 445, and 503 ng TEQ_{DF}-WHO_{98}/body at 681, 772, and 860°C, respectively). Because the operating temperatures are outside the temperature range for the formation of dioxin (200 to 400°C), dioxin concentrations should decrease as temperatures increase. Further analysis of the data shows that as temperatures at the scrubber inlet increased, so did concentrations of PM, HCl, and lead (Table 3-23). The data also indicate that oxygen levels decreased as the temperature increased (U.S. EPA, 1999a). Given these data, one could speculate that as the temperature increased, incomplete combustion conditions arose, leading to an increase in dioxin formation.

Table 3-23. Operational data for the Woodlawn Cemetery crematorium, scrubber inlet

Parameter	Mean value		
	675°C	870°C	980°C
Particulate matter (gr/dscf @ 7% O_2)	0.015	0.033	0.068
Hydrochloric acid (lb/hr)	0.053	0.14	0.26
Lead (g/hr)	0.1	0.32	0.59
Oxygen (%)	9.9	8.6	7.5

Source: U.S. EPA (1999a).

Using data from U.S. crematoria, EPA recommends an average emission factor of 453 ng TEQ_{DF}-WHO_{98}/body (425 ng I-TEQ_{DF}/body). This is derived from the scrubber inlet dioxin concentrations from the Woodlawn Cemetery study and the results from the Camellia Memorial Lawn study. These average congener-specific emission are presented in Table 3-24, and the CDD/CDF congener and congener group emission profiles are presented in Figure 3-17. Because the emission factor was derived using emissions data from only 2 of 1,060 crematoria, the average emission factor is assigned a low confidence rating.

3.4.1.2. *Activity Level Information*

A total of 323,371 cremations were performed in reference year 1987, 488,224 in 1995, and 629,362 in 2000. A high confidence rating is assigned to these activity level estimates because they are based on comprehensive data provided by CANA (CANA, 2006).

Table 3-24. Congener-specific profile for the Camellia Memorial Lawn crematorium and the Woodlawn Cemetery crematorium

Congener/congener group	Mean facility emission factor (ng/body)	
	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	20	20.5
1,2,3,7,8-PeCDD	60.3	66.8
1,2,3,4,7,8-HxCDD	91	91
1,2,3,6,7,8-HxCDD	136	136
1,2,3,7,8,9-HxCDD	140	140
1,2,3,4,6,7,8-HpCDD	1,104	1,104
OCDD	1,725.5	1,725.5
2,3,7,8-TCDF	156	156
1,2,3,7,8-PeCDF	112	116.5
2,3,4,7,8-PeCDF	312	317
1,2,3,4,7,8-HxCDF	318.5	319
1,2,3,6,7,8-HxCDF	308	308
1,2,3,7,8,9-HxCDF	401.5	401.5
2,3,4,6,7,8-HxCDF	300.5	300.5
1,2,3,4,6,7,8-HpCDF	1,325.5	1,388
1,2,3,4,7,8,9-HpCDF	134.5	138.5
OCDF	529.5	529.5
Total I-TEQ_{DF}	424.8	431.9
Total TEQ_{DF}-WHO_{98}	452.9	463.3
Total TCDD	330	330
Total PeCDD	488	488
Total HxCDD	1,254.5	1,254.5
Total HpCDD	1,721.5	1,721.5
Total OCDD	1,304.5	1,304.5
Total TCDF	2,240.5	2,240.5
Total PeCDF	1,514.5	1,514.5
Total HxCDF	2,634	2,634
Total HpCDF	1,097.5	1,097.5
Total OCDF	529.5	529.5
Total CDD/CDF	13,114.5	13,114.5

Sources: CARB (1990a); U.S. EPA (1999a).

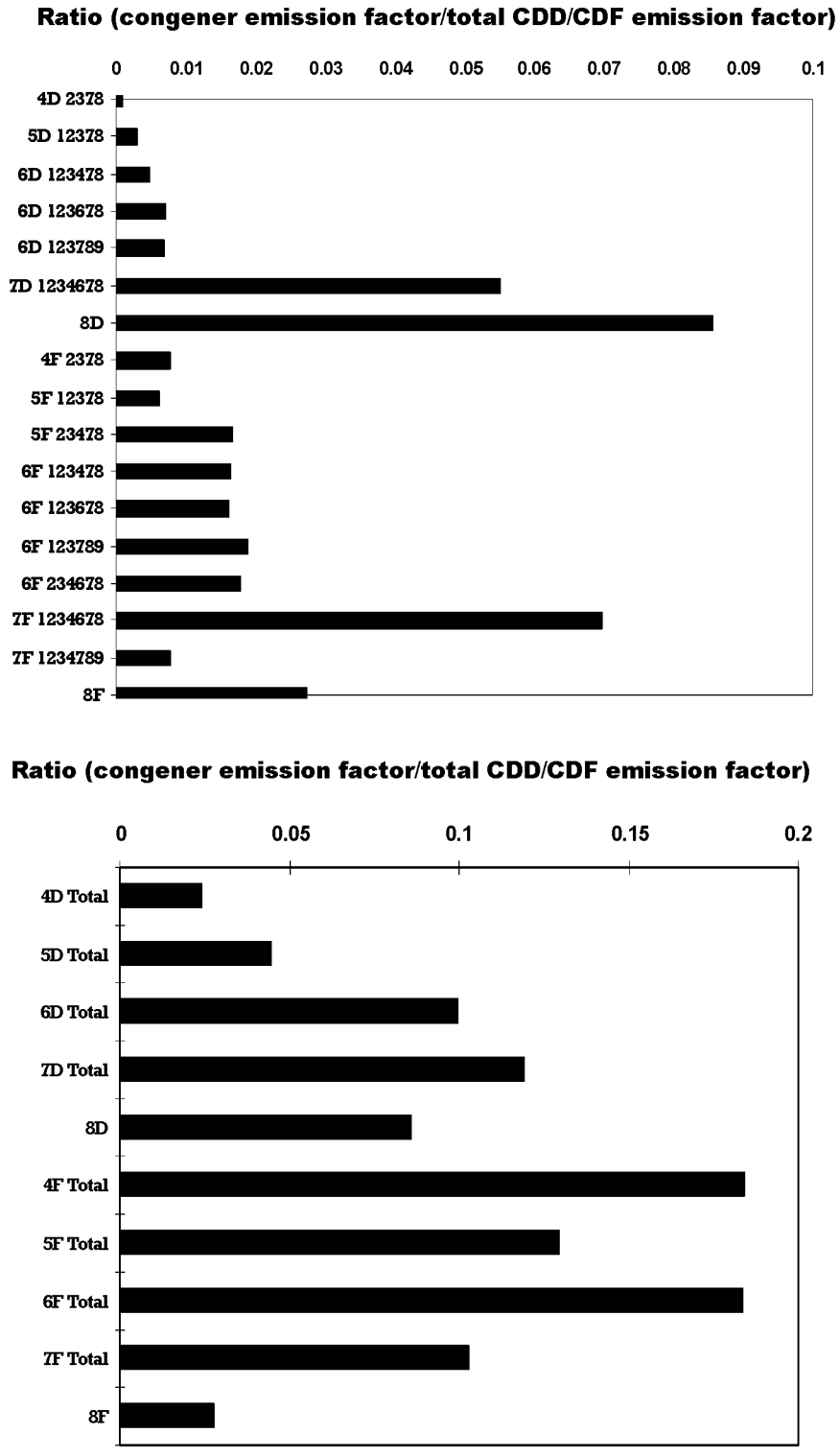


Figure 3-17. Congener and congener group profiles for air emissions from the Camellia Memorial Lawn crematorium and Woodlawn Cemetery crematorium.

Sources: CARB (1990a); U.S. EPA (1999a).

3.4.1.3. *Emission Estimates*

Combining the average emission rate of 453 ng WHO-TEQ_{98}/body (425 ng I-TEQ_{DF}/body) with the number of cremations in 1987, 1995, and 2000 (323,371; 488,224; and 629,362, respectively) yields an estimated annual release of 0.15 g TEQ_{DF}-WHO_{98} (0.14 g I-TEQ_{DF}) in 1987, 0.22 g TEQ_{DF}-WHO_{98} (0.2 g I-TEQ_{DF}) in 1995, and 0.29 g TEQ_{DF}-WHO_{98} (0.27 g I-TEQ_{DF}) in 2000. An overall confidence rating of low was assigned to the emissions because the emission factor had a low rating.

3.4.2. Animal Crematoria

3.4.2.1. *Emissions Data*

Only one study that measured CDD/CDF emissions from animal cremation could be located. In 1999, CDD/CDF emissions from a newly installed animal incineration unit located at the University of Georgia Veterinary School were measured (U.S. EPA, 2000a). The incineration unit, which consists of a primary and a secondary combustion chamber, is used to dispose of animals (mostly cows and horses) used in experimentation. Emissions are uncontrolled, with the exception of an NFPA spark screen located at the stack outlet. Based on four test runs, the average TEQ emission factor was 0.12 TEQ_{DF}-WHO_{98}/kg (0.11 ng I-TEQ_{DF}/kg) of animal cremated. The average emission factors for these test runs are provided in Table 3-25 and a congener-specific profile based on these data is provided as Figure 3-18.

3.4.2.2. *Activity Level Information*

As part of the 2000 inventory, OAQPS calculated a national animal cremation activity level estimate of 81.9 million kg/yr for reference year 2000. This estimate was scaled from the 1999 activity level estimate by applying the ratio of the 2000 national human population (281,421,906) to the 1999 national human population (249,440,000). The 1999 national activity level was based on 1990 data provided by OAQPS' Emission Standards Division. The 1999 and 2000 activity level estimates assume that animal mortality and cremation rates are constant and that the animal population is directly proportional to human population.

3.4.2.3. *Emission Estimates*

Applying the TEQ emission factor of 0.12 ng TEQ_{DF}-WHO_{98}/kg (0.11 ng I-TEQ_{DF}/kg) of animal combusted to the activity level estimated by OAQPS (81.9 million kg/yr) yields estimated annual emissions of 0.0098 g TEQ_{DF}-WHO_{98} (0.009 g I-TEQ_{DF}) in 2000. This estimate does not include events such as the mass burning of animals affected by mad cow disease. These estimates are based on extremely limited data and should be regarded as preliminary indications of possible emissions from this source; further testing is needed to confirm the true magnitude of the emissions.

Table 3-25. Congener-specific profile for the University of Georgia Veterinary School

Congener/congener group	Mean facility emission factor (ng/kg of animal)	
	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	7.51e-03	7.51e-03
1,2,3,7,8-PeCDD	2.13e-02	2.13e-02
1,2,3,4,7,8-HxCDD	4.46e-03	4.46e-03
1,2,3,6,7,8-HxCDD	8.86e-03	8.86e-03
1,2,3,7,8,9-HxCDD	7.17e-03	7.17e-03
1,2,3,4,6,7,8-HpCDD	5.03e-03	5.03e-03
OCDD	1.01e-03	1.01e-03
2,3,7,8-TCDF	1.79e-02	1.79e-02
1,2,3,7,8-PeCDF	6.70e-03	6.70e-03
2,3,4,7,8-PeCDF	1.41e-01	1.41e-01
1,2,3,4,7,8-HxCDF	2.93e-02	2.93e-02
1,2,3,6,7,8-HxCDF	1.85e-02	1.85e-02
1,2,3,7,8,9-HxCDF	7.44e-02	7.44e-02
2,3,4,6,7,8-HxCDF	2.35e-02	2.35e-02
1,2,3,4,6,7,8-HpCDF	4.20e-03	4.20e-03
1,2,3,4,7,8,9-HpCDF	3.16e-03	3.16e-03
OCDF	2.00e-04	2.00e-04
Total CDD/CDF	0.37	0.37
Total I-TEQ_{DF}	0.11	0.11
Total TEQ_{DF}-WHO_{98}	0.12	0.12

Source: U.S. EPA (2000a).

3.5. SEWAGE SLUDGE INCINERATION

The three principal combustion technologies used to incinerate sewage sludge in the United States are multiple-hearth incineration, fluidized-bed incineration, and electric furnace incineration (Brunner, 1992; U.S. EPA, 1995a). All of these technologies are excess-air processes (i.e., they combust sewage sludge with oxygen in excess of theoretical requirements). Approximately 80% of operating sludge incinerators are multiple-hearth design, about 20% are fluidized-bed incinerators, and fewer than 1% are electric incinerators. Other types of furnaces not widely used in the United States are single-hearth cyclones, rotary kilns, and high-pressure, wet-air oxidation units (U.S. EPA, 1997a; e-mail dated July 13, 1998, from K. Maw, Pacific Environmental Services, to G. Schweer, Versar, Inc.).

Multiple-hearth incinerators. These types of furnaces consist of refractory hearths arranged vertically in series, one on top of the other. Dried sludge cake is fed to the top hearth of the furnace. The sludge is mechanically moved from one hearth to another through the length of

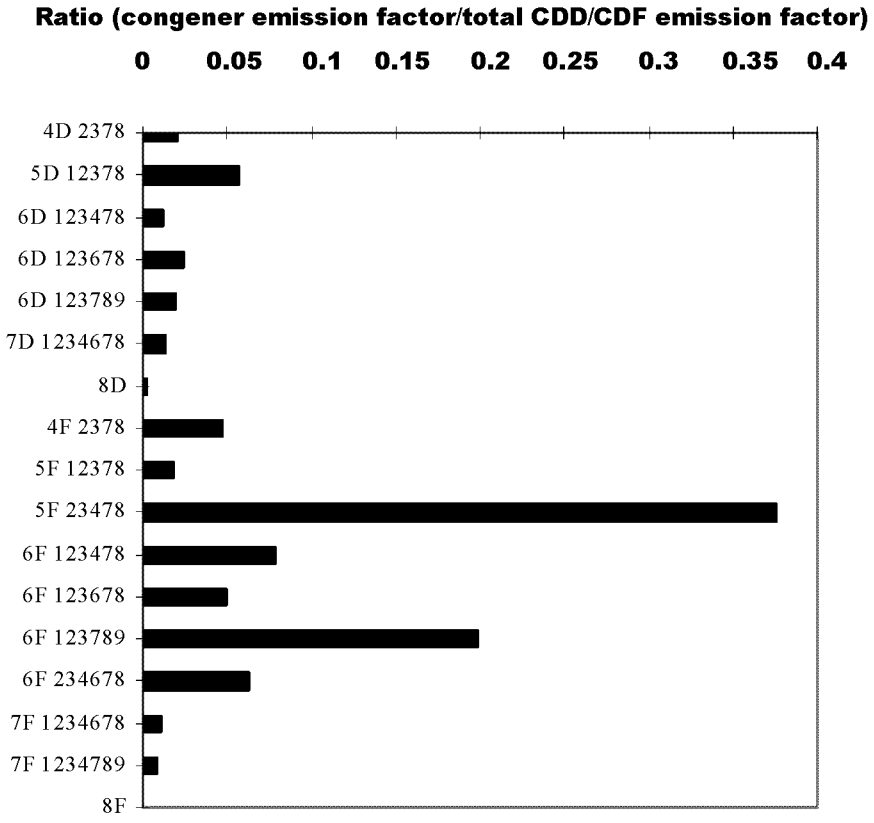


Figure 3-18. Congener profile for air emissions from the University of Georgia animal crematorium.

Source: U.S. EPA (2000a).

the furnace. Moisture is evaporated from the sludge cake in the upper hearths. The center hearths are the burning zone, where gas temperatures reach 871°C. The bottom hearths are the burn-out zone, where the sludge solids become ash. A waste-heat boiler is usually included in the burning zone, where steam is produced to provide supplemental energy at the sewage treatment plant. Air pollution control measures typically include a venturi scrubber, an impingement tray scrubber, or a combination of both. Wet cyclones and dry cyclones are also used (U.S. EPA, 1995a).

Fluidized-bed incinerators. A fluidized-bed incinerator is a cylindrical refractory-lined shell with a steel plate structure that supports a sand bed near the bottom of the furnace (Brunner, 1992). Air is introduced through openings in the bed plate supporting the sand. This causes the sand bed to undulate in a turbulent air flow; hence, the sand appears to have a fluid motion when observed through furnace portals. Sludge cake is added to the furnace at a position just above this fluid motion of the sand bed. The fluid motion promotes mixing in the combustion zone. Sludge ash exits the furnace with the combustion gases; therefore, air pollution control systems

typically consist of high-energy venturi scrubbers or venturi/impingement tray combinations (U.S. EPA, 1995a).

Electric furnaces. Also called infrared furnaces, these consist of a long, rectangular, refractory-lined chamber. A belt conveyer system moves the sludge cake through the length of the furnace. To promote combustion of the sludge, supplemental heat is added by electric infrared heating elements located just above the traveling belt within the furnace. Electric power is required to initiate and sustain combustion. Emissions are usually controlled with a venturi scrubber or some other WS (Brunner, 1992; U.S. EPA, 1995a).

3.5.1. Emissions Estimates from Sewage Sludge Incinerators

EPA measured CDD/CDF emissions at three multiple-hearth incinerators as part of Tier 4 of the National Dioxin Survey (U.S. EPA, 1987a). During the pretest surveys, two of the facilities were judged to have "average" potential and one facility was judged to have "high" potential for CDD/CDF emissions with respect to other sewage sludge incinerators. The results of these tests include congener group concentrations in stack gas but lack measurements for specific congeners other than 2,3,7,8-TCDD and 2,3,7,8-TCDF. The results show a wide variability in the emission factors at these three facilities; total CDD/CDF emission factors ranged from 90 to 3,400 ng/kg (average of 1,266 ng/kg). Total TEQ emissions could not be determined for these facilities because of the lack of congener-specific data.

In 1990, EPA measured CDD/CDF emissions (including all 17 toxic congeners) at another multiple-hearth incinerator and also at a fluidized-bed incinerator (U.S. EPA, 1990d). Assuming nondetects were zero, the total CDD/CDF emission factors for these two facilities were 79 and 846 ng/kg, and the total average TEQ emission factors were 3.6 and 43.2 ng TEQ_{DF}-WHO_{98}/kg (2.4 and 43.3 ng I-TEQ_{DF}/kg) of dry sludge. In 1995, the Association of Metropolitan Sewerage Agencies (AMSA) submitted to EPA the results of stack tests conducted at an additional 13 sewage sludge incinerators (Green et al., 1995). Two of these data sets were considered not usable by EPA because either DLs or feed rates and stack flow rates were not provided. As with the EPA-tested facilities (U.S. EPA, 1987a, 1990d), wide variability was observed in the emission factors for the 11 AMSA facilities. Assuming nondetects were zero, total CDD/CDF emission factors ranged from 0 to 1,392 ng/kg (average of 217 ng/kg), and total average TEQ emission factors ranged from 0 to 16 ng TEQ_{DF}-WHO_{98}/kg (average, 3.47 ng) (3.46 ng I-TEQ_{DF}/kg) of dry sludge.

In 1999, stack tests were conducted at a multiple-hearth incinerator equipped with a venturi scrubber and a three-tray impingement conditioning tower (U.S. EPA, 2000b). Four test runs were conducted; however, the first test run was aborted, and the CDD/CDF results from the fourth test run were determined to be statistical outliers (p>0.05). The back-half emission

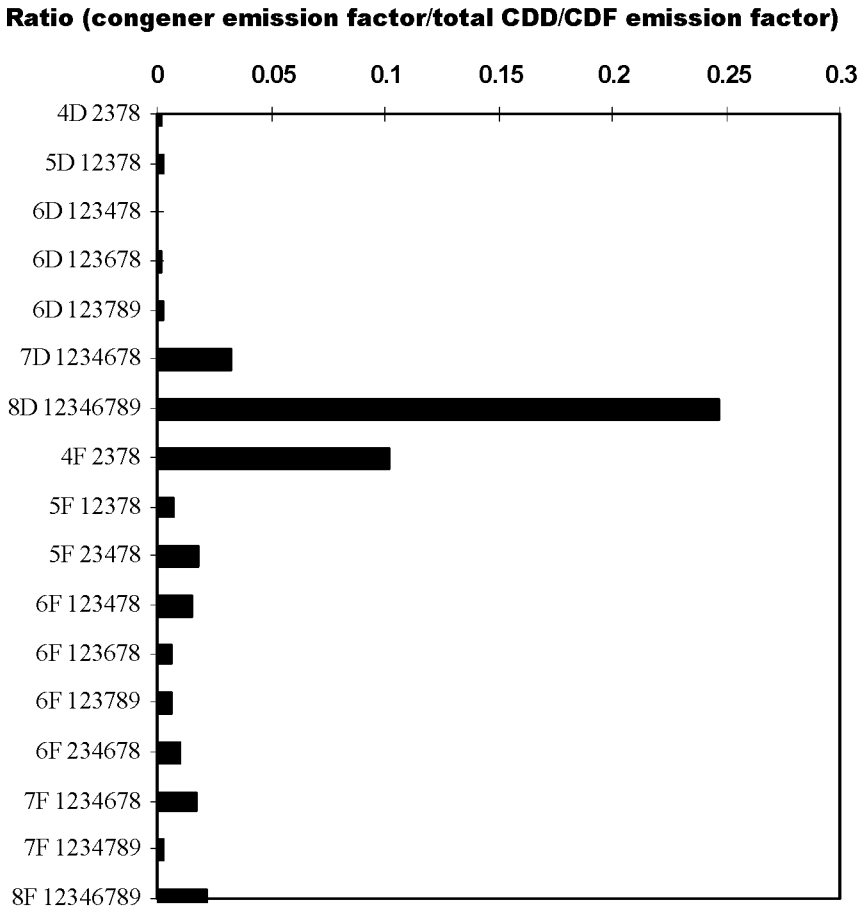
concentrations for test run 4 were 50 to 60% lower than those for test runs 2 and 3. Overall, total CDD/CDF emissions measured during test run 4 were 48 ng/kg, whereas total CDD/CDF emissions measured during test runs 2 and 3 were 120 and 116 ng/kg, respectively. It could not be determined whether the lower concentrations associated with test run 4 were due to analyte loss or whether they represented an accurate reflection of a change in incinerator emission releases.

The average TEQ emission factor, excluding test run 4, was 3.28 ng TEQ_{DF}-WHO_{98}/kg (3.23 ng I-TEQ_{DF}/kg). The average TEQ emission factor based on the data for the 11 AMSA facilities (Green et al., 1995) and the three facilities reported by EPA (U.S. EPA, 2000b, 1990d) is 6.74 ng TEQ_{DF}-WHO_{98}/kg (6.65 ng I-TEQ_{DF}/kg) of dry sludge, assuming nondetect values are zero. Figure 3-19 presents the average congener and congener group profiles based on these data. Additionally, Table 3-26 presents the average congener and congener-specific group emission factors and the average TEQ emission factors for these facilities. Table 3-26 also presents 2,3,7,8-TCDD, 2,3,7,8-TCDF, and congener-specific group emission factors for the three facilities reported by EPA (U.S. EPA, 1987a).

Studies from other countries have reported similar results. Bremmer et al. (1994) reported an emission rate of 5 ng I-TEQ_{DF}/kg for a fluidized-bed sewage sludge incinerator in the Netherlands that was equipped with a cyclone and a WS. Cains and Dyke (1994) measured CDD/CDF emissions at two sewage sludge incinerators in the United Kingdom. The emission rate at an incinerator equipped with an ESP and a WS ranged from 2.75 to 28 ng I-TEQ_{DF}/kg. The emission rate measured at a facility equipped with only an ESP was 43 ng I-TEQ_{DF}/kg.

In 1988, approximately 199 sewage sludge incineration facilities combusted abo 0.865 million metric tons of dry sewage sludge (Federal Register, 1993a). In 1995, approximately 257 sewage sludge incinerators (some of which were backup or alternate incinerators) combusted about 2.11 million dry metric tons of sewage sludge (e-mail dated July 13, 1998, from K. Maw, Pacific Environmental Services, to G. Schweer, Versar, Inc.). Using trends in wastewater flow rates from the 1988 National Sewage Sludge Survey and the 1984 to 1996 Needs Surveys, EPA estimated that in 2000 approximately 6.4 million metric tons of dry sewage sludge would be generated (U.S. EPA, 1999b). Of this amount, EPA projected that 22% (1.42 million metric tons) would be incinerated.

According to EPA, sewage sludge generation would increase to 6.9 million dry tons in 2005 and 7.4 million dry tons in 2010; however, the percentage of sewage sludge incinerated will decrease slightly, to 20% in 2005 and 19% in 2010. EPA estimates that approximately 1.38 million metric tons of dry sewage sludge would be incinerated in 2005 and 1.41 million metric tons will be incinerated in 2010. EPA believes that incineration as a disposal method for sewage sludge will decrease as a result of increasing costs and public concerns about the environmental and health impacts associated with incineration.



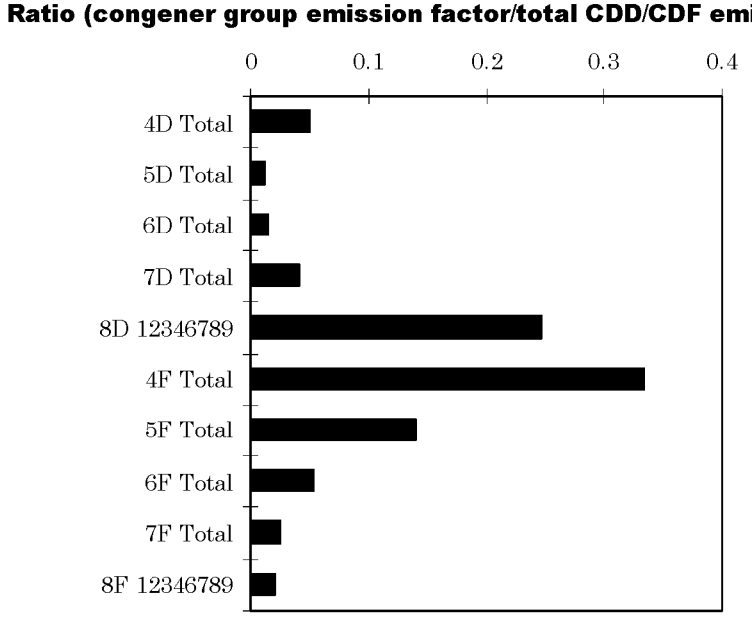


Figure 3-19. Congener and congener group profiles for air emissions from sewage sludge incinerators.

Table 3-26. CDD/CDF emission factors for sewage sludge incinerators

Congener	Mean emission factor (ng/kg) for U.S. EPA (1987a) (3 facilities)		Mean emission factor (ng/kg) for Green et al. (1995) (11 facilities) U.S. EPA (1990d) (2 facilities) U.S. EPA (1999b) (1 facility)	
	Nondetect set to zero	Nondetect set to ½ detection limit	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	0.39	0.44	0.16	0.26
1,2,3,7,8-PeCDD	NR	NR	0.22	0.3
1,2,3,4,7,8-HxCDD	NR	NR	0.04	0.11
1,2,3,6,7,8-HxCDD	NR	NR	0.12	0.17
1,2,3,7,8,9-HxCDD	NR	NR	0.29	0.35
1,2,3,4,6,7,8-HpCDD	NR	NR	2.46	2.59
OCDD	46.2	46.2	12.78	13.16
2,3,7,8-TCDF	179	179	25.41	25.41
1,2,3,7,8-PeCDF	NR	NR	1.92	1.92
2,3,4,7,8-PeCDF	NR	NR	6.47	6.47
1,2,3,4,7,8-HxCDF	NR	NR	2.11	2.11
1,2,3,6,7,8-HxCDF	NR	NR	0.77	0.77
1,2,3,7,8,9-HxCDF	NR	NR	0.03	0.03
2,3,4,6,7,8-HxCDF	NR	NR	1.22	1.22
1,2,3,4,6,7,8-HpCDF	NR	NR	1.46	1.46
1,2,3,4,7,8,9-HpCDF	NR	NR	0.17	0.17
OCDF	109	109	1.17	1.17
Total TCDD	37.6	37.7	35.8	37.81
Total PeCDD	2.66	2.81	1.11	1.63
Total HxCDD	16.6	16.9	1.74	2.25
Total HpCDD	53.9	54	4.39	5.03
Total OCDD	46.2	46.2	12.78	13.16
Total TCDF	528	528	123.85	124.1
Total PeCDF	253	253	59.94	60.16
Total HxCDF	75.4	75.9	12.69	13.5
Total HpCDF	144	144	2.63	3.12
Total OCDF	109	109	1.17	1.55
Total I-TEQ_{DF}	NR	NR	6.65	6.87
Total TEQ_{DF}-WHO_{98}	NR	NR	6.74	7.01
Total CDD/CDF	1,266	1,268	256	262

NR = Not reported

A medium confidence rating is assigned to the average TEQ emission factor because it was derived from stack testing at 14 U.S. sewage sludge incinerators. The 1988 activity level estimate (used as a surrogate for the 1987 activity level) and the 2000 activity level estimate are assigned a high confidence rating because they are based on extensive EPA surveys to support rule-making activities. The 1995 activity level estimate is assigned a medium confidence rating because assumptions were made for numerous facilities concerning hours of operation, operating capacity, and design capacity.

Using the above estimated amounts of sewage sludge incinerated per year and the average TEQ emission factor of 6.74 ng TEQ_{DF}-WHO_{98}/kg (6.65 ng I-TEQ_{DF}/kg), the estimate of TEQ emissions to air is 5.8 g TEQ_{DF}-WHO_{98} (5.8 g I-TEQ_{DF}) in 1987, 14.2 g TEQ_{DF}-WHO_{98} (14 g I-TEQ_{DF}) in 1995, and 9.6 g TEQ_{DF}-WHO_{98}/kg (9.4 g I-TEQ_{DF}/kg) in 2000. Because the emission factor had a medium confidence rating, the overall emission estimates were assigned a medium confidence rating for all years.

3.5.2. Solid Waste from Sewage Sludge Incinerators

In Table 5-16 of U.S. EPA (1987a), data are presented indicating that 2,3,7,8-TCDD was not detected in the bottom ash or scrubber water filtrate from three sewage sludge incinerators. However, total CDDs for the three incinerators and the filtrate were nondetects, 20 ng/kg, 10 ng/kg, and 0.3 ng/kg, respectively. For total CDFs, the respective values were nondetects, 70 ng/kg, 50 ng/kg, and 4 ng/kg. No data were given for any congeners (other than 2,3,7,8-TCDD), nor were there any data on the quantities of ash or filtrate.

3.6. TIRE COMBUSTION

Most discarded tires are combusted in dedicated tire incinerators or cement kilns. Some are combusted as auxiliary fuel in industrial boilers and in pulp and paper mill combustion facilities. Additionally, tires may be unintentionally burned in an uncontrolled fashion at landfills (open burning). This section addresses the total TEQ emissions that may result from the combustion of tires in dedicated tire incinerators, industrial boilers, and pulp and paper mill combustion facilities, but excludes cement kilns (addressed in Section 5.1). The open burning of tires is not discussed in this report due to the lack of information.

Emissions of CDDs/CDFs from the incineration of discarded automobile tires were measured at a dedicated tire incinerator tested by the California Air Resources Board (CARB, 1991). The facility consists of two excess air furnaces equipped with steam boilers to recover the energy from the heat of combustion. Whole tires were fed to the incineration units at rates ranging from 2,800 to 5,700 kg/hr during the three test days. The facility was equipped with a DS and an FF for the control of emissions prior to exiting the stack. Table 3-27 presents the congener-specific emission factors for this facility. Figure 3-20 presents CDD/CDF congener

Table 3-27. CDD/CDF air emission factors for a tire combustion facility

Congener/congener group	Mean facility emission factor (ng/kg)	
	Assuming nondetect set to zero	Assuming nondetect set to ½ detection limit
2,3,7,8-TCDD	0.149	0.149
1,2,3,7,8-PeCDD	0.006	0.026
1,2,3,4,7,8-HxCDD	0.018	0.023
1,2,3,6,7,8-HxCDD	0.055	0.062
1,2,3,7,8,9-HxCDD	0.036	0.048
1,2,3,4,6,7,8-HpCDD	0.379	0.379
OCDD	4.156	4.156
2,3,7,8-TCDF	0.319	0.319
1,2,3,7,8-PeCDF	0.114	0.118
2,3,4,7,8-PeCDF	0.086	0.091
1,2,3,4,7,8-HxCDF	0.103	0.111
1,2,3,6,7,8-HxCDF	0.059	0.09
1,2,3,7,8,9-HxCDF	0.036	0.068
2,3,4,6,7,8-HxCDF	0.1	0.148
1,2,3,4,6,7,8-HpCDF	0.0	0.166
1,2,3,4,7,8,9-HpCDF	0.027	0.095
OCDF	0.756	0.756
Total 2,3,7,8-CDD	4.799	4.843
Total 2,3,7,8-CDF	1.6	1.962
Total I-TEQ_{DF}	0.282	0.312
Total TEQ_{DF}-WHO_{98}	0.281	0.320
Total TCDD	0.153	0.153
Total PeCDD	0.032	0.032
Total HxCDD	0.391	0.391
Total HpCDD	0.695	0.695
Total OCDD	4.156	4.156
Total TCDF	1.204	1.204
Total PeCDF	0.737	0.737
Total HxCDF	0.71	0.71
Total HpCDF	0.119	0.186
Total OCDF	0.802	0.802
Total CDD/CDF	8.999	9.067

Source: CARB (1991).

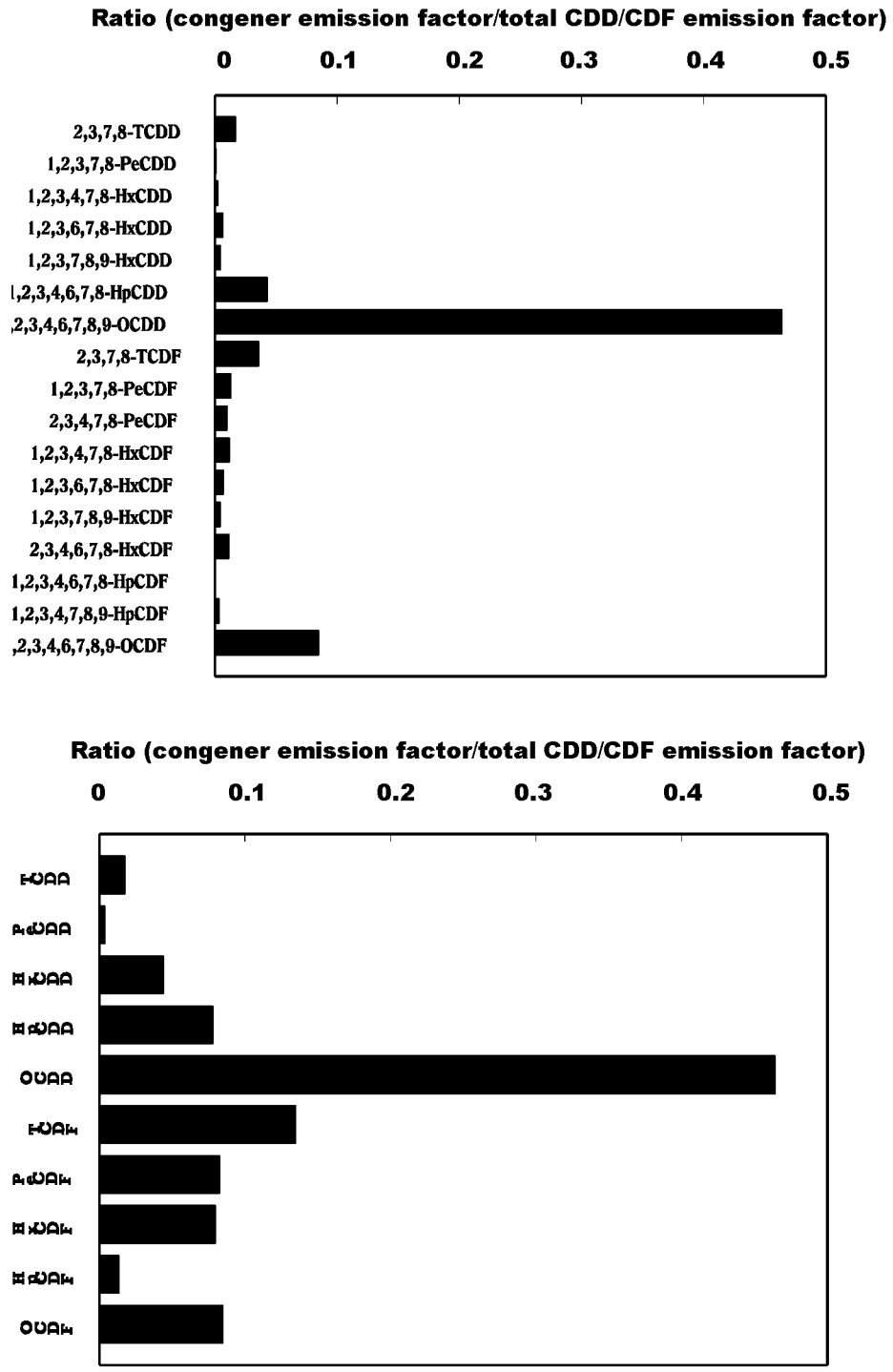


Figure 3-20. Congener and congener group profiles for air emissions from a tire combustor.

and congener group profiles based on these TEQ emission factors. From these data, the average emission factor is estimated to be 0.281 ng TEQ_{DF}-WHO_{98}/kg (0.282 ng I-TEQ_{DF}/kg) of tires incinerated (when all nondetect values are treated as zero). This emission factor was used to estimate annual TEQ releases from the tire combustion source category for the years 1987, 1995, and 2000.

EPA assigned a low confidence rating to the estimated TEQ emission factor because it is possible that it is not representative of TEQ emissions from all tire combustion facilities. It is also possible that this emission factor is an underestimation of emissions from this source category because it was derived from the emissions of a facility equipped with very advanced air pollution control technology specific for the control of dioxin emissions. These devices (DS/FF) are capable of greater than 95% reduction and control of dioxin-like compounds prior to discharge from the stack into the air. Because other facilities may not be equipped with similar air pollution control systems, the TEQ emissions could be higher than the estimates shown above. For example, Cains and Dyke (1994) reported much higher emission rates for two tire incinerators in the United Kingdom that were equipped with only simple grit arrestors. These emissions produced emission factors of 188 and 228 ng I-TEQ_{DF}/kg of tires combusted.

EPA estimated that approximately 500 million kg of tires were combusted in 1990 (U.S. EPA, 1992b). Of this total, 23% (115 million kg) were combusted in cement kilns, and it is assumed that the remaining 385 million kg were combusted in dedicated tire combustion facilities, industrial boilers, and pulp and paper mill combustion facilities. This activity level was adopted for the years 1987 and 1995 and is assigned a medium confidence rating.

The Rubber Manufacturers Association (2002) reported that 281 million scrap tires weighing approximately 5.68 million metric tons were generated in the United States in 2001. Approximately 115 million of these scrap tires were combusted as tire-derived fuel, or roughly 2.32 million metric tons (2.32 billion kg) of tires. Subtracting the 23% of the tires burned in cement kilns yields a total of 1.8 billion kg of tires estimated to have been combusted in facilities other than cement kilns in 2001. This figure is used to represent the activity level for tire combustion in 2000. This activity level is assigned a medium confidence rating.

Annual emissions for the reference years were estimated by multiplying the activity level times the TEQ emission factor. The TEQ emission factor of 0.281 ng TEQ_{DF}-WHO_{98}/kg (0.282 ng I-TEQ_{DF}/kg) of tires combusted was used to estimate annual emissions for all years. Multiplying the emission factor by the activity level (385 million kg of tires) yields an estimate of 0.11 g TEQ_{DF}-WHO_{98}/yr (0.11 g I-TEQ_{DF}/yr) emitted to the air in 1987 and 1995. Using the same emission factor multiplied by the estimated activity level of 1.8 billion kg tires combusted in 2000 gives an estimate of 0.51 g TEQ_{DF}-WHO_{98}/yr (0.51 g I-TEQ_{DF}/yr). The estimated TEQ

emissions to air from tire combustion for 1987, 1995, and 2000 are given a low confidence rating because of the low confidence rating of the emission factor.

3.7. COMBUSTION OF WASTEWATER SLUDGE AT BLEACHED CHEMICAL PULP MILLS

Approximately 20.5% of the wastewater sludges generated at bleached chemical pulp mills are dewatered and burned in bark boilers at the mills. These sludges can contain CDDs/CDFs and elevated levels of chloride. However, the level of heat input from sludge in the mixed feed to bark boilers rarely exceeds 10% (NCASI, 1995).

NCASI (1995) provided congener-specific test results for four wood residue/sludge boilers tested between 1987 and 1993. Sludge comprised 6 to 10% of the solids in the feed. The average congener-specific emission factors derived from the stack test results obtained from these facilities are presented in Table 3-28. The average TEQ emission factor derived from the test results is 0.062 ng I-TEQ_{DF}-WHO_{98} (0.061 ng I-TEQ_{DF}/kg) of feed (i.e., sludge and wood residue), assuming nondetect values were zero. The range in facility-specific emission factors was wide (0.0004 to 0.118 ng I-TEQ_{DF}/kg, assuming nondetect values are zero).

NCASI (1995) also presented stack emission test results for five other bark boilers. These boilers combusted only bark during the tests even though the boilers normally fire bark in combination with sludge and coal. These boilers are discussed in Section 4.2.2 as industrial facilities burning wood scrap/residues. The average TEQ emission factor for these facilities was 0.4 ng I-TEQ_{DF}/kg of feed. The emissions test data presented in NCASI (1995), and discussed above, indicate that the CDD/CDF emission factors for bark/sludge combustors are similar to the emission factor developed in Section 4.2.2 for industrial facilities burning only wood residues/scrap. Based on the fact that wood residues comprise a far greater fraction of the feed to these bark/sludge burners than does sludge, the national TEQ emission estimates derived in Section 4.2.2 for industrial wood-burning facilities are assumed to include emissions from these bark/sludge combustion units.

3.8. BIOGAS COMBUSTION

Using a specially developed sampling apparatus, Schreiner et al. (1992) measured the CDD/CDF content of a flare combusting exhaust gases from an anaerobic sewage sludgedigestor in Germany. The nozzle of the apparatus was moved through three cross-sections of the flame and cooling zone. The CDD/CDF content was 1.4 pg I-TEQ_{DF}/standard cubic meter (Nm^3) at the bottom of the flare, 3.3. pg I-TEQ_{DF}/Nm^3 at the top of the flare, and 13.1 pg I-TEQ_{DF}/Nm^3 in the middle of the flare. Congener-specific results were not reported. Using the theoretical ratio of

Table 3-28. CDD/CDF emission factors for combustion of bleached-kraft mill sludge in wood residue boilers

Congener	Mean emission factors (ng/kg feed)	
	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	0.005	0.013
1,2,3,7,8-PeCDD	0.005	0.012
1,2,3,4,7,8-HxCDD	0.012	0.022
1,2,3,6,7,8-HxCDD	0.05	0.056
1,2,3,7,8,9-HxCDD	0.035	0.043
1,2,3,4,6,7,8-HpCDD	0.301	0.302
OCDD	1.189	1.192
2,3,7,8-TCDF	0.104	0.107
1,2,3,7,8-PeCDF	0.022	0.029
2,3,4,7,8-PeCDF	0.019	0.027
1,2,3,4,7,8-HxCDF	0.069	0.071
1,2,3,6,7,8-HxCDF	0.043	0.046
1,2,3,7,8,9-HxCDF	0.036	0.041
2,3,4,6,7,8-HxCDF	0.004	0.012
1,2,3,4,6,7,8-HpCDF	0.274	0.275
1,2,3,4,7,8,9-HpCDF	0.081	0.083
OCDF	0.187	0.188
Total TCDD	0.101	0.108
Total PeCDD	0.03	0.109
Total HxCDD	0.599	0.6
Total HpCDD	0.956	0.958
Total OCDD	1.189	1.192
Total TCDF	0.56	0.56
Total PeCDF	0.469	0.47
Total HxCDF	0.748	0.748
Total HpCDF	1.102	1.102
Total OCDF	0.187	0.188
Total I-TEQ_{DF}	0.061	0.082
Total TEQ_{DF}-WHO_{98}	0.062	0.087
Total CDD/CDF	5.941	6.035

Source: NCASI (1995).

flare gas volume to digestor gas volume combusted, 78.6:1, and the average CDD/CDF content of the three measurements, 5.9 pg I-TEQ_{DF}/Nm^3, yields an emission rate of 0.46 ng I-TEQ_{DF}/Nm^3 of digestor gas combusted.

During 1996, publicly owned treatment works (POTWs) in the United States treated approximately 122 billion L of wastewater daily (U.S. EPA, 1997b). Although reliable data are

not readily available on the amount of sewage sludge generated by POTWs that is subjected to stabilization by anaerobic digestion, a reasonable approximation is 25% of the total sludge generated (i.e., the sludge generated from treatment of about 30 trillion L per day of wastewater). An estimated 196 kg of sludge solids are generated for every 1 million L of wastewater subjected to primary and secondary treatment (Water Pollution Control Federation, 1990). Thus, multiplying 30 billion L/day (25% of 122 billion L) by 196 kg/million L and 365 days/yr yields an annual estimate of 2 million metric tons of sludge solids that may be anaerobically digested in POTWs annually.

The volume of sludge digestor gas combusted in flares annually can be estimated using operation parameters for a "typical" anaerobic digestor system, as described in Water Pollution Control Federation (1990). Multiplying the annual amount of sludge solids of 2 million metric tons by the following parameters and appropriate conversion factors yields an annual flared digestor gas volume of 467-million Nm^3:

- Fraction of total solids that are volatile solids is 75%.
- Reduction of volatile solids during digestion is 50%.
- Specific gas production is 0.94 m^3/kg volatile solids reduced.
- Fraction of produced gas that is flared is 66%.

Because there are no direct measurements of CDD/CDF emissions from U.S. anaerobic sludge digestor flares and because of uncertainties about the activity level for biogas combustion, no national emissions estimate has been developed for inclusion in the national inventory. However, a preliminary estimate of the potential annual TEQ emissions from this source can be obtained by multiplying the emission factor of 0.46 ng I-TEQ_{DF}/Nm^3 of digestor gas flared by the estimated volume of gas flared annually in the United States, 467 million Nm^3. This calculation yields an annual potential release in 2000 of 0.22 g. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

Table 3-5. National CDD/CDF TEQ emissions (g/yr) for large and small municipal waste combustors (MWCs) operating in 2000

Facility name	State	County/city	MWC type	Unit no.	MSW capacity (tons/day)	MSW combusted (tons/yr)	APCD	Emissions (g I-TEQ/yr)	Emissions (g WHO_{DF}-TEQ/yr)
I. Large MWCs (>250 tpd/unit)									
Huntsville	AL	Madison	MB/WW	1	345	88,154.49	SD/FF/CI/SNCR	0.004	0.004
Huntsville	AL	Madison	MB/WW	2	345	88,633.51	SD/FF/CI/SNCR	0.008	0.008
Long Beach SERRF	CA	Los Angeles	MB/WW	1	360	95,572.00	SD/FF/SNCR	0.028	0.031
Long Beach SERRF	CA	Los Angeles	MB/WW	1	460	154,264.93	SD/FF/SNCR	0.014	0.015
Long Beach SERRF	CA	Los Angeles	MB/WW	2	460	164,072.92	SD/FF/SNCR	0.031	0.033
Long Beach SERRF	CA	Los Angeles	MB/WW	3	460	160,371.15	SD/FF/SNCR	0.018	0.023
Stanislaus (Modesto)	CA	Stanislaus	MB/WW	1	400	131,607.90	SD/FF/CI/SNCR	0.013	0.014
Stanislaus (Modesto)	CA	Stanislaus	MB/WW	2	400	129,798.10	SD/FF/CI/SNCR	0.009	0.01
Wheelabrator Bridgeport, L.P.	CT	Fairfield	MB/WW	1	750	238,974.40	SD/FF/CI	0.019	0.021
Wheelabrator Bridgeport, L.P.	CT	Fairfield	MB/WW	2	750	237,183.53	SD/FF/CI	0.02	0.021
Wheelabrator Bridgeport, L.P.	CT	Fairfield	MB/WW	3	750	231,472.07	SD/FF/CI	0.024	0.027
Bristol RRF	CT	Hartford	MB/WW	2	325	92,453.00	SD/FF/CI/SNCR	0.004	0.004
Bristol RRF	CT	Hartford	MB/WW	2	325	93,627.93	SD/FF/CI/SNCR	0.004	0.004
Mid-Connecticut RRF	CT	Hartford	RDF	1	675	246,570.00	SD/FF/SNCR	0.019	0.022
Mid-Connecticut RRF	CT	Hartford	RDF	2	675	251,454.04	SD/FF/SNCR	0.041	0.046
Mid-Connecticut RRF	CT	Hartford	RDF	3	675	252,415.96	SD/FF/SNCR	0.048	0.048
Southeastern Connecticut RRF	CT	New London	MB/WW	1	345	122,528.01	SD/FF/CI	0.015	0.016
Southeastern Connecticut RRF	CT	New London	MB/WW	2	345	121,053.99	SD/FF/CI	0.046	0.051
Wheelabrator Lisbon Inc.	CT	New London	MB/WW	1	250	89,556.15	SD/FF/CI/SNCR	0.001	0.001
Wheelabrator Lisbon Inc.	CT	New London	MB/WW	2	250	89,452.85	SD/FF/CI/SNCR	0.025	0.028
Wheelabrator South Broward	FL	Ft. Lauderdale	MB/WW	1	750	259,426.57	SD/FF/SNCR	0.023	0.025
Wheelabrator South Broward	FL	Ft. Lauderdale	MB/WW	2	750	244,492.13	SD/FF/SNCR	0.078	0.085
Wheelabrator South Broward	FL	Ft. Lauderdale	MB/WW	3	750	252,013.30	SD/FF/SNCR	0.046	0.051

Table 3-5. National CDD/CDF TEQ emissions (g/yr) for large and small municipal waste combustors (MWCs) operating in 2000 (continued)

Facility name	State	County/city	MWC type	Unit no.	MSW capacity (tons/day)	MSW combusted (tons/yr)	APCD	Emissions (g I-TEQ/yr)	Emissions (g WHO_{DF}-TEQ/yr)
Wheelabrator North Broward	FL	Broward	MB/WW	1	750	260,456.43	SD/FF/SNCR	0.018	0.02
Wheelabrator North Broward	FL	Broward	MB/WW	2	750	255,371.04	SD/FF/SNCR	0.018	0.02
Wheelabrator North Broward	FL	Broward	MB/WW	3	750	259,802.53	SD/FF/SNCR	0.07	0.076
Dade Co. RRF	FL	Dade	RDF	1	672	172,792.98	SD/FF/CI/SNCR	0.384	0.406
Dade Co. RRF	FL	Dade	RDF	2	672	171,880.39	SD/FF/CI/SNCR	0.393	0.419
Dade Co. RRF	FL	Dade	RDF	3	672	167,673.72	SD/FF/CI/SNCR	0.062	0.066
Dade Co. RRF	FL	Dade	RDF	4	672	155,352.91	SD/FF/CI/SNCR	0.444	0.475
Hillsborough Co. RRF	FL	Hillsborough	MB/WW	1	400	116,426.35	SD/FF/CI/SNCR	0.019	0.02
Hillsborough Co. RRF	FL	Hillsborough	MB/WW	2	400	120,265.74	SD/FF/CI/SNCR	0.023	0.025
Hillsborough Co. RRF	FL	Hillsborough	MB/WW	3	400	121,674.90	SD/FF/CI/SNCR	0.039	0.042
McKay Bay REF	FL	Hillsborough	MB/WW	1	250	90,232.04	SD/FF/CI/SNCR	0.014	0.015
McKay Bay REF	FL	Hillsborough	MB/WW	2	250	90,232.04	SD/FF/CI/SNCR	0.016	0.017
McKay Bay REF	FL	Hillsborough	MB/WW	3	250	90,413.44	SD/ESP/CI/SNCR	0.002	0.002
McKay Bay REF	FL	Hillsborough	MB/WW	4	250	90,050.47	SD/ESP/CI/SNCR	0.003	0.003
Lake Co. RRF	FL	Lake	MB/WW	1	264	82,586.03	SD/FF/CI/SNCR	0.034	0.036
Lake Co. RRF	FL	Lake	MB/WW	2	264	83,262.97	SD/FF/CI/SNCR	0.036	0.038
Lee County Solid Waste RRF	FL	Lee	MB/WW	1	600	197,620.93	SD/FF/CI/SNCR	0.101	0.11
Lee County Solid Waste RRF	FL	Lee	MB/WW	2	600	197,203.07	SD/FF/CI/SNCR	0.11	0.12
Pasco County Solid Waste RRF	FL	Pasco	MB/WW	1	350	98,891.97	SD/FF/CI/SNCR	0.012	0.012
Pasco County Solid Waste RRF	FL	Pasco	MB/WW	2	350	102,727.33	SD/FF/CI/SNCR	0.008	0.009
Pasco County Solid Waste RRF	FL	Pasco	MB/WW	3	350	108,759.70	SD/FF/CI/SNCR	0.004	0.004
Pinellas County RRF	FL	Pinellas	MB/WW	1	1000	299,275.82	SD/FF/CI/SNCR	0.013	0.015
Pinellas County RRF	FL	Pinellas	MB/WW	2	1000	289,763.18	SD/FF/CI/SNCR	0.074	0.083
Pinellas County RRF	FL	Pinellas	MB/WW	3	1000	301,717.00	SD/FF/CI/SNCR	0.043	0.047

Table 3-5. National CDD/CDF TEQ emissions (g/yr) for large and small municipal waste combustors (MWCs) operating in 2000 (continued)

Facility name	State	County/city	MWC type	Unit no.	MSW capacity (tons/day)	MSW combusted (tons/yr)	APCD	Emissions (g I-TEQ/yr)	Emissions (g WHO_{DF}-TEQ/yr)
North County RRF	FL	West Palm Beach	RDF	1	1000	273,939.00	SD/ESP	0.279	0.302
North County RRF	FL	West Palm Beach	RDF	2	1000	288,988.00	SD/ESP	0.681	0.747
Savannah RRF	GA	Chatham	MB/WW	1	250	61,886.44	SD/FF/CI/SNCR	0.029	0.032
Savannah RRF	GA	Chatham	MB/WW	2	250	58,830.56	SD/FF/CI/SNCR	0.023	0.025
Honolulu RRF	HI	Honolulu	RDF	1	1080	258,726.76	SD/ESP	0.802	0.888
Honolulu RRF	HI	Honolulu	RDF	2	1080	256,019.24	SD/ESP	1.181	1.318
Indianapolis RRF	IN	Marion	MB/WW	1	787	209,507.33	SD/FF/CI/SNCR	0.025	0.027
Indianapolis RRF	IN	Marion	MB/WW	2	787	220,779.62	SD/FF/CI/SNCR	0.025	0.028
Indianapolis RRF	IN	Marion	MB/WW	3	787	224,095.05	SD/FF/CI/SNCR	0.005	0.005
Haverhill RRF	MA	Essex	MB/WW	1	825	281,121.60	SD/FF/CI/SNCR	0.048	0.051
Haverhill RRF	MA	Essex	MB/WW	2	825	286,516.40	SD/FF/CI/SNCR	0.063	0.067
Wheelabrator North Andover	MA	Essex	MB/WW	1	750	202,456.92	SD/FF/CI/SNCR	0.006	0.007
Wheelabrator North Andover	MA	Essex	MB/WW	2	750	180,415.08	SD/FF/CI/SNCR	0.006	0.006
Wheelabrator Saugus	MA	Essex	MB/WW	1	750	217,656.46	SD/FF/CI/SNCR	0.006	0.006
Wheelabrator Saugus	MA	Essex	MB/WW	2	750	214,057.54	SD/FF/CI/SNCR	0.004	0.005
SEMASS RRF	MA	Plymouth	RDF	1	1000	368,821.00	SD/ESP/FF/CI	0.045	0.051
SEMASS RRF	MA	Plymouth	RDF	2	1000	372,224.92	SD/ESP/FF/CI	0.048	0.052
SEMASS RRF	MA	Plymouth	RDF	3	1000	364,595.08	SD/FF/SNCR	0.033	0.036
Wheelabrator Millbury	MA	Worcester	MB/WW	1	750	230,829.25	SD/ESP/CI/SNCR	0.038	0.042
Wheelabrator Millbury	MA	Worcester	MB/WW	2	750	233,033.75	SD/ESP/CI/SNCR	0.017	0.019
Wheelabrator Baltimore	MD	Independent City	MB/WW	1	750	242,224.16	SD/ESP/CI/SNCR	0.043	0.047

Table 3-5. National CDD/CDF TEQ emissions (g/yr) for large and small municipal waste combustors (MWCs) operating in 2000 (continued)

Facility name	State	County/city	MWC type	Unit no.	MSW capacity (tons/day)	MSW combusted (tons/yr)	APCD	Emissions (g I-TEQ/yr)	Emissions (g WHO_{DF}-TEQ/yr)
Wheelabrator Baltimore	MD	Independent City	MB/WW	2	750	241,753.99	SD/ESP/CI/SNCR	0.176	0.179
Wheelabrator Baltimore	MD	Independent City	MB/WW	3	750	231,232.85	SD/ESP/CI/SNCR	0.177	0.186
Montgomery Co. RRF	MD	Montgomery	MB/WW	1	600	178,986.24	SD/FF/CI/SNCR	0.096	0.107
Montgomery Co. RRF	MD	Montgomery	MB/WW	2	600	170,879.15	SD/FF/CI/SNCR	0.09	0.091
Montgomery Co. RRF	MD	Montgomery	MB/WW	3	600	170,131.61	SD/FF/CI/SNCR	0.099	0.108
Greater Portland Region RRF	ME	Cumberland	MB/WW	1	250	87,323.81	SD/ESP/CI/SNCR	0.051	0.055
Greater Portland Region RRF	ME	Cumberland	MB/WW	2	250	85,676.19	SD/ESP/CI/SNCR	0.108	0.115
Penobscot Energy Recovery	ME	Penobscot	RDF	1	360	108,975.08	SD/FF	0.008	0.008
Penobscot Energy Recovery	ME	Penobscot	RDF	2	360	110,899.92	SD/FF	0.008	0.008
Maine Energy Recovery	ME	York	RDF	1	300	123,654.50	SD/FF/SNCR	0.018	0.02
Maine Energy Recovery	ME	York	RDF	2	300	123,654.50	SD/FF/SNCR	0.019	0.02
Kent Co. WTE Facility	MI	Kent	MB/WW	1	313	90,813.23	SD/FF/CI/SNCR	0.006	0.007
Kent Co. WTE Facility	MI	Kent	MB/WW	2	313	88,925.77	SD/FF/CI/SNCR	0.013	0.013
Central Wayne Energy	MI	Wayne	MB/WW	3	300	61,800.00	SD/FF/CI/SNCR	0.005	0.005
Greater Detroit RRF	MI	Wayne	RDF	1	1100	279,883.11	SD/FF	0.259	0.287
Greater Detroit RRF	MI	Wayne	RDF	2	1100	212,094.32	SD/FF	0.01	0.011
Greater Detroit RRF	MI	Wayne	RDF	3	1100	201,288.58	SD/FF	0.193	0.218
Wilmarth Plant	MN	Blue Earth	RDF	1	360	94,983.00	SD/FF/SNCR	0.028	0.03
Wilmarth Plant	MN	Blue Earth	RDF	2	360	108,339.00	SD/FF/SNCR	0.032	0.034
Red Wing Plant	MN	Goodhue	RDF	1	360	92,993.00	DSI/FF	0.017	0.017
Red Wing Plant	MN	Goodhue	RDF	2	360	89,211.00	DSI/FF	0.066	0.069
Covanta Hennepin	MN	Hennepin	MB/WW	1	600	182,903.45	SD/FF/CI/SNCR	0.009	0.01
Covanta Hennepin	MN	Hennepin	MB/WW	2	600	182,190.55	SD/FF/CI/SNCR	0.049	0.052

Table 3-5. National CDD/CDF TEQ emissions (g/yr) for large and small municipal waste combustors (MWCs) operating in 2000 (continued)

Facility name	State	County/city	MWC type	Unit no.	MSW capacity (tons/day)	MSW combusted (tons/yr)	APCD	Emissions (g I-TEQ/yr)	Emissions (g WHO_{DF}-TEQ/yr)
Great River Energy	MN	Sherburne	RDF	1	250	75,878.19	SD/FF	0.013	0.014
Great River Energy	MN	Sherburne	RDF	2	250	75,122.55	SD/FF	0.013	0.013
Great River Energy	MN	Sherburne	RDF	3	500	133,529.26	SD/FF	0.022	0.024
New Hanover Co. WTE	NC	New Hanover	MB/WW	3	301	126,709.00	SD/FF/CI/SNCR	0.016	0.017
Wheelabrator Concord	NH	Merrimack	MB/WW	1	250	91,065.04	SD/FF/CI/SNCR	0.001	0.001
Wheelabrator Concord	NH	Merrimack	MB/WW	2	250	92,550.96	SD/FF/CI/SNCR	0.006	0.007
Camden RRF	NJ	Camden	MB/WW	1	350	97,654.44	SD/ESP/CI/SNCR	0.098	0.106
Camden RRF	NJ	Camden	MB/WW	2	350	93,330.56	SD/ESP/CI/SNCR	0.218	0.252
Camden RRF	NJ	Camden	MB/WW	3	350	85,658.00	SD/ESP/CI/SNCR	0.062	0.068
Essex Co. RRF	NJ	Essex	MB/WW	1	900	322,862.32	SD/ESP/CI/SNCR	0.07	0.078
Essex Co. RRF	NJ	Essex	MB/WW	2	900	327,332.25	SD/ESP/CI/SNCR	0.049	0.054
Essex Co. RRF	NJ	Essex	MB/WW	3	900	335,288.43	SD/ESP/CI/SNCR	0.039	0.043
Gloucester County	NJ	Gloucester	MB/WW	1	288	90,774.74	SD/FF/CI/SNCR	0.008	0.009
Gloucester County	NJ	Gloucester	MB/WW	2	288	90,397.26	SD/FF/CI/SNCR	0.009	0.01
Union Co. RRF	NJ	Union	MB/WW	1	480	169,630.18	SD/FF/CI/SNCR	0.005	0.005
Union Co. RRF	NJ	Union	MB/WW	2	480	171,047.55	SD/FF/CI/SNCR	0.01	0.011
Union Co. RRF	NJ	Union	MB/WW	3	480	167,844.27	SD/FF/CI/SNCR	0.01	0.011
Hempstead	NY	Nassau	MB/WW	1	835	294,685.61	SD/FF/SNCR	0.015	0.017
Hempstead	NY	Nassau	MB/WW	2	835	299,122.26	SD/FF/SNCR	0.431	0.471
Hempstead	NY	Nassau	MB/WW	3	835	293,532.12	SD/FF/SNCR	0.011	0.012
Niagara Falls	NY	Niagara	MB/WW	3	1100	358,183.15	SD/FF/CI/SNCR	0.209	0.225
Niagara Falls	NY	Niagara	MB/WW	4	1100	355,338.85	SD/FF/CI/SNCR	0.197	0.214
Onondaga Co. RRF	NY	Onondaga	MB/WW	1	330	117,389.13	SD/FF/CI/SNCR	0.002	0.002
Onondaga Co. RRF	NY	Onondaga	MB/WW	2	330	99,956.76	SD/FF/CI/SNCR	0.004	0.004

Table 3-5. National CDD/CDF TEQ emissions (g/yr) for large and small municipal waste combustors (MWCs) operating in 2000 (continued)

Facility name	State	County/city	MWC type	Unit no.	MSW capacity (tons/day)	MSW combusted (tons/yr)	APCD	Emissions (g I-TEQ/yr)	Emissions (g WHO_{DF}-TEQ/yr)
Onondaga Co. RRF	NY	Onondaga	MB/WW	3	330	117,794.12	SD/FF/CI/SNCR	0.007	0.007
Babylon RRF	NY	Suffolk	MB/WW	1	375	112,323.03	SD/FF/CI/SNCR	0.002	0.002
Babylon RRF	NY	Suffolk	MB/WW	2	375	107,951.97	SD/FF/CI/SNCR	0.007	0.008
Huntington RRF	NY	Suffolk	MB/WW	1	250	102,526.89	SD/FF/CI/SNCR	0.003	0.003
Huntington RRF	NY	Suffolk	MB/WW	2	250	102,744.63	SD/FF/CI/SNCR	0.007	0.008
Huntington RRF	NY	Suffolk	MB/WW	3	250	110,853.48	SD/FF/CI/SNCR	0.007	0.008
Adirondack RRF	NY	Washington	MB/WW	1	250	82,458.60	SD/ESP/CI	0.509	0.556
Adirondack RRF	NY	Washington	MB/WW	2	250	79,860.40	SD/ESP/CI	0.437	0.477
Wheelabrator Westchester, L.P.	NY	Westchester	MB/WW	1	750	226,329.03	SD/FF/CI/SNCR	0.025	0.027
Wheelabrator Westchester, L.P.	NY	Westchester	MB/WW	2	750	217,185.24	SD/FF/CI/SNCR	0.017	0.019
Wheelabrator Westchester, L.P.	NY	Westchester	MB/WW	3	750	206,044.73	SD/FF/CI/SNCR	0.026	0.029
Walter B. Hall RRF (Tulsa)	OK	Tulsa	MB/WW	1	375	111,998.10	SD/FF/CI/SNCR	0.012	0.013
Walter B. Hall RRF (Tulsa)	OK	Tulsa	MB/WW	2	375	113,501.52	SD/FF/CI/SNCR	0.006	0.006
Walter B. Hall RRF (Tulsa)	OK	Tulsa	MB/WW	3	375	113,849.38	SD/FF/CI/SNCR	0.003	0.003
Marion Co. WTE	OR	Marion	MB/WW	1	275	92,091.75	SD/FF/CI/SNCR	0.004	0.005
Marion Co. WTE	OR	Marion	MB/WW	2	275	92,288.25	SD/FF/CI/SNCR	0.003	0.003
Lancaster County	PA	Bainbridge	MB/WW	1	400	125,595.02	SD/FF/CI/SNCR	0.017	0.018
Lancaster County	PA	Bainbridge	MB/WW	2	400	127,240.06	SD/FF/CI/SNCR	0.015	0.016
Lancaster County	PA	Bainbridge	MB/WW	3	400	128,049.91	SD/FF/CI/SNCR	0.028	0.029
Wheelabrator Falls RRF	PA	Bucks	MB/WW	1	750	264,839.58	SD/FF/CI/SNCR	0.015	0.016
Wheelabrator Falls RRF	PA	Bucks	MB/WW	2	750	259,729.42	SD/FF/CI/SNCR	0.025	0.027
American Ref-fuel of Delaware Valley	PA	Delaware	MB/RC	1	448	179,845.19	SD/FF	0.126	0.138
American Ref-fuel of Delaware Valley	PA	Delaware	MB/RC	2	448	190,795.79	SD/FF	0.052	0.055

Table 3-5. National CDD/CDF TEQ emissions (g/yr) for large and small municipal waste combustors (MWCs) operating in 2000 (continued)

Facility name	State	County/city	MWC type	Unit no.	MSW capacity (tons/day)	MSW combusted (tons/yr)	APCD	Emissions (g I-TEQ/yr)	Emissions (g WHO_{DF}-TEQ/yr)
American Ref-fuel of Delaware Valley	PA	Delaware	MB/RC	3	448	186,088.66	SD/FF	0.181	0.197
American Ref-fuel of Delaware Valley	PA	Delaware	MB/RC	4	448	189,206.50	SD/FF	0.045	0.05
American Ref-fuel of Delaware Valley	PA	Delaware	MB/RC	5	448	176,939.66	SD/FF	0.023	0.025
American Ref-fuel of Delaware Valley	PA	Delaware	MB/RC	6	448	191,389.21	SD/FF	0.029	0.032
Montenay Montgomery	PA	Montgomery	MB/WW	1	600	204,290.69	SD/FF/CI/SNCR	0.169	0.179
Montenay Montgomery	PA	Montgomery	MB/WW	2	600	198,884.31	SD/FF/CI/SNCR	0.354	0.372
York County	PA	York	MB/RC	1	448	135,266.80	SD/FF/CI/SNCR	0.023	0.025
York County	PA	York	MB/RC	2	448	135,104.31	SD/FF/CI/SNCR	0.025	0.028
York County	PA	York	MB/RC	3	448	126,412.88	SD/FF/CI/SNCR	0.023	0.025
Foster Wheeler Charleston RRF	SC	Charleston	MB/WW	1	300	112,950.14	SD/ESP/CI	0.151	0.16
Foster Wheeler Charleston RRF	SC	Charleston	MB/WW	2	300	98,453.86	SD/ESP/CI	0.15	0.16
Nashville Thermal Transfer Corp.	TN	Davidson	MB/WW	1	330	67,181.87	SD/FF/CI/SNCR	0	0
Nashville Thermal Transfer Corp.	TN	Davidson	MB/WW	2	330	72,257.44	SD/FF/CI/SNCR	0	0
Nashville Thermal Transfer Corp.	TN	Davidson	MB/WW	3	390	85,979.69	SD/FF/CI/SNCR	0	0
Alexandria/Arlington RRF	VA	Alexandria	MB/WW	1	325	113,578.13	SD/FF/CI/SNCR	0.007	0.008
Alexandria/Arlington RRF	VA	Alexandria	MB/WW	2	325	109,442.21	SD/FF/CI/SNCR	0.022	0.024
Alexandria/Arlington RRF	VA	Alexandria	MB/WW	3	325	109,410.66	SD/FF/CI/SNCR	0.02	0.021
I-95 Energy RRF	VA	Fairfax	MB/WW	1	750	270,077.99	SD/FF/CI/SNCR	0.011	0.011
I-95 Energy RRF	VA	Fairfax	MB/WW	2	750	271,967.16	SD/FF/CI/SNCR	0.012	0.013
I-95 Energy RRF	VA	Fairfax	MB/WW	3	750	272,396.24	SD/FF/CI/SNCR	0.006	0.006
I-95 Energy RRF	VA	Fairfax	MB/WW	4	750	271,628.61	SD/FF/CI/SNCR	0.012	0.012

Table 3-5. National CDD/CDF TEQ emissions (g/yr) for large and small municipal waste combustors (MWCs) operating in 2000 (continued)

Facility name	State	County/city	MWC type	Unit no.	MSW capacity (tons/day)	MSW combusted (tons/yr)	APCD	Emissions (g I-TEQ/yr)	Emissions (g WHO_{DF}-TEQ/yr)
SPSA Waste To Energy	VA	Portsmouth	RDF	1	500	122,153.75	SD/FF	0.123	0.133
SPSA Waste To Energy	VA	Portsmouth	RDF	2	500	122,153.75	SD/FF	0.111	0.12
SPSA Waste To Energy	VA	Portsmouth	RDF	3	500	122,153.75	SD/FF	0.103	0.111
SPSA Waste To Energy	VA	Portsmouth	RDF	4	500	122,153.75	SD/FF	0.13	0.141
Spokane Regional Disposal Facility	WA	Spokane	MB/WW	1	400	141,392.12	SD/FF/CI/SNCR	0.009	0.01
Spokane Regional Disposal Facility	WA	Spokane	MB/WW	2	400	143,927.88	SD/FF/CI/SNCR	0.008	0.009
LaCrosse Co.	WI	LaCrosse	RDF	1	288	22,727.86	DSI/FF/H2O/SNCR	0.344	0.36
LaCrosse Co.	WI	LaCrosse	RDF	2	288	21,718.14	DSI/FF/H2O/SNCR	0.344	0.36
Large MWC totals						**2.80e+007**		**12.73**	**13.815**
II. Small MWCs (<250 tpd/unit)									
Juneau RRF	AK	Juneau Borough	MOD/SA	1	35	10,975.85	ESP	0.484	0.533
Juneau RRF	AK	Juneau Borough	MOD/SA	2	35	10,975.85	ESP	0.484	0.533
Wallingford RRF	CT	New Haven	MOD/EA	1	140	43,903.39	SD/FF	0.064	0.07
Wallingford RRF	CT	New Haven	MOD/EA	2	140	43,903.39	SD/FF	0.021	0.023
Wallingford RRF	CT	New Haven	MOD/EA	3	140	43,903.39	SD/FF	0.006	0.007
Bay Resource Management Center	FL	Bay	MB/RC	1	245	76,830.94	ESP	3.442	3.786
Bay Resource Management Center	FL	Bay	MB/RC	2	245	76,830.94	ESP	4.633	5.096
Miami International Airport	FL	Dade	MOD/SA	1	60	18,815.74	Unc	0.649	0.714
Southernmost WTE	FL	Monroe	MB/WW	1	75	23,519.67	ESP	0.322	0.355
Southernmost WTE	FL	Monroe	MB/WW	2	75	23,519.67	ESP	0.322	0.355
Pittsfield RRF	MA	Berkshire	MOD/EA	1	120	37,631.48	WS/ESP	0.978	1.076
Pittsfield RRF	MA	Berkshire	MOD/EA	2	120	37,631.48	WS/ESP	0.978	1.076
Pittsfield RRF	MA	Berkshire	MOD/EA	3	120	37,631.48	WS/ESP	0.978	1.076

Table 3-5. National CDD/CDF TEQ emissions (g/yr) for large and small municipal waste combustors (MWCs) operating in 2000 (continued)

Facility name	State	County/city	MWC type	Unit no.	MSW capacity (tons/day)	MSW combusted (tons/yr)	APCD	Emissions (g I-TEQ/yr)	Emissions (g WHO_{DF}-TEQ/yr)
Springfield RRF	MA	Hampden	MOD/EA	1	120	37,631.48	DSI/FF	0.028	0.03
Springfield RRF	MA	Hampden	MOD/EA	2	120	37,631.48	DSI/FF	0.028	0.03
Springfield RRF	MA	Hampden	MOD/EA	3	120	37,631.48	DSI/FF	0.028	0.03
Harford Co. WTE Fac.	MD	Harford	MOD/SA	1	90	28,223.61	DSI/ESP	1.352	1.488
Harford Co. WTE Fac.	MD	Harford	MOD/SA	2	90	28,223.61	DSI/ESP	1.352	1.488
Harford Co. WTE Fac.	MD	Harford	MOD/SA	3	90	28,223.61	DSI/ESP	1.352	1.488
Harford Co. WTE Fac.	MD	Harford	MOD/SA	4	90	28,223.61	DSI/ESP	1.352	1.488
Mid Maine Waste Action Corp.	ME	Androscoggin	MB	1	100	31,359.57	SD/FF	0.024	0.027
Mid Maine Waste Action Corp.	ME	Androscoggin	MB	2	100	31,359.57	SD/FF	0.024	0.027
Jackson Co. RRF	MI	Jackson	MB/WW	1	100	31,359.57	SD/FF	1.135	1.249
Jackson Co. RRF	MI	Jackson	MB/WW	2	100	31,359.57	SD/FF	1.135	1.249
Central Wayne Co.	MI	Wayne	RDF	1	249	78,085.32	ESP	0.061	0.067
Central Wayne Co.	MI	Wayne	RDF	2	249	78,085.32	ESP	0.061	0.067
Pope-Douglas Waste	MN	Douglas	MOD/EA	1	36	11,289.44	ESP	0.293	0.323
Pope-Douglas Waste	MN	Douglas	MOD/EA	2	36	11,289.44	ESP	0.293	0.323
Red Wing Solid Waste Boiler Facility	MN	Goodhue	MOD/EA	1	36	11,289.44	ESP	0.287	0.316
Red Wing Solid Waste Boiler Facility	MN	Goodhue	MOD/EA	2	36	11,289.44	ESP	0.287	0.316
Olmstead WTE Facility	MN	Olmstead	MB/WW	1	100	31,359.57	ESP	1.449	1.594
Olmstead WTE Facility	MN	Olmstead	MB/WW	2	100	31,359.57	ESP	1.449	1.594
Fergus Falls	MN	Otter Tail	MOD/SA	1	47	14,739.00	WS	0.621	0.683
Fergus Falls	MN	Otter Tail	MOD/SA	2	47	14,739.00	WS	0.621	0.683
Perham Renewable RF	MN	Otter Tail	MOD/SA	1	57	17,874.95	ESP	0.37	0.407
Perham Renewable RF	MN	Otter Tail	MOD/SA	2	57	17,874.95	ESP	0.37	0.407

Table 3-5. National CDD/CDF TEQ emissions (g/yr) for large and small municipal waste combustors (MWCs) operating in 2000 (continued)

Facility name	State	County/city	MWC type	Unit no.	MSW capacity (tons/day)	MSW combusted (tons/yr)	APCD	Emissions (g I-TEQ/yr)	Emissions (g WHO_{DF}-TEQ/yr)
Polk Co.	MN	Polk	MOD/SA	1	40	12,543.83	ESP	0.433	0.476
Polk Co.	MN	Polk	MOD/SA	2	40	12,543.83	ESP	0.433	0.476
Pascagoula	MS	Jackson	MOD/EA	1	75	23,519.67	ESP	0.611	0.672
Pascagoula	MS	Jackson	MOD/EA	2	75	23,519.67	ESP	0.611	0.672
Livingston/Park County	MT	Park	MOD/SA	1	36	11,289.44	Unc	0.389	0.428
Livingston/Park County	MT	Park	MOD/SA	2	36	11,289.44	Unc	0.389	0.428
New Hanover Co.	NC	New Hanover	MB/WW	1	100	31,359.57	SD/FF	0.024	0.027
New Hanover Co.	NC	New Hanover	MB/WW	2	100	31,359.57	SD/FF	0.024	0.027
SES Claremont	NH	Sullivan	MB/WW	1	100	31,359.57	DSI/FF	0.113	0.124
SES Claremont	NH	Sullivan	MB/WW	2	100	31,359.57	DSI/FF	0.095	0.104
Warren Energy RF	NJ	Warren	MB/WW	1	200	62,719.13	SD/FF/CI	0.001	0.002
Warren Energy RF	NJ	Warren	MB/WW	2	200	62,719.13	SD/FF/CI	0.001	0.002
Dutchess Co. RRF	NY	Dutchess	MB/RC	1	200	62,719.13	DSI/FF	0.015	0.016
Dutchess Co. RRF	NY	Dutchess	MB/RC	2	200	62,719.13	DSI/FF	0.027	0.029
Oswego Co. WTE	NY	Oswego	MOD/SA	3	50	15,679.78	SD/FF/CI	0.007	0.008
Oswego Co. WTE	NY	Oswego	MOD/SA	4	50	15,679.78	SD/FF/CI	0.024	0.026
Oswego Co. WTE	NY	Oswego	MOD/SA	1	50	15,679.78	SD/FF/CI	0.015	0.017
Oswego Co. WTE	NY	Oswego	MOD/SA	2	50	15,679.78	SD/FF/CI	0.015	0.017
MacArthur WTE	NY	Suffolk	MB/RC	1	243	76,203.74	DSI/FF	0.001	0.001
MacArthur WTE	NY	Suffolk	MB/RC	2	243	76,203.74	DSI/FF	0.001	0.001
Miami RRF	OK	Ottawa	MOD/SA	1	35	10,975.85	Unc	0.379	0.417
Miami RRF	OK	Ottawa	MOD/SA	2	35	10,975.85	Unc	0.379	0.417
Miami RRF	OK	Ottawa	MOD/SA	3	35	10,975.85	Unc	0.379	0.417
Coos Bay Incinerator	OR	Coos	MOD/SA	1	50	15,679.78	DSI/FF	0	0

Table 3-5. National CDD/CDF TEQ emissions (g/yr) for large and small municipal waste combustors (MWCs) operating in 2000 (continued)

Facility name	State	County/city	MWC type	Unit no.	MSW capacity (tons/day)	MSW combusted (tons/yr)	APCD	Emissions (g I-TEQ/yr)	Emissions (g WHO_{DF}-TEQ/yr)
Coos Bay Incinerator	OR	Coos	MOD/SA	2	50	15,679.78	DSI/FF	0	0
Coos Bay Incinerator	OR	Coos	MOD/SA	3	50	15,679.78	DSI/FF	0	0
Harrisburg WTE	PA	Dauphin	MB/WW	1	245	76,830.94	ESP	12.894	14.184
Harrisburg WTE	PA	Dauphin	MB/WW	2	245	76,830.94	ESP	8.29	9.119
Sumner Co.	TN	Sumner	MB/RC	1	100	31,359.57	ESP	0.43	0.473
Sumner Co.	TN	Sumner	MB/RC	2	100	31,359.57	ESP	0.43	0.473
City of Cleburne	TX	Johnson	MOD/SA	1	38	11,916.63	DSI/ESP	0.526	0.579
City of Cleburne	TX	Johnson	MOD/SA	2	38	11,916.63	DSI/ESP	0.526	0.579
City of Cleburne	TX	Johnson	MOD/SA	3	38	11,916.63	DSI/ESP	0.411	0.452
Panola Co. WTE	TX	Panola	MOD/SA	1	40	12,543.83	WS	0.433	0.476
Center RRF	TX	Shelby	MOD/SA	1	40	12,543.83	WS	0.554	0.609
Davis/Wasatch	UT	Davis	MB/REF	1	200	62,719.13	DSI/ESP	1.275	1.403
Davis/Wasatch	UT	Davis	MB/REF	2	200	62,719.13	DSI/ESP	1.384	1.522
Arlington -Pen tagon	VA	Arlington	MOD/SA	1	50	15,679.78	FF	0.697	0.766
Arlington -Pen tagon	VA	Arlington	MOD/SA	2	50	15,679.78	FF	0.697	0.766
Galax City SW	VA	Grayson	MB/WW/RC	1	56	17,561.36	FF	0.241	0.265
NASA Refuse-fired Steam Generator	VA	Hampton City	MB/WW	1	100	31,359.57	ESP	0.614	0.675
NASA Refuse-fired Steam Generator	VA	Hampton City	MB/WW	2	100	31,359.57	ESP	0.614	0.675
Harrisonburg	VA	Rockingham	MB/WW	1	50	15,679.78	Unc	0.151	0.166
Harrisonburg	VA	Rockingham	MB/WW	2	50	15,679.78	Unc	0.151	0.166
Tacoma	WA	Pierce	FB/RDF	1	150	47,039.35	DSI/FF	0.089	0.098
Tacoma	WA	Pierce	FB/RDF	2	150	47,039.35	DSI/FF	0.089	0.098
Barron Co.	WI	Barron	MOD/SA	1	50	15,679.78	ESP	0.692	0.761

Table 3-5. National CDD/CDF TEQ emissions (g/yr) for large and small municipal waste combustors (MWCs) operating in 2000 (continued)

Facility name	State	County/city	MWC type	Unit no.	MSW capacity (tons/day)	MSW combusted (tons/yr)	APCD	Emissions (g I-TEQ/yr)	Emissions (g WHO_{DF}-TEQ/yr)
Barron Co.	WI	Barron	MOD/SA	2	50	15,679.78	ESP	0.692	0.761
Small MWC totals						**2.60e+006**		**63.583**	**69.941**
All MWCs operating in 2000 (totals)						**3.06e+007**		**76.3**	**83.8**

RRF = Resource recovery facility (steam-generating facility)
MSW = Municipal solid waste
WTE = Waste-to-energy (facility)

APCD (air pollution control device):
- CI = Carbon injection
- DS = Dry scrubber
- DSI = Dry sorbent injection
- ESP = Electrostatic precipitator
- FF = Fabric filter
- SD = Spray dryer
- SNRL = Selective noncatalytic reduction
- Unc = Uncontrolled
- WS = Wet scrubber

MWC type:
- FB/RDF = Fluidized-bed refuse-derived fuel
- MB/REF = Mass burn refractory
- MB/WW = Mass burn waterwall
- MB = Mass burn
- MB/RC = Mass burn rotary kiln
- MOD/EA = Modular excess air
- MOD/SA = Modular starved air
- RDF = Refuse-derived fuel

4. COMBUSTION SOURCES OF CDDs/CDFs: POWER/ENERGY GENERATION

4.1. MOTOR VEHICLE FUEL COMBUSTION

Ballschmiter et al. (1986) reported detecting CDDs/CDFs in used motor oil, thus providing some of the first evidence that CDDs/CDFs might be emitted by the combustion processes in gasoline- and diesel-fueled engines. Incomplete combustion and the presence of a chlorine source in the form of additives such as dichloroethane or pentachlorophenate in the oil or the fuel were speculated to lead to the formation of CDDs/CDFs. The congener patterns found in the used oil samples were characterized by Ballschmiter et al. as being similar to the patterns found in fly ash and stack emissions from municipal waste incinerators.

Since 1986, several studies have been conducted to measure or estimate CDD/CDF concentrations in emissions from vehicles. Although there is no standard approved protocol for measuring CDDs/CDFs in vehicle exhaust, some researchers have developed and implemented several approaches for collecting and analyzing tailpipe emissions. Other researchers have estimated vehicle exhaust emissions of CDDs/CDFs indirectly from studies of tunnel air. The results of these two types of studies are summarized in Sections 4.1.1 and 4.1.2.

Estimates of national annual CDD/CDF TEQ emissions from on-road and off-road motor vehicles fueled with leaded gasoline, unleaded gasoline, and diesel fuel based on the results of those studies are presented in Section 4.1.3. It should be noted, however, that relatively few tests on emissions from diesel- and unleaded gasoline-fueled vehicles are available, considering the variety and number of such vehicles currently in operation and the range of operational, technical, and environmental conditions in which they are operated. As a result, the emission factors developed in this report for on-road and off-road motor vehicles are quite uncertain.

4.1.1. Tailpipe Emission Studies

Marklund et al. (1987) provided the first direct evidence of the presence of CDDs/CDFs in car exhaust by measuring emissions from tailpipes of Swedish cars. Approximately 20 to 220 pg I-TEQ_{DF}/km driven from tetra- and penta-CDDs/CDFs were reported for four cars running on leaded gasoline. For this study, an unleaded gasoline was used, with tetramethyl lead (0.15 g/L [0.57 g/gal]) and 1,2-dichloroethane (0.1 g/L as a scavenger) added. The fuel used may not have accurately represented commercial fuels at that time, which typically contained a mixture of chlorinated and brominated scavengers (Marklund et al., 1990). Also, the lead content of the fuel used (0.15 g lead/L) was the normal content for Swedish fuels at the time, but it was higher than that of leaded gasoline in the United States during the late 1980s (lowered to 0.1 g lead/gal [0.026 g lead/L] effective January 1, 1986). The authors reported a striking similarity between the TCDF and PeCDF congener profiles in the car exhausts and those found in emissions from municipal waste incinerators. For two cars running on unleaded gasoline, CDD/CDF emissions

were below the detection limit (DL), which corresponded to approximately 13 pg I-TEQ_{DF}/km driven.

Table 4-1 presents a summary of the results of Marklund et al. (1987) and subsequent studies, which are discussed below. Tables 4-2 and 4-3 present the results of tailpipe emission studies reported for diesel-fueled cars and trucks, respectively. The results of studies of leaded gasoline-fueled cars are shown in Table 4-4 and those for unleaded gasoline-fueled cars in Tables 4-5 and 4-6. Figures 4-1, 4-2, and 4-3 present congener and congener group profiles for emissions from diesel-fueled vehicles, leaded gasoline-fueled vehicles, and unleaded gasoline-fueled vehicles, respectively.

Virtually no testing of vehicle emissions for CDDs/CDFs in the United States has been reported. In 1987, the California Air Resources Board (CARB) produced a draft report on the testing of exhausts from four gasoline-fueled cars and three diesel-fueled vehicles (one truck, one bus, and one car) (CARB, 1987). However, CARB indicated to EPA that the draft report should not be cited or quoted to support general conclusions about CDDs/CDFs in motor vehicle exhausts because of the small sample size of the study and because the use of low-resolution rather than high-resolution mass spectrometry in the study resulted in high DLs and inadequate selectivity in the presence of interferences (letter dated July 1993, from G. Lew, California Air Resources Board, to J. Schaum, U.S. EPA).

CARB stated that the results of a single sample from the heavy-duty diesel truck could be reported because congeners from most of the homologue groups were present in the sample at levels that could be detected by the analytical method and there were no identified interferences in this sample. This test was conducted under steady-state conditions (50 km/hr) for 6 hr with an engine with a fuel economy of 5.5 km/L. The TEQ emission factor of this one sample was equivalent to 7,190 pg TEQ_{DF}-WHO_{98}/L (7,290 pg I-TEQ_{DF}/L) fuel burned. An assumed fuel economy of 5.5 km/L yields an emission factor of 1,307 pg TEQ_{DF}-WHO_{98}/km (1,325 pg I-TEQ_{DF}/km). Assuming that nondetect values were zero, the TEQ emission factors were 3,280 pg TEQ_{DF}-WHO_{98}/L (3,720 pg I-TEQ_{DF}/L) fuel burned and 596 pg TEQ_{DF}-WHO_{98}/km (676 pg I-TEQ_{DF}/km) driven (letter dated January 11, 1996, from G. Lew, California Air Resources Board, to G. Schweer, Versar, Inc.).

Haglund et al. (1988) sampled exhaust gases from three vehicles (one car fueled with leaded gasoline and one with unleaded gasoline and a heavy-duty diesel truck) for the presence of brominated dibenzo-*p*-dioxins (BDDs) and ethylene dibromide dibenzofurans (BDFs). The authors concluded that the ethylene dibromide scavenger added to the tested gasoline probably acted as a halogen source. Tetra-BDF emissions were measured as 23,000 pg/km in the car with leaded gasoline and 240 pg/km in the car with unleaded gasoline. Tetra- and penta-emissions were measured as 3,200 and 980 pg/km, respectively, in the car with leaded gasoline. All BDDs/BDFs were below DLs in the diesel truck emissions.

Table 4-1. Description and results of vehicle emission testing studies for CDDs and CDFs

Study	Country	Fuel type	Scavenger[a]	Catalyst equipped	Number of test vehicles	TEQ emission factor[b] (pg/km driven)	Driving cycle; sampling location
CARB (1987); letter dated January 11, 1996, from G. Lew, California Air Resources Board, to G. Schweer, Versar, Inc.	United States	Diesel (truck)	No	NR	1	676–1325[c] [597–1307]	6-hr dynamometer test at 50 km/hr
Marklund et al. (1987)	Sweden	Unleaded Leaded	No Yes	Yes No	2 4	Not detected (<13) Approx. 20–220	A10 (2 cycles); muffler exhaust A10 (2 cycles); muffler exhaust
Bingham et al. (1989)	New Zealand	Unleaded Leaded	No Yes	NR NR	1 4	Not detected (<20) 1–39	A10 (3 or 4 cycles); muffler exhaust A10 (3 or 4 cycles); muffler exhaust
Marklund et al. (1990)	Sweden	Unleaded Leaded Unleaded Leaded Diesel (truck)	No Yes No Yes No	No No Yes No NR	2 2 1 2 1	0.36–0.39 2.4–6.3 0.36 1.1–2.6[d] Not detected (<18)[c]	FTP-73 test cycle; before muffler FTP-73 test cycle; before muffler FTP-73 test cycle; in tailpipe FTP-73 test cycle; in tailpipe U.S. federal mode 13 cycle; before muffler
Hagenmaier et al. (1990)	Germany	Unleaded Unleaded Leaded Diesel (car)	No No Yes No	No Yes No NR	1 1 1 1	5.1[c] [6.0] 0.7[c] [0.8] 108[c] [129] 2.1[c] [2.5]	Comparable to FTP-73 test cycle; in tailpipe Comparable to FTP-73 test cycle; in tailpipe Comparable to FTP-73 test cycle; in tailpipe Comparable to FTP-73 test cycle; in tailpipe
Oehme et al. (1991) (tunnel study)	Norway	–	–	–	[e]	520[f] 38[f] Avg = 280 9500[f] 720[f] Avg = 5,100	Cars moving uphill (3.5% incline) at 60 km/hr Cars moving downhill (3.5% decline) at 70 km/hr Car average Trucks moving uphill (3.5% incline) at 60 km/hr Trucks moving downhill (3.5% decline) at 70 km/hr Truck average

Table 4-1. Description and results of vehicle emission testing studies for CDDs and CDFs (continued)

Study	Country	Fuel type	Scavenger[a]	Catalyst equipped	Number of test vehicles	TEQ emission factor[b] (pg/km driven)	Driving cycle; sampling location
Schwind et al. (1991) Hutzinger et al. (1992)	Germany	Leaded Unleaded Unleaded Diesel (car) Diesel (truck)	Yes No No No No	No No Yes No No	1 1 1 1 1	5.2–118[c] [7.2–142] 9.6–17.7[c] [10.2–18.1] 1–2.6[c] [1–2.8] 1–13[c] [1.2–14] 13–15[c] [14–15]	Various test conditions (loads and speeds) Various test conditions (loads and speeds) Various test conditions (loads and speeds) Various test conditions (loads and speeds) Various test conditions (loads and speeds)
Gertler et al. (1996, 1998) (tunnel study)	United States	Diesel (truck)	–	–	[g]	Mean = 172	Mean of seven 12-hr samples
Gullett and Ryan (1997)	United States	Diesel (truck)	No	–	1	Mean = 29	Mean of five sample routes

[a]Except in Marklund et al. (1987), dichloroethane and dibromoethane were used as scavengers.

[b]Values are in units of I-TEQ_{DF}; values in brackets are in units of TEQ_{DF}-WHO_{98}.

[c]Results reported were in units of pg TEQ/L of fuel. For purposes of this table, the fuel economy factor used by Marklund et al. (1990), 10 km/L (24 miles/gal), was used to convert the emission rates into units of pg TEQ/km driven for the cars. For the diesel-fueled truck, the fuel economy factor reported in CARB (1987) for a 1984 heavy-duty diesel truck, 5.5 km/L (13.2 miles/gal), was used.

[d]Table reflects the range of summary results reported in Marklund et al. (1990); however, the congener-specific results for the single run reported indicate an emission rate of about 7.3 pg I-TEQ_{DF}/km.

[e]Tests were conducted over portions of 4 days, with traffic rates of 8,000–14,000 vehicles/day. Heavy-duty vehicles (defined as vehicles over 7 m in length) ranged from 4 to 15% of total.

[f]Emission factors are reported in units of pg Nordic TEQ/km driven; the values in units of I-TEQ_{DF}/km are expected to be about 3 to 6% higher.

[g]Tests were conducted over 5 days, with heavy-duty vehicle rates of 1,800–8,700 vehicles per 12-hr sampling event. Heavy-duty vehicles accounted for 21 to 28% of all vehicles.

NR = Not reported
– = No data

Table 4-2. CDD/CDF congener emission factors (pg/L) for diesel-fueled automobiles

Congener/congener group	Automobile tailpipe emission study results				Mean emission factors	
	63 km/hr[a]	Idling (test no. 25)[b]	57 km/hr (test no. 24)[b]	57 km/hr (full load) (test no. 28)[b]	Assuming nondetect set to zero	Assuming nondetect set to ½ detection limit (DL)
2,3,7,8-TCDD	7.9	13.1	2.4	22	11.4	11.4
1,2,3,7,8-PeCDD	9	6.3	4.1	23	10.6	10.6
1,2,3,4,7,8-HxCDD	ND (5.1)	21.4	1	7.8	7.6	8.2
1,2,3,6,7,8-HxCDD	ND (5.1)	36	1.4	21	14.6	15.2
1,2,3,7,8,9-HxCDD	ND (5.1)	28	2	10	10	10.6
1,2,3,4,6,7,8-HpCDD	44.1	107	22.9	166	85	85
OCDD	440	635	525	560	540	540
2,3,7,8-TCDF	20.5	79	18.1	236	88.4	88.4
1,2,3,7,8-PeCDF	ND (5.1)	171	1.8	111	71	71.6
2,3,4,7,8-PeCDF	7.1	58.7	3.4	85	38.6	38.6
1,2,3,4,7,8-HxCDF	6.5	121	4.1	68	49.9	49.9
1,2,3,6,7,8-HxCDF	6.7	75	3	55	34.9	34.9
1,2,3,7,8,9-HxCDF	ND (5.1)	17.1	0.8	4.7	5.7	6.3
2,3,4,6,7,8-HxCDF	ND (5.1)	52	ND (0.4)	31	20.8	21.4
1,2,3,4,6,7,8-HpCDF	40.7	159	18.9	214	108.2	108.2
1,2,3,4,7,8,9-HpCDF	8.5	11.9	7.1	7.8	8.8	8.8
OCDF	94.4	214	101	305	178.6	178.6
Total 2,3,7,8-CDD	501	846.8	558.8	809.8	679.1	681
Total 2,3,7,8-CDF	184.4	958.7	158.2	1117.5	604.9	606.7
Total I-TEQ_{DF} (nondetect set to 0)	20.8	100.7	10.4	129.6	65.5	
Total I-TEQ_{DF} (nondetect set to ½ DL)	22.2[c]	100.7	10.4	129.6		65.8
Total TEQ_{DF}-WHO_{98} (nondetect set to 0)	24.8	103.1	11.9	140.4	70.1	
Total TEQ_{DF}-WHO_{98} (nondetect set to ½ DL)	26.2	103.1	1.9	140.4		70.5

Table 4-2. CDD/CDF congener emission factors (pg/L) for diesel-fueled automobiles (continued)

Congener/congener group	Automobile tailpipe emission study results				Mean emission factors	
	63 km/hr[a]	Idling (test no. 25)[b]	57 km/hr (test no. 24)[b]	57 km/hr (full load) (test no. 28)[b]	Assuming nondetect set to zero	Assuming nondetect set to ½ detection limit (DL)
Total TCDD	37.4	317	31	394	195	195
Total PeCDD	19.7	214	22	228	121	121
Total HxCDD	23.6	256	20	164	116	116
Total HpCDD	88.5	187	77	356	177	177
Total OCDD	440.5	635	525	560	540	540
Total TCDF	76.7	436	58	3,093	916	916
Total PeCDF	39.3	821	36	1,205	525	525
Total HxCDF	25.6	556	26	472	270	270
Total HpCDF	80.6	321	72	241	179	179
Total OCDF	94.4	214	101	305	179	179
Total CDD/CDF (nondetect set to 0)	926.3	3,957	968	7,018	3,218	
Total CDD/CDF (nondetect set to ½ DL)	926.3	3,957	968	7,018		3,218

[a]Source: Hagenmaier et al. (1990).

[b]Source: Schwind et al. (1991); Hutzinger et al. (1992).

[c]An I-TEQ_{DF} emission factor of 23.6 pg/L is reported in Hagenmaier et al. (1990); however, an I-TEQ_{DF} emission factor of 22.2 pg/L is calculated, based on reported congener levels.

ND = Not detected (value in parenthesis is the detection limit)

Table 4-3. CDD/CDF congener emission factors (pg/L) for diesel-fueled trucks

Congener/congener group	Truck tailpipe study results			Mean emission factors	
	50 km/hr (test no. 40)[a]	90 km/hr (full load) (test no. 42)[a]	50 km/hr [b]	Assuming nondetect set to zero	Assuming nondetect set to ½ detection limit (DL)
2,3,7,8-TCDD	25	16	ND (560)	13.7	107
1,2,3,7,8-PeCDD	5	18	ND (1,340)	7.7	231
1,2,3,4,7,8-HxCDD	14	5.7	ND (2,160)	6.6	367
1,2,3,6,7,8-HxCDD	28	6	ND (1,770)	11.3	307
1,2,3,7,8,9-HxCDD	14	6	ND (2,640)	6.7	446
1,2,3,4,6,7,8-HpCDD	119	74	116,000	38,731	38,731
OCDD	1355	353	344,400	115,369	115,369
2,3,7,8-TCDF	87	53	ND (605)	46.7	148
1,2,3,7,8-PeCDF	45	34	ND (4,750)	26.3	819
2,3,4,7,8-PeCDF	18	51	ND (5,190)	23	887
1,2,3,4,7,8-HxCDF	56	29	ND (8,210)	28.3	1,397
1,2,3,6,7,8-HxCDF	84	31	ND (6,480)	38.3	1,119
1,2,3,7,8,9-HxCDF	4.7	5.1	13,400	4,469	4,469
2,3,4,6,7,8-HxCDF	63	23	ND (7,780)	28.7	1,325
1,2,3,4,6,7,8-HpCDF	375	71	73,460	24,636	24,636
1,2,3,4,7,8,9-HpCDF	40	5.4	ND (11,700)	15.1	1,960
OCDF	397	104	140,400	46,981	46,981
Total 2,3,7,8-CDD	1,560	478.7	460,400	154,146	155,558
Total 2,3,7,8-CDF	1,169.7	406.5	227,260	76,292.4	83,741
Total I-TEQ_{DF} (nondetect set to 0)	81	70	3,720	1,290	
Total I-TEQ_{DF} (nondetect set to ½ DL)	81	70	7,290		2,480
Total TEQ_{DF}-WHO_{98} (nondetect set to 0)	82	79	3,280	1,150	
Total TEQ_{DF}-WHO_{98} (nondetect set to ½ DL)	82	79	7,190		2,450

Table 4-3. CDD/CDF congener emission factors (pg/L) for diesel-fueled trucks (continued)

Congener/congener group	Truck tailpipe study results			Mean emission factors	
	50 km/hr (test no. 40)[a]	90 km/hr (full load) (test no. 42)[a]	50 km/hr [b]	Assuming nondetect set to zero	Assuming nondetect set to ½ detection limit (DL)
Total TCDD	200	208	ND (3,760)	136	762
Total PeCDD	32	117	ND (3,020)	49.7	553
Total HxCDD	130	67	ND (45,300)	65.7	7,620
Total HpCDD	200	155	203,300	67,892	67,892
Total OCDD	1,355	353	344,000	115,252	115,252
Total TCDF	763	694	25,000	8,831	8,831
Total PeCDF	230	736	47,900	16,294	16,294
Total HxCDF	524	268	169,200	56,670	56,670
Total HpCDF	509	76	150,700	50,414	50,414
Total OCDF	397	104	140,300	46,932	46,932
Total CDD/CDF (nondetect set to 0)	4,340	2,778	1,080,400	362,536.4	
Total CDD/CDF (nondetect set to ½ DL)	4,340	2,778	1,106,440		371,220

[a]Source: Schwind et al. (1991); Hutzinger et al. (1992).

[b]Source: Letter dated July 1993, from G. Lew, California Air Resources Board, to J. Schaum, U.S. EPA; letter dated January 11, 1996, from G. Lew, California Air Resources Board, to G. Schweer, Versar, Inc..

ND = Not detected (value in parenthesis is the detection limit)

Table 4-4. CDD/CDF congener emission factors (pg/L) for leaded gasoline-fueled automobiles

Congener/congener group	Automotive tailpipe emission study results							Mean emission factors	
	FTP cycle[a]	63 km/hr[b]	Idling (test no. 12)[c]	Full load (test no. 13)[c]	64 km/hr (test no. 14)[c]	Rated power (test no. 15)[c]	FTP cycle (test no. 22)[c]	Assuming nondetect set to zero	Assuming nondetect set to ½ detection limit (DL)
2,3,7,8-TCDD	ND (14.4)	128	NR	60	141	NR	5	67	68
1,2,3,7,8-PeCDD	ND (36)	425	43	106	468	40	73	165	168
1,2,3,4,7,8-HxCDD	ND (54)	188	17	15	206	16	41	69	73
1,2,3,6,7,8-HxCDD	ND (54)	207	32	35	228	30	62	85	89
1,2,3,7,8,9-HxCDD	ND (54)	188	NR	NR	206	NR	35	107	114
1,2,3,4,6,7,8-HpCDD	ND (54)	503	119	136	554	111	518	277	281
OCDD	ND (90)	498	380	513	549	1,166	1,581	670	676
2,3,7,8-TCDF	432	1,542	NR	678	1,697	78	214	774	774
1,2,3,7,8-PeCDF	21.6	1,081	49	367	1,190	45	218	425	425
2,3,4,7,8-PeCDF	43.2	447	26	156	492	24	225	202	202
1,2,3,4,7,8-HxCDF	ND (54)	856	33	70	942	31	381	330	334
1,2,3,6,7,8-HxCDF	ND (54)	856	22	60	942	20	375	325	329
1,2,3,7,8,9-HxCDF	ND (54)	ND (76)	NR	NR	NR	NR	85	28	50
2,3,4,6,7,8-HxCDF	ND (54)	273	NR	25	301	NR	1,033	326	332
1,2,3,4,6,7,8-HpCDF	ND (54)	4,051	170	NR	4,460	158	2,301	1,857	1,861
1,2,3,4,7,8,9-HpCDF	ND (54)	ND (76)	NR	NR	NR	NR	109	36	58
OCDF	ND (90)	230	1115	NR	253	447	1,128	529	536
Total 2,3,7,8-CDD	ND	2,137	≥591	≥865	2,352	≥1,363	2,315	1,440	1,469
Total 2,3,7,8-CDF	496.8	9,336	≥1,415	≥1,356	≥10,277	≥803	6,069	4,832	4,901
Total I-TEQ_{DF} (nondetect set to 0)	65.9	1,075	≥52	≥300	≥1,184	≥56	419	≥450	
Total I-TEQ_{DF} (nondetect set to ½ DL)	102	1,080	≥52	≥300	≥1,184	≥56	419		≥456
Total TEQ_{DF}-WHO_{98} (nondetect set to 0)	65.9	1,287	≥72	≥352	≥1,417	≥75	454	≥532	
Total TEQ_{DF}-WHO_{98} (nondetect set to ½ DL)	111	1,291	≥72	≥352	≥1,417	≥75	454		≥539

Table 4-4. CDD/CDF congener emission factors (pg/L) for leaded gasoline-fueled automobiles (continued)

Congener/congener group	Automotive tailpipe emission study results							Mean emission factors	
	FTP cycle[a]	63 km/hr[b]	Idling (test no. 12)[c]	Full load (test no. 13)[c]	64 km/hr (test no. 14)[c]	Rated power (test no. 15)[c]	FTP cycle (test no. 22)[c]	Assuming nondetect set to zero	Assuming nondetect set to ½ detection limit (DL)
Total TCDD	5,220	4,555	517	8,134	5,012	4,558	921	4,131	4,131
Total PeCDD	ND (360)	3,338	658	2,161	3,675	6,389	359	2,369	2,394
Total HxCDD	ND (540)	1,868	354	623	2,056	1,973	996	1,124	1,163
Total HpCDD	ND (90)	1,164	194	297	1,281	2,374	988	900	906
Total OCDD	ND (90)	498	380	513	549	1,166	1,581	670	676
Total TCDF	15,300	50,743	2,167	20,513	55,857	29,353	4,290	25,460	25,460
Total PeCDF	2,430	11,591	452	3,608	12,757	10,580	3,165	6,369	6,369
Total HxCDF	ND (540)	6,308	192	477	6,947	12,553	3,132	4,230	4,268
Total HpCDF	ND (270)	5,642	170	NR	6,210	4,767	2,920	3,285	3,307
Total OCDF	ND (90)	230	1,115	NR	253	447	1,128	529	536
Total CDD/CDF (nondetect set to 0)	22,950	85,937	6,199	≥36,326	94,597	74,160	19,480	49,067	
Total CDD/CDF (nondetect set to ½ DL)	23,940	85,937	6,199	≥36,326	94,597	74,160	19,480		49,210

[a]Source: Marklund et al. (1990); values in the table were calculated from the reported units of pg/km to pg/L using a fuel economy of 9 km/L for leaded gas as reported in Marklund et al. (1990).
[b]Source: Hagenmaier et al. (1990).
[c]Source: Schwind et al. (1991); Hutzinger et al. (1992).

ND = Not detected (value in parenthesis is the reported detection limit)
NR = Not reported

Table 4-5. CDD/CDF congener emission factors (pg/L) for unleaded gasoline-fueled automobiles without catalytic converters

Congener/congener group	Automotive tailpipe emission study results						Mean emission factors	
	FTP cycle[a]	63 km/hr[b]	FTP cycle (test no. 21)[c]	64 km/hr (test no. 17)[c]	64 km/hr (test no. 20)[c]	64 km/hr (test no. 31/2)[c]	Assuming nondetect set to zero	Assuming nondetect set to ½ detection limit (DL)
2,3,7,8-TCDD	ND (5)	2.6	24	44	7	8.9	14.4	14.8
1,2,3,7,8-PeCDD	ND (3)	19.1	14	31	11	14.1	14.9	15.1
1,2,3,4,7,8-HxCDD	ND (40)	16.6	24	26	25	16.3	18	21.3
1,2,3,6,7,8-HxCDD	ND (40)	17.1	84	28	42	60.1	38.5	41.9
1,2,3,7,8,9-HxCDD	ND (40)	17.6	15	29	23	17.1	17	20.3
1,2,3,4,6,7,8-HpCDD	ND (40)	40.4	192	66	121	197.8	103	106
OCDD	ND (50)	176	868	280	685	2,634	774	778
2,3,7,8-TCDF	64	44	70	71	77	295.2	104	104
1,2,3,7,8-PeCDF	ND (7)	44.5	40	72	69	161.8	64.6	65.1
2,3,4,7,8-PeCDF	ND (7)	20.7	30	34	184	135.2	67.3	67.9
1,2,3,4,7,8-HxCDF	ND (40)	41.9	68	68	88	129.1	65.8	69.2
1,2,3,6,7,8-HxCDF	ND (40)	21.2	62	34	35	113.2	44.2	47.6
1,2,3,7,8,9-HxCDF	ND (40)	37.8	47	61	ND (1)	36.9	30.5	33.9
2,3,4,6,7,8-HxCDF	ND (40)	54.3	55	88	42	82.1	53.6	56.9
1,2,3,4,6,7,8-HpCDF	ND (40)	27.9	278	45	22	418	132	135
1,2,3,4,7,8,9-HpCDF	ND (40)	16.6	ND (1)	27	24	54.5	20.4	23.8
OCDF	ND (70)	119	374	194	288	991	328	334
Total 2,3,7,8-CDD	ND	289.4	1,221	504	914	2,948.3	979	997.4
Total 2,3,7,8-CDF	64	427.9	1,024	694	829	2,417	910.4	937.4
Total I-TEQ_{DF} (nondetect set to 0)	6.4	50.9	96.4	122	144	177	99.5	
Total I-TEQ_{DF} (nondetect set to ½ DL)	26.2	50.9	96.4	122	144	177		103
Total TEQ_{DF}-WHO_{98} (nondetect set to 0)	6.4	60.2	102	138	148	181	106	
Total TEQ_{DF}-WHO_{98} (nondetect set to ½ DL)	26.9	60.2	102	138	148	181		109

Table 4-5. CDD/CDF congener emission factors (pg/L) for unleaded gasoline-fueled automobiles without catalytic converters (continued)

Congener/congener group	Automotive tailpipe emission study results						Mean emission factors	
	FTP cycle[a]	63 km/hr[b]	FTP cycle (test no. 21)[c]	64 km/hr (test no. 17)[c]	64 km/hr (test no. 20)[c]	64 km/hr (test no. 31/2)[c]	Assuming nondetect set to zero	Assuming nondetect set to ½ detection limit (DL)
Total TCDD	13	435	429	706	500	304	398	398
Total PeCDD	ND (3)	481	837	784	542	170	469	469
Total HxCDD	ND (40)	305	484	496	563	114	327	330
Total HpCDD	ND (10)	93	392	147	225	301	193	194
Total OCDD	ND (5)	176	868	280	685	2,634	774	774
Total TCDF	170	569	718	923	478	6,379	1,540	1,540
Total PeCDF	ND (7)	931	531	1,513	437	1,969	897	897
Total HxCDF	ND (40)	378	165	615	258	1,226	440	444
Total HpCDF	ND (20)	476	278	773	445	1,088	510	512
Total OCDF	ND (7)	119	374	194	288	991	328	328
Total CDD/CDF (nondetect set to 0)	183	3,963	5,076	6,431	4,421	15,176	5,876	
Total CDD/CDF (nondetect set to ½ DL	249	3,963	5,076	6,431	4,421	15,176		5,886

[a]Source: Marklund et al. (1990); the pg/L values in the table were calculated from the reported units of pg/km assuming a fuel economy of 10 km/L for unleaded gas.
[b]Source: Hagenmaier et al. (1990).
[c]Source: Schwind et al. (1991); Hutzinger et al. (1992).

ND = Not detected (value in parenthesis is the reported detection limit)

Table 4-6. CDD/CDF congener emission factors (pg/L) for unleaded gasoline-fueled automobiles with catalytic converters

Congener/congener group	Automotive tailpipe emission study test results				Mean emission factors	
	63 km/hr[a]	64 km/hr (test no. 29)[b]	64 km/hr (test no. 30)[b]	64 km/hr (test no. 18)[b]	Assuming nondetect set to zero	Assuming nondetect set to ½ detection limit (DL)
2,3,7,8-TCDD	1.6	3	ND (7.9)	14	4.7	5.6
1,2,3,7,8-PeCDD	1.6	2.6	ND (7.9)	4	2.1	3
1,2,3,4,7,8-HxCDD	2.4	5.3	ND (7.9)	1	2.2	3.2
1,2,3,6,7,8-HxCDD	3.5	6	6.4	2	4.5	4.5
1,2,3,7,8,9-HxCDD	3.1	6	ND (7.9)	2	2.8	3.8
1,2,3,4,6,7,8-HpCDD	15.3	27.8	78.1	14	33.8	33.8
OCDD	170	275	427	197	267	267
2,3,7,8-TCDF	4.3	10.6	12.7	35	15.7	15.7
1,2,3,7,8-PeCDF	3.3	8.7	5.1	13	7.5	7.5
2,3,4,7,8-PeCDF	2.4	7.2	6.2	6	5.5	5.5
1,2,3,4,7,8-HxCDF	4.8	10.6	4.5	5	6.2	6.2
1,2,3,6,7,8-HxCDF	6.3	9.1	3.9	7	6.6	6.6
1,2,3,7,8,9-HxCDF	0.2	ND (3.8)	2.1	5	1.8	2.3
2,3,4,6,7,8-HxCDF	4.6	18.1	8.2	ND (1)	7.7	7.9
1,2,3,4,6,7,8-HpCDF	16.3	54.3	154.2	51	69	69
1,2,3,4,7,8,9-HpCDF	ND (0.2)	ND (3.8)	7.9	1	2.2	2.7
OCDF	27.9	38	106	140	78	78
Total 2,3,7,8-CDD	197.5	325.7	511.5	234	317.1	320.9
Total 2,3,7,8-CDF	70.1	156.6	310.8	263	200.2	201.4
Total I-TEQ_{DF} (nondetect set to 0)	7.2	16	10.1	26.3	14.9	
Total I-TEQ_{DF} (nondetect set to ½ DL)	7.2	16.2	16.8	26.4		16.6
Total TEQ_{DF}-WHO_{98} (nondetect set to 0)	7.8	17.1	9.6	28	15.6	
Total TEQ_{DF}-WHO_{98} (nondetect set to ½ DL)	7.8	17.3	18.3	28.1		17.9

Table 4-6. CDD/CDF congener emission factors (pg/L) for unleaded gasoline-fueled automobiles with catalytic converters (continued)

Congener/congener group	Automotive tailpipe emission study test results				Mean emission factors	
	63 km/hr[a]	64 km/hr (test no. 29)[b]	64 km/hr (test no. 30)[b]	64 km/hr (test no. 18)[b]	Assuming nondetect set to zero	Assuming nondetect set to ½ detection limit (DL)
Total TCDD	28.6	51	13	82	43.7	43.7
Total PeCDD	25.5	51	ND (15)	101	44.4	46.3
Total HxCDD	26.3	56	36	50	42.1	42.1
Total HpCDD	38.7	50	163	25	69.2	69.2
Total OCDD	170	275	427	197	267.3	267.3
Total TCDF	52.6	152	79	332	153.9	153.9
Total PeCDF	53.4	122	29	84	72.1	72.1
Total HxCDF	33.3	71	60	39	50.8	50.8
Total HpCDF	27.1	62	174	83	86.5	86.5
Total OCDF	27.9	38	106	140	78	78
Total CDD/CDF (nondetect set to 0)	483.4	928	1,087	1,133	908	
Total CDD/CDF (nondetect set to ½ DL)	483.4	928	1,087	1,133		909.9

[a]Source: Hagenmaier et al. (1990).
[b]Source: Schwind et al. (1991); Hutzinger et al. (1992).

ND = Not detected (value in parenthesis is the reported detection limit)

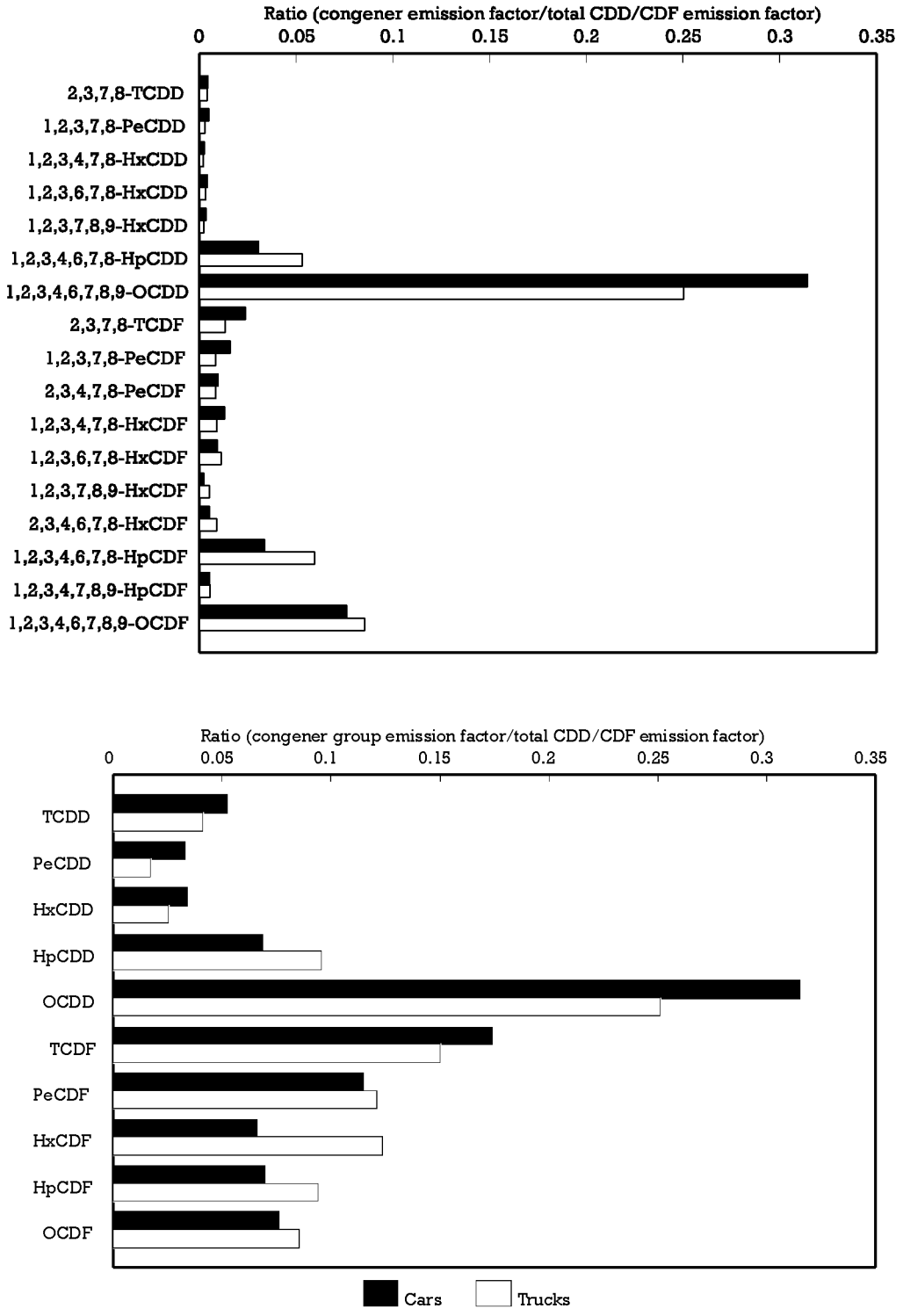


Figure 4-1. Congener and congener group profiles for air emissions from diesel-fueled vehicles (based on profiles calculated from emission factors [nondetects equal one-half the detection limit] from Tables 4-2 and 4-3)**.**

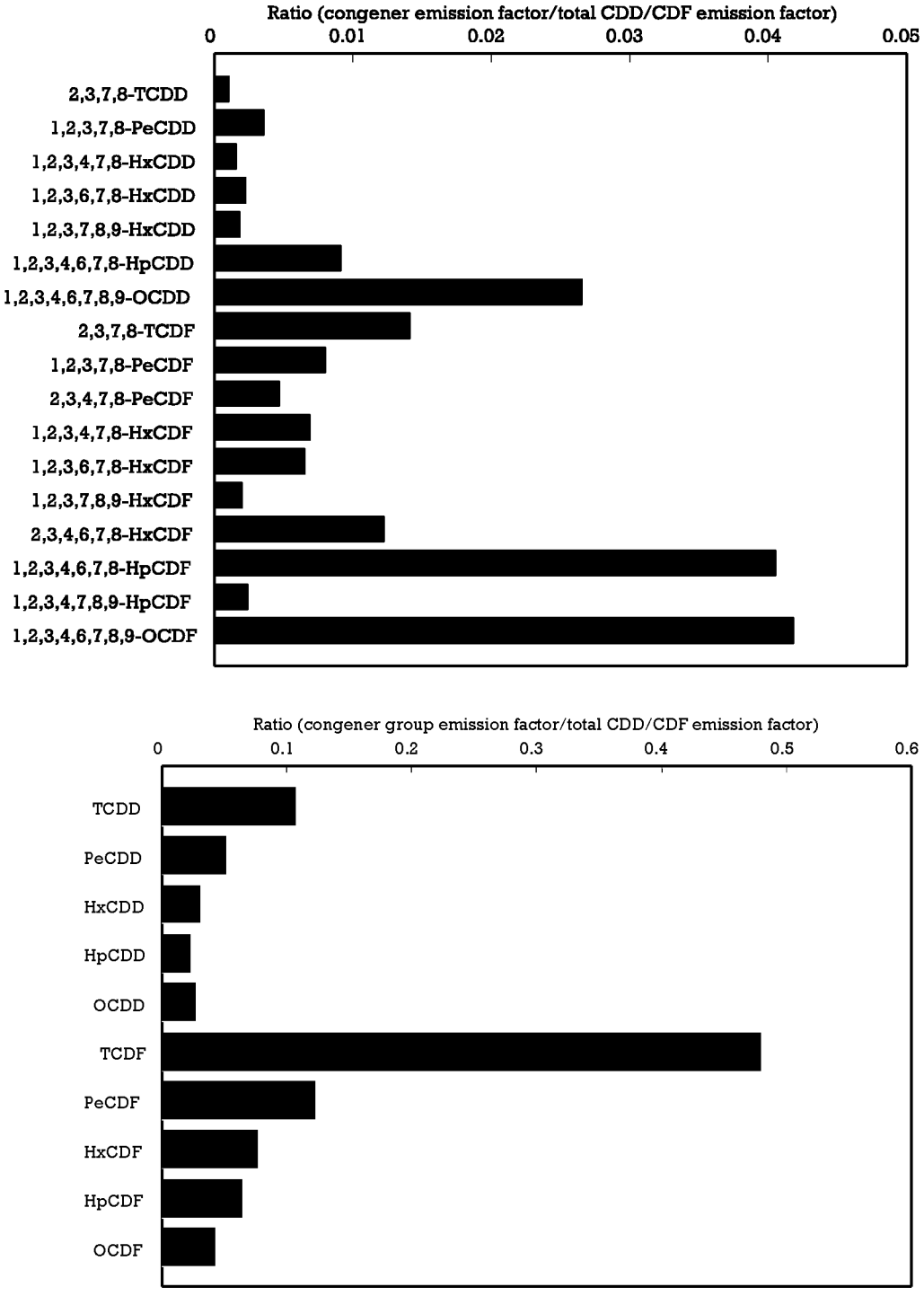
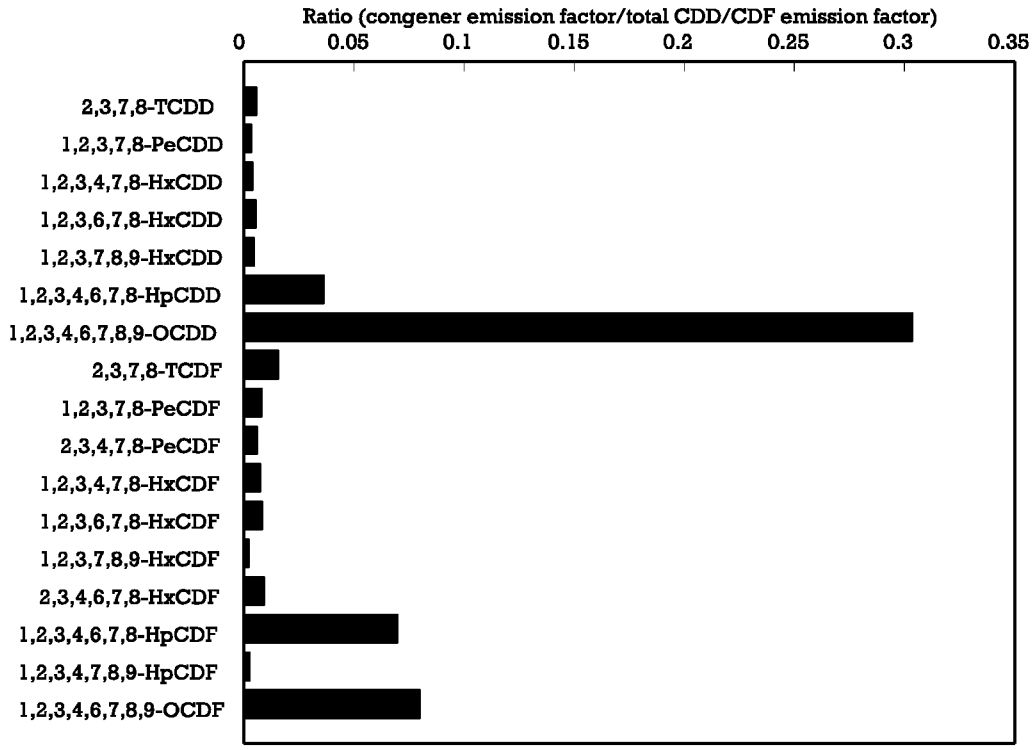


Figure 4-2. Congener and congener group profiles for air emissions from leaded gas-fueled vehicles (based on profiles calculated from emission factors [nondetects equal one-half the detection limit] from Table 4-4).



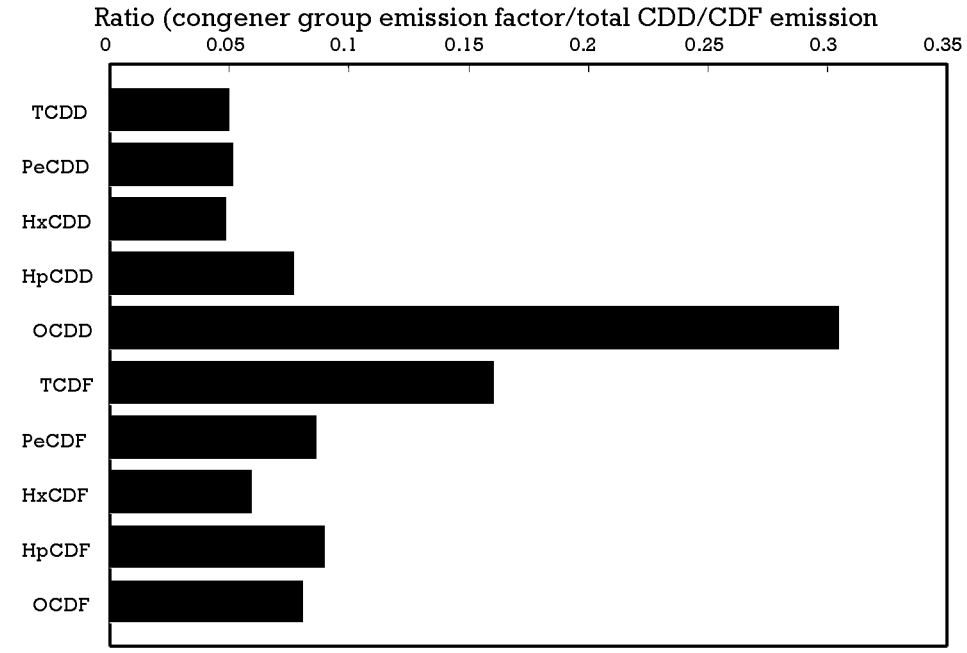


Figure 4-3. Congener and congener group profiles for air emissions from unleaded gas-fueled vehicles (catalytic converter equipped vehicles; based on data from Table 4-6).

Bingham et al. (1989) analyzed the exhausts of four cars using leaded gasoline (uniform lead and organics content of 0.45 g/L tetramethyl lead, 0.22 g/L dichloroethane, and 0.2 g/L dibromoethane) and the exhaust of one car using unleaded gasoline. Analytical results and DLs were reported for only 5 of the 17 toxic CDD/CDF congeners. TEQ emission rates for the cars using leaded fuel, based on detected congeners only, ranged from 1 to 39 pg I-TEQ_{DF}/km. CDDs/CDFs were not detected in the exhaust from the vehicle using unleaded fuel; the total TEQ emission rate for this car, based on one-half the DLs for the five reported congeners, was 20 pg I-TEQ_{DF}/km.

Marklund et al. (1990) tested Swedish cars fueled with commercial fuels, measuring CDD/CDF emissions before and after the muffler. Both new and old vehicles were tested. The tests were done on three cars using unleaded gasoline and two cars using leaded gasoline (0.15 g Pb/L with 1,2-dichloroethane and ethylene dibromide scavengers). CDDs/CDFs were not detected in the fuels at a DL of 2 pg I-TEQ_{DF}/L but were detected at a level of 1,200 pg I-TEQ_{DF}/L in the new semisynthetic engine lube oil used in the engines. The test driving cycle used (31.7 km/hr as a mean speed, 91.2 km/hr as a maximum speed, and 17.9% of time spent idling) yielded fuel economies ranging from approximately 9 to 10 km/L (22 to 24 miles/gal) in the various cars. The reported ranges of emission factors were

- Leaded gas, measured before muffler: 2.4 to 6.3 pg I-TEQ_{DF}/km (21 to 60 pg I-TEQ_{DF}/L fuel consumed)
- Leaded gas, measured in tailpipe: 1.1 to 2.6 pg I-TEQ_{DF}/km (10 to 23 pg I-TEQ_{DF}/L)
- Unleaded gas, catalyst-equipped, measured in tailpipe: 0.36 pg I-TEQ_{DF}/km (3.5 pg I-TEQ_{DF}/L)
- Unleaded gas, measured before muffler: 0.36 to 0.39 pg I-TEQ_{DF}/km (3.5 pg I-TEQ_{DF}/L)

The TEQ levels in exhaust gases from older cars using leaded gasoline were up to six times greater when measured before the muffler than when measured after the muffler. No muffler-related difference was observed in new cars running on leaded gasoline or in old or new cars running on unleaded gasoline.

Marklund et al. (1990) also analyzed the emissions of a heavy-duty, diesel-fueled truck for CDDs/CDFs. None were detected; however, the authors pointed out that the test fuel was a reference fuel and may not have been representative of commercial diesel fuel. Also, due to analytical problems, a much higher DL (about 100 pg I-TEQ_{DF}/L) was realized in this diesel fuel test than in the gasoline tests conducted (5 pg I-TEQ_{DF}/L). Further uncertainty was introduced because the diesel emission samples were collected only before the muffler.

Hagenmaier et al. (1990) ran a set of tests using conditions comparable to the FTP-73 test cycle on gasoline- and diesel-fueled engines for light-duty vehicles in Germany. The following average TEQ emission rates per liter of fuel consumed were reported:

- Leaded fuel: 1,287 pg TEQ_{DF}-WHO_{98}/L (1,080 pg I-TEQ_{DF}/L)
- Unleaded fuel (catalyst equipped): 7.9 pg TEQ_{DF}-WHO_{98}/L (7.2 pg I-TEQ_{DF}/L)
- Unleaded fuel (not catalyst equipped): 60.2 pg TEQ_{DF}-WHO_{98}/L (50.9 pg I-TEQ_{DF}/L)
- Diesel fuel: 24.8 pg TEQ_{DF}-WHO_{98}/L (20.8 pg I-TEQ_{DF}/L)

Schwind et al. (1991) published the major findings of a German study of emissions of halogenated dibenzo-*p*-dioxins and dibenzofurans from internal combustion engines running on commercial fuels. The full report was published in 1992 (Hutzinger et al., 1992). The study was conducted by the universities of Stuttgart, Tübingen, and Bayreuth for the Federal Ministry for Research and Technology, the Research Association for Internal Combustion Engines, and the German Association for the Petroleum Industry and Coal Chemistry. Tests were conducted using engine test benches and rolling test benches under representative operating conditions. Tests were performed on leaded gasoline engines, unleaded gasoline engines, diesel car engines, and diesel truck engines. The reported range of CDD/CDF emission rates across the test conditions in units of pg I-TEQ/L of fuel consumed are presented below.

- Leaded fuel: 72 to 1,417 pg TEQ_{DF}-WHO_{98}/L (52 to 1,184 pg I-TEQ_{DF}/L)
- Unleaded fuel (not catalyst equipped): 102 to 181 pg TEQ_{DF}-WHO_{98}/L (96 to 177 pg I-TEQ_{DF}/L)
- Unleaded fuel (catalyst equipped): 9.6 to 28 pg TEQ_{DF}-WHO_{98}/L (10 to 26 pg I-TEQ_{DF}/L)
- Diesel fuel (cars): 12 to 140 pg TEQ_{DF}-WHO_{98}/L (10 to 130 pg I-TEQ_{DF}/L)
- Diesel fuel (trucks): 79 to 82 pg TEQ_{DF}-WHO_{98}/L (70 to 81 pg I-TEQ_{DF}/L

Tables 4-2 through 4-6 show the results from tests with commercial fuels that were not conducted under normal operating conditions and for which congener-specific emission results were presented in Hutzinger et al. (1992).

Although no specific details on the methodology used were provided, Hagenmaier (1994) reported that analyses of emissions of a diesel-fueled bus run on either the steady-state or the "Berlin cycle" showed no CDDs/CDFs present at a DL of 1 pg/L of fuel consumed for individual congeners.

Gullett and Ryan (1997) reported the results of the first program to sample diesel engine emissions for CDDs/CDFs during actual highway and city driving. The exhaust emissions from a 1991 Freightliner diesel tractor with a 10.3 L, six-cylinder Caterpillar engine—representative of the first generation of computerized fuel-controlled vehicles manufactured in the United States—were sampled during both highway and city routes. The average emission factor for the three highway tests conducted (15.1 pg I-TEQ_{DF}/km; range, 11.7 to 18.7 pg I-TEQ_{DF}/km; standard deviation, 3.5 pg I-TEQ_{DF}/km) was below the average of the two city driving tests by a factor of 3 (49.9 pg I-TEQ_{DF}/kg; range, 3 to 96.8 pg I-TEQ_{DF}/km). DLs were considered to be zero in the calculation of these emission factors. The average of all five tests was 29 pg I-TEQ_{DF}/km, with a standard deviation of 38.3 pg I-TEQ_{DF}/km. This standard deviation reflects the 30-fold variation in the two city driving route tests.

Geueke et al. (1999) analyzed dioxin emissions from heavy-duty vehicle diesel engines in Germany. Table 4-7 shows the results of the analysis. I-TEQ values ranged from 2 to 18 pg I-TEQ/m^3, including one value so high that it could not be reproduced. Miyabara et al. (1999) analyzed CDDs/CDFs found in vehicle exhaust particles from a gasoline engine and a diesel engine in Japan. Table 4-8 presents the data from three tests conducted on the exhaust particles deposited on the tailpipe of the gasoline engine. TEQ values ranged from 3.44 to 5.32 pg TEQ_{DF}-WHO_{98}/g (3.46 to 5.33 pg I-TEQ/g) exhaust particles. Suspended particulate matter (PM) was also collected from an electrostatic precipitator (ESP) connected to a highway tunnel. The I-TEQ for the suspended PM was 257.5 pg TEQ_{DF}-WHO_{98}/g (241.6 pg I-TEQ/g), two orders of magnitude higher than the TEQ for exhaust particles deposited on the tailpipes. Table 4-9 depicts the data from three tests conducted on the exhaust particles deposited on the tailpipe of the diesel engine. TEQ values ranged from 7.14 to 18.1 pg TEQ_{DF}-WHO_{98}/g (7.13 to 14 pg I-TEQ/g) soot.

4.1.2. Tunnel Emission Studies

Several European studies and one U.S. study evaluated CDD/CDF emissions from vehicles by measuring the presence of CDDs/CDFs in tunnel air. This approach has the advantage of allowing the random sampling of exhaust from large numbers of cars with a range of ages and maintenance levels. The disadvantage of this approach is that it relies on indirect measurements (rather than tailpipe measurements), which may introduce bias and make interpretation of the findings difficult. Concerns have been raised that tunnel monitors detect resuspended particulates that have accumulated over time, leading to overestimates of emissions. Also, the driving patterns encountered in these tunnel studies are more or less steady-state driving conditions, which may produce emission levels different from those of the transient driving cycle and cold engine starts that are typical of urban driving conditions. These studies are summarized below in chronological order.

Table 4-7. Total dioxin emission concentrations from heavy-duty diesel engines in Germany

Sample	Concentration in exhaust[a] (pg I-TEQ/m^3)	Sample volume (m^3)
Stationary engine 1 (S1)	6.1	32.89
Stationary engine 2 (S2)	61[b]	10.35
Stationary engine 3 (S3)	18[c]	10.73
Stationary engine 4 (S4)	6.9	10.06
Stationary engine 5 (S5)	6.6	10.06
Truck engine 1 (V1)	9.7	10.03
Truck engine 2 (V2)	2.1	10.07
Truck engine 3 (V3)	2	9.99

[a]Detection limit for sampling: 4.1 pg/m^3 for stationary samples, 4.5 pg/m^3 for truck samples.
[b]Analysis could not be confirmed.
[c]High analytical detection limit (11 pg/m^3).

Source: Geueke et al. (1999).

Rappe et al. (1988) reported the CDD/CDF content of two air samples (60 m^3/sample) collected from a tunnel in Hamburg, Germany, in January 1986 to be 0.44 and 0.59 pg TEQ_{DF}-WHO_{98}/m^3 (0.42 and 0.58 pg I-TEQ_{DF}/m^3). Each sample was collected over a period of about 60 hr. The tunnel handled 65,000 vehicles per day, of which 17% were classified as "heavy traffic." The congener-specific results of the two samples are presented in Table 4-10. Ambient air measured in September 1986 at a nearby highway in Hamburg was reported to contain CDD/CDF levels two to six times lower than those measured in the tunnel.

Larssen et al. (1990) and Oehme et al. (1991) reported the results of a tunnel study in Oslo, Norway, performed during April and May of 1988. Oehme et al. estimated total vehicle emissions by measuring CDD/CDF concentrations in tunnel inlet and outlet air of both the uphill and the downhill lanes. Emission rates for light-duty and heavy-duty vehicle classes were estimated by counting the number of light-duty and heavy-duty vehicles passing through the tunnel on workdays and a weekend and assuming a linear relationship between the percentage of the light- or heavy-duty traffic and the overall emission rate. Thus, the linear relationship for each emission rate was based on only two points (i.e., the weekday and the weekend measurements).

Table 4-8. Levels of 2,3,7,8-chlorine-substituted congeners and total CDDs/CDFs in vehicle exhaust particles (pg/g) for gasoline engines and suspended particulate matter (SPM)

Congener	Gasoline			SPM
	Sample 1	Sample 2	Sample 3	
2,3,7,8-TCDD	<4.4	<2.1	<1.2	<5.2
Other TCDD	6.21	19	7.41	4,580
2,3,7,8-TCDF	3.98	5.17	3.53	108
Other TCDF	36.8	68.8	41.9	2,830
1,2,3,7,8-PeCDD	<7.6	<3.6	<2.1	40.8
Other PeCDD	<7.6	11.5	4.25	1,240
1,2,3,7,8-PeCDF	5.58	6.46	3.07	184
2,3,4,7,8-PeCDF	2.87	5.24	3.66	107
Other PeCDF	24.4	53.9	38.3	29,700
1,2,3,4,7,8-HxCDD	4.3	<1.8	0.86	42.3
1,2,3,6,7,8-HxCDD	<3.8	2.66	1.36	96.7
1,2,3,7,8,9-HxCDD	<3.8	<1.8	0.63	71
Other HxCDD	4.14	20.5	10.5	1,100
1,2,3,4,7,8-HxCDF	6.85	3.95	2.26	243
1,2,3,6,7,8-HxCDF	4.94	4.48	2.35	231
1,2,3,7,8,9-HxCDF	<1.9	<0.9	<0.5	38.6
2,3,4,6,7,8-HxCDF	<1.9	4.94	1.99	387
Other HxCDF	47.2	23.7	15.2	1,600
1,2,3,4,6,7,8-HpCDD	<8.2	11.4	7.64	1,700
Other HpCDD	<8.2	11.3	9	1,360
1,2,3,4,6,7,8-HpCDF	<1.9	12.7	7.41	1,330
1,2,3,4,7,8,9-HpCDF	<1.9	1.06	0.5	143
Other HpCDF	<1.9	8.36	4.88	778
OCDD	8.76	13.8	17	3,650
OCDF	4.78	5.09	3.03	1450
Total CDD/CDF	160.8	294	186.7	53,010.4
I-TEQ	3.73	5.33	3.46	241.6
TEQ_{DF}-WHO_{98}	3.72	5.32	3.44	257.5

Source: Miyabara et al. (1999).

The emission rates estimated in this study, in units of Nordic TEQ, are as follows:

- Light-duty vehicles using gasoline (approximately 70 to 75% using leaded gas): uphill, 520 pg TEQ/km; downhill, 38 pg TEQ/km; mean, 280 pg TEQ/km

Table 4-9. Levels of 2,3,7,8-chlorine-substituted congeners and total CDDs/CDFs in vehicle exhaust particles (pg/g) for diesel engines

Congener	Diesel		
	Sample 1	Sample 2	Sample 3
2,3,7,8-TCDD	2.81	<14.4	<2
Other TCDD	267	117	86.9
2,3,7,8-TCDF	5.71	15.9	7.5
Other TCDF	84.2	335	313
1,2,3,7,8-PeCDD	10.5	<28.8	8.15
Other PeCDD	165	73.5	83.6
1,2,3,7,8-PeCDF	3.17	16.6	15.1
2,3,4,7,8-PeCDF	1.11	<11.5	9.52
Other PeCDF	27.3	211	243
1,2,3,4,7,8-HxCDD	3.39	<17.3	4.01
1,2,3,6,7,8-HxCDD	4.59	<17.3	4.6
1,2,3,7,8,9-HxCDD	2.14	<17.3	<1.5
Other HxCDD	40.9	28.1	26.9
1,2,3,4,7,8-HxCDF	1.29	15.9	9.03
1,2,3,6,7,8-HxCDF	<1.2	31.3	8.22
1,2,3,7,8,9-HxCDF	<1.2	<10.1	0.86
2,3,4,6,7,8-HxCDF	<1.2	<10.1	9.58
Other HxCDF	3.7	182	79
1,2,3,4,6,7,8-HpCDD	8.78	<36	1.24
Other HpCDD	10.1	<36	<1
1,2,3,4,6,7,8-HpCDF	<1	<8.6	4.69
1,2,3,4,7,8,9-HpCDF	<1	<8.6	<1
Other HpCDF	<1	<8.6	6.28
OCDD	<2.8	<23	<0.5
OCDF	<4.4	<36	4.25
Total CDD/CDF	641.7	1,026.3	925.4
I-TEQ	10.6	7.14	14
TEQ_{DF}-WHO_{98}	13.0	7.14	18.1

Source: Miyabara et al. (1999).

- Heavy-duty diesel trucks: uphill, 9,500 pg TEQ/km; downhill, 720 pg TEQ/km; mean, 5,100 pg TEQ/km

The mean values are the averages of the emission rates corresponding to the two operating modes: vehicles moving uphill on a 3.5% incline at an average speed of 37 mph and vehicles

Table 4-10. CDD/CDF concentrations (pg/m^3) from European tunnel air studies

Congener/congener group	Germany[a]	Germany[a]	Belgium[b]	Norway (workdays)[c,d]	Norway (weekend)[c,d]
2,3,7,8-TCDD	ND (0.01)	0.06	0.002	0.02	0.02
1,2,3,7,8-PeCDD	0.31	0.28	0.025	0.18	0.04
1,2,3,4,7,8-HxCDD	0.37	ND (0.17)	0.025	0.06	0.03
1,2,3,6,7,8-HxCDD	1.19	0.66	0.042	0.29	0.03
1,2,3,7,8,9-HxCDD	0.44	ND (0.17)	0.03	0.25	0.06
1,2,3,4,6,7,8-HpCDD	1.9	2	0.468	1.41	0.16
OCDD	6.3	6.4	2.19	0.1	0.5
2,3,7,8-TCDF	0.17	0.72	0.013	0.58	0.07
1,2,3,7,8-PeCDF	0.4	0.36	0.143	0.83	0.75
2,3,4,7,8-PeCDF	0.19	NR	0.039	0.78	0.58
1,2,3,4,7,8-HxCDF	0.26	0.13	0.073	0.79	0.34
1,2,3,6,7,8-HxCDF	0.16	0.15	0.093	0.62	0.31
1,2,3,7,8,9-HxCDF	ND (0.04)	ND (0.05)	0.143	0.04	0.03
2,3,4,6,7,8-HxCDF	0.12	ND (0.05)	0.004	0.74	0.13
1,2,3,4,6,7,8-HpCDF	1.2	0.98	0.499	1.78	0.93
1,2,3,4,7,8,9-HpCDF	ND (0.16)	ND (0.17)	0.074	0.22	0.14
OCDF	ND (1.3)	ND (1)	0.25	1.62	2.54
Total 2,3,7,8-CDD	10.51	9.40	2.78	2.31	0.84
Total 2,3,7,8-CDF	2.5	2.34	1.33	8.0	5.82
Total I-TEQ_{DF} (nondetect set to 0)	0.58	0.42	0.096	0.91	0.48
Total I-TEQ_{DF} (nondetect set to ½ DL)	0.59	0.44	0.096	0.91	0.48
Total TEQ_{DF}-WHO_{98} (nondetect set to 0)	0.73	0.55	0.106	1	0.49
Total TEQ_{DF}-WHO_{98} (nondetect set to ½ DL)	0.74	0.58	0.106	1	0.49
Total TCDD	0.23	0.22	NR	0.26	0.16
Total PeCDD	2.5	1.3	NR	1.78	0.41
Total HxCDD	7.8	2.7	NR	1.32	0.12
Total HpCDD	3.4	3.4	NR	1.31	0.23
Total OCDD	6.3	6.4	NR	0.1	0.5
Total TCDF	3.5	6.2	NR	13.20	1.7
Total PeCDF	3.6	4.1	NR	10.17	7.91
Total HxCDF	2.	1.1	NR	6.42	2.08
Total HpCDF	1.9	1.2	NR	2.62	1.41
Total OCDF	ND (1.3)	ND (1)	NR	1.62	2.54
Total CDD/CDF (nondetect set to 0)	31.2	26.6	NR	38.8	17.06
Total CDD/CDF (nondetect set to ½ DL)	31.9	27.1	NR	38.8	17.06

[a]Source: Rappe et al. (1988).
[b]Source: Wevers et al. (1992).
[c]Source: Oehme et al. (1991).
[d]Listed values are the differences between the concentrations at the inlet and the outlet of the northbound tunnel lanes.

DL = Detection limit
ND = Not detected (value in parenthesis is the detection limit)
NR = Not reported

moving downhill on a 3.5% decline at an average speed of 42 mph. Although Oehme et al. reported results in units of Nordic TEQ, the results in I-TEQ_{DF} should be nearly identical (only about 3 to 6% higher) because the only difference between the two TEQ schemes is the TEF assigned to 1,2,3,7,8-PeCDF (0.1 in Nordic TEQ and 0.05 in I-TEQ_{DF}), a minor component of the toxic CDDs/CDFs measured in the tunnel air. Table 4-10 presents the congener-specific differences in concentrations between the tunnel inlet and outlet concentrations.

Wevers et al. (1992) measured the CDD/CDF content of air samples taken during the winter of 1991 inside a tunnel in Antwerp, Belgium. Background concentrations outside the tunnel were also determined. Two to four samples were collected from each location with two devices: a standard high-volume sampler with a glass fiber filter and a modified two-phase, high-volume sampler equipped with a glass fiber filter and a polyurethane foam (PUF) plug. The I-TEQ_{DF} concentration in the air sampled with the filter with the PUF plug was 74 to 78% of the value obtained with the standard high-volume sampler. However, the results obtained from both sets of devices indicated that the tunnel air had a CDD/CDF TEQ concentration about twice as high as that of the outside air (filter with PUF: 80.3 fg I-TEQ_{DF}/m^3 for tunnel air vs. 35 fg I-TEQ_{DF}/m^3 for outside air; filter only: 100 fg I-TEQ_{DF}/m^3 for tunnel air vs. 58 fg I-TEQ_{DF}/m^3 for outside air). The authors presented the congener-specific results for only one tunnel air measurement; these results are presented in Table 4-10.

During October and November of 1995, Gertler et al. (1996, 1998) conducted a study at the Fort McHenry Tunnel in Baltimore, MD. Their stated objective was to measure CDD/CDF emission factors from in-use vehicles operating in the United States, with particular emphasis on heavy-duty trucks. The air volume entering and leaving the tunnel bore (the area that the traffic goes through) that is used by most of the heavy-duty trucks (i.e., approximately 25% of the vehicles using the bore are heavy-duty trucks) was measured, and the air was sampled for CDDs/CDFs during seven 12-hr sampling periods. Three of the samples were collected during daytime (6 a.m. to 6 p.m.) and four samples were collected during the night (6 p.m. to 6 a.m.). The air volume and concentration measurements were combined with information on vehicle counts (obtained from videotapes) and tunnel length to determine average emission factors.

A total of 33,000 heavy-duty trucks passed through the tunnel during the seven sample runs (21.2 to 28.8% of all vehicles). The emission factors, calculated on the assumption that all CDDs/CDFs emitted in the tunnel were from heavy-duty trucks, are presented in Table 4-11. The average TEQ emission factor was reported to be 181.8 pg TEQ_{DF}-WHO_{98}/km (172 pg I-TEQ_{DF}/km). The major uncertainties identified by the study authors were tunnel air volume measurement, sampler flow volume control, and analytical measurement of CDDs/CDFs.

Table 4-11. Baltimore Harbor tunnel study: estimated emission factors (pg/km) for heavy-duty diesel trucks[a]

Congener/congener group	Run-specific emission factors							Mean emission factors
	Run 2	Run 3	Run 5	Run 6	Run 8	Run 9	Run 10	
2,3,7,8-TCDD	24.5	61.6	0	21.2	37.8	40.1	54.9	34.3
1,2,3,7,8-PeCDD	40.2	20.6	15.4	5.6	38.4	0	83	29
1,2,3,4,7,8-HxCDD	18.2	25.2	46.5	8.3	64.5	0	123	40.8
1,2,3,6,7,8-HxCDD	37.5	28.2	64.3	19.6	153	71.1	186	80
1,2,3,7,8,9-HxCDD	53.6	56.5	91.6	48.4	280	126	370	146.6
1,2,3,4,6,7,8-HpCDD	0	401	729	111	2,438	963	2,080	960.3
OCDD	0	3,361	3,382	1,120	9,730	5,829	7,620	4,434.6
2,3,7,8-TCDF	0	94.3	67.6	152.8	155.8	73.4	61.7	86.5
1,2,3,7,8-PeCDF	0	48.9	72.6	23.6	53.3	0	43.3	34.5
2,3,4,7,8-PeCDF	24.5	75.7	131	46.6	85	63.9	108	76.4
1,2,3,4,7,8-HxCDF	15.4	139	204	93.8	124	164	166	129.5
1,2,3,6,7,8-HxCDF	0.3	75.1	73.7	51	61.3	54.4	95.5	58.8
1,2,3,7,8,9-HxCDF	27.7	14.8	75.6	0	20.6	37.2	63.5	34.2
2,3,4,6,7,8-HxCDF	15.2	82.5	152	55.7	93	86.8	111	85.2
1,2,3,4,6,7,8-HpCDF	12.6	280	445	154	313	354	308	266.7
1,2,3,4,7,8,9-HpCDF	0	58.5	60.8	31.1	25	2.3	34.9	30.4
OCDF	0	239	401	175	416	534	370	305
Total 2,3,7,8-CDD	174	3,954	4,328.8	4,328	1,334.1	7,029	10,516.9	5,725.6
Total 2,3,7,8-CDF	95.7	1,107.8	1,683.3	1,684	783.6	1,370	1,361.9	1,107.2
Total I-TEQ_{DF}	73.8	174.8	170.5	170	95.7	152.9	302.5	172.2
Total TEQ_{DF}-WHO_{98}	93.9	181.8	174.8	175	97.3	147.2	336.8	182.4

Table 4-11. Baltimore Harbor tunnel study: estimated emission factors (pg/km) for heavy-duty diesel trucks[a] (continued)

Congener/congener group	Run-specific emission factors							Mean emission factors
	Run 2	Run 3	Run 5	Run 6	Run 8	Run 9	Run 10	
Total TCDD	245	0	140	165	311	109	97.3	152.5
Total PeCDD	110	21.9	83.3	35.6	174	0	165	84.3
Total HxCDD	677	0	753	54.5	2,009	1,666	2,971	1,161.5
Total HpCDD	0	802	1,498	142	5,696	1,933	4,377	2,064
Total OCDD	0	3,361	3,382	1,120	9,730	5,829	7,620	4,434.6
Total TCDF	0	901	1,314	656	2,416	1,007	687	997.3
Total PeCDF	124	119	1,152	78.4	1,055	282	626	490.9
Total HxCDF	136	319	852	67.6	444	719	619	450.9
Total HpCDF	0	223	814	144	513	354	637	383.6
Total OCDF	0	239	401	175	416	534	370	305
Total CDD/CDF	1,292	5,985.9	10,389.3	2,638.1	22,764	12,433	18,169.3	10,524.5
Heavy-duty vehicles as % of total vehicles	21.2	22	22.6	34	28.8	24.2	27.4	25.7

[a]Values are based on the difference between the calculated chemical mass entering the tunnel and the mass exiting the tunnel. All calculated negative emission factors were set equal to zero. All CDD/CDF emissions were assumed to result from heavy-duty diesel-fueled vehicles.

Source: Gertler et al. (1996, 1998).

EPA's Office of Transportation and Air Quality (OTAQ) reviewed the Gertler et al.(1996) study (Lorang, 1996) and found it to be technologically well done; no major criticisms or comments on the test methodology or protocol were offered, nor did OTAQ find any reason to doubt the validity of the emission factor determined by the study. OTAQ noted that the particulate emission rate for heavy-duty vehicles measured in the study (0.32 g/mile) was lower than the general particulate emission rate used by EPA (about 1 g/mile) and, thus, may underestimate CDD/CDF emissions under different driving conditions. OTAQ cautioned that the reported emission factor should be regarded only as a conservative estimate of the mean emission factor for the interstate trucking fleet under the driving conditions of the tunnel (i.e., speeds on the order of 50 mph, with those of the entering traffic slightly higher and those of the exiting traffic slightly lower).

Figure 4-4 graphically presents the results of the studies by Rappe et al. (1988), Oehme et al. (1991), Wevers et al. (1992), and Gertler et al. (1996, 1998). The figure compares the congener profiles (i.e., congener concentrations or emission factors normalized to total concentration or emission factor of 2,3,7,8-substituted CDDs and CDFs) reported in the four studies. The dominant congeners in the Rappe et al., Wevers et al., and Gertler et al. studies are OCDD; 1,2,3,4,6,7,8-HpCDD; OCDF; and 1,2,3,4,6,7,8-HpCDF. With the exception of OCDD, these congeners are also the major congeners reported by Oehme et al. The Oehme et al. study also differs from the other tunnel studies in that the total of 2,3,7,8-substituted CDFs far exceeds the total of 2,3,7,8-substituted CDDs (by a factor of 2), whereas the other three observed just the opposite.

4.1.3. National Emission Estimates

Estimates of national CDD/CDF TEQ emissions for reference years 1987 and 1995 are presented in this section only for on-road vehicles using gasoline and diesel fuel. For reference year 2000, EPA's Office of Air Quality Planning and Standards (OAQPS) developed national CDD/CDF TEQ emission estimates for on-highway gasoline and diesel vehicles, off-highway gasoline and diesel equipment, diesel railroad equipment, and diesel commercial marine vessels.

4.1.3.1. *Activity Information for On-Road Vehicles*

Reference year 2000 activity information for on-highway gasoline and diesel vehicles was estimated by OAQPS as county-level vehicle miles driven (VMD). The estimates include calculations by month, road type, and vehicle type. To develop the VMD, OAQPS relied on data supplied by the Federal Highway Administration (FHWA).

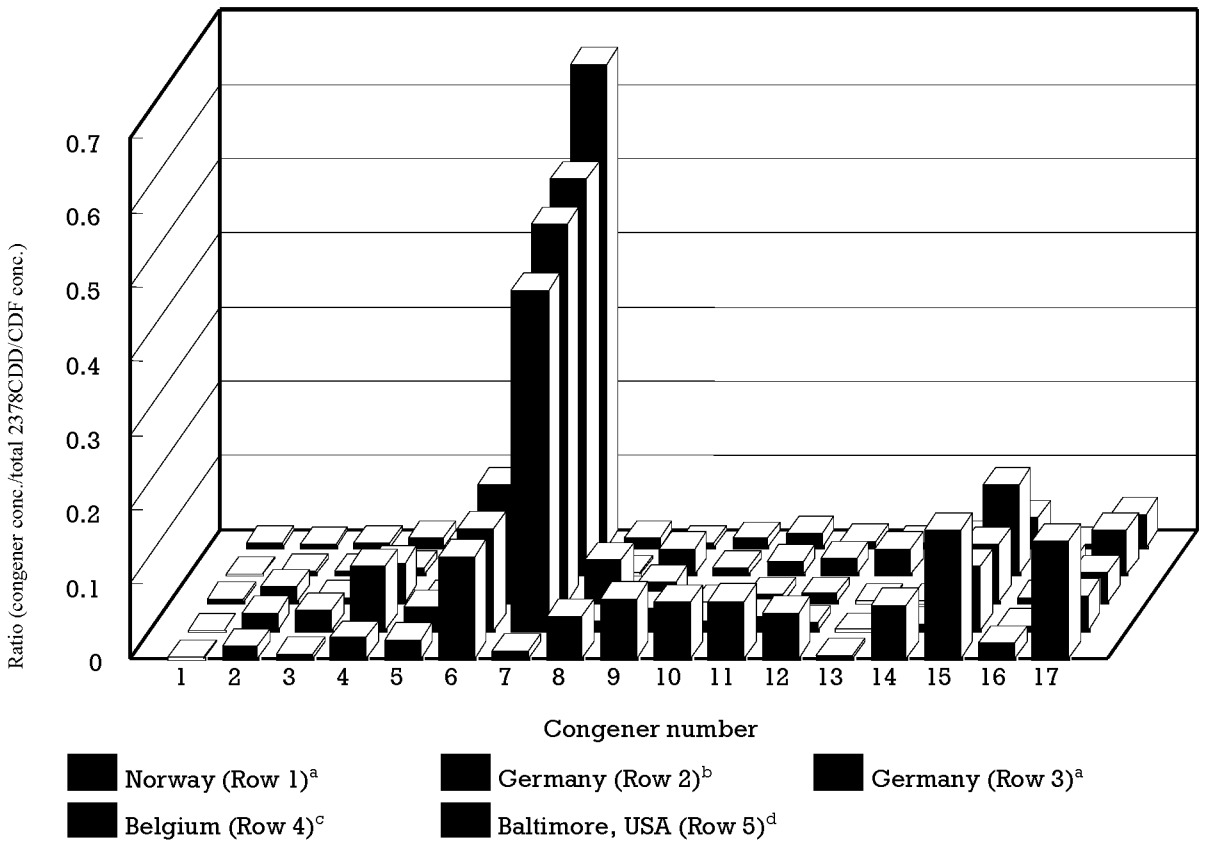


Figure 4-4. Tunnel air concentrations (congener numbers refer to the congeners in order as listed in Table 4-7).

[a]Source: Oehme (1991).
[b]Source: Rappe et al. (1988).
[c]Source: Wevers et al. (1992).
[d]Source: Gertler et al. (1996, 1998).

For on-highway gasoline-driven vehicles, OAQPS calculated a national activity level of 4,071 billion km for 2000. The activity level for each vehicle type was

Vehicle type	Billion kilometers
Light-duty vehicles	2,574.95
Light-duty trucks 1	1,004.23
Light-duty trucks 2	342.79
Heavy-duty vehicles	131.97
Motorcycles	17.70

For on-highway diesel-fueled vehicles, OAQPS estimated a national activity level of 359 billion km for 2000. The activity level for each vehicle type was

Vehicle type	Billion kilometers
Light-duty vehicles	6.44
Light-duty trucks 1	6.44
2B-heavy diesel vehicles	33.80
Light heavy-duty vehicles	25.75
Medium heavy-duty vehicles	59.55
Heavy heavy-duty vehicles	217.26
Buses heavy-duty vehicles	9.66

For reference year 1995, FHWA reported that 1,448 billion total vehicle miles (2,330 billion km) were driven by automobiles and motorcycles in the United States. Trucks accounted for 1,271 billion km (790 billion miles) and buses accounted for 10 billion km (6.2 billion miles) (U.S. DOC, 1997). In 1992, diesel-fueled trucks accounted for 14.4% of total truck vehicle kilometers driven (VKD); gasoline-fueled trucks accounted for the remaining 85.6% (U.S. DOC, 1995a). Applying this factor of 14.4% to the 1995 truck estimate of 1,271 billion km results in an estimate of 183 billion km driven by diesel-fueled trucks in 1995.

All other VKD (2,947 billion km) are assumed to be by gasoline-fueled vehicles (nondiesel trucks, all automobiles, all buses, and all motorcycles); although a fraction of buses and automobiles use diesel fuel, the exact numbers are not known. It is further assumed that all of these kilometers were driven by unleaded gasoline-fueled vehicles because in 1992 only 1.4% of the gasoline supply was leaded fuel (EIA, 1993). Use of leaded fuel should have declined further by 1995 because its use in motor vehicles for highway use in the United States was prohibited as of December 31, 1995 (Federal Register, 1985a).

For reference year 1987, an estimated 3,092 billion km were driven in the United States, of which trucks accounted for 887 billion km (U.S. DOC, 1995b). Diesel-fueled trucks accounted for 17.2% of total truck kilometers driven (U.S. DOC, 1995a). Applying this factor of 17.2% to the 1987 truck kilometer estimate of 887 billion results in an estimate of 153 billion km driven by diesel-fueled trucks. All other VKD (2,939 billion) are assumed to have been by gasoline-fueled vehicles. Leaded gasoline accounted for 24.1% of the gasoline supply in 1987 (EIA, 1993); thus, 708 billion km are estimated to have been driven by leaded gasoline-fueled vehicles. The remaining 2,231 billion km are estimated to have been driven by unleaded gasoline-fueled vehicles. These mileage estimates are given a high confidence rating because they are based on U.S. Census Bureau transportation studies.

4.1.3.2. *Activity Information for Off-Road Uses*

Although on-road vehicles are the largest users of gasoline and diesel fuel, certain sectors of the economy account for significant amounts of farm, railroad, marine vessel, and other off-highway uses. Reference year 2000 activity information for off-highway gasoline and diesel equipment was estimated by OAQPs from NONROAD model runs prepared for the National Emissions Inventory. For off-highway gasoline-driven equipment, OAQPS calculated a national activity level of 23,091.01 million L for 2000. The activity level for each equipment type was

Vehicle type	Million liters
Lawn and garden equipment, 4-stroke engines	8,100.78
Pleasure craft, 2-stroke engines	3,607.50
Commercial equipment, 4-stroke engines	3,255.45
Recreational equipment, 2-stroke engines	2,032.77
Recreational equipment, 4-stroke engines	1,782.93
Pleasure craft, 4-stroke engines	1,374.10
Lawn and garden equipment, 2-stroke engines	1,192.40
Industrial equipment, 4-stroke engines	579.16
Construction and mining equipment, 4-stroke engines	473.18
Agricultural equipment, 4-stroke engines	306.62
Industrial equipment, 4-stroke engines; other oil field equipment	124.92
Construction and mining equipment, 2-stroke engines	102.21
Commercial equipment, 2-stroke engines	79.49
Logging equipment, 4-stroke engines	37.85
Logging equipment, 2-stroke engines	26.50
Airport ground support equipment, 4-stroke engines	7.57
Railroad, 4-stroke engines	3.79
Agricultural equipment, 2-stroke engines	3.40
Industrial equipment, 2-stroke engines	1.14

For reference year 2000, OAQPS calculated national activity levels of 40,125.37 million L for off-highway diesel-driven vehicles, 12,491.86 million L for diesel railroad equipment, and 7,684.39 million L for diesel commercial marine vessels. For diesel commercial marine vessels, the national activity level comprises port emissions (5,905.24 million L) and underway emissions (1,968.41 million L). The activity level for each type of diesel railroad equipment was:

Diesel locomotive type	Million liters
Class I locomotives	10,561.30
Class II/III locomotives	700.30
Yard locomotives	794.94
Passenger trains	230.91
Commuter trains	215.77

The following paragraphs define each of the off-road fuel uses listed at the beginning of this section and present distillate fuel sales (in liters) in each sector for reference years 1987 and 1995 (EIA, 1992, 1997a). For these sectors, the majority of "distillate fuel" sales are diesel fuels; a small fraction are fuel oils. The activity level information for reference years 1987 and 1995 is provided for informational purposes only because emission estimates for these years could not be calculated due to the lack of emission factors.

Farm fuel use includes sales for use in tractors, irrigation pumps, and other agricultural machinery, as well as fuel used for crop drying, in smudge pots, and for space heating of buildings. Sales were 11,352.45 million L in 1987 and 13,158.1 million L in 1995.

Railroad fuel use includes sales to railroads for any use, including diesel fuel for use in locomotives and fuel used for heating buildings operated by railroads. Sales were 10,788.42 L in 1987 and 12,980.18 L in 1995.

Marine vessel fuel use includes sales for the fueling of commercial or private boats such as pleasure craft, fishing boats, tug boats, and oceangoing vessels, including vessels operated by oil companies. Excluded are sales to the U.S. Armed Forces. Sales were 7,059.79 L in 1987 and 8,854.08 L in 1995.

Off-highway fuel use includes sales for use in construction equipment, including, e.g., earthmoving equipment, cranes, stationary generators, and air compressors, and sales for nonconstruction off-highway uses such as logging. Sales were 5,905.24 L in 1987 and 8,225.7 L in 1995.

4.1.3.3 *Emission Estimates*

Using the results of the studies discussed in Section 4.1.1, separate national annual emission estimates were developed for vehicles burning leaded gasoline, unleaded gasoline, and diesel fuel.

Leaded gasoline. The literature indicates that CDD/CDF emissions occur from full combustion in vehicles using leaded gasoline, and that considerable variation occurs depending, at least in part, on the types of scavengers used. Marklund et al. (1987) reported emissions ranging from 20 to 220 pg I-TEQ_{DF}/km from four cars fueled with a reference unleaded fuel to which lead (0.5 g/leaded gal) and a chlorinated scavenger were added. Marklund et al. (1990) reported much lower emissions in the exhaust of cars using a commercial leaded fuel (0.5 g/L) containing both 1,2-dichloroethane and ethylene dibromide as scavengers (1.1 to 6.3 pg I-TEQ_{DF}/km). The difference in the emission measurements in the 1987 and 1990 studies was attributed to the different mix of scavengers used in the two studies, which may have resulted in preferential formation of mixed chlorinated and brominated dioxins and furans.

Hagenmaier et al. (1990) reported TEQ emissions of 1,080 pg I-TEQ_{DF}/L fuel (approximately 129 pg TEQ_{DF}-WHO_{98}/km [108 pg I-TEQ_{DF}/km]) from a car fueled with a commercial leaded fuel (lead content not reported). Bingham et al. (1989) reported emissions ranging from 1 to 39 pg I-TEQ_{DF}/km from four cars using gasoline with a lead content of 1.7 g/L in New Zealand. The German study reported by Schwind et al. (1991) and Hutzinger et al. (1992) measured emissions of 52 to 1,184 pg I-TEQ_{DF}/L (approximately 7.2 to 142 pg TEQ_{DF}-WHO_{98}/km [5.2 to 118 pg I-TEQ_{DF}/km]) for cars under various simulated driving conditions. The tunnel study by Oehme et al. (1991) estimated that emissions from cars running primarily on leaded gasoline (70 to 75% of the cars) ranged from 38 to 520 pg Nordic TEQ/km.

The average emission factor (see Table 4-4) was 532 pg TEQ_{DF}-WHO_{98}/L (450 pg I-TEQ_{DF}/L), as reported for the tailpipe emission studies performed using commercial leaded fuel (Marklund et al., 1990; Hagenmaier et al., 1990; Schwind et al., 1991), which presented analytical results for all 17 toxic CDD/CDF congeners. Assuming an average fuel economy of 10 km/L, this emission factor was approximately 53 pg TEQ_{DF}-WHO_{98}/km (45 pg I-TEQ_{DF}/km). A low confidence rating is assigned to this emission factor because it is based on European fuels and emission control technologies, which may have differed from U.S. leaded-fuel and engine technologies, and because the factor is based on tests with only nine cars.

Combining this average emission factor (53 pg TEQ_{DF}-WHO_{98}/km [45 pg I-TEQ_{DF}/km], assuming nondetect values were zero) with the estimate for kilometers driven by leaded gasoline-fueled vehicles in 1987 (708 billion km) suggests that 37.5 g TEQ_{DF}-WHO_{98} (31.9 g I-TEQ_{DF}) were emitted from vehicles using leaded fuels in 1987. Although some on-road vehicles used leaded fuel in 1995, further use of leaded fuel in motor vehicles for highway use in the United States was prohibited as of December 31, 1995 (Federal Register, 1985a). In 1992, the last year for which data are available on consumption of leaded gasoline by on-road vehicles, only 1.4% of the gasoline supply was leaded gasoline (EIA, 1993). A conservative assumption that 1% of the total VKD in 1995 (29.5 billion km of a total of 2,947 billion km) was by leaded gasoline-fueled vehicles, in conjunction with the emission factor of 53 pg TEQ_{DF}-WHO_{98}/km (45 pg I-TEQ_{DF}/km), yields an annual emission of 1.6 g TEQ_{DF}-WHO_{98} (1.3 g I-TEQ_{DF}) in 1995. These emission estimates are assigned a low confidence rating on the basis of the low rating for the emission factor.

Unleaded gasoline. The literature documenting results of European studies indicates that CDD/CDF emissions from vehicles burning unleaded fuels are lower than emissions from vehicles burning leaded gas with chlorinated scavengers. It also appears, based on the limited data available, that catalyst-equipped cars have lower emission factors than do noncatalyst-equipped cars. Marklund et al. (1987) did not detect CDDs/CDFs in emissions from two catalyst-equipped cars running on unleaded gasoline at a DL of 13 pg I-TEQ_{DF}/km. Marklund et al. (1990)

reported emission factors of 0.36 and 0.39 pg I-TEQ_{DF}/km for two noncatalyst-equipped cars and an emission factor of 0.36 pg I-TEQ_{DF}/km for one catalyst-equipped car. Hagenmaier et al. (1990) reported an emission factor of 5.1 pg I-TEQ_{DF}/km for one noncatalyst-equipped car and 0.7 pg I-TEQ_{DF}/km for one catalyst-equipped car. Schwind et al. (1991) and Hutzinger et al. (1992) reported emission factors of 9.6 to 17.7 pg I-TEQ_{DF}/km for several noncatalyst-equipped cars tested under various conditions; the reported emission factor range for catalyst-equipped cars was 1 to 2.6 pg I-TEQ_{DF}/km.

All automobiles running on unleaded gasoline in the United States are equipped with catalysts. The average emission factor reported for the tailpipe emission studies performed on catalyst-equipped cars (Hagenmaier et al. 1990; Schwind et al., 1991; Hutzinger et al., 1992) was 15.6 pg TEQ_{DF}-WHO_{98}/L (14.9 pg I-TEQ_{DF}/L) (calculated from the mean emission factor in Table 4-6). A low confidence rating is assigned to this emission factor because the European fuels and emission control technology used may have differed from U.S. fuels and technology and also because the emission factor range is based on tests with only three catalyst-equipped cars.

OAQPS calculated emissions for reference year 2000 for dioxins and furans from gasoline-fueled vehicles using the final version of the MOBILE6 model. On-road emissions were calculated by converting the emission factor of 15.6 pg TEQ_{DF}-WHO_{98}/L (14.9 pg I-TEQ_{DF}/L) to a milligram-per-mile basis using a conversion factor of 3.78e–09 and assuming a fuel economy of 21.5 miles/gal. The new emission factor was then multiplied by the corresponding county-level VMD in miles per year. The off-highway gasoline equipment emission estimates for reference year 2000 were developed by multiplying the mean emission factor of 15.6 pg TEQ_{DF}-WHO_{98}/L (14.9 pg I-TEQ_{DF}/L) by 2000 activity estimates developed from NONROAD model runs prepared for the National Emissions Inventory. The activity estimates represent county-level gasoline consumption in gallons. The emission factor was converted from picograms per liter to milligrams per gallon by multiplying by a conversion factor of 3.78e–09. The use of these methodologies resulted in national estimates for reference year 2000 of 7 g TEQ_{DF}-WHO_{98} (6.7 g I-TEQ_{DF}) for on-highway gasoline vehicles and 0.36 g TEQ_{DF}-WHO_{98} (0.35 g I-TEQ_{DF}) for off-highway gasoline equipment.

Applying the same emission factors from Gertler et al. (1996, 1998) and assuming an average fuel economy of 10 km/L yields an emission factor of 1.6 pg TEQ_{DF}-WHO_{98}/km (1.5 pgI-TEQ_{DF}/km). Applying this emission factor to the estimate derived for VKD in 1995 by all gasoline-fueled vehicles (2,947 billion km) suggests that 4.7 g TEQ_{DF}-WHO_{98} (4.4 g I-TEQ_{DF}) were emitted from vehicles using unleaded fuels in 1995. Applying the same emission factors to the estimate derived above for VKD in 1987 by unleaded gasoline-fueled vehicles (2,231 billion km) suggests that 3.6 g TEQ_{DF}-WHO_{98} (3.3 g I-TEQ_{DF}) may have been emitted in 1987. The

emission estimates for all reference years were assigned a low confidence rating on the basis of the low rating given to the emission factor.

Diesel fuel. Limited data are available upon which to base an evaluation of the extent of CDD/CDF emissions resulting from diesel fuel combustion, and these data address only emissions from on-road vehicles; no emissions data are available for off-road diesel uses (construction vehicles, farm vehicles, and stationary equipment). Two U.S. tailpipe studies have been reported: CARB (1987) and Gullett and Ryan (1997). CARB reported a relatively high emission factor of 676 pg I-TEQ_{DF}/km (nondetect values assumed to be zero) for one heavy-duty truck with a fuel economy of 5.5 km/L at 50 km/hr. Gullett and Ryan reported a range of emission factors for one diesel truck tested on six highway or city driving routes of 3 to 96.8 pg I-TEQ_{DF}/km (mean of 29 pg I-TEQ_{DF}/km).

The results of several tailpipe studies conducted in Europe have also been published. Marklund et al. (1990) reported no emissions at a DL of 100 pg I-TEQ_{DF}/L (or 18 pg I-TEQ_{DF}/km, assuming a fuel economy of 5.5 km/L) for one tested truck. Schwind et al. (1991) and Hutzinger et al. (1992) reported emission factors of 32 to 81 pg I-TEQ_{DF}/L (or 6 to 15 pg I-TEQ_{DF}/km, assuming a fuel economy of 5.5 km/L) for a truck engine run under various simulated driving conditions. Hagenmaier (1994) reported no emissions from a bus at a DL of 1 pg/L fuel consumed for individual congeners. For diesel-fueled cars, Hagenmaier et al. (1990) reported an emission factor of 24 pg I-TEQ_{DF}/L (or approximately 2.4 pg I-TEQ_{DF}/km) for one tested car. Schwind et al. and Hutzinger et al. reported emission factors of 5 to 13 pg I-TEQ_{DF}/km for a car engine run under various simulated driving conditions.

The tunnel study by Oehme et al. (1991) generated an estimated mean emission factor of 5,100 pg TEQ/km and a range of 720 to 9,500 pg TEQ/km (in units of Nordic TEQ) for diesel-fueled trucks. Insufficient information was provided in Oehme et al. to enable an exact calculation of emissions in units of I-TEQ_{DF} or TEQ_{DF}-WHO_{98}. However, based on the information that was provided, the mean emission factor in units of TEQ is approximately 5,250 to 5,400 pg I-TEQ_{DF}/km. These indirectly estimated emission factors are considerably larger than those reported in engine studies by Marklund et al. (1990), Schwind et al. (1991), and Hutzinger et al. (1992); the CARB (1987) diesel truck emission factor falls at the low end of the range.

Although aggregate samples representing several thousand heavy-duty diesel vehicles were collected in Oehme et al. (1991), several characteristics of the study introduce considerable uncertainty with regard to the use of the study's results as a basis for estimating emissions in the United States: (a) heavy-duty vehicles represented only 3 to 19% of total vehicle traffic in the tunnel; (b) the majority of the light-duty vehicles were fueled with leaded gasoline, the combustion of which, as noted in Table 4-4, can release considerable amounts of CDD/CDFs; and

(c) technology differences likely existed between the 1988 Norwegian and the 1987 and 1995 U.S. vehicle fleets.

The tunnel study conducted in Baltimore, MD, by Gertler et al. (1996, 1998) shares the disadvantages of all tunnel studies relative to studies that directly measured CDDs and CDFs in tailpipe emissions. Specifically, tunnel studies rely on indirect measurements (rather than tailpipe measurements), which may introduce bias, and the emission factors calculated from these studies reflect driving conditions of only the vehicle fleet using the tunnel and not necessarily of the overall vehicle fleet under other driving conditions.

However, the Gertler et al. study does have strengths that are lacking in the Oehme et al. (1991) tunnel study, and it has advantages over the two U.S. diesel truck tailpipe studies, including: (a) the study was conducted (fairly recently) in the United States and thus reflects current U.S. fuels and technology, (b) virtually no vehicle using the tunnel used leaded gasoline, (c) the tunnel walls and streets were cleaned 1 week prior to the start of sampling and, in addition, the study analyzed road dust and determined that resuspended road dust contributed only about 4% of the estimated emission factors, (d) heavy-duty vehicles comprised, on average, a relatively large proportion (25.7%) of vehicles using the tunnel, and (e) a large number of heavy-duty vehicles—approximately 33,000—passed through the tunnel during the sampling period, which generates confidence that the emission factor is representative of interstate trucks.

Considering the strengths and weaknesses of the available emission factor data from the tailpipe and tunnel studies, the mean TEQ emission factor reported by Gertler et al. (1996, 1998)—182 pg TEQ_{DF}-WHO_{98}/km (172 pg I-TEQ_{DF}/km)—is assumed to represent the best current estimate of the average emission factor for on-road diesel-fueled trucks. This emission factor is assigned a low confidence rating because it may not be representative of emission rates for the entire fleet of diesel-fueled trucks under the wide array of driving conditions encountered on the road.

For reference year 2000, OAQPS developed national CDD/CDF TEQ emission estimates for on-highway diesel vehicles, off-highway diesel equipment, diesel railroad equipment, and diesel commercial marine vessels. For on-highway diesel vehicles, OAQPS combined the calculated mean emission factors from Gertler et al. (1996, 1998) with the OAQPS estimate for VMD. The picogram-per-kilometer emission factors were first converted to a miligram-per-mile basis using a conversion factor of 1.61e–09. OAQPS estimated national emissions of 65.4 g TEQ_{DF}-WHO_{98} (61.7 g I-TEQ_{DF}) from on-highway diesel-fueled vehicles for reference year 2000. For all years, the emissions from diesel vehicles were assigned a low confidence rating because the emission factors were assigned a low confidence rating.

For off-highway diesel equipment, OTAQ developed the NONROAD emissions model to estimate emissions from nonroad (off-road) equipment types. However, the NONROAD model

does not contain emission factors for calculating CDD/CDF emissions. To calculate emissions for 2000, OAQPS estimated fuel consumption, as reported by the May 2002 "Lockdown C" draft version of NONROAD, and multiplied this estimate by an average fuel efficiency of 7 miles/gal and the emission factor from Gertler et al. (1996, 1998). The NONROAD model does not contain activity estimates for commercial marine vessels and railroad equipment.

OAQPS developed estimates for county-level diesel consumption, in gallons, for diesel commercial marine vessels and diesel railroad equipment and multiplied these estimates by an average fuel efficiency of 7 miles/gal and the emission factor from Gertler et al. (1996, 1998). The results from using these methodologies suggest that 22 g TEQ_{DF}-WHO_{98} (21 g I-TEQ_{DF}), 4.3g TEQ_{DF}-WHO_{98} (4 g I-TEQ_{DF}), and 6.8 g TEQ_{DF}-WHO_{98} (6.4 g I-TEQ_{DF}) were emitted from off-highway diesel equipment, diesel commercial marine vessels, and diesel railroad equipment, respectively, in reference year 2000.

The use of the same emission factors from Gertler et al. (1996, 1998) and an assumption of an average fuel economy of 10 km/L results in an emission factor of 1.6 pg TEQ_{DF}-WHO_{98}/km (1.5 pg I-TEQ_{DF}/km). Applying this factor to the estimate for VKD in 1995 in the United States by diesel-fueled trucks (183 billion km) suggests that 33.3 g TEQ_{DF}-WHO_{98} (31.5 g I-TEQ_{DF}) were emitted from diesel-fueled trucks in 1995. Combining the same emission factors with the estimate derived above for VKD in 1987 by diesel-fueled trucks (153 billion km) suggests that 27.8 g TEQ_{DF}-WHO_{98} (26.3 g I-TEQ_{DF}) were emitted from diesel-fueled trucks in 1987.

For 1987 and 1995 off-road diesel emissions, EPA used the emission factor from Gertler et al. (1996, 1998) and multiplied it by an average fuel efficiency of 2.98 km/L (U.S. EPA, 2003b) and a conversion factor of 1.61e–09 g-km/pg-mile to obtain emission factors of 0.51 ng I-TEQ_{DF}/L and 0.54 ng TEQ_{DF}-WHO_{98}/L. These emission factors are assigned a low confidence rating because they possibly are nonrepresentative of the source. Multiplying these emission factors by the 1987 activity factors for off-highway equipment (17,278.61 million L), marine vessels (7,068.35 million L), and railroad use (10,801.5 million L), EPA estimated the following emissions for 1987: 8.8 g I-TEQ_{DF} (9.4 g TEQ_{DF}-WHO_{98}) for off-highway equipment, 3.6 g I-TEQ_{DF} (3.8 g TEQ_{DF}-WHO_{98}) for marine vessels, and 5.5 g I-TEQ_{DF} (5.8 g TEQ_{DF}-WHO_{98}) for railroad use. Similarly, using the 1995 activity factors for off-highway equipment (21,409.71 million L), marine vessels (8,864.81 million L), and railroad use (12,995.91 million L), EPA estimated the following emissions for 1995: 11 g I-TEQ_{DF} (12 g TEQ_{DF}-WHO_{98}) for off-highway equipment, 4.5 g I-TEQ_{DF} (4.8 g TEQ_{DF}-WHO_{98}) for marine vessels, and 6.6 g I-TEQ_{DF} (7 g TEQ_{DF}-WHO_{98}) for railroad use. These emission estimates are given a low confidence rating because the emission factor may possibly be nonrepresentative of the source.

4.2. WOOD COMBUSTION

For reference year 1987, wood energy consumption is estimated to have been 2,437trillion British thermal units (Btu), or 3.2% of the total primary energy consumed in the United States. In 1995, wood fuel (including black liquor solids) provided about 2.6% (2,350 trillion Btu) of the total primary energy consumed (EIA, 1997b). Wood energy consumption in 2000 is estimated to have been 2,473 trillion Btu, or 2.5% of the total primary energy consumed (EIA, 2003a). The industrial sector is the largest consumer of wood fuel, accounting for 65% of total consumption in 1987, 72% in 1995, and 80% in 2000; the residential sector accounted for 35% of total consumption in 1987, 25% in 1995, and 18% in 2000; and the commercial sector accounted for approximately 2% of total consumption in all three reference years (EIA, 2003a).

These energy consumption estimates appear to include the energy value of black liquor solids, which are combusted in recovery boilers by wood pulp mills. In 1987, 1995, and 2000, the energy values of combusted black liquor solids were 950, 1,078, and 998 trillion Btu, respectively (American Paper Institute, 1992; American Forest and Paper Association, 1997; letter dated August 5, 2002, from W. Gillespie, National Council of the Paper Industry for Air and Stream Improvement, to C. Peck, Versar, Inc.). Subtracting the estimates of black liquor energy values from the 1987, 1995, and 2000 national totals for wood fuel yields 1,487, 1,272, and 1,475 trillion Btu, respectively. Assuming that 1 kg of oven-dried wood (2.15 kg of green wood) provides approximately 19,000 Btu (EIA, 1994), an estimated 78.3, 66.9, and 77.6 million metric tons of oven-dried wood equivalents were burned for energy purposes in 1987, 1995, and 2000, respectively. Of these totals, an estimated 44.8, 31.4, and 23 million metric tons were consumed by the residential sector and an estimated 33.2, 32.6, and 51.5 million metric tons were consumed by the industrial sector in 1987, 1995, and 2000, respectively.

The following subsections discuss the results of relevant emission studies for the residential and industrial sectors and present annual TEQ emission estimates for reference years 1987, 1995, and 2000.

4.2.1. Flue Emissions from Wood Combustion (Residential)

Several studies have provided direct measurement of CDDs/CDFs in flue gas emissions from wood-burning stoves and fireplaces (Schatowitz et al., 1993; Vikelsoe et al., 1993; Bremmer et al., 1994; Bröker et al., 1992; Launhardt and Thoma, 2000; Environment Canada, 2000). The findings of each of these studies are summarized below.

4.2.1.1. *Emissions Data*

Schatowitz et al. (1993) measured the CDD/CDF content of flue gas emissions from several types of wood burners used in Switzerland: a household stove (6 kW), automatic chip

furnaces (110 to 1,800 kW), and a wood stick boiler (35 kW). Emissions were measured from the combustion of a variety of wood fuels (natural beech wood, natural wood chips, uncoated chipboard chips, and waste wood chips from building demolition). The results from the testing of the household stove are most relevant for assessing releases from residential combustion. The household stove was tested with the stove door both open and closed. The open-door stove can be assumed to be representative of fireplaces because both have an uncontrolled draft. Although the congener and congener group analytical results were not reported, the following emission factors (dry weight for wood, wet weight for household waste) and emission rates (corrected to 13% oxygen) for the household stoves and furnaces were reported.

Stoves

- Open-door burning of beech wood sticks: 0.77 ng I-TEQ_{DF}/kg (0.064 ng I-TEQ_{DF}/Nm^3)
- Closed-door burning of beech wood sticks: 1.25 ng I-TEQ_{DF}/kg (0.104 ng I-TEQ_{DF}/Nm^3)
- Closed-door burning of household waste: 3,230 ng I-TEQ_{DF}/kg (114.4 ng I-TEQ_{DF}/Nm^3)

Furnaces

- Natural wood chips: 0.79 to 2.57 ng I-TEQ_{DF}/kg
- Chipboard chips (uncoated): 0.29 to 0.91 ng I-TEQ_{DF}/kg
- Waste wood chips from building demolition: 26 to 173.3 ng I-TEQ_{DF}/kg

Vikelsoe et al. (1993) studied emissions of CDD/CDF congener groups from residential wood stoves in Denmark. The wood fuels used in the experiments were seasoned birch, beech, and spruce, equilibrated to 18% absolute moisture. Four different types of stoves (including one experimental stove) were evaluated under both normal and optimal operating conditions (i.e., well controlled, with carbon monoxide [CO] emissions as low as possible). Total CDD/CDF emissions varied widely for the 24 fuel/stove type/operating condition combinations. Emissions from spruce were about twice as high as those from birch and beech. Surprisingly, the optimal operating condition led to significantly higher CDD/CDF emissions for two stove types but not for the other stoves. The predominant congener group for all experiments was TCDF. The weighted average emission factor and the flue gas concentration for wood stoves (considering

wood and stove types) were reported to be 1.9 and 0.18 ng Nordic TEQ/Nm^3, respectively. Because Vickelsoe et al. did not measure congener levels, the reported emission factor and emission rate were estimated by assuming the same congener distribution in each congener group that had been found for municipal waste incinerators.

Bremmer et al. (1994) reported results of testing performed with a cast-iron wood-burning stove with a combustion chamber lined with fire refractory clay. Measurements were conducted at three loads (maximum, average, and minimum) using clean wood as fuel. The emission factors ranged from 1 to 3.3 ng I-TEQ$_{DF}$/kg (average of about 2.2 ng I-TEQ$_{DF}$/kg). Bremmer et al. also reported results of testing conducted with a fireplace of a type that is common in the Netherlands. Measured emission factors from the burning of clean wood ranged from 13 to 28.5 ng I-TEQ$_{DF}$/kg (average of about 20 ng I-TEQ$_{DF}$/kg). The authors noted that the measured emission factors for fireplaces were considerably higher than those reported by others (see Bröker et al., 1992, below) and assigned "great uncertainty" to the emission factors.

Bröker et al. (1992) reported results of a series of three tests with a wood stove and a fireplace. The average, minimum, and maximum emission factors measured for the wood stove tests ranged from 0.53 to 0.94 ng I-TEQ$_{DF}$/kg. The geometric mean of the two average values was 0.71 ng I-TEQ$_{DF}$/kg. The average of the minimum and maximum emission factors measured for the fireplace tests ranged from 0.2 to 1.06 ng I-TEQ$_{DF}$/kg. The geometric mean of these two average values is 0.46 ng I-TEQ$_{DF}$/kg.

Launhardt and Thoma (2000) conducted an investigation on organic pollutants from a domestic heating system using various solid biofuels. Tests were conducted using a multifuel furnace designed for domestic applications. Table 4-12 shows the average dioxin concentration in the flue gas for the four fuels used (spruce wood, wheat straw, hay, and triticale). The concentrations in the flue gas ranged from 52 to 891 pg TEQ/m^3.

Table 4-12. Average CDD/CDF concentration in flue gas while burning wood and crops

Fuel	Concentration (pg TEQ/m^3)	Number of trials
Spruce wood	52	7
Wheat straw	656	5
Hay (set-aside land)	891	4
Triticale (whole crop)	52	5

Source: Launhardt and Thoma (2000).

Environment Canada (2000) conducted a study on the release of dioxins and furans into the atmosphere by residential wood combustors. The study analyzed two wood stoves believed to be representative of stoves used in Canada: a conventional wood stove that was popular in the early 1980s and an advanced combustion, noncatalytic, EPA-certified wood stove. Each stove was tested using hard maple and black spruce wood. Results from the study ranged from 0.222 to 0.952 ng I-TEQ/kg wood (see Table 4-13). Because these tests took place in North America using indigenous wood, and they included the analysis of an EPA-certified wood stove, the mean value of the Environment Canada study (0.5 ng I-TEQ/kg wood) was used to determine the national emissions estimate for residential burning of clean wood in fireplaces and stoves. This emission factor is assigned a low confidence rating because it is judged to be nonrepresentative of all residential wood combustion (e.g., home fireplaces).

Several studies have reported that combustion of treated or manufactured wood in stoves and fireplaces can result in significantly higher CDD/CDF emission factors. A few researchers (e.g., Vikelsoe et al., 1993) have reported high CDD/CDF emission rates when pentachlorophenol (PCP)-contaminated wood is combusted in residential wood stoves and furnaces. The European Inventory (Quab and Fermann, 1997) used the results of these studies to derive best estimates of CDD/CDF emission factors for combustion of "slightly contaminated wood (excluding PCP)" and "PCP-contaminated wood": 50 and 500 ng I-TEQ_{DF}/kg, respectively. Although it is likely that there is some residential combustion of these types of wood in the United States, there are no corresponding activity level data upon which to base a national annual estimate of emissions.

4.2.1.2. *Activity Level Information*

In 1987, 22.5 million households in the United States burned wood (EIA, 1991). Wood was used as the primary heating fuel in 5 million of those households and as a secondary source for aesthetic purposes (i.e., in fireplaces) in 17.4 million (EIA, 1991, 1997b). Lower numbers were reported for 1995; wood was reported to be used as the primary fuel in only 3.53 million households (EIA, 1997b). More rural, low-income households consumed wood as a primary heating fuel than did other sectors of the population. The majority of these households used wood-burning stoves as the primary heating appliance. Although fireplaces were the most common type of wood-burning equipment in the residential sector, only 7% of fireplace users reported using fireplaces for heating an entire home (EIA, 1991, 1994).

Residential wood consumption was 852 trillion Btu (44.8 million metric tons), or 35% of total U.S. wood energy consumption, in 1987 and 596 trillion Btu (31.4 million metric tons), or 25% of total U.S. wood energy consumption, in 1995 (EIA, 1997b). An estimated 433 trillion Btu (23 million metric tons) of wood were consumed in residences in 2000 (EIA, 2003a). These production estimates are given high confidence ratings because they are based on recent government survey data.

Table 4-13. CDD/CDF concentrations (pg TEQ/kg wood) in emissions from residential wood stoves in Canada

	U.S. EPA-certified						Conventional					
	Maple			Spruce			Maple			Spruce		
Congener	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
2,3,7,8-TCDD	212	214	256	82	110	91	68	75	56	63	70	66
1,2,3,7,8-PeCDD	108	138	117	41	66	57	34	56	47	27	39	41
1,2,3,4,7,8-HxCDD	21	16	17	10	18	14	8	13	9	7	7	10
1,2,3,6,7,8-HxCDD	21	16	17	10	18	14	8	13	9	7	7	10
1,2,3,7,8,9-HxCDD	21	16	17	10	18	14	8	13	9	7	7	10
1,2,3,4,6,7,8-HpCDD	2	2	2	1	2	2	1	1	2	1	2	1
OCDD	1	0	0	0	0	0	0	1	1	0	1	0
2,3,7,8-TCDF	129	134	127	95	47	55	28	38	36	27	16	18
1,2,3,7,8-PeCDF	22	24	23	12	13	17	6	4	4	5	2	5
2,3,4,7,8-PeCDF	243	371	350	186	149	302	85	78	66	54	17	33
1,2,3,4,7,8-HxCDF	22	31	23	12	13	23	27	11	10	16	7	18
1,2,3,6,7,8-HxCDF	15	18	20	8	13	15	10	8	6	4	7	8
2,3,4,6,7,8-HxCDF	17	17	14	8	13	10	7	8	6	4	7	8
1,2,3,7,8,9-HxCDF	10	10	11	8	13	10	4	8	6	4	7	8
1,2,3,4,6,7,8-HpCDF	2	1	2	1	2	2	2	2	1	1	1	1
1,2,3,4,7,8,9-HpCDF	2	1	1	1	2	2	1	1	1	0	1	1
OCDF	0	0	0	0	0	0	0	1	0	0	0	0
TOTAL	848	1,009	997	485	497	628	297	331	269	227	198	238
Mean Emission Factor	951			537			299			221		

Source: Environment Canada (2000).

OAQPS developed emission estimates for residential wood combustion from the results of a study by EPA's Emission Factor and Inventory Group (U.S. EPA, 2001a). The activity data for residential wood combustion were based on the type of combustion unit, and the activity data for wood stoves and fireplaces with inserts were estimated on the basis of total amount of wood consumed in a year. OAQPS used 1997 national activity data to extrapolate an estimate for 1999 by applying a growth rate factor based on wood energy consumption data from the Energy Information Administration (EIA). Activity data for fireplaces were estimated on the basis of number of homes in the U.S. with usable fireplaces, as reported by the U.S. Census Bureau.

OAQPS assumed that the extent of wood consumption in residential combustion units is directly related to ambient temperature (with more wood consumption in colder climates). Historical climate data were used to assign each U.S. county to one of five climate zones, as defined by the National Climatic Data Center. Each climate zone was then assigned a percentage of total national wood consumption on the basis of information contained in the EIA's Residential Energy Consumption database.

The consumption in each climate zone was then allocated to individual counties in that zone. Each county was designated as urban or rural to reflect unit location preferences reported in the 1999 American Housing Survey, which estimated that 68% of fireplaces are found in urban areas, compared with 32% in rural areas. An estimated 69% of wood stoves are found in rural areas, compared with 31% in urban areas. Fireplaces with inserts were evenly split between urban and rural areas. In each zone, the total urban and rural county wood consumption was summed and an adjustment was made within the zone for each county's consumption if the urban and rural totals did not match the expected percentage. These steps resulted in final cordwood consumption by county, which was converted to tons of wood consumed using a conversion factor of one cord of wood equaling 1.163 tons.

Wood consumption estimates for stoves and fireplaces with inserts were further categorized to account for the different designs of units that exist in the marketplace. Different designs of stoves and inserts have been found to have different levels of emissions. According to data received from the Hearth Products Association, the three primary types of units currently in use are noncertified (92% of the stoves manufactured), certified noncatalytic (5.7%), and certified catalytic (2.3%). These proportions were applied to the national, state, and county cordwood consumption estimates prior to the application of emission factors.

Activity levels were estimated to be as follows:

Wood combustion category	Activity level (million metric tons/yr)
Fireplaces	2.79
Fireplaces with inserts, certified catalytic	0.92
Fireplaces with inserts, certified noncatalytic	0.47
Fireplaces with inserts, noncertified	7.64
Noncatalytic wood stoves	0.26
Catalytic wood stoves	0.64
Conventional wood stoves	10.60

4.2.1.3. *Emission Estimates*

The emission factor used to determine national emission estimates (0.5 ng I-TEQ/kg wood) was obtained from Environment Canada (2000) because it was the most comprehensive and recent study. Combining this emission factor with the mass of wood consumed in residences in 1987, 1995, and 2000 yields annual TEQ air emissions from this source of approximately 22, 15.7, and 11.3 g I-TEQ_{DF}, respectively. These estimates are given a low confidence rating for all years because the emission factor was judged to be of low confidence.

4.2.2. Stack Emissions from Wood Combustion (Industrial)

4.2.2.1. *Emissions Data*

Congener-specific measurements of CDDs/CDFs in stack emissions from industrial wood-burning furnaces were measured by CARB at four facilities in 1988 (CARB, 1990b, c, d, e). Measurements of CDD/CDF congener groups and 2,3,7,8-TCDD and 2,3,7,8-TCDF were reported for one facility by EPA (U.S. EPA, 1987a). The National Council of the Paper Industry for Air and Stream Improvement (NCASI) presented congener-specific emission factors for five boilers tested during burns of bark and wood residue (NCASI, 1995). The average congener-specific emission factors derived from the four CARB and five NCASI studies are presented in Table 4-14. Average congener and congener group profiles are presented in Figure 4-5a for the four CARB studies and in Figure 4-5b for the five NCASI studies.

CARB (1990b) measured CDDs/CDFs in the emissions from a quad-cell wood-fired boiler used to generate electricity. The fuel consisted of coarse wood waste and sawdust from nonindustrial logging operations. The exhaust gases passed through a multicyclone before entering the stack. From this study, the average TEQ emission factor for total CDDs/CDFs was calculated to be 0.64 ng I-TEQ_{DF}/kg of wood burned.

Table 4-14. CDD/CDF mean emission factors (ng/kg wood) for industrial wood combustors

Congener/congener group	Four facilities tested by CARB		Five facilities tested by NCASI		Nine facilities tested by CARB and NCASI	
	Nondetect set to zero	Nondetect set to ½ detection limit	Nondetect set to zero	Nondetect set to ½ detection limit	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	0.007	0.016	0.066	0.068	0.04	0.046
1,2,3,7,8-PeCDD	0.044	0.054	0.11	0.112	0.079	0.084
1,2,3,4,7,8-HxCDD	0.042	0.055	0.179	0.183	0.115	0.123
1,2,3,6,7,8-HxCDD	0.086	0.096	0.191	0.193	0.138	0.143
1,2,3,7,8,9-HxCDD	0.079	0.132	0.522	0.524	0.321	0.342
1,2,3,4,6,7,8-HpCDD	0.902	0.905	0.635	0.637	0.745	0.748
OCDD	6.026	6.026	1.317	1.317	3.329	0.329
2,3,7,8-TCDF	0.673	0.673	0.707	0.719	0.684	0.69
1,2,3,7,8-PeCDF	0.79	0.79	0.145	0.149	0.406	0.409
2,3,4,7,8-PeCDF	0.741	0.741	0.159	0.164	0.389	0.392
1,2,3,4,7,8-HxCDF	0.761	0.768	0.108	0.111	0.375	0.379
1,2,3,6,7,8-HxCDF	0.941	0.941	0.071	0.073	0.418	0.419
1,2,3,7,8,9-HxCDF	0.343	0.35	0.064	0.067	0.178	0.183
2,3,4,6,7,8-HxCDF	0.45	0.491	0.015	0.017	0.192	0.209
1,2,3,4,6,7,8-HpCDF	2.508	2.749	0.072	0.074	1.062	1.155
1,2,3,4,7,8,9-HpCDF	0.26	0.344	0.017	0.02	0.113	0.152
OCDF	1.587	1.59	0.049	0.06	0.674	0.681
Total TCDD	0.151	0.154	1.628	1.629	0.969	0.97
Total PeCDD	1.039	1.039	1.958	1.98	1.521	1.533
Total HxCDD	1.748	1.748	1.792	1.796	1.663	1.665
Total HpCDD	2.936	2.936	1.12	1.132	1.821	1.823
Total OCDD	6.026	6.026	1.317	1.317	3.329	0.329
Total TCDF	4.275	4.275	4.532	4.552	4.353	4.364
Total PeCDF	9.75	9.75	1.548	1.549	4.93	4.93
Total HxCDF	7.428	7.428	0.536	0.543	3.316	3.32
Total HpCDF	3.747	3.988	0.111	0.116	1.58	1.674
Total OCDF	1.588	1.59	0.049	0.06	0.674	0.681
Total I-TEQ_{DF}	0.82	0.85	0.4	0.41	0.56	0.58
Total TEQ_{DF}-WHO_{98}	0.84	0.87	0.46	0.47	0.6	0.62
Total CDD/CDF	38.69	38.93	14.59	14.67	24.16	21.29

CARB = California Air Resources Board
NCASI = National Council for Air and Stream Improvement

Sources: CARB (1990b, c, d, e); NCASI (1995).

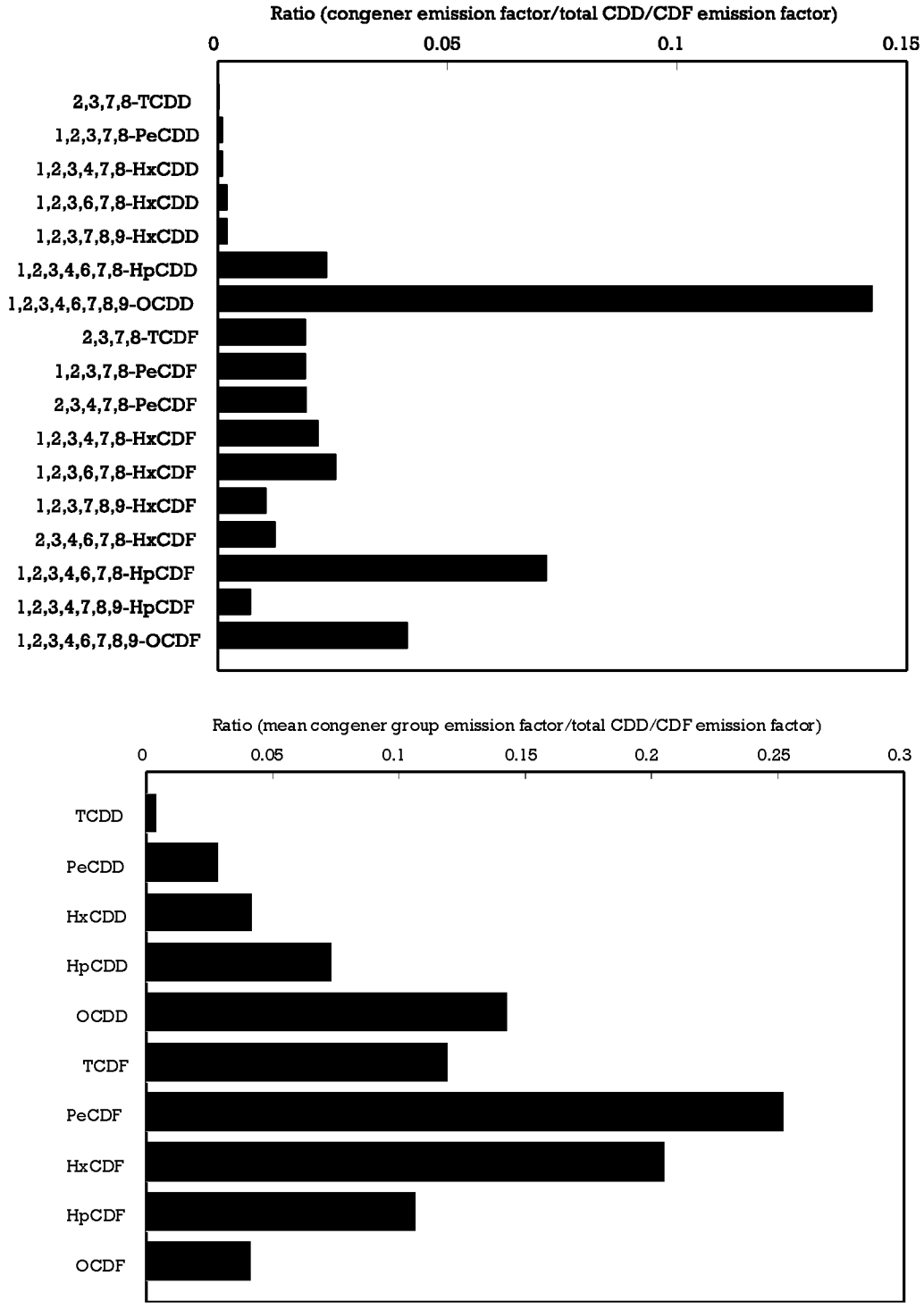


Figure 4-5a. Congener and congener group profiles for air emissions from industrial wood combustors (nondetects set equal to zero).

Sources: CARB (1990b, c, d, e).

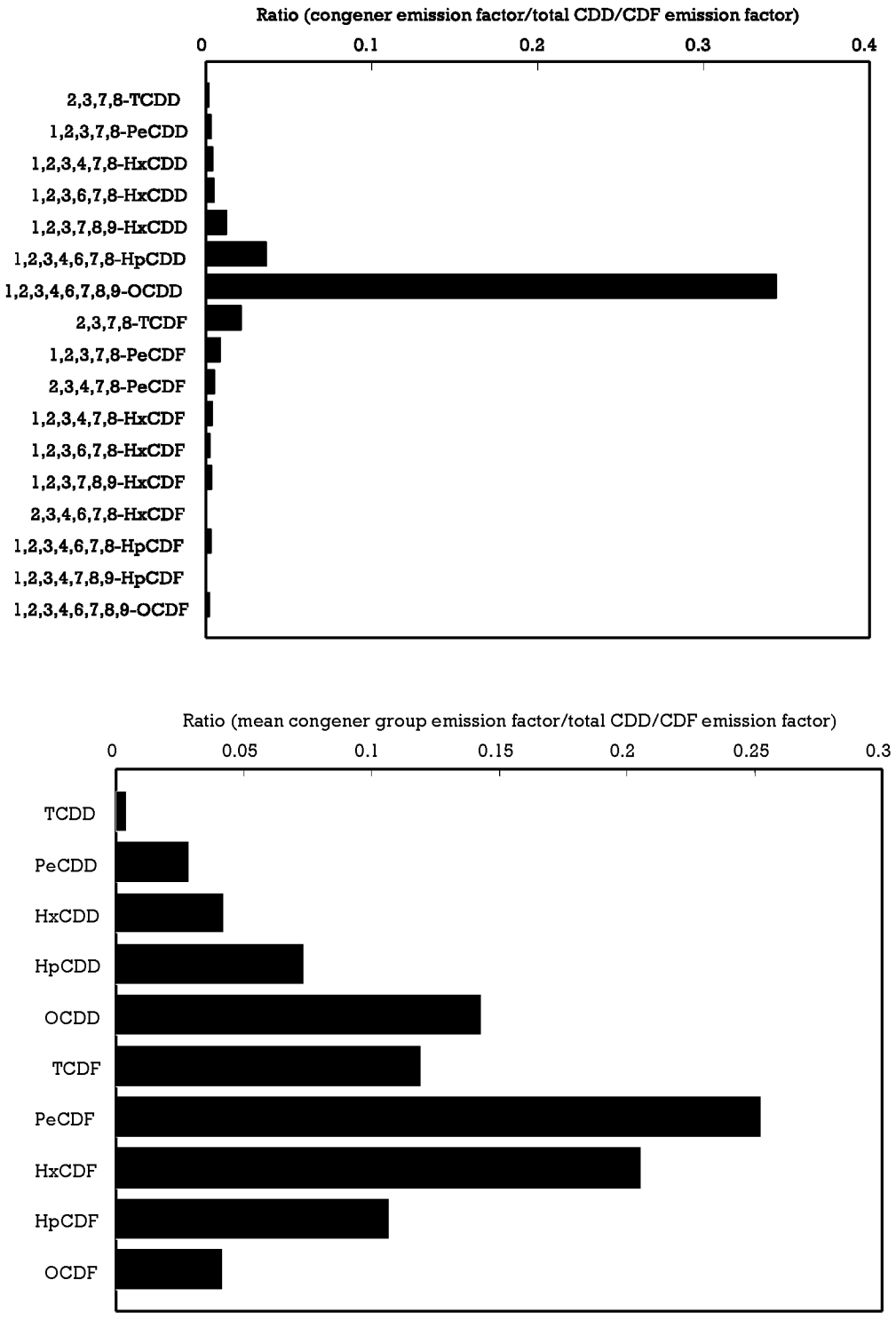


Figure 4-5b. Congener and congener group profiles for air emissions from bleached Kraft mill bark combustors (nondetects set equal to zero).

Source: NCASI (1995).

In the second study (CARB, 1990d), CDDs/CDFs in the emissions from two spreader-stoker wood-fired boilers operated in parallel by an electric utility for generating electricity were measured. The exhaust gas stream from each boiler was passed through a dedicated ESP, after which the gas streams were combined and emitted to the atmosphere through a common stack. Stack tests were conducted when the facility burned fuels allowed by existing permits and when it burned a mixture of permitted fuel supplemented by urban wood waste at a ratio of 7:3. From this study, the average TEQ emission factor for total CDDs/CDFs was calculated to be 0.82 ng I-TEQ_{DF}/kg of wood burned.

In the third study (CARB, 1990e), CDDs/CDFs in the emissions from twin fluidized-bed combustors designed to burn wood chips for the generation of electricity were measured. The air pollution control device (APCD) system consisted of ammonia injection for controlling nitrogen oxides and a multicyclone and ESP for controlling PM. During testing, the facility burned wood wastes and agricultural wastes allowed by existing permits. From this study, the average TEQ emission factor for total CDDs/CDFs was calculated to be 1.32 ng I-TEQ_{DF}/kg of wood burned.

In the fourth study (CARB, 1990f), CDDs/CDFs in the emissions from a quad-cell wood-fired boiler were measured. During testing, the fuel consisted of wood chips and bark. The flue gases passed through a multicyclone and an ESP before entering the stack. From this study, the average TEQ emission factor for total CDDs/CDFs was calculated to be 0.5 ng I-TEQ_{DF}/kg of wood burned.

NCASI (1995) presented stack emission test results for five boilers burning bark or wood residues. One of these facilities, which was equipped with a multicyclone, normally burned bark in combination with sludge and coal. Another facility, which was equipped with an ESP, normally fired pulverized coal. The other three facilities were spreader-stokers equipped with multicyclones or ESPs. Although stack gas flow rates were obtained during these tests, accurate measurements of the amounts of bark and wood fired were not made and had to be estimated from steam production rates. The average TEQ emission factor for these facilities was 0.46 ng TEQ_{DF}-WHO_{98}/kg (0.4 ng I-TEQ_{DF}/kg of feed).

The mean of the emission factors derived from the four CARB studies and five NCASI studies—0.6 ng TEQ_{DF}-WHO_{98}/kg wood (0.56 ng I-TEQ_{DF}/kg wood), assuming nondetect values were zero—is used in this document as the most representative of industrial wood combustion. This emission factor was assigned a medium confidence rating. However, these mean emission factors may not be appropriate for the combustion of waste wood containing elevated chlorine content. NCASI (1995) concluded that CDD/CDF emissions from facilities burning salt-laden wood residue may be considerably higher than those from facilities burning salt-free wood.

Umweltbundesamt (1996) reported the results of stack gas testing at approximately 30 facilities of varying design types burning various types of wood fuel. The author noted that

CDD/CDF emissions were elevated when the combustion conditions were poor, as evidenced by elevated CO emissions, or when the fuel contained elevated chlorine levels. Umweltbundesamt attributed the correlation between elevated CDD/CDF emissions and elevated chlorine content of the fuel to the fire-retardant effects of chlorine, which may have inhibited complete combustion. The chlorine content of untreated wood and bark were reported as 0.001 to 0.01% by weight and 0.01 to 0.02% by weight, respectively. Chipboard can contain up to 0.2% chlorine by weight because of the binding agents used to manufacture the chipboard. Preservative-treated wood and PVC-coated wood were reported to contain chlorine contents as high as 1.2 and 0.3% by weight, respectively.

The facility tested by EPA in 1987 (U.S. EPA, 1987a) was located at a lumber products plant that manufactured overlay panels and other lumber wood products. Nearly all the wood fed to the lumber plant had been stored in sea water adjacent to the facility and therefore had a significant concentration of inorganic chloride. The wood-fired boiler tested was a three-cell dutch oven equipped with a waste heat boiler. The feed wood was a mixture of bark, hogged wood, and green and dry planer shavings. The exhaust gases from the boiler passed through a cyclone and fabric filter (FF) prior to discharge from the stack. From this study, an average emission factor for total CDDs/CDFs of 1,020 ng/kg wood burned (range, 552 to 1,410 ng/kg) was reported for the three collected samples. An average TEQ emission factor of 17.1 ng I-TEQ_{DF}/kg wood burned (range, 7.34 to 22.8 ng/kg) was estimated by EPA using measured congener group concentrations and concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF. Similar emission factors were reported by Luthe et al. (1998) from testing conducted during the 1990s at four Canadian coastal, salt-laden wood-fueled boilers—1.4, 2.6, 17.4, and 27.6 ng I-TEQ_{DF}/kg wood combusted.

The overall average of the five tested facilities in Canada and the United States was 13.2 ng I-TEQ_{DF}/kg of wood combusted. The confidence rating assigned to this emission factor is low because it is based on reporting of limited congener data at one U.S. facility and testing at four non-U.S. sources and because the fraction of salt-laden wood combusted across facilities is likely to have been highly variable.

For reference year 2000, NCASI provided congener-specific estimates of CDD/CDF releases from the pulp and paper industry, including emissions from wood residue-fired boilers (letter dated August 5, 2002, from W. Gillespie, National Council of the Paper Industry for Air and Stream Improvement, to C. Peck, Versar, Inc.). The emission factors were taken from "NCASI Handbook of Chemical Specific Information for SARA (Superfund Amendments and Reauthorization Act) Section 313 Form R Reporting." The factors provided in the handbook were compiled from valid test data supplied to NCASI by a variety of sources, including NCASI member companies that had performed the tests in response to a regulatory program. Data from

11 bark and wood residue-fired boilers used by the forest products industry were used to calculate an emissions estimate. Concentrations of emissions from the wood residue-fired boilers were 0.017 µg TEQ_{DF}-WHO_{98}/ton wood (see Table 4-15).

Table 4-15. NCASI CDD/CDF TEQ concentrations and emissions for wood residue-fired boilers

Congener	Wood-fired boiler emissions		Wood-fired boiler ash not landfilled (72% of total ash landfilled)	
	TEQ_{DF}-WHO_{98} concentrations (median µg/ton)	Emissions (ng/yr)	TEQ concentrations (ng/kg)	Emissions (ng/yr)
2,3,7,8-TCDD	0	0	1.84e+00	3.06e+08
1,2,3,7,8-PeCDD	0	0	1.73e+00	2.88e+08
1,2,3,4,7,8-HxCDD	0	0	3.25e-01	5.41e+07
1,2,3,6,7,8-HxCDD	4.00e-04	1.68e+07	4.28e-01	7.12e+07
1,2,3,7,8,9-HxCDD	5.00e-04	2.10e+07	2.60e-01	4.33e+07
1,2,3,4,6,7,8-HpCDD	1.05e-03	4.41e+07	4.01e-01	6.71e+07
1,2,3,4,6,7,8,9-OCDD	5.69e-04	2.39e+07	1.90e-02	3.96e+06
2,3,7,8-TCDF	4.40e-03	1.85e+08	4.20e+00	7.06e+08
1,2,3,7,8-PeCDF	7.50e-04	3.15e+07	3.35e-01	5.56e+07
2,3,4,7,8-PeCDF	5.00e-03	2.10e+08	3.23e+00	5.37e+08
1,2,3,4,7,8-HxCDF	9.00e-04	3.78e+07	2.21e-01	3.68e+07
1,2,3,6,7,8-HxCDF	7.00e-04	2.94e+07	1.60e-01	2.66e+07
1,2,3,7,8,9-HxCDF	2.10e-03	8.82e+07	5.40e-02	8.98e+06
2,3,4,6,7,8-HxCDF	9.00e-04	3.78e+07	3.80e-02	6.32e+06
1,2,3,4,6,7,8-HpCDF	2.80e-04	1.18e+07	4.10e-03	6.82e+05
1,2,3,4,7,8,9-HpCDF	1.10e-04	4.62e+06	1.30e-03	2.16e+05
1,2,3,4,6,7,8,9-OCDF	2.10e-05	8.82e+05	5.40e-04	1.64e+05
TOTAL	1.72e-02	7.42e+08	1.32e+01	6.19e+08 (ash not landfilled)
				2.21e+09 (ash landfilled)

NCASI = National Council for Air and Stream Improvement

Source: Letter dated August 5, 2002, from W. Gillespie, National Council of the Paper Industry for Air and Stream Improvement, to C. Peck, Versar, Inc.

4.2.2.2. *Activity Level Information*

In 1987, 33.2 million metric tons of wood were burned for fuel in industrial furnaces. In 1995, industrial wood consumption totaled 32.6 million metric tons. EIA (2003b) estimated that industrial wood consumption totaled 1988 trillion Btu (104.6 million metric tons) in 2000. This

total becomes 51.5 million metric tons with the removal of kraft black liquor combustion. The majority of wood fuel consumed in the industrial sector consists of wood waste (chips, bark, sawdust, and hogged fuel). Consumption in the industrial sector is dominated by two industries: paper and allied products and lumber and wood products (EIA, 1994). These activity level estimates are assigned a high confidence rating because they are based on recent government survey data.

Activity level data on combustion of salt-laden wood are not normally collected, even though the associated emission factor is greater than the factor associated with nonsalt-laden wood. Nonetheless, attempts have been made to estimate this activity level. NCASI combined the results from a 1995 survey of combustion units in the pulp and paper industry with those from an ad hoc telephone survey of mills in the Pacific Northwest (Oregon and Washington) to produce a conservative estimate of the amount of salt-laden wood burned at U.S. pulp and paper mills in 1995: 254,000 metric tons (0.8% of the estimated 32.6 million metric tons of industrial wood consumed that year). NCASI suspected that a similar fraction of industrial wood combusted in 1987 by pulp and paper mills was salt laden (letter dated October 8, 1998, from W. Gillespie, National Council of the Paper Industry for Air and Stream Improvement, to G. Schweer, Versar, Inc.).

For purposes of the NCASI survey, salt-laden wood was defined as wood that had been transported, stored, or otherwise exposed to saltwater prior to being processed as fuel. None of the three responding mills in Oregon reported the use of salt-laden wood. Eight of the 13 responding mills in Washington reported some combustion of salt-laden wood. Of the total wood consumed in the Washington mills, 17% was estimated to be salt-laden wood.

As noted above, the majority of industrial wood combustion (97%) occurs in two industries: the paper and allied products industry and the lumber and wood products industry. The relative amount of wood combusted by each of these two industries was the same in 1990 and 1992, the only years for which these statistics are readily available (EIA, 1991, 1994). It can be assumed that the percentage of total wood combusted nationally by the lumber and wood products industry that is salt laden is the same percentage as for the paper and allied products industry, 0.8%; therefore, the total percentage of wood combusted by industry that is salt laden is 1.6%. For reference years 1987, 1995, and 2000, this equates to 0.5, 0.5, and 0.8 million metric tons, respectively. These activity level estimates are assigned a low confidence rating because they are possibly nonrepresentative of the activity levels for the source category combusting salt-laden wood.

4.2.2.3. *Emission Estimates*

Applying the average TEQ emission factor from the four CARB and five NCASI studies (0.6 ng TEQ_{DF}-WHO_{98}/kg wood [0.56 ng I-TEQ_{DF}/kg wood]) to the estimated quantities of nonsalt-laden wood burned by industrial facilities in 1987 (33.2 million metric tons), 1995 (32.6

million metric tons), and 2000 (51.5 million metric tons) yields estimated TEQ emissions to air of 19.9 g TEQ_{DF}-WHO_{98} (18.6 g I-TEQ_{DF}) in 1987, 19.6 g TEQ_{DF}-WHO_{98} (18.3 g I-TEQ_{DF}) in 1995, and 30.9 g TEQ_{DF}-WHO_{98} (28.8 g I-TEQ) in 2000.

Applying the average TEQ emission factor from the five studies on boilers combusting salt-laden wood (13.2 ng I-TEQ_{DF}/kg wood) to the estimated quantities of salt-laden wood burned by industrial facilities in 1987 (0.5 million metric tons), 1995 (0.5 million metric tons), and 2000 (0.8 million metric tons) yields estimated TEQ emissions to air of 6.6 g I-TEQ_{DF} in both 1987 and 1995 and 10.6 g I-TEQ_{DF} in 2000.

Total emissions for 1987, 1995, and 2000 are estimated to have been 26.5, 26.2, and 41.5 g TEQ_{DF}-WHO_{98} (25.2, 24.9, and 39.4 g I-TEQ_{DF}), respectively. Of the 2000 estimate, NCASI estimated that 0.74 g TEQ_{DF}-WHO_{98}/yr of dioxins were emitted from pulp and paper wood-fired boilers (letter dated August 5, 2002, from W. Gillespie, National Council of the Paper Industry for Air and Stream Improvement, to C. Peck, Versar, Inc.). As noted above, the total emissions are based on tests conducted at nine facilities in two industries that account for 97% of total industrial wood fuel combustion. The remaining 3% of industrial combustion and the combustion of wood by the commercial sector (for which no reliable activity level estimates are available) may not be well represented by the emission factors used above, particularly if poorly controlled combustors or treated wood (e.g., treated with PCP or plastics) are burned. The emission estimates for 1987, 1995, and 2000 are given a low confidence level because the activity level estimates were assigned a low confidence rating.

4.2.3. Solid Waste from Wood Combustion (Residential and Industrial)

The measurement of CDDs/CDFs in chimney soot and bottom ash from wood-burning stoves and fireplaces has been reported by several researchers (Bumb et al., 1980; Nestrick and Lamparski, 1982, 1983; Clement et al., 1985; Bacher et al., 1992; Van Oostam and Ward, 1995; and Dumler-Gradl et al., 1995).

Bumb et al. (1980) detected TCDDs (nondetect to 0.4 µg/kg), HxCDDs (0.2 to 3 µg/kg), HpCDDs (0.7 to 16 µg/kg), and OCDD (0.9 to 25 µg/kg) in residues from the wall of a home fireplace and from the firebrick of another home fireplace; for lack of a suitable analytical method, analysis was not performed for PeCDDs. Neither of the fireplaces sampled by Bumb et al. had burned preservative-treated wood.

Nestrick and Lamparski (1982, 1983) expanded the research of Bumb et al. by conducting a survey of CDD concentrations in chimney soot from residential wood-burning units in three rural areas of the United States. Samples were collected from the base of six chimneys in each of the three study areas. Samples were not collected from units where any type of treated or manufactured wood had been burned. For lack of a suitable analytical method, analysis was not performed for PeCDDs. The results of this survey are summarized in Table 4-16. There was

Table 4-16. CDD/CDF concentrations (ng/kg) in residential chimney soot from wood stoves and fireplaces

Congener/ congener group	U.S. east region[a]	U.S. west region[a]	U.S. central region[a]	German farmhouse[b]	Canadian wood stove[c]	Canadian fireplace[c]	Canadian wood stove[d]
2,3,7,8-TCDD	66	13.3	66	150	NR	NR	ND (12)
1,2,3,7,8-PeCDD	NR	NR	NR	70	NR	NR	70
1,2,3,4,7,8-HxCDD	250[e]	522[e]	1,831[e]	35	NR	NR	ND (10)
1,2,3,6,7,8-HxCDD	250[e]	522[e]	1,831[e]	60	NR	NR	625
1,2,3,7,8,9-HxCDD	208	282	1,450	30	NR	NR	281
1,2,3,4,6,7,8-HpCDD	1,143	1,653	6,160	90	NR	NR	948
OCDD	2,033	2,227	13,761	90	NR	NR	530
2,3,7,8-TCDF	NR	NR	NR	930	NR	NR	235
1,2,3,7,8-PeCDF	NR	NR	NR	560	NR	NR	58
2,3,4,7,8-PeCDF	NR	NR	NR	590	NR	NR	68
1,2,3,4,7,8-HxCDF	NR	NR	NR	330	NR	NR	51
1,2,3,6,7,8-HxCDF	NR	NR	NR	400	NR	NR	57
1,2,3,7,8,9-HxCDF	NR	NR	NR	70	NR	NR	8
2,3,4,6,7,8-HxCDF	NR	NR	NR	200	NR	NR	24
1,2,3,4,6,7,8-HpCDF	NR	NR	NR	490	NR	NR	97
1,2,3,4,7,8,9-HpCDF	NR	NR	NR	40	NR	NR	20
OCDF	NR	NR	NR	70	NR	NR	41
Total 2,3,7,8-CDD	3,950	5,219	21,437	525	NR	NR	2,454
Total 2,3,7,8-CDF	NR	NR	NR	3,680	NR	NR	659
Total I-TEQ_{Df}	≥150	≥165	≥286	720	NR	NR	211
Total TEQ_{DF}-WHO_{98}	≥98	≥163	≥81	355	NR	NR	246
Total TCDD	1,987	269	1,511	3,900	ND (10)	ND (10)	11
Total PeCDD	NR	NR	NR	880	ND (10)	500	608
Total HxCDD	2,183	4,273	14,243	600	ND (50)	1,700	3,450
Total HpCDD	2,104	3,243	12,603	200	100	500	1,550
Total OCDD	2,033	2,227	13,761	90	200	400	530
Total TCDF	NR	NR	NR	13,400	ND (10)	300	1,010
Total PeCDF	NR	NR	NR	6,100	ND (10)	1,400	948
Total HxCDF	NR	NR	NR	3,200	ND (50)	1,700	482
Total HpCDF	NR	NR	NR	720	ND (50)	400	154
Total OCDF	NR	NR	NR	70	ND (50)	100	41
Total CDD/CDF	8,307	10,012	42,118	29,160	300	7,000	8,784

[a]Source: Nestrick and Lamparski (1982, 1983); mean values listed, six samples collected in each region.
[b]Source: Bacher et al. (1992).
[c]Source: Clement et al. (1985).
[d]Source: Van Oostdam and Ward (1995); mean of two samples, nondetect values assumed to be zero.
[e]Analytical method could not distinguish between congeners; listed value is the sum of both congeners.

ND = Not detected (value in parenthesis is the reported detection limit)
NR = Not reported

wide variation in the results across soot samples, with standard deviations for congeners and congener groups often equal to or exceeding the mean value; however, CDDs in each congener group were detected in the soot from almost all sampled units. The authors concluded that the results did not appear to present any easily discernible patterns with respect to geographic region, furnace operational parameters, or wood fuel type. They attributed the wide variability observed to differences in design of the units, which affected the sampling point or the conditions at the sampling point, and possible contamination of the fuel wood.

Clement et al. (1985) analyzed chimney soot and bottom ash from residential wood stoves and fireplaces in Canada. The CDD/CDF congener concentrations are presented in Table 4-16 (soot) and Table 4-17 (bottom ash). CDD/CDF congeners were detected in all samples analyzed, although the relative amounts of the different congener groups varied considerably and inconsistently between wood-burning unit types and between ash and soot samples from the same unit.

Table 4-17. CDD/CDF concentrations (ng/kg) in bottom ash from residential wood stoves and fireplaces

Congener/congener group	Canadian wood stove ash	Canadian wood stove ash	Canadian wood stove ash	Canadian fireplace ash
Total TCDD	ND (10)	100	100	ND (10)
Total PeCDD	ND (10)	3,000	200	ND (10)
Total HxCDD	ND (50)	10,000	700	300
Total HpCDD	300	1,200	500	2,000
Total OCDD	2,600	900	100	3,100
Total TCDF	9,100	400	100	ND (10)
Total PeCDF	2,200	4,600	200	ND (10)
Total HxCDF	1,000	9,300	500	100
Total HpCDF	700	1,000	300	400
Total OCDF	ND (50)	100	ND (50)	100
Total CDD/CDF	15,900	30,600	2,700	6,000

[a]No values were reported for individual congeners or for total 2,3,7,8-CDD, 2,3,7,8-CDF, or total TEQ.

ND = Not detected (value in parenthesis is the reported detection limit)

Source: Clement et al. (1985).

Clement et al. also presented total CDD/CDF concentration data for bottom ash from open-air burning of wood. No analyses were reported for individual congeners. The results for the congener groups are shown below. The quantity of ash produced by the open-air burning test was not provided; hence, it is not possible to readily determine the quantities of CDDs/CDFs disposed of.

Congener group	Concentration (µg/kg)
TCDDs	0.8
PeCDDs	4.2
HxCDDs	7.2
HpCDDs	11
OCDD	10
TCDFs	2.2
PeCDFs	7.6
HxCDFs	8.2
HpCDFs	11
OCDF	1.7

Bacher et al. (1992) characterized the full spectrum (mono through octa substitution) of CDD/CDF and BDD/BDF congeners in the soot from an old farmhouse in southern Germany. The chimney carried smoke from an oven that had used untreated wood at the rate of about 5 m^3/yr for more than 10 yr. The sample was taken during the annual cleaning by a chimney sweep. The only BDF detected was mono-BDF (230 ng/kg). No BDDs, BCDDs, or BCDFs were detected at a DL of 20 ng/kg. The results for the tetra- through octa-CDDs/CDFs are presented in Table 4-16. The results indicate that CDFs exceeded the CDDs in each congener group except octa. Also, the lower-chlorinated congener groups exceeded the higher-chlorinated congener groups for both the CDDs and the CDFs. The TEQ content of the chimney soot was 755 ng TEQ_{DF}-WHO_{98}/kg (720 ng I-TEQ_{DF}/kg), of which less than 30% was due to CDDs.

Van Oostdam and Ward (1995) analyzed soot from two wood stoves in British Columbia, Canada. The average TEQ concentration was 246 ng TEQ_{DF}-WHO_{98}/kg (211 ng I-TEQ_{DF}/kg). The congener-specific results are presented in Table 4-16. The soot from a wood stove burning salt-laden wood in a coastal area was found to have an I-TEQ_{DF} content of 7,706 ng I-TEQ_{DF}/kg, or 20 to 90 times more than the concentrations found in the soot from the other two tested stoves.

Dumler-Gradl et al. (1995) analyzed chimney soot samples collected by chimney sweeps from 188 residences in Bavaria, Germany. The summary results of the survey, the largest published survey of its kind to date, are presented in Table 4-18. As in Nestrick and Lamparski (1982, 1983) and Clement et al. (1985), CDDs/CDFs were detected in all samples; however, there was wide variability in total TEQ concentrations within and across unit type/fuel type combinations.

The Washington State Department of Ecology (1998) reported CDD/CDF congener data for ash from hog fuel boilers at three paper mills. The data were compiled and evaluated to determine total I-TEQ concentrations and loading. Nondetect values were included as zero, one-half the DL, or at the DL. The results, assuming nondetect values are at zero, are shown below.

Table 4-18. CDD/CDF concentrations in chimney soot (Bavaria, Germany)

Unit type	Fuel type	Number of samples	Concentration (ng I-TEQ$_{DF}$/kg)		
			Minimum	Mean	Maximum
Oven	Wood	33	10.4	2,015	15,849
Tiled stove	Wood	39	4	3,453	42,048
Heating system	Wood	9	16.9	1,438	20,450
Oven	Wood/coal	27	77.3	2,772	10,065
Tiled stove	Wood/coal	5	53.1	549	4,911
Oven	Wood, wood/coal, waste	5	116.3	6,587	10,652

Source: Dumler-Gradl et al. (1995).

Location	Type of residual	I-TEQ$_{DF}$ (ng/kg)	I-TEQ$_{DF}$ (mg/day)
Daishowa America, Port Angeles	Mixed ash	0.31	0.012
Ft. James	Fly ash	35.4	0.544
Rayonier	Filter ash	12,640	68.9
	Vacuum filter and grate	1,150	6.27
	Filter ash	2,299	12.5
	Fly ash	225	1.23

Pohlandt and Marutzky (1994) presented CDD/CDF concentration data for various types of ash (bottom, furnace, boiler, and fly) from 12 wood-burning boilers. The fly ash samples from two wood-working industry boilers appeared to have the greatest concentrations of CDDs/CDFs. Table 4-19 lists the average congener concentration for the two boilers. Three boiler bottom ash samples contained detectable amounts of only total HpCDDs/HpCDFs and OCDD/OCDF. All the other boiler samples were from boilers that burned copper/chrome/boron-impregnated woods. These samples had total TEQs (assumed to be I-TEQs) ranging from 0.07 to 89 ppt, the highest being for the fly ash samples (52 and 89 ppt). The quantities produced by the boilers that were tested were not reported; hence, it is not possible to readily determine the quantities of CDDs/CDFs disposed of.

The results of analyses of two ash samples from wood-burning facilities in New Hampshire were reported in a facsimile dated January 23, 2001, from Andrew Carpenter, Resource Management, Inc., to Stephen Schwartz, Versar, Inc. Both samples were from the

Table 4-19. CDD/CDF concentrations (ng/kg) in fly ash from wood-working industry

Congener/congener group	Average concentration	I-TEQ_{DF}	TEQ_{DF}-WHO_{98}
2,3,7,8-TCDD	<15	<15	<15
Total TCDD	1,730	–	–
1,2,3,7,8-PeCDD	100	50	100
Total PeCDD	1,250	–	–
1,2,3,4,7,8-HxCDD	130	13	13
1,2,3,6,7,8-HxCDD	150	15	15
1,2,3,7,8,9-HxCDD	140	14	14
Total HxCDD	750	–	–
1,2,3,4,6,7,8-HpCDD	280	3	3
Total HpCDD	470	–	–
Total OCCD	300	0.3	0.03
2,3,7,8-TCDF	130	13	13
Total TCDF	1,300	–	–
1,2,3,7,8-PeCDF	100	5	5
2,3,4,7,8-PeCDF	120	60	60
Total PeCDF	790	–	–
1,2,3,4,7,8-HxCDF	40	4	4
1,2,3,7,8,9-HxCDF	40	4	4
1,2,3,6,7,8-HxCDF	<10	<1	<1
Total HxCDF	150	–	–
1,2,3,4,6,7,8-HpCDF	320	3	3
1,2,3,4,7,8,9-HpCDF	<10	<0.1	<0.1
Total HpCDF	570	–	–
Total OCDF	60	0.06	0.006
Estimated TEQ		89–90	89–90

Source: Pohlandt and Marutzky (1994).

burning of clean (i.e., untreated) wood chips, sawdust, and bark. The first sample was a combination of fly ash and bottom ash. The second sample was fly ash only, but it was a combination of fly ash from two wood-burning boilers. For the first sample, none of the 2,3,7,8-substituted congeners were detected at DLs that ranged from 0.98 ng/kg for 2,3,7,8-TCDD and 2,3,7,8-TCDF to 9.8 ng/kg for OCDD and OCDF. (All other congeners had a DL of 4.9 ng/kg.) For the second sample, all but two congeners were below DLs (which ranged from 0.379 to 0.831 ng/kg). The two congeners that exceeded DLs were OCDD, at 1.261 ng/kg, and 1,2,3,4,6,7,8-HpCDF, at 1.022 ng/kg. For this sample, assuming that the nondetected congeners were not

present, the I-TEQ_{DF} concentration was 0.011 ng/kg. The quantities of the ash produced were not reported.

In a CARB report of emissions from a wood waste-fired incinerator (CARB, 1990b), data are given for CDDs and CDFs for four ash samples. The concentrations of 2,3,7,8-substituted CDD/CDF congeners for each of those four tests were all below the DLs except for OCDD, which was detected in three samples at concentrations of 14, 18, and 32 ng/kg, and 2,3,7,8-TCDF, which was detected in one sample at a concentration of 2.2 ng/kg. The DLs for each CDD and CDF congener ranged from 0.63 ppt (for 2,3,7,8-TCDD) to 9.5 ppt (for HpCDF congeners). Total CDD and CDF values were given for each of the four samples. However, those values assumed that nondetected congeners were at the DL level. Consequently, the total CDD and total CDF values were biased high. The average of the four total CDD values was 28.8 ng/kg (range, 20.3 to 44 ng/kg). The average of the four total CDF values was 21.9 ng/kg (range, 16 to 26.9 ng/kg).

In CARB (1990d), data are presented for CDDs/CDFs for several samples of ESP waste ash from a wood-fired boiler. The report provides sample results for 2 weeks of sampling conducted at the facility. During the first week, the boiler burned fuels that were allowed by the facility permit; during the second week, the boiler burned a mixture containing 70% permitted fuel and 30% urban wood wastes. For the six samples collected over the 3 days of the first week, many of the concentrations of CDD/CDF congeners in the ESP ash were below the DLs. The reported CDD concentrations in ESP waste ash ranged from 24 to 264 ng/kg, and the CDF concentrations ranged from 12 to 151 ng/kg. However, those values assumed that nondetected congeners were present at the detection level. One sample did not have any nondetect values for CDDs. The total CDD concentration for this sample was 264 ng/kg, or about 11.4 ng/kg TEQ_{DF}-WHO_{98} (8.3 ng/kg I-TEQ_{DF}). The TEQ_{DF}-WHO_{98} and I-TEQ_{DF} CDF concentrations for this sample were both less than 1.5 ng/kg. These values were less than 1 ng/kg for the other five samples. All of the samples had some nondetects for the CDF analysis.

Six samples were also collected over 3 days during the second week of sampling, when the 70/30 permitted/urban wood waste mix was burned. For the samples from the second week, the CDD concentrations in ESP waste ash ranged from 1,365 to 3,190 ng/kg, and the CDF concentrations ranged from 2,866 to 11,282 ng/kg. The study authors assumed that nondetected congeners were present at the detection level; however, this is a reasonable estimate for this data set because there was only one nondetect value. Table 4-20 presents the average congener concentrations for these samples. The report did not present quantities of ESP ash produced by the boiler; therefore, it is not possible to readily determine the quantities of CDDs/CDFs disposed of.

Table 4-20. CDD/CDF concentrations (ng/kg) in electrostatic precipitator waste ash from wood-fired industrial boiler

Congener/congener group	Average concentration	I-TEQ_{DF}	TEQ_{DF}-WHO_{98}
2,3,7,8-TCDD	17.85	17.85	17.85
Total TCDD	239	–	–
1,2,3,7,8-PeCDD	30.67	15.33	30.67
Total PeCDD	226.83	–	–
1,2,3,4,7,8-HxCDD	20.33	2.03	2.03
1,2,3,6,7,8-HxCDD	26.33	2.63	2.63
1,2,3,7,8,9-HxCDD	23.33	2.33	2.33
Total HxCDD	300	–	–
1,2,3,4,6,7,8-HpCDD	325	3.25	3.25
Total HpCDD	706.67	–	–
Total OCDD	786.67	0.79	0.08
Total CDD	2,439.17	44.22	58.85
2,3,7,8-TCDF	285	28.5	28.5
Total TCDF	2,713.33	–	–
1,2,3,7,8-PeCDF	154.5	7.73	7.73
2,3,4,7,8-PeCDF	641.67	320.83	320.83
Total PeCDF	2,666.67	–	–
1,2,3,4,7,8-HxCDF	244.83	24.48	24.48
1,2,3,6,7,8-HxCDF	179.67	17.97	17.97
2,3,4,6,7,8-HxCDF	296.67	29.67	29.67
1,2,3,7,8,9-HxCDF	7.28	0.73	0.73
Total HxCDF	1,520	–	–
1,2,3,4,6,7,8-HpCDF	147.67	1.48	1.48
1,2,3,4,7,8,9-HpCDF	21.33	0.21	0.21
Total HpCDF	248.33	–	–
Total OCDF	48.33	0.05	0
Total CDF	7,196.67	431.64	431.6
Estimated TEQ		475.64	490.44

Source: CARB (1990d).

Appendix II in Luthe et al. (1998) shows TEQ concentrations (assumed to be I-TEQ_{DF}) in ashes collected from APCDs from "salt-laden" wood steam boilers. The I-TEQ_{DF} content of ashes from three of the primary multiclone hoppers varied significantly: 0.0978, 0.186, and 9.375

µg/kg. Two samples of ash were taken from the secondary multiclone hoppers. The secondary multiclone removes dust from the primary multiclone emissions; therefore, the ash is finer than primary dust. The I-TEQ_{DF} values for the ash samples were 1.073 and 20.879 µg/kg. The I-TEQ_{DF} values for two samples taken from the ESP that collected dust from the secondary multiclone emissions, which therefore was finer than multiclone dust, were 3.926 and 8.044 µg/kg. No data were given for individual congeners. In fact, because the reference discusses only "dioxins," it is unclear whether the TEQ data are for CDDs or for CDDs plus CDFs. Quantities of collected ash were not given.

Table II in a report by Luthe et al. (1996) presents data for the "TEQs" (assumed to be I-TEQs) on particulates from a secondary collection device for boilers at four paper mills burning salt-laden wood. Eight data points were given (two for each mill), the average of which was 3.6 µg/kg. The range of values was 1.3 to 8 µg/kg. As in Luthe et al. (1998), no data were given for individual congeners. It is also unclear whether the TEQ data were for CDDs or for CDDs plus CDFs. Quantities of collected ash were not given.

Table 5-16 in the National Dioxin Survey (U.S. EPA, 1987a) contains data indicating that the bottom ash from wood combustion from one source (it is not indicated whether it was a boiler) contained 140 ng/kg of 2,3,7,8-TCDD, 138,200 ng/kg of CDDs, and 7,400 ng/kg of CDFs. For a second wood combustion source, the ash contained no detectable 2,3,7,8-TCDD, but it did contain about 125 ng/kg of CDDs and nondetectable levels of CDFs. The FF dust from the second source contained 100 ng/kg of 2,3,7,8-TCDD, 1,143,600 ng/kg of CDDs, and 315,600 ng/kg of CDFs. Specific data for congeners and for ash/dust quantities were not given.

NCASI also provided information on emissions from wood residue boiler ash for reference year 2000 (letter dated August 5, 2002, from W. Gillespie, National Council of the Paper Industry for Air and Stream Improvement, to C. Peck, Versar, Inc.). As with the boiler emissions, emission factors for the boiler ash were taken from "NCASI Handbook of Chemical Specific Information for SARA Section 313 Form R Reporting." Total TEQ concentrations were estimated to be 13.2 ng/kg. Because 72% of the total ash produced is landfilled, emission estimates were 2.21 g TEQ_{DF}-WHO_{98}/yr for ash landfilled and 0.62 g/yr for ash not landfilled (see Table 4-15). It is not known at this time whether the amount of dioxin in nonlandfilled ash results in an environmental release. Therefore, this value was not included in the inventory.

4.3. OIL COMBUSTION

The two major categories of fuel oils that are burned by combustion sources are distillate oils and residual oils. These oils are further distinguished by grade: numbers 1 and 2 are distillate

oils, 5 and 6 are residual oils, and 4 is either distillate oil or a mixture of distillate and residual oils. Number 6 fuel oil is sometimes referred to as Bunker C. Distillate oils are more volatile and less viscous than residual oils. They have negligible nitrogen and ash content and usually contain less than 0.3% sulfur (by weight). Distillate oils are used mainly in domestic and small commercial applications. The heavier residual oils (5 and 6), being more viscous and less volatile than distillate oils, must be heated for ease of handling and to facilitate proper atomization. Because residual oils are produced from the residue after the lighter fractions (gasoline, kerosene, and distillate oils) are removed from the crude oil, they may contain significant quantities of ash, nitrogen, and sulfur. Residual oils are used mainly in utility, industrial, and large commercial applications (U.S. EPA, 1995a).

4.3.1. Institutional/Commercial and Residential Oil Combustion

No testing information on the CDD/CDF content of air emissions from institutional/ commercial or residential oil-fired combustion units in the United States could be located. However, EPA (U.S. EPA, 1997a) estimated CDD/CDF congener group and TEQ emission factors using average CDD/CDF concentrations reported for soot samples from 21 distillate fuel oil-fired furnaces used for central heating in Canada and a particulate emission factor for distillate fuel oil combustors (300 mg/L oil) obtained from AP-42 (U.S. EPA, 1995a). The TEQ emission factor estimate in U.S. EPA (1997a) was derived using the calculated emission factors for 2,3,7,8-TCDD, 2,3,7,8-TCDF, and the 10 congener groups. These emission factors are presented in Table 4-21 and the congener group profile is presented in Figure 4-6.

For reference year 1987, assuming a barrel of oil contains 42 gallons, distillate fuel oil sales to the residential sector and the commercial sector totaled 28.1 billion L (177 million barrels) and 16.2 billion L (102 million barrels), respectively (EIA, 1999). Residual oil sales to the commercial sector in 1987 totaled 6.7 billion L (42 million barrels) (EIA, 1999). Using the emission factor presented in Table 4-21 (150 pg I-TEQ_{DF}/L oil combusted [190 pg TEQ_{DF}-WHO_{98}/L oil combusted]), EPA estimated that 4.22 g I-TEQ_{DF} (5.35 g TEQ_{DF}-WHO_{98}) were emitted in 1987 for the residential sector. For the institutional/commercial sector, EPA estimated TEQ emissions of 1.34 g I-TEQ_{DF} (1.54 g TEQ_{DF}-WHO_{98}) for residual oil and 3.24 g I-TEQ_{DF} (3.73 g TEQ_{DF}-WHO_{98}) for distillate oil for 1987, using an emission factor of 200 pg I-TEQ_{DF}/L oil combusted (230 pg TEQ_{DF}-WHO_{98}/L oil combusted) (see Section 4.3.2). Because the representativeness of the emission factor to 1987 emissions is uncertain and may not be representative, this estimate is assigned a low confidence rating.

Table 4-21. Estimated CDD/CDF emission factors for oil-fired residential furnaces

Congener/ congener group	Mean facility emission factor (pg/L oil)	WHO-TEF	Emission factor (pg TEQ_{DF}-WHO_{98}/L oil)	I-TEF	Emission factor (pg I-TEQ_{DF}/L oil)
2,3,7,8-TCDD	56	1	56	1	56
Total PeCDD	82	1	82	0.5	41
Total HxCDD	66	0.1	7	0.1	7
Total HpCDD	63	0.01	1	0.01	1
OCDD	66	0.0001	0	0.001	0
2,3,7,8-TCDF	53	0.1	5	0.1	5
Total PeCDF	420	0.05	21	0.05	21
Total HxCDF	170	0.1	17	0.1	17
Total HpCDF	73	0.01	1	0.01	1
OCDF	30	0.0001	0	0.001	0
TOTAL			190		149

Source: U.S. EPA (1997a).

For reference year 1995, a low confidence estimate of potential national TEQ emissions from this source category was made using the same emission factors as for the 1987 estimates. Distillate fuel oil sales to the residential and commercial sector totaled 26.2 and 13.5 billion L, respectively, in 1995 (EIA, 1997a). Applying the respective emission factors to these fuel oil sales estimates results in estimated emissions of 3.93 g I-TEQ_{DF} (4.98 g TEQ_{DF}-WHO_{98}) for the residential sector and 2.7 g I-TEQ_{DF} (3.11 g TEQ_{DF}-WHO_{98}) for the institutional/commercial sector in 1995. Residual oil sales to the commercial sector in 1995 totaled 3.7 billion L (23 million barrels) (EIA, 1999). Applying the emission factor of 200 pg I-TEQ_{DF}/L oil combusted (230 pg TEQ_{DF}-WHO_{98}/L oil combusted) (see Section 4.3.2) yields TEQ emissions of 0.73 g I-TEQ_{DF} (0.84 g TEQ_{DF}-WHO_{98}) for residual oil in 1995.

For reference year 2000, EPA/OAQPS developed national emission estimates for residual oil and distillate oil consumed in institutional/commercial heating and distillate oil consumed in residential heating. EPA used state-level 2000 activity data (EIA, 1999), which were allocated to

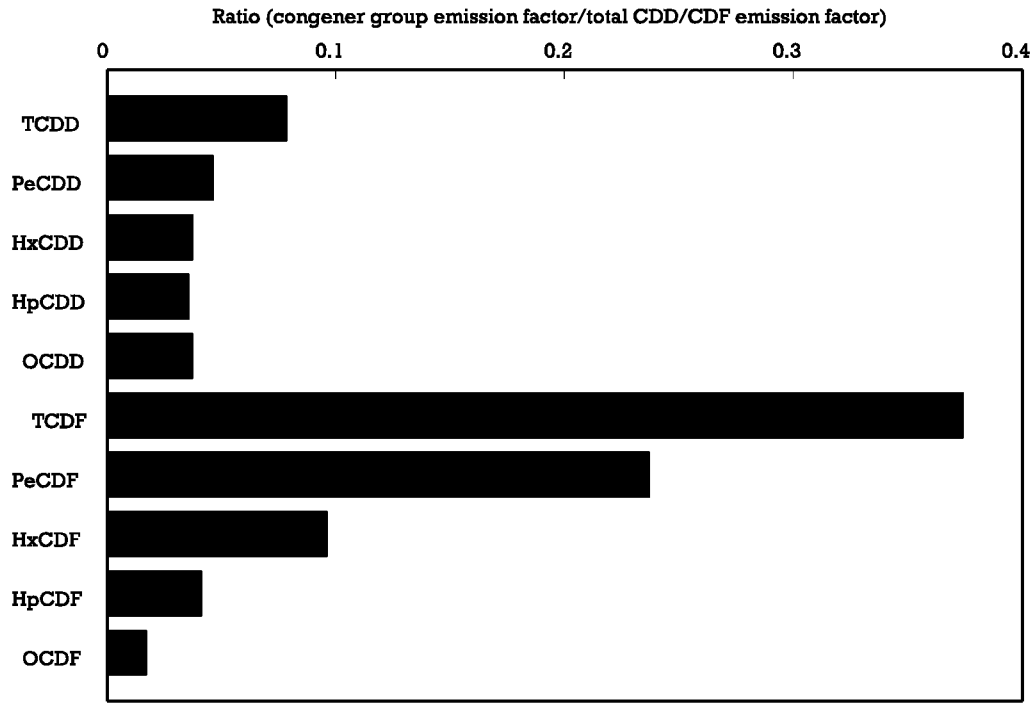


Figure 4-6. Congener group profile for air emissions from residential oil-fueled furnaces.

Source: U.S. EPA (1995b).

counties by the 1999 year county-to-state proportion of employment for numerous SIC codes, as identified in the U.S. Census Bureau's 2000 census. EPA estimated that 2.82 billion L of residual oil and 12.7 billion L of distillate oil were consumed in institutional/commercial heating in 2000. Applying the emission factor of 200 pg I-TEQ_{DF}/L oil combusted (230 pg TEQ_{DF}-WHO_{98}/L oil combusted) (see Section 4.3.2) to these activity levels yields TEQ emissions of 0.56 g I-TEQ_{DF} (0.65 g TEQ_{DF}-WHO_{98}) for residual oil and 2.53 g I-TEQ_{DF} (2.92 g TEQ_{DF}-WHO_{98}) for distillate oil for 2000. EPA/OAQPS estimated that 23.9 billion L of distillate oil were consumed for residential heating in 2000. Using the emission factors discussed above from U.S. EPA (1997a), EPA/OAQPS estimated emissions of 3.59 g I-TEQ_{DF} (4.54 g TEQ_{DF}-WHO_{98}) from distillate oil used for residential heating in 2000.

4.3.2. Utility Sector and Industrial Oil Combustion

Preliminary CDD/CDF emission factors were reported for oil-fired utility boilers using the results of boiler tests conducted over several years (U.S. EPA, 1997a). The data are for a composite of various furnace configurations and APCD systems. Table 4-22 lists the median emission factors presented by EPA. The congener and congener group profiles based on these data are presented in Figure 4-7. The median I-TEQ_{DF} emission factor was reported to be 366 pg TEQ_{DF}-WHO_{98}/L (314 pg I-TEQ_{DF}/L) oil burned.

In 1993, the Electric Power Research Institute (EPRI) sponsored a project to gather information of consistent quality on power plant emissions. The Field Chemical Emissions Measurement (FCEM) project included testing of two cold-sided, ESP-equipped, oil-fired power plants for CDD/CDF emissions (EPRI, 1994). The averages of the congener and congener group emission factors reported for these two facilities are presented in Table 4-22. The average TEQ emission factor was 93.6 pg TEQ_{DF}-WHO_{98}/L (83.1 pg I-TEQ_{DF}/L) oil burned when nondetect values were treated as zero.

The TEQ emission factors reported by EPRI (1994) were less than the median TEQ emission factor reported by EPA by a factor of 3 to 4 (U.S. EPA, 1997a). For purposes of this assessment, the EPA median and EPRI mean emission factors were averaged, for an emission factor of 230 pg TEQ_{DF}-WHO_{98}/L (200 pg I-TEQ_{DF}/L). Although the estimated emission factors are assumed to be the current best estimates for utility/industrial oil burning, they are assigned a low confidence rating.

Residual fuel oil sales totaled 77.3 billion L in 1987 and 46.6 billion L in 1995 (EIA, 1992, 1997a). Vessel bunkering was the largest consumer (48% of sales), followed by electric utilities and the industrial sector. A high confidence rating is assigned to these production estimates. Application of the TEQ emission factor of 230 pg TEQ_{DF}-WHO_{98}/L (200 pg I-TEQ_{DF}/L) to these residual fuel oil sales results in estimated TEQ emissions of 17.8 g TEQ_{DF}-WHO_{98} (15.5 g I-TEQ_{DF}) for 1987 and 10.7 g TEQ_{DF}-WHO_{98} (9.3 g I-TEQ_{DF}) for 1995.

For reference year 2000, OAQPS developed national emission estimates for residual and distillate oil consumption for the industrial sector. OAQPS used state-level 2000 activity data (EIA, 2003a), which were allocated to counties by the 1999 county-to-state proportion of employment for numerous SIC codes, as identified by the 2000 census. OAQPS estimated that 7.33 billion L of residual oil and 31.5 billion L of distillate oil were consumed in the industrial sector in 2000. OAQPS combined these national activity levels with the emission factor of 230 pg TEQ_{DF}-WHO_{98}/L (200 pg I-TEQ_{DF}/L) to estimate 2000 TEQ emissions of 1.69 g TEQ_{DF}-WHO_{98} (1.47 g I-TEQ_{DF}) from residual oil consumption and 7.25 g TEQ_{DF}-WHO_{98}

Table 4-22. CDD/CDF emission factors (pg/L oil) for oil-fired utility/industrial boilers

Congener/congener group	U.S. EPA (1997a) median emission factor[a,b]	EPRI (1994) mean emission factor[a,c]	
		Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	117	0	26.6
1,2,3,7,8-PeCDD	104	24.7	43.1
1,2,3,4,7,8-HxCDD	215	63.3	108
1,2,3,6,7,8-HxCDD	97	65.8	79.3
1,2,3,7,8,9-HxCDD	149	79.7	102
1,2,3,4,6,7,8-HpCDD	359	477	546
OCDD	413	2,055	2,141
2,3,7,8-TCDF	83	0	35.7
1,2,3,7,8-PeCDF	77	64.1	73.9
2,3,4,7,8-PeCDF	86	49.3	59.6
1,2,3,4,7,8-HxCDF	109	76.5	94.9
1,2,3,6,7,8-HxCDF	68	35.4	45.2
1,2,3,7,8,9-HxCDF	104	0	37.7
2,3,4,6,7,8-HxCDF	86	23.8	42.2
1,2,3,4,6,7,8-HpCDF	169	164	218
1,2,3,4,7,8,9-HpCDF	179	0	137
OCDF	179	0	139
Total 2,3,7,8-CDD	1,454	2,765.5	3,046
Total 2,3,7,8-CDF	1,140	413.1	883.2
Total I-TEQ_{DF}	314.6	83.1	147.4
Total TEQ_{DF}-WHO_{98}	366.1	93.6	166.9
Total TCDD	102	NR	NR
Total PeCDD	104	NR	NR
Total HxCDD	145	NR	NR
Total HpCDD	359	NR	NR
Total OCDD	413	NR	NR
Total TCDF	90	NR	NR
Total PeCDF	131	NR	NR
Total HxCDF	172	NR	NR
Total HpCDF	27	NR	NR
Total OCDF	179	NR	NR
Total CDD/CDF	1,722	NR	NR

[a]Assumes a density for residual fuel oil of 0.87 kg/L.
[b]Number of facilities not reported.
[c]Based on two cold-sided power plants equipped with electrostatic precipitators.

NR = Not reported

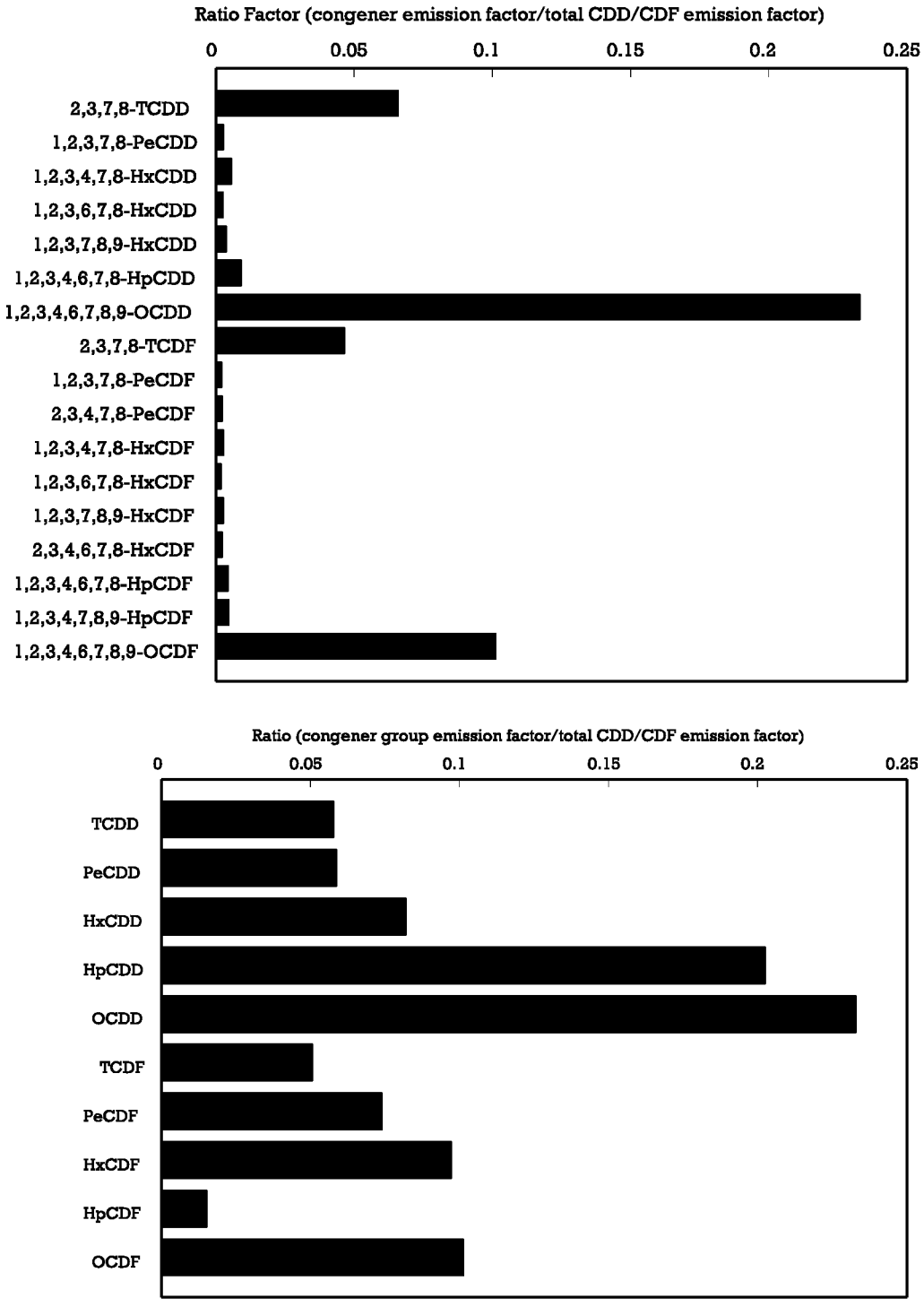


Figure 4-7. Congener and congener group profiles for air emissions from industrial oil-fueled boilers.

Source: U.S. EPA (1995b; 1997a).

(6.3 g I-TEQ_{DF}) from distillate oil combustion. Emission estimates for all reference years are assigned a low confidence rating on the basis of the low rating for the emission factor.

4.3.3. Used Oil Combustion

The emission factors derived by EPA (U.S. EPA, 1997a) and EPRI (1994) were based on combustion of virgin oil by utility boilers. Significantly greater emission factors have been reported by Bremmer et al. (1994) for combustion of used oil by smaller combustion units in the Netherlands. Flue gases from a garage stove consisting of an atomizer fueled by spent lubricating oil from diesel engines (35 mg Cl^-/kg) were reported to contain 0.1 ng I-TEQ_{DF}/Nm^3 (2,000 pg I-TEQ_{DF}/kg) oil burned. The flue gases from a hot water boiler consisting of a rotary cup burner fueled with the organic phase of rinse water from oil tanks (340 mg Cl^-/kg) contained 0.2 ng I-TEQ_{DF}/Nm^3 (4,800 pg I-TEQ_{DF}/kg) oil burned. The flue gases from a steam boiler consisting of a rotary cup burner fueled by processed spent oil (240 mg Cl^-/kg) contained 0.3 ng I-TEQ_{DF}/Nm^3 (6,000 pg I-TEQ_{DF}/kg) oil burned. The emission factor for a ferry burning heavy fuel oil containing 11 ng/kg organic chlorine was 3,200 to 6,500 pg I-TEQ_{DF}/kg oil burned. From these data, Bremmer et al. derived an average emission factor for combustion of used oil of 4,000 pg I-TEQ_{DF}/kg oil burned.

Bremmer et al. (1994) also reported measuring CDD/CDF emissions from a river barge and a container ship fueled with gas oil (less than 2 ng/kg organic chlorine). The exhaust gases contained from 0.002 to 0.2 ng I-TEQ_{DF}/Nm^3. From these data, Bremmer et al. derived an average emission factor for inland oil-fueled vessels of 1,000 pg I-TEQ_{DF}/kg oil burned.

The applicability of these emission factors to used oil combustors in the United States is uncertain. Therefore, estimates of potential emissions from used oil combustion in the United States are not being developed at this time.

4.4. COAL COMBUSTION

During 2000, coal consumption accounted for approximately 18.9% of the energy consumed in the United States from all sources (EIA, 1999). Of the 980 million metric tons of coal consumed in 2000, 891 million metric tons (90.9%) were consumed by electric utilities, including independent power producers; 85.4 million metric tons (8.7%) were consumed by the industrial sector, including 26.2 million metric tons consumed by coke plants; and 3.7 million metric tons (0.4%) were consumed by residential and commercial sources (EIA, 1999).

In 1995, coal consumption (872 million metric tons) accounted for approximately 22% of the energy consumed from all sources in the United States (U.S. DOC, 1997). Of this total,

88.4% (771 million metric tons) were consumed by electric utilities; 11% (96 million metric tons) were consumed by the industrial sector, including consumption of 30 million metric tons by coke plants; and 0.6% (5.3 million metric tons) were consumed by residential and commercial sources (EIA, 1997b).

In 1987 a total of 759 million metric tons of coal were consumed by electric utilities (651 million metric tons), coke plants (33.5 million metric tons), other industries (68.2 million metric tons), and the residential and commercial sectors (6.3 million metric tons) (EIA, 1995).

All of the above estimates are assigned a high confidence rating because they are based on detailed studies specific to the United States.

The following two sections discuss the results of relevant emission studies for the utility/industrial and residential sectors and present annual TEQ emission estimates for reference years 1987, 1995, and 2000.

4.4.1. Utilities and Industrial Boilers

Few studies have been performed to measure CDD/CDF concentrations in emissions from coal-fired plants. Those studies did not have the congener specificity or DLs necessary to fully characterize this potential source (U.S. EPA, 1987a; NATO, 1988; Wienecke et al., 1992). The results of more recent testing of coal-fired utility and industrial boilers in the Netherlands (Bremmer et al., 1994), the United Kingdom (Cains and Dyke, 1994; CRE, 1994), Germany (Umweltbundesamt, 1996), and the United States (Riggs et al., 1995; EPRI, 1994) have achieved lower DLs.

Bremmer et al. (1994) reported the results of emission measurements at two coal-fired facilities in the Netherlands. The emission factor reported for a pulverized coal electric power plant equipped with an ESP and a wet scrubber for sulfur removal was 0.35 ng I-TEQ_{DF}/kg coal combusted (0.02 ng I-TEQ_{DF}/Nm^3 at 11% oxygen). The emission factor reported for a grass-drying chain grate stoker equipped with a cyclone APCD was 1.6 ng I-TEQ_{DF}/kg coal fired (0.16 ng I-TEQ_{DF}/Nm^3 at 11% oxygen).

Cains and Dyke (1994) reported an emission factor of 102 to 109 ng I-TEQ_{DF}/kg of coal at a small-scale facility in the United Kingdom that was equipped with an APCD consisting of only a grit arrester. CRE (1994) reported results of testing at 13 commercial and industrial coal-fired boilers in the United Kingdom, with TEQ emission factors ranging from 0.04 to 4.8 ng I-TEQ_{DF}/kg coal combusted (mean value, 0.6 ng I-TEQ_{DF}/kg). CRE also reported testing results for one coal-fired power plant: 0.06 ng I-TEQ_{DF}/kg of coal combusted. Umweltbundesamt (1996) reported that the I-TEQ_{DF} content of stack gases from 16 coal-burning facilities in Germany

ranged from 0.0001 to 0.04 ng I-TEQ_{DF}/m^3; however, the data provided in that report did not enable emission factors to be calculated.

In 1993, the U.S. Department of Energy (DOE) sponsored a project to assess emissions of hazardous air pollutants at coal-fired power plants. As part of the project, CDD/CDF stack emissions were measured at seven U.S. coal-fired power plants. The preliminary results of the project, concentrations in stack emissions, were reported by Riggs et al. (1995) and are summarized in Table 4-23. The levels reported for individual 2,3,7,8-substituted congeners were typically very low (less than or equal to 0.033 ng/Nm^3) or not detected. In general, CDF levels were higher than CDD levels. OCDF and 2,3,7,8-TCDF were the most frequently detected congeners (at four of the seven plants). Table 4-24 presents characteristics of the fuel used and the APCD employed at each plant. Riggs et al. could not attribute variations in emissions between plants to any specific fuel or operational characteristic.

As mentioned in Section 4.3.2, EPRI sponsored the FCEM project to gather information of consistent quality on power plant emissions. Testing for CDD/CDF emissions was performed on four coal-fired power plants equipped with cold-sided ESPs. Two plants burned bituminous coal and two burned sub-bituminous coal. The results of the testing were integrated into the final results of the DOE project discussed above (Riggs et al., 1995) and published in 1994 (EPRI, 1994). The average congener and congener group emission factors derived from this 11-facility data set, as reported in EPRI (1994), are presented in Table 4-25. Congener and congener group profiles for the data set are presented in Figure 4-8. Assuming nondetect values were zero, the average emission factor was 0.078 ng TEQ_{DF}-WHO_{98}/kg (0.079 ng I-TEQ_{DF}/kg) coal combusted. A medium confidence rating is assigned to the emission factors derived from the DOE and EPRI studies because they were based on recent testing at U.S. power plants.

Because the EPRI and DOE data characterized emissions from units with only cold-sided ESPs, there has been uncertainty regarding the applicability of the emission factors derived from these data to units with hot-sided ESPs. In July 1999, EPA conducted testing of stack emissions at a coal-fired utility equipped with a hot-sided ESP. The preliminary results of this testing indicated that the TEQ emission factor for hot-sided ESPs is of the same order of magnitude as the average TEQ emission factors derived above.

Table 4-23. CDD/CDF concentrations (pg/Nm^3) in stack emissions from U.S. coal-fired power plants

Congener/congener group	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6	Plant 7
2,3,7,8-TCDD			1				
1,2,3,7,8-PeCDD	ND (3.5)	ND (3.5)		ND (2)	ND (3.3)	ND (2.6)	ND (1.7)
1,2,3,4,7,8-HxCDD	ND (0.56)	ND (4.8)	ND (1.8)	ND (10)	ND (4.8)	ND (3.2)	ND (1.8)
1,2,3,6,7,8-HxCDD	ND (0.56)	ND (5.7)	ND (3.6)	ND (10)	ND (15.4)	ND (2.7)	ND (2)
1,2,3,7,8,9-HxCDD	ND (0.44)	5	ND (1.8)	ND (10)	ND (9.9)	ND (4.2)	ND (1.4)
1,2,3,4,6,7,8-HpCDD	ND (0.56)	4.9	ND (1.8)	ND (10)	ND (12.1)	ND (4.3)	ND (1.2)
OCDD	ND (12)	29	ND (1.8)	ND (10)	ND (26.4)	4.3	2.4
		32	ND (14)	ND (20)	ND (131)	20	21.6
2,3,7,8-TCDF		8.1	7.8				0.7
1,2,3,7,8-PeCDF	ND (1.7)		7.2	ND (2)	ND (3.3)	ND (5.7)	
2,3,4,7,8-PeCDF	ND (1)	ND (5.7)	6.6	ND (10)	ND (3.2)	15	ND (1.1)
1,2,3,4,7,8-HxCDF	2.4	ND (19)	8.4	ND (10)	ND (3.2)	ND (4.8)	ND (1.4)
1,2,3,6,7,8-HxCDF	3.3	16	2.9	ND (10)	ND (16.4)	ND (5.1)	ND (1.8)
1,2,3,7,8,9-HxCDF	1.1			ND (10)		ND (4)	ND (1.3)
2,3,4,6,7,8-HxCDF		ND (5)		ND (10)	ND (5.8)	ND (6.9)	ND (1.5)
1,2,3,4,6,7,8-HpCDF	ND (0.44)	11	ND (1.8)	ND (10)	ND (8.8)	ND (2.5)	ND (2)
1,2,3,4,7,8,9-HpCDF	ND (2)	3	3	ND (10)	ND (16.4)		ND (2.2)
OCDF		ND (4.2)	6	ND (10)	ND (23)	ND (30)	ND (2.1)
	ND (0.63)	2		ND (10)	ND (15.4)	ND (5)	11.4
	5.6	ND (6.3)	ND (3.6)	ND (10)	ND (131)		
		33	2.4	ND (20)		ND (19)	
Total 2,3,7,8-CDD	0	70.9	1	0	0	24.3	24
Total 2,3,7,8-CDF	14.4	97.1	44.3	0	0	13	12.1
Total TCDD	1.8	12	12		6.7		
Total PeCDD		4.4	6			ND (2.6)	ND (55)
Total HxCDD	ND (1)	18	2.7	NR	ND (4.7)	ND (3.2)	ND (32)
Total HpCDD	1.3	45		ND (10)	ND (26.3)	ND (4)	ND (24)
Total OCDD	3.4	32	ND (2.4)	ND (10)	ND (26.4)	ND (14)	
Total TCDF	ND (12)	29	ND (14)	ND (10)	ND (131)	20	ND (8.2)
Total PeCDF		33	78	ND (20)		88	21.6
Total HxCDF	ND (5.2)	39	61		ND (3.3)	14	
Total HpCDF	2.4	34	29	ND (2)	ND (6.6)		ND (37)
Total OCDF	7.6	33	9	ND (10)	ND (16.4)		3
	4.3		2.4	ND (10)	ND (29.5)	ND (5)	ND (27)
	5.6			ND (10)	ND (131)	ND (20)	2.9
				ND (20)		ND (19)	11.4
Total CDD/CDF	29.4	279.4	200.1	0	6.7	122	38.9

ND = Not detected; value in parenthesis is the detection limit
NR = Not reported; suspected contamination problem

Source: Riggs et al. (1995).

Table 4-24. Characteristics of U.S. coal-fired power plants tested by the U.S. Department of Energy

Plant no.	Coal type	Coal chlorine content (mg/kg)	Temperature (°C)[a]			
			ESP	FF	FGD	Stack
1	Bituminous	800	160	–	–	160
2	Bituminous	1,400	130	–	–	130
3	Sub-bituminous	300	–	150	–	150
4	Sub-bituminous	390	–	70	130	75
5	Bituminous	1,400	130	–	120	40
6	Lignite	400	170	–	170	110
7	Bituminous	1,000	150	–	–	150

[a]Temperature at pollution control device and stack.

ESP = Electrostatic precipitator
FF = Fabric filter
FGD = Flue gas desulfurization system

Source: Riggs et al. (1995).

Applying the TEQ emission factor of 0.078 ng TEQ_{DF}-WHO_{98}/kg (0.079 ng I-TEQ_{DF}/kg) coal combusted to the consumption totals of 651, 771, and 891 million metric tons of coal consumed by U.S. utility sectors in 1987, 1995, and 2000, respectively, yields estimated annual emissions by the utility sector of 50.89 g TEQ_{DF}-WHO_{98} (51.4 g I-TEQ_{DF}) in 1987, 60.1 g TEQ_{DF}-WHO_{98} (60.9 g I-TEQ_{DF}) in 1995, and 69.5 g TEQ_{DF}-WHO_{98} (70.4 g I-TEQ_{DF}) in 2000. These emission estimates are assigned a medium confidence rating because the emission factor rating for this category was judged to be medium.

No testing results could be located for CDD/CDF content in air emissions from commercial and industrial coal-fired combustion units in the United States. It is uncertain whether the data collected in the European studies (Bremmer et al., 1994; CRE, 1994) accurately represent U.S. sources, but the data suggest that emission factors for commercial/industrial sources might be higher than those reported for U.S. coal-fired utilities. Therefore, no national emission estimate has been derived for this category. However, preliminary estimates of potential national TEQ emissions from this source category can be derived for 1987, 1995, and 2000 using the total coal consumption for each of those reference years, excluding consumption by coke plants, and the average emission factor, 0.6 ng I-TEQ_{DF}/kg coal combusted.

Table 4-25. CDD/CDF emission factors (ng/kg coal) for coal-fired utility/industrial power plants[a]

Congener/congener group	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	0.005	0.018
1,2,3,7,8-PeCDD	0	0.016
1,2,3,4,7,8-HxCDD	0	0.034
1,2,3,6,7,8-HxCDD	0.004	0.028
1,2,3,7,8,9-HxCDD	0.004	0.035
1,2,3,4,6,7,8-HpCDD	0.216	0.241
OCDD	0.513	0.644
2,3,7,8-TCDF	0.109	0.117
1,2,3,7,8-PeCDF	0.007	0.021
2,3,4,7,8-PeCDF	0.074	0.084
1,2,3,4,7,8-HxCDF	0.098	0.12
1,2,3,6,7,8-HxCDF	0.014	0.03
1,2,3,7,8,9-HxCDF	0.013	0.038
2,3,4,6,7,8-HxCDF	0.043	0.06
1,2,3,4,6,7,8-HpCDF	0.354	0.385
1,2,3,4,7,8,9-HpCDF	0.087	0.112
OCDF	0.158	0.281
Total I-TEQ_{DF}	0.078	0.124
Total TEQ_{DF}-WHO_{98}	0.078	0.131
Total TCDD	0.051	0.052
Total PeCDD	0.014	0.015
Total HxCDD	0.03	0.03
Total HpCDD	0.063	0.074
Total OCDD	0.513	0.644
Total TCDF	0.154	0.158
Total PeCDF	0.18	0.18
Total HxCDF	0.104	0.104
Total HpCDF	0.064	0.064
Total OCDF	0.158	0.281
Total CDD/CDF	1.331	1.602

[a]Eleven-facility data set.

Source: EPRI (1994).

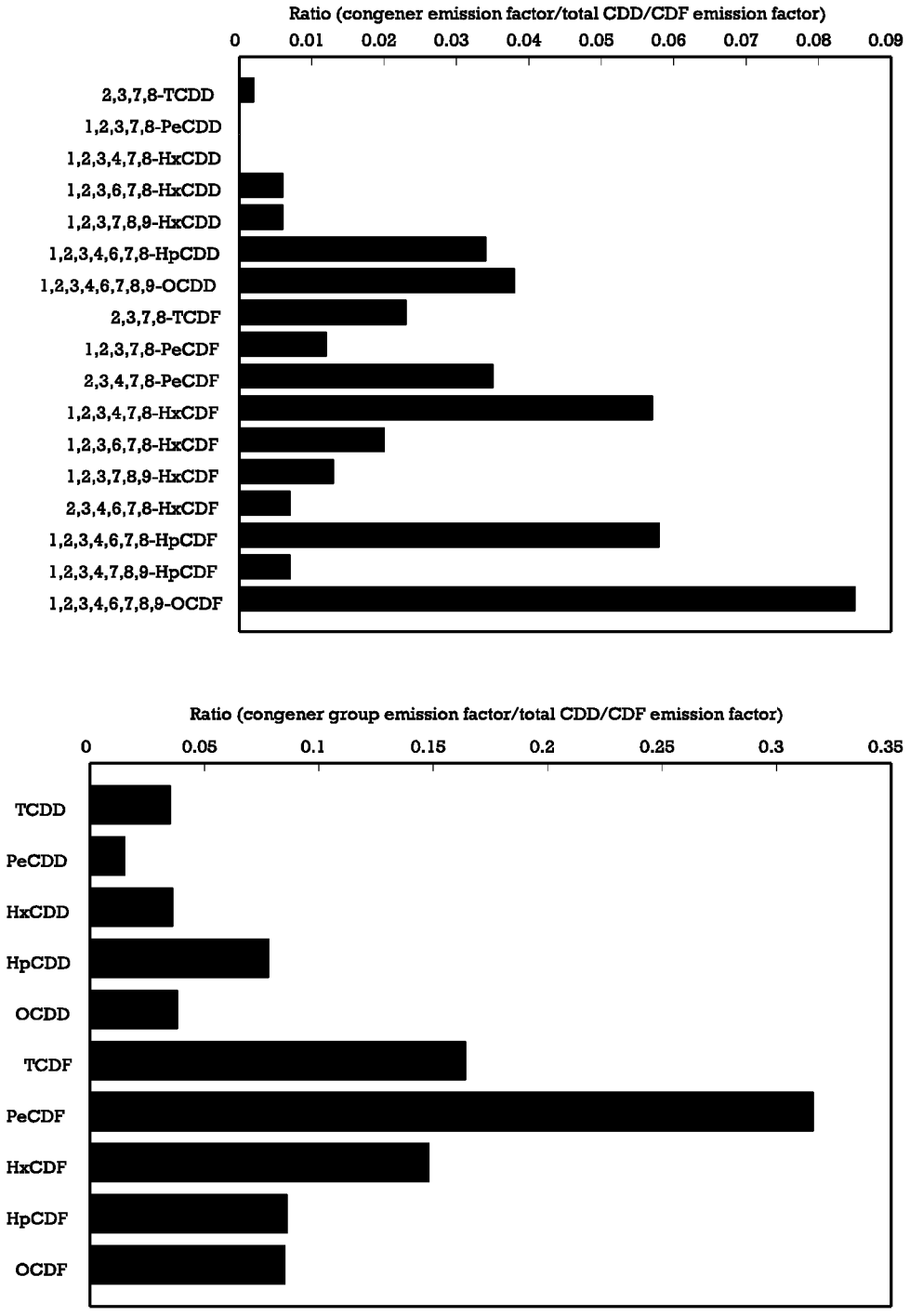


Figure 4-8. Congener and congener group profiles for air emissions from industrial/utility coal-fueled combustors (nondetects set equal to zero**).**

Source: EPRI (1994).

Applying the emission factor to the estimated combustion for 1987, 1995, and 2000 (68.2, 66, and 59.14 million metric tons, respectively) yields 40.9 g I-TEQ_{DF}/kg for 1987, 39.6 g I-TEQ_{DF}/kg for 1995, and 35.4 g I-TEQ_{DF}/kg coal combusted for 2000. These estimates should be regarded as preliminary indications of possible emissions from commercial/industrial coal-fired boilers; further testing is needed to confirm the true magnitude of these emissions. These emission estimates are assigned a Category D uncertainty rating because the emission factor has been judged to be clearly nonrepresentative of commercial and industrial coal-fired combustion units.

4.4.2. Residential Coal Combustion

In the residential sector, coal is usually combusted in underfed or hand-stoked furnaces. Other coal-fired heating units include hand-fed room heaters, metal stoves, and metal and masonry fireplaces. Stoker-fed units are the most common design for warm-air furnaces and for boilers used for steam or hot water production. Most coal combusted in these units is either bituminous or anthracite. These units operate at relatively low temperatures and do not efficiently combust the coal. Coal generally contains small quantities of chlorine; therefore, the potential for CDD/CDF formation exists. Typically, coal-fired residential furnaces are not equipped with PM or gaseous pollutant control devices that may limit emissions of any CDDs/CDFs formed (U.S. EPA, 1997b). No testing results for CDD/CDF content in air emissions from residential/commercial coal-fired combustion units in the United States could be located; however, several relevant studies have been performed in European countries.

Thub et al. (1995) measured flue gas concentrations of CDDs/CDFs from a household heating system in Germany that was fired with either salt lignite coal (total chlorine content of 2,000 ppm) or normal lignite coal (total chlorine content of 300 ppm). CDDs/CDFs were detected in the flue gases generated by combustion of both fuel types (see Table 4-26). The congener profiles and patterns were similar for both fuel types, with OCDD the dominant congener and TCDF the dominant congener group. However, the emissions were higher by a factor of 8 for the "salt" coal (0.109 ng I-TEQ_{DF}/m^3 [2.74 ng I-TEQ_{DF}/kg]) than for the "normal" coal (0.015 ng I-TEQ_{DF}/m^3 [0.34 ng I-TEQ_{DF}/kg]).

Using the results of testing performed by the Coal Research Establishment in the United Kingdom, Eduljee and Dyke (1996) estimated emission factors for residential coal combustion units of 2.1 ng I-TEQ_{DF}/kg for anthracite coal and 5.7 to 9.3 ng I-TEQ_{DF}/kg (midpoint, 7.5 ng I-TEQ_{DF}/kg) for bituminous coal.

Table 4-26. CDD/CDF emission factors (ng/kg coal) for residential coal combustors

Congener	"Salt" lignite[a]	"Normal" lignite[a]	Anthracite[b]	Bituminous[b]
2,3,7,8-TCDD	0.58	0.06	1.6	2.4
1,2,3,7,8-PeCDD	0.73	0.08	NR	NR
1,2,3,4,7,8-HxCDD	0.63	0.06	NR	NR
1,2,3,6,7,8-HxCDD	0.6	0.09	NR	NR
1,2,3,7,8,9-HxCDD	0.4	0.06	NR	NR
1,2,3,4,6,7,8-HpCDD	3.24	0.59	NR	NR
OCDD	16.19	2.42	77	120
2,3,7,8-TCDF	2.49	0.5	42	63
1,2,3,7,8-PeCDF	2.24	0.43	NR	NR
2,3,4,7,8-PeCDF	2.09	0.31	NR	NR
1,2,3,4,7,8-HxCDF	0.38	0.13	NR	NR
1,2,3,6,7,8-HxCDF	1.86	0.36	NR	NR
1,2,3,7,8,9-HxCDF	0.07	0.02	NR	NR
2,3,4,6,7,8-HxCDF	1.01	0.12	NR	NR
1,2,3,4,6,7,8-HpCDF	2.59	0.95	NR	NR
1,2,3,4,7,8,9-HpCDF	0.25	0.06	NR	NR
OCDF	0.63	0.3	4.2	6.3
Total 2,3,7,8-CDD[c]	22.37	3.38	NR	NR
Total 2,3,7,8-CDF[c]	13.6	3.2	NR	NR
Total I-TEQ_{DF}[c]	2.74	0.34	60	98.5
Total TCDD	14.23	9	61.6	92.4
Total PeCDD	14.15	2.22	31	46
Total HxCDD	11.14	1.81	60	90
Total HpCDD	7.06	0.82	57	86
Total OCDD	16.19	2.42	77	120
Total TCDF	80.34	20.33	412	613
Total PeCDF	29.21	8.98	340	550
Total HxCDF	12.72	3.78	130	190
Total HpCDF	3.87	1.27	32	47
Total OCDF	0.63	0.3	4.2	6.3
Total CDD/CDF	189.5	50.9	1,205	1,841

[a]Source: Thub et al. (1995); listed results represent means of three flue gas samples.

[b]Source: U.S. EPA (1997a); based on average particulate CDD/CDF concentrations from chimney soot samples collected from seven coal ovens and particulate emission factors for anthracite and bituminous coal combustion.

[c]Values as reported in sources.

NR = Not reported

CDD/CDF emission factors were estimated (U.S. EPA, 1997a) for coal-fired residential furnaces using average particulate CDD/CDF concentrations from chimney soot samples collected from seven coal ovens and PM emission factors obtained from AP-42 that are specific to anthracite and bituminous coal combustion (U.S. EPA, 1995a). The TEQ emission factors estimated (60 and 98.5 ng I-TEQ_{DF}/kg anthracite and bituminous coal, respectively) were derived using the calculated emission factors for 2,3,7,8-TCDD, 2,3,7,8-TCDF, and the 10 congener groups (U.S. EPA, 1997a). EPA stated that the estimated factors should be considered representative of maximum emission factors because soot may not be representative of the PM actually emitted to the atmosphere. These emission factors are presented in Table 4-26; congener group profiles are presented in Figure 4-9.

Although the congener group profiles of the measurements by Thub et al. (1995) and the estimates by EPA (U.S. EPA, 1997a) are similar, the TEQ emission factors of the two studies differ by factors of 175 to 289. The emission factors used by Eduljee and Dyke (1996) to estimate national annual TEQ emissions from residential coal combustion in the United Kingdom fall in between the other two sets of estimates but are still about one to two orders of magnitude greater than the estimated emission factor for industrial and utility coal combustors (see Section 4.4.1).

For 1987 and 1995, preliminary estimates of potential national TEQs were derived using the emission factors from Eduljee and Dyke (1996). U.S. EPA (1997a) reported that 72.5% of the coal consumed by the residential sector in 1990 was bituminous and 27.5% was anthracite. Assuming that these relative proportions reflect the actual usage in 1987 and 1995, then application of the emission factors from Eduljee and Dyke (2.1 ng I-TEQ_{DF}/kg anthracite coal and 7.5 ng I-TEQ_{DF} bituminous coal) to the consumption values of 6.3 and 5.3 million metric tons in 1987 and 1995, respectively (U.S. DOC, 1997), results in estimated TEQ emissions of 37.9 and 32.0 g I-TEQ_{DF} in 1987 and 1995, respectively. These estimates should be regarded as preliminary indications of possible emissions from this source category because the emission factor is judged to be clearly nonrepresentative of the sources. Further testing is needed to confirm the true magnitude of these emissions.

For 2000, OAQPS developed national emission estimates for coal combustion for residential heating. The activity level for residential coal combustion was taken from state-level 2000 activity data (EIA, 2003a). Because EIA no longer disaggregates coal consumption into anthracite versus bituminous/lignite, OAQPS estimated each state's coal consumption using the state's 1999 proportion of anthracite versus bituminous/lignite to total coal consumption. Emissions were allocated to the county level as a proportion of state population in states that consume anthracite coal and bituminous and lignite coal for residential heating. OAQPS estimated that in 2000, 67,400 metric tons of anthracite coal and 343,000 metric tons of

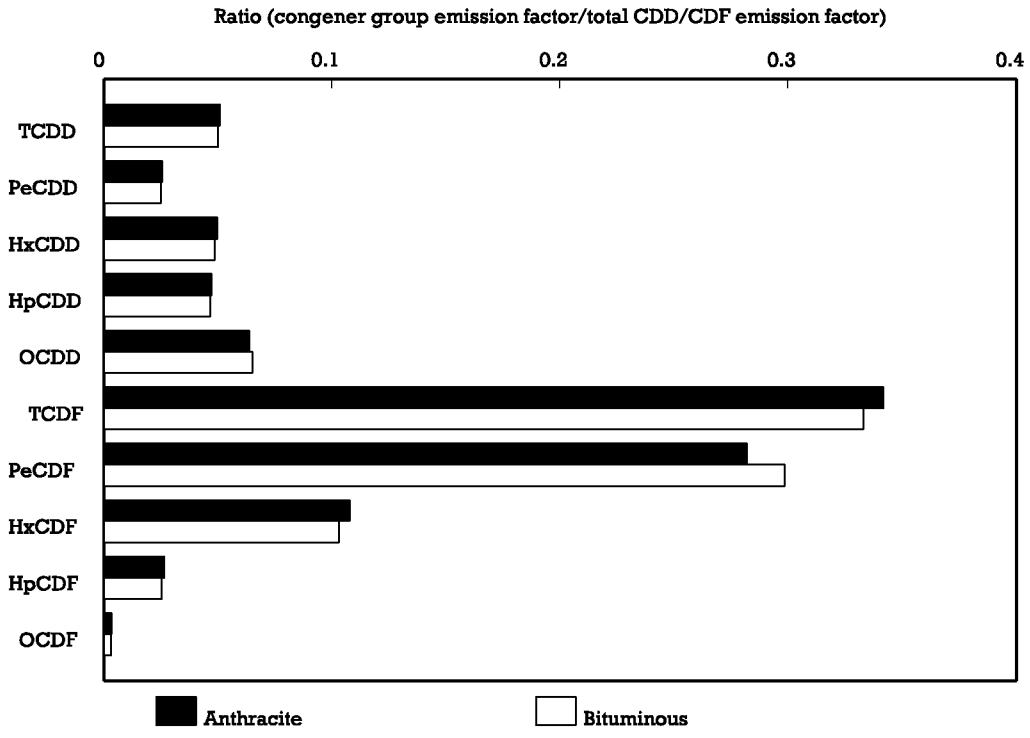


Figure 4-9. Congener group profile for air emissions from residential coal-fueled combustors.

Source: U.S. EPA (1997a).

bituminous and lignite coal were consumed for residential heating. Applying the TEQ emission factors of 2.1 ng I-TEQ_{DF}/kg anthracite coal combusted and 7.5 ng I-TEQ_{DF}/kg bituminous coal combusted (Eduljee and Dyke, 1996) to these production factors yields preliminary estimates of annual emissions of 0.14 g I-TEQ_{DF} of anthracite coal and 2.6 g I-TEQ_{DF} of bituminous/sub-bituminous coal in 2000. These emission estimates are assigned a Category D uncertainty rating because the emission factor has been judged to be clearly nonrepresentative of residential coal combustion.

4.4.3. Solid Wastes from Coal Combustion

A limited amount of CDD/CDF concentration data have been developed for utility industry solid wastes (U.S. EPA, 1999c), and these data are for wastes that are comanaged (i.e., combinations of fly ash, bottom ash, boiler slag, and flue gas desulfurization wastes). A total of 15 samples were taken from 11 disposal sites. The average concentration for each of the CDD

and CDF congeners is presented in the second column of Table 4-27. It should be noted that most of the concentration values shown in Table 4-27 represent DLs. Consequently, the values overestimate actual concentrations.

U.S. EPA (1999d) indicates that approximately 63 million tons (assumed to be short tons, i.e., 2,000 pounds) of large-volume utility coal combustion solid wastes were produced in 1995. Of this amount, about 67% was landfilled and the balance was disposed of in surface impoundments. The concentration data presented in Table 4-27 are for only the 53 million tons that were comanaged (about 84% of the total wastes). For purposes of this analysis it is assumed that the CDD/CDF concentrations in the comanaged wastes are the same as for the entire waste quantity. Combining the concentration data with the 63 million tons of total waste yields the total quantities of each congener disposed of in 1995. These data are presented in the fourth column of Table 4-27. As indicated in Section 4.4 of this document, total consumption of coal for electric utility boilers in 1987 was 98.4% of 1995 consumption. Consequently, the quantities of CDDs/CDFs disposed of in 1987 is assumed to be 98.4% of the 1995 values. These values are presented in column 3 of Table 4-27. The 1995 congener quantities are converted into I-TEQ_{DF} and TEQ_{DF}-WHO_{98} values in columns 5 and 6. Because disposal of these wastes does not constitute an environmental release, the values are not included in the inventory.

Table 4-27. CDD/CDF concentrations and amounts disposed of in solid wastes from coal-fired utilities

Congener	Mean concentration[a] (ng/kg)	Disposed of in solid waste in 1987 (g/yr)[b]	Disposed of in solid waste in 1995 (g/yr)[c]	I-TEQ_{DF} /yr 1995 (g)	TEQ_{DF}-WHO_{98}/yr 1995 (g)
2,3,7,8-TCDD[d]	0.17	10	10	9.72	9.72
1,2,3,7,8-PeCDD[d]	0.25	14	14	7.15	14.3
1,2,3,4,7,8-HxCDD[d]	0.35	20	20	2	2
1,2,3,6,7,8-HxCDD[d]	0.28	16	16	1.6	1.6
1,2,3,7,8,9-HxCDD[e]	0.3	17	17	1.72	1.72
1,2,3,4,6,7,8-HpCDD[f]	0.59	33	34	0.34	0.34
OCDD[g]	10.54	593	603	0.6	0.6
2,3,7,8-TCDF[h]	0.19	11	11	1.09	1.09
1,2,3,7,8-PeCDF[d]	0.17	10	10	0.49	0.49
2,3,4,7,8-PeCDF[d]	0.17	10	10	4.86	4.86
1,2,3,4,7,8-HxCDF[e]	0.25	14	14	1.43	1.43
1,2,3,6,7,8-HxCDF[d]	0.18	10	10	1.03	1.03
2,3,4,6,7,8-HxCDF[d]	0.28	16	16	1.6	1.6
1,2,3,7,8,9-HxCDF[d]	0.24	14	14	1.37	1.37
1,2,3,4,6,7,8-HpCDF[e]	0.29	16	17	0.17	0.17
1,2,3,4,7,8,9-HpCDF[d]	0.35	20	20	0.2	0.2
OCDF[i]	0.59	33	34	0.03	<0.01
TOTAL				35.41	41.98

[a]Source: U.S. EPA (1999c, Table 2-9).
[b]Assumes that solid waste quantity for 1987 was 98.4% of 1995 quantity, based on total utility coal use in those years (see Section 4.4).
[c]Based on EPRI estimate of 63 million tons/yr of large-volume utility coal combustion solid wastes. See Section 3.3 of U.S. EPA (1999d). Assumes all waste characteristics were the same as for comanaged wastes.
[d]All 17 analyses were nondetects.
[e]Sixteen of the 17 analyses were nondetects.
[f]Eleven of the 17 analyses were nondetects.
[g]Five of the 17 analyses were nondetects.
[h]Fourteen of the 17 analyses were nondetects.
[i]Fifteen of the 17 analyses were nondetects.

5. COMBUSTION SOURCES OF CDDs/CDFs: OTHER HIGH-TEMPERATURE SOURCES

5.1. CEMENT KILNS

This section addresses CDD/CDF emissions from Portland cement kilns. These facilities use high temperatures to convert mineral feedstocks into Portland cement and other types of construction materials. For purposes of this analysis, cement kilns are divided into two categories: those that burn hazardous waste as a supplementary fuel and those that do not. For the 1987 and 1995 estimates, the hazardous waste-burning cement kiln category was further divided into kilns with inlet air pollution control device (APCD) temperatures above 232°C and those with APCD temperatures below 232°C. Cement kiln technology, the derivation of TEQ emission factors for cement kilns that burn hazardous waste as supplemental fuel and those that do not, and the derivation of annual TEQ air emissions (g/yr) for reference years 1987, 1995, and 2000 are discussed below.

5.1.1. Process Description of Portland Cement Kilns

In the United States, the primary cement product is Portland cement. Portland cement is a fine, gray powder consisting of a mixture of four basic materials: lime, silica, alumina, and iron compounds. Cement production involves heating (pyroprocessing) the raw materials to a very high temperature in a rotary (rotating) kiln to induce chemical reactions that produce a fused material called clinker. The cement clinker is then ground into a fine powder and mixed with gypsum to form the Portland cement.

The cement kiln is a large, steel, rotating cylindrical furnace lined with refractory material. The kiln is aligned on a slight angle, usually a slope of 3 to 6 degrees, which allows the materials to pass through the kiln by gravity. The kiln rotates at about 50 to 70 revs/hr, and the rotation induces mixing and the downward movement of mixed materials. The upper end of the kiln, known as the cold end, is generally where the raw materials, or meal, are fed into the kiln. Midpoint injection is practiced at some facilities. The lower end of the kiln, known as the hot end, is where the combustion of primary fuels (usually coal and petroleum coke) occurs, producing a high temperature. The cement kiln operates using countercurrents: hot combustion gases are convected up through the kiln while the raw materials pass down toward the lower end. As the meal moves through the cement kiln and is heated by hot combustion gases, water is vaporized and pyroprocessing of materials occurs.

The cement kiln consists of three thermal zones to produce cement clinker. Zone 1 is at the upper end of the kiln where the raw meal is added. Temperatures in this zone typically range from ambient up to 600°C. In this area of the kiln, moisture is evaporated from the raw meal.

Zone 2 is known as the calcining zone. Calcining occurs when the hot gases from the combustion of primary fuels dissociate calcium dioxide from the limestone and form calcium oxide. In this zone, temperatures range from 600 to 900°C. Zone 3, the burning or sintering zone, is the lowest and hottest region of the kiln. Here, temperatures in excess of 1,500°C induce the calcium oxide to react with silicates, iron, and aluminum in the raw materials to form the cement clinker. The formation of clinker actually occurs close to the combustion of primary fuel. The chemical reactions that occur in zone 3 are referred to as pyroprocessing.

The cement clinker, which leaves the kiln at the hot end, is a gray, glass-hard material consisting of dicalcium silicate, tricalcium silicate, calcium aluminate, and tetracalcium aluminoferrite. At this point, the temperature of the clinker is about 1,100°C. The hot clinker is then dumped onto a moving grate, where it cools as it passes under a series of cool-air blowers. After it is cooled to ambient temperature, the clinker is ground into a fine powder and mixed with gypsum to produce the Portland cement product.

Cement kilns can be either wet process or dry process. In the wet process, the raw materials are ground and mixed with water to form a slurry, which is fed into the kiln through a pump. This is an older process. A greater amount of heat energy is needed in the wet process kiln than in other types of kilns. These kilns consume about 5 to 7 trillion Btu per ton of clinker product to evaporate the additional water. In the dry process, a preheater is used to dry the raw meal before it enters the kiln. A typical preheater consists of a vertical tower containing a series of cyclone-type vessels. Raw meal is added at the top of the tower and hot exhaust gases from the kiln operation preheat the meal, thus lowering the fuel consumption of the kiln. Dry kilns are now the most popular type of cement kiln.

Portland cement clinker production in the United States is estimated to have been 52 billion kg in 1987 (U.S. DOC, 1996), 67.6 billion kg in 1995 (U.S. DOC, 1996), and 75.2 billion kg in 2000 (PCA, 2001). The 2000 estimate is based on the assumption that of the annual maximum clinker capacity reported for that reference year (PCA, 2001), only 90% was actually produced (e-mail dated January 31, 2003, from Garth Hawkins, Portland Cement Association, to Karie Riley, Versar, Inc.).

5.1.2. Cement Kilns That Burn Hazardous Waste

The high temperatures achieved in cement kilns make the kilns an attractive technology for combusting hazardous waste as supplemental fuel. Sustaining the relatively high combustion temperatures that are needed to form cement clinker (1,100 to 1,500°C) requires the burning of a fuel with a high energy output. Therefore, coal or petroleum coke is typically used as the primary fuel source. Because much of the cost of operating the cement kiln at high temperatures is associated with the consumption of fossil fuels, some cement kiln operators burn hazardous

liquid and solid waste as supplemental fuel. In 2000, approximately 60% of all facilities burned hazardous waste as the primary fuel to offset the amount of coal/coke purchased and burned by the kiln (PCA, 2001). Organic hazardous waste may have a heating value similar to that of coal (9,000 to 12,000 Btu/lb for coal). The kiln operator may charge the waste generator a disposal fee to combust the hazardous waste; this fee also offsets the cost of kiln operation. The high-energy and ignitable wastes include diverse substances, such as waste oils, spent organic solvents, sludges from the paint and coatings industry, waste paints and coatings from auto and truck assembly plants, and sludges from the petroleum refining industry (Greer et al., 1992).

The conditions in the cement kiln mimic conditions of hazardous waste incineration. For example, the gas residence time in the burning zone is typically 3 sec at temperatures in excess of 1,500°C (Greer et al., 1992). The method of introducing liquid and solid hazardous waste into the kiln is a key factor in the complete consumption of the waste during the combustion of the primary fuel. Liquid hazardous waste is either injected separately or blended with the primary fuel (coal). Solid waste is mixed and burned along with the primary fuel.

Trial burns have consistently shown that destruction and removal efficiencies of 99.99 to 99.9999% can be achieved for very stable organic wastes using cement kilns (Greer et al., 1992). Hazardous waste was combusted at 34 of the 212 kilns operating in 1995 (Federal Register, 1996a) and at 33 of the 201 kilns operating in 2000 (e-mail correspondence dated February 24, 2003, between M. Benoit, Cement Kiln Recycling Coalition, and K. Riley, Versar, Inc.; PCA, 2001). Other types of supplemental fuel used by these facilities include natural gas, fuel oil, automobile tires, used motor oil, sawdust, and scrap wood chips.

5.1.3. Air Pollution Control Devices

The pyroprocessing of raw meal in a cement kiln also produces fine particulates, referred to as cement kiln dust (CKD). CKD is collected and controlled with fabric filters (FFs), electrostatic precipitators (ESPs), or both. Acid gases such as sulfur dioxide (SO_2) can be formed during pyroprocessing of the sulfur-laden minerals and fuels, but the minerals have high alkalinity, which partially neutralizes SO_2 gases. Most APCDs used at cement kilns in 1987 and 1995 were considered to be hot-sided control devices. A hot-sided control device is one that operates at kiln exhaust gas temperatures above 232°C (some EPA rules use different definitions for hot-sided control devices for different industries). Most APCDs currently used at cement kilns are cold-sided devices (i.e., they operate at kiln exhaust gas temperatures below 232°C.

Reducing the temperature at the inlet of the APCD is one factor that has been shown to have a significant impact on limiting dioxin formation and emissions at cement kilns (U.S. EPA, 1997c). Emissions testing at a Portland cement kiln showed that CDDs/CDFs were almost entirely absent at the inlet to a hot-sided ESP, but measurements taken at the exit showed

conclusively that dioxins were formed within the hot-sided ESP (U.S. EPA, 1997c). Reducing the kiln exhaust gas temperature in the APCD to below 232°C has been shown to substantially limit CDD/CDF formation. Lower temperatures are believed to prevent the post-combustion catalytic formation of CDDs/CDFs. Consequently, a number of cement kilns have added exhaust gas-quenching units upstream of the APCD to reduce the inlet APCD temperature, thereby reducing CDD/CDF stack concentrations. A quenching unit usually consists of a water spray system within the flue duct.

5.1.4. CDD/CDF Emissions Data

The general strategy used to derive emission factors for this report was to divide each source category on the basis of design and operation. However, because cement kilns are relatively uniform in terms of kiln design, raw feed material, operating temperatures, and APCDs, they have been categorized, as noted above, only on the basis of whether or not hazardous waste is burned as a supplementary fuel.

CDD/CDF emissions data from tests conducted between 1989 and 1996 were obtained for 16 cement kilns burning hazardous waste and 15 cement kilns burning nonhazardous waste (U.S. EPA, 1996b). More recent CDD/CDF emissions data were also obtained from tests conducted in 2000 at 3 cement kilns burning hazardous waste (U.S. EPA, 2002a) and from tests conducted in June and July of 1999 at one facility burning nonhazardous waste (Bell, 1999). The majority of stack emissions data from cement kilns burning hazardous waste were derived during trial burns and may overestimate the CDD/CDF emissions that most kilns achieve during normal operations. Stack emissions data from kilns burning nonhazardous waste were derived from testing during normal operations.

5.1.4.1. *Emissions Data for 1989 Through 1996* (U.S. EPA, 1996b)

The average TEQ emission factors for this period, based on the data reported by EPA in 1996 (U.S. EPA, 1996b), were 0.000941 to 232 ng TEQ_{DF}-WHO_{98}/kg (average of 22.48 ng TEQ_{DF}-WHO_{98}/kg [20.91 ng I-TEQ_{DF}/kg]) clinker produced for cement kilns burning hazardous waste and 0.000012 to 2.76 ng TEQ_{DF}-WHO_{98}/kg (average of 0.29 ng TEQ_{DF}-WHO_{98}/kg [0.27 ng I-TEQ_{DF}/kg]) clinker produced for cement kilns burning nonhazardous waste.

These data show that the average emission factor for kilns burning hazardous waste was about 90 times greater than that for kilns burning nonhazardous waste. However, it should be noted that the average emission factor for kilns burning hazardous waste was derived from "near worst case" testing of hazardous waste-burning kilns. As discussed in Section 5.1.8, a comparison of CDD/CDF concentrations in CKD samples shows a similar relationship (i.e., the CDD/CDF TEQ concentration of the CKD from kilns burning hazardous waste was about 100

times higher than that of the dust from kilns burning nonhazardous waste). Although the average emission factors for the two groups of kilns differ substantially, the emission factors for individual kilns in the two groups overlap. Therefore, other aspects of the design and operation of the kilns—in particular, the temperature of the APCD equipment (as discussed in Section 5.1.3)—were likely affecting CDD/CDF emissions.

Previous attempts to understand these differences using parametric testing of cement kilns yielded mixed results. EPA (U.S. EPA, 1997c) conducted a limited comparison of CDD/CDF TEQ stack gas concentrations (ng TEQ/dscm) between cement kilns burning hazardous wastes and those not burning hazardous wastes. Those comparisons were made at 14 cement kilns. With the exception of the fuel being burned, operating conditions (e.g., APCD temperature) were the same or similar for each set of comparisons. Baseline conditions used coal as the only primary fuel. The results of these comparisons found:

- seven kilns in which the baseline (i.e., no combustion of hazardous waste) CDD/CDF TEQ stack gas concentrations were about the same as those for the burning of hazardous wastes,
- two kilns in which the baseline CDD/CDF I-TEQ_{DF} stack gas concentrations were about double those for the burning of hazardous wastes, and
- five kilns in which the hazardous waste CDD/CDF I-TEQ_{DF} stack gas concentrations were substantially greater (3- to 29-fold greater) than those for the baseline operating conditions.

Subsequently, EPA's Office of Research and Development (ORD) conducted analyses of the available emissions data to evaluate, on a congener-specific basis, whether there were significant differences in emission factors between (a) kilns burning hazardous waste and those burning nonhazardous waste, (b) kilns with APCD inlet temperatures greater than 232°C and those with temperatures less than 232°C, (c) hazardous waste-burning and nonhazardous waste-burning facilities with APCD inlet temperatures greater than 232°C, (d) hazardous waste-burning and nonhazardous waste-burning facilities with APCD inlet temperatures less than 232°C, (e) hazardous waste-burning facilities with APCD inlet temperatures less than and greater than 232°C, and (f) nonhazardous waste-burning facilities with APCD inlet temperatures less than and greater than 232°C. The results of all analyses showed significant differences in the sample mean values ($p<0.05$).

Given the strong empirical evidence that real differences existed, ORD decided to address the kilns burning hazardous waste separately from those burning nonhazardous waste to develop a CDD/CDF emissions inventory and to subdivide the hazardous waste-burning category into

subcategories by APCD inlet temperature (i.e., less than 232°C and greater than 232°C). APCD inlet temperature data were available for 88 test runs at 14 cement kilns. The number of test runs conducted at individual kilns ranged from 1 to 26. Each test run was treated as an individual facility and each was classified according to APCD inlet temperature and whether or not hazardous waste was burned. The emission factor for each cement kiln test run was calculated using eq 5-1.

$$EF_{CK} = \frac{C \times F_v}{I_{cl}} \quad (5\text{-}1)$$

where:

EF_{CK} = cement kiln emission factor (burning or not burning hazardous waste) (ng TEQ/kg of clinker produced)

C = TEQ or CDD/CDF concentration in kiln exhaust gases (ng TEQ/dscm) (20°C, 1 atm; adjusted to 7% O_2)

F_v = volumetric kiln exhaust gas flow rate (dscm/hr) (20°C, 1 atm; adjusted to 7% O_2)

I_{cl} = average cement kiln clinker production rate (kg/hr)

After developing the emission factor for each cement kiln test run, the overall average congener-specific emission factor was derived for all test runs in each subcategory using eq 5-2.

$$EF_{avgCK} = \frac{EF_{CK_1} + EF_{CK_2} + EF_{CK_3} + \ldots\ldots + EF_{CK_N}}{N} \quad (5\text{-}2)$$

where:

EF_{avgCK} = average emission factor of tested cement kilns burning hazardous waste as supplemental fuel and with APCD inlet temperatures either greater than or less than 232°C (ng TEQ/kg clinker)

N = number of cement kiln test runs

TEQ emission values for hazardous waste-burning cement kilns with APCD inlet temperatures greater than 232°C and less than 232°C were 30.7 and 1.11 ng TEQ_{DF}-WHO_{98}/kg clinker produced, respectively.

5.1.4.2. ***Emissions Data for 1999 and 2000*** (Bell, 1999; U.S. EPA, 2002a)

The results of a test conducted in 1999 for a cement kiln burning nonhazardous waste (Bell, 1999) showed average TEQ_{DF}-WHO_{98} and I-TEQ emission factors of 0.14 ng/kg clinker produced. This value is within the range of emission factor values developed using the 1989 through 1996 data (U.S. EPA, 1996b).

In 1999, EPA's Office of Solid Waste and Emergency Response (OSWER), under the National Emission Standards for Hazardous Air Pollutants (NESHAPs), promulgated Final Standards for Hazardous Air Pollutants for Hazardous Waste Combustors (Federal Register, 1999a). During the development of this rulemaking, a database of national emission estimates for hazardous waste combustors (HWCs), including hazardous waste-burning cement kilns, was established. In this database EPA identified 30 hazardous waste cement kilns operating in 1997. Twenty-four of the 30 kilns had provided emissions sampling data to EPA, including dioxin concentrations. Using the most recent sampling data for each kiln, along with imputed release estimates for the missing six kilns and the assumption that cement kilns were operating 24 hr/day, 365 days/yr, OSWER developed a national emissions estimate of 13 g TEQ/yr for 1997.

A number of parties sought judicial review of the 1999 rule, and in 2001 the standards were vacated. Interim standards were issued in 2002 until EPA could issue revised final standards in 2004. The existing national emissions database was updated to include new sampling data and data for newly operational HWCs and to remove eight of the cement kilns that were identified as no longer burning hazardous waste. From this updated database (U.S. EPA, 2002a), EPA was able to develop new emission estimates for 2000.

5.1.4.3. ***Emission Factor Estimates for Cement Kilns Burning Hazardous Waste***

For reference years 1987 and 1995, EPA estimated the TEQ emission factor by subdividing the emissions data reported in 1996 (i.e., for 1989 through 1996) (U.S. EPA, 1996b) by inlet APCD temperature above and below 232°C. For cement kilns operating at temperatures above 232°C, the TEQ emission factor was 30.7 ng TEQ_{DF}-WHO_{98}/kg clinker produced, and for cement kilns operating at temperatures below 232°C, the TEQ emission factor was 1.11 ng TEQ_{DF}-WHO_{98}/kg clinker produced. These emission factors are presented in Table 5-1 and the average congener profile is presented in Figure 5-1.

Because a vast majority of the facilities had reduced their APCD inlet temperature to below 232°C by 2000, and because only a few new test reports applicable to reference year 2000 were available, EPA removed the 232°C divider and combined the emission factor results (i.e., 1989 through 1996 data) (U.S. EPA, 1996b) for facilities that were still operating in 2000 with

Table 5-1. CDD/CDF emission factors (ng/kg clinker produced) for cement kilns burning hazardous waste for reference years 1987 and 1995

Congener/ congener group	Mean emission factor (nondetect values set equal to zero)	
	APCD inlet temperature >232°C	APCD inlet temperature <232°C
2,3,7,8-TCDD	3.38	0.02
1,2,3,7,8-PeCDD	4.28	0.13
1,2,3,4,7,8-HxCDD	4.85	0.29
1,2,3,6,7,8-HxCDD	6.93	0.42
1,2,3,7,8,9-HxCDD	9.55	0.4
1,2,3,4,6,7,8-HpCDD	27.05	3.16
OCDD	18.61	1.08
2,3,7,8-TCDF	36.26	3.24
1,2,3,7,8-PeCDF	13.36	0.23
2,3,4,7,8-PeCDF	23.48	0.65
1,2,3,4,7,8-HxCDF	22.24	0.55
1,2,3,6,7,8-HxCDF	8.46	0.27
1,2,3,7,8,9-HxCDF	0.96	0.06
2,3,4,6,7,8-HxCDF	13.33	0.52
1,2,3,4,6,7,8-HpCDF	7.73	0.34
1,2,3,4,7,8,9-HpCDF	2.16	0.16
OCDF	2.51	0.37
Total I-TEQ_{DF}	28.58	1.04
Total TEQ_{DF}-WHO_{98}	30.7	1.10
Total TCDD	406.76	1.78
Total PeCDD	608.65	0.89
Total HxCDD	845.99	0.69
Total HpCDD	192.99	0.42
Total OCDD	18.61	1.08
Total TCDF	295.72	11.52
Total PeCDF	127.99	3.83
Total HxCDF	50.75	1.88
Total HpCDF	8.36	0.47
Total OCDF	2.51	0.37
Total CDD/CDF	2,558.33	22.93

APCD = Air pollution control device

Source: U.S. EPA (1996b).

the newer data reported (U.S. EPA, 2002a). Therefore, emission tests from five facilities (U.S. EPA, 1996b) were not used to estimate the 2000 emission factor because the facilities no longer burned hazardous waste in 2000. Using this approach, a conservative TEQ emission estimate of

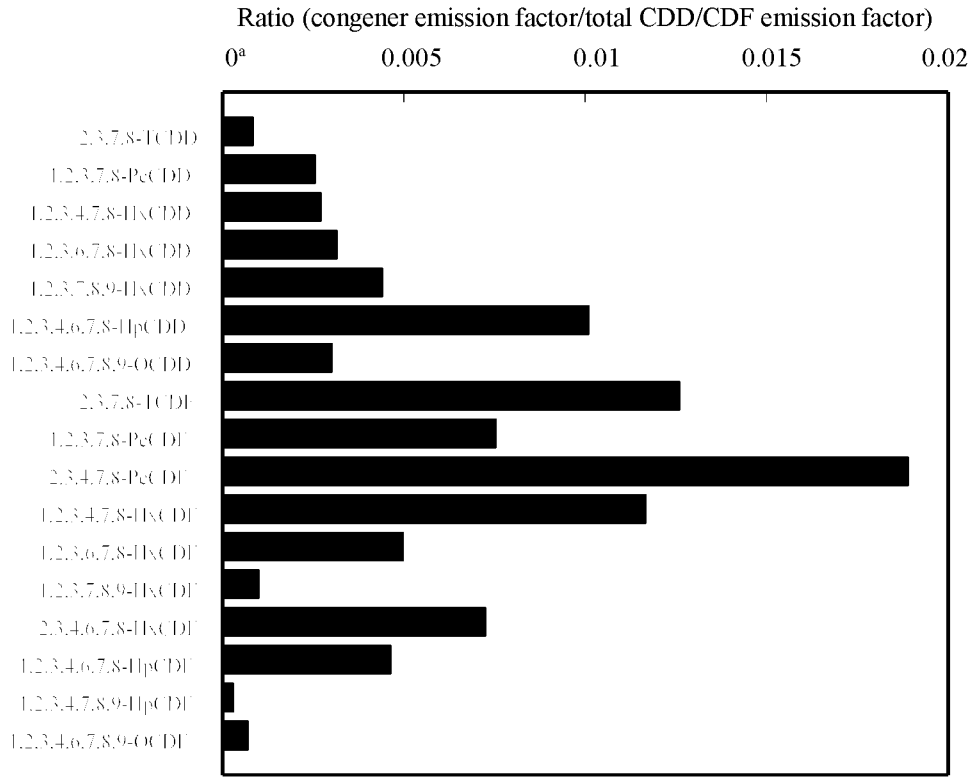


Figure 5-1. Congener profile for air emissions from cement kilns burning hazardous waste for reference years 1987 and 1995 (nondetect set equal to zero).

5.95 ng TEQ_{DF}-WHO_{98}/kg (5.49 ng I-TEQ/kg) clinker produced was developed for reference year 2000. The congener-specific emission factors are presented in Table 5-2 and the average congener and congener group profiles are presented in Figure 5-2.

5.1.4.4. *Emission Factor Estimates for Cement Kilns Burning Nonhazardous Waste*

Because only one test report applicable to reference year 2000 was located for a cement kiln burning nonhazardous waste (Bell, 1999), and the results from the tests were similar to the results reported by EPA in 1996 (U.S. EPA, 1996b), EPA combined the results from the two data sets to obtain a TEQ emission factor estimate of 0.27 ng TEQ_{DF}-WHO_{98}/kg (0.26 ng I-TEQ/kg) clinker produced for reference years 1987, 1995, and 2000. The congener-specific emission factors are presented in Table 5-3 and the average congener and congener group profiles are presented in Figure 5-3.

Table 5-2. CDD/CDF emission factors (ng/hr) for cement kilns burning hazardous waste for reference year 2000

Congener/congener group	Mean emission factor
2,3,7,8-TCDD	9,533
1,2,3,7,8-PeCDD	32,510
1,2,3,4,7,8-HxCDD	48,483
1,2,3,6,7,8-HxCDD	78,043
1,2,3,7,8,9-HxCDD	66,369
1,2,3,4,6,7,8-HpCDD	446,105
OCDD	142,108
2,3,7,8-TCDF	63,866
1,2,3,7,8-PeCDF	37,470
2,3,4,7,8-PeCDF	77,981
1,2,3,4,7,8-HxCDF	59,340
1,2,3,6,7,8-HxCDF	48,179
1,2,3,7,8,9-HxCDF	33,967
2,3,4,6,7,8-HxCDF	47,458
1,2,3,4,6,7,8-HpCDF	47,762
1,2,3,4,7,8,9-HpCDF	15,098
OCDF	12,418
Total I-TEQ_{DF} (g/yr)	16.6
Total TEQ_{DF}-WHO_{98} (g/yr)	18.8

Sources: U.S. EPA (1996b, 2002a).

5.1.4.5. *Confidence Ratings of Emission Factor Estimates*

The TEQ emission factors are given a low confidence rating for all subcategories and all years. The emission factor for nonhazardous waste-burning kilns was given a low rating because test data were available for only 16 facilities. The tested facilities may not be representative of routine CDD/CDF emissions from all kilns burning nonhazardous waste. Although a higher percentage of the kilns burning hazardous waste (with reported APCD temperature data) had been tested, greater uncertainty exists about whether the emissions are representative of normal operations because the tests used trial burn procedures and because a greater majority of the operating facilities had reduced their APCD temperatures to below 232°C. Accordingly, a low confidence rating is also assigned to the estimated emission factors for kilns burning hazardous waste.

5.1.5. Activity Level Information

In 1987, approximately 52 billion kg of cement clinker were produced in the United States (U.S. DOC, 1996). In 1995, approximately 67.6 billion kg of clinker were produced in the

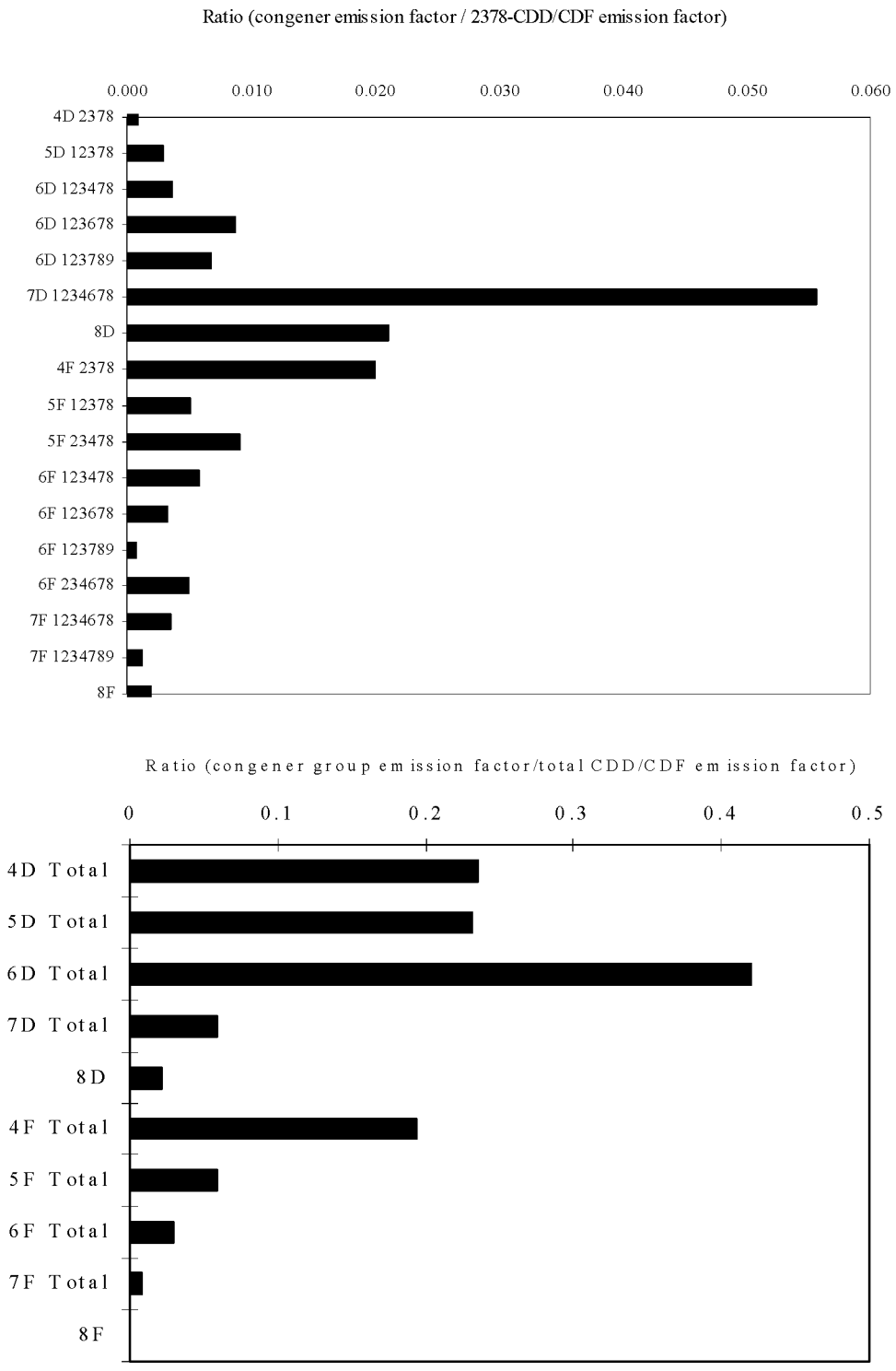


Figure 5-2. Congener profile for air emissions from cement kilns burning hazardous waste for reference year 2000.

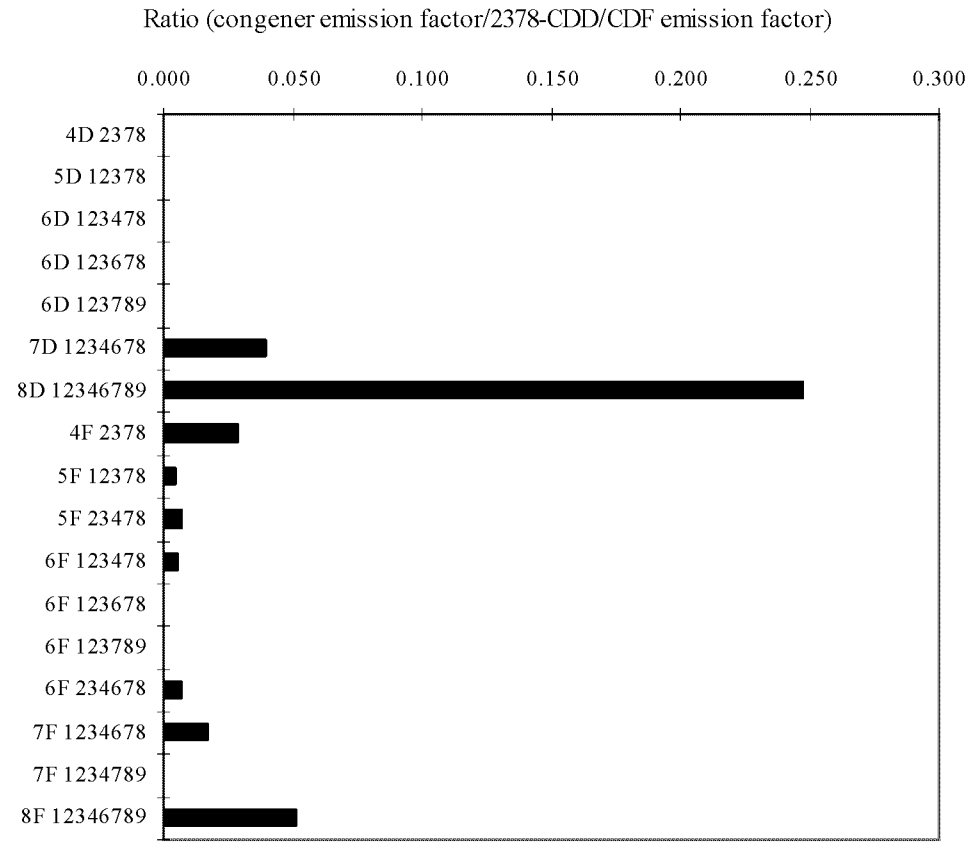
Table 5-3. CDD/CDF emission factors (ng/kg clinker produced) for cement kilns not burning hazardous waste for reference years 1987, 1995, and 2000[a]

Congener/congener group	Mean emission factor	
	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	0.01	0.02
1,2,3,7,8-PeCDD	0.03	0.04
1,2,3,4,7,8-HxCDD	0.03	0.04
1,2,3,6,7,8-HxCDD	0.04	0.05
1,2,3,7,8,9-HxCDD	0.04	0.06
1,2,3,4,6,7,8-HpCDD	0.39	0.39
OCDD	0.64	0.64
2,3,7,8-TCDF	0.73	0.73
1,2,3,7,8-PeCDF	0.1	0.11
2,3,4,7,8-PeCDF	0.22	0.23
1,2,3,4,7,8-HxCDF	0.17	0.18
1,2,3,6,7,8-HxCDF	0.05	0.06
1,2,3,7,8,9-HxCDF	0.01	0.02
2,3,4,6,7,8-HxCDF	0.08	0.08
1,2,3,4,6,7,8-HpCDF	0.13	0.14
1,2,3,4,7,8,9-HpCDF	0	0.02
OCDF	0.22	0.24
Total I-TEQ_{DF}	0.26	0.29
Total TEQ_{DF}-WHO_{98}	0.27	0.31
Total TCDD	1.89	1.89
Total PeCDD	1.92	1.92
Total HxCDD	5.51	5.51
Total HpCDD	0.78	0.78
Total OCDD	0.64	0.64
Total TCDF	7.72	7.72
Total PeCDF	2.06	2.06
Total HxCDF	0.56	0.56
Total HpCDF	0.23	0.23
Total OCDF	0.22	0.24
Total CDD/CDF	21.53	21.55

[a]The same CDD/CDF emission factor was assumed for all three years.

Sources: U.S. EPA (1996b); Bell (1999).

United States (U.S. DOC, 1996), and of this amount, 61.3 billion kg were produced by cement kilns burning nonhazardous waste (Memorandum dated August 23, 1995, from E. Heath, Research Triangle Institute, to J. Wood, U.S. EPA); therefore, approximately 6.3 billion kg were produced by cement kilns burning hazardous waste. Based on the fact that 9.3% of the clinker



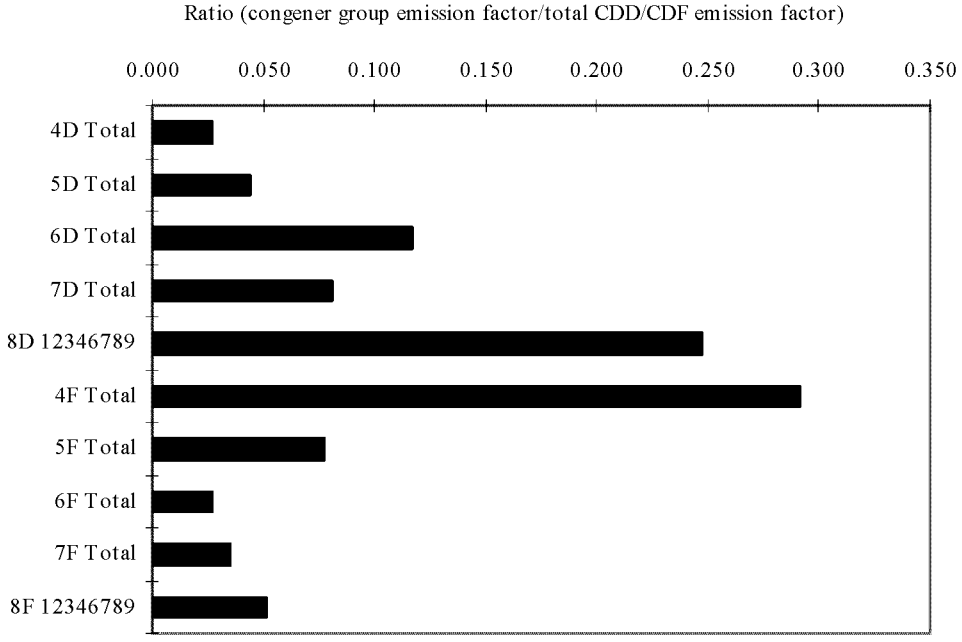


Figure 5-3. Congener profile for air emissions from cement kilns burning nonhazardous waste for reference years 1987, 1995, and 2000.

produced in 1995 was from cement kilns burning hazardous waste, it is assumed that approximately 4.8 billion kg of the clinker produced in 1987 were from cement kilns burning hazardous waste.

In 2000, cement kilns produced approximately 75.2 billion kg of clinker. This amount is based on the assumption that cement kilns operated at 90% of the maximum annual clinker capacity of 83.6 billion kg (e-mail dated January 31, 2003, from Garth Hawkins, Portland Cement Association, to Karie Riley, Versar, Inc.). Based on the annual clinker capacities of individual cement kilns, approximately 11.5 billion kg of clinker (15%) were produced by cement kilns burning hazardous waste and approximately 63.7 billion kg of clinker (85%) were produced by cement kilns not burning hazardous waste (PCA, 2001). The activity level estimates for 1995 and 2000 are given a high confidence rating because they are based on comprehensive survey data, but the rating for 1987 is medium because of uncertainty concerning the proportion produced by hazardous waste-burning kilns (U.S. EPA, 1996b).

5.1.6. National CDD/CDF Emission Estimates

5.1.6.1. *Estimates for Reference Years 1987 and 1995*

National estimates of CDD/CDF air emissions (g TEQ/yr) from all Portland cement kilns for reference years 1987 and 1995 were made by multiplying the average TEQ emission factors by an estimate of the annual activity level (cement clinker produced) for each of the three subcategories (hazardous waste-burning kilns with APCD inlet temperatures greater than 232°C and less than 232°C and kilns burning nonhazardous waste). Of the 10 hazardous waste-burning kilns with APCD temperature data, 8 facilities (80%) had APCD inlet temperatures greater than 232°C and 2 facilities (20%) had APCD inlet temperatures less than 232°C. The percentages of hazardous waste-burning kilns with input temperatures less than and greater than 232°C were assumed to represent the actual distribution of activity level in the industry. These percentages, coupled with the TEQ emission factors presented in Table 5-1 and Table 5-3 (hazardous waste cement kilns and nonhazardous waste cement kilns, respectively) and the activity levels established in Section 5.1.5, were used to calculate the annual national TEQ emission estimates shown in Table 5-4.

Overall, 131 g TEQ_{DF}-WHO_{98} (122 g I-TEQ_{DF}) were produced by cement kilns in 1987. Of this amount, 116.7 g TEQ_{DF}-WHO_{98} (108.6 g I-TEQ_{DF}) were produced by hazardous waste-burning cement kilns with inlet APCD temperatures greater than 232°C, 1.1 g TEQ_{DF}-WHO_{98} (1 g I-TEQ_{DF}) were produced by cement kilns burning hazardous waste with inlet APCD temperatures less than 232°C, and 12.7 g TEQ_{DF}-WHO_{98} (12.3 g I-TEQ_{DF}) were produced by cement kilns burning nonhazardous waste.

Table 5-4. National emission estimates for cement kilns for reference years 1987 and 1995

Category	TEQ emission factor (ng/kg clinker)		Activity level (billion kg clinker/yr)	Annual TEQ emission (g/yr)	
	I-TEQ_{DF}	TEQ_{DF}-WHO_{98}		I-TEQ_{DF}	TEQ_{DF}-WHO_{98}
Reference year 1987					
Hazardous waste >232°C	28.58	30.7	3.8	108.6	116.7
Hazardous waste <232°C	1.04	1.11	1	1	1.1
Nonhazardous waste	0.26	0.27	47.2	12.3	12.7
TOTAL			52	122	131
Reference year 1995					
Hazardous waste >232°C	28.58	30.7	5.04	144	154.7
Hazardous waste <232°C	1.04	1.11	1.26	1.3	1.4
Nonhazardous waste	0.26	0.27	61.3	15.9	16.6
TOTAL			67.6	161	173

In 1995, a total of 173 g TEQ_{DF}-WHO_{98} (161 g I-TEQ_{DF}) were produced by cement kilns. Of this amount, 154.7 g TEQ_{DF}-WHO_{98} (144 g I-TEQ_{DF}) were produced by hazardous waste-burning cement kilns with inlet APCD temperatures greater than 232°C, 1.4 g TEQ_{DF}-WHO_{98} (1.3 g I-TEQ_{DF}) were produced by cement kilns burning hazardous waste with inlet APCD temperatures less than 232°C, and 16.6 g TEQ_{DF}-WHO_{98} (15.9 g I-TEQ_{DF}) were produced by cement kilns burning nonhazardous waste.

The overall rating for these emission estimates is low because the emission factors had a low confidence rating.

5.1.6.2. *Estimates for Reference Year 2000*

National estimates of CDD/CDF air emissions (g TEQ/yr) from all Portland cement kilns for reference year 2000 were made by multiplying the average TEQ emission factors by an estimate of the annual activity level (cement clinker produced) for the nonhazardous waste category. The TEQ emission factors presented in Table 5-3 (above) and the activity levels established in Section 5.1.5 were used to calculate the annual national TEQ emission estimates shown in Table 5-5. For 2000, 17.2 g TEQ_{DF}-WHO_{98} (16.6 g I-TEQ_{DF}) were emitted by cement kilns not burning hazardous waste. The emission estimates for cement kilns not burning hazardous waste in 2000 have an overall low confidence rating because of the small number of tested facilities providing the basis for the emission factor. The emission factor may not be

representative of emissions from cement kilns not burning hazardous waste. However, the activity level is given a high confidence rating because it is based on measured data.

In reference year 2000, 22 cement kilns burning hazardous waste as supplemental fuel were operational in the United States, and most had been stack tested and evaluated for dioxin emissions. Using the measured data from the stack tests, EPA estimated that 18.8 g TEQ_{DF}-WHO_{98} (16.6 g I-TEQ_{DF}) were released from all cement kilns burning hazardous waste in 2000. The emission estimates for cement kilns burning hazardous waste in 2000 have an overall high confidence rating because the emission factors have a high confidence rating due to the large number of tested facilities providing the basis for the emission factor. The activity level is given a high confidence rating because the amount of clinker produced by cement kilns burning hazardous waste is known.

5.1.7. EPA Regulatory Activities

In 1999 EPA promulgated national emission standards for new and existing cement kilns burning and not burning hazardous waste (Federal Register, 1999a, b). A number of parties, representing both industrial and environmental communities, requested judicial review of the rule affecting cement kilns and incinerators burning hazardous waste and challenged EPA's emission standards and several implementation provisions. On July 24, 2001, the U.S. Court of Appeals for the District of Columbia Circuit vacated the emission standards. In response to this action, EPA proposed new standards affecting cement kilns and incinerators burning hazardous waste on April 20, 2004 (Federal Register, 2004), which were made final in December 2005 (Federal Register, 2005).

With regard to dioxin emissions, the regulations are specific to the I-TEQ concentration in the combustion gases leaving the stack. Existing and new cement kilns either combusting or not combusting hazardous waste as supplemental fuel cannot emit more than 0.2 ng I-TEQ/dscm. In addition, the temperature of the combustion gases measured at the inlet to the APCD cannot exceed 232°C. The rule required owners or operators of facilities to test for CDDs/CDFs every 2½ years. EPA expects this rule to reduce I-TEQ_{DF} emissions from existing and new facilities by more than 30% over the next several years (Federal Register, 1999a, b, 2004, 2005).

5.1.8. Solid Waste from Cement Manufacturing: Cement Kiln Dust

EPA characterized CKD (the solid residual material generated during the manufacturing of cement) in a report to Congress (U.S. EPA, 1993a) that was based in part on a 1991 survey of cement manufacturers conducted by the Portland Cement Association (PCA). Survey responses were received from 64% of the active cement kilns in the United States. On the basis of the

Table 5-5. National emission estimates for cement kilns for reference year 2000

Tested facility ID Hazardous waste burning kilns	Estimate in g I-TEQ/yr	Estimate in g WHO-TEQ/yr
200	0.61	0.67
201	0.01	0.01
203	3.77	4.24
204	3.15	3.63
205	0.14	0.16
206	1.12	1.39
207	0.05	0.06
208	0.88	1.26
228	0.06	0.07
300	3.45	3.53
302	0.23	0.27
303	0.13	0.16
318	0.27	0.30
319	0.50	0.59
322	0.04	0.04
323	0.06	0.07
403	0.32	0.38
404	0.06	0.07
473	0.11	0.12
491	1.59	1.75
680	0.01	0.01
681	0.06	0.07
Total Hazardous waste burning kilns	16.6	18.8
Total Non-hazardous waste burning kilns	16.6	17.2
All cement kilns	33.2	36.0

Source: U.S. EPA (2002a).

survey responses, EPA estimated that in 1990 the U.S. cement industry generated about 12.9 million metric tons of gross CKD and 4.6 million metric tons of net CKD, of which 4.2 million metric tons were land-disposed. The material collected by the APCD system is called gross CKD (or as-generated CKD); it is either recycled back into the kiln system or removed from the system for disposal (becoming net CKD or as-managed CKD). As discussed below, low levels of dioxin have been measured in CKD. This material is disposed of in permitted landfills and therefore is not considered to be an environmental release and is not included in the inventory of dioxin releases presented in this report. However, for informational purposes only, estimates of the amount of dioxin in CKD were developed for the reference years 1987, 1995, and 2000.

The PCA recently provided current estimates of the amount of CKD removed from the manufacturing process for beneficial reuse and long-term management units (i.e., landfill disposal) in 1990, 1995, and 2000 (e-mails dated January 31 and March 18, 2003, from Garth Hawkins, Portland Cement Association, to Karie Riley, Versor, Inc.). Possible beneficial reuses include municipal waste daily cover material, municipal waste landfill final cover material, soil stabilization for roadways or other structures, waste neutralization/stabilization/solidification (food wastes, hazardous wastes, etc.), and agricultural soil amendment. The PCA estimated that the amount of CKD beneficially reused on or off site was 752 million kg in 1990, 652 million kg in 1995, and 575 million kg in 2000. The amount of CKD disposed of annually in landfills was estimated to be 2.7 billion kg in 1990, 3.1 billion kg in 1995, and 2.2 billion kg in 2000.

In its report to Congress (U.S. EPA, 1993a), EPA also included the results of sampling and analysis of CKD and clinker conducted in 1992 and 1993. The purposes of the sampling and analysis efforts were to (a) characterize the CDD/CDF content of clinker and CKD, (b) determine the relationship, if any, between the CDD/CDF content of CKD and the use of hazardous waste as fuel, and (c) determine the relationship, if any, between the CDD/CDF content of CKD and the use of wet-process and dry-process cement kilns.

Clinker samples were collected from five cement kilns burning nonhazardous waste and six kilns burning hazardous waste. CDDs/CDFs were not detected in any of the samples. Tetra- through octa-chlorinated CDDs/CDFs were detected in the gross CKD samples obtained from 10 of the 11 kilns and in the net CKD samples obtained from 8 of the 11 kilns. The CDD/CDF content ranged from 0.008 to 247 ng I-TEQ_{DF}/kg for gross CKD and from 0.045 to 195 ng I-TEQ_{DF}/kg for net CKD. Analyses for seven PCB congeners were also conducted, but no congeners were detected in any clinker or CKD sample.

Mean CDD/CDF concentrations in net CKD generated by the kilns burning hazardous waste were higher (35 ng I-TEQ_{DF}/kg) than in net CKD generated by the facilities burning nonhazardous waste (0.003 ng I-TEQ_{DF}/kg). These calculations of mean values treated nondetect values as zero. If the nondetects had been excluded from the calculation of the means, the mean

for net CKD from kilns burning hazardous waste would increase by a factor of 1.2 and the mean for net CKD from kilns burning nonhazardous waste would increase by a factor of 1.7. One sampled kiln had a net CKD TEQ concentration of more than two orders of magnitude greater than the TEQ levels found in samples from any other kiln. If this kiln were considered atypical of the industry (U.S. EPA, 1993a) and were not included in the calculation, then the mean net CKD concentration for hazardous waste-burning kilns would decrease to 2.9 ng I-TEQ_{DF}/kg.

CDD/CDF congener data for CKD from Holnam, Inc., Seattle, WA, were presented in a report by the Washington State Department of Ecology (1998). The data were compiled and evaluated to determine total I-TEQ concentrations and loadings. Nondetect values were included as either zero, one-half of the detection limit (DL), or at the DL. The results of three separate tests of CKD were as follows, assuming that nondetect values were zero:

Date	I-TEQ (ng/kg)	I-TEQ (mg/day)
05/15/96	0.038	0.0038
10/21/97	0.67	0.0674
10/21/97	0.95	0.0948

EPA provided data for ashes from an ESP connected to a cement kiln and an FF connected to a lightweight aggregate (LWA) kiln (U.S. EPA, 1999e). The average congener concentrations for the ash samples are listed in Table 5-6. The average concentrations for the cement kiln were determined from two different waste streams, each with five sample burns. The average concentrations for the LWA kiln were determined using one waste stream with three sample burns.

The amount of CDDs/CDFs associated with CKD was calculated for informational purposes only. National estimates were divided among cement kilns burning hazardous waste and those burning nonhazardous waste for both CKD that was beneficially reused and CKD that was sent landfills. The activity levels used in the estimates were those provided by the PCA (e-mail dated March 18, 2003, from Garth Hawkins, Portland Cement Association, to Karie Riley, Versar, Inc.). The 1990 activity levels provided by PCA were used for reference year 1987. The CDD/CDF concentrations in CKD used in the estimates were 35 ng I-TEQ_{DF}/kg for cement kilns burning hazardous waste (which includes the high value discussed above) and 0.003 ng I-TEQ_{DF}/kg for cement kilns burning nonhazardous waste.

As shown in Table 5-7, by combining the appropriate activity levels and CDD/CDF concentrations, national estimates of CDDs/CDFs in CKD were developed for reference years 1987, 1995, and 2000. For cement kilns burning hazardous waste, approximately 4.2 g I-TEQ_{DF}

Table 5-6. CDD/CDF concentrations (ng/kg) in ash samples from cement kiln electrostatic precipitator and lightweight aggregate (LWA) kiln fabric filter

Congener	Cement kiln	LWA kiln	Cement kiln		LWA kiln	
	Avg. conc.	Avg. conc.	I-TEQ	WHO-TEQ	I-TEQ	WHO-TEQ
2,3,7,8-TCDD	0.429	3.97	0.429	0.429	3.97	3.97
Total TCDD	36.1	333	–	–	–	–
1,2,3,7,8-PeCDD	0.886	17.3	0.443	0.886	8.65	17.3
Total PeCDD	54.9	467	–	–	–	–
1,2,3,4,7,8-HxCDD	1.03	15.4	0.103	0.103	1.54	1.54
1,2,3,6,7,8-HxCDD	2.36	35.6	0.236	0.236	3.56	3.56
1,2,3,7,8,9-HxCDD	2.47	56.6	0.247	0.247	5.66	5.66
Total HxCDD	173	500	–	–	–	–
12,2,3,4,6,7,8-HpCDD	17.7	133	0.177	0.177	1.33	1.33
Total HpCDD	55.2	300	–	–	–	–
OCDD	21	133	0.021	0.0021	0.133	0.133
Total TCDD TEQs			1.66	2.08	24.8	33.5
2,3,7,8-TCDF	4.65	833	0.465	0.465	83.3	83.3
Total TCDF	18.1	4630	–	–	–	–
1,2,3,7,8-PeCDF	1.04	100	0.0518	0.0518	5	5
2,3,4,7,8-PeCDF	2.59	267	1.3	1.3	133	133
Total PeCDF	31.8	2930	–	–	–	–
1,2,3,4,7,8-HxCDF	2.13	267	0.213	0.213	26.7	26.7
1,2,3,6,7,8-HxCDF	0.869	100	0.0869	0.869	10	10
1,2,3,7,8,9-HxCDF	0.523	7.8	0.0523	0.0523	0.780	0.780
2,3,4,6,7,8-HxCDF	2.14	133	0.214	0.214	13.3	13.3
Total HxCDF	9.26	1230	–	–	–	–
1,2,3,4,6,7,8-HpCDF	1.84	167	0.0184	0.0184	1.67	1.67
1,2,3,4,7,8,9-HpCDF	0.739	22.6	0.00739	0.00739	0.226	0.226
Total HpCDF	3.06	2670	–	–	–	–
OCDF	1.43	39.2	0.00143	0.000143	0.0392	0.00392
Total TCDF TEQs			2.41	3.19	274	274

– = No data available

in 1987, 3.6 g I-TEQ_{DF} in 1995, and 3.3 g I-TEQ_{DF} in 2000 were produced from CKD that was beneficially reused, and approximately 14.9 g I-TEQ_{DF} in 1987, 17.7 g I-TEQ_{DF} in 1995, and 12.8 g I-TEQ_{DF} in 2000 were produced from CKD that was disposed of in a landfill. For cement kilns burning nonhazardous waste, approximately 0.0019 g I-TEQ_{DF} in 1987, 0.0016 g I-TEQ_{DF} in 1995, and 0.0014 g I-TEQ_{DF} in 2000 were produced from CKD that was beneficially reused, and

Table 5-7. CDD/CDF estimates in cement kiln dust (CKD) for reference years 1987, 1995, and 2000

Category	CDD/CDF concentration (ng I-TEQ$_{DF}$/kg of CKD)	CKD beneficially reused on or off site		CKD sent to a landfill for disposal	
		Activity level (million kg tons CKD/yr)	Annual TEQ CDD/CDF concentration (g/yr)	Activity level (million kg tons CKD/yr)	Annual TEQ CDD/CDF concentration (g/yr)
Reference year 1987					
HW kilns	35	120	4.2	426	14.9
NHW kilns	0.003	632	0.0019	2,230	0.0067
Reference year 1995					
HW kilns	35	104	3.6	505	17.7
NHW kilns	0.003	547	0.0016	2,642	0.0079
Reference year 2000					
HW kilns	35	94	3.3	365	12.8
NHW kilns	0.003	480	0.0014	1,858	0.0056

HW = Hazardous waste
NHW = Nonhazardous waste

approximately 0.0067 g I-TEQ$_{DF}$ in 1987, 0.0079 g I-TEQ$_{DF}$ in 1995, and 0.0056 g I-TEQ$_{DF}$ in 2000 were produced from CKD that was disposed of in a landfill.

EPA is currently developing CKD storage and disposal requirements. In 1999, a proposed rule for the standards for the management of CKD was developed by EPA (Federal Register, 1999a). Under the rule, CKD would remain a nonhazardous waste, provided that proposed management standards are met, which would protect groundwater and control releases of fugitive dust. Additionally, the rule proposes concentration limits on various pollutants in CKD used for agricultural purposes (Federal Register, 1999c).

5.2. LIGHTWEIGHT AGGREGATE KILNS

LWA kilns heat raw materials such as clay, shale, or slate to expand the particles to form lightweight materials for use in concrete products. In 1995, only 5 of the more than 36 LWA kilns in the United States were burning hazardous waste; in 2000, 9 LWA kilns were burning hazardous waste. LWA kilns are estimated to have emitted 3.3 g I-TEQ$_{DF}$ to air in 1990 (Federal Register, 1998a) and 2.4 g I-TEQ$_{DF}$ in 1997 (Federal Register, 1999a); these estimates are used in this report for reference years 1987 and 1995, respectively.

The CDD/CDF emission factors for 2000 are based on the data for five LWA kilns tested in 2000 (U.S. EPA, 2002a). They were calculated using the process described in Section 3.2.3. The average emission factor for the LWA kilns was 1.986 ng TEQ_{DF}-WHO_{98}/kg (2.063 ng I-TEQ_{DF}/kg) of waste feed, assuming nondetect values of zero. These are assigned a low confidence rating because the emission factor may not be representative of emissions from the source category.

The amount of hazardous waste combusted using LWA kilns in 2000 was conservatively estimated to be 903,000 metric tons, based on estimated activity levels derived for each halogen acid furnace (HAF) in 2000. Data were available for all of the nine facilities operating in 2000. A conservative estimate for the average annual quantity burned per HAF (100,280 metric tons/yr) was derived by assuming that plants operate continuously throughout the year and are always running at 80% of capacity. This quantity, multiplied by the total universe of nine facilities, yielded the final estimate. Because the activity level was not derived from a survey but was estimated, it is given a low confidence rating.

Equation 3-5 (Chapter 3, Section 3.2.4), used to calculate annual TEQ emissions for dedicated hazardous waste incinerators, was also used to calculate annual TEQ emissions for LWA kilns. Multiplying the average TEQ emission factors by the total estimated amount of liquid hazardous waste burned in 2000 yields an annual emissions estimate. From this procedure, the emissions from all LWA kilns burning hazardous waste as supplemental fuel were estimated as 1.86 g TEQ_{DF}-WHO_{98} (1.79 g I-TEQ_{DF}) for 2000. Because of the low confidence rating for the emission factor, the overall confidence rating for the emission estimates is low.

5.3. ASPHALT MIXING PLANTS

Asphalt consists of an aggregate of gravel, sand, and filler mixed with liquid asphalt cement or bitumen. Filler typically consists of limestone, mineral stone powder, and sometimes ash from power plants and municipal waste combustors. The exact composition of an asphalt formulation depends on how it will be used. The aggregate typically constitutes more than 92% by weight of the total asphalt mixture. The components of the aggregate are dried, heated to a temperature ranging from 135 to 163°C, and then mixed and coated with the bitumen at an asphalt mixing installation. "Old" asphalt (i.e., asphalt from dismantled bridges and roads) can be heated and disaggregated to its original components and reused in the manufacture of new asphalt (U.S. EPA, 1996c). "Hot mix" asphalt paving materials can be manufactured by batch mix plants, continuous mix plants, parallel-flow drum mix plants, and counterflow drum mix plants (U.S. EPA, 1998c).

Bremmer et al. (1994) reported the CDD/CDF emissions factor for an asphalt mixing plant in the Netherlands as 47 ng I-TEQ_{DF} per metric ton of produced asphalt. No congener-

specific emission factors were reported. The mixing plant heated old asphalt to about 150°C in an individual recycling drum with kiln exhaust gases that were mixed with ambient air and heated to a temperature of 300 to 400°C. Parallel to this recycling drum was the main drum, which dried and heated the aggregate (sand and gravel/granite chippings) to a temperature of about 220°C. The kiln exhaust gases leaving the recycling drum were led along the main burner of the main drum for incineration. The old asphalt, the minerals from the main drum, and new bitumen from a hot storage tank (about 180°C) were mixed in a mixer to form new asphalt. Natural gas fueled the plant during the sample collection period, and 46% of the feed was old asphalt. The plant's APCD system consisted of cyclones and an FF.

Umweltbundesamt (1996) reported lower emission factors for three tested facilities in Germany that were also equipped with FFs. These three facilities were fueled by oil or butane gas and used old asphalt at rates ranging from 30 to 60% of the feed. The emission factors calculated from the stack gas concentrations, gas flow rates, and hourly throughputs for these three facilities were 0.2, 3.5, and 3.8 ng I-TEQ_{DF}/metric ton of asphalt produced, respectively.

EPA conducted stack emissions testing at two hot-mix asphalt production plants in the United States (U.S. EPA, 2000g). The Midwest Research Institute performed emission tests on outlet of FFs that controlled emissions from the counter-flow rotary dryer process used at the asphalt plant in Clayton, NC, and from the parallel-flow rotary dryer process used at the asphalt plant in Cary, NC. In both processes, virgin aggregate of various sizes was fed to the drum by cold-feed controls in proportions dictated by the final mix specifications. Aggregate was delivered at the opposite end of the burner in the counter-flow continuous drum mix process and at the same end as the burner in the parallel-flow continuous drum mix process. EPA developed average TEQ emission factors from the tested facilities to represent hot-mix asphalt plants in general (U.S. EPA, 2000g). The average TEQ emission factor for hot-mix asphalt plants was 1.40e–03 ng I-TEQ (1.46e–3 ng TEQ_{DF}-WHO_{98}/kg) asphalt produced. Table 5-8 summarizes the TEQ emission factors for hot-mix asphalt plants.

Because only two U.S. facilities have been tested, these emission factors are given a low confidence rating. It is likely that these emission factors are not representative of CDD/CDF emissions from all types of asphalt production facilities in the United States; nevertheless, they are sufficient to derive a preliminary estimate of annual emissions from asphalt production facilities in the United States for 2000.

Approximately 500 million tons of hot-mix asphalt paving materials were produced at approximately 3,600 active asphalt plants in the United States in 1996 (U.S. EPA, 1998c). This activity level was used to represent reference year 2000. The activity level is given a high confidence level because it was based on a comprehensive survey. A preliminary estimate of annual TEQ air releases for 2000 was calculated by multiplying the activity level (in kilograms)

Table 5-8. Congener-specific emission factors (ng/kg asphalt produced) derived from the testing of air emissions at two hot-mix asphalt plants in the United States

Congener	Mean emission factor	
	I-TEQ_{DF}	TEQ_{DF}-WHO_{98}
2,3,7,8-TCDD	9.53e–05	9.53e–05
1,2,3,7,8-PeCD	7.03e–05	1.41e–04
1,2,3,4,7,8-HxCDD	1.91e–05	1.91e–05
1,2,3,6,7,8-HxCDD	5.90e–05	5.90e–05
1,2,3,7,8,9-HxCDD	4.45e–05	4.45e–05
1,2,3,4,6,7,8-HpCDD	2.18e–05	2.18e–05
OCDD	1.13e–05	1.13e–06
2,3,7,8-TCDF	4.40e–05	4.40e–05
1,2,3,7,8-PeCDF	9.75e–05	9.75e–05
2,3,4,7,8-PeCDF	1.91e–04	1.91e–04
1,2,3,4,7,8-HxCDF	1.81e–04	1.81e–04
1,2,3,6,7,8-HxCDF	5.44e–05	5.44e–05
1,2,3,7,8,9-HxCDF	8.62e–05	8.62e–05
2,3,4,6,7,8-HxCDF	3.81e–04	3.81e–04
1,2,3,4,6,7,8-HpCDF	2.95e–05	2.95e–05
1,2,3,4,7,8,9-HpCDF	1.22e–05	1.22e–05
OCDF	2.18e–06	2.18e–07
Total TEQ	1.40e–03	1.50e–03

Source: U.S. EPA (2000g).

by the average emission factor of 1.40e–03 ng I-TEQ (1.46e–3 ng TEQ_{DF}-WHO_{98}/kg) asphalt produced. Approximately 0.70 g I-TEQ (0.73 g TEQ_{DF}-WHO_{98}) were emitted into the air from asphalt plants in the United States in 2000. This estimate is assigned a low confidence level because the emission factors are given a low confidence level rating.

5.4. PETROLEUM REFINING CATALYST REGENERATION

Regeneration of spent catalyst from the reforming process at petroleum refineries is a potential source of CDDs/CDFs, according to limited testing conducted in the United States (Amendola and Barna, 1989; Kirby, 1994), Canada (Maniff and Lewis, 1988; Thompson et al., 1990), and the Netherlands (Bremmer et al., 1994). This section summarizes the catalyst regeneration process, relevant studies performed to date, and the status of EPA regulatory investigations of this source.

Catalytic reforming is the process used to produce high-octane reformates from lower-octane reformates for blending of high-octane gasolines and aviation fuels. The reforming process occurs at high temperature and pressure and requires the use of a platinum or platinum/rhenium catalyst. During the reforming process, a complex mixture of aromatic compounds, known as coke, is formed and deposited onto the catalyst. As coke deposits onto the catalyst, its activity is decreased. The high cost of the catalyst necessitates its regeneration. Catalyst regeneration is achieved by removing the coke deposits via burning at temperatures of 399 to 454°C and then reactivating the catalyst at elevated temperatures (454 to 538°C) using chlorine or chlorinated compounds (e.g., methylene chloride, 1,1,1-trichloroethane, and ethylene dichloride; most refineries use chlorine of perchloroethylene). Burning of the coke produces kiln exhaust gases that can contain CDDs and CDFs along with other combustion products. Because kiln exhaust gases, if not vented directly to the atmosphere, may be scrubbed with caustic or water, internal effluents may become contaminated with CDDs/CDFs (Kirby, 1994; SAIC, 1994).

Three basic catalyst regeneration processes are used: semi-regenerative, cyclic, and continuous. During the semi-regenerative process, the entire catalytic reformer is taken off line. In the cyclic process, one of two (or more) reforming reactors is taken off line for catalyst regeneration; the remaining reactor(s) remains on line so that reforming operations continue. In the continuous process, aged catalyst is continuously removed from one or more on-line stacked or side-by-side reactors, regenerated in an external regenerator, and then returned to the system; the reforming system, consequently, never shuts down (SAIC, 1994).

In 1988, a study by the Canadian Ministry of the Environment (Maniff and Lewis, 1988) detected concentrations of CDDs ranging from 1.8 to 22.2 µg/L and CDFs ranging from 4.4 to 27.6 µg/L in an internal waste stream of spent caustic at a petroleum refinery. The highest concentration of 2,3,7,8-TCDD was 0.0054 µg/L. CDDs were also observed in the refinery's biological sludge at a maximum concentration of 74.5 µg/kg, and CDFs were observed at a maximum concentration of 125 µg/kg. The concentration of CDDs/CDFs in the final combined refinery plant effluent was below the DLs.

Amendola and Barna (1989) reported detecting trace levels of hexa- to octa-CDDs and CDFs in untreated wastewaters (up to 2.9 pg I-TEQ_{DF}/L) and wastewater sludges (0.26 to 2.4 ng I-TEQ_{DF}/kg) at a refinery in Ohio. The levels of detected total CDDs/CDFs in the wastewater and sludge were much lower (<3 ng/L and <1 µg/kg, respectively) than the levels reported by Maniff and Lewis (1988). No CDDs/CDFs were detected in the final treated effluent (less than 0.2 ng I-TEQ_{DF}/L). The data collected in the study were acknowledged to be too limited to enable identifying the source(s) of the CDDs/CDFs within the refinery. The study authors also presented in an appendix to their report the results of analyses of wastewater from the catalyst

regeneration processes at two other U.S. refineries. In both cases, untreated wastewaters contained CDDs/CDFs at levels ranging from high picograms to low nanograms per liter (results were reported for congener group totals, not specific congeners). However, CDDs/CDFs were not detected in the only treated effluent sample collected at one refinery.

Thompson et al. (1990) reported total CDD and CDF concentrations of 8.9 ng/m^3 and 210 ng/m^3, respectively, in stack gas samples from a Canadian petroleum refinery's reforming operation. They also observed CDDs/CDFs in the picogram- to nanogram-per-liter range in the internal washwater from a scrubber of a periodic/cyclic regenerator.

Beard et al. (1993) conducted a series of benchtop experiments to investigate the mechanism(s) of CDD/CDF formation in the catalytic reforming process. A possible pathway for the formation of CDFs was found, but the results could not explain the formation of CDDs. Analyses of the kiln exhaust gas from burning coked catalysts revealed the presence of unchlorinated dibenzofuran in quantities up to 220 µg/kg of catalyst. Chlorination experiments indicated that dibenzofuran and, possibly, biphenyl and similar hydrocarbons act as CDF precursors and can become chlorinated in the catalyst regeneration process. Corrosion products on the steel piping of the process plant seemed to be the most likely chlorinating agent.

In May 1994, EPA's Office of Water conducted a sampling and analytical study of catalyst regeneration wastewater for CDDs/CDFs at three petroleum refining plants (Kirby, 1994). The study objectives were to determine the analytical method best suited for determining CDDs/CDFs in refinery wastewater and to screen and characterize wastewater discharges from several types of reforming operations for CDDs/CDFs. The report for this study (Kirby, 1994) also presented results submitted voluntarily to EPA by two other facilities. The sampled internal untreated wastewaters and spent caustics were found to contain a wide range of CDD/CDF concentrations, 0.1 pg I-TEQ_{DF}/L to 57.2 ng I-TEQ_{DF}/L. The study results also showed that 90% of the TEQ was contained in the wastewater treatment sludges generated during the treatment of wastewater and caustic from the regeneration process.

In 1995, EPA issued a notice of its proposed intent to not designate spent reformer catalysts as a listed hazardous waste under RCRA (Federal Register, 1995b). The final rule was issued in August 1998 (Federal Register, 1998b). The Agency's assessment of current management practices associated with recycling of reforming catalyst found no significant risks to human health or the environment. The Agency estimated that 94% of the approximately 3,600 metric tons of spent reformer catalyst sent off site by refineries were being recycled for their precious metal content. EPA made no determination of the "listability" of spent caustic residuals formed during regeneration of spent reforming catalyst, but it did identify the potential air releases from the combustion of the reforming catalyst prior to reclamation as possibly being of concern. The Agency requested comments on (a) opportunities for removing dioxin prior to

discharge of scrubber water into the wastewater treatment system, (b) opportunities to segregate this wastestream, and (c) potential health risks associated with insertion of dioxin-contaminated media back into the refinery process (such as the coker). In this proposed rulemaking, EPA also noted the possibility of dioxin releases to air during regeneration operations.

As part of its regulatory investigation under RCRA, EPA's Office of Solid Waste commissioned a study to analyze and discuss existing data and information concerning CDD/CDF formation in the treatment of catalytic reformer wastes. This report (SAIC, 1994) also identified potential process modifications that may prevent the formation of CDDs/CDFs. The report's authors concluded that, although the available data indicate that CDDs/CDFs can be generated during the catalyst regeneration process, the available data indicate that CDD/CDF concentrations in treated wastewater and in solid waste are minimal. Releases to air could result from vented kiln exhaust gases at some facilities. In addition, the CDDs/CDFs formed could possibly be reintroduced into other refining operations (e.g., the coker) and resulting products.

In 1998, emissions from the caustic scrubber used to treat gases from the external regeneration unit of a refinery in California were tested (CARB, 1999). This facility uses a continuous regeneration process. The reactor is not taken off line during regeneration; rather, small amounts of catalyst are continuously withdrawn from the reactor and are regenerated. The emissions from the regeneration unit are neutralized by a caustic scrubber before being vented to the atmosphere. The catalyst recirculation rate during the three tests ranged from 733 to 1,000 lb/hr.

All 2,3,7,8-substituted CDDs/CDFs were detected in each of the three samples collected. The average emission factors in units of nanograms per barrel of reformer feed are presented in Table 5-9. The congener profile is presented in Figure 5-4. The samples showed a wide range in concentrations of the CDD/CDF congeners (up to a fivefold difference); however, the congener profile was consistent in all samples. The concentrations of the individual furan congener groups were always higher than the concentrations of the corresponding dioxin congener group. The average TEQ_{DF}-WHO_{98} emission factor for these three tests was 3.18 ng TEQ/barrel and the average I-TEQ_{DF} was 3.04 ng TEQ/barrel.

In 1991, stack testing was performed on the exhaust from one of the three semi-regenerative catalytic reforming units of a refinery in California (Radian Corporation, 1991). At these units, a caustic solution is introduced to the exhaust to neutralize HCl emissions from the catalyst beds prior to release to the atmosphere. The tested unit was considered to be representative of the other units. Each unit is periodically taken off line (approximately once a year) so the catalyst beds can be regenerated. The tested unit has a feed capacity of 7,000 barrels/day. Approximately 59,500 pounds of catalyst were regenerated during the tested regeneration cycle, which lasted for 62 hr.

The average emission factors for this facility (in units of nanogams per barrel of reformer feed) are presented in Table 5-9 and the congener profile is presented in Figure 5-4. The majority of the 2,3,7,8-substituted CDD congeners were not detected during testing. In contrast, the majority of the 2,3,7,8-substituted CDF congeners were detected. The average TEQ_{DF}-WHO_{98} emission factor (assuming nondetect values were zero) was 1.04e–03 ng TEQ/barrel and the average I-TEQ_{DF} emission factor was 1.01e–03 ng TEQ/barrel. These values are three orders of magnitude less than the emission factor reported in CARB (1999). The calculation of these emission factors involved several assumptions: the unit is regenerated once per year, the unit operates at capacity (7,000 barrels/day), and the facility operates 362 days/yr.

The average of the two facility emission factors, 1.59 ng TEQ_{DF}-WHO_{98}/barrel (1.52 ng I-TEQ_{DF}/barrel) of reformer feed, is assumed to apply to all reference years (1987, 1995, and 2000) and is assigned a low confidence rating. Only one continuous and one semiregenerative unit in the United States have been tested. Combined, these two facilities represent less than 1% of the catalytic reforming capacity in U.S. petroleum refineries in 1987 (3.805 million barrels/day), 1995 (3.867 million barrels/day), and 2000 (3.770 million barrels/day) (EIA, 2002a). The average emission factor developed above assumes that emissions are proportional to reforming capacity; however, they may be more related to the amount of coke burned, the APCD equipment present, or other process parameters.

The national daily average catalytic reforming capacities in the United States were 3.805, 3.867, and 3.770 million barrels per day for 1987, 1995, and 2000, respectively (EIA, 2002). These were assigned a high confidence rating because they are based on comprehensive surveys of industry. If it is conservatively assumed that all units operated at full capacity in all three years, then applying the average emission factors of TEQ/barrel yields annual emissions of 2.21 g TEQ_{DF}-WHO_{98} (2.11 g I-TEQ_{DF}) in 1987, 2.24 g TEQ_{DF}-WHO_{98} (2.14 g I-TEQ_{DF}) in 1995, and 2.19 g TEQ_{DF}-WHO_{98} (2.09 g I-TEQ_{DF}) in 2000. These emissions have a low confidence rating because they are based on an emission factor with a low confidence rating.

5.5. CIGARETTE SMOKING

Bumb et al. (1980) were the first to report that cigarette smoking is a source of CDD emissions. Subsequent studies by Muto and Takizawa (1989), Ball et al. (1990), and Löfroth and Zebühr (1992) also reported the presence of CDDs as well as CDFs in cigarette smoke. A study by Matsueda et al. (1994) reported on the CDD/CDF content of tobacco from 20 brands of cigarettes from seven countries. Although a wide range in the concentrations of total CDDs/CDFs and total TEQs were reported in these studies, similar congener profiles and patterns were reported. The findings of each of these studies are described in this section.

Table 5-9. CDD/CDF emission factors (ng/barrel)[a] for petroleum catalytic reforming units

Congener/congener group	Semiregenerative unit		Continuous regeneration unit	
	Nondetect set to zero	Nondetect set to ½ detection limit	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	ND	2.35e−05	1.61e−02	1.61e−02
1,2,3,7,8-PeCDD	5.69e−05	9.58e−05	2.87e−01	2.87e−01
1,2,3,4,7,8-HxCDD	4.22e−05	8.09e−05	3.47e−01	3.47e−01
1,2,3,6,7,8-HxCDD	ND	5.52e−05	8.45e−01	8.45e−01
1,2,3,7,8,9-HxCDD	ND	5.10e−05	5.56e−01	5.56e−01
1,2,3,4,6,7,8-HpCDD	7.02e−04	7.02e−04	3.02e+00	3.02e+00
OCDD	2.55e−03	2.55e−03	1.71e+00	1.71e+00
2,3,7,8-TCDF	2.32e−04	2.32e−04	6.10e−01	6.10e−01
1,2,3,7,8-PeCDF	4.68e−04	4.68e−04	1.72e+00	1.72e+00
2,3,4,7,8-PeCDF	1.09e−03	1.09e−03	2.33e+00	2.33e+00
1,2,3,4,7,8-HxCDF	1.06e−03	1.06e−03	4.70e+00	4.70e+00
1,2,3,6,7,8-HxCDF	1.07e−03	1.07e−03	3.58e+00	3.58e+00
1,2,3,7,8,9-HxCDF	ND	6.82e−05	4.34e−01	4.34e−01
2,3,4,6,7,8-HxCDF	1.24e−03	1.24e−03	3.10e+00	3.10e+00
1,2,3,4,6,7,8-HpCDF	2.94e−03	2.94e−03	1.59e+01	1.59e+01
1,2,3,4,7,8,9-HpCDF	8.32e−04	8.32e−04	1.45e+00	1.45e+00
OCDF	1.01e−03	1.01e−03	3.75e+00	3.75e+00
Total 2,3,7,8-CDD	3.35e−03	3.56e−03	6.78e+00	6.78e+00
Total 2,3,7,8-CDF	9.94e−03	1.00e−02	3.76e+01	2.18e+01
Total I-TEQ_{DF}	1.01e−03	1.07e−03	3.04e+00	3.04e+00
Total TEQ_{DF}-WHO_{98}	1.03e−03	1.12e−03	3.18e+00	3.18e+00
Total TCDD	ND	2.35e−05	6.84e+00	6.84e+00
Total PeCDD	3.56e−04	3.56e−04	5.61e+00	5.61e+00
Total HxCDD	1.28e−03	1.28e−03	8.18e+00	8.18e+00
Total HpCDD	1.39e−03	1.39e−03	6.58e+00	6.58e+00
Total OCDD	2.55e−03	2.55e−03	1.71e+00	1.71e+00
Total TCDF	2.70e−03	2.70e−03	4.68e+01	4.68e+01
Total PeCDF	5.12e−03	5.12e−03	3.30e+01	3.30e+01
Total HxCDF	7.85e−03	7.85e−03	2.96e+01	2.96e+01
Total HpCDF	4.88e−03	4.88e−03	2.11e+01	2.11e+01
Total OCDF	1.01e−03	1.01e−03	3.75e+00	3.75e+00
Total CDD/CDF	2.71e−02	2.72e−02	1.63e+02	1.63e+02

[a]One barrel assumed to be equivalent to 139 kg.

ND = Not detected

Sources: Radian Corporation (1991); CARB (1999).

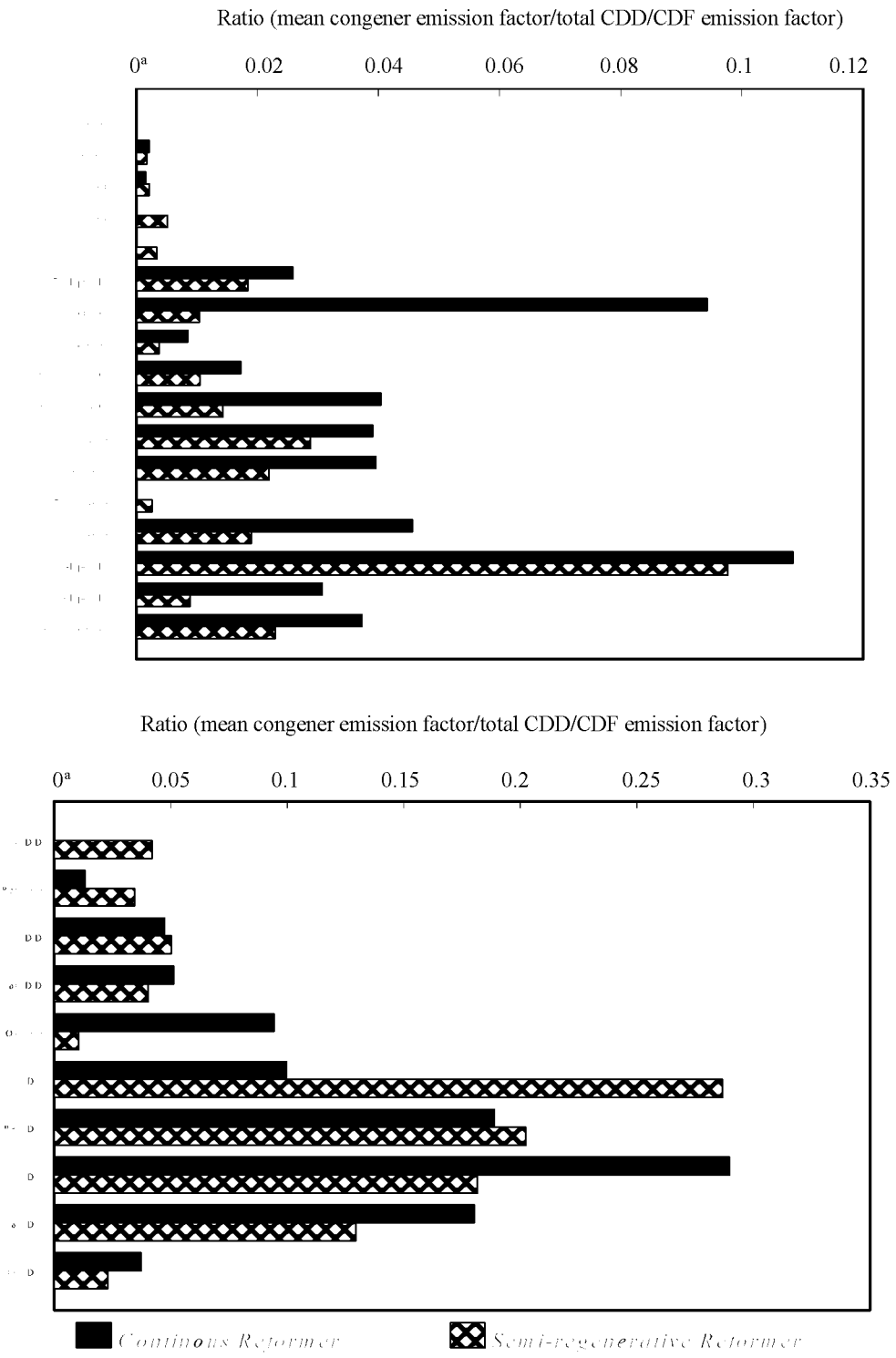


Figure 5-4. Congener and congener group profiles for air emissions from petroleum catalytic reforming units (nondetect set equal to zero)**.**

Sources: CARB (1999); Radian Corporation (1991).

No studies published to date have demonstrated a mass balance, and it is not known whether the CDDs/CDFs measured in cigarette smoke are the result of formation during tobacco combustion, volatilization of CDDs/CDFs present in the unburned tobacco, or a combination of these two source mechanisms. The combustion processes operating during cigarette smoking are complex and could be used to justify both source mechanisms. As reported by Guerin et al. (1992), during a puff on a cigarette, gas-phase temperatures reach 850°C at the core of the firecone, and solid-phase temperatures reach 800°C at the core and 900°C or greater at the char line. Thus, temperatures are sufficient to cause at least some destruction of CDDs/CDFs initially present in the tobacco. Both solid- and gas-phase temperatures rapidly decline to 200 to 400°C within 2 mm of the char line.

Formation of CDDs/CDFs has been reported in combustion studies with other media in this temperature range of 200 to 900°C. However, it is known that a process likened by Guerin et al. (1992) to steam distillation takes place in the region behind the char line because of high, localized concentrations of water and temperatures of 200 to 400°C. At least 1,200 tobacco constituents (e.g., nicotine, n-paraffin, some terpenes) are transferred intact from the tobacco into the smoke stream by distillation in this region, and it is plausible that CDDs/CDFs present in the unburned tobacco would be subject to similar distillation.

Bumb et al. (1980), using low-resolution mass spectrometry, analyzed the CDD content of mainstream smoke from the burning of a U.S. brand of unfiltered cigarette. A package of 20 cigarettes was combusted in each of two experiments. Approximately 20 to 30 puffs of 2 to 3 sec duration were collected from each cigarette on a silica column. Hexa-, hepta-, and octa-CDDs were detected at levels of 0.004 to 0.008, 0.009, and 0.02 to 0.05 ng/g, respectively.

Muto and Takizawa (1989) employed a continuous smoking apparatus to measure CDD congener concentrations in the mainstream smoke generated from the combustion of one kind of filtered cigarette (brand not reported). The apparatus pulled air at a constant continuous rate (rather than a pulsed rate) through a burning cigarette and collected the smoke on a series of traps (glass fiber filter, polyurethane foam, and XAD-II resin). The CDD content of the smoke as well as the CDD content of the unburned cigarette and the ash from the burned cigarettes were also analyzed using low-resolution mass spectrometry. The results are presented in Table 5-10, and the congener group profiles are presented in Figure 5-5. Table 5-11 and Figure 5-6 present the mainstream smoke results on a mass-per-cigarette basis to enable comparison with the results of other studies.

The major CDD congener group found was HpCDD, which accounted for 84% of total CDDs found in the cigarette, 94% of total CDDs found in smoke, and 99% of total CDDs found in the ash. The 2,3,7,8-HpCDDs also accounted for the majority of the measured TEQ in the

Table 5-10. CDD concentrations in Japanese cigarettes, smoke, and ash

Congener/congener group	Cigarette (pg/g)	Concentrations	
		Mainstream smoke (ng/m^3)	Ash (pg/g)
2,3,7,8-TCDD	ND (0.5)	ND (0.22)	ND (0.5)
1,2,3,7,8-PeCDD	ND (0.5)	0.43	ND (0.5)
1,2,3,4,7,8-HxCDD	2.01[a]	2.15[a]	0.56[a]
1,2,3,6,7,8-HxCDD	[a]	[a]	[a]
1,2,3,7,8,9-HxCDD	[a]	[a]	[a]
1,2,3,4,6,7,8-HpCDD	1343	783	ND (0.5)
OCDD	257	240	ND (0.5)
2,3,7,8-TCDF	NR	NR	NR
1,2,3,7,8-PeCDF	NR	NR	NR
2,3,4,7,8-PeCDF	NR	NR	NR
1,2,3,4,7,8-HxCDF	NR	NR	NR
1,2,3,6,7,8-HxCDF	NR	NR	NR
1,2,3,7,8,9-HxCDF	NR	NR	NR
2,3,4,6,7,8-HxCDF	NR	NR	NR
1,2,3,4,6,7,8-HpCDF	NR	NR	NR
1,2,3,4,7,8,9-HpCDF	NR	NR	NR
OCDF	NR	NR	NR
Total 2,3,7,8-CDD	1602.01	1025.58	0.56
Total 2,3,7,8-CDF	NR	NR	NR
Total I-TEQ_{DF}	13.9	8.5	0.06
Total TEQ_{DF}-WHO_{98}	13.7	8.3	0.06
Total TCDD	44.9	68	4.63
Total PeCDD	ND (0.5)	1.51	ND (0.5)
Total HxCDD	13.41	7.51	5.01
Total HpCDD	1629	4939	3211
Total OCDD	257	240	ND (0.5)
Total TCDF	NR	NR	NR
Total PeCDF	NR	NR	NR
Total HxCDF	NR	NR	NR
Total HpCDF	NR	NR	NR
Total OCDF	NR	NR	NR
Total CDD/CDF	1944	5256	3221

[a]Value reported only for total 2,3,7,8-substituted HxCDDs.

ND = Not detected (value in parenthesis is the detection limit)
NR = Not reported

Source: Muto and Takizawa (1989).

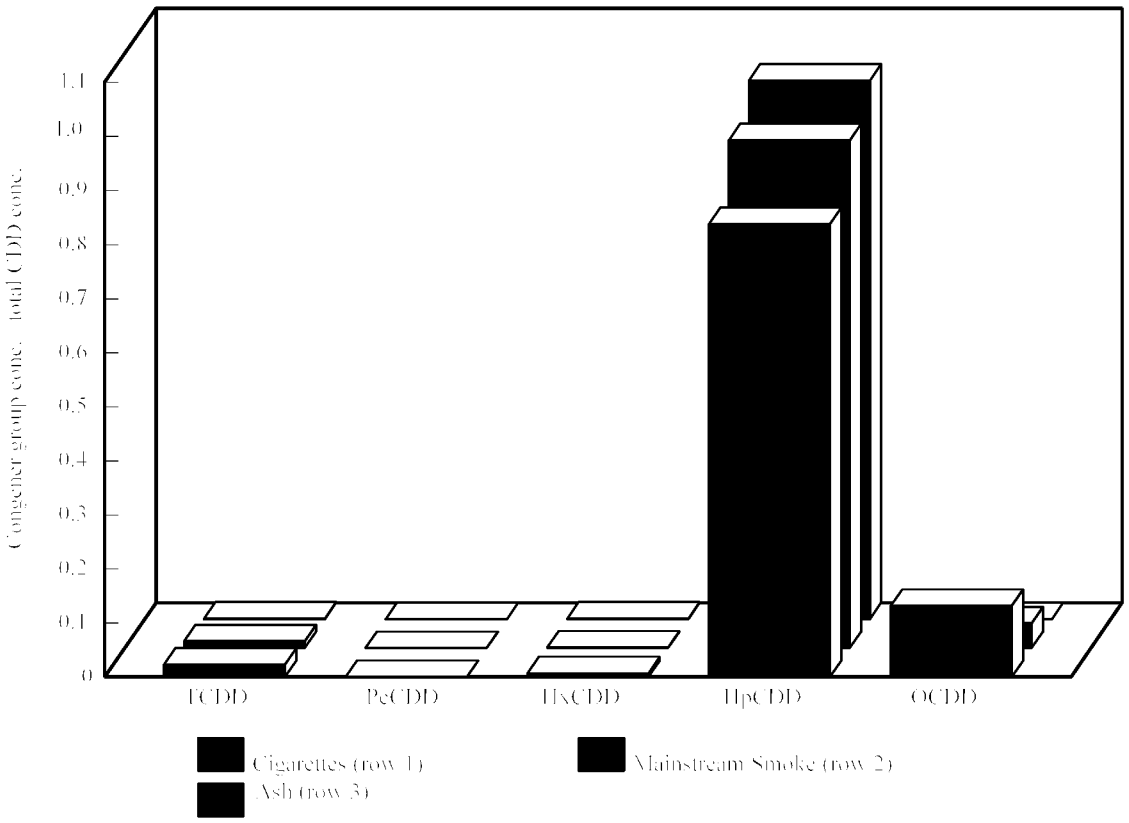


Figure 5-5. CDD profiles for Japanese cigarettes, smoke, and ash.

Source: Matsueda et al. (1994).

cigarettes and smoke; however, none were measured in the ash. Although no PeCDDs were detected in the cigarette, they were detected at low levels in the smoke, indicating probable formation during combustion. On the basis of the similarities in the congener group profiles for the three media, the study authors concluded that most of the CDDs found in the cigarette smoke result from volatilization of CDDs/CDFs present in the unburned cigarette rather than being formed during combustion.

Ball et al. (1990) measured the CDD/CDF content of mainstream smoke for the 10 best-selling German cigarette brands. The international test approach (1 puff/min; puff flow rate of 35 mL/2 sec) was employed with an apparatus that smoked 20 cigarettes at a time in three successive batches and had a large collection device. The average TEQ content (on both an I-TEQ_{DF} and a TEQ_{DF}-WHO_{98} basis) in mainstream smoke for the 10 brands tested, normalized to a mass-per-cigarette basis, was 0.09 pg/cigarette (i.e., 16.5 times less than the value reported by Muto and Takizawa, 1989, for a Japanese cigarette brand). However, the congener group

Table 5-11. CDD/CDF concentrations (pg/cig) in cigarette smoke, normalized to a per-cigarette basis[a]

Congener/congener group	Muto and Takizawa (1989) (1 Japanese brand) (mainstream smoke)	Ball et al. (1990) (avg. of 10 German brands) (mainstream smoke)	Löfroth and Zebühr (1992) (1 Swedish brand) (mainstream smoke)	Löfroth and Zebühr (1992) (1 Swedish brand) (sidestream smoke)
2,3,7,8-TCDD	ND (0.04)	ND (0.03)	0.028	0.07
1,2,3,7,8-PeCDD	0.075	ND (0.03)	0.15	0.32
1,2,3,4,7,8-HxCDD	0.376	0.06	0.1	0.19
1,2,3,6,7,8-HxCDD	[b]	0.05	0.34	0.6
1,2,3,7,8,9-HxCDD	[b]	0.04	0.25	0.55
1,2,3,4,6,7,8-HpCDD	137	1.3	6.05	12.2
OCDD	42	3.4	22.1	38.8
2,3,7,8-TCDF	NR	0.19	1.2[c]	2.1[c]
1,2,3,7,8-PeCDF	NR	0.13	0.34[c]	0.8[c]
2,3,4,7,8-PeCDF	NR	0.04	0.34	0.6
1,2,3,4,7,8-HxCDF	NR	ND (0.03)	1.3[c]	3.8[c]
1,2,3,6,7,8-HxCDF	NR	0.03	0.48	1.2
1,2,3,7,8,9-HxCDF	NR	0.03	0.14	0.39
2,3,4,6,7,8-HxCDF	NR	0.05	0.21	0.5
1,2,3,4,6,7,8-HpCDF	NR	0.16	10	23.5
1,2,3,4,7,8,9-HpCDF	NR	0.03	2.6	5
OCDF	NR	0.11	3.2	10.7
Total 2,3,7,8-CDD	179.45	4.85	29.02	52.7
Total 2,3,7,8-CDF	NR	0.77	19.81	48.6
Total I-TEQ_{DF}	1.49	0.09	0.9	1.96
Total TEQ_{DF}-WHO_{98}	1.49	0.09	0.96	2.08
Total TCDD	11.9	0.51	0.61	0.67
Total PeCDD	0.264	0.14	1.07	2.14
Total HxCDD	1.31	0.53	2.52	5.2
Total HpCDD	864	2.9	12.3	21.3
Total OCDD	42	3.4	22.1	38.8
Total TCDF	NR	1.41	4.5	5.75
Total PeCDF	NR	0.83	3.23	6.35
Total HxCDF	NR	0.35	5.3	12.9
Total HpCDF	NR	0.27	19.8	47.8
Total OCDF	NR	0.11	3.2	10.7
Total CDD/CDF	919.47	10.45	74.63	151.6

[a]Emissions calculated assuming 0.0035 m^3 of smoke are inhaled per 20 cigarettes smoked (Muto and Takizawa, 1992).

[b]Muto and Takizawa (1989) reported a value only for total 2,3,7,8-HxCDDs (0.38 pg/cig).

[c]Concentrations listed include the contribution of a coeluting non-2,3,7,8-substituted congener.

ND = Not detected (value in parenthesis is the detection limit)
NR = Not reported

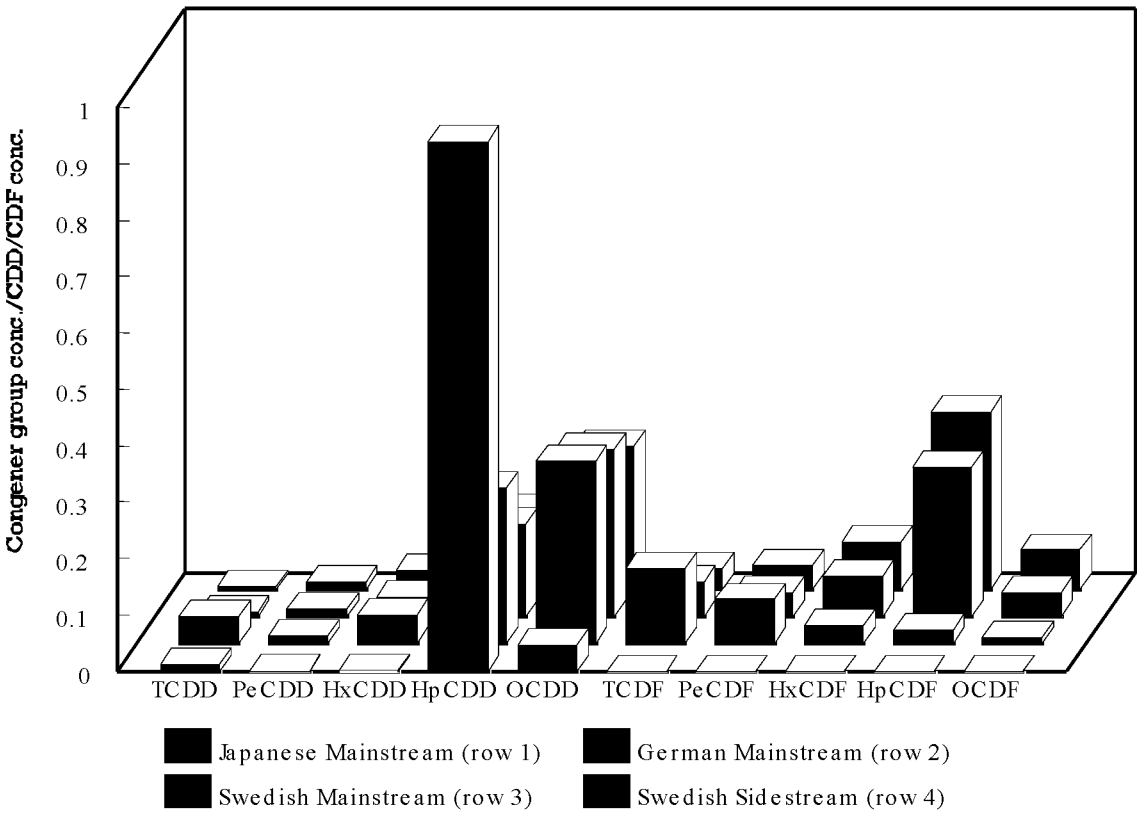


Figure 5-6. Congener group profiles for mainstream and sidestream cigarette smoke.

Source: Matsueda et al. (1994).

profiles were similar to those reported by Muto and Takizawa, with HpCDD and OCDD the dominant congener groups found.

Löfroth and Zebühr (1992) measured the CDD/CDF content of mainstream and sidestream smoke from one common Swedish cigarette brand. The cigarette brand was labeled as giving 17 mg carbon monoxide, 21 mg tar, and 1.6 mg nicotine. The international test approach was used, and the smoke was collected on glass fiber filters followed by two polyurethane plugs. The analytical results for mainstream and sidestream smoke are presented in Table 5-11. The TEQ content in mainstream smoke, normalized to a mass-per-cigarette basis, was 0.96 pg TEQ_{DF}-WHO_{98}/cigarette (0.9 pg I-TEQ_{DF}/cigarette) (i.e., about two times less than the value reported by Muto and Takizawa, 1989, and 10 times greater than the average value reported by Ball et al., 1990). As in the Muto and Takizawa and Ball et al. studies, the dominant congener groups were HpCDDs and OCDD; however, HpCDFs were also relatively high in

comparison with the other congener group totals. The sidestream smoke contained 2.08 pg TEQ_{DF}-WHO_{98}/cigarette (1.96 pg I-TEQ_{DF}/cigarette), or twice that of mainstream smoke.

Using high-resolution mass spectrometry, Matsueda et al. (1994) analyzed the CDD/CDF content of tobacco from 20 brands of commercially available cigarettes collected in 1992 from Japan, the United States, Taiwan, China, the United Kingdom, Germany, and Denmark. Table 5-12 presents the study results. The total CDD/CDF content ranged from 109 to 1,136 pg/pack, and total TEQ_{DF}-WHO_{98} content ranged from 1.9 to 14 pg/pack (1.4 to 12.6 pg/pack on an I-TEQ_{DF} basis). The Chinese cigarette brand contained significantly lower CDDs/CDFs and TEQs than did any other brand of cigarette. Figure 5-7 depicts the congener group profiles for the average results for each country. A high degree of similarity is seen among the CDF congener group profiles of the tested cigarette brands. The Japanese and Taiwanese cigarettes show CDD congener group profiles different from those of the other countries' cigarettes.

Brown (2002) estimated that 440 billion cigarettes were consumed in the United States in 2000. In 1995, approximately 487 billion cigarettes were consumed in the United States and by U.S. overseas armed forces personnel. In 1987, approximately 575 billion cigarettes were consumed. According to The Tobacco Institute (1995), per capita U.S. cigarette consumption, based on the total U.S. population aged 16 and over, was a record high of 4,345 in 1963, declining to 2,415 in 1995 and 1,563 in 2000 (USDA, 1997; U.S. Census Bureau, 2000). The activity level estimates by Brown (2002) were adopted, and a high confidence rating is assigned because they are based on known consumption rates.

The available emission factor data presented above provide the basis for two methods of estimating the amount of TEQs that may have been released to the air in the United States in 2000, 1995, and 1987 from the combustion of cigarettes. The confidence rating assigned to the emission factor is low because of the very limited amount of testing performed to date. First, an annual emission estimate for 2000 of 0.19 g TEQ (on a TEQ_{DF}-WHO_{98} or I-TEQ_{DF} basis) is obtained if it is assumed that (a) the average TEQ content of seven brands of U.S. cigarettes reported by Matsueda et al. (1994)—6.3 pg TEQ_{DF}-WHO_{98}/pack (5.5 pg I-TEQ_{DF}/pack)—is representative of cigarettes smoked in the United States, (b) CDDs/CDFs are not formed and the congener profile reported by Matsueda et al. (1994) is not altered during combustion of cigarettes, and (c) all CDDs/CDFs contributing to the TEQ are released from the tobacco during smoking.

The available emission factor data presented above provide the basis for two methods of estimating the amount of TEQs that may have been released to the air in the United States in 2000, 1995, and 1987 from the combustion of cigarettes. The confidence rating assigned to the emission factor is low because of the very limited amount of testing performed to date. First, an

Table 5-12. CDD/CDF concentrations (pg/pack) in tobacco cigarette brands from various countries

	U.S. (avg. of 7 brands)	Japan (avg. of 6 brands)	United Kingdom (avg. of 3 brands)	Taiwan (1 brand)	China (1 brand)	Denmark (1 brand)	Germany (1 brand)
2,3,7,8-TCDD	1.2	0.5	1.7	1	ND	0.5	1.1
1,2,3,7,8-PeCDD	1.6	1.4	3.1	3.3	1.1	0.8	3.3
1,2,3,4,7,8-HxCDD	6.9	4.8	6.1	12.2	1.1	6.2	5.7
1,2,3,6,7,8-HxCDD	[a]	[a]	[a]	[a]	[a]	[a]	[a]
1,2,3,7,8,9-HxCDD	[a]	[a]	[a]	[a]	[a]	[a]	[a]
1,2,3,4,6,7,8-HpCDD	52.7	17.8	23.9	26.4	2.2	53.3	32.7
OCDD	589.3	244	189.5	272.7	28.2	354.3	288.6
2,3,7,8-TCDF	18.2	4.8	15.6	11	1.2	2.2	7.9
1,2,3,7,8-PeCDF	8.7	5.3	21.2	16	1.5	4.3	14.4
2,3,4,7,8-PeCDF	[b]	[b]	[b]	[b]	[b]	[b]	[b]
1,2,3,4,7,8-HxCDF	8.1	8.1	17	12.9	2.2	4.3	13.2
1,2,3,6,7,8-HxCDF	[c]	[c]	[c]	[c]	[c]	[c]	[c]
1,2,3,7,8,9-HxCDF	[c]	[c]	[c]	[c]	[c]	[c]	[c]
2,3,4,6,7,8-HxCDF	[c]	[c]	[c]	[c]	[c]	[c]	[c]
1,2,3,4,6,7,8-HpCDF	17.6	11.1	13.6	13.2	1.5	7	12.9
1,2,3,4,7,8,9-HpCDF	[d]	[d]	[d]	[d]	[d]	[d]	[d]
OCDF	24.6	10.5	8.3	13.9	0.5	10.5	13.9
Total 2,3,7,8-CDD	651.7	268.5	224.3	315.6	32.6	415.1	331.4
Total 2,3,7,8-CDF	77.2	39.8	75.7	67	6.9	28.3	62.3
Total I-TEQ_{DF}	7.1	3.8	8.8	7.7	1.1	3.4	6.9
Total TEQ_{DF}-WHO_{98}	7.3	4.3	10.1	9.1	1.7	3.4	8.3
Total TCDD	47.1	296.3	85.1	329	9.7	17	49.5
Total PeCDD	27.6	33.6	62.9	150.5	5.2	9.8	40.8
Total HxCDD	40.6	29.2	49.2	99.4	5.4	26.7	40.6
Total HpCDD	108.7	40	47.7	62	3.8	93.1	60.2
Total OCDD	589.3	244	189.5	272.7	28.2	354.3	288.6
Total TCDF	183.8	102.1	348.9	372.1	35.4	97.8	233.4
Total PeCDF	57.7	45.9	134.5	149.1	11.2	35.5	97.5
Total HxCDF	29.1	26.4	51.3	45.8	7.8	18.1	40.8
Total HpCDF	27.3	16.6	19	18.5	1.7	11.1	21.2
Total OCDF	24.6	10.5	8.3	13.9	0.5	10.5	13.9
Total CDD/CDF	1,135.8	844.6	996.4	1513	108.9	673.9	886.5

[a]Value reported only for total 2,3,7,8-substituted HxCDDs.
[b]Value reported only for total 2,3,7,8-substituted PeCDFs.
[c]Value reported only for total 2,3,7,8-substituted HxCDFs.
[d]Value reported only for total 2,3,7,8-substituted HpCDFs.

Source: Matsueda et al. (1994).

annual emission estimate for 2000 of 0.19 g TEQ (on a TEQ_{DF}-WHO_{98} or I-TEQ_{DF} basis) is obtained if it is assumed that (a) the average TEQ content of seven brands of U.S. cigarettes

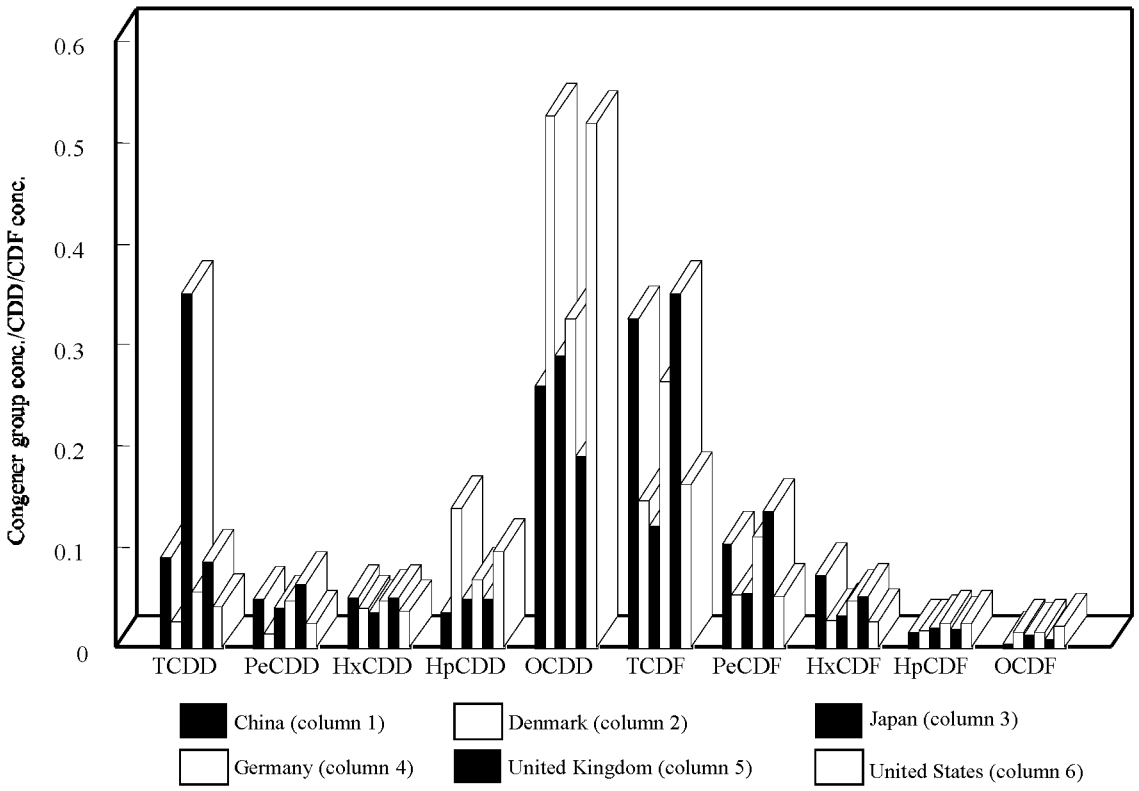


Figure 5-7. Congener group profiles for cigarette tobacco from various countries.

Source: Matsueda et al. (1994).

reported by Matsueda et al. (1994)—6.3 pg TEQ_{DF}-WHO_{98}/pack (5.5 pg I-TEQ_{DF}/pack)—is representative of cigarettes smoked in the United States, (b) CDDs/CDFs are not formed and the congener profile reported by Matsueda et al. (1994) is not altered during combustion of cigarettes, and (c) all CDDs/CDFs contributing to the TEQ are released from the tobacco during smoking.

The second method of estimating is based on the assumption that the TEQ emission rates for a common Swedish brand of cigarette reported by Löfroth and Zebühr (1992) for mainstream smoke (0.96 pg TEQ_{DF}-WHO_{98}/cigarette [0.9 pg I-TEQ_{DF}/cigarette]) and sidestream smoke (2.08 pg TEQ_{DF}-WHO_{98}/cigarette [1.96 pg I-TEQ_{DF}/cigarette]) are representative of the emission rates for U.S. cigarettes. For 2000, the two methods yield estimates of 0.11 g TEQ_{DF}-WHO_{98} (0.1 g I-TEQ) and 0.67 g TEQ_{DF}-WHO_{98} (0.63 g I-TEQ_{DF}). For 1995, the two methods yield estimates of 0.2 g (on a TEQ_{DF}-WHO_{98} or I-TEQ_{DF} basis) and 1.48 g TEQ_{DF}-WHO_{98} (1.41 g I-TEQ_{DF}). For

1987, the two methods yield estimates of 0.14 g TEQ_{DF}-WHO_{98} (0.12 g I-TEQ_{DF} basis) and 1.75 g TEQ_{DF}-WHO_{98} (1.67 g I-TEQ_{DF}).

For purposes of this report, the best estimates of annual emissions are assumed to be the average of the annual emissions estimated by the two methods for 2000, 1995, and 1987 (0.4 g, 0.8 g, and 1 g TEQ_{DF}-WHO_{98} or I-TEQ_{DF}, respectively). These emissions are assigned a low confidence rating because the emission factor has a low confidence rating. Although these emission quantities are relatively small when compared with the emission quantities estimated for various industrial combustion source categories, they are significant because humans are directly exposed to cigarette smoke.

5.6. PYROLYSIS OF BROMINATED FLAME RETARDANTS

The pyrolysis and photolysis of brominated phenolic derivatives and polybrominated biphenyl ethers used as flame retardants in plastics (especially those used in electronic devices), textiles, and paints can generate considerable amounts of polybrominated dibenzo-*p*-dioxins (BDDs) and dibenzofurans (BDFs) (Watanabe and Tatsukawa, 1987; Thoma and Hutzinger, 1989; Luijk et al., 1992). Watanabe and Tatsukawa (1987) observed the formation of BDFs from the photolysis of decabromobiphenyl ether. Approximately 20% of the decabromobiphenyl ether was converted to BDFs in samples that were irradiated with ultraviolet light for 16 hr.

Thoma and Hutzinger (1989) observed the formation of BDFs during combustion experiments with polybutylene-terephthalate polymers containing 9 to 11% decabromodiphenyl ether. Maximum formation of BDFs occurred at 400 to 600°C, with a BDF yield of 16%. Although the authors did not provide specific quantitative results for similar experiments conducted with octabromodiphenyl ether and 1,2-bis(tri-bromophenoxy)ethane, they did report that BDDs and BDFs were formed.

Luijk et al. (1992) studied the formation of BDDs/BDFs during the compounding and extrusion of decabromodiphenyl ether into high-impact polystyrene polymer at 275°C. Hepta- and octa-BDF were formed during repeated extrusion cycles, and the yield of BDFs increased as a function of the number of extrusion cycles. HpBDF increased from 1.5 to 9 ppm (in the polymer matrix), and OBDF increased from 4.5 to 45 ppm after four extrusion cycles.

Insufficient data are available at this time from which to derive annual BDD/BDF emission estimates for this source.

5.7. CARBON REACTIVATION FURNACES

Granular activated carbon (GAC) is an adsorbent that is widely used to remove organic pollutants from wastewater and to treat finished drinking water at water treatment plants. Activated carbon is manufactured from the pyrolytic treatment of nut shells and coal (Buonicore,

1992a). The properties of GAC make it ideal for adsorbing and controlling vaporous organic and inorganic chemicals entrained in combustion plasmas as well as soluble organic contaminants in industrial effluents and drinking water. The high ratio of surface area to particle weight (600:1,600 m^2/g), combined with the extremely small pore diameter of the particles (15 to 25 angstroms), increases the adsorption characteristics (Buonicore, 1992a). GAC eventually becomes saturated, and the adsorption properties significantly degrade. When saturation occurs, GAC usually must be discarded and replaced, which significantly increases the costs of pollution control.

The introduction of carbon reactivation furnace technology in the mid-1980s created a method involving the thermal treatment of used GAC to thermolytically desorb the synthetic compounds and restore the adsorption properties for reuse (Lykins et al., 1987). Large-scale regeneration operations, such as those used in industrial water treatment operations, typically use multiple-hearth furnaces. For smaller-scale operations, such as those used in municipal water treatment operations, fluidized-bed and infrared furnaces are used. Emissions are typically controlled by afterburners followed by water scrubbers (U.S. EPA, 1997a).

The used GAC can contain compounds that are precursors to the formation of CDDs/CDFs during the thermal treatment process. A study by EPA (U.S. EPA, 1987a) measured precursor compounds in spent GAC that was used as a feed material to a carbon reactivation furnace tested during the National Dioxin Study. The total chlorobenzene content of the GAC ranged from 150 to 6,630 ppb. Trichlorobenzene was the most prevalent species present, with smaller quantities of di- and tetra-chlorobenzenes detected. Total halogenated organics were measured to be about 150 ppm.

EPA has stack-tested two GAC reactivation furnaces for the emission of dioxin (U.S. EPA, 1987a; Lykins et al., 1987). One facility was an industrial carbon reactivation plant, and the second facility was used to restore GAC at a municipal drinking water plant. EPA (U.S. EPA, 1997a) reported results of other testing performed at a county water facility in California during 1990.

The industrial carbon reactivation plant processed 36,000 kg/day of spent GAC used in the treatment of industrial wastewater effluents. This facility was chosen for testing because it was considered to be representative of other facilities in the source category (U.S. EPA, 1987a). Spent carbon was reactivated in a multiple-hearth furnace, cooled in a water quench, and shipped back to primary chemical manufacturing facilities for reuse. The furnace was fired by natural gas and consisted of seven hearths arranged vertically in series. The hearth temperatures ranged from 480 to 1,000°C. Air pollutant emissions were controlled by an afterburner, a sodium spray cooler, and an FF. Temperatures in the afterburner were about 930°C. The estimated I-TEQ_{DF} emission factor (treating nondetect values as zero) was 0.76 ng TEQ_{DF}-WHO_{98}/kg (0.64 ng

I-TEQ_{DF}/kg) carbon processed. The emission factor for total CDDs/CDFs was 58.6 ng/kg. Because analyses were performed only for 2,3,7,8-TCDD; 2,3,7,8-TCDF; OCDD; and OCDF and the congener groups, equivalent concentrations were assumed for all toxic and nontoxic congeners in each of the penta, hexa, and hepta congener groups.

The second GAC reactivation facility tested by EPA consisted of a fluidized-bed furnace located at a municipal drinking water treatment plant (Lykins et al., 1987). The furnace was divided into three sections: a combustion chamber, a reactivation section, and a dryer section. The combustion chamber was fired by natural gas and consisted of a stoichiometrically balanced stream of fuel and oxygen. Combustion temperatures were about 1,038°C. Gases from the reactivation section and combustion chamber were directed through an acid gas scrubber and high-temperature afterburner prior to discharge from a stack. Although measurable concentrations of dioxin-like compounds were detected in the stack emissions, measurements of the individual CDD/CDF congeners were not performed; therefore, it was not possible to derive TEQ emission factors for this facility. With the afterburner operating, no CDD congeners below HpCDD were detected in the stack emissions. Concentrations of HpCDDs and OCDD ranged from 0.001 to 0.05 ppt/volume basis (ppt/v) and 0.006 to 0.28 ppt/v, respectively. All CDF congener groups were detected in the stack emissions even with the afterburner operating. Total CDFs emitted from the stack averaged 0.023 ppt/v.

EPA (U.S. EPA, 1997a) reported a TEQ emission factor of 1.73 ng I-TEQ_{DF}/kg of carbon processed for the reactivation unit at a county water facility in California in 1990. The emission factor for total CDDs/CDFs was reported to be 47 ng/kg (i.e., similar to the total CDD/CDF emission factor of 58.6 ng/kg at the industrial GAC facility). Because congener-specific results were not reported, it was not possible to calculate the TEQ_{DF}-WHO_{98} emission factor. The report also did not provide the configuration and type of furnace tested; however, it did state that the emissions from the furnace were controlled by an afterburner and a scrubber.

The industrial GAC reaction furnace test data indicate that an average of 0.64 ng I-TEQ_{DF}/kg of GAC may be released. The I-TEQ_{DF} emission rate for the reactivation unit at the county water treatment facility was 1.73 ng I-TEQ_{DF}/kg carbon. Low confidence ratings are given to these emission factors because only two GAC reactivation furnaces were stack tested, and not all congeners were analyzed at the industrial GAC facility.

The mass of GAC that is reactivated annually in carbon reactivation furnaces is not known. However, a rough estimate, to which a low confidence rating is assigned, is the mass of virgin GAC shipped each year by GAC manufacturers. According to the U.S. Department of Commerce (U.S. DOC, 1990c), 48,000 metric tons of GAC were shipped in 1987. EPA reported that in 1990, water and wastewater treatment operations consumed 65,000 metric tons of GAC

(U.S. EPA, 1995b, 1997a). The 1990 activity level was used in this document as a surrogate for the 1995 and 2000 activity levels.

Applying the average TEQ emission factor of 1.2 ng (TEQ_{DF}-WHO_{98} or I-TEQ_{DF}) per kg of reactivated carbon for the two tested facilities to the estimates of potential GAC reactivation volumes yields annual release estimates of 0.06 g (TEQ_{DF}-WHO_{98} or I-TEQ_{DF}) in 1987 and 0.08 g (TEQ_{DF}-WHO_{98} or I-TEQ_{DF}) in 1995 and 2000 (assuming that the activity level for 1990 is representative of the 1995 and 2000 activity levels). These emission estimates are assigned a low confidence rating because both the activity and emission factor estimates had low confidence ratings.

5.8. KRAFT BLACK LIQUOR RECOVERY BOILERS

Kraft black liquor recovery boilers are associated with the production of pulp in the making of paper using the Kraft process. In this process, wood chips are cooked in large vertical vessels called digesters at elevated temperatures and pressures in an aqueous solution of sodium hydroxide and sodium sulfide. Wood is broken down into two phases: a soluble phase containing primarily lignin, and an insoluble phase containing the pulp. The spent liquor (called black liquor) from the digester contains sodium sulfate and sodium sulfide, which the industry recovers for reuse in the Kraft process.

In the recovery of black liquor chemicals, weak black liquor is first concentrated in multiple-effect evaporators to about 65% solids. The concentrated black liquor also contains 0.5 to 4% chlorides by weight, which are recovered through combustion. The concentrated black liquor is sprayed into a Kraft black liquor recovery furnace equipped with a heat recovery boiler. The bulk of the inorganic molten smelt that forms in the bottom of the furnace contains sodium carbonate and sodium sulfide in a ratio of about 3:1. The combustion gas is usually passed through an ESP that collects PM prior to being vented out the stack. The PM can be processed to further recover and recycle sodium sulfate (Someshwar and Pinkerton, 1992).

In 1987, EPA stack-tested three Kraft black liquor recovery boilers for the emission of dioxin in conjunction with the National Dioxin Study (U.S. EPA, 1987a). The three sites tested by EPA were judged to be typical of Kraft black liquor recovery boilers at that time. During pretest surveys, two facilities were judged to have average potential for CDD/CDF emissions and one was judged to have high potential, based on the amount of chlorine found in the feed to these units. Dry-bottom ESPs controlled emissions from two of the boilers; a wet-bottom ESP controlled emissions from the third. The results of these tests included congener group concentrations but lacked measurement results for specific congeners other than 2,3,7,8-TCDD and 2,3,7,8-TCDF.

NCASI (1995) provided congener-specific emission test results for six additional boilers tested during 1990 to 1993. Three boilers were of the direct contact type, and three were noncontact type. All were equipped with ESPs. The average congener and congener group emission factors are presented in Table 5-13 for the three facilities reported by EPA (U.S. EPA, 1987a) and the six facilities reported by NCASI (1995). Figure 5-8 presents the average congener and congener group profiles based on the test results presented by NCASI (1995).

The average TEQ emission factor, based on the data for the six NCASI facilities with complete congener data, was 0.028 ng TEQ_{DF}-WHO_{98}/kg (0.029 ng I-TEQ_{DF}/kg) of black liquor solids, assuming nondetect values were zero, and 0.078 ng TEQ_{DF}-WHO_{98}/kg (0.068 ng I-TEQ_{DF}/kg), assuming nondetect values were present at one-half the DL. This value is assumed to apply to all three reference years (1987, 1995, and 2000). The results for the three facilities reported by EPA were not used in the derivation of the TEQ emission factor because congener-specific measurements for most 2,3,7,8-substituted congeners were not made in the study (U.S. EPA, 1987a). A medium confidence rating is assigned to those emission factors because they were derived from the stack testing of six Kraft black liquor recovery boilers that were judged to be fairly representative of technologies used at Kraft pulp mills in the United States.

A 1995 survey of the industry indicated that 215 black liquor recovery boilers were in operation at U.S. pulp and paper mills. All but one of these boilers used ESPs for control of particulate emissions; the one unique facility used dual scrubbers. In addition, ESPs were reported to have been the predominant means of particulate control at recovery boilers for the past 20 years (letter dated October 8, 1998, from W. Gillespie, National Council of the Paper Industry for Air and Stream Improvement, Inc., to G. Schweer, Versar, Inc.).

The amounts of black liquor solids burned in Kraft black liquor recovery boilers in the United States during 1987 and 1995 were 69.8 million metric tons and 80.8 million metric tons, respectively (American Paper Institute, 1992; American Forest and Paper Association, 1997). These activity level estimates are assigned a high confidence rating because they are based on comprehensive industry survey data. Combining the emission factors derived above with the activity level estimates for 1987 and 1995 yields estimated annual emissions from this source of approximately 2 g (TEQ_{DF}-WHO_{98} or I-TEQ_{DF}) in 1987 and 2.3 g (TEQ_{DF}-WHO_{98} or I-TEQ_{DF}) in 1995. These emission estimates are assigned a medium confidence rating because the emission factor have a medium confidence rating.

For 2000, NCASI provided estimates of activity levels for Kraft recovery furnaces and Kraft lime kilns and CDD/CDF releases, including emissions from 11 Kraft recovery furnaces and four Kraft lime kilns (Gillespie, 2002). The activity levels were reported to be 90.7 million

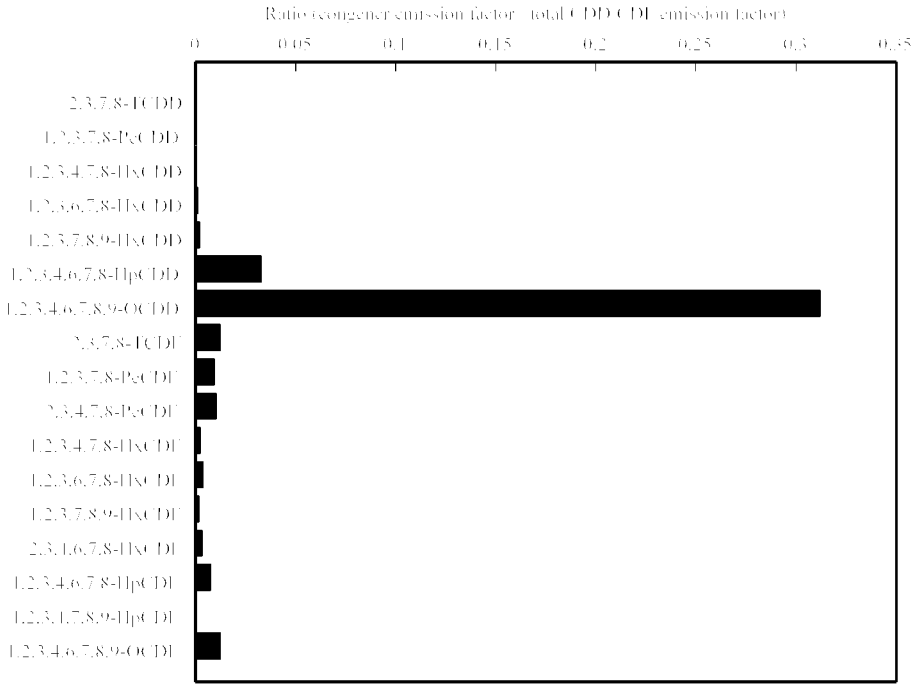
Table 5-13. CDD/CDF mean emission factors (ng/kg feed) for black liquor recovery boilers

Congener	U.S. EPA (1987a) (3 facilities)		NCASI (1995) (6 facilities)	
	Nondetect set to zero	Nondetect set to ½ detection limit	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	0	0.04	0	0.016
1,2,3,7,8-PeCDD	NR	NR	0	0.016
1,2,3,4,7,8-HxCDD	NR	NR	0.001	0.018
1,2,3,6,7,8-HxCDD	NR	NR	0.003	0.015
1,2,3,7,8,9-HxCDD	NR	NR	0.006	0.019
1,2,3,4,6,7,8-HpCDD	NR	NR	0.108	0.135
OCDD	4.24	4.24	1.033	1.054
2,3,7,8-TCDF	0.04	0.06	0.04	0.049
1,2,3,7,8-PeCDF	NR	NR	0.03	0.036
2,3,4,7,8-PeCDF	NR	NR	0.033	0.037
1,2,3,4,7,8-HxCDF	NR	NR	0.007	0.022
1,2,3,6,7,8-HxCDF	NR	NR	0.012	0.021
1,2,3,7,8,9-HxCDF	NR	NR	0.005	0.016
2,3,4,6,7,8-HxCDF	NR	NR	0.01	0.021
1,2,3,4,6,7,8-HpCDF	NR	NR	0.024	0.035
1,2,3,4,7,8,9-HpCDF	NR	NR	0	0.014
OCDF	0.35	0.35	0.113	0.13
Total TCDD	0.21	0.36	0.106	0.123
Total PeCDD	0.27	0.35	0.013	0.059
Total HxCDD	0.8	1.02	0.104	0.122
Total HpCDD	2.05	2.05	0.252	0.279
Total OCDD	4.24	4.24	1.033	1.054
Total TCDF	0.95	1	1.27	1.275
Total PeCDF	0.64	0.77	0.37	0.376
Total HxCDF	1.16	1.2	0.102	0.109
Total HpCDF	1.05	1.05	0.024	0.038
Total OCDF	0.35	0.35	0.113	0.13
Total I-TEQ_{DF}	0.10[a]	0.15[a]	0.029	0.065
Total TEQ_{DF}-WHO_{98}	0.10[a]	0.16[a]	0.028	0.072
Total CDD/CDF	11.72	12.39	3.39	3.57

[a]Estimate based on the measured data for 2,3,7,8-TCDD; 2,3,7,8-TCDF; OCDD; and OCDF and congener group emissions (i.e., for the penta-, hexa-, and hepta-CDD and CDFs, it was assumed that the measured emission factor within a congener group was the sum of equal emission factors for all congeners in that group, including non-2,3,7,8-substituted congeners).

NR = Not reported

metric tons for Kraft recovery furnaces and 13 million metric tons for Kraft lime kilns. These activity level estimates are assigned a high confidence rating because they are based on comprehensive industry survey data. Emission factors were taken from "NCASI Handbook of Chemical Specific Information for SARA Section 313 Form R Reporting." The factors provided



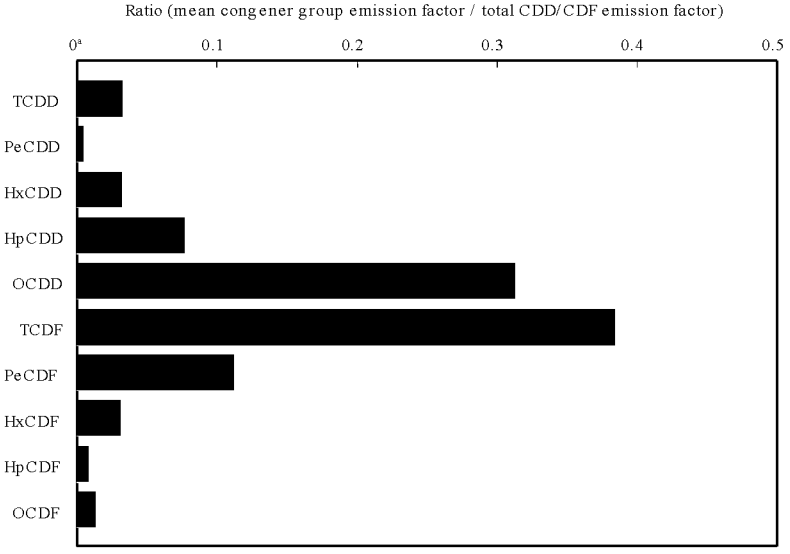


Figure 5-8. Congener and congener group profiles for air emissions from Kraft black liquor recovery boilers (nondetect set equal to zero**).**

Source: NCASI (1995).

in this handbook were compiled from valid test data supplied to NCASI by a variety of sources, including NCASI member companies who had performed the tests in response to a regulatory program. They are assigned a high confidence rating because they are based on a comprehensive survey of stack emissions. Congener-specific CDD/CDF TEQ emission factors were provided for both source categories (Table 5-14). Using the congener-specific emission factors and the activity levels provided above, NCASI estimated CDD/CDF TEQ_{DF}-WHO_{98} emissions for each congener (Table 5-14) and reported total emissions of 0.75 g TEQ_{DF}-WHO_{98}/yr and 6.9e−5 g TEQ_{DF}-WHO_{98}/yr for Kraft recovery furnaces and Kraft lime kilns, respectively. This 2000 emissions estimate has a high confidence rating because both the emission factor and activity level are rated as high confidence.

5.9. OTHER IDENTIFIED SOURCES

Several manufacturing processes are identified as potential sources of CDD/CDF formation because the processes use chlorine-containing components or involve application of high temperatures. However, no testing of emissions from these processes has been performed in the United States, and only minimal emission rate information has been reported for these processes in other countries. Therefore, these sources are rated as Category E sources, meaning their emissions cannot be quantified.

Burning of candles. Schwind et al. (1995) analyzed the wicks and waxes of uncolored candles as well as the fumes of burning candles for CDDs/CDFs, total chlorophenol, and total chlorobenzene content. The results, presented in Table 5-15, show that beeswax contained the highest levels of CDDs/CDFs and total chlorophenols. In contrast, the concentration of total chlorobenzenes in stearin wax was higher than that in paraffin or beeswax by a factor of 2 to 3. The concentrations of the three analyte groups were significantly lower in the wicks than in the waxes. Emissions of CDDs/CDFs from all three types of candles were very low during burning. In fact, comparison of the emission factor with the original CDD/CDF concentrations in the wax indicates a net destruction of the CDDs/CDFs originally present in the wax. Information on the activity level is lacking, therefore, no estimate of environmental release can be made at this time.

Glass manufacturing. Annual emissions of less than 1 g I-TEQ_{DF}/yr have been estimated for glass manufacturing facilities in the Netherlands (Bremmer et al., 1994) and the United Kingdom (Douben et al., 1995). Glass is manufactured by heating a mixture of sand and, depending on the type of glass, lime, sodium carbonate, dolomite, clay, or feldspar to a temperature of 1,400 to 1,650°C. In addition, various coloring and clarifying agents may be added. Chlorine enters the process as a contaminant (NaCl) in sodium carbonate (Bremmer et al. 1994). However, the emission factors used by Bremmer et al. and Douben et al. were not reported. Umweltbundesamt (1996) reported relatively low emission factors (approximately 0.002 and 0.007 ng I-TEQ_{DF}/kg) for two glass manufacturing facilities in Germany.

Table 5-14. CDD/CDF TEQ emission factors and emission estimates from Kraft recovery furnaces and Kraft lime kilns

Congener	Kraft recovery furnaces		Kraft lime kilns	
	TEQ_{DF}-WHO_{98} (ng/lb BLS)	Emissions (ng/yr)	TEQ_{DF}-WHO_{98} (ng/lb CaO)	Emissions (ng/yr)
2,3,7,8-TCDD	0.00e+00	0.00e+00	0.00e+00	0.00e+00
1,2,3,7,8-PeCDD	0.00e+00	0.00e+00	0.00e+00	0.00e+00
1,2,3,4,7,8-HxCDD	0.00e+00	0.00e+00	0.00e+00	0.00e+00
1,2,3,6,7,8-HxCDD	2.00e−04	3.33e+07	1.00e–04	2.60e+03
1,2,3,7,8,9-HxCDD	5.00e−04	8.31e+07	0.00e+00	0.00e+00
1,2,3,4,6,7,8-HpCDD	4.90e−04	8.15e+07	2.80e−04	7.27e+03
1,2,3,4,6,7,8,9-OCDD	1.42e−04	2.36e+07	2.56e−04	6.65e+03
2,3,7,8-TCDF	5.00e−04	8.31e+07	8.00e−04	2.08e+04
1,2,3,7,8-PeCDF	1.00e−04	1.66e+07	1.00e−04	2.60e+03
2,3,4,7,8-PeCDF	1.50e−03	2.49e+08	0.00e+00	0.00e+00
1,2,3,4,7,8-HxCDF	4.00e−04	6.65e+07	9.00e−04	2.34e+04
1,2,3,6,7,8-HxCDF	2.00e−04	3.33e+07	2.00e−04	5.20e+03
1,2,3,7,8,9-HxCDF	0.00e+00	0.00e+00	0.00e+00	0.00e+00
2,3,4,6,7,8-HxCDF	4.00e−04	6.65e+07	0.00e+00	0.00e+00
1,2,3,4,6,7,8-HpCDF	6.00e−05	9.98e+06	0.00e+00	0.00e+00
1,2,3,4,7,8,9-HpCDF	0.00e+00	0.00e+00	0.00e+00	0.00e+00
1,2,3,4,6,7,8,9-OCDF	2.60e−05	4.32e+06	0.00e+00	0.00e+00

BLS = Black liquor solids
CaO = Calcium oxide

Table 5-15. CDD/CDF concentrations in candle materials and emissions

Wax material	Candle component	Concentration			Emission factor
		CDD/CDF (ng I-TEQ_{DF}/kg)	Total chlorophenols (µg/kg)	Total chlorobenzenes (µg/kg)	CDD/CDF (ng I-TEQ_{DF}/kg burnt wax)
Paraffin	Wax	0.59	14.8	130	0.015
Stearin	Wax	1.62	32.3	330	0.027
Beeswax	Wax	10.99	256	120	0.004
Paraffin	Wick	0.18	1.23	0.67	NR
Stearin	Wick	0.12	0.94	0.34	NR
Beeswax	Wick	0.08	0.74	0.35	NR

Source: Schwind et al. (1995).

Lime kilns. Annual emissions from lime kilns in Belgium and the United Kingdom have been reported by Wevers and De Fre (1995) and Douben et al. (1995), respectively. However, the emission factors used to generate those estimates were not provided. Umweltbundesamt (1996) reported low emissions (0.016 to 0.028 ng I-TEQ_{DF}/kg) during tests at two lime kilns in Germany.

Ceramics and rubber manufacturers. Douben et al. (1995) estimated annual emissions from ceramic manufacturers and rubber manufacturers in the United Kingdom. Lexen et al. (1993) had previously detected high concentrations of CDDs/CDFs in emissions from a ceramic manufacturer in Sweden that occasionally glazed ceramics by volatilization of sodium chloride in a coal-fired oven. Lexen et al. (1993) also detected high pg/L levels of I-TEQ_{DF} in the scrubber water from the vulcanization process at a Swedish rubber manufacturer.

6. COMBUSTION SOURCES OF CDDs/CDFs: MINIMALLY CONTROLLED AND UNCONTROLLED COMBUSTION SOURCES

This chapter discusses combustion sources of CDDs/CDFs that have some (in the case of combustion of landfill gas) or no post-combustion pollution control equipment for conventional pollutant emissions.

6.1. COMBUSTION OF LANDFILL GAS

6.1.1. Emissions Data

Although no data could be located on levels in untreated landfill gas, several studies have reported detecting CDDs/CDFs in the emissions resulting from the combustion of landfill gas. Only one study of CDD/CDF emissions from a landfill flare has been reported for a U.S. landfill (CARB, 1990c). The TEQ_{DF}-WHO_{98} and I-TEQ_{DF} emission factor calculated from the results of this study is approximately 2.4 ng TEQ/m^3 landfill gas combusted. The congener-specific results of this study are presented in Table 6-1. Figure 6-1 presents the CDD/CDF congener emission profile based on these emission factors. Bremmer et al. (1994) reported a lower emission factor, 0.4 ng I-TEQ_{DF}/m^3, from the incineration of untreated landfill gas in a flare at a facility located in the Netherlands. No congener-specific emission factors were provided. The average TEQ emission factor for the CARB and Bremmer et al. studies is 1.4 ng I-TEQ_{DF}/m^3 landfill gas combusted.

Umweltbundesamt (1996) reported even lower TEQ emission factors for landfill gas burned in engines or boiler mufflers rather than in a flare. The reported results for 30 engines and mufflers tested in Germany ranged from 0.001 to 0.28 ng I-TEQ_{DF}/m^3, with most values below 0.1 ng I-TEQ_{DF}/m^3. However, Bremmer et al. (1994) reported an emission factor of 0.5 ng I-TEQ_{DF}/m^3 from a landfill gas-fired engine in the Netherlands.

6.1.2. Activity Level Information

In 1996 EPA promulgated emission standards and guidelines to control emissions of landfill gas from existing and future landfills under the Clean Air Act (Federal Register, 1996b). Those regulations require the largest landfills in the United States (on the basis of design capacity) to periodically measure and determine their annual emissions of landfill gas. Landfills that emit more than 50 metric tons of nonmethane organic compounds (NMOC) annually must collect landfill gas and reduce its NMOC content by 98% weight through the use of a control device.

Table 6-1. CDD/CDF emission factors for a landfill flare

Congener/congener group	Mean facility emission factor[a] (ng/m^3 gas combusted)
2,3,7,8-TCDD	0.02
1,2,3,7,8-PeCDD	0.09
1,2,3,4,7,8-HxCDD	0.07
1,2,3,6,7,8-HxCDD	0.07
1,2,3,7,8,9-HxCDD	0.26
1,2,3,4,6,7,8-HpCDD	0.76
OCDD	4.41
2,3,7,8-TCDF	14.07
1,2,3,7,8-PeCDF	0.39
2,3,4,7,8-PeCDF	1.14
1,2,3,4,7,8-HxCDF	1.46
1,2,3,6,7,8-HxCDF	0.42
1,2,3,7,8,9-HxCDF	0.11
2,3,4,6,7,8-HxCDF	0.68
1,2,3,4,6,7,8-HpCDF	1.22
1,2,3,4,7,8,9-HpCDF	0.07
OCDF	0.64
Total 2,3,7,8-CDD	5.68
Total 2,3,7,8-CDF	20.20
Total I-TEQ_{DF}	2.39
Total TEQ_{DF}-WHO_{98}	2.43
Total TCDD	NR
Total PeCDD	NR
Total HxCDD	NR
Total HpCDD	NR
Total OCDD	NR
Total TCDF	NR
Total PeCDF	NR
Total HxCDF	NR
Total HpCDF	NR
Total OCDF	NR
Total CDD/CDF	NR

[a]Assumes heat content of 1.86e+07 J/m^3 for landfill gas (Federal Register, 1996a).

NR = Not reported

Source: CARB (1990c).

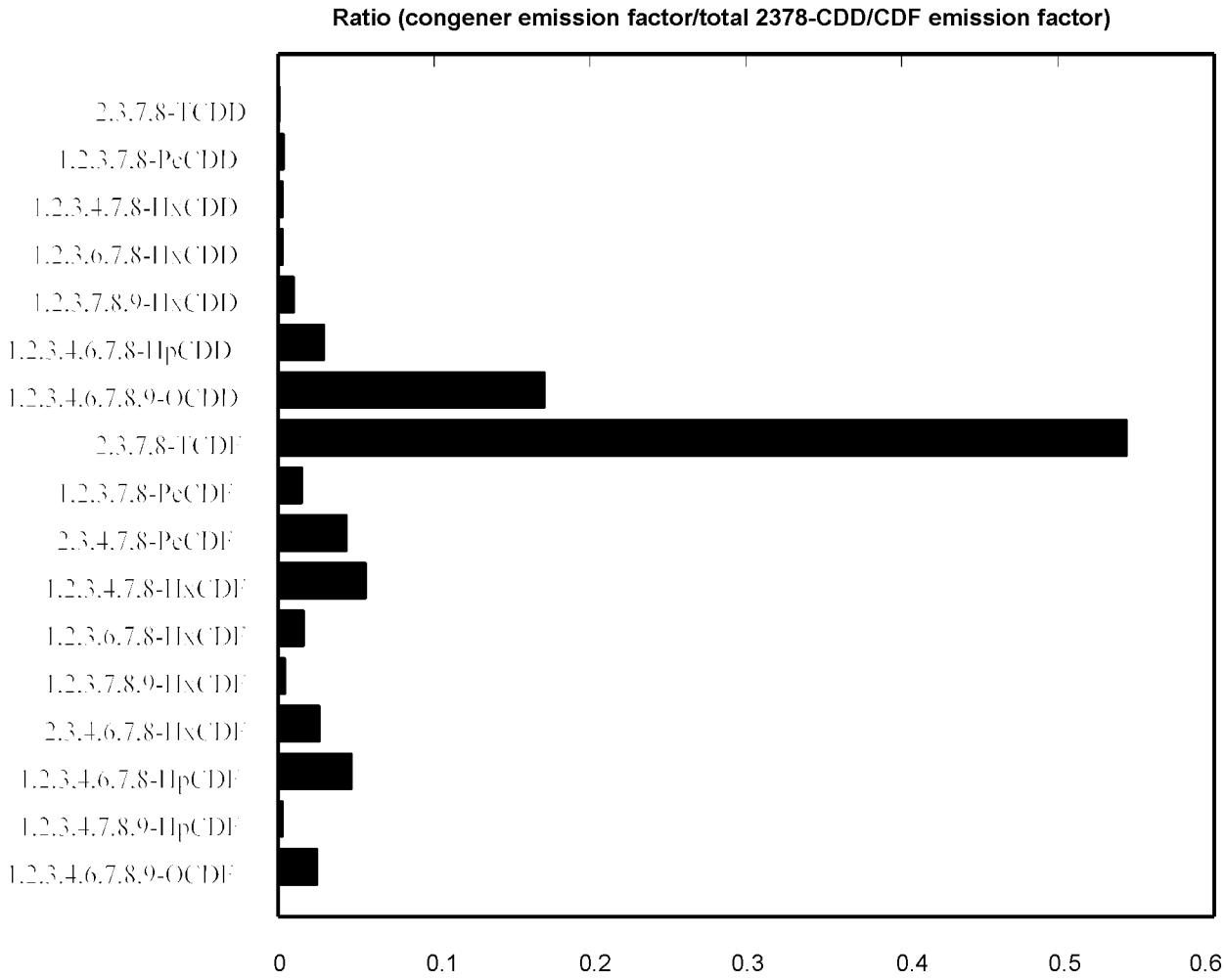


Figure 6-1. Congener profile for landfill flare air emissions.

Source: CARB (1990c).

6.1.2.1. *Activity Levels for 1987 and 1995*

EPA estimated that when the 1996 regulations were implemented, the controls would reduce annual NMOC emissions from existing landfills by 77,600 metric tons. The cost analysis supporting this rulemaking based control device costs on open flares because flares are applicable to all the regulated facilities. Assuming that the mass reduction would be achieved by the use of flares, the corresponding volume of landfill gas burned would be approximately 14 billion m^3/yr. The calculation was based on an assumed default NMOC concentration in landfill gas of 1,532 ppmv and a conversion factor of 3.545 mg/m^3 NMOC per 1 ppmv NMOC (Federal Register, 1993b).

Of the approximately 312 landfills that were affected by the promulgation of the emission standards and guidelines in 1996, EPA estimated that more than 100 had some form of collection or control system (or both) in place in 1991 (Federal Register, 1991c). Thus, a rough approximation of the volume of landfill gas combusted in 1995 was 4.7 billion m^3/yr (or 33% of the future expected 14 billion m^3/yr reduction). This estimate is similar to the 2 to 4 billion m^3 landfill gas estimated by the Energy Information Administration (EIA, 1994) as collected and consumed for energy recovery purposes in 1992.

EIA (1992) estimated that between 0.9 and 1.8 billion m^3 of landfill gas were collected and burned in 1990 for energy recovery purposes. Because there were no specific data available for 1987, EPA assumed that the mean of this range, 1.35 billion m^3, would serve as an approximate estimate of the volume of landfill gas combusted in 1987.

6.1.2.2. *Activity Level for 2000*

According to the EPA 2001 inventory of greenhouse gas emissions, approximately 7.7 billion m^3 of landfill gas were combusted in 2000 through 477 landfill flares (average of 16.5 million m^3 of landfill gas per flare). As of 2003, there were more than 1,000 landfill flares in the United States (e-mails dated February 28, 2003, and March 7, 2003, from B. Guzzone, U.S. EPA, to K. Riley, Versar). Assuming that the amount of landfill gas combusted through the 477 landfill flares inventoried is representative of the landfill gas combusted through these 1,000+ flares, approximately 16 billion m^3 of landfill gas were combusted in the United States through flares in 2000.

6.1.3. Emission Estimates

The limited emission factor data that are available were judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary estimate of the potential annual TEQ releases from landfills can be obtained using the estimated volume of combusted gas and the available emission factors. Combining the estimates of landfill gas volume that was combusted (1.35 billion m^3 in 1987, 4.7 billion m^3 in 1995, and 16 billion m^3 in 2000) with the emission factor of 1.4 ng I-TEQ_{DF}/m^3 of flare-combusted gas yields annual emission estimates of 1.9, 6.6, and 22 g I-TEQ_{DF}/m^3 for 1987, 1995, and 2000, respectively. These estimates should be regarded as preliminary indications of possible emissions from this source; further testing is needed to confirm the true magnitude of those emissions.

6.2. ACCIDENTAL FIRES

Accidental fires in buildings and vehicles are uncontrolled combustion processes that, because of poor combustion conditions, typically result in relatively high emissions of incomplete combustion products (Bremmer et al., 1994), which can include CDDs and CDFs. Polyvinyl chloride (PVC) building materials and furnishings, chloroparaffin-containing textiles and paints, and other chlorinated organic compound-containing materials appear to be the primary sources of the chlorine (Rotard, 1993). Although the results of several studies have demonstrated the presence of CDD/CDF concentrations in soot deposits and residual ash from such fires, few direct measurements of CDDs/CDFs in the fumes or smoke of fires have been reported. The results of some of those studies are described below, and an evaluation of the available data follows.

6.2.1. Soot and Ash Studies

Christmann et al. (1989a) analyzed the soot formed during combustion and pyrolysis of pure PVC and PVC cable sheathings in simple laboratory experiments designed to mimic the conditions of fires. For the combustion experiments, 2 g of a PVC sample were incinerated with a laboratory gas burner. The combustion products were collected on the inner walls of a cooled gas funnel placed above the sample. For the pyrolysis experiments, about 50 mg of the sample were placed in a quartz tube and heated to about 950°C for 10 min in either an air atmosphere or a nitrogen atmosphere. The combustion experiments yielded CDD/CDF concentrations in soot of 110 µg I-TEQ_{DF}/kg for a low-molecular-weight PVC, 450 µg I-TEQ_{DF}/kg for a high-molecular-weight PVC, and 270 µg I-TEQ_{DF}/kg for PVC cable. The pyrolysis experiments in the air atmosphere yielded lower CDD/CDF concentrations in soot: 24.4 µg I-TEQ_{DF}/kg for a low-molecular-weight PVC, 18.7 µg I-TEQ_{DF}/kg for a high-molecular-weight PVC, and up to 41 µg I-TEQ_{DF}/kg for PVC cable.

In general, more CDFs than CDDs were formed. The lower-chlorinated CDF congeners were dominant in the combustion experiments; however, the HpCDF and OCDF congeners were dominant in the pyrolysis experiments. No CDDs/CDFs were detected in pyrolysis experiments under a nitrogen atmosphere. Also, no CDDs/CDFs were detected when chlorine-free polyethylene samples were subjected to the same combustion and pyrolysis conditions.

Deutsch and Goldfarb (1988) reported finding CDD/CDF concentrations ranging from 0.04 to 6.6 µg/kg in soot samples collected after a 1986 fire in a State University of New York lecture hall. The fire consumed or melted plastic furnishings and cleaning products containing chlorine, wood, and paper.

In a study that analyzed 200 ash and soot samples from sites of accidental fires in which PVC was involved (Funcke et al., 1988, as reported in Bremmer et al., 1994; Rotard, 1993),

CDDs/CDFs were detected in more than 90% of the samples at concentrations in the ng I-TEQ_{DF}/kg to µg I-TEQ_{DF}/kg range. Fires involving the combustion of materials containing relatively large amounts of PVC and other chlorinated organic substances resulted in the highest levels of CDDs/CDFs, with concentrations ranging from 0.2 to 110 µg I-TEQ_{DF}/kg residue.

Thiesen et al. (1989) analyzed residues from surfaces of PVC-containing materials that were partially burned during accidental fires at sites in Germany that manufactured or stored plastics. CDD/CDF concentrations in residues were reported as 0.5 µg I-TEQ_{DF}/kg for soft PVC, 4.6 µg I-TEQ_{DF}/kg for PVC fibers, and 28.3 µg I-TEQ_{DF}/kg for a hard PVC. The ratio of total CDFs to total CDDs in the three samples ranged from 4:1 to 7:1. The dominant 2,3,7,8-substituted CDF and CDD congeners in all three samples were 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,6,7,8-HpCDD.

In an accidental fire at a Swedish carpet factory in 1987, 200 metric tons of PVC and 500 metric tons of PVC-containing carpet were burned. Marklund et al. (1989) analyzed snow samples up to 1,500 m downwind from the fire site and found CDD/CDF concentrations in the top 2 cm ranging from 0.32 µg I-TEQ_{DF}/m^2 at 10 m from the site to 0.01 µg I-TEQ_{DF}/m^2 at 1,500 m. Because of an atmospheric inversion and very light wind at the time of the fire, the smoke from the fire remained close to the ground. The soot deposited onto the snow was thus assumed to be representative of the soot generated and released from the fire. Wipe samples of soot from interior posts of the plant that were 5 and 20 m from the fire contained Eadon TEQ concentrations of 0.18 and 0.05 µg/m^2, respectively. On the basis of these deposition measurements, the investigators estimated total CDD/CDF emissions from the fire to be less than 3 mg I-TEQ_{DF}.

Carroll (1996) estimated a soot-associated CDD/CDF emission factor for the Swedish carpet factory fire (i.e., not including volatile emissions) of 28 to 138 ng I-TEQ_{DF}/kg PVC burned using the following assumptions: the PVC carpet backing was one-half the weight of the carpet, the carpet backing contained 30% by weight PVC resin, and 20 to 100% of the PVC and PVC carpet backing present in the warehouse actually burned. Using the results of wipe samples collected at downwind distances of up to 6,300 m, Carroll (1996) also estimated a similar soot-associated emission factor (48 to 240 ng I-TEQ_{DF}/kg of PVC burned) for a fire at a plastics recycling facility in Lengerich, Germany.

Fiedler et al. (1993) presented a case study of CDD/CDF contamination and associated remedial actions taken at a kindergarten in Germany following a fire that destroyed parts of the roof, windows, and furnishings. Soot collected from the building contained CDDs/CDFs at a concentration of 45 µg I-TEQ_{DF}/kg (15 µg I-TEQ_{DF}/m^2). The study authors attributed the CDDs/CDFs detected to the combustion of plastic and wooden toys, floors, and furnishings; however, no information was provided on the quantities of those materials.

Fiedler and Lindert (1998) presented results of soot sampling following a serious fire at the airport in Düsseldorf, Germany. Polystyrene sheets and PVC-coated cables were involved in the fire, together with PCB-containing condensers (bulbs). Surface wipe samples contained up to 0.33 μg I-TEQ_{DF}/m^2. Concentrations in soot ranged from 7 to 130 μg I-TEQ_{DF}/kg. Concentrations of polybrominated dibenzo-*p*-dioxins and dibenzofurans were detected in soot at concentrations as high as 0.9 mg/kg soot.

Wichmann et al. (1993, 1995) measured the CDD/CDF content of ash and debris and deposited surface residues that resulted from experimental test burns of two cars (a 1974 Ford Taurus [old car] and a 1988 Renault Espace [new car]), one subway car, and one railway coach in a tunnel in Germany. On the basis of measurements obtained from the sampled ash and debris and from soot collectors placed at regular intervals up to 420 m downwind of the burn site, the total estimated amount of CDDs/CDFs in the ash/debris and tunnel surface residues from each vehicle burn experiment was 0.044 mg I-TEQ_{DF} for the 1974 model car, 0.052 mg I-TEQ_{DF} for the 1988 model car, 2.6 mg I-TEQ_{DF} for the subway car, and 10.3 mg I-TEQ_{DF} for the railway coach. For each vehicle burn experiment, the mass of TEQ in tunnel surface residue exceeded the mass in ash and debris: 73 to 89% were accounted for by the tunnel surface residues and 11 to 27% by ash and debris. The average CDD/CDF content of the ash and debris from each experimental burn was: 0.14 μg I-TEQ_{DF}/kg for the new car, 0.3 μg I-TEQ_{DF}/kg for the old car, 3.1 μg I-TEQ_{DF}/kg for the subway car, and 5.1 μg I-TEQ_{DF}/kg for the railway coach.

6.2.2. Fume and Smoke Studies

Merk et al. (1995) collected fume and smoke generated during the burning of 400 kg of wood and 40 kg of PVC in a building (4,500 m^3 volume) over a 45-min period. The sampling device consisted of dual glass fiber filters to collect particles greater than 0.5 μm followed by a polyurethane foam filter to collect vapor-phase CDDs/CDFs. The particulate phase (particles greater than 0.5 μm diameter) and the gas phase showed the same congener pattern: decreasing concentration with increasing degree of chlorination, thus indicating no preferential sorption of higher-chlorinated congeners to smoke particulates. However, the CDDs/CDFs found in the gas phase (about 5 ng I-TEQ_{DF}/m^3) accounted for more than 90% of the detected CDDs/CDFs. The authors also reported that the soot deposited from this fire onto a 1 m^2 aluminum sheet resulted in surface contamination of 0.05 μg I-TEQ_{DF}/m^2.

Although it was stated in Merk et al. (1995) that the building was "closed," subsequent communication with one of the coauthors (telephone conversation on September 29, 1998, between Karl-Werner Schramm, GSF-Institute of Ecological Chemistry, and Greg Schweer, Versar, Inc.) clarified that a "gas cleaning" system was in operation. Because a ventilation system was in operation, there was likely some loss of vapor-phase CDDs/CDFs from the hall;

therefore, the deposits (from particulate deposition and vapor-phase condensation) on the test aluminum plate may not have reflected total CDD/CDF formation during the fire.

Dyke and Coleman (1995) reported a fourfold increase in CDD/CDF TEQ concentrations in the ambient air during "bonfire night" (an annual event held on November 5 during which it is customary to set off fireworks and have bonfires) in Oxford, England. Air concentrations before and after bonfire night ranged from 0.15 to 0.17 pg I-TEQ_{DF}/m^3. The air concentration during bonfire night was 0.65 pg I-TEQ_{DF}/m^3. The dominant congeners in all samples were the hepta- and octa-CDDs. The study was not designed to collect data that would enable calculation of an emission rate or to differentiate the relative importance of the various materials combusted. However, the results do indicate that open burning of materials likely to be combusted in accidental fires (with the exception of fireworks) results in the release of CDDs and CDFs.

6.2.3. Data Evaluation

6.2.3.1. *Structural Fires*

6.2.3.1.1. ***Emissions data.*** Only limited emissions data for structural fires were located. Most of the studies obtained involved situations (field and laboratory) where relatively high loadings of PVC or plastics were combusted. The effects of different mixes of combusted materials, oxygen supplies, building configurations, and durations of burn, for example, that are likely to occur or be found in accidental fires cannot be accounted for by the factors that can be derived from these studies. Also, most of the studies addressed only soot or ash residues and did not address potential volatile emissions of CDDs/CDFs, which, according to Merk et al. (1995), may represent 90% of the CDDs/CDFs generated during the burning of PVC.

Two reports (Carroll, 1996; Thomas and Spiro, 1995) attempted to quantify CDD/CDF emissions from U.S. structural fires, and Lorenz et al. (1996) estimated emissions from structural fires in Germany.

Carroll (1996) estimated the total CDD/CDF content of soot and ash generated from the 358,000 residential fires in the United States in 1993 (as reported in U.S. DOC, 1995b). Detailed estimates were developed of the PVC content of items in typical homes, including plumbing, wiring, siding and windows, wallpaper, blinds and shades, and upholstery. The typical percentage of PVC burned in household fires was assumed to be 9.5%. Extrapolating to all 358,000 one- to two-family unit fires yielded an annual mass of 2,470 metric tons PVC burned. Carroll then developed TEQ emission factors from the results of Thiesen et al. (1989) and Marklund et al. (1989). The estimated CDD/CDF content ranged from 0.47 to 22.8 g I-TEQ_{DF}, with 0.07 to 8.6 g I-TEQ_{DF} in soot and 0.4 to 14.2 g I-TEQ_{DF} in ash. A soot emission factor (i.e., grams of soot produced per gram of PVC combusted) was derived from the investigator's assumptions regarding the surface area of the soot collection funnel used by Christmann et al.

(1989b) and the soot deposition rate on that funnel. These I-TEQ_{DF} emission factors were then applied to the estimated 2,470 metric tons of PVC burned annually in one- to two-family unit residential fires to obtain estimates of the annual mass of TEQ that would be found in the soot and ash of residential fires (0.48 to 22.8 g I-TEQ_{DF}/yr). The average emission per fire is thus 1.3 to 64 µg I-TEQ_{DF}.

Thomas and Spiro (1995) estimated that 20 g I-TEQ_{DF} may be released annually to air from structural fires. This estimate assumes an emission factor of 4 ng I-TEQ_{DF}/kg material combusted (i.e., the emission rate for "poorly" controlled wood combustion), a material combustion factor of 6,800 kg per fire, and 688,000 structural fires per year. The average emission per fire is thus 29 µg I-TEQ_{DF}.

Lorenz et al. (1996) estimated annual generation of CDDs/CDFs in Germany using data on the number of residential and industrial/commercial structural fires coupled with data on CDD/CDF content in soot and ash residues remaining after fires. The potential annual I-TEQ_{DF} generation was estimated to be 78 to 212 g.

Using the emissions data estimated by Carroll (1996) and Thomas and Spiro (1995) provides an average emission factor of 32 µg I-TEQ/fire.

6.2.3.1.2. ***Activity level information.*** In 1987, there were approximately 2,330,000 fires in the Unites States, of which approximately 745,600 (32%) were structural fires (FEMA, 1997). In 1995, approximately 574,000 structural fires were reported in the United States. Of these, 426,000 were reported to be in residential structures, including 320,000 in one- to two-family units, 94,000 in apartments, and 12,000 in other residential settings. The types of structures for the remaining 148,000 fires were public assembly, 15,000; educational, 9,000; institutional, 9,000; stores and offices, 29,000; special structures, 29,000; storage, 39,000; and industry, utility, and defense, 18,000. The latter two categories may be underreported, as some incidents were not recorded because they were handled by private fire brigades or fixed suppression systems (U.S. DOC, 1997). For 2000, the National Fire Data Center estimated that approximately 1,708,000 fires occurred in the United States, of which approximately 512,400 (30%) were structural fires (FEMA, 2001).

6.2.3.1.3. ***Emission estimates.*** The limited data available on structural fires were judged inadequate for developing national emission estimates. This conclusion was also reached for national emission inventories developed for the Netherlands (Bremmer et al., 1994) and the United Kingdom (U.K. Department of the Environment, 1995). However, preliminary estimates were calculated by combining the average emission factor of 32 µg I-TEQ/fire and the number of structural fires in the Unites States (745,600 in 1987; 426,000 in 1995; and 512,400 in 2000),

yielding an annual release of 24 g I-TEQ_{DF} in 1987, 14 g I-TEQ_{DF} in 1995, and 16 g I-TEQ_{DF} in 2000. Confidence in these estimated emissions is very low because of the numerous assumptions employed in their derivation. If the conclusion by Merk et al. (1995) is assumed to be correct, that 90% of the CDDs/CDFs formed in fires are in the gaseous phase rather than particulate phase, and it is also assumed that the estimates by Carroll (1996) and Thomas and Spiro (1995) did not totally account for volatile emissions, then the total CDD/CDF emissions estimated by Carroll and Thomas and Spiro may be underestimates. Further testing is needed to confirm the true magnitude of these releases.

6.2.3.2. *Vehicle Fires*

As with structural fires, the limited data available on vehicle fires were judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary estimate of the range of potential CDD/CDF emissions that may result from vehicle fires can be calculated using the results reported by Wichmann et al. (1993, 1995) for controlled vehicle fires in a tunnel (0.044 mg I-TEQ_{DF} for an old car to 2.6 mg I-TEQ_{DF} for a subway car). Although Wichmann et al. did not measure volatile CDDs/CDFs (which were reported by Merk et al., 1995, to account for the majority of CDDs/CDFs formed during a fire), the study was conducted in a tunnel, and it is likely that a significant fraction of the volatile CDDs/CDFs sorbed to tunnel and collector surfaces and were thus measured as surface residues.

The number of vehicle fires reported in the United States was approximately 561,530 in 1987 (FEMA, 1997), 406,000 in 1995 (U.S. DOC, 1997), and 341,600 in 2000 (FEMA, 2001). If it is assumed that 99% of those fires involved cars and trucks (the approximate percentage of all U.S. motor vehicles that are in-service cars and trucks; U.S. DOC, 1995b) and that the applicable emission rate is 0.044 mg I-TEQ_{DF} per incident, then the annual TEQ formation was 24.4 g I-TEQ_{DF} for 1987, 17.7 g I-TEQ_{DF} for 1995, and 14.9 g I-TEQ_{DF} for 2000. The emission factor of 2.6 mg I-TEQ_{DF}/fire is assumed to be applicable to the remaining 1% of vehicle fires, thus yielding emissions of 14.6 g I-TEQ_{DF}/yr for 1987, 10.6 g I-TEQ_{DF}/yr for 1995, and 8.9 g I-TEQ_{DF}/yr for 2000. Total TEQ annual emissions for 1987, 1995, and 2000 were roughly estimated to have been 39, 28.3, and 23.8 g I-TEQ_{DF}/yr, respectively. These estimates should be regarded as preliminary indications of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

6.3. LANDFILL FIRES

6.3.1. Emissions Data

In the late 1980s, two serious fires occurred in landfills near Stockholm, Sweden. The first fire was in a large pile of refuse-derived fuel. Using measurements of chlorobenzenes in the air emissions, it was estimated that 50 to 100 kg of chlorobenzenes were released. CDD/CDF emissions were estimated to be several tens of grams, on the assumption that the ratio of CDDs/CDFs to chlorobenzenes in landfill fire emissions is similar to the ratio observed in stack gases of municipal waste combustors. To measure releases in connection with the second fire, which occurred at a large conventional landfill, birch leaves were collected from trees close to the fire and at distances up to 2 km downwind of the fire, as well as from nearby areas not affected by smoke from the fire. The discharge of CDDs/CDFs necessary to cause the concentrations measured on the leaves was estimated to be several tens of grams (Persson and Bergström, 1991).

In response to these incidents, Persson and Bergström (1991) also measured CDD/CDF emissions from experimental fires designed to simulate surface landfill fires and deep landfill fires. The experiments used 9-month-old domestic waste. The tests showed no significant difference in CDD/CDF content of the fire gases produced by the simulated surface and that of the deep fires. The average CDD/CDF emission rate was reported to be 1 µg Nordic TEQ/kg waste burned.

Persson and Bergström (1991) and Bergström and Björner (1992) estimated annual CDD/CDF Nordic TEQ emissions in Sweden from landfill fires to be 35 g. The estimate was based on the emission rate of 1 µg Nordic TEQ/kg waste burned, an assumed average density of landfill waste of 700 kg/m^3, an assumed waste burn of 150 m^3 for each surface landfill fire (167 fires in Sweden per year), and an assumed waste burn of 500 m^3 for each deep landfill fire (50 fires in Sweden per year). The estimates of waste burn mass for each type of fire were the average values obtained from a survey of 62 surface fires and 25 deep fires. The estimated number of fires per year was based on the results of a survey of all Swedish municipalities for fires reported during 1988 and 1989. In 1991, Sweden had an estimated 400 municipal landfills (Persson and Bergström, 1991).

Ruokojärvi et al. (1995) measured ambient air concentrations of CDDs/CDFs in the vicinity of real and experimental landfill fires in Finland. The most abundant toxic congeners were the hepta- and octa-CDDs and the penta-, hepta-, and octa-CDFs. The highest contributors to the measured TEQ were 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF. In Finland, annual CDD/CDF emissions from landfill fires are estimated to be 50 to 70 g Nordic TEQ (Aittola, 1993, as reported in Ruokojärvi et al., 1995).

6.3.2. Activity Level Information and Emission Estimates

Although no U.S. monitoring studies are available, an emission factor similar to the Swedish emission factor would be expected for the United States because the content of municipal waste in the United States and Sweden are expected to be similar. Because no data could be located on characterization of landfill fires in the United States (i.e., number, type, mass of waste involved), the limited data available were judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary estimate of the potential magnitude of TEQ emissions associated with landfill fires in the United States can be obtained by assuming a direct correlation of emissions to population size for the United States and Sweden or by assuming a direct correlation between emissions and the number of landfills in each country.

Both the United States and Sweden are industrialized countries. Although the per capita waste generation rate in the United States is nearly 1.5 times that of Sweden, the composition of municipal waste and the fraction of municipal waste disposed of in landfills in the two countries are nearly identical (U.S. EPA, 1996d). The population of Sweden was 8,825,417 in 1995 (U.S. DOC, 1995b) and 8,873,052 in 2000 (U.S. DOC, 2002). Based on these population estimates and the estimated annual Nordic TEQ emission factor of 35 g, the per capita landfill fire–associated Nordic TEQ emission factor was 4 µg TEQ per person per year for both 1995 and 2000. Because congener-specific results were not provided in Persson and Bergström (1991) or Bergström and Björner (1992), it was not possible to derive emission factors in units of TEQ_{DF}-WHO_{98} or I-TEQ_{DF}. Applying this factor to the U.S. population of 263,814,000 in 1995 (U.S. DOC, 1995b) and 281,421,906 in 2000 (U.S. DOC, 2003) results in an estimated annual emission of 1,050 g TEQ for 1995 and 1,126 g TEQ for 2000. These estimates should be regarded as preliminary indications of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

6.4. FOREST AND BRUSH FIRES

6.4.1. Emissions Data

Because CDDs/CDFs have been detected both in the soot from residential wood burning (Bumb et al., 1980; Nestrick and Lamparski, 1982, 1983; Bacher et al., 1992) and in the flue gases from residential wood burning (Schatowitz et al., 1993; Vickelsoe et al., 1993; Launhardt and Thoma, 2000; Environment Canada, 2000), it is reasonable to assume that wood burned in forest and brush fires may also be a source of CDDs/CDFs (Section 4.2 contains details on these studies).

Only one study (Tashiro et al., 1990) could be found that reported direct measurements of CDDs/CDFs in emissions from forest fires. This study reported detection of total CDDs/CDFs in

air at levels ranging from about 15 to 400 pg/m^3. The samples were taken from fixed collectors located 10 m above the ground and from aircraft flying through the smoke. Background samples collected before and after the tests indicated negligible levels in the atmosphere. These results were presented in a preliminary report; however, no firm conclusions were drawn about whether forest fires are a CDD/CDF source. The final report on this study, Clement and Tashiro (1991), showed total CDD/CDF levels in the smoke of about 20 pg/m^3. The authors concluded that CDDs/CDFs are emitted during forest fires but recognized that some portion of these emissions could represent resuspension from residues deposited on leaves rather than newly formed CDDs/CDFs.

Although not designed to directly assess whether CDDs/CDFs are formed during brush fires, Buckland et al. (1994) measured CDD/CDF levels in soil samples from both burnt and unburnt areas in national parks in New Zealand 6 weeks after large-scale brush fires. Four surface soil cores (2 cm depth) were collected and composited from each of three burnt and three unburnt areas. Survey results indicated that brush fires did not have a major impact on CDD/CDF levels in soil. The I-TEQ_{DF} content in the soil sample composites was 3, 8.7, and 10 ng/kg for the three unburnt areas and 2.2, 3.1, and 36.8 ng/kg for the three burnt areas. Total CDD/CDF content ranged from 1,050 to 7,700 ng/kg in the unburnt area soil samples and from 1,310 to 27,800 ng/kg in the burnt area soil samples. OCDD accounted for 94 to 97% of total CDD/CDF content in all samples.

Similarly, a survey of controlled straw-field burning in the United Kingdom (Walsh et al., 1994) indicated that the straw burning did not increase the CDD/CDF burden in the soil; however, a change in congener distribution was observed. Soils from three fields were sampled immediately before and after burning, along with ash from the fire. The mean I-TEQ_{DF} concentrations in the preburn soil, postburn soil, and ash were 1.79, 1.72, and 1.81 ng/kg, respectively. Concentrations of 2,3,7,8-TCDF were lower in the postburn soils than in the preburn soils. Conversely, concentrations of OCDD were higher in the postburn soils, indicating possible formation of OCDD during the combustion process.

Van Oostdam and Ward (1995) reported finding no detectable levels of 2,3,7,8-substituted CDDs/CDFs in three soil samples and four ash samples following a forest fire in British Columbia. The detection limits (DLs), on a congener-specific basis (unweighted for TEQ), ranged from 1 to 2 ng/kg. Nondetect values were also reported for ashes at a slash and burn site: the soil contained about 0.05 ng I-TEQ_{DF}/kg, whereas background soil contained about 0.02 ng I-TEQ_{DF}/kg.

The concentrations presented by Clement and Tashiro (1991) cannot accurately be converted to an emission factor because the corresponding rates of combustion gas production

and wood consumption are not known. As a result, the following four alternative approaches were considered for developing an emission factor.

Soot-based approach. This approach assumes that the levels of CDDs/CDFs in chimney soot are representative of the CDDs/CDFs in emissions. The CDD/CDF emission factor is calculated as the product of the CDD/CDF concentration in soot and the total particulate emission factor. This calculation involves first assuming that the CDD/CDF levels measured in chimney soot by Bacher et al. (1992) (720 ng I-TEQ_{DF}/kg) are representative of the CDD/CDF concentrations of particles emitted during forest fires. Second, the total particulate generation factor must be estimated. Using primarily data for head fires, Ward et al. (1976) estimated the national average particulate emission factor for wildfires as 150 lb/ton biomass dry weight. Ward et al. (1993) estimated the national average particulate emission factor for prescribed burning to be 50 lb/ton biomass dry weight. Combining the total particulate generation rates with the I-TEQ_{DF} level in soot results in emission factor estimates of 54 ng of I-TEQ_{DF} and 18 ng of I-TEQ_{DF}/kg of biomass burned in wildfires and prescribed burns, respectively. These estimated factors are likely to be overestimates because the levels of CDDs/CDFs measured in chimney soot by Bacher et al. (1992) may represent the accumulation and enrichment of CDDs/CDFs measured in chimney soot over time, leading to much higher assumed levels than the actual levels on emitted particles.

Carbon monoxide (CO) approach. CO is a general indicator of the efficiency of combustion, and the emission factors of many emission products can be correlated with the CO emission factor. Data from Schatowitz et al. (1993) for emissions during natural wood burning in open stoves suggest an emission factor of 10 µg I-TEQ_{DF}/kg CO. Combining this factor with the CO emission factor during forest fires (roughly 0.1 kg CO/kg of biomass [Ward et al., 1993]) yields an emission factor of 1,000 ng I-TEQ_{DF}/kg biomass. This factor is higher than the soot-based factor discussed above, which is itself considered to be an overestimate. In addition, although the formation kinetics of CDDs/CDFs during combustion are not well understood, CDD/CDF emissions have not been shown to correlate well with CO emissions from other combustion sources.

Wood stove approach. This approach assumes that the emission factor for residential wood burning (using natural wood and open door, i.e., uncontrolled draft) applies to forest fires. As discussed in Section 4.2.1, this approach suggests an emission factor of about 0.5 ng I-TEQ/kg wood combusted. This value appears more reasonable than the factors suggested by the soot and CO approaches because it is based on direct measurement of CDDs/CDFs from combustion of wood rather than on indirect techniques. However, forest fire conditions differ significantly from combustion conditions in wood stoves. For example, forest fire combustion

does not occur in an enclosed chamber, and the biomass consumed in forest fires is usually green and includes underbrush, leaves, and grass.

Forest fire simulation approach. This approach quantifies CDD/CDF emissions through the combustion of forest biomass in a controlled-burn facility. Using this approach, Gullet and Touati (2003) estimated CDD/CDF emissions through the testing of three biomass samples collected from the Oregon coast near Seal Rock and from four biomass samples collected from the North Carolina Piedmont region, approximately 200 km from the Atlantic coast. The samples generally consisted of equal portions of live shoots (needles cut from tree branches) and needle litter gathered from the forest floor. The Oregon samples were composed of pine needles (*Pinus contorta* and *Pinus monticola*) and hemlock needles (*Tyuga heterophylla*); the North Carolina samples were composed entirely of lobolly pine (*Pinus taeda*). The combustion of these seven samples, piled approximately 10 cm high, took place on top of an open, flat combustion platform. CDD/CDF emissions were measured using a Graseby PS-1 sampler and EPA's ambient TO-9 method.

As shown in Table 6-2, the overall average total TEQ emission factor for the seven samples was 19.9 ng TEQ_{DF}-WHO_{98}/kg (18.6 ng I-TEQ_{DF}), assuming nondetects were zero. Separately, the average total TEQ emission factors for the three Oregon samples and the four North Carolina samples were 15 ng and 25 ng TEQ_{DF}-WHO_{98}/kg, respectively. Even though the average TEQ emission factors for the Oregon and North Carolina runs were similar, CDF congeners were dominant in the Oregon samples, whereas CDD congeners were dominant in the North Carolina samples. Figure 6-2 shows the congener profile for the Oregon and North Carolina samples combined.

To test an alternative CDD/CDF sampling method, CDD/CDF emissions from one of the Oregon samples were also measured using a "Nomad" (a prototype portable sampler designed for mobile, in-field sampling). The results from both sampling methods showed very similar CDD/CDF TEQ values, total values, and ratio values. An additional Oregon sample was also combusted to test influences of fuel configuration on emissions. In this experiment, the biomass was placed in a metal barrel with air holes cut into the bottom. The results showed the highest total TEQ emission value calculated in this study (47 ng TEQ_{DF}-WHO_{98}/kg); however, this value is similar to the next highest total TEQ value (46 ng TEQ_{DF}-WHO_{98}/kg).

Because the waxy cuticle layer on pine needles has been demonstrated to absorb lipophilic compounds from the atmosphere, Gullet and Touati (2003) also extracted a raw, as-received Oregon biomass sample to determine whether the observed emissions were due to simple vaporization of existing CDDs/CDFs or the formation of new CDDs/CDFs in the combustion process. The CDD/CDF concentration in the sample measured 1.3 ng TEQ_{DF}-WHO_{98}/kg, which is approximately 20 times lower than the Oregon CDD/CDF emission

Table 6-2. CDD/CDF mean emission factors (ng/kg) for forest fires[a]

Congener	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	1.15	1.28
1,2,3,7,8-PeCDD	3.83	3.83
1,2,3,4,7,8-HxCDD	5.68	5.68
1,2,3,6,7,8-HxCDD	10.70	10.70
1,2,3,7,8,9-HxCDD	17.34	17.34
1,2,3,4,6,7,8-HpCDD	166.27	166.27
OCDD	663.67	663.67
2,3,7,8-TCDF	6.98	6.98
1,2,3,7,8-PeCDF	6.34	6.35
2,3,4,7,8-PeCDF	10.09	10.11
1,2,3,4,7,8-HxCDF	16.72	16.74
1,2,3,6,7,8-HxCDF	7.14	7.16
1,2,3,7,8,9-HxCDF	1.11	1.20
2,3,4,6,7,8-HxCDF	9.81	9.85
1,2,3,4,6,7,8-HpCDF	25.39	25.39
1,2,3,4,7,8,9-HpCDF	3.06	3.12
OCDF	10.27	10.32
Total CDD/CDF	965.55	965.99
Total TEQ_{DF}-WHO_{98}	19.90	20.06
Total I-TEQ_{DF}	18.60	18.75

[a]Values were derived from a total of seven biomass samples from Oregon and North Carolina.

Source: Gullet and Touati (2003).

concentrations (average, 25 ng TEQ_{DF}-WHO_{98}/kg; range, 14 to 46 ng TEQ_{DF}-WHO_{98}/kg). The CDD/CDF isomer patterns of the extracted biomass samples and the emission samples were similar. Therefore, this preliminary evidence suggests CDD/CDF emissions are not due solely to vaporization of cuticle-bound CDDs/CDFs but are formed anew during forest fires. Additionally, the new CDDs/CDFs formed may be adsorbed to the waxy cuticle layer in such a manner that the isomer pattern reflects the ambient CDD/CDF concentrations.

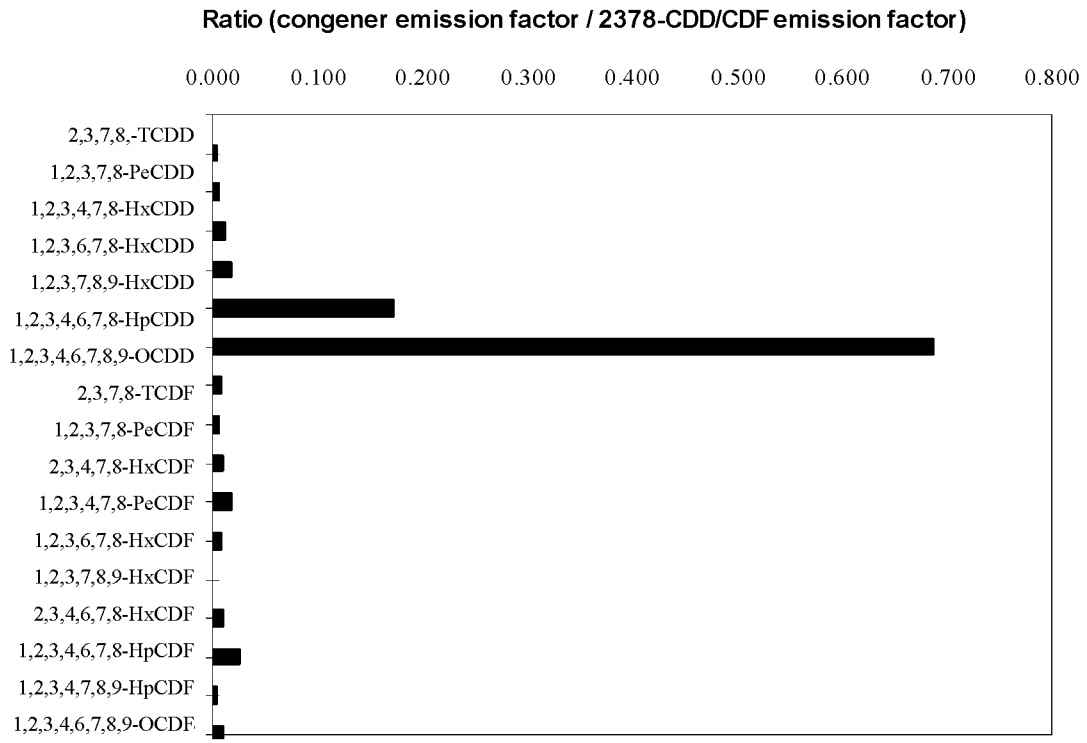


Figure 6-2. Congener profile for forest fire simulation approach emissions.

Source: Gullet and Touati (2003).

Many factors may affect forest fire CDD/CDF emissions, such as the type of fire (crown vs. understory and duff), types of species combusted, and location of the fire (near coastal vs. inland). Additionally, combustion conditions such as wind speed and fuel moisture content may also result in variations in emissions. These variables, therefore, yield uncertainties in the calculation of a representative emission factor through forest fire simulations. However, the emission factor of 19.9 ng TEQ_{DF}-WHO_{98}/kg (18.6 ng I-TEQ_{DF}) calculated through this approach appears to be more reasonable than the factors suggested by the soot, CO, and wood stove approaches because the forest fire simulation approach directly measures CDD/CDF emissions from forest biomass combusted in an open pile. Additionally, the forest biomass samples consisted of both live shoots and needle litter of representative species from two distinct locations.

6.4.2. Activity Level Information

6.4.2.1. *Approach for Reference Year 2000 (Office of Air Quality Planning and Standards [OAQPS])*

As part of the 2000 National Emissions Inventory, OAQPS developed activity levels of wildfires and prescribed burning on a county-level basis for reference year 2000. The number of acres burned by wildfires and prescribed burning was obtained from the U.S. Forest Service (USFS) and four U.S. Department of Interior agencies: Bureau of Land Management, National Park Service, U.S. Fish and Wildlife Service, and Bureau of Indian Affairs (BIA). USFS provided data for federal, state, and private lands. All data were provided on a state level except for the BIA wildfire data and the USFS prescribed burning data, which were provided on a regional level.

Prior to allocating the forest fire activity to the county level, the BIA and USFS regional data were first allocated to the state level. The BIA data were allocated using the number of acres of tribal land in each state. The USFS data were allocated using factors developed from landcover data in the Biogenic Emissions Landcover Database (BELD2) within EPA's Biogenic Emissions Inventory System; however, the BELD2 data for California were replaced with data from the 1996 National Toxics Inventory because USFS's Region 5 contains both Hawaii and California.

For each of the forest fire categories, the activity from all the agencies were then totaled by state and allocated to the county level using state-to-county land cover factors developed from BELD2. These BELD2 factors were based on the acreage of rural forest, brush, and grass in each county. This procedure was used for all states except Alaska and Hawaii, for which BELD2 does not contain land cover data. For Alaska and Hawaii, state-to-county factors were derived from data contained in the allocation factor file used for the 1996 National Emissions Inventory.

Using this approach, OAQPS estimated that approximately 8,357,958 acres were burned by wildfires in 2000 and approximately 1,261,607 acres were burned by prescribed fires in 2000. To obtain the amount of biomass consumed by wildfires and prescribed burning, the acres of forest burned were combined with region-specific fuel loading factors, as shown in Table 6-3. Nationally, approximately 228 million tons of biomass were consumed by wildfires and 15.8 million metric tons of biomass were consumed by prescribed burning in 2000.

6.4.2.2. *Approach for Reference Years 1987 and 1995*

According to the Council on Environmental Quality's 25th annual report (CEQ, 1997), 5 million acres of forest were lost to wildfires in 1987 and 7 million acres were lost in 1995. Estimates of the acreage consumed annually during prescribed burns are not readily available for

Table 6-3. Forest fire fuel loading factors (tons/acre)

Region	Wildfires	Prescribed burning
Alaska	6	12.6
California	18	14.2
Intermountain	8	6.3
North Central	11	8.7
Northern	60	47.3
Pacific Northwest	60	47.3
Rocky Mountain	30	23.7
Southern	9	7.1
Southwestern	10	7.9

Source: U.S. EPA (2002b).

1995 and 1997. An estimated 5.1 million acres of biomass were burned in 1989 during prescribed burns (Ward et al., 1993). This value was assumed to be appropriate for use for reference years 1987 and 1995.

To obtain the amount of biomass consumed by wildfires and prescribed burning, the acres of forest burned were combined with biomass consumption rates of 9.43 metric tons/acre in areas consumed by wildfires (Ward et al., 1976) and 7.44 metric tons/acre in areas consumed in prescribed burns. For 1987 and 1995, approximately 38 million tons were consumed by prescribed burns. Approximately 47 million metric tons of biomass were consumed by wild fires in 1987 and approximately 66 million metric tons of biomass were consumed in 1995.

6.4.3. Emission Estimates

Combining the emission factor developed using the forest fire simulation approach (19.9 ng TEQ_{DF}-WHO_{98}/kg biomass [18.6 ng I-TEQ_{DF}/kg biomass]) with the amount of biomass consumed annually in wildfires and prescribed fires (total of 85 million metric tons in 1987, 104 million metric tons in 1995, and 244 million metric tons in 2000) yields annual emission estimates of 1,700 g TEQ_{DF}-WHO_{98} (1,581 g I-TEQ_{DF}) for 1987; 2,080 g TEQ_{DF}-WHO_{98} (1,934 g I-TEQ_{DF}) for 1995; and 4,880 g TEQ_{DF}-WHO_{98} (4,538 g I-TEQ_{DF}) for 2000. For wildfires specifically, annual reference year emission estimates are 940 g TEQ_{DF}-WHO_{98} (874.2 g I-TEQ_{DF}) for 1987; 1,320 g TEQ_{DF}-WHO_{98} (1,228 g I-TEQ_{DF}) for 1995; and 4,560 g TEQ_{DF}-WHO_{98} (4,241 g I-TEQ_{DF}) for 2000. For prescribed fires specifically, annual emission estimates

are 760 g TEQ_{DF}-WHO_{98} (706.8 g I-TEQ_{DF}) for reference years 1987 and 1995 and 320 g TEQ_{DF}-WHO_{98} (297 g I-TEQ_{DF}) for reference year 2000.

These estimates should be regarded as preliminary indications of possible emissions from this source; further testing is needed to confirm the true magnitude of emissions. The activity level for both forest fires and biomass combustion is given a low confidence rating because these values were estimated and may not be representative. The emission factor is highly variable and dependent on type of biomass burned, therefore, it is judged to be clearly nonrepresentative.

6.5. BACKYARD BARREL BURNING

6.5.1. Emissions Data

In many rural and nonurban areas of the United States, residences may dispose of household refuse through open backyard burning. This practice usually consists of burning refuse in a 208-L capacity steel drum. Holes are punched near the bottom of the drum to allow combustion air to enter. The fire is ignited with a petroleum fuel, e.g., kerosene. The low combustion temperatures and oxygen-starved conditions associated with household refuse burning in these "burn barrels" results in poor and uncontrolled combustion conditions. Under such conditions, products of incomplete combustion are formed and visible smoke is emitted into the air.

The practice of open burning in burn barrels causes CDDs and CDFs to be formed and released as toxic air contaminants. In 1997, EPA's Control Technology Center, in cooperation with the New York State's Department of Health and Department of Environmental Conservation, conducted an initial study that examined, characterized, and quantified emissions from simulated open burnings of household waste materials in barrels (Lemieux, 1997). The representative waste was prepared on the basis of the typical percentages of various waste materials disposed of by New York State residents; hazardous wastes (e.g., chemicals, paints, oils) were not included in the test waste. A variety of compounds, including CDDs/CDFs, were measured in the emissions from two simulated open burnings of this "baseline" waste.

Combustion studies were subsequently performed by EPA to provide additional baseline waste tests and an initial indication of the impact of limited variation in waste composition and combustion conditions on CDD/CDF emissions from a simulated domestic backyard barrel burn of 6.8 kg of unshredded household waste (Gullet et al., 1999, 2000a, b; Lemieux et al., 2000; e-mail dated September 7, 2000, from P. Lemieux, U.S. EPA, to D. Cleverly, U.S. EPA). The results of seven baseline open burning waste tests were reported in these EPA studies. These tests exhibited variation in the emissions of CDDs/CDFs, with a one to two order-of-magnitude spread between the lowest and highest values for individual congeners, congener groups, total CDDs/CDFs, and TEQ values. The average TEQ emission factor for the seven baseline tests was

72.8 ng I-TEQ_{DF}/kg waste burned (setting nondetect values equal to zero) and 73.7 ng I-TEQ_{DF}/kg waste burned (setting nondetect values equal to one-half the DL). The corresponding TEQ_{DF}-WHO_{98} values were 76.8 and 77.7 ng/kg. Table 6-4 presents the average congener and congener group results for these tests.

In addition to the baseline tests, the combustion experiments included testing at three different PVC levels: 0, 1, and 7.5% by weight PVC. The average emissions were 14, 201, and 4,916 ng I-TEQ_{DF}/kg waste burned, respectively. Two tests using waste impregnated with inorganic chloride ($CaCl_2$) at a concentration of 7.5% by weight (and no PVC) averaged 734 ng I-TEQ_{DF}/kg. Qualitative comparisons suggest that the tests conducted with higher chlorine, via PVC or $CaCl_2$, resulted in substantial increases in TEQ emissions.

Other variations in baseline waste composition included conducting one test with compressed waste, one test with a double load of waste, and one test in which some of the waste paper was wetted to simulate high-moisture burns. These tests resulted in a higher mean TEQ emission factor (534 ng I-TEQ_{DF}/kg) than that of the baseline runs.

Several waste combustion variables were evaluated, such as average temperatures at prescribed barrel heights, length of time temperatures (favorable temperature ranges) for CDD/CDF formation, and measurement of CO, CO_2, O_2, particulate matter, and HCl. Statistical analyses of the results indicated that CO emissions and temperature measured in the uppermost portion of the barrel were the best predictors of TEQ variation. However, the wide variability in test results (from less than 10 to more than 6,000 ng I-TEQ_{DF}/kg) also indicates that a high degree of CDD/CDF emission variation can be expected due to factors that are not wholly related to waste composition or burning practice, such as waste orientation. A mean emission factor of the baseline tests (without PVC added) was developed from the data. This mean emission factor was 78.6 mg TEQ_{DF}-WHO/kg, and it was used to estimate releases from barrel burning. The emission factor is given a low confidence rating because it is possibly nonrepresentative of barrel-burning emissions.

6.5.2. Activity Level Information

The amount of refuse that is combusted annually in the United States in residential backyard burn barrels is largely unknown. Although no national statistics are available, a limited number of telephone surveys have attempted to measure the prevalence of backyard barrel burning in a few geographical areas. This limited number of surveys, combined with census data on the rural and nonurban population of the United States, were used to estimate annual activity level in terms of the quantity of refuse combusted in burn barrels per reference year. The following is a summary of this estimation procedure.

Table 6-4. CDD/CDF average air emission factors (ng/kg waste burned) from barrel burning of household waste[a]

Congener/congener group	Nondetect set to ½ detection limit	Nondetect set to zero
2,3,7,8-TCDD	3.4	2.7
1,2,3,7,8-PeCDD	8.2	8.1
1,2,3,4,7,8-HxCDD	6.6	6.4
1,2,3,6,7,8-HxCDD	9.9	9.7
1,2,3,7,8,9-HxCDD	19.1	19
1,2,3,4,6,7,8-HpCDD	39.8	39.8
OCDD	49.7	49.7
2,3,7,8-TCDF	45.6	45.6
1,2,3,7,8-PeCDF	37.2	37.2
2,3,4,7,8-PeCDF	65.2	65.2
1,2,3,4,7,8-HxCDF	113.8	113.8
1,2,3,6,7,8-HxCDF	38.5	38.5
2,3,4,6,7,8-HxCDF	61.9	61.9
1,2,3,7,8,9-HxCDF	3	2.5
1,2,3,4,6,7,8-HpCDF	128.6	124.4
1,2,3,4,7,8,9-HpCDF	14.6	15
OCDF	37.5	36.4
Total 2,3,7,8-CDD	136.7	135.4
Total 2,3,7,8-CDF	545.9	540.5
Total I-TEQ_{DF}	73.7	72.8
Total TEQ_{DF}-WHO_{98}	77.7	76.8
Total TCDD	413	413
Total PeCDD	281	281
Total HxCDD	221	221
Total HpCDD	105	105
Total OCDD	43	43
Total TCDF	1,880	1,880
Total PeCDF	1,021	1,021
Total HxCDF	492	492
Total HpCDF	169	169
Total OCDF	32	30
Total CDD/CDF	4,657	4,655

[a]Listed values are the arithmetic averages of seven tests for the congeners and the averages of five tests for the congener groups.

Sources: E-mail dated September 7, 2000, from P. Lemieux, U.S. EPA, to D. Cleverly, U.S. EPA; Gullett et al. (1999, 2000, 2001).

6.5.2.1. *Summary of Barrel Burn Surveys*

A total of seven surveys of the prevalence of backyard combustion of domestic refuse in burn barrels were identified in the literature. For the most part, these surveys were an attempt to estimate the barrel-burning activity in a specific state, county, or region in support of regulatory determinations on barrel burning. In general, the results of the surveys showed a prevalence of barrel burning within the rural population to range from 12 to 40%, with a mean of 28%. The following is a review of the surveys.

The Two Rivers Region Council of Public Officials (TRRCPO) and Patrick Engineering conducted a telephone survey in the early 1990s of residents of five central Illinois counties. They found that about 40% of the residents in a typical rural county burned household waste. The survey also indicated that, on average, those households that burned waste disposed of approximately 63% of their household waste by burning it in barrels (TRRCPO, 1994).

Similar results were obtained in a survey conducted by Zenith Research Group, Inc., (2000) for the Western Lake Superior Sanitary District of Minnesota. This survey of 760 residents of selected portions of northwestern Wisconsin and northeastern Minnesota addressed, in part, the use of burn barrels or other devices to burn household garbage or other materials. Among all survey respondents, 27.5% said they used burn barrels or other devices to burn household garbage or other materials.

Environics Research Group conducted a household garbage disposal and burning survey of 1,516 residents of Ontario, Canada. All respondents resided in detached single-family homes. Approximately 24% of all respondents reported burning their household refuse in burn barrels (Environics Research Group, 2001).

E.H. Pechan and Associates conducted a residential municipal solid waste survey for the Mid-Atlantic/Northeast Visibility Union (MANE-VU) states and tribes (Pechan and Associates, 2002). The MANE-VU entities include Connecticut, Delaware, the District of Columbia, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, New York, Pennsylvania, the Penobscot Indian Nation, Rhode Island, the St. Regis Mohawk Tribe, and Vermont. Household waste burning surveys were conducted by telephone for 72 residents of rural, suburban, and urban jurisdictions, as classified by the 1990 census. The residents were asked to estimate the number of households in their jurisdiction that burned household waste or trash. In general, the survey estimated that 11.9% of the rural population burned refuse in backyard burn barrels.

The State of California Air Resources Board (CARB) undertook a study of the prevalence of backyard refuse burning in rural areas of 21 air management districts in California (CARB, 2002). From this study, CARB estimated that approximately 18% of the rural population in California combusted their household refuse in backyard burn barrels.

In 1993, the St. Lawrence County Planning Office in Canton, NY, conducted a survey of open burning of domestic refuse (St. Lawrence County, 1993). From the survey, it was concluded that 48.2% of 9,926 households in rural areas of the county burned household refuse in burn barrels.

In 1997, the State of Maine Department of Conservation Forestry Bureau surveyed rural town fire wardens and state fire rangers regarding the prevalence of backyard burning of household waste. It was revealed through the survey that each day approximately 19,147 kg of domestic refuse was being combusted state wide in approximately 8,510 burn barrels. In relation to the total population, it was noted that one burn barrel existed for every 144 individuals.

6.5.2.2. *Estimates of Activity Level*

The following chart summarizes the steps taken to estimate the quantity of household refuse combusted in backyard burn barrels in1987, 1995, and 2000.

Step	Assumption	2000	1995	1987
1	U.S. population	281,400,000	260,600,000	242,300,000
2	Population in rural and nonurban areas	59,000,000	52,700,000	50,700,000
3	Percent nonurban population burning household refuse	28	40	40
4	Adjusted population burning household refuse in barrels	16,726,500	21,080,000	20,280,000
5	Per capita household refuse generation rate (kg/yr)	616	616	616
6	Percent of household refuse generated burned at homes	63	63	63
7	Adjusted per capita household refuse burned (kg/yr)	388	388	388
8	Total refuse generated by rural and nonurban population burning household refuse (kg/yr)	6,491,220,120	8,180,726,400	7,870,262,400

For steps 1 and 2, the U.S. Census Bureau Statistical Abstract of the United States was used to determine population size. For step 3, the assumption of the percent of rural population

combusting refuse in burn barrels in 2000 was derived from the overall mean prevalence rate from six surveys (CARB, 2002; Zenith Research Group, 2001; Environics Research Group, 2001: Pechan and Associates, 2004; St. Lawrence County, 1993; and TRRCPO, 1994). This produced a mean prevalence of 28%, which should reflect the impact of state bans or restrictions on the practice of open burning of refuse. The 1995 and 1987 population was estimated using the survey by TRRCPO (1994). This produced a prevalence of 40%, which should reflect the fact that the practice of open burning of refuse was not banned or restricted by the majority of the states.

The above mean prevalence rates were used in step 4 to calculate the number of people residing in rural areas assumed to have burned household refuse in burn barrels in each reference year (assumption in step 2 multiplied by the percentage in step 3). The annual per capita household refuse generation rate in step 5 is from *Municipal Solid Waste Fact Book* (2000). The figure of 616 kg/person/yr is the result of subtracting out weight of yard waste from the per capita generation rate. The assumption in step 6 is that 63% of the household refuse generated in rural areas is burned in backyard burn barrels. This percentage was derived from the survey conducted in rural counties of Illinois by TRRCPO (1994).

These activity levels are adopted and assigned a confidence rating of low because they are derived from limited surveys that are possibly nonrepresentative of the national activity level.

6.5.2.3. *Alternative Approach to Estimating Activity Level*

The actual amount of refuse combusted in burn barrels in the United States is unknown and must be estimated. OAQPS developed activity levels of residential MSW combusted in backyard barrels for reference year 2000. The activity levels were determined by first estimating the amount of waste generated for each county in the United States. The amount of waste generated was estimated by using a national average per capita waste generation factor, which is 1.5 kg/person/day. This value was calculated using population data from the 2000 census and 2000 waste generation data (U.S. EPA, 2002c). To better reflect the actual amount of household residential waste subject to being burned, noncombustibles (glass and metals) and yard waste were excluded. This factor was then applied to the portion of the county's total population that is considered rural, since open burning is generally not practiced in urban areas.

Using data from TRRCPO (1994), it was estimated that for rural populations, 25 to 32% of generated MSW is burned. A median value of 28% was assumed for the nation, and this correction factor was applied to the total amount of waste generated. Controls (or burning bans) were accounted for by assuming that no burning takes place in counties where the urban population is at least 80% of the total population (i.e., urban plus rural). Zero emissions from open burning were attributed to these counties. This technique produced an estimated annual

activity level of 7.79 billion kg of residential household waste combusted in burn barrels in 2000. This estimate is approximately 16.5% greater than the estimate used in this report.

6.5.3. Emission Estimates

CDD/CDF emissions from burn barrels for reference years 1987, 1995, and 2000 were calculated by multiplying the estimated annual total weight of household refuse combusted in burn barrels (see Section 6.5.2.2) by the dioxin emission factor. The emission factor was 76.8 ng TEQ_{DF}-WHO_{98}/kg (72.8 ng I-TEQ_{DF}/kg) waste burned.

Annual nationwide TEQ emissions for 1987, 1995, and 2000 were calculated using the following equation:

$$E_{TEQ} = EF_{TEQ} \times AL$$

where:

E_{TEQ} = Annual TEQ_{DF} emissions (g/yr)

EF_{TEQ} = TEQ_{DF} emission factor (76.8 ng TEQ_{DF}-WHO_{98}/kg waste burned)

AL = Annual activity level (7,870,262,400 kg in 1987; 8,180,726,400 kg in 1995; and 6,491,220,120 kg in 2000).

Using this equation, estimated nationwide TEQ_{DF} emissions were 604 g TEQ_{DF}-WHO_{98} (573 g I-TEQ_{DF}) in 1987, 628 g TEQ_{DF}-WHO_{98} (595 g I-TEQ_{DF}) in 1995, and 498.53 g TEQ_{DF}-WHO_{98} (472.56 g I-TEQ_{DF}) in 2000. A low confidence rating is given to both the emission factor and the estimate of activity level, therefore, the confidence rating is low for the estimate of TEQ emissions from backyard barrel burning of refuse.

6.5.4. Composition of Ash from Barrel Burning

Ash samples were collected from open barrel burning (Lemieux, 1997) and analyzed for CDDs/CDFs and PCBs. Ash samples from the experiments were combined, resulting in two composite samples, one for recyclers and one for nonrecyclers. The results for PCBs depict only the data for specific PCB congeners. The remaining PCB data reported in Lemieux (1997) could not be related to a particular congener. The results are presented in Tables 6-5 and 6-6.

6.6. RESIDENTIAL YARD WASTE BURNING

6.6.1. Emissions Data

It is reasonable to assume that residential yard waste burning may be a source of CDDs/CDFs, as they have been detected in forest and brush fires. No direct measurements of CDD/CDF emissions from residential yard waste burning have been performed; however, Gullet

Table 6-5. CDD/CDF analysis for composite ash samples from barrel burning (ng/kg ash)

Congener/congener group	Average concentration in composite ash sample		I-TEQ_{DF}		TEQ_{DF}-WHO_{98}	
	Avid recycler	Non-recycler	Avid recycler	Non-recycler	Avid recycler	Non-recycler
2,3,7,8-TCDD	31	9	31	9	31	9
1,2,3,7,8-PeCDD	230	53	115	26.5	230	53
1,2,3,4,7,8-HxCDD	270	44	27	4.4	27	4.4
1,2,3,6,7,8-HxCDD	420	74	42	7.4	42	7.4
1,2,3,7,8,9-HxCDD	300	56	30	5.6	30	5.6
1,2,3,4,6,7,8-HpCDD	4,000	630	40	6.3	40	6.3
OCDD	9,600	690	9.6	0.69	0.96	0.069
2,3,7,8-TCDF	830	220	83	22	83	22
1,2,3,7,8-PeCDF	1,000	270	50	13.5	50	13.5
2,3,4,7,8-PeCDF	2,500	690	1,250	345	1,250	345
1,2,3,4,7,8-HxCDF	2,300	480	230	48	230	48
1,2,3,6,7,8-HxCDF	2,100	490	210	49	210	67
2,3,4,6,7,8-HxCDF	2,900	670	290	67	290	15
1,2,3,7,8,9-HxCDF	810	150	81	15	81	21
1,2,3,4,6,7,8-HpCDF	12,000	2,100	120	21	120	1.7
1,2,3,4,7,8,9-HpCDF	1,400	170	14	1.7	14	0.056
OCDF	8,200	560	8.2	0.56	0.82	
Total TCDD	2,500	490	-	-	-	-
Total PeCDD	4,100	740	-	-	-	-
Total HxCDD	5,600	1,300	-	-	-	-
Total HpCDD	7,600	1,300	-	-	-	-
Total OCDD	9,600	690	-	-	-	-
Total TCDF	25,000	8,200	-	-	-	-
Total PeCDF	21,000	6,600	-	-	-	-
Total HxCDF	19,000	4,600	-	-	-	-
Total HpCDF	17,000	2,900	-	-	-	-
Total OCDF	8,200	560	-	-	-	-
Total CDD	29,400	4,520	-	-	-	-
Total CDF	90,200	22,860	-	-	-	-
Total CDD/CDF	119,600	27,380	-	-	-	-

Source: Lemieux (1997).

Table 6-6. PCB analysis for composite ash samples from barrel burning (ng/kg ash)

Compound	Avid recycler	Nonrecycler
2-Chlorobiphenyl	<2,500	4,900
2,3'-Dichlorobiphenyl	3,700	4,700
2,2',6-Trichlorobiphenyl	<500	5,600
2,2',5-Trichlorobiphenyl	32,000	6,300
2,3',5-Trichlorobiphenyl	800	800
2,3',4-Trichlorobiphenyl	<500	700
2,4',5-Trichlorobiphenyl	1,500	900
2,4,4'-Trichlorobiphenyl	<500	500
2,2',4,6'-Tetrachlorobiphenyl	<500	1,500
2,2',3,6'-Tetrachlorobiphenyl	5,300	1,300
2,2',5,5'-Tetrachlorobiphenyl	3,100	1,800
2,2',3,5'-Tetrachlorobiphenyl	2,600	1,200
2,2',4,4',5-Pentachlorobiphenyl	3,400	1,300
2,2',3,3',5-Pentachlorobiphenyl	400	<500
2,2',3,4,5,5'-Hexachlorobiphenyl	1,200	<500

Source: Lemieux (1997).

and Touati (2003) measured an average CDD/CDF emission factor of 20 ng TEQ_{DF}-WHO_{98}/kg during forest fire simulations where biomass samples from Oregon and North Carolina were burned on an open platform (see Section 6.4). Therefore, the emission factor of 20 ng TEQ_{DF}-WHO_{98}/kg developed by Gullet and Touati (2003) was used for residential yard waste burning.

6.6.2. Activity Level Information

Pechan and Associates (2002) estimated that approximately 233 lb of yard waste per household per year (based on a four-person household) were burned in 2000. This is similar to the estimate of 106 to 319 lb yard waste per household per year (based on a four-person household) that Pechan calculated using the results of a household yard waste burning survey. Pechan's telephone survey was completed by 181 rural, suburban, and urban jurisdictions of the MANE-VU entities. The results indicated that approximately 28% of the population in rural areas burned household yard waste and that households typically conducted two to three burns

per year. Additionally, as indicated by information provided by three respondents, 1 to 3 cubic yards of yard waste was typically burned at a time.

As part of the 2000 National Emissions Inventory, OAQPS determined on a county-level basis the amount of yard waste burned in 2000. The activity level estimates were based on the assumption that yard waste was generated at a rate of 0.54 lb/person/day in 2000, which in turn was derived using population data for 2000 and the assumption that 27.7 million tons of yard waste were generated in 2000 (U.S. EPA, 2002c). Of the total amount of yard waste generated, the composition was assumed to be 25% leaves, 25% brush, and 50% grass by weight (U.S. EPA, 2001b). Because open burning of grass clippings is not typically practiced by homeowners, only 50% of the yard waste generated was assumed to be burnable. Additionally, OAQPS assumed that burning primarily occurs in rural areas (i.e., the per capita yard waste generation factor was applied to only the rural population in each county) and that only 28% of the total yard waste generated was actually burned (see Section 6.5).

The amount of yard waste assumed to be generated in each county was then adjusted for variation in vegetation using BELD2. For counties with 10 to 50% forested land, the amount of yard waste generated was reduced to 50% and for counties with less than 10% forested land, to zero (i.e., no yard waste was generated). Adjustments for variation in vegetation were not made to counties where the percentage of forested acres was greater than or equal to 50%. Before calculating the percentage of forested acres per county, the acreage of agricultural lands was subtracted from the acreage of forested lands to better account for the native vegetation that would likely be occurring in the residential yards of farming states. Controls (or burning bans) were accounted for by assuming that no burning took place in counties where the urban population exceeded 80% of the total population (i.e., urban plus rural). Using this method, OAQPS estimated that 255,000 metric tons of leaf and 255,000 metric tons of brush (total of 510,000 metric tons of yard waste) were burned in 2000.

6.6.3. Emission Estimates

Using the emission factor of 20 ng TEQ_{DF}-WHO_{98}/kg (18.6 ng I-TEQ_{DF}/kg) and the activity level of 510,000 metric tons yard waste burned in 2000, CDD/CDF emissions from open burning of yard waste were 10.2 g TEQ_{DF}-WHO_{98} (9.5 g I-TEQ_{DF}) in 2000. Assuming 772 and 754 million kg of yard waste were burned in 1987 and 1995, respectively, then 15.4 g TEQ_{DF}-WHO_{98} (14.4 g I-TEQ_{DF}) and 15.19 g TEQ_{DF}-WHO_{98} (14 g I-TEQ_{DF}) were emitted in 1987 and 1995, respectively. These numbers should be regarded as preliminary estimates of possible emissions from this source; further testing is needed to confirm the true magnitude of emissions because both the emission factor and activity levels are judged to be clearly nonrepresentative of the source category.

6.7. LAND-CLEARING DEBRIS BURNING

6.7.1. Emissions Data

During the clearing of land for the construction of new buildings (residential and nonresidential) and highways, trees, shrubs, and brush are often torn out, collected in piles, and burned. As with residential yard waste burning, it is assumed that the burning of land-clearing debris may generate CDDs/CDFs because emissions have been detected from forest and brush fires. No direct measurements of CDD/CDF emissions from the burning of land-clearing debris have been performed, so the average emission factor of 20 ng TEQ_{DF}-WHO_{98}/kg, which was used for both forest fires and residential yard waste burning, is also used for burning of land clearing debris (see Sections 6.4 and 6.6).

6.7.2. Activity Level Information

Activity levels associated with land-clearing debris were calculated by OAQPS on a county-level basis using the number of acres disturbed through residential, nonresidential, and roadway construction.

6.7.2.1. *Residential Construction*

In 2000, approximately 330,551 acres were disturbed by residential construction. This number is based on county-level housing permit data and regional housing start data obtained from the U.S. Census Bureau for single-family units, two-family units, and apartment buildings. The county permit data were first adjusted to equal regional housing-start data, and then the number of buildings in each housing category was estimated. The total number of acres disturbed by residential construction was then determined by applying the following conversion factors to the housing-start data for each category:

Unit type	Acres per building
Single-family unit	1/4
Two-family unit	1/3
Apartments	1/2

6.7.2.2. *Nonresidential Construction*

In 2000, approximately 336,224 acres were disturbed by nonresidential construction. This number is based on the national value of construction put in place, as reported by the U.S. Census Bureau. The national value was allocated to counties using construction employment data from the Bureau of Labor Statistics and Dun & Bradstreet. A conversion factor of 1.6 acres disturbed per $100,000 spent was applied to the county-level estimates of the value of

construction put in place to obtain the acres disturbed by nonresidential construction per county. The conversion factor was developed using the Price and Cost Indices for Construction by adjusting the 1992 value of 2 acres per $100,000 for 2000.

6.7.2.3. *Roadway Construction*

In 2000, approximately 190,367 acres were disturbed by roadway construction. This number is based on 1999 Federal Highway Administration state expenditure data for capital outlay within the following six road classifications: interstate (urban and rural), other arterial (urban and rural), and collectors (urban and rural). The expenditure data were converted to miles of road constructed based on data from the North Carolina Department of Transportation (NCDOT). According to NCDOT, approximately $4 million per mile is spent for freeway and interstate projects, and approximately $1.9 million per mile is spent for arterial and collector projects. The number of miles was then converted to acres disturbed using the following conversion factors for each road classification category:

Road type	Acres per mile
Interstate, urban	15.2
Interstate, rural	15.2
Other arterial, urban	15.2
Other arterial, rural	12.7
Collectors, urban	9.8
Collectors, rural	7.9

For 1995, state expenditure for capital outlay was assumed to be 74% of total funding. This percentage was derived using 2000 data (U.S. DOT, 2002). For 1987, 74% of the total capital outlay of the average of 1985 and 1989 was used (capital outlays for 1985 and 1989 are reported in U.S. DOT, 2002). Therefore, approximately 83,110 and 123,140 acres were disturbed as the result of roadway construction in 1987 and 1995, respectively.

6.7.2.4. *Fuel Loading Factors*

To obtain the amount of biomass consumed by the burning of land-clearing debris, the total acreage of land disturbed in each county by residential, nonresidential, and roadway construction was distributed according to vegetation type (hardwood, softwood, and grass) and then combined with vegetation-specific fuel loading factors. The percentage of vegetation type within each county was determined using BELD2. The average loading factors used for each fuel type were 99 tons/acre for hardwood, 57 tons/acre for softwood, and 4.5 tons/acre for grass.

Using this method, OAQPS estimated that 28.4 million metric tons of biomass were burned through land clearing activities in 2000. EPA developed a national average biomass loading factor of 33 metric tons burned per acre in 2000. Using this loading factor combined with total acreage disturbed, EPA estimated that approximately 27.7 and 26.4 million metric tons of biomass were burned by land clearing in 1987 and 1995, respectively.

6.7.3. Emission Estimates

Using the emission factor of 20 ng TEQ_{DF}-WHO_{98}/kg (18.6 ng I-TEQ_{DF}/kg) and the activity level estimates in Section 6.7.2.4, CDD/CDF emissions from land clearing burning were 568 g TEQ_{DF}-WHO_{98} (528 g I-TEQ_{DF}) in 2000, 528 g TEQ_{DF}-WHO_{98} (491 g I-TEQ_{DF}) in 1995, and 553 g TEQ_{DF}-WHO_{98} (515 g I-TEQ_{DF}) in 1987. These should be regarded as preliminary estimates of possible emissions from this source because the emission factor is clearly nonrepresentative; further testing is needed to confirm the true magnitude of emissions.

6.8. UNCONTROLLED COMBUSTION OF POLYCHLORINATED BIPHENYLS

The accidental combustion of PCB-containing electrical equipment or intentional combustion of PCBs in incinerators and boilers not approved for PCB burning (40 CFR 761) may produce CDDs/CDFs. At elevated temperatures, such as in transformer fires, PCBs can undergo reactions to form CDFs and other by-products. More than 30 accidental fires and explosions involving PCB transformers and capacitors in the United States and Scandinavia that involved the combustion of PCBs and the generation of CDDs/CDFs have been documented (Hutzinger and Fiedler, 1991a; O'Keefe and Smith, 1989; Williams et al., 1985). For example, analyses of soot samples from a Binghamton, NY, office building fire detected 20 µg/g total CDDs (0.6 to 2.8 µg/g 2,3,7,8-TCDD) and 765 to 2,160 µg/g total CDFs (12 to 270 µg/g 2,3,7,8-TCDF). At that site, the fire involved a mixture containing PCBs (65%) and chlorobenzene (35%). Laboratory analyses of soot samples from a PCB transformer fire that occurred in Reims, France, indicated total CDD and CDF levels in the range of 4 to 58,000 ng/g and 45 to 81,000 ng/g, respectively.

Using a bench-scale thermal destruction system, Erickson et al. (1984) determined the optimum conditions for CDF formation to be a temperature of 675°C, an excess oxygen concentration of 8%, and a residence time of 0.8 sec (or longer). Combusting mineral oil and silicone oil containing 5, 50, and 500 ppm of Aroclor 1254 at these conditions yielded PCB to CDF conversion efficiencies as high as 4%. Up to 3% conversion efficiency was observed when an Askarel (70% Aroclor 1260) was combusted under the same conditions.

The use of PCBs in new transformers in the United States is banned, and their use in existing transformers and capacitors is being phased out under regulations promulgated under the Toxic Substances Control Act.

Because of the accidental nature of these incidents, the variation in duration and intensity of elevated temperatures, the variation in CDD/CDF content of residues, and uncertainty regarding the amount of PCBs still in service in electrical equipment, EPA judged the available data inadequate for developing any quantifiable emission estimates. However, Thomas and Spiro (1995) conservatively estimated that about 15 g of TEQ may be generated annually from fires in commercial and residential buildings each year. This estimate is based on the following assumptions: (a) the I-TEQ_{DF} emission rate is 20 μg/kg of PCB burned, (b) 74,000 metric tons of PCB are still in use in various electrical equipment, and (c) 1% of the in-use PCBs are burned during the course of structural fires annually.

6.9. VOLCANOES

To date, no studies demonstrating the formation of CDDs/CDFs by volcanoes have been published. Given the available information from the studies discussed below, volcanoes do not appear to be sources of CDD/CDF release to the environment.

Gribble (1994) summarized some of the existing information on the formation of chlorinated compounds by natural sources, including volcanoes. Gribble reported that several studies had demonstrated the presence of chlorofluorocarbons and simple halogenated aliphatic compounds (one and two carbon chain length) in volcanic gases. In addition, several chlorinated monoaromatic compounds as well as three PeCB congeners were detected in the ash from the 1980 eruption of Mount St. Helens. Gribble hypothesized that the formation of these PCB compounds was the result of rapid, incomplete, high-temperature combustion of chloride-containing plant material in the eruption zone. However, no information was presented to indicate the formation of CDDs/CDFs by volcanoes.

Lamparski et al. (1990) analyzed groundfall ash samples collected at various distances and locations from Mount St. Helens following the eruption in 1980. The findings of this study indicate that volcanic particulate emissions were free of detectable PCBs and nearly free of detectable CDDs (0.8 ng/kg HpCDD detected) upon exiting the volcano and remained so throughout their period of deposition in the blast zone. However, upon transport through the atmosphere, measurable and increasing levels of CDDs and PCBs were detected in deposited ash as it passed from rural to urban environments. The authors hypothesized that CDDs and PCBs in the atmosphere became associated with the volcanic ash particulates through gas-phase sorption or particulate agglomeration.

Takizawa et al. (1994) investigated the CDD/CDF content of volcanic dust fall from two active volcanoes in Japan (Mt. Fugendake and Sakurajima). The study was not designed to determine whether the CDDs/CDFs observed were formed by the volcanoes or were scavenged from the atmosphere by the falling dust and ash. The dust fall was collected for one-month periods during July and October 1992; two samples of the volcanic ash were collected in 1992. The results of the sample analyses for 2,3,7,8-substituted CDDs and CDFs, presented in Table 6-7, show that no 2,3,7,8-substituted congeners with less than seven chlorines were detected; however, the authors reported that non-2,3,7,8-substituted congeners in the lower-chlorinated congener groups were detected.

Table 6-7. CDDs/CDFs in dust fall and ashes from volcanoes

2,3,7,8-substituted congener group	Dust fall (mg/km^2/month)[a]		Volcanic ash (ng/kg)[b]	
	July 1992	Oct. 1992	Ash no. 1	Ash no. 2
TCDD	<0.5	<0.5	<0.1	<0.1
PeCDD	<0.5	<0.5	<0.1	<0.1
HxCDD	<0.5	<0.5	<0.1	<0.1
HpCDD	9.2	5.2	2.5	1.8
OCDD	14	11	1.7	2.2
TCDF	<0.5	<0.5	<0.1	<0.1
PeCDF	<0.5	<0.5	<0.1	<0.1
HxCDF	<0.5	<0.5	<0.1	<0.1
HpCDF	1.9	2.8	1.2	1.2
OCDF	4.2	1.8	<0.5	<0.5

[a]Dust fall measured from the active volcano Fugendake.
[b]Volcanic ash measured from the active volcano Sakurajima.

Source: Takizawa et al. (1994).

6.10. FIREWORKS

In order to produce various effects and illuminations, modern fireworks contain black powder and substances such as chlorine-based oxidizers, flame-coloring copper salts, and pulverized polyvinylchloride, which are known to be involved in dioxin-forming processes. During deflagration of pyrotechnics, core temperatures reach as high as 2,500°C, which would most likely inhibit the formation of organic pollutants. However, CDDs/CDFs may be generated in the areas adjacent to the combustion zone, where temperatures are lower and dwell times are longer. Therefore, CDDs/CDFs may be generated during the cooling period of the deflagration

products because the temperatures of the smoke and ash are within the possible temperature range of dioxin formation (Fleischer et al., 1999).

During a celebration in Oxford, England, that was accompanied by fireworks and bonfires, Dyke and Coleman (1995) reported a fourfold increase in CDD/CDF TEQ concentrations in the ambient air (see Section 6.2.2). Fleischer et al. (1999) conducted an experiment to measure the air emissions resulting specifically from the following seven types of fireworks: firecracker, cone fountain, jumping jack, whistler, sparkling rocket, roman candle, and four-color fountain. The paper cartridges and charges were separated from each firework and deflagrated separately in a steel chamber. CDD/CDF concentrations were measured both in air samples and in paper and ash samples. The results indicated that dioxins were not present in significant quantities in the air samples collected. Therefore, Fleisher et al. suspected that the increased background concentrations of CDDs/CDFs detected by Dyke and Coleman (1995) were due mainly to the bonfires and not the fireworks. However, concentrations of HpCDD and OCDD/OCDF were present in the paper and ash collected after the fireworks were detonated at concentrations ranging from less than the DL (10 ng/kg) to 1,200 ng/kg. Table 6-8 depicts the results of Fleischer's tests.

Table 6-8. Residue of HpCDD/HpCDF and OCDD/OCDF (ng/kg) in paper cartridges and charges of select pyrotechnic products

Product	Paper Cartridges			Charge		
	HpCDD	OCDD	OCDF	HpCDD	OCDD	OCDF
Firecracker	16	322	79	<10	535	26
Cone fountain	111	384	22	<10	<10	<10
Jumping Jack	<10	33	24	<10	28	<10
Whistler	22	353	121	<10	35	1200
Sparkling rocket	30	129	12	<10	13	<10
Roman candle	<10	426	39	<10	<10	22
Four-color fountain	<10	18	<10	<10	<10	<10

Source: Fleischer et al. (1999).

Given the lack of information on the potential for CDD/CDF emissions from fireworks, emissions cannot be quantified.

6.11. OPEN BURNING AND OPEN DETONATION OF ENERGETIC MATERIALS

Open burning and open detonation (OB/OD) practices are routinely used to destroy surplus or unserviceable energetic materials. Mitchell and Suggs (1998) conducted a study to determine emission factors from OB/OD. Air samples were collected for CDD/CDF analysis during four burns and after three detonations. The results of the study indicated that emission levels of CDDs/CDFs as a result of disposal of energetic materials by OB/OD were nondetectable.

7. METAL SMELTING AND REFINING SOURCES OF CDDs/CDFs

7.1. PRIMARY NONFERROUS METAL SMELTING/REFINING

Little information has been published on the potential for the formation and environmental release of CDDs/CDFs from primary nonferrous metal smelting facilities. CDD/CDF releases from these facilities were first reported in the wastewater of a magnesium refining facility and in the receiving water sediments downstream of a nickel refining facility in Norway (Oehme et al., 1989). This study resulted in the evaluation of the potential for CDD/CDF releases from primary nonferrous metal smelting operations in the United States. Air emissions from several U.S. smelting operation facilities have been sampled. The findings of these studies are reviewed in the following sections.

7.1.1. Primary Copper Smelting and Refining

Environmental Risk Sciences (1995) prepared an analysis for the National Mining Association on the potential for CDD/CDF emissions from operations in the primary copper smelting industry. The analysis included reviewing the process chemistry and technology of primary copper smelting, identifying operating conditions, and comparing process stream compositions from seven of the eight U.S. primary copper smelters that are members of the National Mining Association. The analysis also included stack testing for CDDs/CDFs at two facilities. The stack testing involved the principal off-gas streams for copper smelters: the main stack stream, the plant tail gas stack stream, and vent fume exhaust (Secor International, Inc., 1995b). The two facilities that were tested (Phelps Dodge Mining Co. in Playas, NM, and Cyprus Miami Mining Co. in Claypool, AZ) were selected as representative of the industry because of their similarity to other facilities in terms of process chemistry, process stream composition, and process stream temperatures. CDDs/CDFs were not detected in the air emissions from either facility.

The results of the analysis indicate that although there is some potential for CDD/CDF formation in this industry's operations, several factors lessen the probability, including the following: (a) most of the energy used to melt copper is derived from oxidation of copper sulfide ore minerals ($CuFeS_2$) rather than carbon (fossil fuels), (b) low concentrations of organic carbon and chloride are present in raw materials and reagents, (c) high concentrations of SO_2 are present in process gases (6 to 40% by volume), (d) high temperatures are maintained in the furnaces and converters (1,100 to 1,500°C), and (e) copper (II) chloride is apparently absent in process emissions.

Although CDDs/CDFs have not been detected in U.S. facilities, CDD/CDF emissions have been measured in the stack of a primary copper smelter in Canada. In 2001, emission

measurements for various persistent, bioaccumulative, and toxic substances, including CDDs/CDFs, were collected in Canada as a voluntary initiative under the Great Lakes Binational Toxics Strategy (Cianciarelli, 2001). One of the facilities tested was the Falconbridge Kidd Metallurgical plant in Timmins, Ontario, a copper smelting plant. Emission summaries are provided in Table 7-1 as TEQ concentrations corrected for 11% oxygen for the average of three runs. The total concentrations for the three runs were 3.8, 1.7, and 0.7 pg TEQ/m^3. Annual CDD/CDF emission rates were estimated to be 0.002 g I-TEQ/yr.

In 2002, Environment Canada began developing a generic dioxin/furan emissions testing protocol for use by the base metals smelting sector (Charles E. Napier Company, Ltd., 2002). Several base metals smelting and refining complexes were identified, and a summary of readily available published information on dioxin/furan emissions from the base metals smelter processes was compiled. A summary of this information is provided in Table 7-2. Four facilities were identified as primary copper smelters and had CDD/CDF emission concentrations ranging from less than 1 to 559 pg I-TEQ/dscm.

Table 7-1. CDD/CDF emission concentrations (pg TEQ/m^3 @ 11% oxygen) for primary copper smelters

Congener/congener group	Run 1	Run 2	Run 3
2,3,7,8-TCDD	0	0	0
1,2,3,7,8-PeCDD	0	0	0.1
1,2,3,4,7,8-HxCDD	0	0	0
1,2,3,6,7,8-HxCDD	0.1	0	0
1,2,3,7,8,9-HxCDD	0.1	0	0
1,2,3,4,6,7,8-HpCDD	0.1	0.1	0
OCDD	0	0	0
2,3,7,8-TCDF	0.7	0.2	0.1
1,2,3,7,8-PeCDF	0.1	0	0
2,3,4,7,8-PeCDF	2.2	0.9	0
1,2,3,4,7,8-HxCDF	0	0.2	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0
2,3,4,6,7,8-HxCDF	0.3	0.2	0.1
1,2,3,7,8,9-HxCDF	0	0	0
1,2,3,4,6,7,8-HpCDF	0.1	0.1	0
1,2,3,4,7,8,9-HpCDF	0	0	0
OCDF	0	0	0
TOTAL	3.8	1.8	0.4

Source: Cianciarelli (2001).

Table 7-2. CDD/CDF emissions data from primary and secondary copper and secondary lead smelters

Company, location	Process units	Emission control technology	CDD/CDF emission concentration (pg I-TEQ/dscm)
Primary copper smelters			
Norddeutsche Affinerie, Germany	Outokumpu flash smelting furnace	Waste heat boiler, ESP	< 20
	Peirce-Smith converter	ESP	NA
Falconbridge, Sudbury, Ontario (nickel and copper)	Roasting Electric smelting Peirce-Smith converters	Cyclone/ESP	559
Noranda, Horne smelter, Noranda, Quebec	Noranda reactor Noranda continuous converter	ESP	<1
Noranda, Gaspe smelter, Murdockville, Quebec	Reverberatory furnace	ESP	NA
	Peirce-Smith converter		82
Secondary copper smelters			
Norddeutsche Affinerie, Germany	Peirce-Smith converter	FF	<500
Huttenwerke Kayser, Germany	Blast furnace	Post-combustion, waste heat boiler, FF	<500
	Peirce-Smith converters Hearth furnace (for tin/lead)	FF	<100
	Reverberatory anode furnace	Waste heat boiler, FF	
Mansfelder Kupfer und Messing, Germany	Blast furnace	Post-combustion, waste heat boiler, cooler, FF, FF with lime/coke injection	<500
Unknown company, Germany	Shaft furnace	Post-combustion, dry quench with secondary off-gas, FF	<100
Unknown company, Germany	Rotary furnace	FF	<100–1,000
Unknown company, Germany	Rotary furnace	Gas cooling, FF	<100
Unknown company, Germany	Rotary furnace	Gas cooling, FF, activated carbonized lignite adsorbent boxes	<100

ESP = Electrostatic precipitator
FF = Fabric filter
NA = Not available

Source: Charles E. Napier Company, Ltd. (2002).

In 1995, eight primary smelters were in operation in the United States, one of which closed at the end of that year (Edelstein, 1995). Total refinery production was 1.60 million metric tons in 1995, including 0.36 million metric tons from scrap material (Edelstein, 1995), and 1.13 million metric tons in 1987 (USGS, 1997a). In 2000, four primary smelters of copper were in operation in the United States, producing 1.61 million metric tons of copper (USGS, 2002).

CDD/CDF emission estimates for primary copper smelters were developed using the stack test data from the two tested facilities in the United States. Conservatively assuming that all nondetect values were present at one-half the detection limit, Environmental Risk Sciences, Inc. (1995) calculated the annual TEQ emission to air to be less than 0.5 g I-TEQ_{DF} in 1995 for the seven facilities (out of a total of eight) belonging to the National Mining Association. Assuming that 1987 feed and processing materials were similar, 1987 releases can be estimated at less than 0.5 g I-TEQ_{DF} as well. Because the number of facilities was reduced in 2000, the national emissions estimate was reduced proportionally to 0.29 g I-TEQ. The activity level estimates are assigned a high confidence rating and the emission factor estimates a medium rating; therefore, the emission estimates are assigned a medium confidence rating. The activity levels are based on comprehensive surveys. The emission factors are reasonably representative of emissions from the source category.

7.1.2. Primary Magnesium Smelting and Refining

Oehme et al. (1989) reported that the production of magnesium can lead to the formation of CDDs and CDFs. They estimated that 500 g of I-TEQ_{DF} were released to the environment in wastewater and 6 g I-TEQ_{DF} were released to air annually from a magnesium production facility in Norway; CDFs predominated, with a CDF-to-CDD concentration ratio of 10:1. At the time of sampling, the magnesium production process involved formation of magnesium oxide (MgO) from calcinated dolomite followed by a step in which magnesium chloride ($MgCl_2$) was produced by heating MgO/coke pellets in a shaft furnace in a pure chlorine atmosphere to about 700 to 800°C. The $MgCl_2$ was then electrolyzed to form metallic magnesium and chloride. The chloride excess from the $MgCl_2$ process and the chloride formed during electrolysis were collected by water scrubbers and directly discharged to the environment. The discharged wastewater contained 200 to 500 ppm of suspended particulate matter. All but trace quantities of the hexa through octa congeners were associated with the particulates; up to 10% of the tetra and penta congeners were present in the water phase.

A study by the firm operating the facility (Musdalslien et al., 1998) indicated that installation of a water treatment system had reduced annual emissions to water to less than 1 g Nordic TEQ, and emissions to air had been reduced to less than 2 g Nordic TEQ. This study also

presented results demonstrating that the carbon-reducing agent used in the $MgCl_2$ production step and the operating conditions of the shaft furnace greatly affected the formation of CDDs/CDFs. Gases from the furnace were measured nine times over sampling periods of 6 to 8 hr. The calculated emission factor to air (i.e., before any air pollution control device [APCD] controls) ranged from 468 to 3,860 ng Nordic TEQ per kg of $MgCl_2$ produced. The APCD controls consisted of three water scrubbers, a wet electrostatic precipitator (ESP), and an incinerator.

From 1950 to 2000, the United States was the world's largest producer of metallic magnesium (Kramer, 1995). In 1995, three magnesium production facilities were operating in the United States. As in the Norwegian plant, an electrolytic process (electrolysis of $MgCl_2$) was used at the plants in Texas (capacity of 65,000 metric tons/yr) and Utah (capacity of 40,000 metric tons/yr) to recover metallic magnesium from $MgCl_2$. However, these two facilities reportedly used seawater and lake brines as the source of magnesium, and the procedures to obtain and purify $MgCl_2$ did not involve chlorinating furnaces and carbonized pellets (Lockwood et al., 1981). A thermic process was used to recover magnesium from dolomite at the facility in Washington (capacity of 40,000 metric tons/yr) (Kramer, 1995). In thermic processes, MgO, a component of calcinated dolomite, is reacted with a metal such as silicon (usually alloyed with iron) to produce metallic magnesium. In 2000, the Magnesium Corporation of America facility near Rowley, UT, was the only operational magnesium smelting facility in the United States.

Monitoring of wastewater discharges from U.S. magnesium production facilities for CDD/CDF content has not been reported. Wastewater discharges of CDDs/CDFs reported for the Norwegian facility (Oehme et al., 1989), discussed in the previous paragraphs, are not adequate to support development of wastewater emission factors for U.S. facilities because of possible differences in the processes used to manufacture $MgCl_2$ and pollution control equipment.

Monitoring of air emissions for CDD/CDF content has been reported for the Magnesium Corporation of America facility near Rowley, UT (Western Environmental Services and Testing, Inc., 2000). The average emission rates (for three tests) reported for the melt reactor stack and the cathode stack were 0.31 mg I-TEQ_{DF}/hr and 0.16 mg I-TEQ_{DF}/hr, respectively.

Emissions data were judged inadequate for developing national emission estimates for 1987 that could be included in the national inventory. The confidence in the degree to which the one tested facility represents emissions from the other two U.S. facilities is low. However, an estimate of the potential TEQ annual emissions for 1995 from U.S. primary magnesium production facilities can be made by assuming that the average total emission factor for the Utah facility measured in May 2000 (0.47 mg I-TEQ_{DF}/hr) is representative of the other two facilities for magnesium production. Specifically, if it is assumed that this facility operated for 24 hr/day for 365 days in 1995, then the annual release in 1995 would have been 4.1 g I-TEQ_{DF}. If it is

further assumed that this facility operated at 98% of its rated capacity of 40,000 metric tons/yr, then the production-based emission factor would be 105 ng I-TEQ_{DF}/kg of magnesium produced. Applying this emission factor to 98% of the industry's production capacity in 1995 (142,000 metric tons) yields a preliminary annual emissions estimate of 14.6 g I-TEQ_{DF} in 1995.

In 2000, the Magnesium Corporation of America facility near Rowley, UT, was the only magnesium smelting facility operating in the United States. Production of primary magnesium at this facility was 41,000 metric tons in 2000. Using the emission factor of 105 ng I-TEQ_{DF}/kg of magnesium produced, the national estimate for dioxin releases in 2000 due to primary magnesium smelting is 4.3 g I-TEQ/yr. The emission factor has a high confidence rating because it was developed using data from this facility; therefore, the emissions estimate is assigned a high confidence level.

7.1.3. Primary Nickel Smelting and Refining

Oehme et al. (1989) reported that certain primary nickel refining processes generate CDDs and CDFs, primarily CDFs. Although the current low-temperature process used at a Norwegian facility was estimated to result in releases to water of only 1 g I-TEQ_{DF}/yr, a high-temperature (800°C) process to convert nickel chloride to nickel oxide that had been used for 17 yr at the facility is believed to have resulted in significant releases in earlier years, based on the parts-per-billion levels of CDFs detected in aquatic sediments downstream of the facility.

According to Kuck (1995), the only nickel mining and smelting complex in the United States (located in Oregon) had a capacity of 16,000 metric tons/yr. The facility had been on standby since August 1993 and had no production in 1994. The facility restarted operations in April 1995 and produced 8,290 metric tons of nickel that year. In 1998, the smelter closed because of low nickel prices (USGS, 2002). Monitoring for discharges of CDDs/CDFs at this facility has not been reported. Emissions of CDDs/CDFs were reported for a Norwegian facility in the late 1980s, as discussed above (Oehme et al., 1989). The emissions information contained in the Norwegian study is not adequate to support development of emission factors for the U.S. facility for 1987 and 1995. Because the facility closed in 1998, emission estimates for 2000 for primary nickel smelting are zero.

7.1.4. Primary Aluminum Smelting and Refining

No sampling of air emissions for the presence of CDDs/CDFs has been reported for this industry. Lexen et al. (1993) reported that samples of filter powder and sludge from a lagoon at the only primary aluminum production plant in Sweden showed no or little CDDs/CDFs. Because the primary smelting process does not use chlorine, there is widespread belief that

dioxin emissions from primary aluminum smelting facilities do not exist; therefore, no sampling has been done.

In the primary aluminum smelting process, bauxite ore, a hydrated oxide of aluminum consisting of 30 to 56% alumina (Al_2O_3), is refined into alumina by the Bayer process. The alumina is then shipped to a primary aluminum smelter for electrolytic reduction to aluminum. Electrolytic reduction of alumina occurs in shallow rectangular cells, or pots, which are steel shells lined with carbon. Carbon electrodes (petroleum coke mixed with a pitch binder) extending into the pot serve as the anodes, and the carbon lining serves as the cathode. Three types of pots are used: prebaked anode cell, horizontal stud Soderberg anode cell, and vertical stud Soderberg anode cell. Most of the aluminum produced in the United States is produced using the prebaked cells. Molten cryolite (Na_3AlF_6) functions as both the electrolyte and the solvent for the aluminum. Aluminum is deposited on the cathode as molten metal (U.S. EPA, 1998a).

Prior to casting, the molten aluminum may be batch treated in reverberatory furnaces (such as those used in secondary aluminum smelting) to remove oxides, gaseous impurities, and active metals such as sodium and magnesium. One process consists of adding a flux of chloride and fluoride salts and then bubbling chlorine gas through the molten mixture (U.S. EPA, 1998a).

U.S. production of primary aluminum was 3.343 million metric tons in 1987 and 3.375 million metric tons in 1995. In 1995, 13 companies operated 22 primary aluminum reduction plants (USGS, 1997b, c). In 2000, 12 companies operated 23 primary aluminum reduction plants, and primary aluminum smelters produced 3.7 million metric tons of aluminum (USGS, 2002). Because emission factors have not been developed for this sector, there are no emission estimates for this category.

7.1.5. Primary Titanium Smelting and Refining

It has been suggested that carbochlorination processes used in this industry may be a source of CDDs/CDFs (Bramley,1998; ERG, 1998). As discussed below, CDDs/CDFs have been measured in titanium dioxide production sludges. A brief summary of the processes used in this industry is presented in the following paragraphs.

In primary titanium smelting, titanium oxide ores and concentrates are chlorinated in fluidized-bed reactors in the presence of coke at 925 to 1,010°C to form titanium tetrachloride ($TiCl_4$). The $TiCl_4$ is separated from other chlorides by double distillation. The $TiCl_4$ is then either oxidized at 985°C to form pigment-grade titanium dioxide or reduced using sodium or magnesium to form titanium sponge (i.e., metallic titanium) (Knittel, 1983). Titanium ingot is produced by melting titanium sponge or scrap or a combination of both using electron beam,

plasma, and vacuum arc methods. Scrap currently supplies about 50% of ingot feedstock (Gambogi, 1996).

Titanium sponge is produced at two facilities in the United States, one in Albany, OR, and the other in Henderson, NV. In 1995, the U.S. production volume of titanium sponge was withheld to avoid disclosing proprietary data; domestic sponge capacity was 29,500 metric tons/yr. In 1987, U.S. production of titanium sponge was 17,849 metric tons.

More than 90% of titanium dioxide is produced using the process described above. Titanium dioxide pigment is used in paints, plastics, and paper products. In 1995, titanium dioxide was produced at nine facilities in the United States. Production volumes in 1987 and 1995 were 821,000 and 1.8 million metric tons, respectively (Gambogi, 1996; USGS, 1997d). In 2000, four companies at eight facilities in seven states produced 1.44 million metric tons of titanium dioxide (USGS, 2002).

Titanium dioxide production creates a sludge waste, and CDDs/CDFs have been measured in these sludges (U.S. EPA, 2001c). For the most part, these sludges have been disposed of in either on-site or off-site RCRA Subtitle D solid waste disposal facilities. However, given the potential for leaching of the heavy metals from the sludge in the Subtitle D landfill, EPA has listed this waste as hazardous waste under Subtitle C. These sludges are now considered a hazardous waste under RCRA and must be disposed of in permitted landfills (U.S. EPA, 2001c). Therefore, they are not considered to cause environmental releases under the definition in this document and are not included in the inventory.

7.2. SECONDARY NONFERROUS METAL SMELTING

Secondary smelters primarily engage in the recovery of nonferrous metals and alloys from new and used scrap and dross. The principal metals of this industry, both in terms of volume and value of product shipments, are aluminum, copper, lead, zinc, and precious metals (U.S. DOC, 1990a). Scrap metal and metal wastes may contain organic impurities such as plastics, paints, and solvents. Secondary smelting and refining processes for some metals (e.g., aluminum, copper, and magnesium) use chemicals such as sodium chloride, potassium chloride, and other salts. The combustion of these impurities and chlorine salts in the presence of various types of metal during reclamation processes can result in the formation of CDDs/CDFs, as evidenced by their detection in the stack emissions of secondary aluminum, copper, and lead smelters (Aittola et al., 1992; U.S. EPA, 1987a, 1997a).

7.2.1. Secondary Aluminum Smelters

Secondary aluminum smelters reclaim aluminum from scrap using two processes: precleaning and smelting. Both processes may produce CDD/CDF emissions.

Precleaning processes involve sorting and cleaning scrap to prepare it for smelting. Cleaning processes that may produce CDD/CDF emissions use heat to separate aluminum from contaminants and other metals. These techniques are "roasting" and "sweating." Roasting uses rotary dryers with a temperature high enough to vaporize organic contaminants but not high enough to melt aluminum. An example of roasting is the delacquering and processing of used beverage cans. Sweating involves heating aluminum-containing scrap metal to a temperature above the melting point of aluminum but below the melting temperature of other metals such as iron and brass. The melted aluminum trickles down and accumulates in the bottom of the sweat furnace and is periodically removed (U.S. EPA, 1997a).

After precleaning, the treated aluminum scrap is smelted and refined. This usually takes place in a reverberatory furnace. Once smelted, flux is added to remove impurities. The melt is demagged to reduce the magnesium content of the molten aluminum by adding chlorine gas. The molten aluminum is then transferred to a holding furnace and alloyed to final specifications (U.S. EPA, 1997a).

CDD/CDF emissions to air have been measured at seven U.S. secondary aluminum operations. Five facilities were tested in 1995 and 1996 and two facilities were tested in 1992. Four of the 1995 tests were conducted by EPA in conjunction with The Aluminum Association, Inc., to identify emission rates from facilities with potentially maximum-achievable-control-technology-grade operations and APCD equipment. The fourth test was performed by EPA (U.S. EPA, 1995c). Results from two facilities tested by the California Air Resources Board (CARB) in 1992 were presented in two confidential reports.

The first facility tested in 1995 was a top-charge melt furnace (Advanced Technology Systems, Inc., 1995). During testing, the charge material to the furnace was specially formulated to contain no oil, paint, coatings, rubber, or plastics other than incidental amounts. The TEQ emission factor from such a clean charge, 0.27 ng TEQ_{DF}-WHO_{98}/kg (0.26 ng I-TEQ_{DF}/kg) charge material, would be expected to represent the low end of the normal industry range.

The second facility operated a sweat furnace to preclean the scrap and a reverberatory furnace to smelt the precleaned aluminum (U.S. EPA, 1995c). Stack emissions were controlled by an afterburner operated at 788°C. The TEQ emission factor for this facility was 3.37 ng TEQ_{DF}-WHO_{98}/kg (3.22 ng I-TEQ_{DF}/kg) aluminum produced.

The third facility employed a crusher/roasting dryer as a precleaning step followed by a reverberatory furnace (Galson Corporation, 1995). The emissions from the two units were vented separately. The exhaust from the crusher/dryer was treated with an afterburner and a fabric filter (FF). The exhaust from the furnace passed through an FF with lime injection. Both stack exhausts were tested, and the combined TEQ emission factor was 13.55 ng TEQ_{DF}-WHO_{98}/kg (12.95 ng I-TEQ_{DF}/kg) aluminum produced. Because the activity level of the facility

at the time of sampling was treated as confidential business information, the calculated emission factor was based on the reported typical production rates of the two operations: 26,000 lb/hr for the crusher/dryer and 6,700 lb/hr for the furnace.

The fourth facility operated a scrap roasting dryer followed by a sidewell reverberatory furnace (Weston,1996). The emissions from the two units were vented separately. Exhaust from the dryer passed through an afterburner and a lime-coated FF. The exhaust from the furnace passed through a lime-coated FF. Both stack exhausts were tested, and the combined TEQ emission factor was 8.52 ng TEQ_{DF}-WHO_{98}/kg (7.93 ng I-TEQ_{DF}/kg) of charge material.

The two facilities tested by CARB in 1992, which were reported in two confidential reports (CARB, 1992a, b, as reported in U.S. EPA, 1997a) had TEQ emission factors of 55.68 and 23.44 ng TEQ_{DF}-WHO_{98}/kg (52.21 and 21.67 ng I-TEQ_{DF}/kg) of scrap aluminum consumed. One facility was equipped with a venturi scrubber; the other was assumed to be uncontrolled (U.S. EPA, 1997a).

The seventh facility was tested in 1995 by Commonwealth Aluminum Corp. (1995). The test involved sampling air emissions from a delaquering kiln. The facility was equipped with an FF as the primary APCD.

The CDD/CDF congener and congener group emission factors derived from these stack tests were used to represent emissions from secondary aluminum facilities operating in 2000, 1995, and 1987. Table 7-3 shows the TEQ emission factors for facilities operating in 2000, and Table 7-4 shows those for 1995 and 1987. The 2000 emission factors do not include the results from the two facilities tested by CARB (1992a, b) because it was assumed that all facilities operating in 2000 were equipped with APCDs on all vents and stacks. The average congener and congener group profiles are presented in Figure 7-1. The average of the TEQ emission factors measured at the five tested facilities representative of the year 2000 is 5.17 ng TEQ_{DF}-WHO_{98}/kg (4.90 ng I-TEQ_{DF}/kg) of scrap feed. A low confidence rating is assigned to the average emission factor for 2000 because it is based on the results of testing at only five facilities, and they may not be representative of all facilities operating in the United States in that year.

The emission factors for facilities operating in 1995 and 1987 do include the results from the two facilities tested by CARB in 1992. The average of the TEQ emission factor measured at the seven tested facilities representative of the years 1995 and 1987 is 15.0 ng TEQ_{DF}-WHO_{98}/kg (14.05 ng I-TEQ_{DF}/kg) of scrap feed. A low confidence rating is assigned to the average emission factor for 1995 and 1987 because it is based on the results of testing at only seven facilities, and that may not be representative of all facilities operating in the United States in those reference years.

Table 7-3. CDD/CDF emission factors (ng/kg scrap feed) for secondary aluminum smelters for 2000

Congener	Mean facility emission factor					Overall mean emission factor
	a	b	c	d	e	
2,3,7,8-TCDD	ND (0.01)	0.13	0.51	0.40	0.01	0.21
1,2,3,7,8-PeCDD	0.02	0.39	1.19	1.19	0.02	0.56
1,2,3,4,7,8-HxCDD	0.05	0.24	1.35	0.72	0.02	0.48
1,2,3,6,7,8-HxCDD	0.13	0.86	1.52	0.94	0.03	0.70
1,2,3,7,8,9-HxCDD	0.15	1.26	2.51	1.62	0.05	1.12
1,2,3,4,6,7,8-HpCDD	0.51	7.67	2.6	3.49	0.10	2.87
OCDD	0.42	14.97	1.01	NR	NR	5.47
2,3,7,8-TCDF	0.44	0.74	14.20	10.46	0.07	5.18
1,2,3,7,8-PeCDF	0.06	1.51	10.47	12.52	0.08	4.93
2,3,4,7,8-PeCDF	0.17	2.44	11.06	6.98	0.12	4.15
1,2,3,4,7,8-HxCDF	0.32	2.44	21.84	8.14	0.16	6.58
1,2,3,6,7,8-HxCDF	0.11	2.69	7.1	2.74	0.06	2.54
1,2,3,7,8,9-HxCDF	0.02	1.02	0.47	0.14	0.01	0.33
2,3,4,6,7,8-HxCDF	0.3	3.82	7.09	4.30	0.08	3.12
1,2,3,4,6,7,8-HpCDF	0.07	11.39	14.61	3.18	0.17	5.88
1,2,3,4,7,8,9-HpCDF	0.03	5.5	1.21	0.45	0.04	1.45
OCDF	0.3	30.4	3.15	1.23	0.06	7.03
Total I-TEQ_{DF}[f]	0.26	3.22	12.95	8.09	0.14	4.93
Total TEQ_{DF}-WHO_{98}[f]	0.27	3.37	13.55	8.68	0.15	5.20

[a]Source: Advanced Technology Systems, Inc. (1995).
[b]Source: U.S. EPA (1995c).
[c]Source: Galson Corporation (1995).
[d]Source: Weston (1996).
[e]Source: Commonwealth Aluminum Corp. (1995).
[f]TEQ calculations assume nondetect values were zero.

NR = Not reported
ND = Not detected (value in parenthesis is the detection limit)

For comparison purposes, the European Commission uses 22 ng I-TEQ_{DF}/kg scrap aluminum as the typical emission factor for the European Dioxin Inventory (Quab and Fermann, 1997). Umweltbundesamt (1996) reported stack testing results for 25 aluminum smelters and foundries in Germany. This study provided sufficient data to enable calculation of TEQ emission factors for 11 of the tested facilities. The calculated emission factors ranged from 0.01 to 167 ng

Table 7-4. CDD/CDF emission factors (ng/kg scrap feed) for secondary aluminum smelters for 1995 and 1987

Congener	Mean facility emission factor							Overall mean emission factor
	a	b	c	d	e	f	f	
2,3,7,8-TCDD	ND (0.01)	0.13	0.51	0.40	0.01	1.97	0.85	0.54
1,2,3,7,8-PeCDD	0.02	0.39	1.19	1.19	0.02	7.1	3.64	1.94
1,2,3,4,7,8-HxCDD	0.05	0.24	1.35	0.72	0.02	4.26	2.82	1.35
1,2,3,6,7,8-HxCDD	0.13	0.86	1.52	0.94	0.03	5.3	4.12	1.84
1,2,3,7,8,9-HxCDD	0.15	1.26	2.51	1.62	0.05	5.3	2.02	1.84
1,2,3,4,6,7,8-HpCDD	0.51	7.67	2.6	3.49	0.10	28.9	19.3	8.94
OCDD	0.42	14.97	1.01	NR	NR	33.2	24.3	14.78
2,3,7,8-TCDF	0.44	0.74	14.20	10.46	0.07	23.2	4.84	7.71
1,2,3,7,8-PeCDF	0.06	1.51	10.47	12.52	0.08	33.8	1.18	8.52
2,3,4,7,8-PeCDF	0.17	2.44	11.06	6.98	0.12	48	23.3	13.15
1,2,3,4,7,8-HxCDF	0.32	2.44	21.84	8.14	0.16	46.1	17.6	13.80
1,2,3,6,7,8-HxCDF	0.11	2.69	7.1	2.74	0.06	46.1	16.9	10.81
1,2,3,7,8,9-HxCDF	0.02	1.02	0.47	0.14	0.01	22	1.35	3.57
2,3,4,6,7,8-HxCDF	0.3	3.82	7.09	4.30	0.08	39	16	10.08
1,2,3,4,6,7,8-HpCDF	0.07	11.39	14.61	3.18	0.17	122	42.6	27.71
1,2,3,4,7,8,9-HpCDF	0.03	5.5	1.21	0.45	0.04	27.1	6.2	5.79
OCDF	0.3	30.4	3.15	1.23	0.06	60.5	29.5	17.88
Total I-TEQ_{DF}[g]	0.26	3.22	12.95	8.09	0.14	52.21	21.68	14.08
Total TEQ_{DF}-WHO_{98}[g]	0.27	3.37	13.55	8.68	0.15	55.68	23.45	15.02

[a]Source: Advanced Technology Systems, Inc. (1995).
[b]Source: U.S. EPA (1995c).
[c]Source: Galson Corporation (1995).
[d]Source: Weston (1996).
[e]Source: Commonwealth Aluminum Corp. (1995).
[f]Source: CARB (1992a, b), as reported in U.S. EPA (1997a).
[g]TEQ calculations assume nondetects were zero.

NR = Not reported
ND = Not detected (value in parenthesis is the detection limit)

I-TEQ_{DF}/kg of scrap feed. Three facilities had emission factors exceeding 100 ng I-TEQ_{DF}/kg, and two facilities had emission factors of less than 1 ng I-TEQ_{DF}/kg. The mean emission factor for the 11 facilities was 42 ng I-TEQ_{DF}/kg.

Approximately 727,000 metric tons of scrap aluminum were consumed by 67 secondary aluminum smelters in the United States in 1987 (U.S. DOC, 1995c). In 1995, consumption of

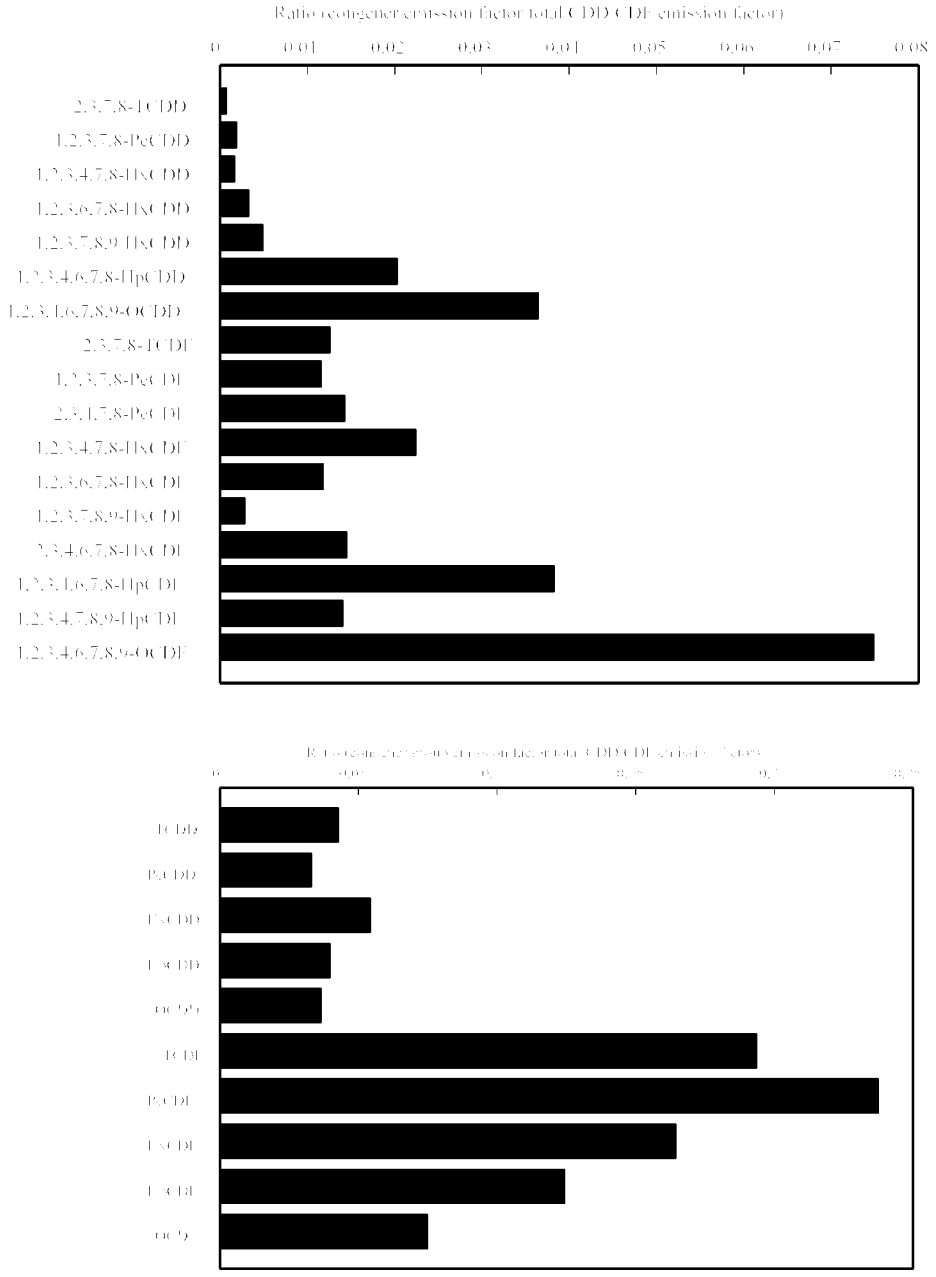


Figure 7-1. Congener and congener group profiles for air emissions from secondary aluminum smelters.

Sources: U.S. EPA (1995c); Galson Corporation (1995).

scrap aluminum by the 76 facilities that composed the secondary aluminum smelting industry had nearly doubled, to 1.3 million metric tons (USGS, 1997e; The Aluminum Association, Inc., 1997). In 2000, secondary aluminum smelters consumed 1.6 million metric tons of scrap aluminum (USGS, 2002). A high confidence rating is assigned to these production estimates

because they are based on government survey data. Applying the 15.0 ng TEQ_{DF}-WHO_{98}/kg (14.05 ng I-TEQ_{DF}/kg) emission factor to the metric tons of scrap aluminum processed in 1987 and 1995 yields estimated annual emissions of 10.9 g TEQ_{DF}-WHO_{98} (10.21 g I-TEQ) in 1987 and 19.5 TEQ_{DF}-WHO_{98} (18.27 g I-TEQ_{DF}) in reference year 1995. Applying the emission factor of 5.17 ng TEQ_{DF}-WHO_{98}/kg (4.9 ng I-TEQ_{DF}/kg) to the metric tons of scrap aluminum processed in 2000 yields estimated annual emissions of 8.27 g TEQ_{DF}-WHO_{98} (7.84 g I-TEQ) in reference year 2000. These emission estimates are assigned a low confidence rating because the rating given to the emission factor was low.

It should be noted that a significant amount of scrap aluminum is also consumed by other segments of the aluminum industry. However, this scrap is generally from metal manufacturing processes, including metal and alloy production (e.g., borings, turnings, and dross), rather than old scrap that results from recycling of consumer products (e.g., cans, radiators, auto shredders). In 1995, integrated aluminum companies consumed 1.4 million metric tons of scrap aluminum, and independent mill fabricators consumed 0.68 million metric tons (USGS, 1997e).

7.2.2. Secondary Copper Smelters

Secondary copper smelting is part of the scrap copper, brass, and bronze reprocessing industry. Brass is an alloy of copper and zinc; bronze is an alloy of copper and tin. Facilities in this industry fall into three general classifications: secondary smelting, ingot making, and remelting. Similar processing equipment may be used at all three types of facilities, so the distinguishing features are not immediately apparent (U.S. EPA, 1994b).

The feature that distinguishes secondary smelters from ingot makers and remelters is the extent to which pyrometallurgical purification is performed. A typical charge at a secondary smelter may contain from 30 to 98% copper. The secondary smelter upgrades the material by reducing the quantity of impurities and alloying materials, thereby increasing the relative concentration of copper. This degree of purification and separation of the alloy constituents does not occur at ingot makers and remelters. Feed material to a secondary copper smelter is a mixture of copper-bearing scrap such as tubing, valves, motors, windings, wire, radiators, turnings, mill scrap, printed circuit boards, telephone switching gear, and ammunition casings. Nonscrap items such as blast furnace slags and drosses from ingot makers or remelters may represent a portion of the charge. Secondary smelter operators use a variety of processes to separate the alloy constituents. Some purify the scrap in the reductive atmosphere of a blast furnace and then purify the charge in the oxidizing atmosphere of a converter; others perform all purification by oxidation in top-blown rotary converters or in reverberatory furnaces (U.S. EPA, 1994b).

Ingot maker operators blend and melt scrap copper, brass, and bronze of various compositions to produce a specification brass or bronze ingot. When necessary, they add ingots of other metals (e.g., zinc or tin) to adjust the metallurgy of the final product. The feed materials for ingot makers contain relatively high amounts of copper. Examples of feed materials include copper tubing, valves, brass and bronze castings, ammunition shell casings, and automobile radiators. "Fire-refined" anode copper or cathode copper may also be charged. Items such as motors, telephone switchboard scrap, circuit board scrap, and purchased slags are not used by ingot makers. The reductive step (melting in a reducing atmosphere, as in a blast furnace) that some secondary smelters employ is not used by ingot makers. Ingot makers do, however, use some of the other types of furnaces used by secondary smelters, including direct-fired converters, reverberatory furnaces, and electric induction furnaces (U.S. EPA, 1994b).

Remelting facilities do not conduct substantial purification of the incoming feeds. These facilities typically melt the charge and then cast or extrude a product. The feeds to a remelter are generally alloy material of approximately the desired composition of the product (U.S. EPA, 1994b).

7.2.2.1. *Emissions Data*

Stack emissions of CDDs/CDFs from a secondary copper smelter were measured by EPA during 1984 and 1985 as part of the National Dioxin Tier 4 Study (U.S. EPA, 1987a). The facility chosen for testing was estimated to have a high potential for CDD/CDF emissions because of the abundance of chlorinated plastics in the feed. This facility ceased operations in 1986. The facility was chosen for testing by EPA because the process technology and APCD equipment in place were considered typical for the source category.

During operations, copper and iron-bearing scrap were fed in batches to a cupola blast furnace, which produced a mixture of slag and black copper. Approximately 4 to 5 tons of metal-bearing scrap were fed to the furnace per charge, with materials typically being charged 10 to 12 times per hour. Coke fueled the furnace and represented approximately 14% (by weight) of the total feed. During the stack tests, the feed consisted of electronic telephone scrap and other plastic scrap, brass and copper shot, iron-bearing copper scrap, precious metals, copper-bearing residues, refinery by-products, converter furnace slag, anode furnace slag, and metallic floor-cleaning material. The telephone scrap made up 22% (by weight) of the feed and was the only scrap component that contained plastic materials. Oxygen-enriched combustion air for combustion of the coke was blown through tuyeres (nozzles) at the bottom of the furnace. At the top of the blast furnace were four natural gas-fired afterburners to aid in completing combustion of the exhaust gases. Particulate emissions were controlled by FFs, and the flue gas was then discharged into a common stack. The estimated emission factors derived for this site are

presented in Table 7-5. The emission factors are based on the total weight of scrap fed to the furnace. Based on the measured congener and congener group emission factors, the TEQ emission factor is 779 ng I-TEQ_{DF}/kg (810 ng TEQ_{DF}-WHO_{98}/kg) of scrap metal smelted. Figure 7-2a presents the congener group profile based on these emission factors.

In 1992, stack testing of the blast furnace emissions of a secondary smelter located in Philadelphia, PA (Franklin Smelting and Refining Co.), was conducted by Applied Geotechnical & Environmental Services Corporation (AGES, 1992). Like the facility tested by EPA during 1984 and 1985, this facility processed low-purity copper-bearing scrap, telephone switch gear, and slags, as well as higher-copper-content materials (U.S. EPA, 1994b). The facility used a blast (cupola-type) furnace coupled with a pair of rotary converters to produce blister copper. The blast furnace used coke as both the fuel and the agent to maintain a reducing atmosphere. The black copper-slag mixture from the blast furnace was charged to the rotary converters for further refining with the aid of oxygen, sand, and oak logs (AGES, 1992; U.S. EPA, 1994b). The APCD equipment installed on the blast furnace included an afterburner, a cooling tower, and an FF. During testing, the afterburner was reported to be operating erratically and was particularly low during one of the two sampling episodes. Stack gas flow was also low during both sampling episodes because one or more FF compartments were inoperable (AGES, 1992). The estimated emission factors derived for this site from the AGES results are presented in Table 7-5. The emission factors were based on the total weight of scrap fed to the blast furnace. The TEQ emission factor was 16,618 ng I-TEQ_{DF}/kg (16,917 ng TEQ_{DF}-WHO_{98}/kg) of scrap. Figure 7-2b presents the congener and congener group profiles based on these emission factors.

In 1991, stack testing of the rotary furnace stack emissions of a secondary smelter (Chemetco, Inc.) located in Alton, IL, was conducted by Sverdrup Corp. (1991). The Chemetco facility used four tap-down rotary (i.e., oxidizing) furnaces. Furnace-processed gas emissions were controlled by a primary quencher and a venturi scrubber. The feed was relatively high-purity copper scrap containing minimal, if any, plastics. The same manufacturing process and APCD equipment were in place in 1987 and 1995 (U.S. EPA, 1994b). Because this facility operated under oxidizing rather than reducing conditions and processed relatively high-purity scrap, the potential for CDD/CDF formation and release was expected to be dramatically different from that of the two tested facilities reported above. The estimated emission factors derived for this site from the results of Sverdrup Corp. (1991) are presented in Table 7-5. The emission factors were based on the total weight of scrap feed going to the furnace. The TEQ emission factor was 3.60 ng I-TEQ_{DF}/kg (3.66 ng TEQ_{DF}-WHO_{98}/kg) of scrap.

Table 7-5. CDD/CDF mean emission factors (ng/kg scrap feed) for secondary copper smelters

Congener/ congener group	EPA Tier 4 facility[a,b]	Franklin smelting facility[c]	Chemetco smelting facility[d]
2,3,7,8-TCDD	127	227	ND (0.05)
1,2,3,7,8-PeCDD	NR	846	0.21
1,2,3,4,7,8-HxCDD	NR	1,476	0.39
1,2,3,6,7,8-HxCDD	NR	1,746	0.70
1,2,3,7,8,9-HxCDD	NR	2,132	1.26
1,2,3,4,6,7,8-HpCDD	NR	17,065	8.95
OCDD	1,350	55,668	22.45
2,3,7,8-TCDF	2,720	4,457	2.11
1,2,3,7,8-PeCDF	NR	9,455	1.47
2,3,4,7,8-PeCDF	NR	5,773	2.63
1,2,3,4,7,8-HxCDF	NR	70,742	7.30
1,2,3,6,7,8-HxCDF	NR	20,524	2.15
1,2,3,7,8,9-HxCDF	NR	5,362	4.06
2,3,4,6,7,8-HxCDF	NR	12,082	0.27
1,2,3,4,6,7,8-HpCDF	NR	37,251	11.48
1,2,3,4,7,8,9-HpCDF	NR	7,570	2.74
OCDF	2,520	82,192	21.61
Total I-TEQ_{DF}[e]	779[f]	16,618	3.59
Total TEQ_{DF}-WHO_{98}[e]	810[f]	16,917	3.66
Total TCDD	736	14,503	3.05
Total PeCDD	970	30,248	5.19
Total HxCDD	1,260	55,765	9.62
Total HpCDD	2,080	38,994	16.71
Total OCDD	1,350	55,668	22.45
Total TCDF	13,720	108,546	46.42
Total PeCDF	8,640	71,136	27.99
Total HxCDF	4,240	164,834	27.96
Total HpCDF	3,420	66,253	23.38
Total OCDF	2,520	82,192	21.61
Total CDD/CDF	38,936	688,139	204.38

[a]No nondetect values were reported for 2,3,7,8-TCDD, 2,3,7,8-TCDF, or any congener group in the three test runs.
[b]Source: U.S. EPA (1987a).
[c]Source: AGES (1992).
[d]Source: Sverdrup Corp. (1991).
[e]TEQ calculations assume nondetect values were zero.
[f]Estimated using the measured data for 2,3,7,8-TCDD, 2,3,7,8-TCDF, OCDD, and OCDF and congener group emissions (i.e., for the penta-, hexa-, and hepta-CDDs and CDFs, it was assumed that the measured emission factor within a congener group was the sum of equal emission factors for all congeners in that group, including non-2,3,7,8-substituted congeners).

NR = Not reported
ND = Not detected (value in parenthesis is the detection limit)

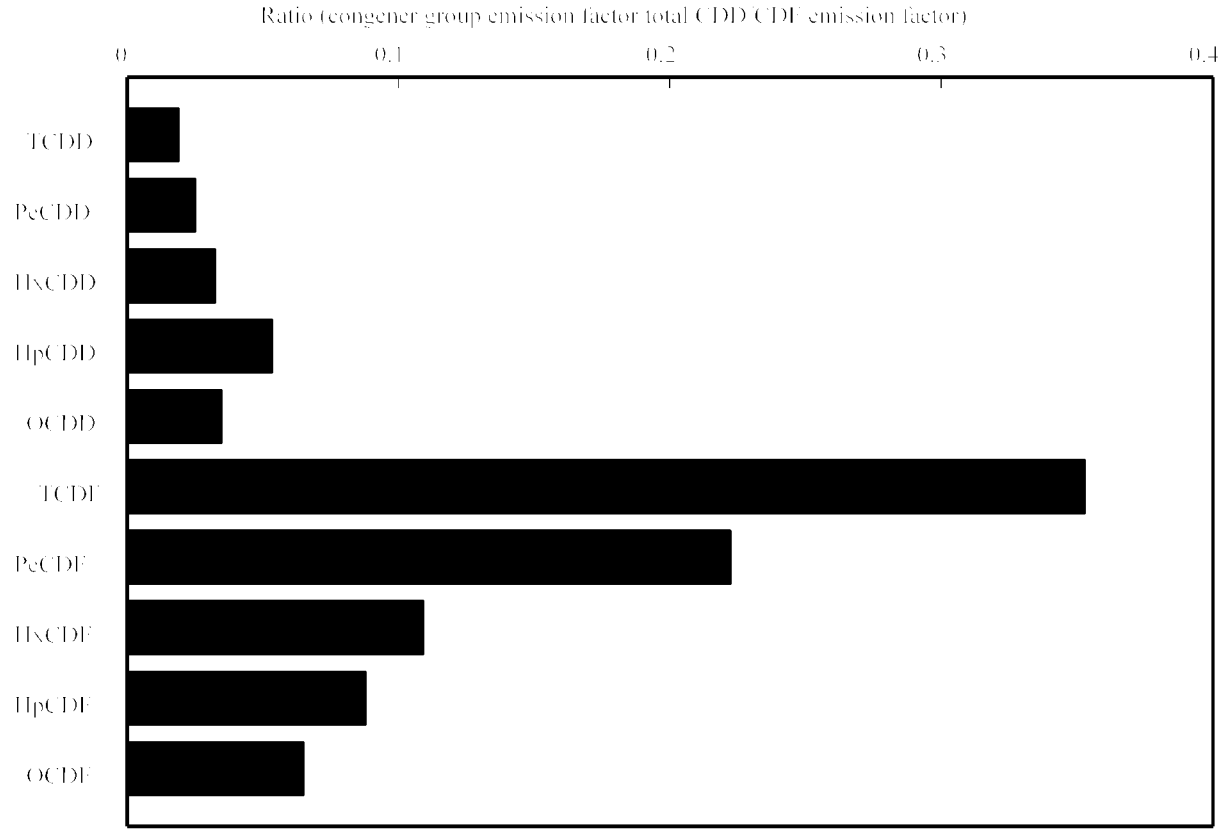


Figure 7-2a. Congener group profile for air emissions from a secondary copper smelter.

Source: U.S. EPA (1987d).

Only limited data on emissions from secondary copper smelters are reported in the European Dioxin Inventory (LUA, 1997). TEQ emission factors reported for German shaft furnaces/converters and reverberatory furnaces range from 5.6 to 110 ng I-TEQ_{DF}/kg and from 0.005 to 1.56 ng I-TEQ_{DF}/kg, respectively. Emission factors reported for two smelter and casting furnaces in Sweden in which relatively clean scrap is used as input are 0.024 and 0.04 ng I-TEQ_{DF}/kg. A smelter in Austria is reported to have a TEQ emission factor of 4 ng I-TEQ_{DF}/kg. The minimum, typical, and maximum default emission factors selected in LUA (1997) are 5, 50, and 400 ng I-TEQ_{DF}/kg, respectively.

In the 2002 Environment Canada report on CDD/CDF emissions from the base metals smelting sector (Charles E. Napier Company, Ltd., 2002), three secondary copper smelters were identified (see Table 7-2). CDD/CDF emission concentrations were reported as ranging from less than 100 to less than 500 pg I-TEQ/dscm.

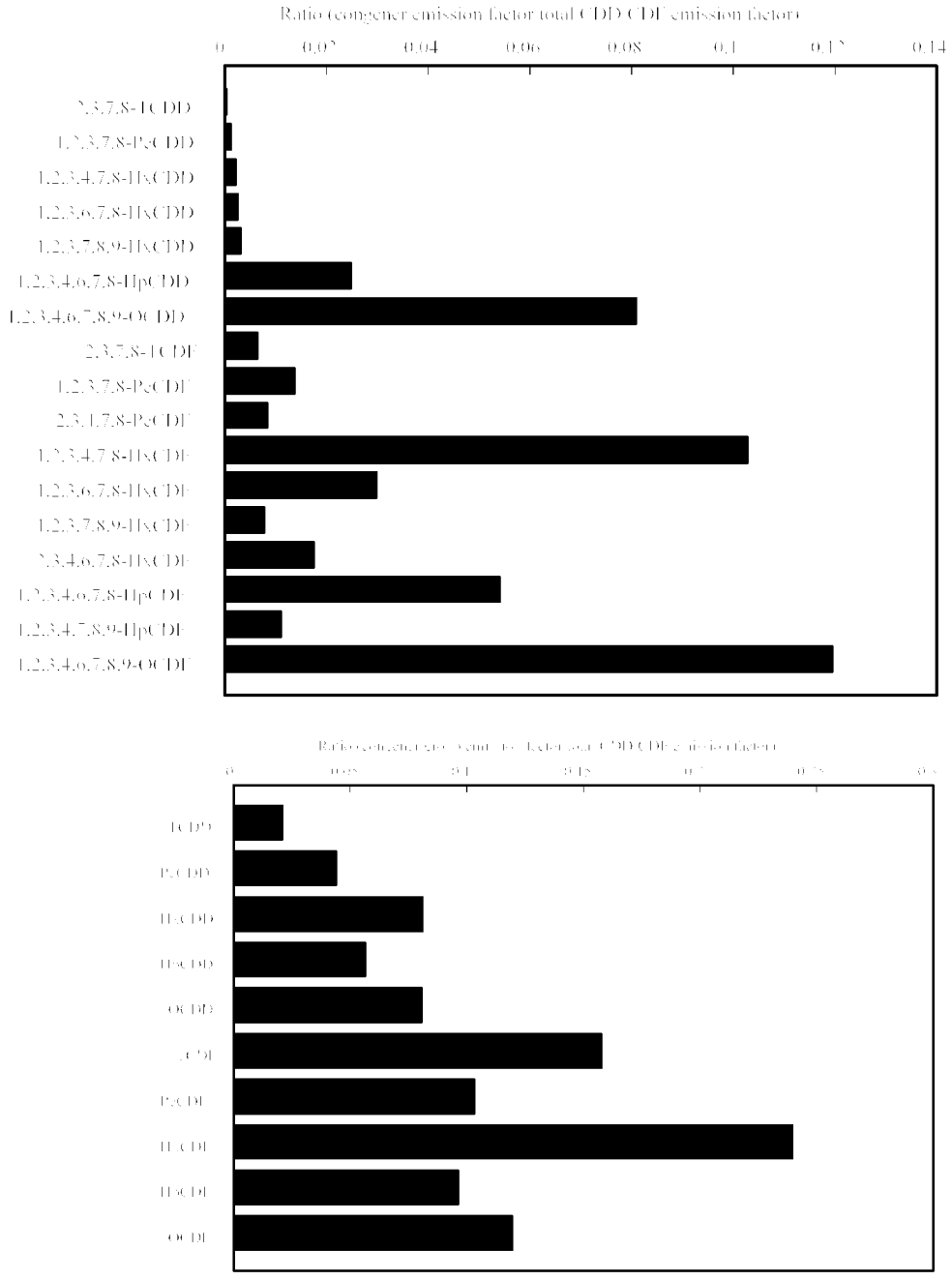


Figure 7-2b. Congener and congener group profiles for a closed secondary copper smelter.

Source: AGES (1992).

7.2.2.2. *Activity Level Information*

In 1987, four secondary copper smelters were in operation: Franklin Smelting and Refining Co. (Philadelphia, PA), Chemetco, Inc. (Alton, IL), Southwire Co. (Carrollton, GA), and a facility located in Gaston, SC, that was owned by American Telephone and Telegraph (AT&T) until 1990, when it was purchased by Southwire Co. In 1987, estimated smelter capacities were 13,600 metric tons for the Franklin facility, 120,000 metric tons for the Chemetco facility, 48,000 metric tons for the Southwire facility, and 85,000 metric tons for the AT&T facility (telephone conversation on August 17, 1999, between D. Edelstein, U.S. Geological Survey, and G. Schweer, Versar, Inc.). In 1995, only three of these four facilities were still in operation. The Southwire facility in Gaston was closed in January 1995. The Franklin facility ceased operations in August 1997. Estimated smelter capacities in 1995 were 16,000 metric tons for the Franklin facility, 135,000 metric tons for the Chemetco facility, and 92,000 metric tons for the Southwire Georgia facility (Edelstein, 1999). In May 2000, the Southwire Co. closed its Georgia facility and ceased operations (Edelstein, 2000). In November 2001, Chemetco closed its facility and ceased operations (Edelstein, 2001).

According to Edelstein (2001), smelters and refineries consumed 255,000 metric tons of purchased copper-based scrap in 2000 and 196,000 metric tons in 2001. Assuming Chemetco was the sole smelter facility operating in 2001, and that it operated for 10 of 12 months in 2001, its estimated annual consumption of copper-based scrap would be 235,000 metric tons per year. Assuming Chemetco's annual consumption rate did not change from 2000 to 2001, the estimated consumption of copper-based scrap for the Southwire Co. in 2000 was 20,000 metric tons.

7.2.2.3. *Emission Estimates*

Although little research has been done to define the CDD/CDF formation mechanisms in secondary copper smelting operations, two general observations have been made (Buekens et al., 1997). First, the presence of chlorinated plastics in copper scraps used as feed for smelters is believed to increase CDD/CDF formation. Second, the reducing or pyrolytic conditions in blast furnaces can lead to high CDD/CDF concentrations in the furnace process gases. As noted in Section 7.2.2.1, two of the U.S. facilities that have been tested (U.S. EPA, 1987a; AGES, 1992) had the following characteristics: both processed low-purity copper-bearing scrap containing significant quantities of plastics and telephone switch gears, and both used blast furnaces. The APCD equipment at both facilities consisted of an afterburner, a cooling tower (Franklin facility only), and an FF (U.S. EPA, 1994b). The other tested U.S. facility used oxidizing rather than reducing conditions and processed relatively high-purity scrap (Sverdrup Corp., 1991).

Annual TEQ emissions for 1987, 1995, and 2000 were derived as the sum of the TEQ emissions for each secondary copper facility in operation during the reference years. The following discussion summarizes the procedure used to estimate annual TEQ air emissions.

The Franklin Smelting facility operated in 1987 and 1995 but not in 2000. The TEQ emission factor measured at this facility in 1992 is assumed to be representative of the TEQ emission factors in 1987 and 1995. Combining this emission factor (16,618 ng I-TEQ_{DF}/kg [16,917 ng TEQ_{DF}-WHO_{98}/kg] of scrap feed) with the estimated smelter capacities (data are not available on the amount of scrap processed) for this facility in 1987 (13,600,000 kg) and 1995 (16,000,000 kg) yields TEQ emission estimates of 226 g I-TEQ_{DF} (230 g TEQ_{DF}-WHO_{98}) in 1987 and 266 g I-TEQ_{DF} (271 g TEQ_{DF}-WHO_{98}) in 1995. This facility ceased operations in 1997.

The Chemetco facility operated in 1987, 1995, and 2000. Similarly, for purposes of this report, the TEQ emission factor for the Chemetco facility is considered to be representative of the TEQ emission factor for this facility for 1987, 1995, and 2000. Combining this emission factor (3.60 ng I-TEQ_{DF}/kg [3.66 ng TEQ_{DF}-WHO_{98}/kg] of scrap feed) with the estimated smelter capacities of 120,000,000 kg in 1987 and 135,000,000 kg in 1995 yields TEQ estimates of 0.43 g I-TEQ_{DF} (0.44 g TEQ_{DF}-WHO_{98}) in 1987 and 0.49 g I-TEQ_{DF} (0.49 g TEQ_{DF}-WHO_{98}) in 1995. Combining the same emission factor with the scrap consumption for this facility in 2000 (235,000,000 kg) yields a TEQ estimate of 0.85 g I-TEQ_{DF} (0.86 g TEQ_{DF}-WHO_{98}) for 2000.

The facility in Gaston, SC, was in operation during 1987 but ceased operations in 1995. Prior to 1990, when this facility was owned by AT&T, the plant processed a great deal of high-plastics-content scrap (such as whole telephones). This scrap was fed to a pyrolysis unit prior to entering the blast furnace. In addition to a blast furnace, the facility also had an oxidizing reverberatory furnace for processing higher-purity scrap. The facility had separate FFs for the blast furnace, the converters, and the reverberatory furnace (U.S. EPA, 1994b). Because this facility processed low-purity, high-plastics-content scrap in 1987, and presumably processed much of this in the reducing atmosphere of a pyrolysis unit and blast furnace, the average of the TEQ emission factors for the Tier 4 EPA-tested facility (U.S. EPA, 1987a) and the Franklin facility (8,700 ng I-TEQ_{DF}/kg [8,860 ng TEQ_{DF}-WHO_{98}/kg]) was used to estimate potential emissions in 1987 of 740 g I-TEQ_{DF} (753 g TEQ_{DF}-WHO_{98}) (assuming an activity level of 85,000,000 kg). This activity level is the estimated capacity of the facility; data were not available on the amount of scrap processed.

The Southwire facility had both a blast furnace and a reverberatory furnace. In 1992, approximately 50% of incoming scrap was processed in each furnace (U.S. EPA, 1994b). Unlike the Franklin, Chemetco, and Gaston secondary copper smelters, the Southwire facility stopped processing plastic-coated scrap in the 1970s. In addition, this facility had a more complex APCD system, which may have reduced the formation and release of CDDs/CDFs. The blast furnace-

processed gases passed through an afterburner (871°C), U-tube coolers, and an evaporative spray system before entering the FF at a temperature of 107 to 191°C. For these reasons, EPA has determined that the existing emissions data for secondary smelters cannot reliably be used to generate a quantitative estimate of potential emissions during 1987, 1995, or 2000 for this facility.

Total secondary copper smelter emissions for 1987 are the sum of the Franklin smelting facility emissions (271 g TEQ_{DF}-WHO_{98} [266 g I-TEQ_{DF}]), the Chemetco smelter facility (0.44 g TEQ_{DF}-WHO_{98} [0.43 g I-TEQ_{DF}]) and the Gaston, SC, facility (753 g TEQ_{DF}-WHO_{98} [740 g I-TEQ_{DF}]). Total secondary copper smelter emissions for 1987 are 983.44 g TEQ_{DF}-WHO_{98} (966.43 g I-TEQ_{DF}).

Total secondary copper smelter emissions for 1995 are the sum of the Franklin smelting facility emissions (271 g TEQ_{DF}-WHO_{98} [266 g I-TEQ_{DF}]) and the Chemetco smelter facility (0.49 g TEQ_{DF}-WHO_{98} [0.49 g TEQ_{DF}-WHO_{98}]). Total secondary copper smelter emissions for 1995 are 271.49 g TEQ_{DF}-WHO_{98} (266.49 I-TEQ_{DF}).

The Chemetco smelter provides the TEQ emissions estimate for the year 2000. Total secondary copper smelter emissions for 2000 are 0.86 g TEQ_{DF}-WHO_{98} (0.85 g I-TEQ_{DF}).

A high confidence rating is assigned to the production and consumption estimates because they are based on government survey data. A low confidence rating is assigned to the TEQ emission estimates because they are based on limited measurements made at three smelters, one of which was not in operation in 1987 or 1995.

It should be noted that a significant amount of scrap copper is consumed by other segments of the copper industry. In 1995 and 2000, brass mills and wire-rod mills consumed 886,000 and 1,070,000 metric tons of copper-based scrap, respectively; foundries and iscellaneous manufacturers consumed 71,500 and 96,200 metric tons, respectively (USGS, 1997e; Edelstein, 2001). As noted above, however, these facilities generally do not conduct any significant purification of the scrap. Rather, the scrap consumed is already of alloy quality, and processes employed typically involve only melting, casting, and extruding. Thus, the potential for formation of CDDs/CDFs is expected to be much less than the potential during secondary smelting operations.

7.2.3. Secondary Lead Smelters

The secondary lead smelting industry produces elemental lead through the chemical reduction of lead compounds in a high-temperature furnace (1,200 to 1,260°C). Smelting is performed in reverberatory, blast, rotary, or electric furnaces. Blast and reverberatory furnaces are the most common types of smelting furnaces used by the 23 facilities that make up the current secondary lead smelting industry in the United States. Of the 45 furnaces at these 23

facilities, 15 are reverberatory furnaces, 24 are blast furnaces, 5 are rotary furnaces, and 1 is an electric furnace. The electric furnace and 11 of the 24 blast furnaces are co-located with reverberatory furnaces, and most share a common exhaust and emissions control system (U.S. EPA, 1994c).

Furnace charge materials consist of lead-bearing raw materials, lead-bearing slag and drosses, fluxing agents (blast and rotary furnaces only), and coke. Scrap motor vehicle lead-acid batteries represent about 90% of the lead-bearing raw materials at a typical lead smelter. Fluxing agents consist of iron, silica sand, and limestone or soda ash. Coke is used as fuel in blast furnaces and as a reducing agent in reverberatory and rotary furnaces. Organic emissions from co-located blast and reverberatory furnaces are more similar to the emissions of a reverberatory furnace than to those of a blast furnace (U.S. EPA, 1994c).

In 1987, the lead smelting industry consisted of 24 facilities producing 0.72 million metric tons of lead (U.S. EPA, 1994c). In 1995, there were 23 companies producing 0.97 million metric tons (USGS, 1997e), and in 2000 there were 27 secondary lead smelters in operation in the United States producing 1.02 million metric tons (USGS, 2002). In 1995, the total annual production capacity of the 23 companies that made up the U.S. lead smelting industry was 1.36 million metric tons. Blast furnaces not co-located with reverberatory furnaces accounted for 21% of capacity (0.28 million metric tons). Reverberatory furnaces and blast and electric furnaces co-located with reverberatory furnaces accounted for 74% of capacity (1.01 million metric tons). Rotary furnaces accounted for the remaining 5% of capacity (0.07 million metric tons) (U.S. EPA, 1994c).

Actual production volume statistics by furnace type were not available. However, if it is assumed that the total actual production volume of the industry reflects the production capacity breakdown by furnace type, then the estimated actual production volumes of blast furnaces (not co-located), reverberatory and co-located blast/electric and reverberatory furnaces, and rotary furnaces were 0.15, 0.53, and 0.04 million metric tons, respectively, in 1987; 0.2, 0.72, and 0.05 million metric tons, respectively, in 1995; and 0.29, 1, and 0.07 million metric tons, respectively, in 2000.

A report commissioned by Environment Canada (Charles E. Napier Company, Ltd., 2000) reviewed published literature and other information on the dioxin/furan formation mechanisms; dioxin/furan emissions; emission control technology, including cost; and dioxin/furan published emission standards pertinent to steel production processes of plants in Canada. The report included four facilities identified as primary lead smelters. CDD/CDF emission concentrations were reported to range from less than 100 to less than 1,000 pg I-TEQ/dscm.

CDD/CDF emission factors were estimated for secondary lead smelters using the results of emission tests performed by EPA at three smelters (a blast furnace [U.S. EPA, 1995d], a co-located blast/reverberatory furnace [U.S. EPA, 1992c], and a rotary kiln furnace [U.S. EPA, 1995e]). The air pollution control systems at the three tested facilities consisted of both FFs and scrubbers. Congener-specific measurements were made at both APCD exit points at each facility. Table 7-6 presents the congener and congener group emission factors for the FF and the scrubber for each site. Figure 7-3 presents the corresponding profiles for the FF emissions from the tested blast furnace and reverberatory furnace. For the facilities in operation in 1995, all 23 smelters employed FFs, with only 9 employing scrubber technology. Facilities with scrubbers accounted for 14% of the blast furnace (not co-located) production capacity, 52% of the reverberatory and co-located furnace production capacity, and 57% of the rotary furnace production capacity. TEQ emission factors (ng TEQ/kg lead produced when nondetect values are set equal to zero) from the reported data for each of the three furnace configurations, presented as a range reflecting the presence or absence of a scrubber, are

- Blast furnace: 0.64 to 8.81 ng TEQ_{DF}-WHO_{98}/kg (0.63 to 8.31 ng I-TEQ_{DF}/kg)
- Reverberatory/co-located furnace: 0.05 to 0.42 ng TEQ_{DF}-WHO_{98}/kg (0.05 to 0.41 ng I-TEQ_{DF}/kg)
- Rotary furnace: 0.24 to 0.66 ng TEQ_{DF}-WHO_{98}/kg (0.24 to 0.66 ng I-TEQ_{DF}/kg)

If these ranges of emission rates are assumed to be representative of those at nontested facilities with the same basic furnace configuration, with and without scrubbers, then combining these emission rates with the estimated production volumes derived above and the percentage of each configuration type that have scrubbers yields the estimated air emissions shown in Table 7-7 for reference years 1987, 1995, and 2000.

A medium confidence rating is assigned to the emission factors because stack test data were available for 3 of the 27 smelters operating in the United States (of which only 16 were in operation as of December 1993), and the stack test data used represent the three major furnace configurations. The activity level estimate has been assigned a medium confidence rating because, although it is based on a U.S. Department of Commerce estimate of total U.S. production, no production data were available on a furnace type or furnace configuration basis. Therefore, a medium confidence rating is assigned to the emission estimates.

Table 7-6. CDD/CDF emission factors (ng/kg lead produced) for secondary lead smelters[a]

Congener/congener group	Blast furnace[b]		Blast/reverberatory furnace[c]		Rotary kiln[d]	
	Before scrubber/ FF	After scrubber/ FF	Before scrubber/ FF	After scrubber/ FF	Before scrubber/ FF	After scrubber/ FF
2,3,7,8-TCDD	2.11	0.25	0	0	0.1	0.24
1,2,3,7,8-PeCDD	0.99	0.03	0	0	0.01	0
1,2,3,4,7,8-HxCDD	0.43	0	0	0	0	0
1,2,3,6,7,8-HxCDD	0.99	0.03	0	0	0	0
1,2,3,7,8,9-HxCDD	1.55	0.03	0	0	0	0
1,2,3,4,6,7,8-HpCDD	2.06	0.08	0.1	0.06	0	0.22
OCDD	1.4	0.39	0.57	0.55	0.24	2.41
2,3,7,8-TCDF	8.73	0.93	1.46	0.49	0.40	1.2
1,2,3,7,8-PeCDF	3.88	0.43	0.24	0.02	0.14	0.4
2,3,4,7,8-PeCDF	6.65	0.36	0.31	0	0.14	0.46
1,2,3,4,7,8-HxCDF	5.83	0.37	0.63	0	0.11	0.27
1,2,3,6,7,8-HxCDF	1.67	0.11	0.19	0	0.02	0.1
1,2,3,7,8,9-HxCDF	0.11	0	0	0	0.04	0.13
2,3,4,6,7,8-HxCDF	2.06	0.11	0.15	0	0	0
1,2,3,4,6,7,8-HpCDF	2.34	0.19	0.48	0	0.03	0.13
1,2,3,4,7,8,9-HpCDF	0.63	0.06	0	0	0	0
OCDF	1.39	0.18	0.29	0	0	0
Total 2,3,7,8-CDD	9.53	0.81	0.67	0.61	0.35	2.87
Total 2,3,7,8-CDF	33.29	2.74	3.75	0.51	0.88	2.69
Total I-TEQ_{DF} (nondetect set to zero)	8.31	0.63	0.42	0.05	0.24	0.67
Total TEQ_{DF}-WHO_{98} (nondetect set to zero)	8.81	0.64	0.42	0.05	0.24	0.66
Total TCDD	74.33	7.39	0.97	1.58	3.4	7.9
Total PeCDD	39.29	1.73	0.15	0.16	0.29	0.27
Total HxCDD	20.05	0.81	0.14	0.02	0.1	0.23
Total HpCDD	4.2	9.72	0.09	0.09	0.01	0.29
Total OCDD	1.39	0.18	0.57	0.55	0.24	2.41
Total TCDF	145.71	17.34	8.21	4.71	10.82	28.57
Total PeCDF	69.59	3.45	3.07	0.36	1.69	5.04
Total HxCDF	19.73	1.02	1.14	0.19	0.15	0.73
Total HpCDF	4.74	0.11	0.72	0.01	0.05	0.14
Total OCDF	1.39	0.18	0.29	0.00	0	0
Total CDD/CDF (nondetect set to zero)	380.42	41.93	15.35	7.67	16.75	45.58

[a]Except where noted, emission factors were calculated assuming nondetect values were zero.
[b]Source: U.S. EPA (1995d).
[c]Source: U.S. EPA (1992c).
[d]Source: U.S. EPA (1995e).

FF = Fabric filter

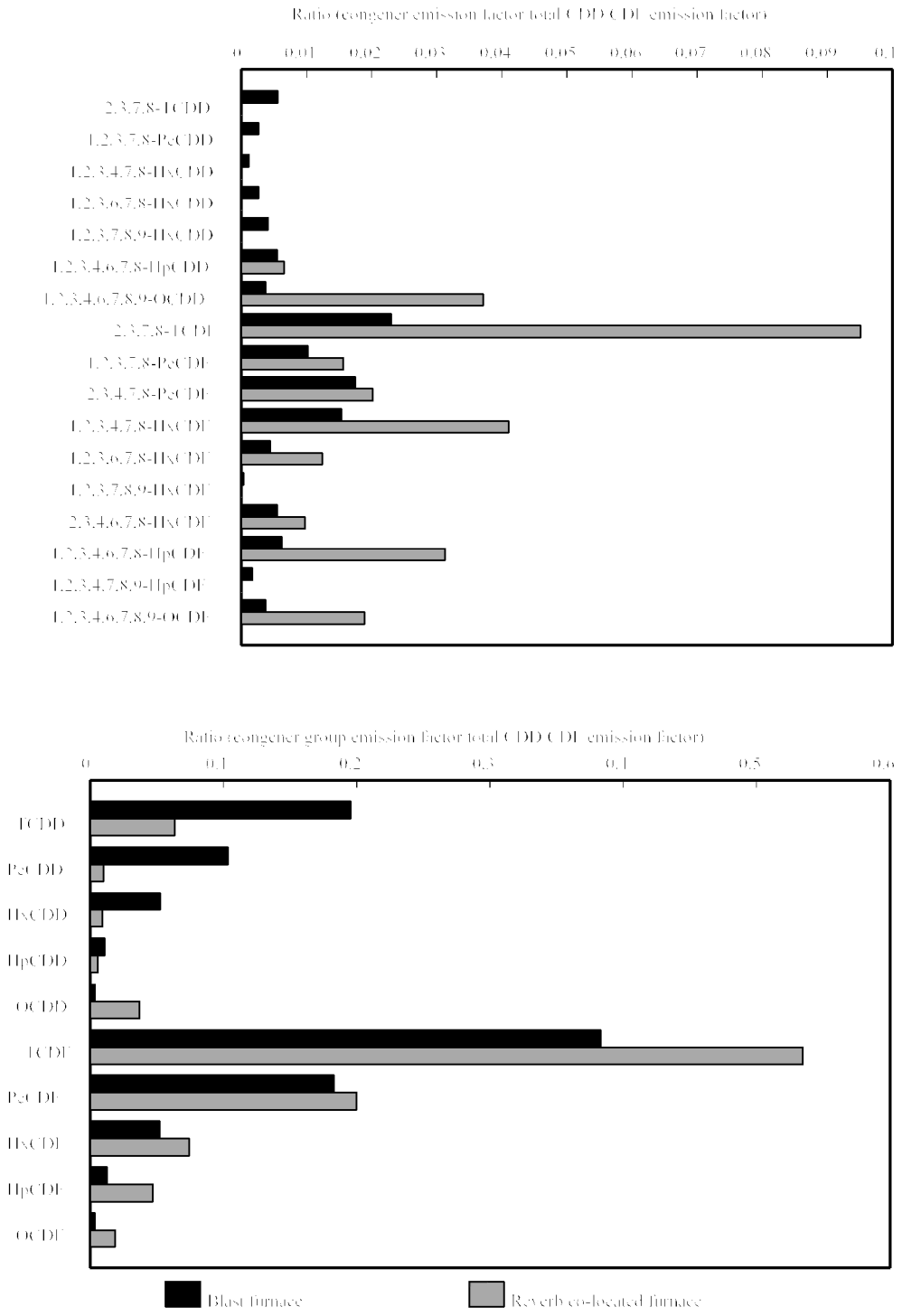


Figure 7-3. Congener and congener group profiles for air emissions from secondary lead smelters. Profiles are for emissions from fabric filters; nondetect values set equal to zero.

Sources: U.S. EPA (1992c, 1995d, e).

Table 7-7. Estimated annual TEQ emissions (g TEQ)[a]

Configuration	Ref. year 1987		Ref. year 1995		Ref. year 2000	
	TEQ_{DF}-WHO_{98}	I-TEQ_{DF}	TEQ_{DF}-WHO_{98}	I-TEQ_{DF}	TEQ_{DF}-WHO_{98}	I-TEQ_{DF}
Blast furnaces w/scrubbers	0.013	0.013	0.018	0.018	0.026	0.026
Blast furnaces w/o scrubbers	1.136	1.072	1.515	1.429	2.197	2.073
Reverberatory furnaces w/scrubbers	0.014	0.014	0.019	0.019	0.026	0.026
Reverberatory furnaces w/o scrubbers	0.106	0.104	0.145	0.142	0.202	0.197
Rotary furnaces w/scrubbers	0.015	0.015	0.019	0.019	0.026	0.026
Rotary furnaces w/o scrubbers	0.004	0.004	0.005	0.005	0.007	0.007
TOTAL	1.288	1.222	1.721	1.632	2.484	2.355

[a]Calculated using emission factors based on nondetect values set equal to zero.

7.3. PRIMARY FERROUS METAL SMELTING/REFINING

Iron is manufactured from its ores (magnetic pyrites, magnetite, hematite, and carbonates of iron) in a blast furnace, and the iron obtained from this process is further refined in steel plants to make steel. The primary production of iron and steel involves two operations identified by European researchers as potential emission sources of CDDs/CDFs: iron ore sinter production and coke production. Each of these potential sources is discussed in the following subsections.

7.3.1. Sinter Production

At some iron manufacturing facilities, iron ores and waste iron-bearing materials undergo sintering to convert the materials to usable feed for the blast furnace. In the sintering process, iron ore fines and waste materials are mixed with coke fines, and the mixture is placed on a grate that is then heated to a temperature of 1,000 to 1,400°C. The heat generated during combustion sinters the small particles. Iron-bearing dusts and slags from processes in the steel plant are the types of iron-bearing waste materials used as a feed mix for the sintering plant (Knepper, 1981; Capes, 1983; U.S. EPA, 1995b).

Several European investigators have reported that iron ore sintering plants are major sources of airborne emissions of CDDs/CDFs (Rappe, 1992a; Lexen et al., 1993; Lahl, 1993, 1994). Lahl reported that the practice of recycling dusts and scraps from other processes in the steel plant for use in the sintering plant introduces traces of chlorine and organic compounds that generate the CDDs/CDFs found in these plants.

Organic compounds that are potential precursors to CDD/CDF formation come primarily from oil, which is found in mill scale, as well as from some blast furnace sludges that are used as part of the sinter feed mixture. Most U.S. plants limit the amount of oil because it increases emissions of volatile organic compounds and may create a fire hazard. In addition, plants with FFs must limit the oil content because the oil tends to blind the FFs. Typical oil content of the feed at U.S. sintering plants ranges from 0.1 to 0.75% (Calcagni et al., 1998).

Sintering plants in Sweden have been reported to emit up to 3 ng I-TEQ_{DF}/Nm^3 stack gas, or 2 to 4 g I-TEQ_{DF}/yr (Rappe, 1992a; Lexen et al., 1993). Bremmer et al. (1994) reported the results of stack testing at three iron ore sintering plants in the Netherlands. One facility equipped with wet scrubbers (WSs) had an emission factor of 1.8 ng I-TEQ_{DF}/dscm (at 11% oxygen). The other two facilities, both equipped with cyclones, had emission factors of 6.3 and 9.6 ng I-TEQ_{DF}/dscm (at 7% oxygen). Lahl (1993, 1994) reported stack emissions for sintering plants in Germany (after passage through mechanical filters and ESPs) ranging from 3 to 10 ng I-TEQ_{DF}/Nm^3. A compilation of emission measurements by the German Federal Environmental Agency indicated stack emission concentrations ranging from 1.2 to 60.6 ng I-TEQ_{DF}/m^3 (at 7% oxygen); the majority of emissions in 1996 were around 3 ng I-TEQ_{DF}/m^3 (Umweltbundesamt, 1996).

The report commissioned by Environment Canada in 2000 to review steel production processes in Canadian plants (Charles E. Napier Company, Ltd., 2000) included information on emissions from iron sintering. For iron sintering, the CDD/CDF emissions from one facility, the Stelco Hilton Works sintering plant, were assumed to be representative of the 1998 sinter production. The average emission rate was 19.9 ng I-TEQ/day. Applying a production rate of 1,143 metric tons/day yields a mass emission factor of 17.4 ng I-TEQ/kg of sinter.

EPA conducted tests at two of the nine U.S. sintering plants operating in 1997 in order to quantify emissions of CDDs/CDFs (Calcagni et al., 1998). In choosing representative plants for testing, EPA considered a variety of issues, including the types and quantities of feed materials, the types of emission controls, and the oil content of the sinter feed. EPA decided to test a plant with an FF and a plant with a venturi (or wet) scrubber. FFs and WSs are the principal APCDs used to control emissions from the sintering plant windbox. Four plants used an FF and five plants used a WS. The types of feed materials and oil content at the two selected plants were

determined to be representative of other plants in the industry. Sampling was performed over 3 days (4 hr/day) at each plant.

The average CDD/CDF TEQ concentrations measured in the stack emissions were 0.19 ng I-TEQ_{DF}/Nm^3 and 0.81 ng I-TEQ_{DF}/Nm^3 for the WS and the FF, respectively. The corresponding TEQ emission factors are 0.62 ng TEQ_{DF}-WHO_{98}/kg (0.55 ng I-TEQ_{DF}/kg) sinter and 4.61 ng TEQ_{DF}-WHO_{98}/kg (4.14 ng I-TEQ_{DF}/kg) sinter, respectively, for WSs and FFs. These emission factors are assigned a high rating because they are based on EPA testing at two facilities considered by EPA to be representative of both current and 1995 standard industry practices.

Congener-specific emission factors for these two facilities are presented in Table 7-8. Figure 7-4 presents the congener profiles for these facilities. Although concentrations were higher from the FF than from the WS, both concentrations were low relative to what had been reported from testing at German, Dutch, Swedish, and Canadian sintering plants. This disparity may be due to differences in the operation or APCDs of U.S. sintering plants and the tested European plants.

Most of the U.S. integrated iron and steel plants, including those with sintering plants, have eliminated the purchase and use of chlorinated organics in their facilities, and their rolling mill oils (lubricants and hydraulic fluids) do not contain chlorinated compounds. In addition, routine analyses of waste materials going to the sintering plant have not detected any chlorinated solvents.

Finally, none of the U.S. plants use an ESP to control emissions from the sinter windbox (Calcagni et al., 1998).

In 1996 (data were not readily available for 1995), 11 sintering plants were operating in the United States, with a total annual production capacity of about 17.6 million metric tons (Metal Producing, 1996). Since the 1980s, the size of this industry has decreased dramatically. In 1982, 33 facilities were in operation, with a combined total capacity of 48.3 million metric tons (U.S. EPA, 1982a). The nine U.S. sintering plants operating in 1995 had a combined capacity of 15.6 million metric tons (Calcagni et al., 1998). In 1987, sinter consumption by iron and steel plants was 14.5 million metric tons (AISI, 1990); in 1995, consumption was 12.4 million metric tons (Fenton, 1996), or approximately 70% of production capacity, assuming that production capacity in 1995 was the same as in 1996. These activity level estimates are assigned a confidence rating of medium.

Based on the production capabilities shown in Table 7-9, 59% of 1998 sinter production capacity was at facilities with WSs and 41% was at facilities with FFs. If it is assumed that these proportions of APCD-to-production capacity existed in 1995 and that actual production in 1995 was equal to sinter consumption at iron and steel plants (12.4 million metric tons), then estimated

Table 7-8. CDD/CDF emission factors (ng/kg sinter) for sintering plants

Congener/congener group	Wet scrubber		Fabric filter	
	Nondetect set to zero	Nondetect set to ½ detection limit	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	0.049	0.049	0.406	0.406
1,2,3,7,8-PeCDD	0.138	0.138	0.937	0.937
1,2,3,4,7,8-HxCDD	0.03	0.03	0.135	0.135
1,2,3,6,7,8-HxCDD	0.612	0.612	1.469	1.469
1,2,3,7,8,9-HxCDD	0.288	0.288	0.609	0.609
1,2,3,4,6,7,8-HpCDD	0.696	0.696	0.698	0.698
OCDD	0.496	0.496	0.695	0.695
2,3,7,8-TCDF	0.602	0.602	10.232	10.232
1,2,3,7,8-PeCDF	0.343	0.343	3.518	3.518
2,3,4,7,8-PeCDF	0.349	0.349	3.228	3.228
1,2,3,4,7,8-HxCDF	0.421	0.421	1.382	1.382
1,2,3,6,7,8-HxCDF	0.164	0.164	0.495	0.495
1,2,3,7,8,9-HxCDF	0.011	0.014	0.029	0.057
2,3,4,6,7,8-HxCDF	0.142	0.142	0.285	0.285
1,2,3,4,6,7,8-HpCDF	0.247	0.247	0.316	0.316
1,2,3,4,7,8,9-HpCDF	0.036	0.036	0	0.115
OCDF	0.103	0.103	0.05	0.192
Total 2,3,7,8-CDD	2.309	2.309	4.949	4.949
Total 2,3,7,8-CDF	2.418	2.421	19.820	19.82
Total I-TEQ_{DF}	0.55	0.55	4.14	4.14
Total TEQ_{DF}-WHO_{98}	0.62	0.62	4.61	4.61
Total TCDD	NR	NR	NR	NR
Total PeCDD	NR	NR	NR	NR
Total HxCDD	NR	NR	NR	NR
Total HpCDD	NR	NR	NR	NR
Total OCDD	0.496	0.496	0.695	0.695
Total TCDF	NR	NR	NR	NR
Total PeCDF	NR	NR	NR	NR
Total HxCDF	NR	NR	NR	NR
Total HpCDF	NR	NR	NR	NR
Total OCDF	0.103	0.103	0.050	0.192
Total 2,3,7,8 CDD/CDF[a]	4.73	4.73	24.77	24.77

[a]The listed values for total CDD/CDF include only the 17 toxic congeners.

Source: Calcagni et al. (1998).

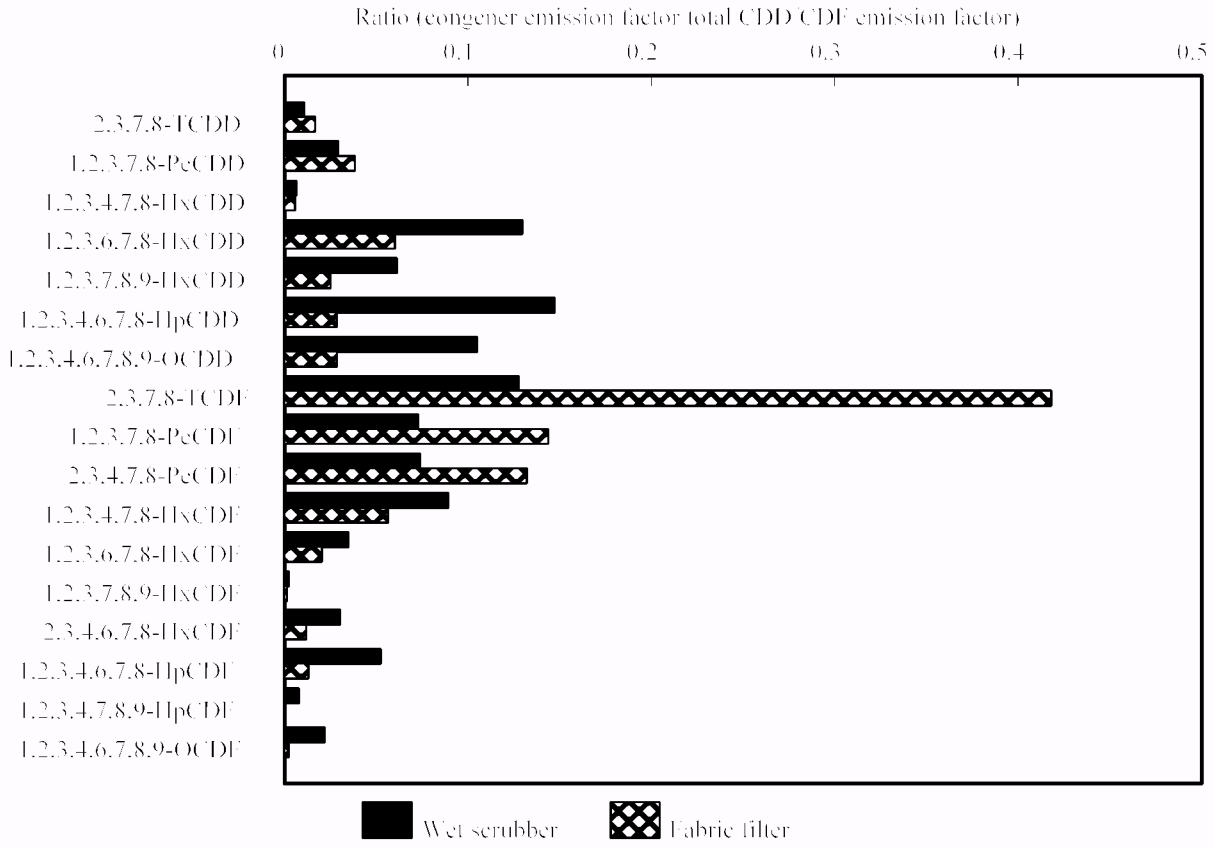


Figure 7-4. Congener profiles for air emissions from U.S. iron ore sintering plants.

Source: Calcagni et al. (1998).

TEQ emissions from WS-equipped facilities were 4.5 g TEQ_{DF}-WHO_{98} (4 g I-TEQ_{DF}) and emissions from FF-equipped facilities were 23.4 g TEQ_{DF}-WHO_{98} (21 g I-TEQ_{DF}), for a total of 27.9 g TEQ_{DF}-WHO_{98} (25.1 g I-TEQ_{DF}). These emission estimates are assigned an overall medium confidence rating on the basis of the medium rating for the activity level estimates.

If these same assumptions are applied to the 1987 sinter consumption rate of 14.5 million metric tons, then estimated TEQ emissions from WS-equipped facilities were 5.3 g TEQ_{DF}-WHO_{98} (4.7 g I-TEQ_{DF}) and emissions from FF-equipped facilities were 27.4 g TEQ_{DF}-WHO_{98} (24.6 g I-TEQ_{DF}), for a total of 32.7 g TEQ_{DF}-WHO_{98} (29.3 g I-TEQ_{DF}). These emission estimates are less certain than the estimates for 1995 because of uncertainties concerning actual APCDs in place in 1987 and the content of waste feed (i.e., oil content and presence of

Table 7-9. Operating parameters for U.S. iron ore sintering plants

Company	Location	1998 capacity (1,000 metric tons/yr)	Current air pollution control device
AK Steel	Middletown, OH	907	Wet scrubber
AK Steel[a]	Ashland, KY	816[a]	NA
Bethlehem Steel	Burns Harbor, IN	2,676	Wet scrubber
Bethlehem Steel	Sparrows Point, MD	3,856	Wet scrubber
Geneva Steel	Provo, UT	816	Fabric filter
Inland Steel	East Chicago, IN	1,089	Fabric filter
LTV Steel	East Chicago, IN	1,270	Wet scrubber
U.S. Steel	Gary, IN	3,992	Fabric filter
Weirton Steel[a]	Weirton, WV	1,179[a]	NA
Wheeling-Pittsburgh Steel	East Steubenville, WV	519	Wet scrubber
WCI Steel	Warren, OH	477	Fabric filter
TOTAL		17,597[b]	

[a]Not in operation during 1998 (Calcagni et al., 1998).
[b]When the Ashland, KY, and Weirton, WV, facilities are excluded, total 1998 capacity was 15,600,000 metric tons.

NA = Not available

Sources: Metal Producing (1991, 1996); Calcagni et al. (1998).

chlorinated organics in the oil) at that time. Consequently, a low confidence rating is assigned to the emission factor and the emissions estimate.

In 2000, a total of 10,600 million metric tons of sinter were consumed in blast furnaces (Fenton, 2001). This activity level has a high confidence rating because it is based on a comprehensive survey. Assuming the same proportions for facilities with WSs and facilities with FFs as in 1995 and 1987, then estimated TEQ emissions from WS-equipped facilities were 3.9 g TEQ_{DF}-WHO_{98} (3.4 g I-TEQ_{DF}) and emissions from FF-equipped facilities were 23.7 g TEQ_{DF}-WHO_{98} (21.3 g I-TEQ_{DF}), for a total of 27.6 TEQ_{DF}-WHO_{98} (24.4 g I-TEQ_{DF}) for 2000. This emissions estimate is assigned a high confidence rating on the basis of the high ratings given to the activity level and emission factor for reference year 2000.

7.3.2. Coke Production

Coke is the principal fuel used in the manufacture of iron and steel. It is the solid carbonaceous material produced by the destructive distillation of coal in high-temperature ovens.

No testing of CDD/CDF emissions from U.S. coke facilities has been reported. However, at a facility in the Netherlands, Bremmer et al. (1994) measured a CDD/CDF emission rate to air during the water quenching of hot coke of 0.23 ng I-TEQ_{DF}/kg of coal consumed. Bremmer et al. estimated minimal CDD/CDF air emissions (0.002 ng I-TEQ_{DF}/kg of coal) for flue gases generated during the charging and emptying of the coke ovens.

The report commissioned by Environment Canada in 2000 to review steel production processes in Canadian plants (Charles E. Napier Company, Ltd., 2000) also provided information on emissions from coke ovens. Mean emission factors (ng I-TEQ/kg) of the four Canadian coke oven facilities (as indicated in Table 7-10) were 0.3 ng I-TEQ/kg coke produced.

Although there are no testing data on which to base an estimate of CDD/CDF emissions in the United States, a preliminary estimate of potential TEQ annual emissions from U.S. coke plants can be made by combining the estimated consumption values of 33.5 million metric tons in 1987, 29.9 million metric tons in 1995, and 26.2 million metric tons in 2000 (EIA, 2002) with the emission factor reported by Bremmer et al. (1994) for a Dutch coke plant (0.23 ng I-TEQ_{DF}/kg of coal consumed). These calculations yield annual emissions of 7.7, 6.9, and 6.03 g I-TEQ_{DF} for 1987, 1995, and 2000, respectively. These estimates should be regarded as preliminary indications of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

7.4. SECONDARY FERROUS METAL SMELTING/REFINING

Electric arc furnaces in Europe have been reported to be sources of CDD/CDF emissions; no testing has been reported at U.S. facilities. Electric arc furnaces are used to produce carbon and steel alloys, primarily from scrap material, using a batch process. The input material is typically 100% scrap. Scrap, alloying agents, and fluxing materials are loaded into the cylindrical, refractory-lined furnace, and then carbon electrodes are lowered into the mix. The current of the opposite-polarity electrodes generates heat through the scrap. Processing time of a batch ranges from about 1.5 to 5 hr to produce carbon steel and from 5 to 10 hr to produce alloy steel (U.S. EPA, 1995b).

The melting of scrap ferrous material contaminated with metalworking fluids and plastics that contain chlorine provides the conditions conducive to formation of CDDs/CDFs. Tysklind et al. (1989) studied the formation and release of CDDs/CDFs at a pilot 10-ton electric furnace in Sweden. Scrap ferrous metal feedstocks containing varying amounts of chlorinated compounds (PVC plastics, cutting oils, or calcium chloride) were charged into the furnace under different operating conditions (continuous feed, batch feed into the open furnace, or batch feed through the furnace lid). During continuous charging operations, the highest emissions, 1.5 ng Nordic

Table 7-10. CDD/CDF emission estimates for Canadian coke oven facilities, blast furnace facilities, and electric arc furnaces

Company/facility	Location	Plant capacity (1,000 net tonnes/yr)	Estimated production (1,000 net tonnes)	Estimated CDD/CDF emissions (g I-TEQ)	Estimated CDD/CDF emission factor (ng I-TEQ/kg)
Coke oven facilities					
Algoma Steel Inc.	Sault Ste. Marie, Ontario	1,021	979	0.29	0.296
Dofasco Inc.	Hamilton, Ontario	1,656	1,588	0.48	0.302
Stelco Inc., Lake Erie Steel	Nanticoke, Ontario	563	540	0.16	0.296
Stelco Inc., Hilton Works	Hamilton, Ontario	1,035	993	0.30	0.302
TOTAL		4,275	4,100	1.23	
Blast furnace facilities					
Algoma Steel Inc.	Sault Ste. Marie, Ontario	2,270	2,177	<0.01	NA
Dofasco Inc.	Hamilton, Ontario	2,725	2,613	<0.01	NA
Stelco Inc., Lake Erie Steel	Nanticoke, Ontario	1,680	1,611	<0.01	NA
Stelco Inc., Hilton Works	Hamilton, Ontario	2,720	2,608	<0.01	NA
TOTAL		9,395	9,009	<0.01	
Electric arc furnaces					
AltaSteel Ltd.	Edmonton, Alberta	295	256	0.67	2.62
Atlas Specialty Steels	Welland, Ontario	218	189	0.49	2.59
Atlas Stainless Steels	Tracy, Quebec	118	103	0.27	2.62
Co-Steel Lasco	Whitby, Ontario	907	788	0.79	1.00
Dofasco Inc.	Hamilton, Ontario	1,225	1,065	0.50	0.469
Gerdau MRM Steel Inc.	Cambridge, Ontario	290	252	0.66	2.62
Gerdan MRM Steel Inc.	Selkirk, Manitoba	281	244	0.63	2.58
IPSCO Inc.	Regina, Saskatchewan	907	788	1.13	1.43
Ispat Sidbec Inc.	Contrecoeur, Quebec	1,633	1,419	3.69	2.60
Ivanco Rolling Mills Inc.	L'Original, Ontario	408	355	0.92	2.59
Slater Steels, Hamilton Specialty Bar Div.	Hamilton, Ontario	363	315	0.82	2.60
Stelco-McMaster Ltèe	Contrecoeur, Quebec	499	434	1.13	2.60
Sydney Corp.	Sydney, Nova Scotia	454	395	0.40	1.01
TOTAL		7,598	6,603	12.10	

NA = Not available

Source: Charles E. Napier Company, Ltd. (2000).

TEQ/dry Nm^3 (after an FF), were observed with a feedstock consisting of scrap metal with PVC plastics (1.3 g chlorine/kg feedstock). This emission rate equates to 7.7 ng Nordic TEQ/kg of feedstock.

The highest emissions during batch charging also occurred when the scrap metal with PVC plastic was combusted (0.3 ng Nordic TEQ/dry Nm^3 [1.7 ng Nordic TEQ/kg] feedstock). Much lower emissions (0.1 ng Nordic TEQ/dry Nm^3 [0.6 ng Nordic TEQ/kg] feedstock) were observed when scrap metal with cutting oils that contained chlorinated additives (0.4 g chlorine/kg feedstock) was melted. Although these cutting oil-related emissions were not significantly different from the emissions observed from the melting of no-chlorine scrap metal, relatively high levels of CDDs/CDFs (110 ng Nordic TEQ/dry Nm^3) were detected in flue gases prior to the FF.

The congener profiles of raw flue gas samples (prior to the APCD) showed that CDFs rather than CDDs were predominant in all three feedstock types. The congener profile from the test burn with PVC-containing feedstock showed a higher chlorinated congener content than was observed with the other feedstocks.

Eduljee and Dyke (1996) used a range of 0.7 to 10 ng I-TEQ_{DF}/kg of scrap feed to estimate national emissions for the United Kingdom. This range was assumed to be representative of no-chlorine and high-chlorine operations. However, the study authors provided little information on the supporting emission test studies (i.e., tested facility operational materials, feed rates, congener-specific emission rates).

Umweltbundesamt (1996) reported stack testing results for a variety of electric arc furnaces in Germany. Sufficient data were provided in the report to enable calculation of TEQ emission factors for six of the tested facilities. Two facilities had emission factors exceeding 1 ng I-TEQ_{DF}/kg of scrap processed, and two facilities had emission factors of less than 0.1 ng I-TEQ_{DF}/kg of scrap. The mean emission factor was 1.15 ng I-TEQ_{DF}/kg of scrap. The TEQ concentrations in the stack gases at these facilities (corrected to 7% oxygen) ranged from less than 0.1 to 1.3 ng I-TEQ_{DF}/m^3.

The report commissioned by Environment Canada in 2000 to review steel production processes at Canadian plants (Charles E. Napier Company, Ltd., 2000) included information on emissions from iron sintering and provided information on emissions from electric arc furnaces, which were estimated on the basis of plant capacity and estimated production. Mean emission factors (ng I-TEQ/kg) of the 13 Canadian electric arc furnace facilities (as indicated in Table 7-10) were 2.1 ng I-TEQ_{DF}/kg steel produced.

In March 2000, Environment Canada reported on source testing to determine CDD/CDF emissions from a facility in Ontario (Cianciarelli, 2000). Sampling was conducted on the exhaust stack of the electric arc furnace of Dofasco Inc., and both concentrations and emission

rates were provided (see Table 7-11). Total CDD/CDF concentrations were reported to be 51.15 pg TEQ/m^3, and the total emission rate was reported to be 0.47 ng TEQ/kg steel produced. In August 2000, the Emissions Research and Measurement Division of Environment Canada conducted source testing to determine CDDs/CDFs from the electric arc furnace of another facility, Gerdau Courtice Steel Inc. (Cianciarelli, 2001). These results (presented in Table 7-11) are being used to support the Canadian dioxin/furan inventory for electric arc furnaces. The total CDD/CDF concentrations were reported to be 125.5 pg TEQ/m^3, and the total emission rate was reported to be 1.1 ng TEQ/kg steel produced.

In 1987, electric arc furnaces accounted for 38.1% of U.S. steel production, or 30.8 billion kg of raw steel produced (Peters, 1988). In 1995, electric arc furnaces accounted for 40.4% of U.S. steel production, or 38.4 of the total 95.2 million metric tons of raw steel produced (Fenton, 1996). In 2000, electric arc furnaces accounted for 46.2% of U.S. steel production, or 49 of the 106 million metric tons of raw steel produced (USGS, 2002).

No testing of CDD/CDF emissions from U.S. electric arc furnaces on which to base an estimate of national emissions has been reported. A preliminary estimate of potential TEQ annual emissions from U.S. electric arc furnaces can be made by combining the production estimate of steel and an average emission factor of 1.21 ng I-TEQ_{DF}/kg steel derived from the data reported in Umweltbundesamt (1996) and the three Environment Canada reports (Charles E. Napier Company, Ltd., 2000; Cianciarelli, 2000, 2001). This calculation yields an annual emissions estimate of 37.3 g I-TEQ_{DF} in 1987, 46.5 g I-TEQ_{DF} in 1995, and 59.3 g I-TEQ_{DF} in 2000. These estimates should be regarded as preliminary indications of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

7.5. FERROUS FOUNDRIES

Ferrous foundries produce high-strength iron and steel castings used in industrial machinery, pipes, and heavy transportation equipment. Iron and steel castings are solid solutions of iron, carbon, and various alloying materials. Castings are produced by injecting or pouring molten metal into cavities of a mold made of sand, metal, or ceramic material. Metallic raw materials are pig iron, iron and steel scrap, foundry returns, and metal turnings (U.S. EPA, 1995b, 1997a).

The melting process takes place primarily in cupola (or blast) furnaces and to a lesser extent in electric arc furnaces. About 70% of all iron castings are produced using cupolas, although steel foundries rely almost exclusively on electric arc furnaces or induction furnaces for melting. The cupola is typically a vertical, cylindrical steel shell with either a refractory-lined or a water-cooled inner wall. Charges are loaded at the top of the unit; the iron is melted as it flows

Table 7-11. CDD/CDF emission concentrations and rates for Canadian electric arc furnaces

Congener	Mean facility concentration (pg TEQ/m^3)				Mean facility emission rate (ng TEQ/tonne steel)			
	Run 1	Run 2	Run 3	Avg.	Run 1	Run 2	Run 3	Avg.
Dofasco Inc.								
2,3,7,8-TCDD	0	1.99	0	0.66	0	17.2	0	5.7
1,2,3,7,8-PeCDD	1.96	4.09	6.44	4.16	20.5	35.3	60.5	38.8
1,2,3,4,7,8-HxCDD	0	0	0	0	0	0	0	0
1,2,3,6,7,8-HxCDD	0	0.33	1.13	0.49	0	2.8	10.6	4.5
1,2,3,7,8,9-HxCDD	0.25	0	0.63	0.29	2.7	0	5.9	2.9
1,2,3,4,6,7,8-HpCDD	0.11	0	0.05	0.05	1.2	0	0.5	0.6
OCDD	0.04	0.01	0	0.02	0.4	0	0	0.1
2,3,7,8-TCDF	9.96	37.11	29.45	25.51	104.2	320.9	276.5	233.9
1,2,3,7,8-PeCDF	0.48	1.23	1.60	1.1	5	10.6	15	10.2
2,3,4,7,8-PeCDF	5.88	14.9	22.98	14.59	61.6	128.8	215.7	135.4
1,2,3,4,7,8-HxCDF	1.12	2.23	3.86	2.4	11.7	19.3	36.3	22.4
1,2,3,6,7,8-HxCDF	0.51	0.81	2.02	1.11	5.3	7	19	10.4
2,3,4,6,7,8-HxCDF	0	0.52	1.43	0.65	0	4.5	13.4	6
1,2,3,7,8,9-HxCDF	0	0	0	0	0	0	0	0
1,2,3,4,6,7,8-HpCDF	0.11	0.05	0.16	0.11	1.1	0.4	1.5	1
1,2,3,4,7,8,9-HpCDF	0	0	0	0	0	0	0	0
OCDF	0.01	0	0	0	0.1	0	0	0
TOTAL	20.43	63.27	69.75	51.14	213.8	546.8	654.9	471.9
Gerdau Courtice Steel Inc.								
2,3,7,8-TCDD	6.3	2.7	2.6	3.9	57	21	22	33.3
1,2,3,7,8-PeCDD	8.3	4.7	3.1	5.4	75	37	27	46.3
1,2,3,4,7,8-HxCDD	0.6	0.4	0.2	0.4	5	3	2	3.3
1,2,3,6,7,8-HxCDD	1	0.7	0.4	0.7	9	6	3	6
1,2,3,7,8,9-HxCDD	0.8	0.5	0.3	0.5	8	4	3	5
1,2,3,4,6,7,8-HpCDD	0.2	0.1	0.1	0.1	1	1	1	1
OCDD	0	0	0	0	0	0	0	0
2,3,7,8-TCDF	65	29.4	18	37.5	588	232	154	324.7
1,2,3,7,8-PeCDF	5.5	2.9	1.7	3.4	50	23	15	29.3
2,3,4,7,8-PeCDF	95.5	46.2	26	55.9	864	364	222	483.3
1,2,3,4,7,8-HxCDF	12.5	7.9	4.3	8.2	113	63	37	71
1,2,3,6,7,8-HxCDF	6.9	4.6	2.4	4.6	62	36	20	39.3
2,3,4,6,7,8-HxCDF	5.8	4.3	1.7	3.9	52	34	14	33.3
1,2,3,7,8,9-HxCDF	0.5	0.5	0.2	0.4	5	4	2	3.7
1,2,3,4,6,7,8-HpCDF	0.7	0.5	0.2	0.5	6	4	2	4
1,2,3,4,7,8,9-HpCDF	0.1	0.1	0	0.1	1	1	0	0.7
OCDF	0	0	0	0	0	0	0	0
TOTAL	209.7	105.5	61.2	125.5	1,896	833	524	1,084.2

Source: Cianciarelli (2000).

down the cupola and is removed at the bottom. Electric induction furnaces are batch-type furnaces in which the charge is melted by a fluctuating electromagnetic charge produced by electrical coils surrounding the unit (U.S. EPA, 1995b, 1997a).

Iron and steel foundries, particularly those using electric arc furnaces, are highly dependent on iron and steel scrap. Of the estimated 72 million metric tons of iron and steel scrap consumed by the iron and steel industry in 1995, 25% (18 million metric tons) were used by ferrous foundries. The other 75% were used by primary ferrous metal smelters (principally those using electric arc furnaces) (USGS, 1997f). In 2000, 20% (12.4 million metric tons) were used by ferrous foundries; the remaining 80% were used by primary ferrous smelters (USGS, 2000).

In 2000, there were approximately 1,100 ferrous foundries in the United States producing 1.3 million metric tons of steel castings and 10 metric tons of iron castings. Thus, foundries face the same potential for CDD/CDF emissions as do electric arc furnaces because of their use of scrap that contains chlorinated solvents, plastics, and cutting oils (see Section 7.4) The potential for formation and release of CDDs/CDFs during the casting process is not known.

In 1993, emissions testing was conducted at a U.S. ferrous foundry (CARB, 1993, as reported in U.S. EPA, 1997a). The tested facility consisted of a batch-operated, coke-fired cupola furnace charged with pig iron, scrap iron, scrap steel, coke, and limestone. Emission control devices operating during the testing were an oil-fired afterburner and an FF. The congener and congener group emission factors derived from the testing are presented in Table 7-12. The calculated TEQ emission factor for this set of tests is 0.42 ng TEQ_{DF}-WHO_{98} (0.37 ng I-TEQ_{DF}/kg) of metal charged to the furnace.

Umweltbundesamt (1996) reported stack testing results for a variety of ferrous foundries in Germany. Sufficient data were provided to enable calculation of TEQ emission factors for eight of the tested facilities. Three facilities had emission factors exceeding 1 ng I-TEQ_{DF}/kg of metal charge, and four facilities had emission factors less than 0.1 ng I-TEQ_{DF}/kg of metal charge. The emission factors span more than four orders of magnitude. The mean emission factor was 1.26 ng I-TEQ_{DF}/kg of metal feed.

In 1997, EPA conducted testing for emissions of dioxins at two ferrous foundries (U.S. EPA, 1999c, f). One study was conducted on the cupola's WS; the second study was performed on the cupola's FF. A summary of the results is presented in Table 7-13. The emission factor developed from these tests is 2.05 ng I-TEQ/kg of metal processed.

Because of the wide range of emissions for the tested German foundries reported in Umweltbundesamt (1996), the confidence in the degree to which the three tested U.S. facilities represent the mean emission factor for the approximately 1,100 U.S. foundries is considered very low. Therefore, the limited data available were judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary

Table 7-12. CDD/CDF emission factors for a U.S. ferrous foundry

Congener/congener group	Mean facility emission factor (ng/kg scrap feed)
2,3,7,8-TCDD	0.033
1,2,3,7,8-PeCDD	0.086
1,2,3,4,7,8-HxCDD	NR
1,2,3,6,7,8-HxCDD	0.051
1,2,3,7,8,9-HxCDD	NR
1,2,3,4,6,7,8-HpCDD	0.093
OCDD	NR
2,3,7,8-TCDF	0.52
1,2,3,7,8-PeCDF	0.305
2,3,4,7,8-PeCDF	0.35
1,2,3,4,7,8-HxCDF	0.19
1,2,3,6,7,8-HxCDF	0.17
1,2,3,7,8,9-HxCDF	NR
2,3,4,6,7,8-HxCDF	0.101
1,2,3,4,6,7,8-HpCDF	0.193
1,2,3,4,7,8,9-HpCDF	NR
OCDF	0.059
Total 2,3,7,8-CDD	0.263
Total 2,3,7,8-CDF	1.888
Total I-TEQ_{DF} (for reported congeners)	0.372
Total TEQ_{DF}-WHO_{98}	0.415
Total TCDD	3.96
Total PeCDD	1.76
Total HxCDD	0.55
Total HpCDD	0.19
Total OCDD	NR
Total TCDF	25.8
Total PeCDF	850
Total HxCDF	1.74
Total HpCDF	0.24
Total OCDF	0.06
Total CDD/CDF (not including OCDD)	884.3

NR = Not reported

Source: CARB (1993), as reported in U.S. EPA (1997a).

estimate of potential TEQ annual emissions from U.S. ferrous foundries can be made by combining the mean emission factor (1.23 ng I-TEQ_{DF}/kg of metal feed) derived from the data reported in Umweltbundesamt (1996), CARB (1993), and U.S. EPA (1997a) with an estimated activity level for U.S. foundries.

Table 7-13. Congener-specific profile for ferrous foundries

Congener	Mean emission factor (2 facilities) (ng I-TEQ/kg)	
	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	0.11	0.11
1,2,3,7,8-PeCD	0.15	0.15
1,2,3,4,7,8-HxCDD	0.012	0.012
1,2,3,6,7,8-HxCDD	0.023	0.023
1,2,3,7,8,9-HxCDD	0.028	0.028
1,2,3,4,6,7,8-HpCDD	0.0033	0.0033
OCDD	0.16	0.16
2,3,7,8-TCDF	0.084	0.084
1,2,3,7,8-PeCDF	1.08	1.08
2,3,4,7,8-PeCDF	0.21	0.21
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.0079	0.0079
1,2,3,7,8,9-HxCDF	0.075	0.075
2,3,4,6,7,8-HxCDF	0.0082	0.0082
1,2,3,4,6,7,8-HpCDF	0.0014	0.0014
1,2,3,4,7,8,9-HpCDF	0.00009	0.00009
OCDF	0.00007	0.00007
Total I-TEQ	2.05	2.05

Sources: U.S. EPA (1999c, f).

In 1987, U.S. shipments from ferrous foundries were 9.19 million metric tons, of which about 90% were iron castings and 10% were steel castings (Houck, 1991). In 1995, U.S. shipments from the approximately 1,000 U.S. ferrous foundries were 13.9 million metric tons, of which about 90% were iron castings and 10% were steel castings (Fenton, 1996). In 2000, U.S. shipments from the approximate 1,100 U.S. ferrous foundries were 11.3 million metric tons, of which about 89% were iron castings and 11% were steel castings (USGS, 2001). Using the mean emission factors and these activity levels yields annual emission estimates of 11.3 g I-TEQ_{DF}, 17.1 g I-TEQ_{DF}, and 13.9 g I-TEQ_{DF} for 1987, 1995, and 2000, respectively. These estimates should be regarded as preliminary indications of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

7.6. SCRAP ELECTRIC WIRE RECOVERY

The objective of wire recovery is to reclaim the metal (copper, lead, silver, and gold) in the electric wire by removing the insulating material. The recovery facility then sells the reclaimed metal to a secondary metal smelter. Wire insulation commonly consists of a variety of

plastics, asphalt-impregnated fabrics, or burlap. Chlorinated organics are used to preserve the cable casing in below-ground cables. The combustion of chlorinated organic compounds in the cable insulation, catalyzed by the presence of wire metals such as copper and iron, can lead to the formation of CDDs and CDFs (Van Wijnen et al., 1992).

Although, in the past, scrap electric wire was commonly recovered using thermal processing to burn off the insulating material, current recovery operations typically no longer involve thermal treatment, according to industry and trade association representatives. Instead, scrap electric wire is mechanically chopped into fine particles. The insulating material is then removed by mixing, followed by settling of the heavier metal (telephone conversations between T. Leighton, Versar, Inc., and R. Garino, Institute of Scrap Recycling Industries, March 2, 1993, and T. Leighton and J. Sullivan, Triple F. Dynamics, March 8, 1993).

EPA measured dioxin-like compounds emitted to the air from a scrap wire reclamation incinerator during its 1986 National Dioxin Study of combustion sources (U.S. EPA, 1987a). EPA determined that the tested facility was typical of this industrial source category at that time. Insulated wire and other metal-bearing scrap material were fed to the incinerator on a steel pallet. The incinerator operated in a batch mode, with the combustion cycles for each batch of scrap feed lasting between 1 and 3 hr. Natural gas was used to incinerate the material. Although most of the wire had a tar-based insulation, PVC-coated wire was also fed to the incinerator. Temperatures during combustion in the primary chamber furnace were about 570°C. The tested facility was equipped with a high-temperature, natural gas-fired afterburner (980 to 1090°C). Emission factors estimated for this facility are presented in Table 7-14. The estimated TEQ emission factor (based only on 2,3,7,8-TCDD, 2,3,7,8-TCDF, OCDD, and OCDF) is 15.8 ng TEQ_{DF}-WHO_{98} (16.9 ng I-TEQ_{DF}/kg) of scrap feed. Figure 7-5 presents a congener group profile based on these emission factors.

Bremmer et al. (1994) reported emission factors for three facilities in the Netherlands that subsequently ceased operations. Emission rates at a facility burning underground cables and cables containing PVC ranged from 3.7 ng I-TEQ_{DF}/kg to 14 ng I-TEQ_{DF}/kg. The emission rates at a second facility ranged from 21 ng I-TEQ_{DF}/kg of scrap (when burning copper core coated with greasy paper) to 2,280 ng I-TEQ_{DF}/kg of scrap (when burning lead cable). The third facility, which burned motors, was reported to have an emission rate of 3,300 ng I-TEQ_{DF}/kg of scrap. On the basis of these measurements, Bremmer et al. used emission rates of 40 ng I-TEQ_{DF}/kg of scrap and 3,300 ng I-TEQ_{DF}/kg of scrap for estimating national emissions in the Netherlands for facilities burning wires and cables and those burning motors, respectively.

Although limited emissions testing has been conducted at one U.S. facility, the activity level for this industry sector in reference years 1987, 1995, and 2000 is unknown; therefore, an

Table 7-14. CDD/CDF emission factors for a scrap wire incinerator

Congener/congener group	Mean facility emission factor[a] (ng/kg scrap feed)
2,3,7,8-TCDD	0.374
1,2,3,7,8-PeCDD	NR
1,2,3,4,7,8-HxCDD	NR
1,2,3,6,7,8-HxCDD	NR
1,2,3,7,8,9-HxCDD	NR
1,2,3,4,6,7,8-HpCDD	NR
OCDD	1,000
2,3,7,8-TCDF	2.67
1,2,3,7,8-PeCDF	NR
2,3,4,7,8-PeCDF	NR
1,2,3,4,7,8-HxCDF	NR
1,2,3,6,7,8-HxCDF	NR
1,2,3,7,8,9-HxCDF	NR
2,3,4,6,7,8-HxCDF	NR
1,2,3,4,6,7,8-HpCDF	NR
1,2,3,4,7,8,9-HpCDF	NR
OCDF	807
Total 2,3,7,8-CDD	NR
Total 2,3,7,8-CDF	NR
Total I-TEQ_{DF}	16.9[b]
Total TEQ_{DF}-WHO_{98}	15.8
Total TCDD	1,000
Total PeCDD	4.42
Total HxCDD	13.7
Total HpCDD	71.1
Total OCDD	347
Total TCDF	107
Total PeCDF	97.4
Total HxCDF	203
Total HpCDF	623
Total OCDF	807
Total CDD/CDF	3,274

[a]No nondetect values were reported for 2,3,7,8-TCDD, 2,3,7,8-TCDF, or any congener group in the three test runs.
[b]Estimated on the basis of the measured data for 2,3,7,8-TCDD, 2,3,7,8-TCDF, OCDD, and OCDF and congener group emissions (i.e., for the penta-, hexa-, and hepta-CDDs and CDFs, it was assumed that the measured emission factor within a congener group was the sum of equal emission factors for all congeners in that group, including non-2,3,7,8-substituted congeners).

NR = Not reported

Source: U.S. EPA (1987a).

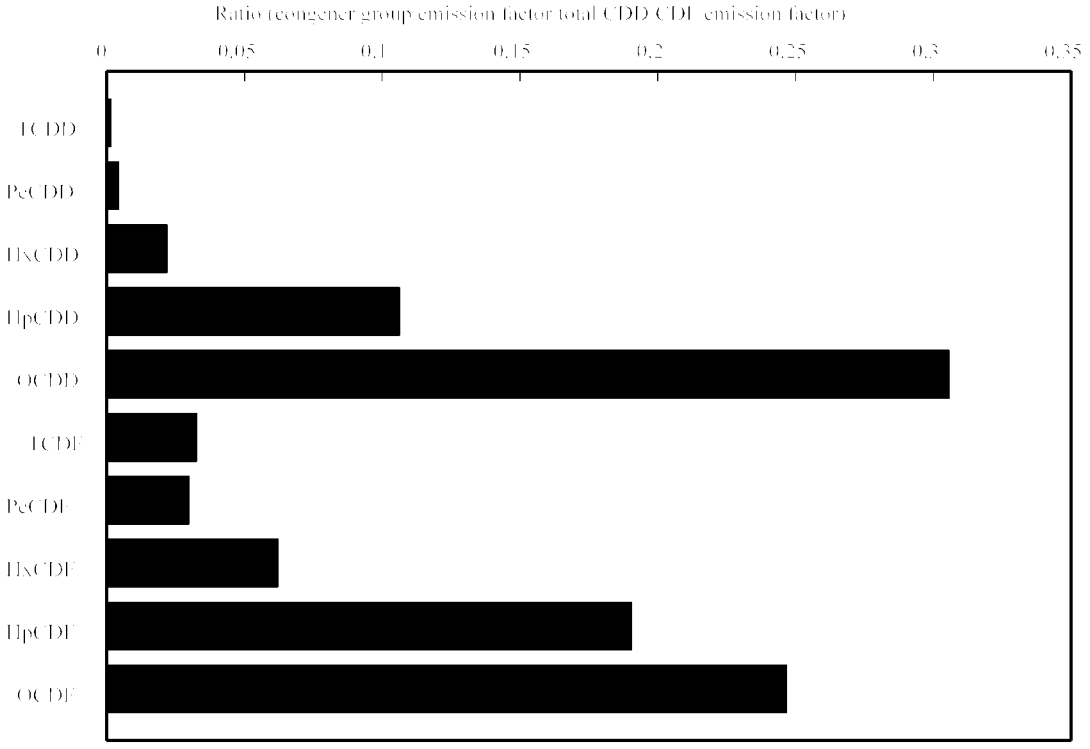


Figure 7-5. Congener group profile for air emissions from a scrap wire incinerator.

Source: U.S. EPA (1987a).

estimate of national emissions cannot be made. It is uncertain how many facilities in the United States still combust scrap wire. Trade association and industry representatives state that U.S. scrap wire recovery facilities now burn only minimal quantities of scrap wire. However, an inventory of CDD/CDF sources in the San Francisco Bay area noted that two facilities thermally treated electric motors to recover electrical windings (BAAQMD, 1996).

In addition to releases from regulated recovery facilities, CDD/CDF releases from small-scale burning of wire at unregulated facilities and open air sites have occurred; however, the current magnitude of these types of activity in the United States is not known. Harnly et al. (1995) analyzed soil/ash mixtures from three closed metal recovery facilities and from three closed sites using open burning for copper recovery near a California desert town. The geometric means of the total CDD/CDF concentrations at the facility sites and the open burning sites were 86,000 and 48,500 ng/kg, respectively. The geometric mean TEQ concentrations were 2,900 and 1,300 ng I-TEQ_{DF}/kg, respectively. A significantly higher geometric mean concentration (19,000 ng I-TEQ_{DF}/kg) was found in fly ash located at two of the facility sites. The congener-specific

and congener group results from this study are presented in Table 7-15. The results show that the four dominant congeners in the soil samples at both the facility and the open burning sites were OCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8-HxCDF, and 2,3,7,8-TCDF. A slightly different profile was observed in the fly ash samples, with 1,2,3,7,8-PeCDF and 1,2,3,4,7,8,9-HpCDF replacing OCDD and 2,3,7,8-TCDF as the dominant congeners.

Table 7-15. CDD/CDF concentrations in fly ash and ash/soil at metal recovery sites

Congener/congener group	Metal recovery facilities				Open burn sites	
	Fly ash (2 sites)		Ash/soil (3 sites)		Ash/soil (3 sites)	
	Geometric mean (µg/kg)	Relative percent of total CDD/CDF	Geometric mean (µg/kg)	Relative percent of total CDD/CDF	Geometric mean (µg/kg)	Relative percent of total CDD/CDF
2,3,7,8-TCDD	[a]		[a]		[a]	
1,2,3,7,8-PeCDD	400	0.1	0.24	0.3	0.24	0.5
1,2,3,4,7,8-HxCDD	1,200	0.2	0.25	0.3	0.13	0.3
1,2,3,6,7,8-HxCDD	2,300	0.5	0.49	0.6	0.33	0.7
1,2,3,7,8,9-HxCDD	1,700	0.3	1.3	1.5	0.39	0.8
1,2,3,4,6,7,8-HpCDD	12,000	2.4	2.6	3.1	1.2	2.5
OCDD	18,000	3.5	7.2	8.5	3.4	7
2,3,7,8-TCDF	15,000	2.9	6.4	7.5	1.7	3.5
1,2,3,7,8-PeCDF	35,000	6.9	2.9	3.4	0.58	1.2
2,3,4,7,8-PeCDF	10,000	2	1.4	1.6	0.66	1.4
1,2,3,4,7,8-HxCDF	46,000	9	5.9	6.9	2.7	5.6
1,2,3,6,7,8-HxCDF	12,000	2.4	1.8	2.1	0.76	1.6
1,2,3,7,8,9-HxCDF	5,000	1	0.92	1.1	0.66	1.4
2,3,4,6,7,8-HxCDF	5,000	1	1.6	1.9	0.49	1
1,2,3,4,6,7,8-HpCDF	71,000	13.9	12	14.1	4.3	8.9
1,2,3,4,7,8,9-HpCDF	25,000	4.9	3	3.5	0.71	1.5
OCDF	100,000	19.6	14	16.5	6.6	13.6
Total TCDD	[a]	[a]	[a]	[a]	[a]	[a]
Total PeCDD	2,000	0.4	1.4	1.6	2.8	5.8
Total HxCDD	4,000	0.8	2.7	3.2	0.98	2
Total HpCDD	24,000	4.7	4.1	4.8	2	4.1
Total OCDD	18,000	3.5	7.2	8.5	3.4	7
Total TCDF	23,000	4.5	14	16.5	5.6	11.5
Total PeCDF	110,000	21.6	12	14.1	7	14.4
Total HxCDF	88,000	17.3	12	14.1	7.6	15.7
Total HpCDF	110,000	21.6	17	20	7.4	15.3
Total OCDF	100,000	19.6	14	16.5	6.6	13.6
Total I-TEQ_{DF}	16,968		3		1.3	
Total CDD/CDF	479,000		84.4		48.4	

[a]Analytical method used had low sensitivity for TCDDs; results were not reported.

Source: Harnly et al. (1995).

Van Wijnen et al. (1992) reported similar results for soil samples collected from unpermitted incineration sites of former scrap wire and cars in the Netherlands. Total CDD/CDF concentrations in the soil ranged from 60 to 98,000 ng/kg, with 9 of the 15 soil samples having levels above 1,000 ng/kg. Chen et al. (1986) reported finding high levels of CDDs/CDFs in residues from open air burning of wire in Taiwan, and Huang et al. (1992) reported elevated levels in soil near wire scrap recovery operations in Japan. Bremmer et al. (1994) estimated an emission rate to air of 500 ng I-TEQ_{DF}/kg of scrap for illegal, unregulated burning of cables in the Netherlands.

7.7. DRUM AND BARREL RECLAMATION FURNACES

Hutzinger and Fiedler (1991a) reported detecting CDDs/CDFs in stack gas emissions from drum and barrel reclamation facilities at levels ranging from 5 to 27 ng/m^3. EPA measured dioxin-like compounds in the stack gas emissions of a drum and barrel reclamation furnace as part of the National Dioxin Study (U.S. EPA, 1987a).

Drum and barrel reclamation facilities operate a burning furnace to thermally clean used 55-gallon steel drums of residues and coatings. The drums processed at these facilities come from a variety of sources in the petroleum and chemical industries. The thermally cleaned drums are then repaired, repainted, relined, and sold for reuse. The drum-burning process subjects the used drums to an elevated temperature in a tunnel furnace fired by auxiliary fuel for a sufficient time so that the paint, interior linings, and previous contents are burned or disintegrated. Used drums are loaded onto a conveyor that moves at a fixed speed. As the drums pass through the preheat and ignition zone of the furnace, residual contents of the drums drain into the furnace ash trough. A drag conveyor moves these sludges and ashes to a collection pit. The drums are air-cooled as they exit the furnace. Exhaust gases from the burning furnace are typically drawn through a breeching fan to a high-temperature afterburner.

The afterburner at the facility tested by EPA operated at an average of 827°C during testing and achieved a 95% reduction in CDD/CDF emissions (U.S. EPA, 1987a). Emission factors estimated for this facility are presented in Table 7-16. On the basis of the measured congener and congener group emissions, the average TEQ emission factor is estimated to be 17.5 ng TEQ_{DF}-WHO_{98}/drum (16.5 ng I-TEQ_{DF}/drum). The congener group profile is presented in Figure 7-6.

Approximately 2.8 to 6.4 million 55-gallon drums are reclaimed by incineration annually in the United States (telephone conversation between C. D. Ruiz, Versar, Inc., and P. Rankin, Association of Container Reconditioners, December 21, 1992). This estimate is based on the assumption that 23 to 26 incinerators are in operation; each incinerator, on average, handles 500

Table 7-16. CDD/CDF emission factors for a drum and barrel reclamation facility

Congener/congener group	Mean facility emission factor[a] (ng/drum)
2,3,7,8-TCDD	2.09
1,2,3,7,8-PeCDD	NR
1,2,3,4,7,8-HxCDD	NR
1,2,3,6,7,8-HxCDD	NR
1,2,3,7,8,9-HxCDD	NR
1,2,3,4,6,7,8-HpCDD	NR
OCDD	37.5
2,3,7,8-TCDF	36.5
1,2,3,7,8-PeCDF	NR
2,3,4,7,8-PeCDF	NR
1,2,3,4,7,8-HxCDF	NR
1,2,3,6,7,8-HxCDF	NR
1,2,3,7,8,9-HxCDF	NR
2,3,4,6,7,8-HxCDF	NR
1,2,3,4,6,7,8-HpCDF	NR
1,2,3,4,7,8,9-HpCDF	NR
OCDF	22.4
Total 2,3,7,8-CDD	NR
Total 2,3,7,8-CDF	NR
Total I-TEQ_{DF}	16.5[b]
Total TEQ_{DF}-WHO_{98}	17.5
Total TCDD	50.29
Total PeCDD	29.2
Total HxCDD	32.2
Total HpCDD	53.4
Total OCDD	37.5
Total TCDF	623
Total PeCDF	253
Total HxCDF	122
Total HpCDF	82.2
Total OCDF	22.4
Total CDD/CDF	1,305.2

[a]No nondetect values were reported for 2,3,7,8-TCDD, 2,3,7,8-TCDF, or any congener group in the three test runs.
[b]Estimated on the basis of the measured data for 2,3,7,8-TCDD, 2,3,7,8-TCDF, OCDD, and OCDF and congener group emissions (i.e., for the penta-, hexa-, and hepta-CDDs and CDFs, it was assumed that the measured emission factor within a congener group was the sum of equal emission factors for all congeners in that group, including non-2,3,7,8-substituted congeners).

NR = Not reported

Source: U.S. EPA (1987a).

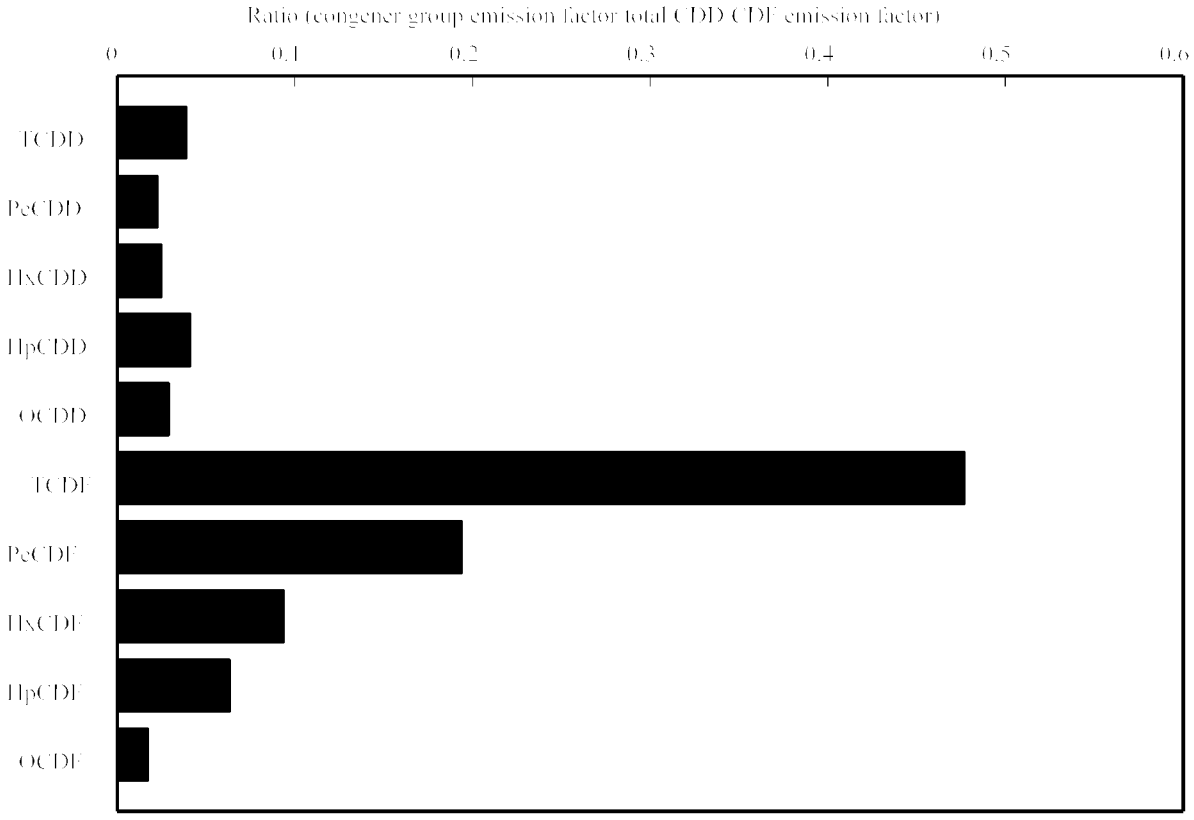


Figure 7-6. Congener group profile for air emissions from a drum incinerator.

Source: U.S. EPA (1987a).

to 1,000 drums each day and, on average, each incinerator operates 5 days/wk, with 14 downtime days annually for maintenance activities. The weights of 55-gallon drums vary considerably; however, on average, a drum weighs 38 lb (or 17 kg); therefore, an estimated 48 to 109 million kg of drums are incinerated annually. For 1987 and 1995, EPA assumed that 4.6 million drums were burned each year (i.e., the midpoint of the range); applying the emission factors developed above, the estimated annual emission is 0.08 g TEQ_{DF}-WHO_{98} (0.08 g I-TEQ_{DF}).

The Reusable Industrial Packaging Association estimated that approximately 35 million 55-gallon barrels were reclaimed in 1997 (RIPA, 1997). Assuming the number of drums treated has remained constant through 2000, the estimate for 2000 would be 0.61 g TEQ_{DF}-WHO_{98} (0.58 g I-TEQ_{DF}).

A low confidence rating is assigned to the activity level estimates for all reference years because they are based on expert judgment rather than a published reference. A low confidence

rating is also assigned to the emission factor because it was developed from stack tests conducted at just one U.S. drum and barrel furnace and thus may not represent average emissions from current operations in the United States. Based on these ratings, the emission estimates are assigned a low confidence rating.

7.8. SOLID WASTE FROM PRIMARY/SECONDARY IRON/STEEL MILLS/FOUNDRIES

Table 17 in Quab and Fermann (1997) contains summary data on the typical annual quantities and ranges of TEQ (Norwegian-TEQ [NTEQ] and I-TEQ) from various solid residuals from the metallurgical industries in Europe, but support information and specific congeners were not discussed. The summary data for annual TEQ generation are presented below (in grams) for informational purposes only and are not included in the inventory of dioxin releases presented in this report because they are disposed of in permanent landfills and are not considered an environmental release.

- Grey iron foundries, FF dust and scrubber sludge: 0.817 NTEQ
- Steel mill coke oven door leakage dust: 0.31 NTEQ
- Steel mill coke oven door leakage dust: 0.04 I-TEQ
- Pig iron tapping slag: 0.041 NTEQ
- Basic oxygen furnace scrubber sludge: 1.53 NTEQ (range, 0.3–7.81)
- Electric furnace FF dust: 3.1 I-TEQ (range of 0.4–2.4)
- Electric furnace slag or FF dust: 19.2 NTEQ

8. CHEMICAL MANUFACTURING AND PROCESSING SOURCES

8.1. BLEACHED CHEMICAL WOOD PULP AND PAPER MILLS

In March 1988, EPA and the U.S. pulp and paper industry jointly released the results of a screening study that provided the first comprehensive data on the formation and discharge of CDDs/CDFs from pulp and paper mills (U.S. EPA, 1988d). This early screening study of five bleached kraft mills (the Five Mill Study) confirmed that the pulp bleaching process was primarily responsible for the formation of CDDs/CDFs. The study results showed that 2,3,7,8-TCDD was present in seven of nine bleached pulps, five of five wastewater treatment sludges, and three of five treated wastewater effluents. The study results also indicated that 2,3,7,8-TCDD and 2,3,7,8-TCDF were the principal CDDs/CDFs formed.

To provide EPA with more complete data on the release of these compounds, EPA and the pulp and paper industry jointly conducted a survey during 1988 of 104 pulp and paper mills in the United States to measure levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF in effluent, sludge, and pulp. The survey study, commonly called the 104 Mill Study, was managed by the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI), with oversight by EPA, and included all mills where chemically produced wood pulps were bleached with chlorine or chlorine derivatives. The final study report (U.S. EPA, 1990e) was released in July 1990.

An initial phase of the 104 Mill Study involved the analysis of bleached pulp (10 samples), wastewater sludge (9 samples), and wastewater effluent (9 samples) from eight kraft mills and one sulfite mill for all 2,3,7,8-substituted CDDs/CDFs. These analyses were conducted to test the conclusion drawn in the Five Mill Study that 2,3,7,8-TCDD and 2,3,7,8-TCDF were the principal CDDs/CDFs found in pulp, wastewater sludge, and wastewater effluent on a TEQ basis. Although at the time of the study there were no reference analytical methods for many of the 2,3,7,8-substituted CDDs/CDFs, the data obtained were considered valid by EPA for the purposes intended because of the identification and quantification criteria used, duplicate sample results, and limited matrix spike experiments. Table 8-1 presents a summary of the results obtained in terms of the median concentrations and the range of concentrations observed for each matrix (pulp, sludge, and effluent). Figures 8-1, 8-2, and 8-3 present congener profiles for each matrix (normalized to total CDD/CDF) using the median reported concentrations.

After examination of the raw, mill-specific data, EPA concluded that the congener profiles were fairly consistent across matrices within mills and that 2,3,7,8-TCDD and 2,3,7,8-TCDF accounted for the majority of TEQ in the samples (U.S. EPA, 1990e). Using the median concentrations and treating nondetect values as either zero or one-half the detection limit (DL),

Table 8-1. CDD/CDF concentrations in pulp and paper mill bleached pulp, wastewater sludge, and wastewater effluent (circa 1988)

Congener/congener group	Bleached pulp			Wastewater sludge			Wastewater effluent		
	Median (ng/kg)	Range (ng/kg)	No. of detects (10 samples)	Median (ng/kg)	Range (ng/kg)	No. of detects (9 samples)	Median (pg/L)	Range (pg/L)	No. of detects (9 samples)
2,3,7,8-TCDD	6.4	0.4 to 124	10	63	ND(6.3) to 180	8	42	ND(11) to 98	8
1,2,3,7,8-PeCDD	ND(0.3)	ND(0.1) to 1.4	2	ND(2.5)	ND(1.4) to 28	1	ND(9.6)	ND(2.8) to ND(25)	0
1,2,3,4,7,8-HxCDD	ND(0.4)	ND(0.2) to 0.4	1	ND(3.1)	ND(1.5) to 40	1	ND(12)	ND(6.6) to ND(12)	0
1,2,3,6,7,8-HxCDD	ND(0.5)	ND(0.2) to 1.6	2	ND(3.2)	ND(1.7) to 95	1	ND(12)	ND(6.6) to ND(24)	0
1,2,3,7,8,9-HxCDD	ND(0.5)	ND(0.2) to 0.5	1	ND(3.9)	ND(1.7) to 80	1	ND(12)	ND(6.6) to ND(23)	0
1,2,3,4,6,7,8-HpCDD	3.3	2.3 to 8.4	10	37	18 to 490	9	170	77 to 270	9
OCDD	46	28 to 81	10	698	263 to 1,780	9	3,000	1,000 to 4,600	9
2,3,7,8-TCDF	18	1.4 to 716	10	233	13 to 1150	9	120	12 to 840	9
1,2,3,7,8-PeCDF	ND(0.7)	ND(0.1) to 3.9	4	6.2	ND(1.2) to 22	6	ND(7.2)	ND(2.2) to 36	2
2,3,4,7,8-PeCDF	ND(0.2)	ND(0.1) to 4.7	3	4.7	ND(0.9) to 38	6	ND(6.3)	ND(2.2) to 33	2
1,2,3,4,7,8-HxCDF	ND(0.3)	ND(0.2) to ND(0.6)	0	ND(2.5)	ND(0.9) to 31	2	ND(8.4)	ND(4.8) to ND(15)	0
1,2,3,6,7,8-HxCDF	ND(0.3)	ND(0.1) to ND(0.4)	0	ND(1.4)	ND(0.9) to 33	1	ND(7.1)	ND(4.8) to ND(15)	0
1,2,3,7,8,9-HxCDF	ND(0.3)	ND(0.1) to ND(0.4)	0	ND(1.7)	ND(0.9) to ND(4)	0	ND(6.2)	ND(2.5) to ND(15)	0
2,3,4,6,7,8-HxCDF	ND(0.3)	ND(0.2) to ND(0.4)	0	ND(1.7)	ND(0.9) to 34	1	ND(8.2)	ND(4.8) to ND(15)	0
1,2,3,4,6,7,8-HpCDF	ND(0.6)	ND(0.1) to 0.8	3	6.6	ND(3.6) to 70	7	ND(23)	ND(13) to 44	3
1,2,3,4,7,8,9-HpCDF	ND(0.6)	ND(0.1) to ND(2.1)	0	ND(1.6)	ND(1.2) to 10	1	ND(22)	ND(6.4) to ND(41)	0
OCDF	2.2	ND(2.8) to 4.3	8	22	ND(54) to 168	8	190	ND(180) to 230	8
Total 2,3,7,8-CDD[a,b]	55.7			798			3,212		
Total 2,3,7,8-CDF[a,b]	20.2			272.5			310		
Total I-TEQ_{DF} (nondetect = 0)[b]	8.28			90.12			58.89		
Total I-TEQ_{DF} (nondetect = ½ DL)[b]	8.56			91.72			66.57		
Total TEQ_{DF}-WHO_{98} (nondetect = 0)[b]	8.24		89.47				56.02		
Total TEQ_{DF}-WHO_{98} (nondetect = ½ DL)[b]	8.59		91.7				66.09		
Total CDD/CDF[b]	75.9			1,070.5			3,522		

[a]Calculated assuming nondetect values were zero.
[b]Sum of median values.

DL = Detection limit
ND = Not detected (value in parenthesis is the detection limit)

Source: U.S. EPA (1990e).

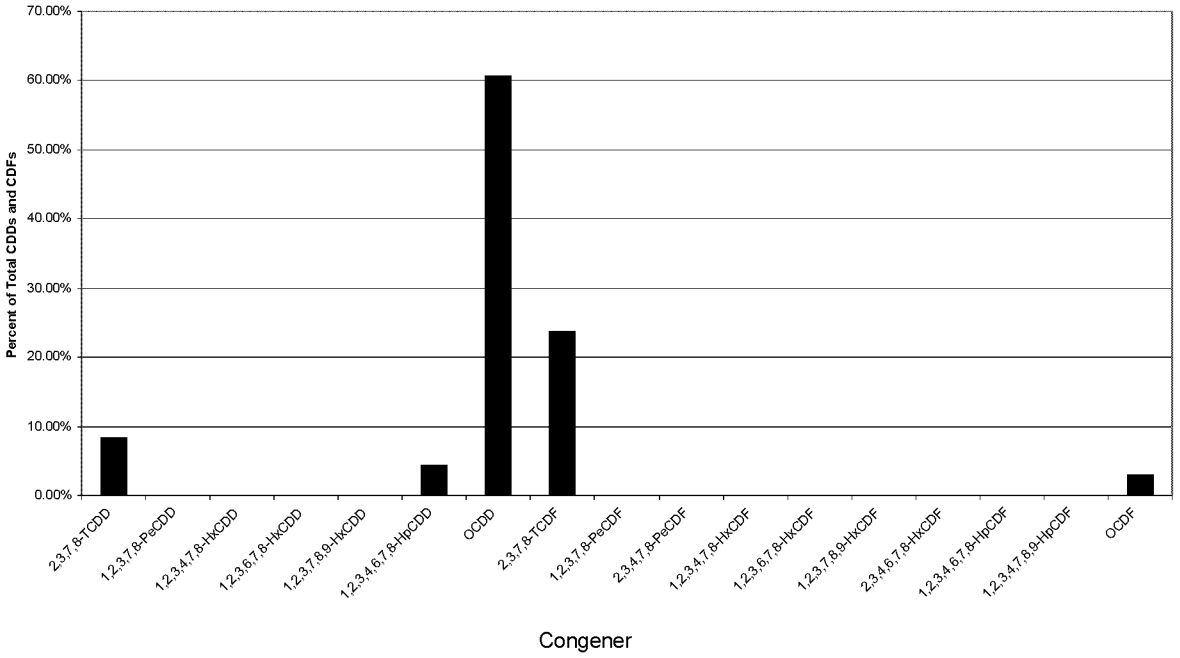


Figure 8-1. 104 Mill Study full congener analysis results for pulp (nondetects equal to zero).

Source: Median concentrations from U.S. EPA (1990e).

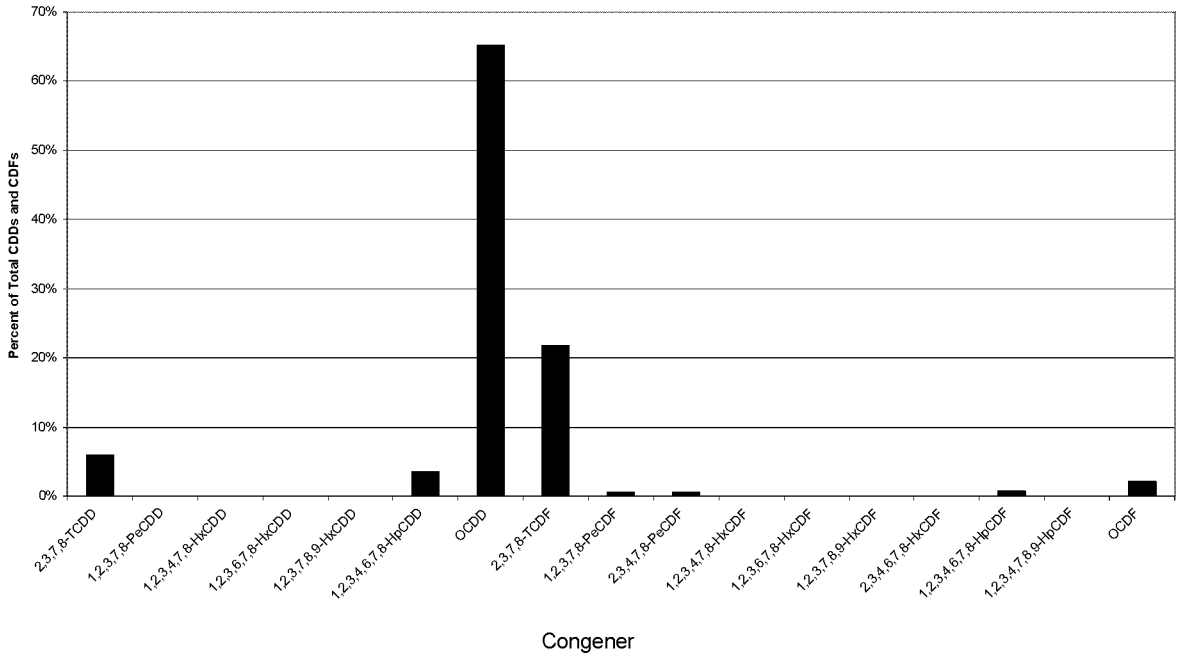


Figure 8-2. 104 Mill Study full congener analysis results for sludge.

Source: Median concentrations from U.S. EPA (1990e).

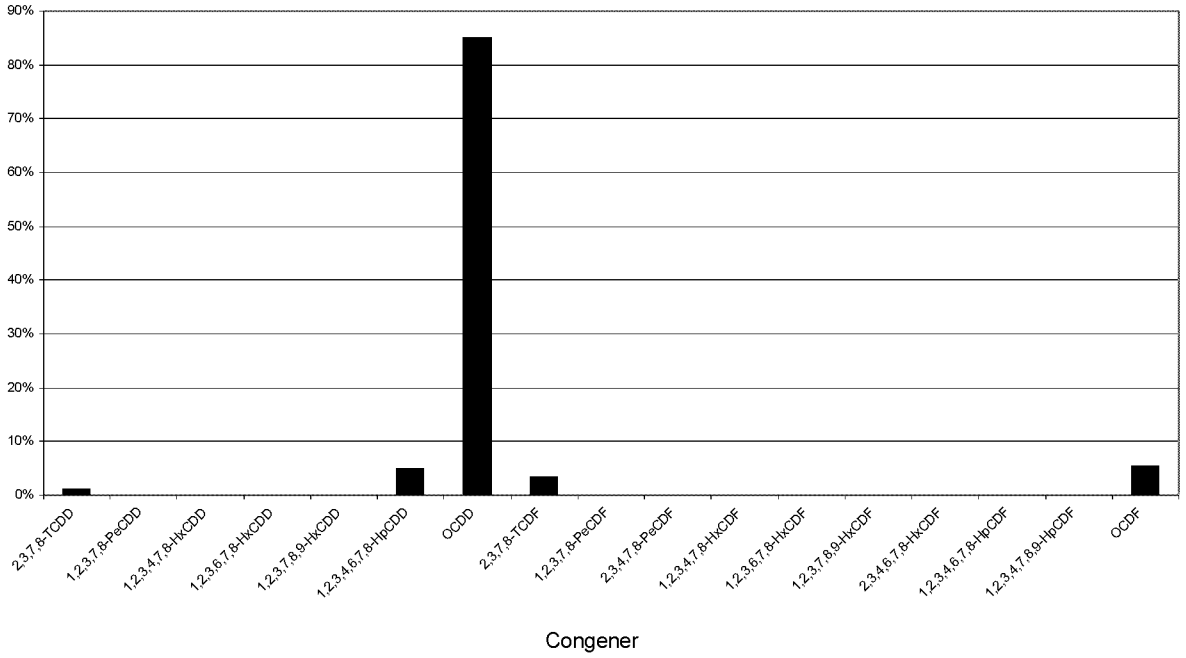


Figure 8-3. 104 Mill Study full congener analysis results for effluent.

Source: Median concentrations from U.S. EPA (1990e).

EPA concluded that 2,3,7,8-TCDF accounted for 77.8 to 99.5% of the total TEQ_{DF}-WHO_{98} (77.3 to 99% of the total I-TEQ_{DF}) in pulp, 70.4 to 96.5% of the TEQ_{DF}-WHO_{98} (69.9 to 95.8% of the I-TEQ_{DF}) in sludge, and 75.0 to 96.4% of the TEQ_{DF}-WHO_{98} (71.3 to 91.7% of the I-TEQ_{DF}) in effluent.

NCASI reported on a similar full-congener analysis study for samples collected from eight mills during the mid-1990s (letter dated February 10, 1997, from W. Gillespie, National Council of the Paper Industry for Air and Stream Improvement, Inc., to G. Schweer, Versar, Inc.). The results of these analyses are presented in Table 8-2. The frequency of detection of 2,3,7,8-TCDD and 2,3,7,8-TCDF was significantly lower than in the 1988 study; therefore, deriving meaningful summary statistics concerning the relative importance of 2,3,7,8-TCDD and 2,3,7,8-TCDF to the total TEQ is difficult. With all nondetect values assumed to be zero, 2,3,7,8-TCDD and 2,3,7,8-TCDF accounted for 97% of the total effluent TEQ_{DF}-WHO_{98} (91% of the I-TEQ_{DF}), 53% of the total sludge TEQ_{DF}-WHO_{98} (46% of the I-TEQ_{DF}), and 87% of the total pulp TEQ_{DF}-WHO_{98} (87% of the I-TEQ_{DF}). Because of the high frequency of nondetects when all nondetect values are one-half the DL, 2,3,7,8-TCDD and 2,3,7,8-TCDF accounted for only 13% of the total effluent I-TEQ_{DF}, 13% of the total sludge I-TEQ_{DF}, and 28% of the total pulp I-TEQ_{DF}.

Table 8-2. CDD/CDF concentrations in pulp and paper mill bleached pulp, wastewater sludge, and wastewater effluent (mid-1990s)

Congener/congener group	Bleached pulp				Wastewater sludge				Wastewater effluent			
	Mean nondetect = 0 (ng/kg)	Median (ng/kg)	Range (ng/kg)	No. of detects/ samples	Mean nondetect = 0 (ng/kg)	Median (ng/kg)	Range (ng/kg)	No. of detects/ samples	Mean nondetect = 0 (pg/L)	Median (ng/kg)	Range (pg/L)	No. of detects/ samples
2,3,7,8-TCDD	0.3	ND(1)	ND(1) to 5	1/18	0.8	ND(1)	ND(1) to 4	4/12	1.2	ND(11)	ND(10) to 21	1/18
1,2,3,7,8-PeCDD	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/12	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,4,7,8-HxCDD	0	ND(5)	ND(3) to ND(7)	0/18	0.5	ND(5)	ND(4) to 7	1/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,6,7,8-HxCDD	0	ND(5)	ND(3) to ND(7)	0/18	2.3	ND(5)	ND(4) to 18	2/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,7,8,9-HxCDD	0	ND(5)	ND(3) to ND(7)	0/18	1.6	ND(5)	ND(4) to 14	2/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,4,6,7,8-HpCDD	0	ND(5)	ND(3) to ND(7)	0/18	41.4	7	ND(4) to 330	9/13	3.2	ND(53)	ND(50) to 58	1/18
OCDD	2.4	ND(10)	ND(10) to 15	3/16	445	150	21 to 2,900	10/10	99	ND(110)	ND(100) to 370	6/14
2,3,7,8-TCDF	10.3	ND(1)	ND(1) to 170	7/18	6.2	3	ND(1) to 31	9/12	2.3	ND(11)	ND(10) to 23	2/18
1,2,3,7,8-PeCDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13		ND(53)	ND(50) to ND(55)	0/18
2,3,4,7,8-PeCDF	0.4	ND(5)	ND(3) to 7	1/18	0.5	ND(5)	ND(4) to 7	1/13		ND(53)	ND(50) to ND(55)	0/18
1,2,3,4,7,8-HxCDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13		ND(53)	ND(50) to ND(55)	0/18
1,2,3,6,7,8-HxCDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13		ND(53)	ND(50) to ND(55)	0/18
1,2,3,7,8,9-HxCDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13		ND(53)	ND(50) to ND(55)	0/18
2,3,4,6,7,8-HxCDF	0	ND(5)	ND(3) to ND(7)	0/18	0.5	ND(5)	ND(4) to 6	1/13		ND(53)	ND(50) to ND(55)	0/18
1,2,3,4,6,7,8-HpCDF	0	ND(5)	ND(3) to ND(7)	0/18	1.2	ND(5)	ND(4) to 10	2/13		ND(53)	ND(50) to ND(55)	0/18
1,2,3,4,7,8,9-HpCDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13		ND(53)	ND(50) to ND(55)	0/18
OCDF	0	ND(10)	ND(6) to ND(14)	0/18	0	ND(10)	ND(9) to ND(100)	0/13		ND(106)	ND(104) to ND(110)	0/18
Total 2,3,7,8-CDD[a]	2.7				491.6				103			
Total 2,3,7,8-CDF[a]	10.7				8.4				2.3			
Total I-TEQ_{DF} (nondetect = 0)[a]	1.53				3				1.5 53.6			
Total I-TEQ_{DF} (nondetect = ½ DL)[a]	6.4				12.9				1.4 66.5			
Total TEQ_{DF}-WHO_{98} (nondetect = 0)[a]	1.5				2.6							
Total TEQ_{DF}-WHO_{98} (nondetect = ½ DL)[a]	7.6				15.2							

[a] Sum of mean values.

DL = Detection limit
ND = Not detected (value in parenthesis is the detection limit)

Source: Letter dated February 10, 1997, from W. Gillespie, National Council of the Paper Industry for Air and Stream Improvement, Inc., to G. Schweer, Versar, Inc.

In 1992, the pulp and paper industry conducted its own NCASI-coordinated survey of 2,3,7,8-TCDD and 2,3,7,8-TCDF emissions (NCASI, 1993). Ninety-four mills participated in the study, and NCASI assumed that the remaining 10 (of 104) operated at the same levels as measured in the 1988 104 Mill Study. All nondetect values were counted as one-half the DL. If a DL was not reported, it was assumed to be 10 pg/L for effluent and 1 ng/kg for sludge or bleached pulp. The data used in the report were provided by individual pulp and paper companies that had been requested by NCASI to generate the data using the same protocols used in the 104 Mill Study.

In 1993, as part of its efforts to develop revised effluent guidelines and standards for the pulp, paper, and paperboard industry, EPA published the development document for the guidelines and standards being proposed for this industry (U.S. EPA, 1993b). The development document presented estimates of the 2,3,7,8-TCDD and 2,3,7,8-TCDF annual discharges in wastewater from the mills in this industry as of January 1, 1993. To estimate these discharges, EPA used the most recent information about each mill from four databases (104 Mill Study, EPA short-term monitoring studies at 13 mills, EPA long-term monitoring studies at eight mills, and industry self-monitoring data submitted to EPA). The 104 Mill Study data were used for only those mills that did not report making any process changes subsequent to the 104 Mill Study and did not submit any more recent effluent monitoring data.

Gillespie (1994) and Gillespie (1995) reported the results of 1993 and 1994 updates, respectively, to the 1992 NCASI survey. As in the 1992 survey, companies were requested to follow the same protocols for generating data that were used in the 104 Mill Study. Gillespie (1994, 1995) reported that fewer than 10% of mills had 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in effluent above the nominal DLs of 10 pg/L and 100 pg/L, respectively. EPA obtained similar results in its short- and long-term sampling for 18 mills; 2,3,7,8-TCDD was detected at four mills, and 2,3,7,8-TCDF was detected at nine mills (U.S. EPA, 1993b).

Gillespie (1994) reported that wastewater sludges at most mills (90%) contained less than 31 ng/kg of 2,3,7,8-TCDD and less than 100 ng/kg of 2,3,7,8-TCDF. Gillespie (1995) reported that 90% of the mills had 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in sludge of less than 17 ng/kg and 76 ng/kg, respectively, in 1994. U.S. EPA (1993b) reported similar results but found detectable levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF in sludges from 64% and 85%, respectively, of the facilities sampled.

Gillespie (1994) reported that nearly 90% of the bleached pulps contained less than 2 ng/kg of 2,3,7,8-TCDD and less than 160 ng/kg of 2,3,7,8-TCDF. Gillespie (1995) reported that 90% of the bleached pulps contained 1.5 ng/ng or less of 2,3,7,8-TCDD and 5.9 ng/kg or less of 2,3,7,8-TCDF. The final levels in white paper products would correspond to levels in bleached pulp, so bleached paper products would also be expected to contain less than 2 ng/kg of 2,3,7,8-TCDD.

On April 15, 1998, EPA promulgated effluent limitation guidelines and standards for certain segments of the pulp, paper, and paperboard industry (Federal Register, 1998c). The industry segments covered by this rulemaking (i.e., the bleached paper-grade kraft and soda subcategory and the paper-grade sulfite subcategory) are those segments responsible for more than 90% of the bleached chemical pulp production in the United States. For this rule, EPA updated the estimates of baseline loadings made in 1993 for the proposed rule by using more recent data collected by EPA, NCASI (including the 1994 NCASI survey), and individual facilities (U.S. EPA, 1997d). These revised estimates are presented in the last column in Table 8-3. EPA projects that, after full compliance with these rules, annual TEQ discharges will be reduced to 5 g in effluent and 7 g in sludge.

Table 8-3. Summary of bleached chemical pulp and paper mill discharges (g/yr) of 2,3,7,8-TCDD and 2,3,7,8-TCDF

Matrix	Congener	U.S. EPA 1988[a]	NCASI 1992[b]	U.S. EPA 1993[c]	NCASI 1993[b]	NCASI 1994[b]	U.S. EPA 1995[d]
Effluent	2,3,7,8-TCDD	201	22	71	19	14.6	16
	2,3,7,8-TCDF	1,550	99	341	76	49.0	120
	TEQ	356	32	105	27	19.5	28
Sludge[e]	2,3,7,8-TCDD	210	33	--	24	18.9	--
	2,3,7,8-TCDF	1,320	118	--	114	95.2	--
	TEQ	343	45	177	35	28.4	50
Pulp	2,3,7,8-TCDD	262	24	--	22	16.2	--
	2,3,7,8-TCDF	2,430	124	--	106	78.8	--
	TEQ	505	36	149	33	24.1	40

[a]Data from the 104 Mill Study (U.S. EPA, 1990e). The total discharge rate of congener or TEQ (based only on 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations) was summed across all 104 mills.

[b]The total discharge rate of congener or TEQ (based only on 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations) was summed across all 104 mills. The daily discharge rates reported in NCASI (1993) and Gillespie (1994, 1995) were multiplied by a factor of 350 days/yr to obtain estimates of annual discharge rates. NCASI 1992 survey (NCASI, 1993), 1993 update (Gillespie, 1994), and 1994 update (Gillespie, 1995).

[c]The discharges in effluent and sludge were estimated in U.S. EPA (1993b, 1997d) for January 1, 1993. The TEQ discharge in pulp was estimated by multiplying the 1988 discharge estimate by the ratio of the 1988 and1993 effluent discharge estimates (i.e., the estimate of the reduction in 1988 discharges achieved by pollution prevention measures taken by the industry between 1988 and 1993).

[d]The discharges in effluent and sludge were estimated in U.S. EPA (1997d) for mid-1995. The TEQ discharge in pulp was estimated by multiplying the 1988 discharge estimate by the ratio of the 1988 and1995 effluent discharge estimates (i.e., the estimate of the reduction in 1988 discharges achieved by pollution prevention measures taken by industry between 1988 and 1995).

[e]Approximately 20.5% of the sludge generated in 1990 was incinerated. The remaining 79.5% was predominantly landfilled (56.5%) or placed in surface impoundments (18.1%); 4.1% was land-applied directly or as compost, and 0.3% was distributed or marketed (U.S. EPA, 1993e).

NCASI = National Council of the Paper Industry for Air and Stream Improvement, Inc.
-- = No information given

8.1.1. Estimates of National Emissions in 1987 and 1995

The U.S. annual discharges of 2,3,7,8-TCDD and 2,3,7,8-TCDF are summarized in Table 8-3 for each of the six surveys discussed above. EPA release estimates for 1988 (U.S. EPA, 1990e) and 1995 (U.S. EPA, 1997d) are believed to best represent emissions in reference years 1987 and 1995, respectively. During the period between EPA's 104 Mill Study and issuance of the development document (U.S. EPA, 1993b), the U.S. pulp and paper industry reduced releases of CDDs/CDFs, primarily by instituting numerous process changes to reduce the formation of CDDs/CDFs during the production of chemically bleached wood pulp. Details on the process changes implemented are provided in U.S. EPA (1993b) and Gillespie (1995). Much of the reduction between 1988 and 1995 can be attributed to process changes for pollution prevention.

The confidence ratings for these release estimates are judged to be high because direct measurements were made at virtually all facilities, providing a high level of confidence in both the production and the emission factor estimates. The best estimates of annual emissions in 1987 (i.e., the 1988 estimates presented in Table 8-3) are 356 g TEQ/yr for effluent and 343 g TEQ/yr for sludge. The best estimates of annual emissions in 1995 (i.e., the 1995 estimates presented in Table 8-3) are 28 g TEQ/yr for effluent and 50 g TEQ/yr for sludge. The CDD/CDF content in bleached chemical wood pulp as a product is estimated to be approximately 505 g TEQ and 40 g TEQ in 1987 and 1995, respectively. Although EPA provided an estimate of contaminant levels of CDDs/CDFs in wood pulp, it is currently not known whether the dioxin contamination in the product actually resulted in a release to the open and circulating environment.

In 1990, the majority (75.5%) of the wastewater sludge generated by these facilities was placed in landfills or in surface impoundments, with the remainder incinerated (20.5%), applied to land directly or as compost (4.1%), or distributed as a commercial product (less than 1%) (U.S. EPA, 1993e). Data on the disposition of wastewater sludges are available only for years 1988 through 1995. On the basis of these data, the best estimate of TEQ applied to land (i.e., not incinerated or landfilled) is 14.1 g TEQ (4.1% of 343 g) for 1987 and 2 g (4.1% of 50 g) for 1995. These emission estimates are assigned a high level of confidence on the basis of the high confidence ratings given to both the activity level and the emission factor estimates.

8.1.2. Estimates of National Emissions in 2000

In 2000, NCASI provided estimates of congener-specific CDD/CDF releases from the pulp and paper industry in effluent, wastewater residuals, and pulp (Gillespie, 2002). Emission factors were taken from "NCASI Handbook of Chemical Specific Information for SARA (Superfund Amendments and Reauthorization Act) Section 313 Form R Reporting." Emission factors were compiled from valid test data supplied to NCASI by a variety of sources, including member companies that had performed the tests in response to a regulatory program. The mass

throughput parameter of total pulp production (31.9 million metric tons/yr) was provided by the American Forest and Paper Association and included data from 12 elemental chlorine-free mills. The effluent flow from chemical pulp mills with aerated stabilization basins (1,509 million gal/day) and with activated sludge treatment (660 million gal/day) was taken from the NCASI database and included data from five aerated stabilization basin mills and three activated sludge treatment mills. The primary waste treatment residuals from pulp mills (0.974 million dry metric tons/yr) and the combined, secondary, and dredged waste treatment residuals from pulp mills (1.37 million dry metric tons/yr) were also taken from the NCASI database and included data from five mills for the primary residuals and data from three mills for the secondary residuals (Gillespie, 2002).

Table 8-4 provides a breakdown of TEQ_{DF}-WHO_{98} concentrations and emissions by congener. Total TEQ_{DF}-WHO_{98} concentrations were reported to be 0.49 pg/L, 1.76 ng/kg, and 0.02 pg/g for effluent, sludge, and pulp, respectively. CDD/CDF emission estimates were reported as 1.02 g TEQ_{DF}-WHO_{98}/yr, 1.93 g TEQ_{DF}-WHO_{98}/yr, and 0.582 g TEQ_{DF}-WHO_{98}/yr for effluent, sludge, and pulp, respectively.

Fifty-one percent of the sludge generated in 2000 was sent to landfills or lagoons. It is uncertain how much of the remaining 49% of the sludge was applied to land. However, a conservative estimate can be developed by applying the 4.1% used to develop the 1987 and 1995 estimates. In this case, 0.08 g TEQ_{DF}-WHO_{98}/yr of sludge is estimated to have been applied to land in 2000. These estimates are assigned a high confidence rating because they are based on recent industry survey data; however, EPA is working with NCASI to develop a QA/QC protocol to monitor the data being collected.

8.2. MANUFACTURE OF CHLORINE, CHLORINE DERIVATIVES, AND METAL CHLORIDES

Testing of CDD/CDF emissions to air, land, or water from U.S. manufacturers of chlorine, chlorine derivatives, and metal chlorides on which to base estimates of national emissions has not been reported. Sampling of graphite electrode sludges from European chlorine manufacturers indicates high levels of CDFs. Limited sampling of chlorine derivatives and metal chlorides in Europe indicates low-level contamination in some products.

8.2.1. Manufacture of Chlorine

Chlorine gas is produced by electrolysis of brine electrolytic cells. Until the late 1970s, the primary type of electrolytic process used in the chlor-alkali industry to produce chlorine consisted of the use of mercury cells containing graphite electrodes. As shown in Table 8-5, high levels of CDFs have been found in several samples of graphite electrode sludge from facilities in

Table 8-4. CDD/CDF TEQ concentrations and emissions for the paper and pulp industry by source

Congener	Effluent		Waste treatment residuals not lagooned or landfilled (sludge) (49% not landfilled)		Pulp	
	TEQ conc.[a] (pg/L)	TEQ emissions (ng/yr)	TEQ conc.[a] (ng/kg)	TEQ emissions (ng/yr)	TEQ conc.[a] (pg/g pulp)	TEQ emissions (ng/yr)
2,3,7,8-TCDD	0	0.00e+00	4.00e-01	4.63e+08	1.00e-02	2.90e+08
1,2,3,7,8-PeCDD	0.00e+00	0.00e+00	5.00e-02	6.24e+07	0.00e+00	0.00e+00
1,2,3,4,7,8-HxCDD	0.00e+00	0.00e+00	1.00e-02	1.25e+07	0.00e+00	0.00e+00
1,2,3,6,7,8-HxCDD	1.30e-01	2.71e+08	8.00e-02	8.53e+07	0.00e+00	0.00e+00
1,2,3,7,8,9-HxCDD	9.00e-02	1.88e+08	9.00e-02	9.05e+07	0.00e+00	0.00e+00
1,2,3,4,6,7,8-HpCDD	7.00e-02	1.46e+08	1.82e-01	1.97e+08	3.00e-03	8.69e+07
1,2,3,4,6,7,8,9-OCDD	7.37e-02	1.54e+08	2.80e-01	2.81e+08	3.04e-03	8.80e+07
2,3,7,8-TCDF	1.00e-01	2.08e+08	4.00e-01	4.66e+08	1.00e-03	2.90e+07
1,2,3,7,8-PeCDF	0.00e+00	0.00e+00	1.00e-02	1.25e+07	0.00e+00	0.00e+00
2,3,4,7,8-PeCDF	0.00e+00	0.00e+00	1.00e-01	1.25e+08	0.00e+00	0.00e+00
1,2,3,4,7,8-HxCDF	0.00e+00	0.00e+00	4.00e-02	4.63e+07	0.00e+00	0.00e+00
1,2,3,6,7,8-HxCDF	0.00e+00	0.00e+00	1.00e-02	1.25e+07	0.00e+00	0.00e+00
1,2,3,7,8,9-HxCDF	0.00e+00	0.00e+00	5.00e-02	5.15e+07	2.00e-03	5.79e+07
2,3,4,6,7,8-HxCDF	0.00e+00	0.00e+00	0.00e+00	0.00e+00	0.00e+00	0.00e+00
1,2,3,4,6,7,8-HpCDF	1.90e-02	3.96e+07	1.70e-02	1.83e+07	1.00e-03	2.90e+07
1,2,3,4,7,8,9-HpCDF	5.00e-03	1.04e+07	0.00e+00	0.00e+00	0.00e+00	0.00e+00
1,2,3,4,6,7,8,9-OCDF	2.00e-03	4.17e+06	3.70e-03	3.93e+06	6.00e-05	1.74e+06
TEQ_{DF}-WHO_{98}	0.49	1.02e+09	1.76		0.02	5.83e+08
Residuals total				1.93e+09		
Residuals not landfilled				9.44e+08		

[a]TEQ concentrations are in TEQ_{DF}-WHO_{98}.

Source: Gillespie (2002).

Europe. The CDFs predominate in these sludges, and the 2,3,7,8-substituted congeners account for a large fraction of the respective congener totals (Rappe et al., 1990a, 1991; Rappe, 1993; Strandell et al., 1994). During the 1980s, titanium metal anodes were developed to replace graphite electrodes (U.S. EPA, 1982b; Curlin and Bommaraju, 1991). Currently, no U.S. facility is believed to use graphite electrodes in the production of chlorine gas (telephone conversation between L. Phillips, Versar, Inc., and T. Fielding, U.S. EPA, Office of Water, February 1993).

Table 8-5. CDD/CDF concentrations (µg/kg) in graphite electrode sludge from chlorine production

Congener/congener group	Sludge 1	Sludge 2	Sludge 3	Sludge 4
2,3,7,8-TCDD	ND (0.006)	ND (0.009)	ND (0.009)	ND
1,2,3,7,8-PeCDD	ND (0.007)	ND (0.009)	ND (0.009)	ND (0.033)
1,2,3,4,7,8-HxCDD	ND (0.018)	ND (0.026)	ND (0.029)	ND (0.49)
1,2,3,6,7,8-HxCDD	ND (0.012)	ND (0.016)	ND (0.019)	ND (0.053)
1,2,3,7,8,9-HxCDD	ND (0.016)	ND (0.022)	ND (0.025)	ND (1.2)
1,2,3,4,6,7,8-HpCDD	0.095	0.21	0.25	0.055
OCDD	0.92	2	2.2	0.65
2,3,7,8-TCDF	26	56	57	52
1,2,3,7,8-PeCDF	25	55	56	55
2,3,4,7,8-PeCDF	12	25	24	27
1,2,3,4,7,8-HxCDF	32	71	73	44
1,2,3,6,7,8-HxCDF	7	16	15	12
1,2,3,7,8,9-HxCDF	1.3	2.8	2.6	1.7
2,3,4,6,7,8-HxCDF	0.87	1.9	2	1.3
1,2,3,4,6,7,8-HpCDF	9.1	19	19	15
1,2,3,4,7,8,9-HpCDF	8.1	19	20	14
OCDF	31	76	71	81
Total 2,3,7,8-CDD[a]	1.02	2.21	2.45	0.7
Total 2,3,7,8-CDF[a]	152.37	341.7	339.6	303
Total I-TEQ_{DF}[a]	14.2	30.5	30.2	27.7
Total TEQ_{DF}-WHO_{98}[a]	14.1	30.4	30.2	27.6
Total TCDD	ND (0.006)	ND (0.009)	ND (0.009)	--
Total PeCDD	ND (0.070)	ND (0.009)	ND (0.009)	--
Total HxCDD	ND (0.046)	ND (0.064)	ND (0.074)	--
Total HpCDD	0.22	0.48	0.56	--
Total OCDD	0.92	2	2.2	0.65
Total TCDF	64	150	140	--
Total PeCDF	75	240	240	--
Total HxCDF	68	140	140	--
Total HpCDF	24	53	54	--
Total OCDF	31	76	71	81
Total CDD/CDF[a]	263.14	661.48	647.76	--

[a]Calculated assuming nondetect values were zero.

ND = Not detected (value in parenthesis is the reported detection limit)
-- = No information given

Sources: Rappe et al. (1991); Rappe (1993).

Although the origin of the CDFs in graphite electrode sludge is uncertain, chlorination of the cyclic aromatic hydrocarbons (such as dibenzofuran) present in the coal tar used as a binding agent in the graphite electrodes has been proposed as the primary source (Strandell et al., 1994).

For this reason, sludges produced using metal electrodes were not expected to contain CDFs. However, results of an analysis of metal electrode sludge from a facility in Sweden, analyzed as part of the Swedish Dioxin Survey, showed that the sludge contained high levels of CDFs (similar to those of the graphite sludge) and primarily nondetectable levels of CDDs (Strandell et al., 1994). The sludge showed the same type of CDF congener pattern reported by Rappe et al. (1991) and Rappe (1993). Strandell et al. suggested that chlorination of polyaromatic hydrocarbons present in the rubber linings of the electrolytic cell may have produced the CDFs found in the one sample analyzed.

Although EPA does not regulate CDDs/CDFs specifically, it issued restrictions under RCRA on the land disposal of wastewater and sludges generated by chlorine manufacturers that use the mercury cell process and the diaphragm process (with graphite electrodes) (waste codes K071, K073, and K106) (40 CFR 268).

The Chlorine Chemistry Council (CCC), a trade association representing manufacturers that produce and/or use chlorine, sampled the treated wastewater discharges to surface waters at seven chlor-alkali facilities in the U.S. (CCC, 2004). The results of this study are presented in Table 8-6. The measurements are intended to represent wastewater discharges in both 2000 and 1995. As indicated in Table 8-6, 1.79 g TEQ_{DF}-WHO_{98} (1.81 g I-TEQ) were released to water from chlor-alkali facilities in 2000 and 1995. The emission estimates for 2000 and 1995 are assigned a high confidence rating, because they were derived from the testing of chlor-alkali facility treated wastewater.

The CCC reported on air emissions from two chlor-alkali production facilities in 2000 (CCC, 2004). Table 8-7 summarizes the CDD/CDF congener-specific and TEQ annual releases to air from the Dow Chemical chlor-alkali facility in Midland, MI, and the PPG Industries facility in Natrium, WV. Total releases to air in 2000 were 0.08 g TEQ_{DF}-WHO_{98} (0.08 g I-TEQ). There are no data showing air releases from chlor-alkali facilities in 1995 and 1987. A high confidence rating is to assigned the estimate for 2000 because it is based on actual measurements of chlor-alkali facilities.

8.2.2. Manufacture of Chlorine Derivatives and Metal Chlorides

The limited sampling of chlorine-derivative products indicates that they contain very low, if any, concentrations of CDDs/CDFs. Rappe et al. (1990b) analyzed a sample of chlorine bleach consisting of 4.4% sodium hypochlorite. Most of the 2,3,7,8-substituted CDD/CDF congeners were below the limits of detection (0.3 to 7 pg/L for all congeners except OCDD and OCDF, which were 12 and 20 pg/L, respectively). No 2,3,7,8-substituted CDDs were detected. Tetra-, penta-, and hexa-CDFs were detected at levels of 13 pg/L or lower. The TEQ content of the sample was 4.9 pg I-TEQ_{DF}/L. Hutzinger and Fiedler (1991b) reported finding no CDDs/CDFs at

Table 8-6. Releases of dioxin-like compounds in wastewater discharges from chlor-alkali and mixed chemical manufacturing facilities to surface water in reference years 2000 and 1995

Congener	Occidental Chemical Corporation						PPG Industries	Total
	Battleground, TX	Deer Park, TX	Delaware City, DE	Hahnville, LA	Mobile, AL	Muscle Shoals, AL	Natrium, WV	
2,3,7,8 TCDD	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.02
1,2,3,7,8 PeCDD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2,3,4,7,8 HxCDD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2,3,6,7,8 HxCDD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2,3,7,8,9 HxCDD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2,3,4,6,7,8 HpCDD	0.00	0.08	0.00	0.01	0.00	0.00	0.22	0.31
OCDD	0.48	21.50	4.09e-03	0.10	1.15e-03	1.13e-09	3.13	25.22
2,3,7,8 TCDF	0.00	0.63	1.02e-03	0.19	2.88e-04	3.94e-08	0.06	0.89
1,2,3,7,8 PeCDF	0.00	1.20	0.00	0.90	0.00	1.33e-07	0.06	2.16
2,3,4,7,8 PeCDF	0.00	0.21	0.00	0.85	0.00	7.99e-08	0.33	1.39
1,2,3,4,7,8 HxCDF	0.00	2.11	0.00	2.96	0.00	1.85e-07	0.11	5.18
1,2,3,6,7,8 HxCDF	0.00	0.38	0.00	1.18	0.00	9.76e-08	0.00	1.56
1,2,3,7,8,9 HxCDF	0.00	2.03e-03	0.00	0.63	0.00	2.29e-08	0.00	0.63
2,3,4,6,7,8 HxCDF	0.00	0.00	0.00	0.60	0.00	3.28e-08	0.00	0.60
1,2,3,4,6,7,8 HpCDF	0.00	0.59	2.31e-03	4.47	6.49e-04	1.32e-07	0.15	5.22
1,2,3,4,7,8,9 HpCDF	0.00	5.66e-03	0.00	0.69	0.00	6.30e-08	0.00	0.69
OCDF	0.00	4.88	0.00	1.75	0.00	1.34e-07	0.66	7.29
Total I-TEQ	4.83e-04	0.53	1.29e-04	1.08	3.64e-05	8.65e-08	0.19	1.80
Total TEQ_{DF}-WHO_{98}	4.83e-05	0.51	1.26e-04	1.08	3.54e-05	8.63e-08	0.19	1.59

Source: CCC (2004).

a DL of 4 µg/kg in chlorine gas or in samples of 10% sodium hypochlorite, 13% sodium hypochlorite, and 31 to 33% hydrochloric acid at a DL of 1 µg/kg.

Hutzinger and Fiedler (1991b) reported the results of analyses of samples of ferric trichloride ($FeCl_3$), aluminum trichloride ($AlCl_3$), copper chloride ($CuCl_2$), cuprous chloride (CuCl), silicon tetrachloride ($SiCl_4$), and titanium tetrachloride ($TiCl_4$) for their HpCDF, OCDF, HpCDD, and OCDD content. The sample of $FeCl_3$ contained HpCDF and OCDF in the low micrograms per kilogram range, but no HpCDD or OCDD was detected at a DL of 0.02 µg/kg. One of the two samples of $AlCl_3$ analyzed also contained a low (µg/kg) concentration of OCDF. The samples of $CuCl_2$ and CuCl contained concentrations of HpCDF, OCDF, and OCDD of less than 1 µg/kg. The results are presented in Table 8-8.

Table 8-7. Congener-specific and TEQ annual releases to air (g/yr) from chlor-alkali and mixed chemical production facilities in 2000

Congener	Dow Chemical Co. Midland, MI	PPG Industries Natrium, WV
2,3,7,8-TCDD	0.027	0.003
1,2,3,7,8-PeCDD	0.004	0.000
1,2,3,4,7,8-HxCDD	0.008	0.000
1,2,3,6,7,8-HxCDD	0.000	0.002
1,2,3,7,8,9-HxCDD	0.003	0.002
1,2,3,4,6,7,8-HpCDD	0.020	0.087
OCDD	0.086	0.208
2,3,7,8-TCDF	0.023	0.044
1,2,3,7,8-PeCDF	0.009	0.003
2,3,4,7,8-PeCDF	0.008	0.030
1,2,3,4,7,8-HxCDF	0.066	0.044
1,2,3,6,7,8-HxCDF	0.000	0.006
1,2,3,7,8,9-HxCDF	0.002	0.006
2,3,4,6,7,8-HxCDF	0.009	0.022
1,2,3,4,6,7,8-HpCDD	0.148	0.142
1,2,3,4,7,8,9-HpCDD	0.028	0.039
OCDF	0.225	0.064
Total I-TEQ_{DF}	0.047	0.034
Total TEQ_{DF}-WHO_{98}	0.049	0.033

Source: Chlorine Chemistry Council (2004).

8.3. MANUFACTURE OF HALOGENATED ORGANIC CHEMICALS

Several chemical production processes generate CDDs/CDFs (Versar, Inc., 1985; Hutzinger and Fiedler, 1991b). CDDs/CDFs can be formed during the manufacture of chlorophenols, chlorobenzenes, and chlorobiphenyls (Versar, 1985; Ree et al., 1988). Consequently, disposal of industrial wastes from manufacturing facilities producing these compounds may result in the release of CDDs/CDFs to the environment. Also, the products themselves may contain these compounds, and their use or consumption may result in additional releases to the environment.

CDD/CDF congener distribution patterns indicative of noncombustion sources have been observed in sediments in southwest Germany and the Netherlands. According to Ree et al. (1988), the congener patterns found suggest that wastes from the production of chlorinated organic compounds may be important historical sources of CDD/CDF contamination in these

Table 8-8. CDD/CDF concentrations (µg/kg) in metal chlorides

Congener group	$FeCl_3$	$AlCl_3$[a]	$AlCl_3$[a]	$CuCl_2$	CuCl	$TiCl_4$	$SiCl_4$
Total TCDD	--	--	--	--	--	--	--
Total PeCDD	--	--	--	--	--	--	--
Total HxCDD	--	--	--	--	--	--	--
Total HpCDD	ND	ND	ND	0.03	ND	ND	ND
Total OCDD	ND	ND	0.1	0.60	0.03	ND	ND
Total TCDF	--	--	--	--	--	--	--
Total PeCDF	--	--	--	--	--	--	--
Total HxCDF	--	--	--	--	--	--	--
Total HpCDF	12	ND	ND	0.10	0.08	ND	ND
Total OCDF	42	ND	34.0	0.50	0.20	ND	ND

[a]$AlCl_3$ was tested twice.

ND = Not detected; detection limit of 0.02 µg/kg
-- = No information given

Source: Hutzinger and Fiedler (1991b).

regions. The production and use of many of the chlorophenols, chlorophenoxy herbicides, and PCB products are now banned or strictly regulated in most countries. However, these products may have been a source of the environmental contamination that occurred prior to the 1970s and may continue to be a source of environmental releases under certain limited use and disposal conditions (Rappe, 1992b).

8.3.1. Chlorophenols

Chlorophenols have been widely used for a variety of pesticidal applications. The higher-chlorinated phenols (tetrachlorophenol and pentachlorophenol [PCP]) and their sodium salts have been used primarily for wood preservation. The lower-chlorinated phenols have been used primarily as chemical intermediates in the manufacture of other pesticides. For example, 2,4-dichlorophenol is used to produce the herbicides 2,4-dichlorophenoxyacetic acid (2,4-D), 4-(2,4-dichlorophenoxy)butanoic acid (2,4-DB), 2-(2,4-dichlorophenoxy)-propanoic acid (2,4-DP), Nitrophen, Genite, and Zytron and 2,4,5-trichlorophenol was used to produce hexachlorophene, 2,4,5-T, Silvex, Erbon, Ronnel, and Gardona (Gilman et al., 1988; Hutzinger and Fiedler, 1991b). (Sections 8.3.7 and 8.3.8 contain information on EPA actions to control CDD/CDF contamination of pesticides, including PCP and its salts, and to obtain additional data on CDD/CDF contamination of pesticides.)

The two major commercial methods used to produce chlorophenols are (1) electrophilic chlorination of molten phenol by chlorine gas in the presence of catalytic amounts of a metal chloride and organic chlorination promoters and stabilizers, and (2) alkaline hydrolysis of chlorobenzenes under heat and pressure using aqueous methanolic sodium hydroxide. Other manufacturing methods include conversion of diazonium salts of various chlorinated anilines and chlorination of phenolsulfonic acids and benzenesulfonic acids, followed by the removal of the sulfonic acid group (Gilman et al., 1988; Hutzinger and Fiedler, 1991b).

Because of the manufacturing processes employed, commercial chlorophenol products can contain appreciable amounts of impurities (Gilman et al., 1988). During the direct chlorination of phenol, CDDs/CDFs can form either by the condensation of tri-, tetra-, and pentachlorophenols or by the condensation of chlorophenols with hexachlorocyclohexadienone (which forms from excessive chlorination of phenol). During alkaline hydrolysis of chlorobenzenes, CDDs/CDFs can form through chlorophenate condensation (Ree et al., 1988; Gilman et al., 1988; Hutzinger and Fiedler, 1991b).

The limited information on CDD/CDF concentrations in chlorophenols published in the 1970s and early 1980s was compiled by Versar, Inc. (1985) and Hutzinger and Fiedler (1991b). The results of several major studies cited by these reviewers (Firestone et al., 1972; Rappe et al., 1978a, b) are presented in Table 8-9. Typically, CDDs/CDFs were not detected in mono- and dichlorophenols but were reported in tri- and tetrachlorophenols. More recent results of testing of 2,4-dichlorophenol, performed in response to the Toxic Substances Control Act (TSCA) dioxin/furan test rule, showed no detectable concentrations of 2,3,7,8-substituted tetra- through hepta-CDD/CDFs.

Other than a study by Hagenmaier (1986), which reported finding 2,3,7,8-TCDD at a concentration of 0.3 µg/kg in a sample of 2,3,4,5-tetrachlorophenol, no more recent data on concentrations of CDDs and CDFs could be found in the literature for the mono- through tetrachlorophenols. Tables 8-10 and 8-11 present summaries of several studies that reported CDD/CDF concentrations in PCP and in PCP-Na products, respectively. Many of these studies do not report congener-specific concentrations, and many are based on products obtained from non-U.S. sources.

8.3.1.1. *Regulatory Actions for Chlorophenols*

Section 8.3.8 of this report describes regulatory actions taken by EPA to control the manufacture and use of chlorophenol-based pesticides. In the mid-1980s, EPA's Office of Solid Waste (OSW) promulgated, under RCRA, land disposal restrictions on wastes (wastewaters and nonwastewaters) resulting from the manufacture of chlorophenols (40 CFR 268). Table 8-12 lists all wastes in which CDDs/CDFs are specifically regulated by EPA as hazardous

Table 8-9. CDD/CDF concentrations (mg/kg) in mono- through tetrachlorophenols

Congener/ congener group	2-CP[a]	2,4-DCP[a]	2,6-DCP[a]	2,4,5-TrCP (Na salt)[a]	2,4,5-TrCP[a]	2,4,6-TrCP[a]	2,4,6-TrCP (Na salt)[b]	2,3,4,6-TeCP[a]	2,3,4,6-TeCP (Na salt)[b]
Total TCDD	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02) to 14	ND (0.02) to 6.5	ND (0.02) to 49	<0.02	ND (0.02)	0.7
Total PeCDD	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02) to 1.5	ND (0.02)	<0.03	ND (0.02)	5.2
Total HxCDD	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	<0.03	ND (0.02) to 15	9.5
Total HpCDD	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	<0.1	ND (0.02) to 5.1	5.6
Total OCDD	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	<0.1	ND (0.02) to 0.17	0.7
Total TCDF	+	ND	ND	ND	ND	+	1.5	+	0.5
Total PeCDF	ND	ND	ND	ND	ND	+	17.5	+	10
Total HxCDF	ND	ND	ND	ND	ND	+	36	+	70
Total HpCDF	ND	ND	ND	ND	ND	ND	4.8	+	70
Total OCDF	ND	ND	ND	ND	ND	ND	--	+	10
TOTAL	--	--	--	--	--	--	--	--	--

[a]Source: Firestone et al. (1972); because of poor recoveries, the authors stated that actual CDD/CDF levels may have been considerably higher than those reported.

[b]Sources: Rappe et al. (1978a, b); common Scandinavian commercial chlorophenols.

ND = Not detected (value in parenthesis is the detection limit, if reported)
+ = Detected but not quantified
-- = No information given

Table 8-10. CDD/CDF concentrations (historical and current) (µg/kg) in technical-grade pentachlorophenol (PCP) products

Congener/ congener group	1973[a]	1978[b]	1979[c]	1984[d]	1985[e]	1986[e]	1987[f]	1987[g]	1985–88[h]	1991[i]	1988–99[e]	1988–99[j]	Un-known[k]
2,3,7,8-TCDD	--	--	--	ND (10)	ND (0.05)	ND (0.05)	ND (0.03)	ND (0.05)	ND (0.05)	ND	--	ND (0.5)	ND (10)
1,2,3,7,8-PeCDD	--	--	--	ND (10)	ND (1)	ND (1)	1	2	ND (1)	ND	--	--	ND (10)
1,2,3,4,7,8-HxCDD	--	--	--	--	6	8	ND (1)	ND (1)	8	--	--	--	ND (10)
1,2,3,6,7,8-HxCDD	--	--	--	2,200	2,565	1,532	831	1,480	600	--	--	--	860
1,2,3,7,8,9-HxCDD	--	--	--	100	44	28	28	53	13	--	--	--	20
1,2,3,4,6,7,8-HpCDD	--	--	--	100,000	210,000	106,000	78,000	99,900	89,000	--	--	--	36,400
OCDD	--	--	--	610,000	1,475,000	930,000	733,000	790,000	2,723,000	1,100,000	--	--	296,810
2,3,7,8-TCDF	--	--	--	ND (10)	ND (0.5)	ND (0.5)	ND (0.1)	ND (0.1)	ND (0.5)	ND	--	--	ND (10)
1,2,3,7,8-PeCDF	--	--	--	--	ND (1)	ND (1)	0.5	0.2	ND (1)	ND	--	--	ND (10)
2,3,4,7,8-PeCDF	--	--	--	--	ND (1)	ND (1)	1.5	0.9	ND (1)	ND	--	--	ND (10)
1,2,3,4,7,8-HxCDF	--	--	--	--	49	34	125	163	67	--	--	--	200
1,2,3,6,7,8-HxCDF	--	--	--	--	5	4	ND (1)	ND (1)	2	--	--	--	ND (20)
1,2,3,7,8,9-HxCDF	--	--	--	--	5	ND (1)	32	146	ND (1)	--	--	--	ND (20)
2,3,4,6,7,8-HxCDF	--	--	--	--	ND (1)	ND (1)	ND (1)	ND (1)	ND (1)	--	--	--	ND (20)
1,2,3,4,6,7,8-HpCDF	--	--	--	--	34,000	29,000	11,280	19,940	22,000	--	--	--	2,000
1,2,3,4,7,8,9-HpCDF	--	--	--	--	4,100	6,200	637	980	3,400	--	--	--	140
OCDF	--	130,000	--	130,000	222,000	233,000	118,000	137,000	237,000	170,000	--	--	19,940
Total 2,3,7,8-CDD[1]	--	--	--	712,300	1,687,615	1,037,568	811,860	891,435	2,812,621	1,100,000	--	--	334,090
Total 2,3,7,8-CDF[1]	--	--	--	130,000	260,159	268,238	130,076	158,230	262,469	170,000	--	--	22,280
Total I-TEQ_{DF}[1]	--	--	--			2,735	1,853	2,321	4,173	≥1,270	--	--	810
Total TEQ_{DF}-WHO_{98}[1]	--	--	--	1,970	4,445		1,088	1,488		>127	--	--	525
				1,304	2,918	1,689			1,509				
Total TCDD	ND (20)	--	--	ND (10)	ND	ND	1.9	0.4	ND	ND (10)	ND (1)	ND	--
Total PeCDD	ND (30)	--	--	ND (10)	ND	ND	6.5	15.2	ND	ND (10)	ND (10)	3	--
Total HxCDD	5,500	--	10,100	4,500	4,694	2,925	1,700	3,300	912	8,900	1,440	1,490	--
Total HpCDD	98,000	--	296,000	135,000	283,000	134,000	154,000	198,000	117,000	130,000	55,560	48,430	--
Total OCDD	220,000	--	1,386,000	610,000	1,475,000	930,000	733,000	790,000	2,723,000	1,100,000	--	191,700	--
Total TCDF	40	900	--	ND (10)	6	ND	0.8	0.4	ND	ND (10)	ND (10)	48	--
Total PeCDF	250	4,000	1,400	--	10	3	141	343	200	ND (10)	ND (10)	520	--
Total HxCDF	22,000	32,000	9,900	--	1,982	1,407	4,300	13,900	1,486	14,000	3,070	13,650	--
Total HpCDF	150,000	120,000	88,000	62,000	125,000	146,000	74,000	127,000	99,000	36,000	36,530	76,090	--
Total OCDF	160,000	130,000	43,000	130,000	222,000	233,000	118,000	137,000	237,000	170,000	--	136,310	--
Total CDD/CDF[1]	655,790	286,900	1,834,400	941,500	2,111,692	1,447,335	1,085,150	1,269,559	3,178,598	1,458,900	960,000	468,241	--

[a]Source: Buser and Bosshardt (1976); mean of 10 samples of "high" CDD/CDF-content PCP received from Swiss commercial sources in 1973.

[b]Source: Rappe et al. (1978b); sample of U.S. origin, "presumably prepared by alkaline hydrolysis of hexachlorobenzene."

[c]Source: U.S. Department of Health and Human Services (1989); composite of technical-grade materials produced in 1979 by Monsanto Industrial Chemical Co. (St. Louis, MO), Reichhold Chemicals, Inc. (White Plains, NY), and Vulcan Materials Co. (Birmingham, AL).

Table 8-10. CDD/CDF concentrations (historical and current) in technical-grade pentachlorophenol (PCP) products (µg/kg) (continued)

[d] Source: Cull et al. (1984); mean of four "recent" production batches from each of two manufacturers of technical PCP using three different analytical methods; ANOVA showed no statistically significant difference in CDD/CDF concentrations between the eight samples (samples obtained in the United Kingdom).
[e] Source: Letter dated February 7, 1997, from John Wilkinson, Pentachlorophenol Task Force, to Matthew Lorber, U.S. EPA; average of monthly batch samples for the period January 1987 to August 1996.
[f] Source: Hagenmaier and Brunner (1987); sample of Witophen P (Dynamit Nobel - Lot no. 7777) (obtained in Germany).
[g] Source: Hagenmaier and Brunner (1987); sample of PCP produced by Rhone Poulenc (obtained in Germany).
[h] Source: Letter dated February 7, 1997, from John Wilkinson, Pentachlorophenol Task Force, to Matthew Lorber, U.S. EPA; samples of "penta" manufactured in 1985, 1986, and 1988.
[i] Source: Harrad et al. (1991); PCP-based herbicide formulation from the New York State Department of Environmental Conservation.
[j] Source: Letter dated March 5, 1997, from Thomas Mitchell, KMG-Bernuth, to Matthew Lorber, U.S. EPA; average of monthly batch samples for the period February 1987 to December 1996 (excluding the following months, for which data were not available: February 1993, January 1992, December 1991, September 1991, December 1988, and September 1988).
[k] Source: Schecter et al. (1997); sample found stored in a barn in Vermont.
[l] Calculated assuming nondetects were zero.

ND = Not detected (value in parenthesis is the detection limit)
-- = No information given

Table 8-11. Historical CDD/CDF concentrations (µg/kg) in pentachlorophenol-Na (PCP-Na)

Congener/congener group	1969[a]	1973[b]	1973[c]	1987[d]	1987[e]	1992[f]	1980s[g]
2,3,7,8-TCDD	--	--	--	0.23	0.51	0.076	ND (1.4)
1,2,3,7,8-PeCDD	--	--	--	18.2	3.2	18.7	28.3
1,2,3,4,7,8-HxCDD	--	--	--	28.3	13.3	96	ND (6.1)
1,2,3,6,7,8-HxCDD	--	--	--	2,034	53	4,410	4,050
1,2,3,7,8,9-HxCDD	--	--	--	282	19	328	ND (1.4)
1,2,3,4,6,7,8-HpCDD	--	--	--	9,100	3,800	175,400	33,800
OCDD	3,600	--	--	41,600	32,400	879,000	81,000
2,3,7,8-TCDF	--	--	--	1.8	0.79	ND (1)	149
1,2,3,7,8-PeCDF	--	--	--	8.2	1.9	ND (4)	319
2,3,4,7,8-PeCDF	--	--	--	6.6	1.1	ND (4)	324
1,2,3,4,7,8-HxCDF	--	--	--	48	4.6	27.6	ND (2.8)
1,2,3,6,7,8-HxCDF	--	--	--	69	1.3	21.9	225
1,2,3,7,8,9-HxCDF	--	--	--	ND (1)	1.3	9.8	480
2,3,4,6,7,8-HxCDF	--	--	--	87	4.6	103	ND (385)
1,2,3,4,6,7,8-HpCDF	--	--	--	699	197	9,650	6,190
1,2,3,4,7,8,9-HpCDF	--	--	--	675	36	2,080	154
OCDF	--	--	--	37,200	4,250	114,600	36,000
Total 2,3,7,8-CDD[h]	--	--	--	53,062.7	36,289	1,059,252.8	118,878.3
Total 2,3,7,8-CDF[h]	--	--	--	38,794.6	4,498.6	126,492.3	43,841
Total I-TEQ_{DF}[h]	--	--	--	452	89.5	3,374	1,201
Total TEQ_{DF}-WHO_{98}[h]	--	--	--	390	58.1	2,489	1,110
Total TCDD	--	140	50	27	52	3.6	1.9
Total PeCDD	--	40	ND (30)	213	31	142.7	140
Total HxCDD	17,000	140	3,400	3,900	230	9,694	14,000
Total HpCDD	9,600	1,600	38,000	18,500	5,800	260,200	100,000
Total OCDD	3,600	4,000	110,000	41,600	32,400	879,000	81,000
Total TCDF	--	ND (20)	ND (20)	82	12	10.1	1,200
Total PeCDF	--	60	40	137	27	88.4	6,400
Total HxCDF	--	1,400	11,000	3,000	90	9,082.3	49,000
Total HpCDF	--	4,300	47,000	13,200	860	75,930	91,000
Total OCDF	--	4,300	26,500	37,200	4,250	114,600	36,000
Total CDD/CDF[h]	30,200	15,980	235,990	117,859	43,752	1,348,751	378,742

[a]Source: Firestone et al. (1972); mean of two samples of PCP-Na obtained in the United States between 1967 and 1969.

[b]Source: Buser and Bosshardt (1976); mean of five samples of "low" CDD/CDF-content PCP-Na received from Swiss commercial sources.

[c]Source: Buser and Bosshardt (1976); sample of "high" CDD/CDF-content PCP-Na received from a Swiss commercial source.

[d]Source: Hagenmaier and Brunner (1987); sample of Dowicide-G purchased from Fluka; sample obtained in Germany.

[e]Source: Hagenmaier and Brunner (1987); sample of Preventol PN (Bayer AG); sample obtained in Germany.

[f]Source: Santl et al. (1994); 1992 sample of PCP-Na from Prolabo, France.

[g]Source: Palmer et al. (1988); sample of a PCP-Na formulation collected from a closed sawmill in California in the late 1980s.

[h]Calculated assuming nondetect values were zero.

ND = Not detected (value in parenthesis is the detection limit)
-- = No information given

Table 8-12. Summary of specific dioxin-containing wastes that must comply with land disposal restrictions[a]

EPA hazardous waste number	Waste description	Land disposal restriction effective date	Regulated waste constituent
F020	Wastes (except wastewater and spent carbon from HCl purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri- or tetrachlorophenol or of intermediates used to produce their pesticide derivatives. (This listing does not include wastes from the production of hexachlorophene from highly purified 2,4,5-trichlorophenol.)	November 8, 1988	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs
F021	Wastes (except wastewater and spent carbon from HCl purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of pentachlorophenol or of intermediates used to produce its derivatives.	November 8, 1988	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs
F022	Wastes (except wastewater and spent carbon from HCl purification) from the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzenes under alkaline conditions.	November 8, 1988	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs
F023	Wastes (except wastewater and spent carbon from HCl purification) from the production of materials on equipment previously used for the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri- and tetrachlorophenols. (This listing does not include wastes from equipment used only for the production or use of hexachlorophene from highly purified 2,4,5-trichlorophenol.)	November 8, 1988	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs
F026	Wastes (except wastewater and spent carbon from HCl purification) from the production of materials on equipment previously used for the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzene under alkaline conditions.	November 8, 1988	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs

Table 8-12. Summary of specific dioxin-containing wastes that must comply with land disposal restrictions[a] (continued)

EPA hazardous waste number	Waste description	Land disposal restriction effective date	Regulated waste constituent
F027	Discarded unused formulations containing tri-, tetra-, or pentachlorophenol or discarded unused formulations containing compounds derived from these chlorophenols. (This listing does not include formulations containing hexachlorophene synthesized from prepurified 2,4,5-trichlorophenol as the sole component.)	November 8, 1988	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs
F028	Residues resulting from the incineration or thermal treatment of soil contaminated with EPA Hazardous Wastes No. F020–F023, F026, and F027	November 8, 1988	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs
F039	Leachate (liquids that have percolated through land-disposed wastes) resulting from the disposal of more than one restricted waste classified as hazardous under Subpart D of 40 CFR 268. (Leachate resulting from the disposal of one or more of the following EPA hazardous wastes and no other hazardous wastes retains its EPA hazardous waste number(s): F020, F021, F022, F026, F027, and/or F028.)	August 8, 1990 (wastewater) May 8, 1992 (nonwastewater)	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs
K043	2,6-Dichlorophenol waste from the production of 2,4-D	June 8, 1989	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs
K099	Untreated wastewater from the production of 2,4-D	August 8, 1988	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs

[a]For wastewater, the treatment standard for all regulated waste constituents except PeCDFs is 0.063 µg/L; the standard for PeCDFs is 0.035 µg/L. For nonwastewater, the treatment standard for all regulated waste constituents is 1 µg/kg. Treatment standards are based on incineration to 99.9999% destruction and removal efficiency.

Source: 40 CFR 268.

constituents, including chlorophenol wastes (waste codes F020 and F021). The regulations prohibit the land disposal of these wastes until they are treated to a level below the routinely achievable DLs for the EPA hazardous waste numbers listed in Table 8-12 for each of the following congener groups: TCDDs, PeCDDs, HxCDDs, TCDFs, PeCDFs, and HxCDFs. Wastes from PCP-based wood-preserving operations (waste codes K001 and F032) are also regulated as hazardous wastes under RCRA (40 CFR 261).

EPA's Office of Water promulgated effluent limitations for facilities that manufacture chlorinated phenols and discharge treated wastewater (40 CFR 414.70). These effluent limitations do not specifically regulate CDDs or CDFs. The effluent limitations for the individually regulated chlorinated phenols are less than or equal to 39 μg/L for facilities that use biological end-of-pipe treatment.

Di- and trichlorophenols are subject to reporting under the dioxin/furan test rule, which is discussed in Section 8.3.7 of this report. Since the effective date of that rule (June 5, 1987), only the 2,4-dichlorophenol isomer has been commercially produced in (or imported to) the United States, and as noted in Table 8-9, no CDDs/CDFs were detected in the product. Testing is required for the other di- and trichlorophenols if manufacture or importation resumes. Similarly, tetrachlorophenols were subject to reporting under the Dioxin/Furan Pesticide Data Call-In (DCI) (discussed in Section 8.3.8 of this report). Since issuance of the DCI, the registrants of tetrachlorophenol-containing pesticide products have elected to no longer support the registration of their products in the United States.

In January 1987, EPA entered into a settlement agreement with PCP manufacturers that set limits, effective in February 1989, on the allowed uses of PCP and its salts and the maximum allowable concentrations of 2,3,7,8-TCDD and HxCDDs. Section 8.3.8 discusses the 1987 PCP settlement agreement and includes estimates of current releases of CDDs/CDFs associated with the use of PCP in the United States. Section 11.3.1 (Chapter 11) provides an estimate of the amount of CDDs/CDFs that may have entered the environment or that are contained in treated wood products as a result of prior use of PCP and PCP-Na.

Since the late 1980s, U.S. commercial production of chlorophenols has been limited to 2,4-dichlorophenol and PCP. As noted above, disposal of wastes generated during the manufacture of chlorophenols is strictly regulated, and thus releases to the environment are expected to be negligible. With regard to releases associated with the use of 2,4-dichlorophenol, no CDDs/CDFs have been detected in 2,4-dichlorophenol. Releases associated with the use of PCP are presented in Sections 8.3.8 and 11.3.1.

8.3.2. Chlorobenzenes

Chlorobenzenes have been produced in the United States since 1909. U.S. production operations were developed primarily to provide chemical raw materials for the production of phenol, aniline, and various pesticides based on the higher-chlorinated benzenes. Because of (incremental) changes in the processes used to manufacture phenol and aniline and the phaseout of highly chlorinated pesticides such as DDT and hexachlorobenzene, U.S. production of chlorobenzenes in 1988 had decreased to 50% of the peak production level, in 1969.

Chlorobenzenes can be produced via three methods: (1) electrophilic substitution of benzene (in liquid or vapor phase) with chlorine gas in the presence of a metal salt catalyst, (2) oxidative chlorination of benzene with HCl at 150 to 300°C in the presence of a metal salt catalyst, and (3) dehydrohalogenation of hexachlorocyclohexane wastes at 200 to 240°C with a carbon catalyst to produce trichlorobenzene, which can be further chlorinated to produce higher-chlorinated benzenes (Ree et al., 1988; Hutzinger and Fiedler, 1991b; Bryant, 1993).

All chlorobenzenes currently manufactured in the United States are produced by the electrophilic substitution process using liquid-phase benzene (i.e., temperature is at or below 80°C). $FeCl_3$ is the most common catalyst employed. Although this method can be used to produce mono- through hexachlorobenzene, the extent of chlorination is controlled to yield primarily monochlorobenzene and dichlorobenzene. The finished product is a mixture of chlorobenzenes, and refined products must be obtained by distillation and crystallization (Bryant, 1993).

CDDs/CDFs can be produced inadvertently during the manufacture of chlorobenzenes by nucleophilic substitution and pyrolysis mechanisms (Ree et al., 1988). The criteria required for production of CDDs/CDFs via nucleophilic substitution are oxygen as a nuclear substituent (i.e., presence of chlorophenols) and production or purification of the substance under alkaline conditions. Formation via pyrolysis requires reaction temperatures above 150°C (Ree et al., 1988; Hutzinger and Fiedler, 1991b). The liquid-phase electrophilic substitution process currently used in the United States does not meet either of these criteria. Although Ree et al. and Hutzinger and Fiedler state that the criteria for formation of CDDs/CDFs via nucleophilic substitution may be present in the catalyst neutralization and purification/distillation steps of the manufacturing process, Opatick (1995) states that the chlorobenzene reaction product in U.S. processes remains mildly acidic throughout these steps.

Table 8-13 summarizes the very limited published information on CDD/CDF contamination of chlorobenzene products. The presence of CDDs/CDFs has been reported in tri-, penta-, and hexachlorobenzene. No CDDs/CDFs have been reported in mono- or dichlorobenzene. Conflicting data exist concerning the presence of CDDs/CDFs in

Table 8-13. CDD/CDF concentrations (µg/kg) in chlorobenzenes

Congener/ congener group	MCBz[a]	1,2-DCBz (for synthesis)[a]	1,2,4-TrCBz ("pure")[b]	Mixed TrCBz (47%)[a]	1,2,4,5-TCBz (99%)[a]	PeCBz (98%)[a]	HCBz (97%)[a]	HCBz[b]
Total TCDD	ND (0.02)		ND (0.1)	0.027			ND (20)	--
Total PeCDD	ND (0.02)	ND (0.02)	ND (0.1)	0.14	ND (0.02) 0.2	ND (0.02)	ND (20)	--
Total HxCDD	ND (0.02)	ND (0.02) 0.3	ND (0.1)	0.259	0.5	ND (0.02) 0.02	ND (20)	--
Total HpCDD	ND (0.02)	ND (0.02)	ND (0.1)	0.253	0.8	0.02	470	--
Total OCDD	ND (0.02)	ND (0.02)	ND (0.1)	0.081	0.4	0.05	6,700	50–212,000
Total TCDF	ND (0.02)	ND (0.02)	ND (0.1)	0.736	0.03	0.02	ND (20)	--
Total PeCDF	ND (0.02)		ND (0.1)	0.272	0.2		ND (20)	--
Total HxCDF	ND (0.02)	ND (0.02)	ND (0.1)	0.091	0.8	ND (0.02)	ND (20)	--
Total HpCDF	ND (0.02)	ND (0.02) 0.3	ND (0.1)	0.03	1.5	ND (0.02) 0.1	455	--
Total OCDF	ND (0.02)	ND (0.02)	ND (0.1)	0.016	2.1	0.1	2,830	350–58,300
Total CDD/CDF	ND	0.8	ND	1.9	6.5	0.3	10,455	400–270,300

[a]Source: Hutzinger and Fiedler (1991b); unpublished results of tests performed at the University of Bayreuth, Germany, and by Dr. H. Hagenmaier.
[b]Source: Villanueva et al. (1974); range of three samples of commercially available HCBz.

ND = Not detected (value in parenthesis is the detection limit, if reported)
-- = No information given

trichlorobenzene. One study (Villanueva et al., 1974) detected no CDDs/CDFs in one sample of 1,2,4-TCBz at a DL of 0.1 µg/kg. Hutzinger and Fiedler (1991b) reported unpublished results of a study by Dr. Hans Hagenmaier showing CDD/CDF congener group concentrations ranging from 0.02 to 0.074 µg/kg in a sample of mixed trichlorobenzene. Because the TCBz examined by Hagenmaier contained about 2% hexachlorocyclohexane, it is reasonable to assume that it was produced by dehydrohalogenation of hexachlorocyclohexane (a manufacturing process not currently used in the United States).

8.3.2.1. *Regulatory Actions for Chlorobenzenes*

EPA determined, as part of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) DCI (discussed in Section 8.3.8), that the 1,4-dichlorobenzene manufacturing processes used in the United States are not likely to form CDDs/CDFs. Mono-, di-, and trichlorobenzene are listed as potential precursor chemicals under the TSCA dioxin/furan test rule and are subject to reporting (see Section 8.3.7). In addition, EPA issued a Significant New Use Rule (SNUR) under Section 5(a)(2) of TSCA on December 1, 1993 (effective January 14, 1994) for pentachlorobenzene and 1,2,4,5-tetrachlorobenzene (Federal Register, 1993c). This rule requires that EPA be notified at least 90 days before the manufacture, import, or processing of either of these compounds in amounts of 10,000 pounds or greater per year per facility for any use. All registrations of pesticide products containing hexachlorobenzene were cancelled in the mid-1980s (Carpenter et al., 1986).

OSW promulgated land disposal restrictions on wastes (i.e., wastewaters and nonwastewaters) resulting from the manufacture of chlorobenzenes (40 CFR 268). Table 8-12 lists all solid wastes for which EPA specifically regulates CDDs and CDFs, including chlorobenzene wastes, as hazardous constituents. The regulations prohibit the land disposal of these wastes until they are treated to a level below the routinely achievable DLs in the waste extract listed in Table 8-12 for each of the following congener groups: TCDDs, PeCDDs, HxCDDs, TCDFs, PeCDFs, and HxCDFs.

EPA's Office of Water promulgated effluent limitations for facilities that manufacture chlorinated benzenes and discharge treated wastewater (40 CFR 414.70). These effluent limitations do not specifically address CDDs and CDFs. The following chlorinated benzenes are regulated: chlorobenzene; 1,2-dichlorobenzene; 1,3-dichlorobenzene; 1,4-dichlorobenzene; 1,2,4-trichlorobenzene; and hexachlorobenzene. The effluent limitations for the individual regulated chlorinated benzenes are less than or equal to 77 µg/L for facilities that use biological end-of-pipe treatment and less than or equal to 196 µg/L for facilities that do not use biological end-of-pipe treatment.

Since at least 1993, U.S. commercial production of chlorobenzenes has been limited to monochlorobenzene, 1,2-dichlorobenzene, 1,4-dichlorobenzene, and, to a much lesser extent, 1,2,4-trichlorobenzene. As noted above, CDD/CDF formation is not expected under the normal operating conditions of the processes currently used in the United States to produce these four chemicals. No tetra-, penta-, or hexachlorinated benzenes are now intentionally produced or used in the United States (Bryant, 1993). Thus, releases of CDDs/CDFs from the manufacture of chlorobenzenes in 1995 were estimated to be negligible. Because the information available on CDD/CDF content of mono- through pentachlorobenzene is very limited and is based primarily on unpublished European data, and because information on the chlorobenzene manufacturing processes in place during 1987 is not readily available, no emission estimates can be made for 1987.

8.3.3. Chlorobiphenyls

PCBs are manufactured by the direct batch chlorination of molten biphenyl in the presence of a catalyst, followed by separation and purification of the desired chlorinated biphenyl fractions. During the manufacture of PCBs, the inadvertent production of CDFs also occurs. This section focuses on levels of CDD/CDF contamination that may have been present in PCB products.

CDFs have been shown to form when PCB-containing transformers and capacitors undergo malfunctions or are subjected to fires that result in accidental combustion of the dielectric fluid. The direct releases of dioxin-like PCBs from sources is reviewed in Chapter 10.

During the commercial production of PCBs, thermal oxidative cyclization under alkaline conditions resulted in the inadvertent production of CDFs in most of the commercial PCB mixtures (Brown et al., 1988; ATSDR, 1993). Bowes et al. (1975a) first reported detection of CDFs in Aroclor products; samples of unused Aroclors manufactured in 1969 and 1970 were found to have CDF (TCDF through HxCDF) concentrations ranging from 0.8 to 2 mg/kg. Bowes et al. used congener-specific analytical methodology and detected 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF at concentrations ranging from 0.11 to 0.33 mg/kg and 0.12 to 0.83 mg/kg, respectively, in unused samples of Aroclor 1254 and Aroclor 1260. The presence of CDDs in commercial PCB mixtures, although at much lower concentrations than those of the CDFs, was reported by Hagenmaier (1987) and Malisch (1994). Table 8-14 presents the CDF and CDD congener group concentrations reported by Bowes et al. (1975a) and those reported in subsequent years for unused PCBs by Erickson (1986), ATSDR (1993), Hagenmaier (1987), and Malisch (1994).

Several researchers have reported concentrations of specific CDD/CDF congeners in commercial PCB mixtures (Bowes et al., 1975b; Brown et al., 1988; Hagenmaier, 1987; Malisch, 1994). Table 8-15 presents the results of these four studies. Only the Hagenmaier and Malisch

Table 8-14. Concentrations of CDD/CDF congener groups in unused commercial polychlorinated biphenyl (PCB) mixtures (mg/kg)

PCB mixture	Year of manufacture	CDD congener group concentrations						CDF congener group concentrations						Source
		TCDD	PeCDD	HxCDD	HpCDD	OCDD	Total CDD	TCDF	PeCDF	HxCDF	HpCDF	OCDF	Total CDF	
Aroclor 1016	1972	--	--	--	--	--	--	ND	ND	ND	--	--	ND	a
Aroclor 1242	--	--	--	--	--	--	--	0.07	0.03	0.003	--	--	0.15	b, c
Aroclor 1242	--	--	--	--	--	--	--	2.3	2.2	ND	--	--	4.5	b, c
Aroclor 1242	--	--	--	--	--	--	--	0.25	0.7	0.81	--	--	1.9	b
Clophen A-30	--	0.0007	ND	0.001	0.006	0.031	0.039	6.377	2.402	0.805	0.108	0.016	9.708	d
Clophen A-30	--	ND	ND	ND	0.005	0.025	0.030	0.713	0.137	0.005	0.001	ND	0.855	e
Aroclor 1248	1969	--	--	--	--	--	--	0.5	1.2	0.3	--	--	22.2352	b
Clophen A-40	--	ND	ND	ND	0.012	0.030	0.042	1.289	0.771	0.144	0.02	0.011		e
Kanechlor 400	--	--	--	--	--	--	--	--	--	--	--	--		b, c
Aroclor 1254	1969	--	--	--	--	--	--	0.1	0.2	1.4	--	--	1.7	a
Aroclor 1254	1970	--	--	--	--	--	--	0.2	0.4	0.9	--	--	1.5	a
Aroclor 1254	--	--	--	--	--	--	--	0.02	0.2	0.6	--	--	0.8	b, c
Aroclor 1254	--	--	--	--	--	--	--	0.05	0.1	0.02	--	--	0.2	b
Clophen A-50	--	ND	ND	ND	0.011	0.027	0.038	5.402	2.154	2.214	0.479	0.069	10.318	e
Aroclor 1260	--	--	--	--	--	--	--	0.3	1	1.1	1.35	--	3.8	b, c
Aroclor 1260	1969	--	--	--	--	--	--	0.1	0.4	0.5	--	--	1	a
Aroclor 1260	--	--	--	--	--	--	--	0.8	0.9	0.5	--	--	2.2	b, c
Aroclor 1260	--	--	--	--	--	--	--	0.2	0.3	0.3	--	--	0.8	a
Clophen A-60	--	0.0004	0.002	0.002	0.003	0.015	0.022	15.786	11.655	4.456	1.517	0.639	34.052	d
Clophen A-60	--	ND	ND	ND	0.014	0.032	0.046	16.34	21.164	7.63	2.522	1.024	48.681	e
Clophen A-60	--	--	--	--	--	--	--	1.4	5	2.2	--	--	8.6	a
Phenoclor DP-6	--	--	--	--	--	--	--	0.7	10	2.9	--	--	13.6	a
Clophen T-64	--	--	--	--	--	--	--	0.3	1.73	2.45	0.82	--	5.4	b
Prodelec 3010	--	--	--	--	--	--	--	1.08	0.35	0.07	--	--	2	b

[a]Source: Bowes et al. (1975a).
[b]Source: Erickson (1986).
[c]Source: ATSDR (1993).
[d]Source: Malisch (1994).
[e]Source: Hagenmaier (1987).

ND = Not detected
-- = No information given

Table 8-15. 2,3,7,8-Substituted congener concentrations in unused polychlorinated biphenyl (PCB) mixtures (µg/kg)

Congener	Congener concentrations in Clophens						Congener concentrations in Aroclors									
	A-30[a]	A-30[b]	A-40[b]	A-50[b]	A-60[a]	A-60[b]	1016[c]	1242[c]	1248[d]	1254[c]	1254[c]	1254[c]	1254[d]	1260[c]	1260[c]	1260[c]
2,3,7,8-TCDD	ND	ND	ND	ND	ND	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,7,8-PeCDD	ND	ND	ND	ND	0.1	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,4,7,8-HxCDD	ND	ND	ND	ND	0.2	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,6,7,8-HxCDD	0.8	ND	ND	ND	ND	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,7,8,9-HxCDD	ND	ND	ND	ND	ND	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,4,6,7,8-HpCDD	5.6	2.4	4.4	5.3	2.5	6.8	--	--	--	--	--	--	--	--	--	--
OCDD	31.1	24.7	30.3	26.9	14.9	32.3	--	--	--	--	--	--	--	--	--	--
2,3,7,8-TCDF	1,032.6	36.9	250.2	1,005.7	2,287.7	3,077.2	0.1	40.1	330	28	20.9	55.8	110	63.5	6.88	29
1,2,3,7,8-PeCDF	135.8	14.9	52.7	155.2	465.2	1,750.8	--	--	--	--	--	--	--	--	--	--
2,3,4,7,8-PeCDF	509.2	13.1	171.3	407.5	1,921.9	2,917.0	1.75	40.8	830	110	179	105	120	135	58.2	112
1,2,3,4,7,8-HxCDF	301.4	1.9	48.4	647.5	1,604.2	2,324.1	--	--	--	--	--	--	--	--	--	--
1,2,3,6,7,8-HxCDF	65.3	0.8	19.6	227.5	157.6	351.3	--	--	--	--	--	--	--	--	--	--
1,2,3,7,8,9-HxCDF	ND	ND	0.7	8.3	42.8	19	0.08	0.26	--	28.8	28.7	19.4	--	5.1	9.7	10.7
2,3,4,6,7,8-HxCDF	50.6	0.1	6.8	62.5	369.5	4,08.3	--	--	--	--	--	--	--	--	--	--
1,2,3,4,6,7,8-HpCDF	43.7	0.6	7	205.5	480.6	1,126.1	--	--	--	--	--	--	--	--	--	--
1,2,3,4,7,8,9-HpCDF	22.5	ND	2.8	72.2	321.7	304	--	--	--	--	--	--	--	--	--	--
OCDF	15.7	ND	11.4	69.2	639.2	1,024.3	--	--	--	--	--	--	--	--	--	--
Total TCDD	0.7	ND	ND	ND	0.4	ND	--	--	--	--	--	--	--	--	--	--
Total PeCDD	ND	ND	ND	ND	2	ND	--	--	--	--	--	--	--	--	--	--
Total HxCDD	1.2	ND	ND	ND	1.8	ND	--	--	--	--	--	--	--	--	--	--
Total HpCDD	5.6	5.4	11.6	11	3	13.5	--	--	--	--	--	--	--	--	--	--
Total OCDD	31.1	24.7	30.3	26.9	14.9	32.3	--	--	--	--	--	--	--	--	--	--
Total TCDF	6,376.6	713	1,289.4	5,402.3	15,785.7	16,340	--	--	--	--	--	--	--	--	--	--
Total PeCDF	2,402.4	136.5	770.8	2,153.7	11,654.6	21,164	--	--	--	--	--	--	--	--	--	--
Total HxCDF	804.8	5.1	143.6	2,213.8	4,455.8	7,630.2	--	--	--	--	--	--	--	--	--	--
Total HpCDF	108.3	0.8	19.5	478.8	1,517	2,522.3	--	--	--	--	--	--	--	--	--	--
Total OCDF	15.7	ND	11.4	69.2	639.2	1,024.3	--	--	--	--	--	--	--	--	--	--
Total CDD/CDF[e]	9,746.4	885.5	2,276.6	10,355.7	34,074.4	48,726.6	--	--	--	--	--	--	--	--	--	--
Total I-TEQ_{DF}[e]	407.2	11.3		409.6	1,439.2	2,179	--	--	--	--	--	--	--	--	--	--
Total TEQ_{DF}-WHO_{98}[e]	407.2	11.3		409.5	1,439	2,178	--	--	--	--	--	--	--	--	--	--

[a]Source: Malisch (1994).
[b]Source: Hagenmaier (1987).
[c]Source: Brown et al. (1988).
[d]Source: Bowes (1975b).
[e]Calculated assuming nondetect values were zero.

ND = Not detected
-- = No information given

studies, however, reported the concentrations of all 2,3,7,8-substituted CDDs and CDFs. It is evident from the table that major variations are found in the levels of 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF in the Clophen mixtures reported by Hagenmaier and Malisch and the corresponding levels in the Aroclor mixtures reported by Bowes et al. and Brown et al.

Brown et al. (1988) compared the levels of 2,3,7,8-TCDF; 2,3,4,7,8-PeCDF; and 1,2,3,7,8,9-HxCDF in used samples (from previously used capacitors and transformers) and unused samples of Aroclor 1016, 1242, 1254, and 1260. The concentration ranges reported for the used and unused Aroclors were similar, leading Brown et al. (1988) to conclude that CDFs are not formed during the normal use of PCBs in electrical equipment.

8.3.4. Ethylene Dichloride/Vinyl Chloride Monomer/Polyvinyl Chloride Manufacturing

In the United States the manufacture of PVC is an integrated manufacturing process. This means that most manufacturing facilities produce all the precursors and chemical intermediates necessary to manufacture PVC as well as PVC resins and products. For example, ethylene dichloride (EDC) is used to produce vinyl chloride monomer (VCM). VCM is then converted to PVC resins. The resins are used to manufacture various PVC products.

PVC resins are produced from the polymerization of VCM. VCM is typically produced by the thermal dehydrochlorination (commonly known as cracking) of EDC. The cracking of EDC requires elevated pressure (20 to 30 atm) and temperature (450 to 650°C) and yields VCM and HCl at about a 1:1 molar ratio. EDC is produced by two different methods: (1) direct chlorination of ethylene with chlorine in the presence of a catalyst at a temperature of 50 to 60°C and pressure of 4 to 5 atm, and (2) oxychlorination, which involves reaction of ethylene with HCl and oxygen in the presence of a catalyst at temperatures generally less than 325°C. The primary source of HCl for the oxychlorination process is the HCl produced from the cracking of EDC to form VCM. Most VCM manufacturing facilities are integrated with EDC production facilities (The Vinyl Institute, 1998).

Although it has been generally recognized that CDDs/CDFs can be formed during the manufacture of EDC, VCM, and PVC, manufacturers and environmental public interest groups have disagreed as to the quantity of CDDs/CDFs that are formed and released to the environment in wastes and possibly in PVC products. Although EPA regulates emissions from EDC/VCM production facilities under the Clean Water Act (40 CFR 61), the Clean Air Act (40 CFR 414), and RCRA (40 CFR 268, waste codes F024, K019, and K020), CDDs/CDFs are not specifically regulated pollutants; as a consequence, monitoring data for CDDs/CDFs in emissions were generally lacking until the early 1990s.

Greenpeace International initially determined that CDDs and CDFs can be formed during the manufacture of PVC. In 1993, it issued a report on CDD/CDF emissions associated with the

production of EDC/VCM (Greenpeace, 1993). Greenpeace estimated that 5 to 10 g I-TEQ_{DF} were released to the environment (air, water, and ground combined) annually for every 100,000 metric tons of VCM produced. This emission factor was based on data gathered by Greenpeace on four European plants. The Vinyl Institute responded with a critique of the Greenpeace report (ChemRisk, 1993). Miller (1993) summarized the differing views of the two parties. According to Miller, European PVC manufacturers claimed the emission factor was 0.01 to 0.5 g I-TEQ_{DF}/100,000 metric tons of VCM, but although Greenpeace and ChemRisk used basically the same monitoring information to develop their emission factors, Greenpeace adjusted the emission factor to account for unquantified fugitive emissions and waste products that contain unspecified amounts of CDDs/CDFs.

In 1995, Greenpeace issued a second report (Stringer et al., 1995) reiterating the organization's concern that the generation and emission of CDDs/CDFs may be significant and urging that further work be initiated to quantify and prevent emissions. Stringer et al. presented the results of analyses of three samples of chlorinated wastes obtained from U.S. EDC/VCM manufacturing facilities. The three wastes were characterized according to EPA hazardous waste classification numbers as an F024 waste (waste from the production of short-chain aliphatics by free radical-catalyzed processes), a K019 waste (heavy ends from the distillation of ethylene from EDC production), and a probable K020 waste (heavy ends from distillation of vinyl chloride in VCM manufacture). Table 8-16 presents the analytical results reported by Stringer et al. This study acknowledged that because EDC/VCM production technologies and waste treatment and disposal practices are very site-specific, the limited information available on CDD/CDF generation and emissions made it difficult to quantify amounts of CDDs/CDFs generated and emitted.

In response to the lack of definitive studies, and at the recommendation of EPA, U.S. PVC manufacturers began an extensive monitoring program, the Dioxin Characterization Program (DCP). The objective of the DCP was to evaluate the extent and magnitude of potential CDD/CDF releases to air, water, and land, as well as the potential for PVC product contamination. Manufacturers performed emissions and product testing at several facilities that were representative of various manufacturing and process control technologies. In 1998, The Vinyl Institute completed studies of CDD/CDF releases in wastewater, wastewater treatment plant solids, and stack gases, as well as studies of the CDD/CDF content of products (PVC resins and EDC sold as products) (The Vinyl Institute, 1998).

In September 2002, the CCC met to review dioxin release estimates for 2000 submitted by various EDC/VCM manufacturing facilities. Several companies provided stack gas emissions and wastewater release data as well as a discussion of how they generated the release and transfer estimates reported in the Toxics Release Inventory for 2000. In March 2004, the CCC met again

Table 8-16. Reported CDD/CDF concentrations (µg/kg) in wastes from polyvinyl chloride (PVC) manufacture

Congener/congener group	F024 waste	K019 waste	K020 waste
2,3,7,8-TCDD	0.37	260	0.06
1,2,3,7,8-PeCDD	0.14	890	0.05
1,2,3,4,7,8-HxCDD	0.3	260	0.08
1,2,3,6,7,8-HxCDD	0.14	330	0.06
1,2,3,7,8,9-HxCDD	0.11	620	0.07
1,2,3,4,6,7,8-HpCDD	4.2	920	0.89
OCDD	15	1,060	3
2,3,7,8-TCDF	0.91	680	0.44
1,2,3,7,8-PeCDF	9.5	975	1.8
2,3,4,7,8-PeCDF	1.6	1,050	0.58
1,2,3,4,7,8-HxCDF	110	10,100	11
1,2,3,6,7,8-HxCDF	24	9,760	2.4
1,2,3,7,8,9-HxCDF	9.5	21,800	1.3
2,3,4,6,7,8-HxCDF	3.1	930	0.89
1,2,3,4,6,7,8-HpCDF	250	13,400	38
1,2,3,4,7,8,9-HpCDF	51	1,340	6
OCDF	390	43,500	650
Total 2,3,7,8-CDD	20.3	4,340	4.21
Total 2,3,7,8-CDF	849.6	103,535	712.4
Total I-TEQ_{DF}	20	5,928	3.2
Total TEQ_{DF}-WHO_{98}	19.7	6,333	2.6
Total TCDD	3.1	1,230	1.9
Total PeCDD	3.6	3,540	1.7[a]
Total HxCDD	1.3	3,950	1.7
Total HpCDD	5	1,270	3
Total OCDD	15	1,060	6
Total TCDF	15	20,600	11
Total PeCDF	65	45,300	27
Total HxCDF	300	63,700	58
Total HpCDF	450	16,600	650
Total OCDF	390	43,500	
Total CDD/CDF	1,248	200,750	760.3

[a]Congener group concentration reported in source is not consistent with reported congener concentrations.

Source: Stringer et al. (1995).

to discuss the results, to date, of its CDD/CDF data validation study for PVC/EDC/VCM and chlor-alkali facilities. The study's goal was to provide facility-specific water, air, and land release estimates for 2000 and 2002. As of the date of this report, data validation studies were provided for 17 of 20 facilities in the CCC that were considered chlor-alkali production facilities and PVC/EDC/VCM manufacturing plants.

8.3.4.1. *Water Releases*

This section presents estimates of releases of dioxin-like compounds in wastewater discharges to surface waters for 2000 and 1995 from the integrated EDC, VCM, and PVC manufacturing facilities in the United States. Site-specific testing of the wastewater from facilities operated by Dow Chemical Co., Occidental Chemical Corp., Georgia Gulf Corp., PPG Industries, and DuPont provide the basis for estimating annual releases of dioxin-like compounds in 2000 (CCC, 2005, 2003a, b, c, d). In total, these tests represent site-specific analysis of 17 manufacturing facilities throughout the United States. The site-specific releases of dioxin-like compounds for these facilities are shown in Table 8-17. In 2000, approximately 23.08 g TEQ_{DF}-WHO_{98} (23.94 g I-TEQ) were released from 17 EDC/VCM/PVC manufacturing facilities in the United States. These estimates are assigned a high confidence rating because they were derived from the testing of individual manufacturing facilities and the activity level is known with a high degree of certainty.

Estimating TEQ wastewater discharges for 1995 from EDC/VCM/PVC integrated chemical manufacturing facilities is problematic. A report by The Vinyl Institute (1998) did not represent a comprehensive testing of the wastewaters from all existing EDC/VCM/PVC manufacturing facilities in 1995. The report presented results for treated wastewater samples collected during April and May of 1995 at only 10 manufacturing sites (6 that manufactured only PVC, 3 that manufactured EDC and VCM, and 1 that manufactured EDC, VCM, and PVC). In terms of production, the 10 sites represented only about 27% of the total estimated 1995 EDC/VCM/PVC production.

The representativeness of these sites to total EDC/VCM/PVC manufacturing is questionable because the testing program did not include some of the higher-emitting facilities discovered in 2000 (CCC, 2003a). For example, the CCC reports that provided the basis for the 2000 release estimates (CCC, 2005, 2003a, b, c, d) indicated that the Dow facility in Freemont, TX, and the Occidental facility in Ingleside, TX, released approximately 3 g and 1.6 g TEQ_{DF}-WHO_{98}, respectively, as wastewater discharges into surface waters. These two facilities are about an order of magnitude higher in wastewater releases than are the 10 facilities tested in 1995 (The Vinyl Institute, 1998). In an attempt to overcome this deficiency, it is assumed that the wastewater releases from EDC/VCM/PVC integrated chemical production facilities in 1995 were

Table 8-17. Releases of dioxin-like compounds (g/yr) in wastewater discharges from EDC/VCM/PVC and integrated chlorine chemical manufacturing facilities to surface water in reference years 2000 and 1995

Company	Facility	2,3,7,8 TCDD	1,2,3,7,8 PeCDD	1,2,3,4,7,8 HxCDD	1,2,3,6,7,8 HxCDD	1,2,3,7,8,9 HxCDD	1,2,3,4,6,7,8 HpCDD	OCDD	2,3,7,8 TCDF	1,2,3,7,8 PeCDF	2,3,4,7,8 PeCDF	1,2,3,4,7,8 HxCDF	1,2,3,6,7,8 HxCDF	1,2,3,7,8,9 HxCDF	2,3,4,6,7,8 HxCDF	1,2,3,4,6,7,8 HpCDF	1,2,3,4,7,8,9 HpCDF	OCDF	I-TEQ	TEQ_{DF}-WHO_{98}
Dow[a]	Freeport, TX	0.00	0.00	0.57	0.00	0.35	15.61	74.61	2.63	3.57	1.68	26.28	0.00	0.00	5.00	125.74	19.36	297.94	6.48	6.14
Dow	Midland, MI	0.00	0.00	0.02	0.00	0.00	0.54	3.63	0.02	0.00	0.01	0.06	0.00	0.00	0.04	0.88	0.01	1.25	0.04	0.03
Dow	Plaquemine, LA	0.06	0.12	0.87	0.00	0.33	18.72	285.79	4.78	3.77	1.97	21.42	0.00	0.98	3.14	161.57	11.81	374.10	7.03	6.50
DuPont[b]	DeLisle, MS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DuPont	Edge Moor, DE	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.14	0.12	13.49	0.02	0.01
DuPont	Johnsonville, TN	0.00	0.00	0.00	0.00	0.00	0.00	1.41	0.00	0.00	0.00	0.44	0.00	0.00	0.00	1.23	0.00	11.03	0.07	0.06
Georgia Gulf[c]	Plaquemine, LA	0.00	0.00	0.00	0.00	0.00	0.03	0.12	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.11	0.02	0.41	0.02	0.02
Occidental[d]	Convent, LA	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.04	0.002	0.002
Occidental	Deer Park, TX	0.00	0.00	0.00	0.00	0.00	0.08	1.19	0.00	0.00	0.00	0.04	0.03	0.03	0.01	0.69	0.26	5.85	0.03	0.02
Occidental	Ingleside, TX	0.02	0.09	0.08	0.09	0.08	0.09	0.18	0.02	0.09	0.09	0.09	0.10	0.10	0.10	0.10	0.10	0.19	0.18	0.23
Occidental	LaPorte, TX	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.12	0.03	0.67	0.01	0.01
Occidental	Mobile, AL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3e−04	0.00	0.00	0.00	0.00	0.00	0.00	6e−04	0.00	0.00	4e−05	4e−05
Occidental	Battleground, TX	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5e−04	5e−05
Occidental	Delaware City, DE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1e−03	0.00	0.00	0.00	0.00	0.00	0.00	2e−03	0.00	0.00	1e−04	1e−04
Occidental	Hahnville, LA	0.00	0.00	0.00	0.00	0.00	0.01	0.10	0.19	0.90	0.85	2.96	1.18	0.63	0.60	4.47	0.69	1.75	1.08	1.08
Occidental	Muscle Shoals, AL	0.00	0.00	0.00	0.00	0.00	0.00	1e−09	4e−08	1e−07	8e−08	2e−07	1e−07	2e−08	3e−08	1e−07	6e−08	1e−07	9e−08	9e−08
PPG Industries	Lake Charles, LA	0.00	0.00	0.01	0.01	0.00	0.40	2.97	6.47	14.30	10.83	12.29	3.96	3.23	1.57	4.41	2.64	12.13	8.98	8.97
	TOTAL	0.08	0.22	1.55	0.10	0.77	35.49	370.78	14.13	22.64	15.46	63.73	5.29	4.98	10.47	299.47	35.03	718.85	23.94	23.08

Table 8-17. Releases of dioxin-like compounds (g/yr) in wastewater discharges from EDC/VCM/PVC and integrated chlorine chemical manufacturing facilities to surface water in reference years 2000 and 1995 (continued)

[a]Dow Chemical Company.
[b]DuPont.
[c]Georgia Gulf Corporation.
[d]Occidental Chemical Corporation.

Source: Chlorine Chemistry Council (2004).

EDC = Ethylene dichloride
PVC = Polyvinyl chloride
VCM = Vinyl chloride monomer

equal to wastewater discharges in 2000. Based on this assumption, approximately 23.08 g TEQ_{DF}-WHO_{98} (23.94 g I-TEQ) were released from 17 EDC/VCM/PVC manufacturing facilities in the United States in reference year 1995. These estimates are assigned a low confidence rating because they may not be representative of wastewater discharges from facilities operating in 1995, although the activity level is known with a high degree of certainty and is assigned a high confidence rating. The site-specific releases of dioxin-like compounds for facilities operating in 1995 are shown in Table 8-17.

A number of EDC/VCM/PVC manufacturing facilities have reported significant reductions in CDD/CDF wastewater discharges to surface water in 2002 from 2000 levels. For example, the Dow facility in Freemont, TX, achieved a 47% reduction (from 6.4 g TEQ_{DF}-WHO_{98} in 2000 to 3.43 g TEQ_{DF}-WHO_{98} in 2002) (CCC, 2003a), the Dow facility in Plaquemine, LA, achieved a 69% reduction (from 6.86 g TEQ_{DF}-WHO_{98} in 2000 to 2.16 g TEQ_{DF}-WHO_{98} in 2002) (CCC, 2003a), and the PPG Industries facility in Lake Charles, LA, achieved a 28% reduction (from 8.97 g TEQ_{DF}-WHO_{98} in 2000 to 6.47 g TEQ_{DF}-WHO_{98} in 2002) (CCC, 2003b).

8.3.4.2. *Land Releases*

Only one EDC/VCM/PVC manufacturing facility (the Georgia Gulf facility in Plaquemine, LA) reported CDD/CDF releases to land from the land application of wastewater sludge in 2000 (CCC, 2003c). The congener-specific and TEQ releases are presented in Table 8-18. Releases to land from EDC/VCM/PVC manufacturing in 2000 and 1995 were 1.36 g TEQ_{DF}-WHO_{98} (1.45 g I-TEQ_{DF}), assuming that the land application rates were the same in both years.

These emission estimates for 2000 are assigned a high confidence rating because the releases to land were determined from the actual measurements taken from the single facility that applies the wastewater sludge to land. The emission estimates for 1995 are assigned a medium confidence rating because the estimates were based on assuming that the CDD/CDF levels of contamination in the wastewater solids and the land application rates were the same in both reference years.

8.3.4.3. *Air Releases*

The Vinyl Institute conducted a study of releases of EDC/VCM/PVC to air (The Vinyl Institute, 1998). Based on similarities in design and service, thermal destruction units at EDC/VCM and/or PVC manufacturing units were subcategorized into three types: type A, vent gas incinerators at PVC-only resin plants; type B, vent gas thermal oxidizers at EDC/VCM plants; and type C, liquid-only and liquid/vent gas thermal oxidizers at EDC/VCM plants. Using

Table 8-18. Congener-specific releases to land from an EDC/VCM/PVC integrated chemical manufacturing facility[a] in reference years 2000 and 1995

Congener	Annual release to land (g/yr)
2,3,7,8-TCDD	0.004
1,2,3,7,8-PeCDD	0.039
1,2,3,4,7,8-HxCDD	0.123
1,2,3,6,7,8-HxCDD	0.122
1,2,3,7,8,9-HxCDD	0.078
1,2,3,4,6,7,8-HpCDD	1.710
OCDD	8.640
2,3,7,8-TCDF	0.077
1,2,3,7,8-PeCDF	0.354
2,3,4,7,8-PeCDF	0.370
1,2,3,4,7,8-HxCDF	2.690
1,2,3,6,7,8-HxCDF	2.110
1,2,3,7,8,9-HxCDF	1.540
2,3,4,6,7,8-HxCDF	0.595
1,2,3,4,6,7,8-HpCDD	28.100
1,2,3,4,7,8,9-HpCDD	6.540
OCDF	118.000
Total I-TEQ_{DF}	1.450
Total TEQ_{DF}-WHO_{98}	1.360

[a]Georgia Gulf, Plaquemine, LA.

Source: CCC (2004).

EDC = Ethylene dichloride
PVC = Polyvinyl chloride
VCM = Vinyl chloride monomer

an industry-wide survey, The Vinyl Institute identified 22 type A units at 11 facilities, 23 type B units at 10 facilities, and 17 type C units at 10 facilities. Test data were gathered from 5 of the 22 type A units (3 facilities representing 7% of total U.S. and Canadian EDC/VCM/PVC production in 1995), 14 of the 23 type B units (8 facilities), and 13 of the 17 type C units (7 facilities). The sampled type B and C units represented 70% of total U.S. and Canadian EDC/VCM/PVC production in 1995.

Annual I-TEQ_{DF} emission estimates were generated by combining estimated emissions from tested units (based on measured stack gas results and plant-specific activity data) with an estimate of emissions from untested units. The emissions from the untested units were estimated by multiplying the average emission factor for the tested units in the category (the most likely

estimate) or the average emission factor of the tested units with the highest emissions in each class (the upper-bound estimate) by the activity level for the untested units. It is not possible to calculate emission factors for TEQ_{DF}-WHO_{98} using the data presented in The Vinyl Institute report.

The Vinyl Institute estimates of most likely and upper-bound emissions during 1995 for these three categories are as follows:

Category	Most likely emissions estimate (g I-TEQ_{DF}/yr)	Upper-bound emissions estimate (g I-TEQ_{DF}/yr)
PVC-only incinerators	0.0014	0.0019
EDC/VCM liquid and liquid/vents	3.7	7.2
EDC/VCM vents for VCM only	6.9	21.6

The study also estimated emissions that may have resulted from incineration of EDC/VCM/PVC wastes processed by off-site, third-party processing. Using the emission factors for liquid and liquid/vents developed in its study, it was estimated that potential emissions to air from this source category would be 0.65 g I-TEQ_{DF}/yr (most-likely estimate) and 2.3 g I-TEQ_{DF}/yr (upper-bound estimate). Combining these third-party release estimates with those developed above yields a 1995 estimate of 11.2 g I-TEQ_{DF}/yr.

Data validation studies by the CCC indicate that eight EDC/VCM/PVC manufacturing facilities released 5.51 g TEQ_{DF}-WHO_{98} (5.56 g I-TEQ_{DF}) to air (CCC, 2004); more than 85% of the releases occurred at two facilities. Congener-specific and TEQ release estimates to air from EDC/VCM/PVC manufacturing facilities are shown in Table 8-19. The emission estimates for 1995 and 2000 are assigned a high confidence rating because they were based on emissions testing of on-site incinerator and vent releases.

8.3.4.4. *Transfers to Secure Landfills*

The CCC reported on the amount of CDDs/CDFs contained in wastewater treatment plant sludges used to secure landfills in 2000 (CCC, 2004). These data were determined on the basis of sampling wastewater sludges at 16 integrated EDC/VCM/PVC manufacturing facilities. Table 8-20 summarizes the estimated CDD/CDF congener-specific and TEQ amounts (based on actual test data) transferred from specific facilities in 2000. It should be noted that, because the wastes were transferred to secure landfills, this is not considered to have been an environmental release; therefore, these transfers were not incorporated into the inventory.

Table 8-19. Congener-specific and TEQ releases to air (g/yr) from EDC/VCM/PVC integrated chemical manufacturing facilities in reference years 2000 and 1995

Company	Facility	2,3,7,8 TCDD	1,2,3,7,8 PeCDD	1,2,3,4,7,8 HxCDD	1,2,3,6,7,8 HxCDD	1,2,3,7,8,9 HxCDD	1,2,3,4,6,7,8 HpCDD	OCDD	2,3,7,8 TCDF	1,2,3,7,8 PeCDF	2,3,4,7,8 PeCDF	1,2,3,4,7,8 HxCDF	1,2,3,6,7,8 HxCDF	1,2,3,7,8,9 HxCDF	2,3,4,6,7,8 HxCDF	1,2,3,4,6,7,8 HpCDF	1,2,3,4,7,8,9 HpCDF	OCDF	I-TEQ	TEQ_{DF}-WHO_{98}
Dow[a]	Freeport, TX	0.01	0.20	1.01	0.00	0.39	3.73	9.46	1.26	1.80	1.28	11.98	0.00	0.34	2.50	32.35	5.34	66.92	3.08	3.11
Dow	Midland, MI	0.026	0.004	0.008	0.000	0.003	0.02	0.086	0.023	0.009	0.008	0.066	0.000	0.002	0.009	0.148	0.028	0.225	0.05	0.05
Dow	Plaquemine, LA	0.00	0.00	0.03	0.00	0.01	0.10	0.27	0.03	0.04	0.03	0.40	0.00	0.00	0.05	1.47	0.10	3.21	0.09	0.09
DuPont[b]	DeLisle, MS	0.000	0.001	0.000	0.000	0.000	0.004	0.011	0.004	0.004	0.006	0.007	0.005	0.002	0.013	0.028	0.003	0.042	0.007	0.007
DuPont	Edge Moor, DE	0.000	0.001	0.000	0.000	0.000	0.003	0.016	0.001	0.002	0.002	0.003	0.002	0.005	0.003	0.011	0.018	0.204	0.004	0.004
DuPont	Johnsonville, TN	0.000	0.001	0.000	0.000	0.000	0.003	0.007	0.005	0.006	0.008	0.010	0.008	0.004	0.023	0.043	0.003	0.043	0.011	0.011
Georgia Gulf[c]	Plaquemine, LA	0.00	0.00	0.00	0.00	0.00	0.02	0.12	0.09	0.07	0.03	0.17	0.07	0.04	0.01	0.32	0.03	1.01	0.07	0.07
Occidental[d]	Convent, LA	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.02	0.02	0.01	0.01	0.01	0.00	0.00	0.02	0.00	0.02	0.02	0.03
Occidental	Deer Park, TX	0.00	0.01	0.05	0.03	0.06	1.37	13.54	0.06	0.12	0.14	1.38	0.58	0.55	0.06	11.88	2.32	52.83	0.58	0.53
Occidental	Ingleside, TX	0.01	0.03	0.11	0.12	0.09	1.58	9.51	0.04	0.35	0.37	3.58	3.38	0.77	1.94	25.71	5.13	46.90	1.61	1.58
Occidental	LaPorte, TX	0.00	0.01	0.01	0.02	0.01	0.15	0.48	0.01	0.02	0.03	0.04	0.04	0.01	0.04	0.25	0.02	0.23	0.04	0.04
	TOTAL	0.05	0.27	1.21	0.18	0.56	6.99	33.49	1.54	2.45	1.92	17.65	4.09	1.74	4.64	72.22	13.01	171.64	5.56	5.51

[a]Dow Chemical Company.
[b]DuPont.
[c]Georgia Gulf Corporation.
[d]Occidental Chemical Corporation.

Source: Chlorine Chemistry Council (2004).

EDC = Ethylene dichloride
PVC = Polyvinyl chloride
VCM = Vinyl chloride monomer

Table 8-20. Congener-specific and TEQ transfers to secure landfills (g/yr)[a] from EDC/VCM/PVC integrated chemical production facilities in 2000

Company	Facility	2,3,7,8 TCDD	1,2,3,7,8 PeCDD	1,2,3,4,7,8 HxCDD	1,2,3,6,7,8 HxCDD	1,2,3,7,8,9 HxCDD	1,2,3,4,6,7,8 HpCDD	OCDD	2,3,7,8 TCDF	1,2,3,7,8 PeCDF	2,3,4,7,8 PeCDF	1,2,3,4,7,8 HxCDF	1,2,3,6,7,8 HxCDF	1,2,3,7,8,9 HxCDF	2,3,4,6,7,8 HxCDF	1,2,3,4,6,7,8 HpCDF	1,2,3,4,7,8,9 HpCDF	OCDF	TEQ_{DF}-WHO_{98}
Dow[b]	Freeport, TX	0.00	0.00	0.57	0.00	0.35	15.61	74.61	2.63	3.57	1.68	26.28	0.00	0.00	5.00	125.74	19.36	297.94	6.14
Dow	Midland, MI	0.00	0.00	0.02	0.00	0.00	0.54	3.63	0.02	0.00	0.01	0.06	0.00	0.00	0.04	0.88	0.01	1.25	0.03
Dow	Plaquemine, LA	0.06	0.12	0.87	0.00	0.33	18.72	285.79	4.78	3.77	1.97	21.42	0.00	0.98	3.14	161.57	11.81	374.10	6.50
DuPont[c]	DeLisle, MS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DuPont	Edge Moor, DE	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.14	0.12	13.49	0.01
DuPont	Johnsonville, TN	0.00	0.00	0.00	0.00	0.00	0.00	1.41	0.00	0.00	0.00	0.44	0.00	0.00	0.00	1.23	0.00	11.03	0.06
Georgia Gulf[c]	Plaquemine, LA	0.00	0.00	0.00	0.00	0.00	0.03	0.12	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.11	0.02	0.41	0.02
Occidental[e]	Convent, LA	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.04	0.002
Occidental	Deer Park, TX	0.00	0.00	0.00	0.00	0.00	0.08	1.19	0.00	0.00	0.00	0.04	0.03	0.03	0.01	0.69	0.26	5.85	0.02
Occidental	Ingleside, TX	0.02	0.09	0.08	0.09	0.08	0.09	0.18	0.02	0.09	0.09	0.09	0.10	0.10	0.10	0.10	0.10	0.19	0.23
Occidental	LaPorte, TX	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.12	0.03	0.67	0.01
Occidental	Mobile, AL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3e−04	0.00	0.00	0.00	0.00	0.00	0.00	6e−04	0.00	0.00	4e−05
Occidental	Battleground, TX	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5e−05
Occidental	Delaware City, DE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1e−03	0.00	0.00	0.00	0.00	0.00	0.00	2e−03	0.00	0.00	1e−04
Occidental	Hahnville, LA	0.00	0.00	0.00	0.00	0.00	0.01	0.10	0.19	0.90	0.85	2.96	1.18	0.63	0.60	4.47	0.69	1.75	1.08
Occidental	Muscle Shoals, AL	0.00	0.00	0.00	0.00	0.00	0.00	1e−09	4e−08	1e−07	8e−08	2e−07	1e−07	2e−08	3e−08	1e−07	6e−08	1e−07	9e−08
	TOTAL	0.08	0.22	1.54	0.09	0.76	35.09	367.81	7.65	8.33	4.62	51.44	1.32	1.75	8.90	295.06	32.40	706.72	14.11

[a]Not considered to be environmental releases.
[b]Dow Chemical Company.
[c]DuPont.
[d]Georgia Gulf Corporation.
[e]Occidental Chemical Corporation.

EDC = Ethylene dichloride
PVC = Polyvinyl chloride
VCM = Vinyl chloride monomer

Source: CCC (2004).

8.3.4.5 *Products*

The Vinyl Institute (1998) presented results for 22 samples from 14 of the 24 U.S. and Canadian facilities manufacturing suspension and mass PVC resins (13 pipe resins, 3 bottle resins, and 6 packaging resins). The results for U.S. manufacturers are summarized in Table 8-21. The 14 sampled sites represented approximately 74% of estimated 1995 U.S. and Canadian suspension and mass PVC resin production. CDDs/CDFs were detected in only one sample (0.043 ng I-TEQ_{DF}/kg, assuming nondetects equal to zero). The overall mean TEQ concentrations were 0.002 ng I-TEQ_{DF}/kg (assuming nondetects equal to zero) and 0.7 ng I-TEQ_{DF}/kg (assuming nondetects equal to one-half the DL). The DLs were 2 ng/kg or less for all congeners in all samples except for OCDD and OCDF, which had DLs of 6 ng/kg or less.

The same study also presented results for six samples from four of the seven U.S. facilities manufacturing dispersion PVC resins. CDDs/CDFs were detected in five of the samples. The results are summarized in Table 8-21. In terms of production, the four sampled sites represent approximately 61% of estimated 1995 U.S. dispersion PVC resin production. The results ranged from not detected to 0.008 ng I-TEQ_{DF}/kg (overall mean = 0.001 ng I-TEQ_{DF}/kg, assuming nondetects equal to zero, and 0.4 ng I-TEQ_{DF}/kg, assuming nondetects equal to one-half the DL). The DLs were 2 ng/kg or less for all congeners in all samples except for OCDD and OCDF, which had DLs of 4 ng/kg or less.

Results were also presented for five samples from 5 of the 15 U.S. facilities manufacturing EDC. The results are summarized in Table 8-21. In terms of production, the five sampled sites represented approximately 71% of the estimated EDC produced in the United States in 1995. CDDs/CDFs were detected in only one sample (0.03 ng I-TEQ_{DF}/kg). The overall mean TEQ concentrations were 0.006 ng I-TEQ_{DF}/kg (nondetects equal to zero) and 0.21 ng I-TEQ_{DF}/kg (nondetects equal to one-half the DL). The DLs for all congeners were 1 ng/kg or less.

Using 1995 U.S. production data, 4.846 million metric tons of suspension and mass PVC, 0.367 million metric tons of dispersion PVC resins, and 1.362 million metric tons of EDC were produced. Based on the average TEQ concentration observed, The Vinyl Institute estimated that the total I-TEQ_{DF} contents of suspension/mass PVC resins, dispersion PVC resins, and EDC were 0.01 g, 0.004 g, and 0.008 g, respectively (nondetects equal to zero), and 3.39 g, 0.15 g, and 0.29 g, respectively (nondetects equal to one-half the DL). Therefore, total I-TEQ_{DF} present in PVC in 1995 was estimated to be between 0.02 g (nondetects equal to zero) and 3.83 g (nondetects equal to one-half the DL). It is not possible using the data presented in The Vinyl Institute report to calculate emission factors for TEQ_{DF}-WHO_{98}. However, because neither 1,2,3,7,8-PeCDD nor OCDD was detected in any sample, the TEQ_{DF}-WHO_{98} emission factors would be very similar to the I-TEQ_{DF} emission factors.

Table 8-21. CDD/CDF concentrations in products from U.S. EDC/VCM/PVC manufacturers

Congener/congener group	Suspension and mass PVC resins			Dispersion PVC resins			EDC sold as product[d]		
	No. detects/ samples[a]	Range[b] (ng/kg)		No. of detects/ samples	Range[c] (ng/kg)		No. detects/ samples	Range[e] (ng/kg)	
		Min.	Max.		Min.	Max.		Min.	Max.
2,3,7,8-TCDD	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
1,2,3,7,8-PeCDD	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
1,2,3,4,7,8-HxCDD	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
1,2,3,6,7,8-HxCDD	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
1,2,3,7,8,9-HxCDD	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
1,2,3,4,6,7,8-HpCDD	1/22	ND	0.64	1/6	ND	0.8	0/5	ND	ND
OCDD	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
2,3,7,8-TCDF	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
1,2,3,7,8-PeCDF	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
2,3,4,7,8-PeCDF	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
1,2,3,4,7,8-HxCDF	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
1,2,3,6,7,8-HxCDF	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
1,2,3,7,8,9-HxCDF	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
2,3,4,6,7,8-HxCDF	1/22	ND	0.37	0/6	ND	ND	0/5	ND	ND
1,2,3,4,6,7,8-HpCDF	0/22	ND	ND	0/6	ND	ND	1/5	ND	1.1
1,2,3,4,7,8,9-HpCDF	0/22	ND	ND	0/6	ND	ND	1/5	ND	0.4
OCDF	0/22	ND	ND	2/6	ND	0.38	1/5	ND	11
Mean I-TEQ_{DF} (nondetect = 0)		0.002			0.001			0.001	
Mean I-TEQ_{DF} (nondetect = ½ DL)			0.7			0.4			0.21
Total TCDD	0/22	ND	ND	1/6	ND	0.24	0/5	ND	ND
Total PeCDD	0/22	ND	ND	1/6	ND	0.32	0/5	ND	ND
Total HxCDD	0/22	ND	ND	5/6	ND	0.97	0/5	ND	ND
Total HpCDD	1/22	ND	0.64	1/6	ND	1.3	0/5	ND	ND
Total OCDD	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
Total TCDF	0/22	ND	ND	0/6	ND	ND	0/5	ND	ND
Total PeCDF	0/22	ND	ND	1/6	ND	0.3	0/5	ND	ND
Total HxCDF	1/22	ND	0.37	0/6	ND	ND	0/5	ND	ND
Total HpCDF	0/22	ND	ND	0/6	ND	ND	1/5	ND	2.02
Total OCDF	0/22	ND	ND	2/6	ND	0.38	1/5	ND	11

Table 8-21. CDD/CDF concentrations in products from U.S. EDC/VCM/PVC manufacturers (continued)

[a]Two of these 22 samples were duplicate samples from two sites. The results were averaged and treated as one sample for each site.
[b]Detection limits (DLs) for individual samples were less than 2 ng/kg for all congeners and congener groups except OCDD and OCDF, which had DLs less than 6 ng/kg.
[c]DLs for individual samples were less than 2 ng/kg for all congeners and congener groups except OCDD and OCDF, which had DLs less than 4 ng/kg.
[d]"Sales" EDC is defined as EDC sold commercially for non-VCM uses or exported from the United States.
[e]DLs were less than 1 ng/kg for all congeners in all samples.

DL = Detection limit
EDC = Ethylene dichloride
ND = Not detected
PVC = Polyvinyl chloride
VCM = Vinyl chloride monomer

Source: The Vinyl Institute (1998).

Approximately 6.55 million metric tons of PVC and 9.91 million metric tons of EDC were produced in North America in 2000 and approximately 5.58 million metric tons of PVC and 7.83 million metric tons of EDC were produced in 1995 (C&EN, 2002). Approximately 94% of PVC production and approximately 17% of EDC production in 1995 occurred in the United States. Of the PVC produced, 87% was for suspension and mass PVC products and 7% was for dispersion PVC resins. Assuming these product percentages remained the same for 2000, it is estimated that approximately 5.69 million metric tons of suspension and mass PVC and 0.46 million metric tons of dispersion PVC resins were produced and 1.69 million metric tons of EDC product were produced. Applying the same average TEQ observed in The Vinyl Institute samples from 1998, EPA estimated the total I-TEQ_{DF} contents of suspension/mass PVC resins, dispersion PVC resins, and EDC produced in 2000 to be 0.01 g, 0.0004 g, and 0.01 g, respectively (nondetects equal to zero) and 3.99 g, 0.17 g, and 0.36 g, respectively (nondetects equal to one-half the DL). Therefore, total I-TEQ_{DF} present in PVC in 2000 was estimated to be between 0.02 g (nondetects equal to zero) and 4.52 g (nondetects equal to one-half the DL).

8.3.5. Other Aliphatic Chlorine Compounds

Aliphatic chlorine compounds are used as monomers in the production of plastics, as solvents and cleaning agents, and as precursors for chemical synthesis (Hutzinger and Fiedler, 1991b). These compounds are produced in large quantities. In 1992, 14.6 million metric tons of halogenated hydrocarbons were produced in the United States (U.S. ITC, 1946–1994), with 1,2-dichloroethane and vinyl chloride accounting for 82% of total production. Highly chlorinated CDDs/CDFs (hexa- to octa-chlorinated congeners) have been found in nanograde-quality samples of 1,2-dichloroethane (55 ng/kg of OCDF in one of five samples), tetrachloroethene (47 ng/kg of OCDD in one of four samples), epichlorohydrin (88 ng/kg of CDDs and 33 ng/kg of CDFs in one of three samples), and hexachlorobutadiene (360 to 425 ng/kg of OCDF in two samples) obtained in Germany from Promochem (Hutzinger and Fiedler, 1991b; Heindl and Hutzinger, 1987). No CDDs/CDFs were detected in two samples of allyl chloride, three samples of 1,1,1-trichloroethane, and four samples of trichloroethylene (DL ranged from 5 to 20 ng/kg) (Heindl and Hutzinger, 1987). Because no more recent or additional data could be found in the literature to confirm these values for products manufactured or used in the United States, no national estimates of CDD/CDF emissions were made for the inventory.

EPA's Office of Water promulgated effluent limitations for facilities that manufacture chlorinated aliphatic chlorine compounds and discharge treated wastewater (40 CFR 414.70). These effluent limitations do not specifically address CDDs/CDFs. Regulated limits for chlorinated aliphatic compounds are 68 µg/L for 1,2-dichloroethane and 22 µg/L for tetrachloroethylene. Similarly, OSW promulgated restrictions on land disposal of wastes

generated during the manufacture of many chlorinated aliphatics (40 CFR 268); however, these restrictions do not specifically regulate CDDs/CDFs.

8.3.6. Dyes, Pigments, and Printing Inks

Several researchers have analyzed various dyes, pigments, and printing inks obtained in Canada and Germany for the presence of CDDs/CDFs (Williams et al., 1992; Hutzinger and Fiedler, 1991b; Santl et al., 1994). The following subsections discuss the findings of those studies.

8.3.6.1. *Dioxazine Dyes and Pigments*

Williams et al. (1992) analyzed the CDD/CDF content in dioxazine dyes and pigments available in Canada. As shown in Table 8-22, OCDD and OCDF concentrations in the nanogram-per-kilogram range and HpCDD, HxCDD, and PeCDD concentrations in the microgram-per-kilogram range were found in Direct Blue 106 dye (three samples), Direct Blue 108 dye (one sample), and Violet 23 pigments (six samples). These dioxazine pigments are derived from chloranil, which has been found to contain high levels of CDDs/CDFs and has been suggested as the source of contamination among these dyes (Christmann et al., 1989b; Williams et al., 1992; U.S. EPA, 1992d). In May 1990, EPA received test results showing that chloranil was heavily contaminated with dioxins; levels as high as 2,903 µg TEQ_{DF}-WHO_{98}/kg (3,065 µg I-TEQ_{DF}/kg) were measured in samples from four importers (mean value of 1,388 µg TEQ_{DF}-WHO_{98}/kg [1,754 µg I-TEQ_{DF}/kg]) (U.S. EPA, 1992d; Remmers et al., 1992). (See Section 8.3.6 for analytical results.)

In the early 1990s, EPA learned that I-TEQ_{DF} levels in chloranil could be reduced by more than two orders of magnitude (to less than 20 µg/kg) through manufacturing feedstock and process changes. EPA's Office of Pollution Prevention and Toxics subsequently began efforts to complete an industry-wide switch from the use of contaminated chloranil to low-dioxin chloranil. Although chloranil is not manufactured in the United States, significant quantities are imported. As of May 1992, EPA had negotiated agreements with all chloranil importers and domestic dye/pigment manufacturers known to EPA that used chloranil in their products to switch to low-dioxin chloranil. In May 1993, when U.S. stocks of chloranil with high levels of CDDs/CDFs had been depleted, EPA proposed a SNUR under Section 5 of TSCA that would require industry to notify EPA at least 90 days prior to the manufacture, import, or processing, for any use, of chloranil containing CDDs/CDFs at a concentration greater than 20 µg I-TEQ_{DF}/kg (Federal Register, 1993a; U.S. EPA, 1993d).

Table 8-22. CDD/CDF concentrations (µg/kg) in samples of dioxazine dyes and pigments (Canada)

Congener/congener group	Blue 106			Blue 108	Violet 23					
2,3,7,8-TCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,7,8-PeCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,4,7,8-HxCDD	--	--	--	--	--	--	--	--	--	--
1,2,3,6,7,8-HxCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,7,8,9-HxCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,4,6,7,8-HpCDD	31	6	9	ND (0.3)	9	1	16	10	2	4
OCDD	41,953	28,523	18,066	23	7,180	806	11,022	7,929	1,627	1,420
2,3,7,8-TCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,7,8-PeCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	0.5	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
2,3,4,7,8-PeCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,4,7,8-HxCDF	12	2	2	ND (0.3)	76	4	39	31	9	7
1,2,3,6,7,8-HxCDF[a]										
1,2,3,7,8,9-HxCDF	--	--	--	--	--	--	--	--	--	--
2,3,4,6,7,8-HxCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,4,6,7,8-HpCDF	50	10	14	9	13	10	11	4	1	12
1,2,3,4,7,8,9-HpCDF	--	--	--	--	--	--	--	--	--	--
OCDF	12,463	1,447	1,006	11	941	125	3,749	1,556	147	425
Total 2,3,7,8-CDD	41,984	28,529	18,075	23	7,189	807	11,038	7,939	1,629	1,424
Total 2,3,7,8-CDF	12,525	1,459	1,022	20	1,030.5	139	3,799	1,591	157	444
Total I-TEQ_{DF}[b]	56.4	30.3	19.5	0.1	16	1.4	18.9	12.7	2.7	2.7
Total TEQ_{DF}-WHO_{98}[b]	7.45	3.4	2.3	0.1	8.7	0.6	5.6	4.2	1.1	1
Total TCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
Total PeCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
Total HxCDD	ND (0.3)	ND (0.3)	ND (0.3)	1	21	2	7	ND (0.3)	ND (0.3)	1
Total HpCDD	34	8	12	ND (0.3)	30	5	36	11	2	6
Total OCDD	41,953	28,523	18,066	23	7,180	806	11,022	7,929	1,627	1,420
Total TCDF	ND (0.3)	0.3	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	0.4	ND (0.3)
Total PeCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	0.5	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
Total HxCDF	12	2	2	ND (0.3)	76	5	39	31	9	7
Total HpCDF	71	32	26	12	26	14	29	13	2	21
Total OCDF	12,463	1,447	1,006	11	941	125	3,749	1,556	147	425
Total CDD/CDF[b]	54,533	30,012.3	19,112	47	8,274.5	957	14,882	9,540	1,787.4	1,880

Table 8-22. CDD/CDF concentrations in samples of dioxazine dyes and pigments (µg/kg) (Canada) (continued)

[a]Results listed for 1,2,3,4,7,8-HxCDF include concentrations for 1,2,3,6,7,8-HxCDF.
[b]Calculations assume nondetected values were equal to zero.

ND = Not detected (value in parenthesis is the detection limit)
-- = Not reported

Source: Williams et al. (1992).

In 1983, approximately 36,500 kg of chloranil were imported (U.S. ITC, 1984). The U.S. International Trade Commission has not published quantitative import data for chloranil since 1984. If it is assumed that this import volume reflects actual usage of chloranil in the United States during 1987 and that the CDD/CDF contamination level was 1,388 µg TEQ_{DF}-WHO_{98}/kg (1,754 µg I-TEQ_{DF}/kg), then the maximum release to the environment via processing wastes and finished products was 50.6 g TEQ_{DF}-WHO_{98} (64 g I-TEQ_{DF}). If it is assumed that the import volume in 1995 was also 36,500 kg but that the imported chloranil contained 10 µg I-TEQ_{DF}/kg on average, then the total potential annual TEQ release associated with chloranil in 1995 was 50.6 g TEQ_{DF}-WHO_{98} (64 g I-TEQ_{DF}).

In 1986, EPA promulgated the Inventory Update Rule (IUR) that requires the partial updating of the TSCA Chemical Inventory database. Every four years, chemical manufacturers and importers of chemicals listed in the TSCA inventory that produce at one plant site or import at production volume levels of 10,000 lb or more must report the range of chemical production or import. According to information entered in the TSCA database, 10,000 to 500,000 lb (4,540 to 227,000 kg) of chloranil were imported in 1994 and 2000 (http://www.epa.gov/opptintr/iur /iur02/search03.htm). Assuming the imported chloranil contained the same concentration of dioxin as the 1995 estimate (10 µg I-TEQ_{DF}/kg), the total potential annual TEQ release associated with chloranil in 2000 was 0.05 to 2.27 g I-TEQ_{DF}-WHO_{98} (mean of 1.16 g I-TEQ_{DF}).

8.3.6.2. *Phthalocyanine Dyes and Printing Inks*

Hutzinger and Fiedler (1991b) found CDDs/CDFs (tetra-, penta-, and hexa-chlorinated congeners) in the microgram-per-kilogram range in a sample of a Ni-phthalocyanine dye. No CDDs/CDFs were detected (DL of 0.1 to 0.5 µg/kg) in two samples of Cu-phthalocyanine dyes and in one Co-phthalocyanine dye (Hutzinger and Fiedler, 1991b).

Santl et al. (1994) reported the results of analyses of four printing inks obtained from a supplier in Germany. Two of the inks are used for rotogravure printing and two are used for offset printing. The results of the analyses are presented in Table 8-23. The TEQ_{DF}-WHO_{98} content of the inks ranged from 17.7 to 87.2 ng/kg (15 to 88.6 ng/kg on an I-TEQ_{DF} basis). Primarily non-2,3,7,8-substituted congeners were found. The identities of the dyes and pigments in these inks were not reported.

Although EPA provided an estimate of potential environmental releases based on limited information of contaminant levels of CDDs/CDFs in the product, the estimate is still too uncertain to include in the quantitative inventory of sources. It is currently not known whether the dioxin contamination in the product actually results in a release to the open and circulating environment.

Table 8-23. CDD/CDF concentrations (ng/kg) in printing inks (Germany)

Congener/congener group	Rotogravure (2-color)	Rotogravure (4-color)	Offset (4-color)	Offset (4-color)
2,3,7,8-TCDD	ND (1)	ND (1.5)	ND (2)	ND (2)
1,2,3,7,8-PeCDD	8	ND (4)	15	6
1,2,3,4,7,8-HxCDD	19	ND (5)	16	11
1,2,3,6,7,8-HxCDD	325	310	82	21
1,2,3,7,8,9-HxCDD	155	105	42	14
1,2,3,4,6,7,8-HpCDD	2,770	1,630	540	240
OCDD	5,810	2,350	890	230
2,3,7,8-TCDF	2.5	14	7	7
1,2,3,7,8-PeCDF	ND (2)	ND (4)	ND (4)	ND (3)
2,3,4,7,8-PeCDF	ND (2)	ND (4)	ND (4)	ND (3)
1,2,3,4,7,8-HxCDF	4	7	27	35
1,2,3,6,7,8-HxCDF	ND (3)	ND (5)	ND (5)	ND (5)
1,2,3,7,8,9-HxCDF	ND (3)	ND (5)	ND (5)	ND (5)
2,3,4,6,7,8-HxCDF	ND (3)	ND (5)	ND (5)	ND (5)
1,2,3,4,6,7,8-HpCDF	40	14	315	42
1,2,3,4,7,8,9-HpCDF	ND (4)	ND (7)	11	ND (6)
OCDF	129	ND (10)	960	165
Total 2,3,7,8-CDD	9,087	4,395	1,585	522
Total 2,3,7,8-CDF	175.5	35	1,320	249
Total I-TEQ_{DF} [a]	88.6	62.4	35.4	15
Total TEQ_{DF}-WHO_{98}	87.2	60.3	41.2	18
Total TCDD	4	ND (2)	77	38
Total PeCDD	58	145	35	25
Total HxCDD	2,679	2,485	660	246
Total HpCDD	5,630	3,460	1,100	445
Total OCDD	5,810	2,350	890	230
Total TCDF	5.5	28	90	35
Total PeCDF	13	ND (4)	340	110
Total HxCDF	29	45	95	94
Total HpCDF	64	14	566	63
Total OCDF	129	ND (10)	960	165
Total CDD/CDF	14,421.5	8,527	4,813	1,451

[a]Calculations assume nondetect values were zero.

ND = Not detected (value in parenthesis is the detection limit)

Source: Santl et al. (1994).

8.3.7. TSCA Dioxin/Furan Test Rule

Citing evidence that halogenated dioxins and furans may be formed as by-products during chemical manufacturing processes (Versar, Inc., 1985), EPA issued a rule under Section 4 of TSCA that requires chemical manufacturers and importers to test for the presence of CDDs/CDFs and brominated dibenzo-*p*-dioxins (BDDs) and brominated dibenzofurans (BDFs) in certain commercial organic chemicals (Federal Register, 1987a). The rule listed 12 manufactured or imported chemicals that required testing and 20 chemicals not currently manufactured or imported that would require testing if manufacture or importation resumed. These chemicals are listed in Table 8-24. The specific dioxin and furan congeners that require quantitation and the target limits of quantitation (LOQs) that are specified in the rule are listed in Table 8-25. Under Section 8(a) of TSCA, the final rule also required that chemical manufacturers submit data on manufacturing processes and reaction conditions for chemicals produced using any of the 28 precursor chemicals listed in Table 8-26. The rule stated that subsequent to this data-gathering effort, testing may be proposed for additional chemicals if any of the manufacturing conditions used favored the production of dioxins and furans.

Twenty-three sampling and analytical protocols and test data for 10 of the 12 chemicals that required testing were submitted to EPA (U.S. EPA, 2003a, c). Manufacture or import of two substances (tetrabromobisphenol-A-bis-2,3-dibromopropylether and tetrabromobisphenol-A-diacrylate) have stopped since the test rule was promulgated. (All data and reports in the EPA TSCA docket are available for public review and inspection at EPA Headquarters in Washington, DC.)

Table 8-27 presents the results of analytical testing for CDDs/CDFs for the chemicals that have data available in the TSCA docket. Five of these 10 chemicals contained CDDs/CDFs. Positive results were obtained for 2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione (chloranil), pentabromodiphenyloxide, octabromodiphenyloxide, decabromodiphenyloxide, and 1,2-bis(tribromophenoxy)-ethane. Table 8-28 presents the quantitative analytical results for four submitted chloranil samples, as well as the results of an EPA analysis of a sample of carbazole violet, which is manufactured from chloranil.

Although testing conducted under this test rule for 2,4,6-tribromophenol indicated no halogenated dioxins or furans above the LOQs, Thoma and Hutzinger (1989) reported detecting BDDs and BDFs in a technical-grade sample of this substance. Total TBDD, TBDF, and PeBDF were found at 84 µg/kg, 12 µg/kg, and 1 µg/kg, respectively. No hexa-, hepta-, or octa-BDFs were detected. The investigators also analyzed analytical-grade samples of two other brominated flame retardants, pentabromophenol and tetrabromophthalic anhydride; no BDDs or BDFs were detected (DLs not reported).

Table 8-24. Chemicals requiring Toxic Substances Control Act Section 4 testing under the dioxin/furan rule

CAS No.	Chemical name
Currently manufactured or imported as of June 5, 1987	
79-94-7	Tetrabromobisphenol-A
118-75-2	2,3,5,6-Tetrachloro-2,5-cyclohexadiene-1,4-dione
118-79-6	2,4,6-Tribromophenol
120-83-2	2,4-Dichlorophenol
1163-19-5	Decabromodiphenyloxide
4162-45-2	Tetrabromobisphenol-A-bisethoxylate
21850-44-2	Tetrabromobisphenol-A-bis-2,3-dibromopropylether[a]
25327-89-3	Allyl ether of tetrabromobisphenol-A
32534-81-9	Pentabromodiphenyloxide
32536-52-0	Octabromodiphenyloxide
37853-59-1	1,2-Bis(tribromophenoxy)-ethane
55205-38-4	Tetrabromobisphenol-A-diacrylate[a]
Not manufactured or imported as of June 5, 1987[b]	
79-95-8	Tetrachlorobisphenol-A
87-10-5	3,4',5-Tribromosalicylanide
87-65-0	2,6-Dichlorophenol
95-77-2	3,4-Dichlorophenol
95-95-4	2,4,5-Trichlorophenol
99-28-5	2,6-Dibromo-4-nitrophenol
120-36-5	2[2,4-(Dichlorophenoxy)]-propanoic acid
320-72-9	3,5-Dichlorosalicyclic acid
488-47-1	Tetrabromocatechol
576-24-9	2,3-Dichlorophenol
583-78-8	2,5-Dichlorophenol
608-71-9	Pentabromophenol
615-58-7	2,4-Dibromophenol
933-75-5	2,3,6-Trichlorophenol
1940-42-7	4-Bromo-2,5-dichlorophenol
2577-72-2	3,5-Dibromosalicylanide
3772-94-9	Pentachlorophenyl laurate
37853-61-5	Bismethylether of tetrabromobisphenol-A
-	Alkylamine tetrachlorophenate
-	Tetrabromobisphenol-B

[a]No longer manufactured in or imported into the United States (memorandum dated May 4, 1993, from Gordon Cash, U.S. EPA/OPPTS, to John Schaum, U.S. EPA/ORD).

[b]As of August 5, 1995, neither manufacture nor importation of any of these chemicals had resumed in the United States (memorandum dated August 2, 1995, from T.S. Holderman, U.S. EPA, to A. Adenuga, Versar, Inc.).

Table 8-25. Congeners and limits of quantitation (LOQs) for which quantitation is required under the dioxin/furan test rule and pesticide Data Call-In

Chlorinated dioxins and furans	Brominated dioxins and furans	LOQ (µg/kg)
2,3,7,8-TCDD	2,3,7,8-TBDD	0.1
1,2,3,7,8-PeCDD	1,2,3,7,8-PeBDD	0.5
1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-HxBDD	2.5
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxBDD	2.5
1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-HxBDD	2.5
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpBDD	100
2,3,7,8-TCDF	2,3,7,8-TBDF	1
1,2,3,7,8-PeCDF	1,2,3,7,8-PeBDF	5
2,3,4,7,8-PeCDF	2,3,4,7,8-PeBDF	5
1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxBDF	25
1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-HxBDF	25
1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-HxBDF	25
2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-HxBDF	25
1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpBDF	1,000
1,2,3,4,7,8,9-HpCDF	1,2,3,4,7,8,9-HpBDF	1,000

8.3.8. Halogenated Pesticides and FIFRA Pesticides Data Call-In

In the late 1970s and early 1980s, attention began to focus on pesticides as potential sources of CDDs/CDFs in the environment. Up to that time, CDD/CDF levels were not regulated in end-use pesticide products. However, some of the active ingredients in pesticides, particularly chlorinated phenols and their derivatives, were known or suspected to be contaminated with CDDs/CDFs. During the 1980s and 1990s, EPA took several actions to investigate and control CDD/CDF contamination of pesticides.

In 1983, EPA cancelled the sale of Silvex and 2,4,5-T for all uses (Federal Register, 1987a). Earlier, in 1979, EPA had ordered emergency suspension of the forestry, rights-of-way, and pasture uses of 2,4,5-T. Emergency suspensions of the forestry, rights-of-way, pasture, home and garden, commercial/ornamental turf, and aquatic weed control/ditch bank uses of Silvex were also ordered (Federal Register, 1979; Plimmer, 1980). The home and garden, commercial/ornamental turf, and aquatic weed control/ditch bank uses of 2,4,5-T had been suspended in 1970.

Table 8-26. Precursor chemicals subject to reporting requirements under Toxic Substances Control Act Section 8(a)[a]

CAS No.	Chemical name
85-22-3	Pentabromoethylbenzene
87-61-6	1,2,3-Trichlorobenzene
87-84-3	1,2,3,4,5-Pentabromo-6-chlorocyclohexane
89-61-2	1,4-Dichloro-2-nitrobenzene
89-64-5	4-Chloro-2-nitrophenol
89-69-0	2,4,5-Trichloronitrobenzene
92-04-6	2-Chloro-4-phenylphenol
97-74-6	4-Chloro-o-toloxy acetic acid
94-81-5	4-(2-Methyl-4-chlorophenoxy) butyric acid
95-50-1	o-Dichlorobenzene
95-56-7	o-Bromophenol
95-57-8	o-Chlorophenol
95-88-5	4-Chlororesorcinol
95-94-3	1,2,4,5-Tetrachlorobenzene
95-50-7	5-Chloro-2,4-dimethoxyaniline
99-30-9	2,6-Dichloro-4-nitroaniline
99-54-7	1,2-Dichloro-4-nitrobenzene
106-46-7	p-Dichlorobenzene
108-70-3	1,3,5-Trichlorobenzene
108-86-1	Bromobenzene
108-90-7	Chlorobenzene
117-18-0	1,2,4,5-Tetrachloro-3-nitrobenzene
120-82-1	1,2,4-Trichlorobenzene
348-51-6	o-Chlorofluorobenzene
350-30-1	3-Chloro-4-fluoronitrobenzene
615-67-8	Chlorohydroquinone
626-39-1	1,3,5-Tribromobenzene
827-94-1	2,6-Dibromo-4-nitroaniline

[a]Dibromobenzene (CAS No. 106-37-6) was identified in the preamble to 52 FR 21412 as one of 29 precursor chemicals; however, it was inadvertently omitted from the regulatory text. Because the regulatory text identified only 28 chemicals, 28 chemicals appear in 40 CFR 766.38 and in this table.

In 1984, EPA issued a notice of intent to cancel registrations of pesticide products containing PCP (including its salts) for all wood preservative uses (Federal Register, 1984). This notice specified modifications to the terms and conditions of product registrations that were required in order to avoid cancellation of the products. In response to this notice, several trade associations and registrants requested administrative hearings to challenge EPA's determinations. After carefully considering the comments and alternatives suggested during the prehearing stage of the administrative proceedings, EPA concluded that certain changes to the 1984 notice were appropriate. These changes, finalized in 1986 (Federal Register, 1986), included the following:

Table 8-27. Results of analytical testing for dioxins and furans in the chemicals tested to date under Section 4 of the dioxin/furan test rule

CAS No.	Chemical name	No. of chemical companies that submitted data	No. of positive studies	Congeners detected (detection range in µg/kg)
79-94-7	Tetrabromobisphenol-A	3	0	[a]
118-75-2	2,3,5,6-Tetrachloro-2,5-cyclohexadiene-1,4-dione (chloranil)	6	5	See Table 8-28
118-79-6	2,4,6-Tribromophenol	1	0	[a]
120-83-2	2,4-Dichlorophenol	1	0	[a]
1163-19-5	Decabromodiphenyl oxide	3	3	2,3,7,8-PeBDD (ND–0.1) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD (ND–0.5) 1,2,3,7,8,9-HxBDD (ND–0.76) 1,2,3,7,8-PeBDF (ND–0.7) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (ND–0.8) 1,2,3,4,6,7,8-HpBDF (17–186)
25327-89-3	Allyl ether of tetrabromobisphenol-A	1	0	[a]
32536-52-0	Octabromodiphenyl oxide	3	3	2,3,7,8-TBDD (ND–0.71) 1,2,3,7,8-PeBDD (ND–0.1) 2,3,7,8-TBDF (ND–12.6) 1,2,3,7,8-PeBDF (ND–6.3) 2,3,4,7,8-PeBDF (ND–83.1) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (ND–67.8) 1,2,3,7,8,9-HxBDF (ND–56.0) 1,2,3,4,6,7,8-HpBDF (ND–330)
378-53-59-1	1,2-Bis(tribromo-phenoxy)-ethane	1	1	2,3,7,8-TBDF (ND–0.04) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (ND–0.03) 1,2,3,4,6,7,8-HpBDF (ND–0.33)
32534-81-9	Pentabromodiphenyl oxide	3	3	1,2,3,7,8-PeBDD (ND–5.9) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD (ND–6.8) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD (ND–6.8) 1,2,3,7,8,9-HxBDD (ND–0.02) 2,3,7,8-TBDF(ND–3.1) 1,2,3,7,8-PeBDF (0.7–10.2) 2,3,4,7,8-PeBDF (0.1–2.9) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (15.6–61.2) 1,2,3,4,6,7,8-HpBDF (0.7–3.0)
4162-45-2	Tetrabromobisphenol-A-bisethoxylate	1	0	[a]

[a]No 2,3,7,8-substituted dioxins and furans detected above the test rule target limits of quantitation (see Table 8-20).

ND = Not detected

Source: Holderman and Cramer (1995).

Table 8-28. CDD/CDF concentrations (µg/kg) in chloranil and carbazole violet samples analyzed pursuant to the EPA dioxin/furan test rule

Congener	Chloranil				Carbazole violet
	Importer 1	Importer 2	Importer 3	Importer 4	
2,3,7,8-TCDD	ND (1)	ND (1)	ND (2)	ND (2)	ND (0.8)
1,2,3,7,8-PeCDD	ND (2)	ND (2)	ND (5)	ND (6)	ND (0.5)
1,2,3,4,7,8-HxCDD	ND (3)	ND (10)	ND (5)	ND (3)	ND (1.2)
1,2,3,6,7,8-HxCDD	ND (3)	75	ND (5)	6	ND (1.2)
1,2,3,7,8,9-HxCDD	ND (1)	48	ND (5)	9	ND (1.2)
1,2,3,4,6,7,8-HpCDD	110	8,200	390	2,300	28
OCDD	240,000	180,000	760,000	71,000	1,600
2,3,7,8-TCDF	ND (1)	ND (2)	ND (1)	ND (2)	ND (1.6)
1,2,3,7,8-PeCDF	ND (1)	ND (1)	ND (3)	ND (5)	ND (0.9)
2,3,4,7,8-PeCDF	ND (1)	ND (1)	ND (3)	ND (5)	ND (0.9)
1,2,3,4,7,8-HxCDF	35	ND (860)	ND (4)	5,600	ND (20)
1,2,3,6,7,8-HxCDF	ND (5)	ND (860)	ND (4)	ND (600)	ND (20)
1,2,3,7,8,9-HxCDF	6	ND (680)	ND (4)	ND (600)	ND (20)
2,3,4,6,7,8-HxCDF	ND (5)	ND (680)	ND (4)	ND (600)	ND (20)
1,2,3,4,6,7,8-HpCDF	33	240,000	36	230,000	15,000
1,2,3,4,7,8,9-HpCDF	ND (15)	ND (100)	ND (15)	ND (400)	ND (20)
OCDF	18,000	200,000	50,000	110,000	59,000
Total I-TEQ_{DF}[a]	263	2,874	814	3,065	211
Total TEQ_{DF}-WHO_{98}[a]	31	2,532	85	2,903	156

[a]Calculated assuming nondetect values are zero.

ND = Not detected (value in parenthesis is the minimum detection limit)

Source: Remmers et al. (1992).

(a) all wood preservative uses of PCP and its salts were classified as "restricted use" only by certified applicators, (b) specific worker protection measures were required, (c) limits were placed on the HxCDD content of PCP, and (d) label restrictions for home and farm uses of PCP prohibited its application indoors and to wood intended for interior use (with a few exceptions) as well as its application in a manner that might result in direct exposure of domestic animals or livestock or in the contamination of food, feed, or drinking and irrigation water.

EPA subsequently amended its Notice on the wood preservative uses to establish reliable and enforceable methods for implementing certified limits for HxCDD and 2,3,7,8-TCDD in registered wood preservative pesticide products (Federal Register, 1987b). Levels of 2,3,7,8-TCDD were not allowed to exceed 1 ppb in any product, and after February 2, 1989, any manufacturing-use PCP released for shipment could not contain HxCDD levels that exceeded an

average of 2 ppm over a monthly release or a batch level of 4 ppm (a gradually phased-in requirement). On January 21, 1987, EPA prohibited the registration of PCP and its salts for most nonwood uses (Federal Register, 1987c). EPA deferred action on several uses (uses in pulp/paper mills, oil wells, and cooling towers) pending receipt of additional exposure, use, and ecological effects data. On January 8, 1993, EPA issued a press advisory stating that its special review of these deferred nonwood uses was being terminated because all of these uses had been either voluntarily cancelled by the registrants or cancelled by EPA for failure of the registrants to pay the required annual maintenance fees (U.S. EPA, 1993e).

PCP was one of the most widely used biocides in the United States prior to the regulatory actions to cancel and restrict certain of its wood and nonwood preservative uses. PCP was registered for use as a herbicide, defoliant, mossicide, and mushroom house biocide. It also found use as a biocide in pulp-paper mills, oil wells, and cooling towers. These latter three uses were terminated on or before 1993 (U.S. EPA, 1993e). However, the major use (greater than 80% of consumption) of PCP was and continues to be wood preservation.

The production of PCP for wood preserving began on an experimental basis in the 1930s. In 1947, nearly 3,200 metric tons of PCP were reported to have been used in the United States by the commercial wood preserving industry. Use in this industry steadily increased through the mid-1970s (American Wood Preservers Institute, 1977). Although domestic consumption volumes are not available for all years, it is estimated, on the basis of historical production/export data for PCP reported in Mannsville (1983), that 90 to 95% of production volume has typically been consumed domestically rather than exported. A reasonable estimate of average annual domestic PCP consumption during the period of 1970 to 1995 is about 400,000 metric tons. This estimate assumes an average annual consumption rate of 20,000 metric tons/yr during the 1970s, 15,000 metric tons/yr during the 1980s, and 10,000 metric tons/yr during the 1990s.

Table 8-10 presents a compilation of published data on the CDD/CDF content of technical-grade PCP. The only samples that have been analyzed for all dioxin-like CDDs/CDFs were manufactured in the mid to late 1980s. Figure 8-4 presents these data in graphical form. It is evident from the figures that the predominant congener groups are OCDD, OCDF, HpCDF, and HpCDD and the dominant 2,3,7,8-substituted congeners are OCDD, 1,2,3,4,6,7,8-HpCDD, and OCDF. Waddell et al. (1995) tested analytical-grade PCP (from Aldrich Chemical Co.) for CDD/CDF content and found the same congener profile; however, the CDD/CDF levels were three to four orders of magnitude lower. Table 8-11 presents a similar compilation of published data on the CDD/CDF content of PCP-Na. The table shows the same patterns of dominant congeners and congener groups reported for PCP.

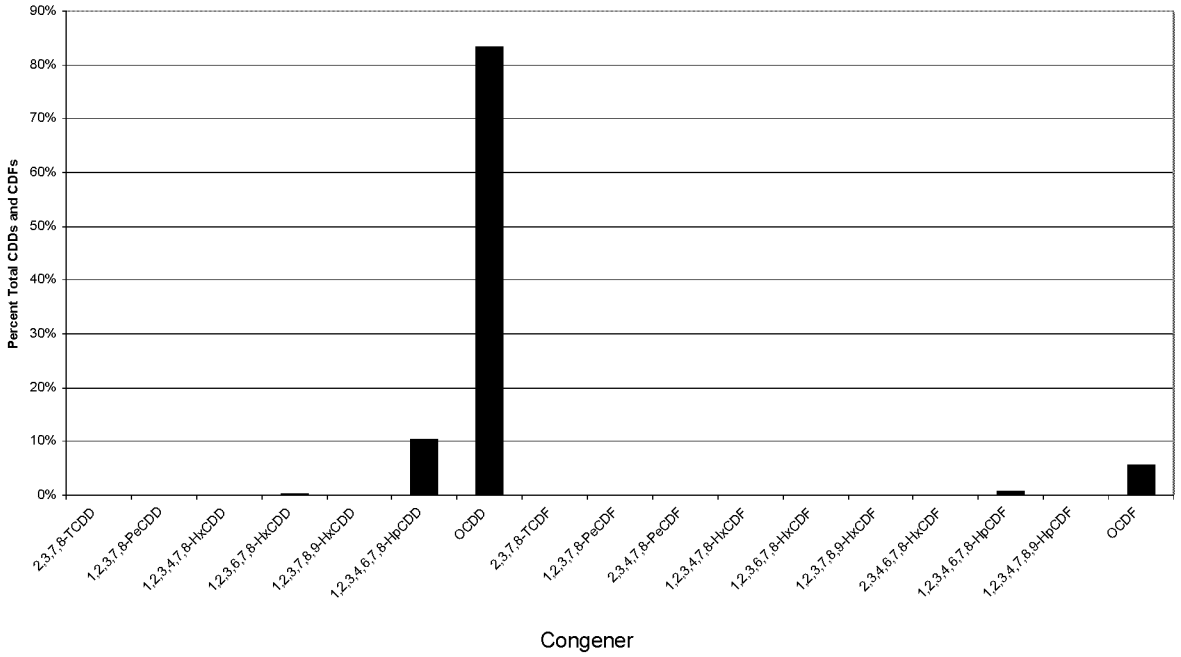


Figure 8-4. Congener profile for technical-grade PCP (developed from data in last column in Table 8-10).

Samples of technical-grade PCP manufactured during the mid to late 1980s contained about 1.7 mg TEQ_{DF}-WHO_{98}/kg (3 mg I-TEQ/kg), based on the data presented in Table 8-10. No published reports could be located that present the results of any congener-specific analyses of PCP manufactured since the late 1980s. However, monthly measurements of CDD/CDF congener group concentrations in technical PCP manufactured for use in the United States have been reported to EPA from 1987 to the present (letter dated March 5, 1997, from Thomas Mitchell, KMG-Bernuth, to Matthew Lorber, U.S. EPA; letter dated February 7, 1997, from John Wilkinson, Pentachlorophenol Task Force, to Matthew Lorber, U.S. EPA; U.S. EPA, 1999a). The average congener group concentrations reported to EPA for the years 1988 (i.e., one year after EPA regulations were imposed limiting HxCDD and 2,3,7,8-TCDD concentrations in PCP) to 1999 are presented in Table 8-10. In general, the average congener group concentrations during the period of 1988 to 1999 are lower by factors of 2 to 4 than those observed in the mid to late 1980s' full congener analysis samples. If it is assumed that the toxic CDD/CDF congeners have also been reduced by similar factors, then the TEQ content of PCP manufactured since 1988 is about 0.6 mg TEQ_{DF}-WHO_{98}/kg (1 mg I-TEQ/kg).

An estimated 12,000 metric tons of PCP were used for wood preservation in the United States in 1987 (WHO, 1991). An estimated 8,400 metric tons were used in 1994 (American Wood Preservers Institute, 1995); for purposes of this report, it is assumed that an identical amount was used in 1995. In 1999, approximately 7,710 metric tons of PCP were produced annually in the United States (Council of Great Lakes Industries, 1999); for purposes of this report, it is assumed that an identical amount was produced in 2000. Assuming that 95% of the production volume was consumed domestically (Mannsville, 1983), and that all of the PCP produced in 2000 was used for wood preservation, approximately 7,325 metric tons of PCP was used in the United States for wood preservation. Combining these activity level estimates with the TEQ concentration estimates presented above indicates that 20,000 µg TEQ_{DF}-WHO_{98} (36,000 µg I-TEQ_{DF}), 4,800 µg TEQ_{DF}-WHO_{98} (8,400 µg I-TEQ_{DF}), and 4,175 µg TEQ_{DF}-WHO_{98} (7,325 µg I-TEQ_{DF}) were incorporated into PCP-treated wood products in 1987, 1995, and 2000, respectively. These amounts in PCP products are not considered an environmental release and therefore are not included in the inventory. As discussed below, there is some evidence that releases could occur, but no consistent estimation approach could be found.

Although the estimates of the mass of TEQ in treated wood are fairly certain, no studies are available that provide measured CDD/CDF release rate data from which a reliable estimate can be made of the amount of CDDs/CDFs that have or will volatilize or leach from treated wood. Several recent field studies, discussed in the following paragraphs, demonstrate that CDDs/CDFs do apparently leach into soil from PCP-treated wood, but the studies do not provide release rate data. No studies were located that provide any measured CDD/CDF volatilization rates from PCP-treated wood. Although CDDs/CDFs have very low vapor pressures, they are not bound to, nor do they react with, the wood in any way that would preclude volatilization. Several studies, discussed below, have attempted to estimate potential CDD/CDF volatilization releases using conservative assumptions or modeling approaches, but these estimates span many orders of magnitude.

Gurprasad et al. (1995) analyzed three PCP-treated utility poles and their surrounding surface soils for penta- through octa-CDD content. All three poles showed significant levels of HxCDD (0.29 to 0.47 mg/kg), HpCDD (4.69 to 6.63 mg/kg), and OCDD (27.9 to 42.1 mg/kg), but no PeCDD. Surface soils collected 2 cm from the poles also had detectable levels of HxCDD, HpCDD, and OCDD; however, no consistent pattern was found between the CDD concentrations in the poles and those in the adjacent soils. The soil concentrations did, however, show the same relative congener group pattern observed in the wood. CDD concentrations in soils obtained 20 cm from the poles were an order of magnitude less than those measured at 2 cm. Soils 26 m from the poles showed nondetect values or values close to the DL of 0.01 to 0.02 mg/kg.

In a study of the leaching of PCP from 31 utility poles, the Electric Power Research Institute (EPRI, 1995) found patterns of PCP distribution in soils surrounding poles similar to those found by Gurprasad et al. (1995) for CDDs. PCP concentrations decreased by as much as two orders of magnitude between 7.5 cm from the poles and 20 cm from the poles, with an average decrease of slightly more than one order of magnitude over this distance. The EPRI study also found no obvious trend between PCP concentration in the wood (eight poles analyzed) and the age of the poles (4 to 11 years) or the PCP concentration in the surface soil. On the basis of their results and those of the EPRI study, Gurprasad et al. concluded that CDDs probably leach from PCP-treated utility poles with the PCP/oil carrier and travel in the soil in a similar manner.

Wan (1995) and Wan and Van Oostdam (1995) measured CDD/CDF concentrations in waters and sediments from ditches surrounding utility poles and railroad ties and demonstrated that chlorophenol-treated wood could serve as a source of CDD/CDFs to the aquatic environment. Ten samples were collected at each of six utility pole sites and five railroad tie sites 1 to 2 days after major rainfall events and then were composited into one sample per site prior to analyses. Total CDDs (mean value of 76.7 mg/kg) and total CDFs (mean value of 18.7 mg/kg) detected in chlorophenol/creosote-treated utility poles were about six to eight times greater, respectively, than the CDD and CDF concentrations detected in chlorophenol/creosote-treated railroad ties.

Total CDDs found in water from railway ditches without utility poles (i.e., only treated railroad ties were present) were approximately 20 times higher than the background level found in farm ditch water. Total CDDs in railway ditches with utility poles were 4,300 times higher than the background levels. Water from railway ditches without utility poles contained total CDF levels 13 times higher than background levels, whereas water in ditches adjacent to poles had levels 8,500 times higher than background levels. Total CDDs in ditch sediments adjacent to and 4 m downstream of utility poles were about 5,900 and 2,200 times higher, respectively, than background levels; total CDFs for the same sites were about 8,100 and 1,700 times higher, respectively, than background levels. Total CDDs found in ditch sediments of railway and ditch sediments adjacent to utility poles were about 5 and 700 times higher, respectively, than background levels, and total CDFs were about 9 and 1,800 times higher, respectively, than background levels. Both CDDs and CDFs were found in utility ditch sediments 4 m downstream of treated power poles, but at levels 200 and 400 times lower, respectively, than those found adjacent to poles, indicating that they were transported from point sources of contamination. The corresponding values for CDFs were 5,400 and 8,000 times higher, respectively, in concentration.

Bremmer et al. (1994) estimated an annual release of 15 to 125 g I-TEQ_{DF} from PCP-treated wood in the Netherlands. The lower estimate was based on three basic assumptions:

(1) the half-life of PCP in treated wood is 15 years (according to industry sources), (2) the half-life of CDDs/CDFs in treated wood is 10 times that of PCP (i.e., 150 years) because of the lower vapor pressures of CDDs/CDFs relative to PCP, and (3) the typical CDD/CDF concentration in PCP has been 3,000 µg/kg. The higher estimate was based on an assumed half-life of PCP in wood of 15 years and the results of an indoor air study by Papke et al. (1989) conducted at several kindergartens where PCP-treated wood had been used. Although Papke et al. found no clear correlation between indoor air concentrations of CDDs/CDFs and PCP across the range of CDD/CDF concentrations observed in the 20-plus samples (2.6 to 427 pg CDD/CDF/m^3), there did appear to be a positive correlation at the sites with more elevated CDD/CDF concentrations. Bremmer et al. (1994) reported the average ratio of PCP to I-TEQ $_{DF}$ air concentrations at these elevated sites to be $1{:}5 \times 10^{-6}$ (or about the same ratio as the concentration of I-TEQ $_{DF}$ in technical PCP). The results of the Papke et al. (1989) study imply that CDDs/CDFs may be released from PCP-treated wood at the same rate as is PCP rather than at a rate 10 times slower.

Rappe (1995) used the emission factor approach developed by Bremmer et al. (1994) and an assumed U.S. usage volume of PCP over the past 50 years (0.5 million metric tons) to estimate that as much as 10.5 kg I-TEQ_{DF} could volatilize from PCP-treated wood in the United States annually. Eitzer and Hites (1987) derived a dramatically different estimate: 3 kg/yr of total CDDs/CDFs (or 66 g I-TEQ_{DF} per year, assuming an I-TEQ_{DF} content in PCP of 3 mg/kg). Eitzer and Hites based their estimate on an assumption that 0.1% of the PCP produced annually enters the atmosphere and that the CDD/CDF contaminants present in the PCP (assumed to be 130 mg/kg) are released to the atmosphere at the same rate as the PCP (i.e., 0.1%). The basis for the first assumption by Eitzer and Hites is not clear because U.S. EPA (1980), which was cited as the source of the 0.1% emission factor, does not appear to address volatilization of PCP from in-service treated wood. The report does, however, estimate that most PCP in treated wood leaches relatively rapidly from the wood, presumably to land, within a period of 12 years.

Eduljee and Dyke (1996) and Douben et al. (1995) estimated that 0.8 g I-TEQ_{DF} is released to the air annually from PCP-treated wood in the United Kingdom. This estimate was based on the assumed emission of 0.1% of the CDDs/CDFs present in PCP-treated wood during the first year of the service life of the wood that was assumed by Eitzer and Hites (1987). No emissions were assumed for subsequent years of use of the treated wood.

The California Air Resources Board (Chinkin et al., 1987) generated estimates of CDD/CDF volatilization releases at wood treatment facilities from bundles of treated wood that remain on site for 1 month prior to shipment. An "adapted" version of a model developed by McCord (1981) was used for estimating volatile releases from a constantly filling lagoon. The model is primarily driven by chemical-specific vapor pressures and air diffusivity coefficients. Chinkin et al. did not provide all model input parameter values used to generate the emission estimates. However, running the model with typical dimensions for treated poles yields an I-

TEQ_{DF} emission rate on the order of 6E-12 g/yr-pole, an extremely low number (170 billion poles would together emit 1 g TEQ/yr).

In addition to cancelling some pesticide registrations and establishing product standards, EPA's Office of Pesticide Programs (OPP) issued two DCIs in 1987. Pesticide manufacturers are required to register their products with EPA in order to market them commercially in the United States. Through the registration process, mandated by FIFRA, EPA can require that the manufacturer of each active ingredient generate a wide variety of scientific data through several mechanisms. The most common process is the five-phase reregistration process, with which the manufacturers (i.e., registrants) of older pesticide products must comply. In most registration activities, registrants must generate data under a series of strict testing guidelines, 40 CFR 158—Pesticide Assessment Guidelines (U.S. EPA, 1988c). EPA can also require additional data from registrants, when necessary, through various mechanisms, including the DCI process.

The purpose of the first DCI, dated June and October 1987, "Data Call-In Notice for Product Chemistry Relating to Potential Formation of Halogenated Dibenzo-*p*-dioxin or Dibenzofuran Contaminants in Certain Active Ingredients," was to identify, using an analysis of raw materials and process chemistry, those pesticides that might contain halogenated dibenzo-*p*-dioxin (HDD) and halogenated dibenzofuran (HDF) contaminants. The 93 pesticides (76 pesticide active ingredients) to which the DCI applied, along with their corresponding Shaughnessey and Chemical Abstract code numbers, are presented in Table 8-29. (The Shaughnessey code is an internal EPA tracking system. It is of interest because chemicals with similar code numbers are similar in chemical nature [e.g., salts, esters, and acid forms of 2,4-D].)

All registrants supporting registrations for these chemicals were subject to the requirements of the DCI unless their product qualified for a Generic Data Exemption (i.e., a registrant exclusively used a FIFRA-registered pesticide product as a source of an active ingredient identified in Table 8-29 in formulating a product). Registrants whose products did not meet the Generic Data Exemption were required to submit the types of data listed below to enable EPA to assess the potential for formation of tetra- through hepta-HDD or -HDF contaminants during manufacture.

- Product identity and disclosure of ingredients. EPA required submittal of a Confidential Statement of Formula (CSF), based on the requirements specified in 40 CFR 158.108 and 40 CFR 158.120, Subdivision D: Product Chemistry. Registrants who had previously submitted still-current CSFs were not required to resubmit this information.

- Description of beginning materials and manufacturing process. Under the requirements mandated by 40 CFR 158.120, Subdivision D, EPA required submittal of a manufacturing process description for each step of the manufacturing process, including specification of the range of acceptable conditions of temperature, pressure, or pH at each step.

Table 8-29. Status of first pesticide Data Call-In: pesticides suspected of having the potential to become contaminated with dioxins if synthesized under conditions favoring dioxin formation

Shaughnessey code	Pesticide [active ingredient]	CAS No.	Support withdrawn	Testing required
000014	Dichlorodifluoromethane	75-71-8	Yes	--
008706	O-(4-Bromo-2,5-dichlorophenyl) O,O-dimethyl phosphorothioate	2104-96-3	Yes	--
009105	Dimethylamine 2,3,5-triiodobenzoate	17601-49-9	Yes	--
012001	Neburon	555-37-3	Yes	--
012101	Crufomate	299-86-5	Yes	--
019201	MCPB, 4-butyric acid [4-(2-Methyl-4-chlorophenoxy)butyric acid]	94-81-5	No	Yes
019202	MCPB, Na salt [Sodium 4-(2-methyl-4-chlorophenoxy)butyrate]	6062-26-6	No	No
019401	4-Chlorophenoxyacetic acid	122-88-3	No	Yes
025501	Chloroxuron	1982-47-4	Yes	--
027401	Dichlobenil	1194-65-6	No	Yes
28201	Propanil [3',4'-Dichloropropionanilide]	709-98-8	No	No
028601	Dichlofenthion [O-(2,4-Dichlorophenyl) O,O-diethyl phosphorothioate)]	97-17-6	Yes	--
029201	DDT [Dichloro diphenyl trichloroethane]	50-29-3	Yes	--
29601	Dichlone [2,3-dichloro-1,4-naphthoquinone]	117-80-6	Yes	--
029902	Ammonium chloramben [3-amino-2,5-dichlorobenzoic acid]	1076-46-6	Yes	--
029906	Sodium chloramben [3-amino-2,5-dichlorobenzoic acid]	1954-81-0	Yes	--
030602	Sodium 2-(2,4-dichlorophenoxy)ethyl sulfate	136-78-7	Yes	--
031301	DCNA [2,6-Dichloro-4-nitroaniline]	99-30-9	No	Yes
031503	Potassium 2-(2-methyl-4-chlorophenoxy)propionate	1929-86-8	Yes	--
031516	MCCP, DEA Salt [Diethanolamine 2-(2-methyl-4-chlorophenoxy)propionate]	1432-14-0	Yes	--
031563	MCPP, IOE [Isooctyl 2-(2-methyl-4-chlorophenoxy)propionate]	28473-03-2	No	No
034502	Dicapthon [O-(2-chloro-4-nitrophenyl) O,O-dimethyl phosphorothioate]	2463-84-5	Yes	--
035502	Monuron trichloroacetate [3-(4-chlorophenyl)-1,1-dimethylurea trichloroacetate]	140-41-0	Yes	--
35505	Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea]	330-54-1	No	No
35506	Linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea]	330-55-2	No	No
35901	Metobromuron [3-(p-bromophenyl)-1-methoxy-1-methylurea]	3060-89-7	Yes	--

Table 8-29. Status of first pesticide data call-in: pesticides suspected of having the potential to become contaminated with dioxins if synthesized under conditions favoring dioxin formation (continued)

Shaughnessey code	Pesticide [active ingredient]	CAS No.	Support withdrawn	Testing required
53501	Methyl parathion [O,O-Dimethyl O-p-nitrophenyl phosphorothioate]	298-00-0	No	No
55001	Dichlorophene [Sodium 2,2'-methylenebis(4-chlorophenate)]	97-23-4	Yes	--
55005	Dichlorophene, sodium salt [Sodium 2,2'-methylenebis(4-chlorophenate)]	10254-48-5	Yes	--
55201	1,2,4,5-Tetrachloro-3-nitrobenzene	117-18-0	Yes	--
57501	Ethyl parathion [O,O-diethyl O-p-nitrophenyl phosphorothioate]	56-38-2	No	No
58102	Carbophenothion [S-(((p-chlorophenyl)thio)methyl) O,O-diethyl phosphorodithioate]	786-19-6	Yes	--
58301	Ronnel [O,O-dimethyl O-(2,4,5-trichlorophenyl) phosphorothioate]	229-84-3	Yes	--
58802	Mitin FF [Sodium 5-chloro-2-(4-chloro-2-(3-(3,4-dichlorophenyl)ureido)phenoxy) benzenesulfonate]	3567-25-7	No	No
59401	Orthodichlorobenzene	95-50-1	Yes	--
61501	Paradichlorobenzene	106-46-7	No	No
62201	Chlorophene [2-Benzyl-4-chlorophenol]	120-32-1	No	No
62202	Potassium 2-benzyl-4-chlorophenate	35471-49-9	No	In review
62203	Sodium 2-benzyl-4-chlorophenate	3184-65-4	No	In review
62204	2-Chlorophenol	95-57-8	Yes	--
62206	2-Chloro-4-phenylphenol	92-04-6	Yes	--
62207	Potassium 2-chloro-4-phenylphenate	18128-16-0	Yes	--
62208	4-Chloro-2-phenylphenol	NA	Yes	--
62209	4-Chloro-2-phenylphenol, potassium salt	53404-21-0	Yes	--
62210	6-Chloro-2-phenylphenol	85-97-2	Yes	--
62211	6-Chloro-2-phenylphenol, potassium salt	18128-17-1	Yes	--
62212	4-Chloro-2-phenylphenol, sodium salt	10605-10-4	Yes	--
62213	6-Chloro-2-phenylphenol, sodium salt	10605-11-5	Yes	--
62214	4 and 6-Chloro-2-phenylphenol, diethanolamine salt	53537-63-6	Yes	--
62215	2-Chloro-4-phenylphenol, sodium salt	31366-97-9	Yes	--
64202	4-Chloro-2-cyclopentylphenol	13347-42-7	Yes	--

Table 8-29. Status of first pesticide data call-in: pesticides suspected of having the potential to become contaminated with dioxins if synthesized under conditions favoring dioxin formation (continued)

Shaughnessey code	Pesticide [active ingredient]	CAS No.	Support withdrawn	Testing required
64208	Fentichlor [2,2'-Thiobis(4-chloro-6-methylphenol)]	4418-66-0	Yes	--
64209	Fentichlor [2,2'-Thiobis(4-chlorophenol)]	97-24-5	Yes	--
64214	4-Chloro-2-cyclopentylphenol, potassium salt of	35471-38-6	Yes	--
64218	4-Chloro-2-cyclopentylphenol, sodium salt	53404-20-9	Yes	-
67707	Chlorophacinone	3691-35-8	No	No
69105	ADBAC [Alkyl* dimethyl benzyl ammonium chloride *(50% C14, 40% C12, 10% C16)]	68424-85-1	No	No
69144	ADBAC [Alkyl* dimethyl 3,4-dichlorobenzyl ammonium chloride *(61% C12, 23% C14, 11% C16, 5% C18)]	NA	No	No
77401	Niclosamide [2-Aminoethanol salt of 2',5-dichloro-4'-nitrosalicylanilide]	1420-04-8	No	No
77406	5-Chlorosalicylanilide	4638-48-6	Yes	--
78780	2-Methyl-4-isothiazolin-3-one	NA	Yes	--
79202	Tetradifon [4-chlorophenyl 2,4,5-trichlorophenyl sulfone]	116-29-0	Yes	--
79301	Chloranil [tetrachloro-p-benzoquinone]	118-75-2	Yes	--
80403	6-Chlorothymol	89-68-9	Yes	--
80811	Anilazine [2,4-Dichloro-6-(o-chloroanilino)-s-triazine]	101-05-3	Yes	--
81901	Chlorothalonil [tetrachloroisophthalonitrile]	1897-45-6	No	Yes
82602	Sodium 2,3,6-Trichlorophenylacetate	2439-00-1	Yes	--
84101	Chlorfenvinphos	470-90-6	Yes	--
84901	O-(2-Chloro-1-(2,5-dichlorophenyl)vinyl) O,O-diethyl phosphorothioate	1757-18-2	Yes	--
86801	PCMX [4-Chloro-3,5-xylenol]	88-04-0	No	No
97003	Piperalin [3-(2-Methylpiperidino)propyl 3,4-dichlorobenzoate]	3478-94-2	No	No
100601	Fenamiphos	NA	No	No
101001	p-Chlorophenyl diiodomethyl sulfone	20018-12-6	Yes	--
101101	Metribuzin	21087-64-9	No	No
104301	Bifenox [methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate]	42576-02-3	Yes	--
106001	Methazole [2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione]	20354-26-1	Yes	--

Table 8-29. Status of first pesticide data call-in: pesticides suspected of having the potential to become contaminated with dioxins if synthesized under conditions favoring dioxin formation (continued)

Shaughnessey code	Pesticide [active ingredient]	CAS No.	Support withdrawn	Testing required
108201	Diflubenzuron [N-(((4-chlorophenyl)amino)carbonyl)-2,6-difluorobenzamide]	35367-38-5	No	Yes
109001	Oxadiazon [2-tert-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)- delta 2 -1,3,4-oxadiazoline-5-one]	19666-30-9	No	Yes
109301	Fenvalerate	51630-58-1	No	In review
109302	Fluvalinate [N-2-Chloro-4-trifluoromethyl)phenyl-DL-valine (+-)-cyano(3-phenoxy-phenyl)methyl ester]	69409-94-5	No	No
109801	Iprodione [3-(3,5-Dichlorophenyl)-N-(1-methylethyl)-2,4-dioxo-1-imidazolidinecarboxamide (9CA)]	36734-19-7	No	No
109901	Triadimefon [1-(4-Chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone]	43121-43-3	No	No
110902	Diclofop - methyl [methyl 2-(4-(2,4-dichlorophenoxy)phenoxy)propanoate]	51338-27-3	No	Yes
111401	Profenofos [O-(4-Bromo-2-chlorophenyl)-O-ethyl S-propyl phosphorothioate]	41198-08-7	No	In review
111601	Oxyfluorfen [2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene]	42874-03-3	No	In review
111901	Imazalil [1-(2-(2,4-Dichlorophenyl)-2-(2-propenyloxy)ethyl)-1H-imidazole]	35554-44-0	No	No
112802	Bromothalin [N-Methyl-2,4-dinitro-n-(2,4,6-tribromophenyl)-6-(trifuloromethyl)benzenamine]	63333-35-7	No	No
113201	Vinclozolin [3-(3,5-Dichlorophenyl)-5-ethenyl-5-methyl-2,4-oxazolidinedione (9CA)]	50471-44-8	No	No
119001	Fenridazon [Potassium 1-(p-chlorophenyl)-1,4-dihydro-6-methyl-4-oxo- pyridazine-3-carboxylate]	83588-43-6	No	In review
123901	Tridiphane [2-(3,5-Dichlorophenyl)-2-(2,2,2-trichloroethyl) oxirane]	58138-08-2	No	No
125601	Paclobutrazol	76738-62-0	No	No
128838	Linalool	78-70-6	No	In review
206600	Fenarimol [a-(2-chlorophenyl)-a-(4-chlorophenyl)-5-pyrimidinemethanol]	60168-88-9	No	No

NA = Not available
-- = No information given

- Discussion of the formation of impurities. Under the requirements mandated by 40 CFR 158.120, Subdivision D, EPA required submittal of a detailed discussion and assessment of the possible formation of HDDs and HDFs.

Registrants had the option of voluntarily canceling their product or "reformulate to remove an active ingredient" to avoid having to comply with the DCI.

The second DCI, dated June and October 1987, "Data Call-In for Analytical Chemistry Data on Polyhalogenated Dibenzo-*p*-Dioxins/Dibenzofurans (HDDs and HDFs)," was issued for 68 pesticides (16 pesticide active ingredients) suspected to be contaminated with CDDs/CDFs (see Table 8-30). All registrants supporting registrations for these pesticides were subject to the requirements of this DCI unless the product qualified for various exemptions or waivers. Pesticides covered by the second DCI were strongly suspected by EPA of containing detectable levels of CDDs/CDFs. Under the second DCI, registrants whose products did not qualify for an exemption or waiver were required to generate and submit the following types of data in addition to the data requirements of the first DCI:

- Quantitative method for measuring CDDs or CDFs. Registrants were required to develop an analytical method for measuring the HDD/HDF content of their products. The DCI established a regimen for defining the precision of the analytical method. Target LOQs were established in the DCI for specific CDD/CDF congeners (see Table 8-25).

- Certification of limits of CDDs or CDFs. Registrants were required to submit a "Certification of Limits" in accordance with 40 CFR 158.110 and 40 CFR 158.120, Subdivision D. Analytical results were required that met the guidelines described above.

Registrants could select one of two options to comply with the second DCI. The first option was to submit relevant existing data, develop new data, or share the cost of developing new data with other registrants. The second option was to alleviate the DCI requirements through several exemption processes, including a Generic Data Exemption, voluntary cancellation, reformulation to remove the active ingredient of concern, an assertion that the data requirements did not apply, or the application or award of a low-volume, minor-use waiver.

The data contained in CSFs, as well as any other data generated under 40 CFR 158.120, Subdivision D, are typically considered confidential business information (CBI) under the guidelines prescribed in FIFRA because they usually contain information regarding proprietary manufacturing processes. In general, all analytical results submitted to EPA in response to both DCIs are considered CBI and cannot be released by EPA into the public domain. Summaries

Table 8-30. Status of second pesticide Data Call-In: pesticides suspected of being contaminated with dioxins

Shaughnessey code	Pesticide [active ingredient]	CAS No.	Support withdrawn	Testing required
29801	Dicamba [3,6-dichloro-o-anisic acid]	1918-00-9	No	Yes
29802	Dicamba dimethylamine [3,6-dichloro-o-anisic acid]	2300-66-5	No	Yes
29803	Diethanolamine dicamba [3,6-dichloro-2-anisic acid]	25059-78-3	Yes	--
30001	2,4-Dichlorophenoxyacetic acid	94-75-7	No	Yes
30002	Lithium 2,4-dichlorophenoxyacetate	3766-27-6	No	No
30003	Potassium 2,4-dichlorophenoxyacetate	14214-89-2	Yes	--
30004	Sodium 2,4-dichlorophenoxyacetate	2702-72-9	No	No
30005	Ammonium 2,4-dichlorophenoxyacetate	2307-55-3	Yes	--
30010	Alkanol* amine 2,4-dichlorophenoxyacetate *(salts of the ethanol and ispropanol series)	NA	Yes	--
30011	Alkyl* amine 2,4-dichlorophenoxyacetate *(100% C12)	2212-54-6	Yes	--
30013	Alkyl* amine 2,4-dichlorophenoxyacetate *(100% C14)	28685-18-9	Yes	--
30014	Alkyl* amine 2,4-dichlorophenoxyacetate *(as in fatty acids of tall oil)	NA	Yes	--
30016	Diethanolamine 2,4-dichlorophenoxyacetate	5742-19-8	No	No
30017	Diethylamine 2,4-dichlorophenoxyacetate	20940-37-8	Yes	--
30019	Dimethylamine 2,4-dichlorophenoxyacetate	2008-39-1	No	No
30020	N,N-Dimethyloleylamine 2,4-dichlorophenoxyacetate	53535-36-7	Yes	--
30021	Ethanolamine 2,4-dichlorophenoxyacetate	3599-58-4	Yes	--
30023	Heptylamine 2,4-dichlorophenoxyacetate	37102-63-9	Yes	--
30024	Isopropanolamine 2,4-dichlorophenoxyacetate	6365-72-6	Yes	--
30025	Isopropylamine 2,4-dichlorophenoxyacetate	5742-17-6	No	No
30028	Morpholine 2,4-dichlorophenoxyacetate	6365-73-7	Yes	--
30029	N-Oleyl-1,3-propylenediamine 2,4-dichlorophenoxyacetate	2212-59-1	Yes	--
30030	Octylamine 2,4-dichlorophenoxyacetate	2212-53-5	Yes	--
30033	Triethanolamine 2,4-dichlorophenoxyacetate	2569-01-9	Yes	--
30034	Triethylamine 2,4-dichlorophenoxyacetate	2646-78-8	No	No
30035	Triisopropanolamine 2,4-dichlorophenoxyacetate	32341-80-3	No	No

Table 8-30. Status of second pesticide Data Call-In: pesticides suspected of being contaminated with dioxins (continued)

Shaughnessey code	Pesticide [active ingredient]	CAS No.	Support withdrawn	Testing required
30039	N,N-Dimethyl oleyl-linoleyl amine 2,4-dichlorophenoxyacetate	55256-32-1	Yes	--
30052	Butoxyethoxypropyl 2,4-dichlorophenoxyacetate	1928-57-0	Yes	--
30053	Butoxyethyl 2,4-dichlorophenoxyacetate	1929-73-3	No	No
30055	Butoxypropyl 2,4-dichlorophenoxyacetate	1928-45-6	Yes	--
30056	Butyl 2,4-dichlorophenoxyacetate	94-80-4	Yes	--
30062	Isobutyl 2,4-dichlorophenoxyacetate	1713-15-1	Yes	--
30063	Isooctyl(2-ethylhexyl) 2,4-dichlorophenoxyacetate	1928-43-4	No	Yes
30064	Isooctyl(2-ethyl-4-methylpentyl) 2,4-dichlorophenoxyacetate	25168-26-7	Yes	--
30065	Isooctyl(2-octyl) 2,4-dichlorophenoxyacetate	1917-97-1	Yes	--
30066	Isopropyl 2,4-dichlorophenoxyacetate	94-11-1	No	No
30072	Propylene glycol butyl ether 2,4-dichlorophenoxyacetate	1320-18-9	Yes	--
30801	4-(2,4-Dichlorophenoxy)butyric acid	94-82-6	No	Yes
30804	Sodium 4-(2,4-dichlorophenoxy)butyrate	10433-59-7	No	No
30819	Dimethylamine 4-(2,4-dichlorophenoxy)butyrate	2758-42-1	No	No
30853	Butoxyethanol 4-(2,4-dichlorophenoxy)butyrate	32357-46-3	Yes	--
30856	Butyl 4-(2,4-dichlorophenoxy)butyrate	6753-24-8	Yes	--
30863	Isooctyl 4-(2,4-dichlorophenoxy)butyrate	1320-15-6	Yes	--
31401	2-(2,4-Dichlorophenoxy)propionic acid	120-36-5	No	Yes
31419	Dimethylamine 2-(2,4-dichlorophenoxy)propionate	53404-32-3	No	No
31453	Butoxyethyl 2-(2,4-dichlorophenoxy)propionate	53404-31-2	No	No
31463	Isooctyl 2-(2,4-dichlorophenoxy)propionate	28631-35-8	No	No
31501	MCPP acid [2-(2-Methyl-4-chlorophenoxy)propionic acid]	7085-19-0	No	Yes
31519	MCPP, DMA [Dimethylamine 2-(2-methyl-4-chlorophenoxy)propionate]	32351-70-5	No	No
35301	Bromoxynil [3,5-dibromo-4-hydroxybenzonitrile]	1689-84-5	No	Yes
44901	Hexachlorophene [2,2'-Methylenebis(3,4,6-trichlorophenol)]	70-30-4	Yes	--

Table 8-30. Status of second pesticide Data Call-In: pesticides suspected of being contaminated with dioxins (continued)

Shaughnessey code	Pesticide [active ingredient]	CAS No.	Support withdrawn	Testing required
44902	Hexachlorophene, Na salt [Monosodium 2,2'-methylenebis(3,4,6-trichlorophenate)]	5736-15-2	Yes	--
44904	Hexachlorophene, K salt [Potassium 2,2'-methylenebis(3,4,6-trichlorophenate)]	67923-62-0	Yes	--
54901	Irgasan [5-Chloro-2-(2,4-dichlorophenoxy)phenol]	3380-34-5	No	Yes
63004	Tetrachlorophenols	25167-83-3	Yes	--
63005	Tetrachlorophenols, sodium salt	25567-55-9	Yes	--
63006	Tetrachlorophenols, alkyl* amine salt*(as in fatty acids of coconut oil)	NA	Yes	--
63007	Tetrachlorophenols, potassium salt	53535-27-6	Yes	--
64203	Bithionolate sodium [Disodium 2,2'-thiobis(4,6-dichlorophenate)]	6385-58-6	Yes	--
64212	Phenachlor [2,4,6-Trichlorophenol]	88-06-2	Yes	--
64219	Potassium 2,4,6-trichlorophenate	2591-21-1	Yes	--
64220	2,4,6-Trichlorophenol, sodium salt	3784-03-0	Yes	--
64501	Phenothiazine	92-84-2	Yes	--
78701	Dacthal-DCPA [Dimethyl tetrachloroterephthalate]	1861-32-1	No	Yes
79401	Endosulfan [hexachlorohexahydromethano-2,4,3-benzodioxathiepin-3-oxide]	115-29-7	No	No
82501	Silvex [2-(2,4,5-trichlorophenoxy)propionic acid]	93-72-1	Yes	--
83701	Tetrachlorvinphos [2-Chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate]	961-11-5	No	Yes
104101	Edolan [Sodium 1,4',5'-trichloro-2'-(2,4,5-trichlorophenoxy) methanesulfonanilide]	69462-14-2	Yes	--

NA = Not available
-- = No information given

based on the trends identified in those data as well as in data made public by EPA are summarized below.

The two DCIs included 161 pesticides. Of these, 92 are no longer supported by registrants. Following evaluation of the process chemistry submissions required under the DCIs, OPP determined that formation of CDDs/CDFs was not likely during the manufacture of 43 of the remaining 69 pesticides; thus, analysis of samples of these 43 pesticides was not required by OPP. Evaluation of process chemistry data is ongoing at OPP for an additional 7 pesticides. Table 8-30 indicates which pesticides are no longer supported and those for which OPP has required further testing to determine whether CDDs/CDFs are present as contaminants (U.S. EPA, 1995g). OPP required that analysis of production samples be performed on the remaining 19 pesticides (see Table 8-31). The status of the analytical data generation/evaluation to date is summarized as follows: (a) no detection of CDDs/CDFs above the LOQs in registrant submissions for 13 active ingredients, (b) detection of CDDs/CDFs above the LOQs for 2,4-D acid (two submissions) and 2,4-D 2-ethyl hexyl acetate (one submission), and (c) ongoing data generation or evaluation for four pesticides.

Table 8-32 presents a summary of results obtained by EPA for CDDs/CDFs in eight technical 2,4-D herbicides; these data were extracted from program files in OPP. Because some of these files contained CBI, the data in this table were reviewed by OPP staff to ensure that no CBI was being disclosed (memorandum dated May 28, 1996, from S. Funk, U.S. EPA, to W. Hazel, U.S. EPA). Figure 8-5 presents a congener profile for 2,4-D based on the average congener concentrations reported in Table 8-32.

Schecter et al. (1997) reported the results of analyses of samples of 2,4-D manufactured in Europe, Russia, and the United States (see Table 8-33). The total TEQ concentrations measured in the European and Russian samples were similar to those measured in the EPA DCI samples; however, the levels reported by Schecter et al. for U.S. samples were significantly lower. Similarly, Masunaga et al. (2001) reported the analyses of two agrochemical formulations containing 2,4-D manufactured in Japan (Table 8-33). The total TEQ concentration measured in one of the samples was similar to what Schecter et al. (1997) reported for the U.S. samples; no TEQ was detected in the other sample.

As discussed in Section 11.2.1 (Chapter 11), an estimated 28,100 metric tons of 2,4-D were used in the United States in 2000, making it one of the top 10 pesticides in terms of quantity used (EPA proprietary data). The pesticide 2,4-D is the only product judged to have the potential for environmental release through its agricultural use. However, no estimate of environmental release can be made for 2000. Since 1995, the chemical manufacturers of 2,4-D have been undertaking voluntary actions to significantly reduce the dioxin content of the product. No information is available on the level of dioxin contamination, if any, that may have been present

Table 8-31. Summary of analytical data submitted to EPA in response to pesticide Data Call-In(s)

Shaughnessey code	Pesticide		Number of positive[a] submissions to date
	Common name	Chemical name	
019201	MCPB, 4-butyric acid	4-(2-methyl-4-chlorophenoxy)butyric acid	0
019401	4-CPA	4-Chlorophenoxyacetic acid	0
027401	Dichlobenil	2,6-Dichlorobenzonitrile	0
029801	Dicamba	3,6-Dichloro-o-anisic acid	0
029802	Dicamba, dimethylamine	3,6-Dichloro-o-anisic acid, dimethylamine salt	0
030001	2,4-D	2,4-Dichlorophenoxy acetic acid	2
030063	2,4-D, 2EH	Isooctyl(2-ethylhexyl)2,4-dichlorophenoxyacetate	1
030801	2,4-DB	4-(2,4-Dichlorophenoxy)butyric acid	0
031301	DCNA	2,6-Dichloro-4-nitroaniline	Pending
031401	2,4-DP	2-(2,4-Dichlorophenoxy)propionic acid	0
031501	Mecoprop (MCPP)	2-(2-methyl-4-chlorophenoxy)propionic acid	0
035301	Bromoxynil	3,5-Dibromo-4-hydroxybenzonitrile	0
054901	Irgasan	5-Chloro-2-(2,4-dichlorophenoxy)phenol	0
078701	Dacthal (DCPA)	Dimethyl tetrachloroterephthalate	Pending
081901	Chlorothalonil	Tetrachloroisophthalonitrile	Pending
083701	Tetrachlorvinphos	2-Chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate	0
108201	Diflubenzuron	N-(((4-chlorophenyl)amino)carbonyl)-2,6-difluorobenzamide	0
109001	Oxadiazon	2-Tert-butyl-4(2,4-dichloro-5-isopropoxyphenyl)-delta2-1,3,4-oxadiazoline-5-one	Pending
110902	Dichlofop-methyl	Methyl-2-(4-(2,4-dichlorophenoxy)phenoxy) propanoate	0

[a]Positive is defined as the detection of any congener at a concentration equal to or exceeding the limits of quantitation listed in Table 8-27.

Sources: U.S. EPA (1995f); facsimile dated March 27, 1996 from S. Funk, U.S. EPA, to D. Cleverly, U.S. EPA.

Table 8-32. Summary of results for CDDs/CDFs in technical 2,4-D and 2,4-D ester herbicides

Congener	EPA LOQ[a] (µg/kg)	Total no. of technicals	Number of technicals greater than LOQ	Observed maximum conc. (µg/kg)	Average conc.[b] (µg/kg)
2,3,7,8-TCDD	0.1	8	2	0.13	0.06
1,2,3,7,8-PeCDD	0.5	8	3	2.6	0.78
1,2,3,4,7,8-HxCDD	2.5	8	0	0.81	0.31
1,2,3,6,7,8-HxCDD	2.5	8	0	0.77	0.39
1,2,3,7,8,9-HxCDD	2.5	8	0	0.68	0.24
1,2,3,4,6,7,8-HpCDD	100.0	8	0	1.5	0.21
OCDD	--	--	--	--	--
2,3,7,8-TCDF	1	8	0	0.27	0.07
1,2,3,7,8-PeCDF	5	8	0	0.62	0.38
2,3,4,7,8-PeCDF	5	7	0	0.73	0.07
1,2,3,4,7,8-HxCDF	25	8	0	1.6	0.36
1,2,3,6,7,8-HxCDF	25	8	0	1.2	0.11
1,2,3,7,8,9-HxCDF	25	8	0	1.4	0.16
2,3,4,6,7,8-HxCDF	25	8	0	1.1	0.14
1,2,3,4,6,7,8-HpCDF	1,000	8	0	8.3	2.17
1,2,3,4,7,8,9-HpCDF	1,000	8	0	1.2	0.18
OCDF	--	--	--	--	--
TOTAL[c]					5.6
I-TEQ_{DF}					0.7
TEQ_{DF}-WHO_{98}					1.1

[a]LOQ required by EPA in the data call-in.
[b]Average of the mean results for multiple analyses of four technical 2,4-D and/or 2,4-D ester products for which detectable CDD/CDF congener concentrations less than the LOQs were quantified; nondetect values were assumed to be zero.
[c]Total equals the sum of the individual congener averages.

LOQ = Limit of quantitation
-- = Analyses not performed

Source: U.S. EPA Office of Pesticide Programs file.

in 2,4-D in 2000. An estimated 26,300 and 30,400 metric tons were used during 1995 and 1987, respectively (U.S. EPA, 1997e, 1988d). On the basis of the average CDD/CDF congener concentrations in 2,4-D presented in Table 8-33 (not including OCDD and OCDF), the corresponding TEQ_{DF}-WHO_{98} concentration is 1.1 µg/kg (0.7 µg I-TEQ_{DF}/kg). Combining this

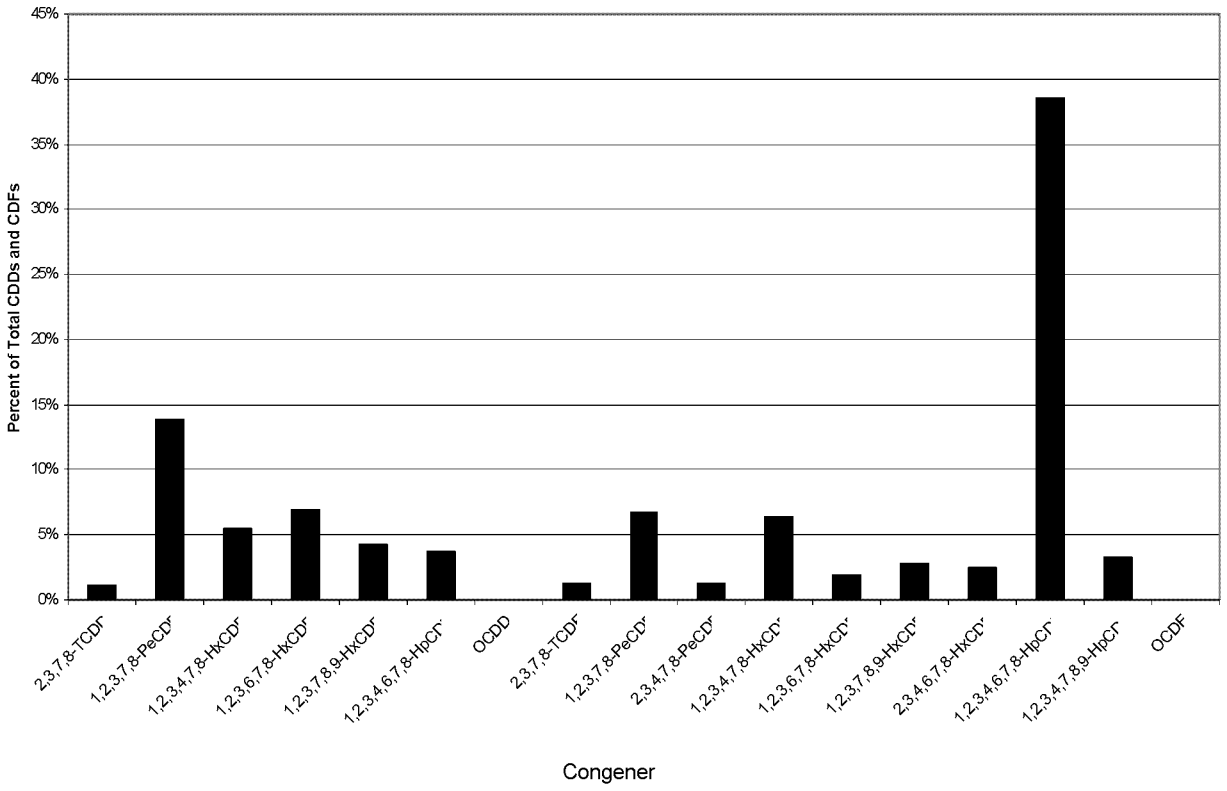


Figure 8-5. Congener profile for 2,4-D (salts and esters) (based on mean concentrations reported in Table 8-34).

TEQ concentration with the activity level estimates for 1995 and 1987 indicates that 28.9 g TEQ_{DF}-WHO_{98} (18.4 g I-TEQ_{DF}) were released in 1995 and 33.4 g TEQ_{DF}-WHO_{98} (21.3 g I-TEQ_{DF}) in 1987. The release estimates for 1987 and 1995 are assigned a high confidence rating, indicating high confidence in both the production and the emission factor estimates. Because no estimate can be made for 2000, it is rated as Category E (no estimate of environmental release of CDDs/CDFs can be made because of the poor quality of existing information).

8.4. OTHER CHEMICAL MANUFACTURING AND PROCESSING SOURCES

8.4.1. Municipal Wastewater Treatment Plants

8.4.1.1. *Sources*

CDDs/CDFs have been measured in nearly all sewage sludges tested, although the concentrations and, to some extent, the congener profiles and patterns differ widely. Potential sources of the CDDs/CDFs include microbial formation (discussed in Chapter 9), runoff to

Table 8-33. CDD/CDF concentrations (µg/kg) in samples of 2,4-D and pesticide formulations containing 2,4-D

Congener/congener group	Acbar Super (Gaza City[a])	Amco Super (Gaza City[a])	(Bethlehem)[a]	Chimprom (Russia)	Dragon Lawn Weed Killer	KGRO (U.S.)	Pro Care Premium (U.S.)	Ortho Weed-B-Gone (U.S.)	Sigma Co. (U.S.)	American Brand Chemical Co. (U.S.)	Ishihara Sangyo Kaisha, Ltd. (Japan)	Nissan Chemical Industries, Ltd. (Japan)
2,3,7,8-TCDD	ND (0.1)	ND (0.1)	ND (0.1)	ND (0.02)	ND (0.001)	--	--	--	--	--	0.0021	ND (0.002)
1,2,3,7,8-PeCDD	0.1	ND (0.1)	1.2	0.03	0.0014	--	--	--	--	--	0.011	ND (0.002)
1,2,3,4,7,8-HxCDD	ND (0.1)	ND (0.1)	ND (0.1)	0.02	ND (0.001)	--	--	--	--	--	ND (0.005)	ND (0.005)
1,2,3,6,7,8-HxCDD	ND (0.1)	0.2	0.6	0.05	0.0024	--	--	--	--	--	ND (0.005)	ND (0.005)
1,2,3,7,8,9-HxCDD	ND (0.1)	ND (0.1)	0.4	ND (0.02)	0.001	--	--	--	--	--	ND (0.005)	ND (0.005)
1,2,3,4,6,7,8-HpCDD	0.1	1.2	0.3	0.23	0.0017	--	--	--	--	--	ND (0.005)	ND (0.005)
OCDD	0.1	2.6	0.1	0.85	0.0063	--	--	--	--	--	ND (0.01)	ND (0.01)
2,3,7,8-TCDF	0.3	ND (0.1)	ND (0.1)	ND (0.1)	0.0036	--	--	--	--	--	ND (0.002)	ND (0.002)
1,2,3,7,8-/1,2,3,4,8-PeCDF	ND (0.1)	0.2	0.7	1.2	0.001	--	--	--	--	--	0.0038	ND (0.002)
2,3,4,7,8-PeCDF	ND (0.1)	ND (0.1)	0.1	0.06	0.0011	--	--	--	--	--	ND (0.002)	ND (0.002)
1,2,3,4,7,8-/1,2,3,4,7,9 -HxCDF	ND (0.1)	0.1	0.4	0.08	0.0013	--	--	--	--	--	ND (0.005)	ND (0.005)
1,2,3,6,7,8-HxCDF	ND (0.1)	ND (0.1)	0.1	0.11	ND (0.001)	--	--	--	--	--	ND (0.005)	ND (0.005)
1,2,3,7,8,9-HxCDF	ND (0.1)	ND (0.1)	ND (0.1)	ND (0.02)	ND (0.001)	--	--	--	--	--	ND (0.005)	ND (0.005)
2,3,4,6,7,8-HxCDF	ND (0.1)	ND (0.1)	0.1	0.05	0.0011	--	--	--	--	--	ND (0.005)	ND (0.005)
1,2,3,4,6,7,8-HpCDF	0.1	0.8	0.1	0.24	0.0016	--	--	--	--	--	ND (0.005)	ND (0.005)
1,2,3,4,7,8,9-HpCDF	ND (0.1)	ND (0.1)	ND (0.1)	0.02	ND (0.001)	--	--	--	--	--	ND (0.005)	ND (0.005)
OCDF	0.2	3.8	0.4	0.46	0.0039	--	--	--	--	--	ND (0.010)	ND (0.01)
Total 2,3,7,8-CDD (nondetect = 0)	0.3	4	2.6	1.18	0.0128	0.0144	0.0143	0.0091	0.127	0.0278	0.013	--
Total 2,3,7,8-CDF (nondetect = 0)	0.6	4.9	1.9	2.22	0.0136	0.1628	0.4253	0.1095	3.0507	0.0822	0.004	--
Total I-TEQ_{DF} (nondetect = 0)[b]	0.082	0.066	0.85	0.142	0.0023	0.0009	0.0012	0.0014	0.0013	0.0019		ND
Total TEQ_{DF}-WHO_{98} (nondetect = 0)[b]	0.134	0.061	1.449	0.156	0.003						0.0078	ND
Total TCDD	--	--	--	--	--	--	--	--	--	--	0.013 0.041	ND (0.002)
Total PeCDD	--	--	--	--	--	--	--	--	--	--	0.018	ND (0.002)
Total HxCDD	--	--	--	--	--	--	--	--	--	--	0.008	ND (0.005)
Total HpCDD	--	--	--	--	--	--	--	--	--	--	ND (0.005)	ND (0.005)
Total OCDD	--	--	--	--	--	--	--	--	--	--	ND (0.01)	ND (0.01)
Total TCDF	--	--	--	--	--	--	--	--	--	--	2.7	0.0093
Total PeCDF	--	--	--	--	--	--	--	--	--	--	0.89	ND (0.002)
Total HxCDF	--	--	--	--	--	--	--	--	--	--	0.019	ND (0.005)
Total HpCDF	--	--	--	--	--	--	--	--	--	--	0.006	ND (0.005)
Total OCDF	--	--	--	--	--	--	--	--	--	--	ND (0.01)	ND (0.01)
Total CDD/CDF	--	--	--	--	--	--	--	--	--	--	3.7	0.0093

Table 8-33. CDD/CDF concentrations (µg/kg) in samples of 2,4-D and pesticide formulations containing 2,4-D (continued)

[a]2,4-D manufactured in Europe and packaged in Palestine.
[b]Calculated assuming nondetect values are zero.

ND = not detected (value in parenthesis is the detection limit)
-- = No information given

Sources: Schecter et al. (1997); Masunaga et al. (2001).

sewers from lands or urban surfaces contaminated by product uses or deposition of previous emissions to air (discussed in Chapter 11, Section 11.2.1), household wastewater, industrial wastewater, and chlorination operations within the wastewater treatment facility (Rappe, 1992b; Rappe et al., 1994; Horstmann et al., 1992; Sewart et al., 1995; Cramer et al., 1995; Horstmann and McLachlan, 1995).

The major source(s) for a given publicly owned treatment works (POTW) is likely to be site specific, particularly in industrialized areas. For example, Rieger and Ballschmiter (1992) traced the origin of CDDs/CDFs found in municipal sewage sludge in Ulm, Germany, to metal manufacturing and urban sources. The characteristics of both sources were similar and suggested generation via thermal processing. However, a series of studies by Horstmann et al. (1992, 1993a, b) and Horstmann and McLachlan (1994a, b, 1995) demonstrated that wastewater generated by laundering and bathing could be the major source at many, if not all, POTWs that serve primarily residential populations. Although runoff from streets during precipitation events, particularly from streets with high traffic density, was reported by these researchers as contributing measurably, the total contribution of TEQ from household wastewater was eight times greater than that from surface runoff at the study city.

Horstmann et al. (1992) provided initial evidence that household wastewater could be a significant source. Horstmann et al. (1993a) measured CDD/CDF levels in the effluent from four different loads of laundry from two different domestic washing machines. The concentrations of total CDDs/CDFs in the four samples ranged from 3,900 to 7,100 pg/L and were very similar in congener profile, with OCDD being the dominant congener, followed by the hepta- and hexa-CDDs. Because of the similar concentrations and congener profiles found, the authors concluded that the presence of CDDs/CDFs in washing machine wastewater is widespread. A simple mass balance performed using the results (Horstmann and McLachlan, 1994a) showed that the CDDs/CDFs found in the four washing machine wastewater samples could account for 27 to 94% of the total CDDs/CDFs measured in the sludge of the local wastewater treatment plant.

Horstmann et al. (1993a) performed additional experiments that showed that detergents, commonly used bleaching agents, and the washing cycle process itself were not responsible for the observed CDDs/CDFs. To determine whether the textile fabric or fabric finishing processes could account for the observed CDDs/CDFs, Horstmann et al. (1993b), Horstmann and McLachlan (1994a, b), and Klasmeier and McLachlan (1995) analyzed the CDD/CDF content of raw cotton cloth, white synthetic materials, and more than 100 new textile finished products. Low concentrations were found in most products (less than 50 ng/kg of total CDDs/CDFs), but a small percentage contained high concentrations, up to 290 µg/kg of total CDDs/CDFs. On the basis of the concentrations and patterns found, the authors concluded that neither unfinished new fabrics nor common cotton finishing processes could explain the CDD/CDF levels found in

wastewater; rather, the use of CDD-/CDF-containing textile dyes and pigments and the use in some developing countries of PCP to treat unfinished cotton appeared to be the sources of the detected CDDs/CDFs.

Horstmann and McLachlan (1994a, b, 1995) reported the results of additional experiments showing that the small percentage of clothing items with high CDD/CDF levels could be responsible for the quantity of CDDs/CDFs observed in household wastewater and sewage sludge. They demonstrated that the CDDs/CDFs can be gradually removed from the fabric during washing; they can be transferred to the skin, subsequently transferred back to other textiles, and then washed out, or they can be transferred to other textiles during washing and then removed during subsequent washing.

8.4.1.2. *Releases to Water*

8.4.1.2.1. ***Emissions data***. The presence of CDDs/CDFs in sewage sludge suggests that CDDs/CDFs may also be present in the wastewater effluent discharges of POTWs; however, few studies reporting the results of effluent analyses for CDDs/CDFs have been published.

Rappe et al. (1989a) tested the effluent from two Swedish POTWs for all 2,3,7,8-substituted CDD/CDF congeners. OCDD was detected in the effluents from both facilities at concentrations ranging from 14 to 39 pg/L. The investigators detected 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF in the effluent of one facility at concentrations of 2.8 and 2 pg/L, respectively. No 2,3,7,8-substituted tetra-, penta-, and hexa-CDDs or CDFs were detected (DLs of 0.2 to 20 pg/L).

Ho and Clement (1990) reported the results of sampling during the late 1980s of 37 POTWs in Ontario, Canada, for each of the five CDD/CDF congener groups with four to eight chlorines. The sampled facilities included 27 secondary treatment facilities, seven primary treatment facilities, one tertiary plant, and two lagoons. The facilities accounted for about 73% of the sewage discharged by POTWs in Ontario. No CDDs/CDFs were detected (DL in the low ng/L range) in the effluents from the lagoons and the tertiary treatment facility. Only OCDD and TCDF were detected in the effluents from the primary treatment facilities (two and one effluent samples, respectively). HpCDD, OCDD, TCDF, and OCDF were detected in the effluents from the secondary treatment facilities (detected in four or fewer samples at levels ranging from 0.1 to 11 ng/L).

Gobran et al. (1995) analyzed the raw sewage and final effluent of an Ontario, Canada, wastewater treatment plant for CDD/CDF congeners over a 5-day period. Although HpCDD, OCDD, HpCDF, and OCDF were detected in the raw sewage (12 to 2,300 pg/L), no CDDs/CDFs were detected in the final effluent at congener-specific DLs ranging from 3 to 20 pg/L.

The California Regional Water Quality Control Board reported the results of effluent testing at nine POTWs in the San Francisco area (memorandum dated March 21, 1996, from Lila Tang, California Regional Water Quality Control Board, to David Cleverly, U.S. EPA). A total of 30 samples were collected between 1992 and 1995, and 1 to 6 samples were analyzed for each POTW. The mean concentrations of CDDs/CDFs are shown in Table 8-34. The overall mean TEQ concentration was 0.27 pg TEQ_{DF}-WHO_{98}/L (0.29 pg I-TEQ_{DF}/L). With the exception of OCDD, most 2,3,7,8-substituted CDD/CDF congeners were seldom detected.

Rappe et al. (1998) analyzed effluent samples from 17 POTWs in Mississippi, 10 of which receive input from industrial facilities. Treatment processes at the facilities include the use of one or more of the following: lagoons, activated sludge, aerated digestion, wetlands, oxidative ditch, and trickling filter. Additionally, 12 of the facilities use chlorine gas in the treatment process. The wastewater flows at the facilities range from 0.11 to 39.75 million L/day; however, wastewater flow rates were not known for two facilities. Table 8-35 presents the concentrations of dioxins measured in the effluent samples for each facility and total TEQ emission factors. Concentrations were congener-specific for only 2,3,7,8-TCDD; 2,3,7,8-TCDF; 1,2,3,7,8-PeCDD; 2,3,4,7,8-PeCDF; OCDD; and OCDF. Also provided were concentrations for total HxCDD and total HpCDD. The total I-TEQ concentrations reported by Rappe et al. (assuming nondetect values equal to one-half the DL) ranged from 0.274 to 3.84 pg I-TEQ_{DF}/L (average of 0.81 pg/I-TEQ_{DF}/L). Because concentrations for all congeners were not provided, emission factors could not be calculated in TEQ_{DF}-WHO_{98}.

The CRWQCB data (memorandum dated March 21, 1996, from Lila Tang, California Regional Water Quality Control Board, to David Cleverly, U.S. EPA) were collected to provide representative effluent concentrations for the San Francisco area. These data cannot be considered to be representative of CDD/CDF effluent concentrations at the 16,000-plus POTWs nationwide. Therefore, the data can be used only to generate a preliminary estimate of the potential mass of CDD/CDF TEQ that may be released annually by U.S. POTWs.

8.4.1.2.2. ***Activity level information.*** Based on the results of the 1996 and 2000 Clean Water Needs Surveys, an estimated 122 billion L and 148 billion L of wastewater were treated daily by POTWs in the United States in 1996 and 2000, respectively (U.S. EPA, 1997c, 2004).

Wastewater treatment data were not available for 1987; however, an estimate was developed using the population of the United States as a surrogate. In 2000, the population of the United States was approximately 281 million people. Using the estimate of water treated daily by POTWs in 2000, approximately 527 L/person of wastewater were treated daily by POTWs. In 1990, the population of the United States was approximately 249 million people. Assuming the

Table 8-34. Mean CDD/CDF concentrations and range of detection limits (DLs) (pg/L) in effluents from nine U.S. publicly owned treatment works (POTWs)

Congener/congener group	No. of detections/ samples	Range of DLs	Range of detected concentrations (POTW mean basis)		Overall mean concentrations[a]	
			Minimum	Maximum	Nondetect set to 0	Nondetect set to ½ DL
2,3,7,8-TCDD	0/30	0.31–8.8	ND	ND	0	0.98
1,2,3,7,8-PeCDD	0/30	0.45–15	ND	ND	0	1.32
1,2,3,4,7,8-HxCDD	0/30	0.43–9.8	ND	ND	0	1.38
1,2,3,6,7,8-HxCDD	0/30	0.81–10	ND	ND	0	1.42
1,2,3,7,8,9-HxCDD	0/30	0.42–9.7	ND	ND	0	1.31
1,2,3,4,6,7,8-HpCDD	3/30	0.75–18	ND	5	1.06	3.61
OCDD	13/30	6.2–57	ND	99.75	29.51	37.95
2,3,7,8-TCDF	1/27	0.74–4.4	ND	1.3	0.14	0.98
1,2,3,7,8-PeCDF	1/30	0.64–9.4	ND	2	0.22	1.58
2,3,4,7,8-PeCDF	1/30	0.61–14	ND	2.8	0.31	1.68
1,2,3,4,7,8-HxCDF	1/30	0.25–6.8	ND	2.4	0.27	1.22
1,2,3,6,7,8-HxCDF	1/30	0.23–6.8	ND	1.5	0.17	0.97
1,2,3,7,8,9-HxCDF	1/30	0.57–10	ND	2	0.22	1.72
2,3,4,6,7,8-HxCDF	1/30	0.25–7.9	ND	ND	0	0.93
1,2,3,4,6,7,8-HpCDF	2/30	0.36–6.9	ND	4.6	0.68	1.83
1,2,3,4,7,8,9-HpCDF	0/30	0.19–11	ND	ND	0	1.18
OCDF	1/30	0.86–28	ND	3.2	0.36	3.4
Total 2,3,7,8-CDD			ND	104.75	30.57	47.97
Total 2,3,7,8-CDF	--	--	ND	19.8	2.37	15.49
Total I-TEQ_{DF}			ND	2.42	0.29	3.66
Total TEQ_{DF}-WHO_{98}			ND	2.33	0.27	4.28
Total TCDD	4/27	1.2–8.8	ND	9.7	1.23	2.61
Total PeCDD	0/27	0.62–200	ND	ND	0	6.27
Total HxCDD	1/30	0.84–11	ND	1.7	0.19	1.93
Total HpCDD	3/30	0.75–18	ND	8.4	1.83	4.77
Total OCDD	13/30	6.2–57	ND	99.75	29.51	37.95
Total TCDF	2/30	0.39–6.8	ND	25	6.61	7.7
Total PeCDF	1/30	0.64–25	ND	20	2.22	4.72
Total HxCDF	1/30	0.93–17	ND	13	1.44	3.43
Total HpCDF	2/30	0.36–19	ND	4.6	0.68	2.41
Total OCDF	1/30	0.86–28	ND	3.2	0.36	3.4
Total CDD/CDF			ND	185.35	44.07	75.19

[a]The overall means are the means of the individual POTW mean concentrations rather than the means of the individual sample concentrations.

DL = Detection limit
ND = Not detected
-- = No information given

Source: Memorandum dated March 21, 1996, from Lila Tang, California Regional Water Quality Control Board, to David Cleverly, U.S. EPA.

Table 8-35. Effluent concentrations (pg/L) of CDDs/CDFs from publicly owned treatment works in Mississippi

Facility	2,3,7,8-TCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDD	2,3,4,7,8-PeCDF	Total HxCDD	Total HpCDD	OCDD	OCDF	Total I-TEQ
Waynesboro	ND (0.17)	0.18	ND (0.2)	ND (0.1)	ND	3.5	13	1.8	0.316
Meridian	0.18	0.12	ND (0.16)	ND (0.09)	1.3	7.6	58	1.8	0.445
Pascagoula	ND (0.13)	0.15	ND (0.15)	0.11	ND	0.82	3.6	0.46	0.264
W. Biloxi	0.18	0.24	ND (0.15)	0.082	ND	0.9	4	ND (0.34)	0.378
Gulfport	0.16	0.24	ND (0.15)	0.094	ND	2.3	9.9	0.78	0.371
Laurel	ND (0.18)	0.15	ND (0.23)	ND (0.12)	ND	2.9	38	ND (0.48)	0.334
Brookhaven	ND (0.18)	0.54	0.45	0.16	0.85	3.2	28	1.7	0.796
Natchez	ND (0.16)	0.41	0.6	0.34	2.5	2.4	9.1	1.8	1.03
Picayune	ND (0.22)	0.56	ND (0.27)	ND (0.14)	6.5	38	120	2	0.715
Picayune[a]	ND (0.13)	0.54	ND (0.12)	ND (0.07)	6	30	53	106	0.397
Waveland	ND (0.18)	17	0.22	0.66	ND	3	14		2.4
Corinth	ND (0.15)	0.17	ND (0.16)	ND (0.09)	0.77	2.7	18	0.9	0.276
New Augusta	ND (0.1)	1.3	0.28	0.085	21	120	2,500	1.1	3.84
Beaumont	ND (0.1)	0.14	ND (0.13)	0.088	0.64	2.4	11	0.66	0.274
Leaksville	ND (0.12)	0.72	0.25	0.15	8.9	46	780	3.2	1.6
McLain	ND (0.06)	ND (0.05)	ND (0.10)	ND (0.06)	2.5	14	200		0.377
Hattiesburg South	ND (0.16)	ND (0.24)	ND (0.24)	ND (0.11)	1.2	4.5	59	0.77	0.32
Hattiesburg North	ND (0.19)	0.18	ND (0.26)	ND (0.13)	0.96	9.1	73	2.9	0.457
AVERAGE	0.17	1.42	0.36	0.2	4.43	16.3	221.76	8.99	0.81

[a]Blind double.

ND = Not detected (value in parenthesis is the detection limit). When calculating the average, NDs were not included.

Source: Rappe et al. (1998).

population did not change drastically between 1987 and 1990, and assuming that the daily domestic wastewater treatment per person remained constant between 1987 and 2000, EPA estimates that approximately 131 billion L of wastewater were treated daily at POTWs in 1987.

8.4.1.2.3. ***Emission Estimates.*** Multiplying the amount of wastewater treated by 365 days/yr by the overall mean TEQ concentrations reported by CRWQCB (memorandum dated March 21, 1996, from Lila Tang, California Regional Water Quality Control Board, to David Cleverly, U.S. EPA) (0.27 pg TEQ_{DF}-WHO_{98}/L [0.29 pg I-TEQ_{DF}/L]) yields annual TEQ release estimates of 12.9 g TEQ_{DF}-WHO_{98} (13.9 g I-TEQ_{DF}), 12 g TEQ_{DF}-WHO_{98} (13 g I-TEQ_{DF}), and 14.6 g TEQ_{DF}-WHO_{98} (15.7 g I-TEQ_{DF}) for 1987, 1995, and 2000, respectively. These estimates should be regarded as preliminary indications of possible emissions from this source.

8.4.1.3. *Sewage Sludge Land Disposal*

Sewage sludge is the solid, semi-solid, or liquid residue generated during the treatment of wastewater. During wastewater treatment, nutrients, pathogens, inorganic compounds (metals and trace elements), and organic compounds (CDDs/CDFs, PCBs, and surfactants) from the incoming wastewater are partitioned to the resulting sewage sludge (NRC, 2002). The sludge is either disposed of through methods such as incineration or landfill/surface disposal or beneficially used through methods such as land application.

Sewage sludge that is applied to land is referred to as biosolids. In order to be applied to land, the biosolids must be treated to meet land application regulatory requirements (Federal Register, 1993a). Biosolids are often used for crop production, gardening, forestry, turf growth, and landscaping. Some other uses include strip mine and gravel pit reclamation and wetland restoration. Land application of biosolids is beneficial because it improves the physical and chemical properties of the soil needed for plant growth, it reduces the need for other disposal methods, and it reduces or eliminates the need for commercial fertilizers. Commercial fertilizers often have higher nutrient contents than do biosolids; therefore, the application of biosolids to land in lieu of commercial fertilizers may reduce the impacts of high levels of excess nutrients entering the environment (U.S. EPA, 1999b).

8.4.1.3.1. ***Emissions data.*** EPA conducted the National Sewage Sludge Survey in 1988 and 1989 to obtain national data on sewage sludge quality and management. As part of this survey, EPA analyzed sludges from 174 POTWs that employed at least secondary wastewater treatment for more than 400 analytes, including CDDs/CDFs. Although sludges from only 16% of the POTWs had detectable levels of 2,3,7,8-TCDD, all sludges had detectable levels of at least one CDD/CDF congener (U.S. EPA, 1996e). I-TEQ_{DF} concentrations as high as 1,820 ng/kg dry

weight were measured. The congener-specific results of the survey are presented in Table 8-36. If all nondetect values found in the study are assumed to be zero, then the mean and median I-TEQ_{DF} concentrations of the sludges from the 174 POTWs are 50 and 11.2 ng/kg (dry-weight basis), respectively. If the nondetect values are set equal to the DL, then the mean and median I-TEQ_{DF} concentrations are 86 and 50.4 ng/kg, respectively (U.S. EPA, 1996e; Rubin and White, 1992).

Table 8-36. CDD/CDF concentrations (ng/kg) measured in the 1998/1999 National Sewage Sludge Survey[a]

Congener	Percent detected	Maximum concentration detected	Median concentration		Mean concentration	
			Nondetect set to detection limit	Nondetect set to zero	Nondetect set to detection limit	Nondetect set to zero
2,3,7,8-TCDD	16	116	6.86	0	--	--
1,2,3,7,8-PeCDD	18	736	9.84	0	--	--
1,2,3,4,7,8-HxCDD	25	737	22.5	0	--	--
1,2,3,6,7,8-HxCDD	49	737	27.3	0	--	--
1,2,3,7,8,9-HxCDD	39	737	28	0	--	--
1,2,3,4,6,7,8-HpCDD	98	52,500	335	335	--	--
OCDD	100	905,000	3,320	3,320	--	--
2,3,7,8-TCDF	65	337	17	3.9	--	--
1,2,3,7,8-PeCDF	22	736	9.6	0	--	--
2,3,4,7,8-PeCDF	26	736	10.4	0	--	--
1,2,3,4,7,8-HxCDF	43	1,500	28	0	--	--
1,2,3,6,7,8-HxCDF	35	737	18	0	--	--
1,2,3,7,8,9-HxCDF	16	1,260	18	0	--	--
2,3,4,6,7,8-HxCDF	27	737	18	0	--	--
1,2,3,4,6,7,8-HpCDF	71	7,100	57	36	--	--
1,2,3,4,7,8,9-HpCDF	26	842	23	0	--	--
OCDF	80	69,500	110	80	--	--
Total I-TEQ_{DF}		1,820	50.4	11.2	86[b]	50[b]
Total 2,3,7,8-CDD/CDF		--	--	--	--	--

[a]For publicly owned treatment works with multiple samples, the pollutant concentrations were averaged before the summary statistics presented in the table were calculated.
[b]Values presented by Rubin and White (1992) for 175 rather than 174 publicly owned treatment works.

-- = No information given

Source: U.S. EPA (1996e).

Green et al. (1995) and Cramer et al. (1995) reported the results of analyses of 99 samples of sewage sludge collected from wastewater treatment plants across the United States during the summer of 1994 as part of the 1994/1995 Association of Metropolitan Sewerage Agencies (AMSA) survey. These data are summarized in Table 8-37. To calculate average results in units of TEQ, Green et al. averaged the results from all samples collected from the same facility to ensure that the results were not biased toward the concentrations found at facilities from which more than one sample was collected. Also, eight samples were excluded from the calculation of the overall TEQ averages because it was unclear whether they were duplicate samples from other POTWs. POTW average TEQ concentrations were calculated for 74 POTWs. If all nondetect values are assumed to be zero, then the overall study mean and median I-TEQ_{DF} concentrations were 47.7 and 33.4 ng I-TEQ_{DF}/kg (dry weight basis), respectively (standard deviation of 44.7 ng I-TEQ_{DF}/kg). The corresponding mean and median TEQ_{DF}-WHO_{98} concentrations were 36.3 and 25.5 ng/kg, respectively (standard deviation, 38.6).

The mean and median results reported by Green et al. (1995) and Cramer et al. (1995) are very similar in terms of total TEQ to those reported by EPA for samples collected 5 years earlier (U.S. EPA, 1996e; Rubin and White, 1992). The predominant congeners in both data sets are the octa- and hepta-CDDs and CDFs. Although not present at high concentrations, 2,3,7,8-TCDF was commonly detected.

In addition to effluents, Rappe et al. (1998) analyzed the levels of CDDs/CDFs in municipal sewage sludge from the 17 POTWs in Mississippi. Table 8-38 presents the concentrations of dioxins measured in the sewage sludge samples and total TEQ emission factors reported by Rappe et al. Concentrations were only congener specific for 2,3,7,8-TCDD; 2,3,7,8-TCDF; 1,2,3,7,8-PeCDD; 2,3,4,7,8-PeCDF; OCDD; and OCDF. Also provided were concentrations for total HxCDD and total HpCDD. The TEQ emission factors (assuming nondetects equal to one-half the DL) ranged from 2.26 to 1,270 ng I-TEQ_{DF}/kg. The predominant congeners in all samples were the octa- and hepta-CDDs. The sludge with the highest concentrations of octa- and hepta-CDDs was from the Picayune POTW, which receives industrial inputs, including effluents from wood treatment facilities that likely contain PCP. In general, the sludges with the lowest TEQ values were from the facilities that do not receive effluent from industrial facilities. Additionally, the samples with the two lowest TEQ values were from facilities that do not use free chlorine as a disinfectant.

In 1999, sewage sludge samples from a POTW in Ohio were collected and analyzed for CDDs/CDFs (U.S. EPA, 2000b). The facility, which accepts both domestic and industrial wastewater, employs secondary wastewater technology. Assuming nondetects are zero, the mean TEQ emission factor was 21.9 ng TEQ_{DF}-WHO_{98}/kg (dry-weight basis). These results are presented in Table 8-39.

Table 8-37. CDD/CDF concentrations (ng/kg) measured in 99 sludges collected from U.S. publicly owned treatment works (POTWs) during 1994

Congener	Percent detected	Maximum concentration detected	Median concentration		Mean concentration			
			Nondetect set to detection limit	Nondetect set to zero	Nondetect set to detection limit[a]		Nondetect set to zero[a]	
2,3,7,8-TCDD	40	12.3	1.95	0	2.72	(2.4)	1.71	(2.86)
1,2,3,7,8-PeCDD	23	37.5	8.23	0	10.9	(7.8)	3.34	(7.43)
1,2,3,4,7,8-HxCDD	34	45.6	5.25	0	11.1	(8.13)	6.03	(10.2)
1,2,3,6,7,8-HxCDD	87	130	25.6	24.7	33.8	(27.6)	32.2	(28.8)
1,2,3,7,8,9-HxCDD	64	88.8	12.3	9.48	20.2	(17.7)	17	(19.8)
1,2,3,4,6,7,8-HpCDD	98	5,380	642	642	981	(977)	981	(977)
OCDD	99	65,500	6,630	6,630	11,890	(12,540)	11,890	(12,540)
2,3,7,8-TCDF	76	156	7.53	6.28	12.8	(19.6)	11.1	(20.2)
1,2,3,7,8-PeCDF	21	60.3	7.91	0	10.7	(11.3)	3.53	(9.36)
2,3,4,7,8-PeCDF	42	155	9.7	0	15.7	(19.8)	10.5	(21.6)
1,2,3,4,7,8-HxCDF	48	170	11.5	0	20.4	(25.3)	14	(25.9)
1,2,3,6,7,8-HxCDF	17	200	14	0	30.4	(53.6)	5.13	(21.9)
1,2,3,7,8,9-HxCDF	4	115	7.53	0	11.1	(13.6)	1.56	(11.7)
2,3,4,6,7,8-HxCDF	35	356	9.85	0	21.8	(40.4)	13.6	(41)
1,2,3,4,6,7,8-HpCDF	64	1,460	91.7	31.8	223	(271)	97.5	(207)
1,2,3,4,7,8,9-HpCDF	31	213	11.7	0	27.1	(34.8)	15	(33.4)
OCDF	93	11,200	286	281	786	(1,503)	775	(1,506)
Average I-TEQ$_{DF}$ (facility basis)[b]		246	49.6	33.4	64.5	(50.1)	47.7	(44.7)
Total 2,3,7,8-CDD/CDF		85,279.5	7,782.8	7,625.3	14,108.7	(15,573)	13,878.2	(15,484.2)
Average TEQ$_{DF}$-WHO$_{98}$ (facility basis)[b]			44.6	25.5	57.2	(44.4)	36.3	(38.6)

[a]Value in parenthesis is the standard deviation.

[b]For POTWs with multiple samples, the sample TEQ concentrations were averaged to POTW averages before calculation of the total TEQ mean and median values presented in the table. A total of 74 POTW average concentrations were used in the calculations. In addition, the following sample ID numbers were not included in the averaging because, according to Green et al. (1995), it was not possible to determine whether they were duplicate or multiple samples from other POTWs: 87, 88, 89, 90, 91, 97, 98, and 106.

Sources: Green et al. (1995); Cramer et al. (1995).

Table 8-38. Concentrations of CDDs/CDFs (ng/kg dry matter) in sewage sludge from publicly owned treatment works in Mississippi

Facility	2,3,7,8-TCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDD	2,3,4,7,8-PeCDF	Total HxCDD	Total HpCDD	OCDD	OCDF	Total I-TEQ
Waynesboro	2.1	2.9	3.5	1.4	85	920	7,400	410	23.7
Meridian	ND (0.06)	2.1	6.4	2.8	10	100	7,400	410	27.6
Pascagoula	2	3.6	5.3	3.5	170	970	4,300	170	26.4
W. Biloxi	0.84	2.4	3.2	1.3	78	280	1,800	70	13.7
Gulfport	1.9	9.1	9.5	3.4	200	1,100	7,700	310	30.9
Laurel	0.17	0.3	0.37	0.25	22	160	2,700	21	4.83
Brookhaven	2	2.5	11	2.5	130	1,400	9,300	230	36.7
Natchez	ND (0.58)	8.3	8.4	ND (1.5)	270	1,100	6,800	270	37.7
Picayune	5.3	69	74	24	17,000	250,000	480,000	16,000	1,270
Picayune[a]	4.1	66	60	17	16,000	210,000	420,000	17,000	1,240
Waveland	1.6	2.6	5.1	1.9	130	580	3,500	150	31.7
Corinth	0.3	1.8	0.97	0.93	42	230	3,300	36	7.4
New Augusta	ND (0.13)	0.17	0.15	0.094	21	140	1,400	8.8	2.67
Beaumont	0.17	0.67	0.78	0.37	59	470	1,900	42	6.18
Leaksville	ND (0.051)	0.14	0.32	0.11	16	92	560	26	2.26
McLain	0.076	0.17	0.11	0.031	39	140	2,600	0.74	3.55
Hattiesburg S	1	1.1	9.1	2.2	170	1,3000	4,400	180	33
Hattiesburg N	ND (0.035)	1.7	4	2	310	3,600	27,000	980	70.4
Average	1.7	9.7	11.2	3.8	1,930.7	26,904.6	55,114.4	2,017.5	159.4 ± 399

[a]Blind double.

ND = Not detected (value in parenthesis is the detection limit). When calculating the average, NDs were not included.

Source: Rappe et al. (1998).

Table 8-39. CDD/CDF median concentrations (ng/kg) measured in 1999 from a publicly owned treatment works facility in Ohio

Congener	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	ND	0.0018
1,2,3,7,8-PeCD	ND	0.0082
1,2,3,4,7,8-HxCDD	2.67	2.67
1,2,3,6,7,8-HxCDD	21.33	21.33
1,2,3,7,8,9-HxCDD	30.33	30.33
1,2,3,4,6,7,8-HpCDD	298	298
OCDD	2,963	2,963
2,3,7,8-TCDF	26.67	26.67
1,2,3,7,8-PeCDF	4.33	4.34
2,3,4,7,8-PeCDF	10	10
1,2,3,4,7,8-HxCDF	21	21
1,2,3,6,7,8-HxCDF	5.33	5.33
1,2,3,7,8,9-HxCDF	ND	0.0033
2,3,4,6,7,8-HxCDF	9	9
1,2,3,4,6,7,8-HpCDF	171	171
1,2,3,4,7,8,9-HpCDF	ND	0.01
OCDF	364.67	364.67
Average total TEQ_{DF}-WHO_{98}	21.87	21.88

ND = Not detected

Source: U.S. EPA (2000b).

In 2000 and 2001, AMSA conducted another survey of dioxin-like compounds in sewage sludge (Alvarado et al., 2001). A total of 200 sewage sludge samples were collected from 171 POTWs located in 31 states. Assuming nondetects are zero, TEQ emission factors range from 0.08 to 3,578.61 ng TEQ_{DF}-WHO_{98}/kg. The mean and median TEQ emission factors were 34.5 and 11.79 ng TEQ_{DF}-WHO_{98}/kg, respectively.

EPA conducted another National Sewage Sludge Survey to characterize the dioxin and dioxin-like equivalence levels in biosolids produced by 6,857 POTWs operating in the United States in 2001 (U.S. EPA, 2002d). Samples were collected from 94 POTWs using secondary or higher treatment practices. All facilities had been sampled previously as part of the 1988/1989 National Sewage Sludge Survey. The overall mean and median TEQ_{DF}-WHO_{98} concentrations were 75 and 15 ng/kg, respectively. However, when the data were weighted using the daily influent wastewater flow rates (i.e., the number of facilities with wastewater flow rate

>100 Mg/day, >10 but ≤100 Mg/day, >1 but ≤10 Mg/day, and ≤1 Mg/day), the overall mean and median TEQ_{DF}-WHO_{98} concentrations were 21.7 and 15.5 ng/kg, respectively. These data are summarized in Table 8-40.

Table 8-40. CDD/CDF mean concentrations (ng/kg) measured in the 2001 National Sewage Sludge Survey

Congener	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	1.41	1.1
1,2,3,7,8-PeCD	5.76	4.57
1,2,3,4,7,8-HxCDD	11.8	7.49
1,2,3,6,7,8-HxCDD	21.3	15.1
1,2,3,7,8,9-HxCDD	3.6	2.22
1,2,3,4,6,7,8-HpCDD	492	273
OCDD	6,780	2,730
2,3,7,8-TCDF	3.11	2.3
1,2,3,7,8-PeCDF	2.61	1.5
2,3,4,7,8-PeCDF	6.03	2.8
1,2,3,4,7,8-HxCDF	1.37	1
1,2,3,6,7,8-HxCDF	0.27	0
1,2,3,7,8,9-HxCDF	5.21	2.6
2,3,4,6,7,8-HxCDF	5.5	3.36
1,2,3,4,6,7,8-HpCDF	9.13	2.8
1,2,3,4,7,8,9-HpCDF	167	88.2
OCDF	802	279
Average total TEQ_{DF}-WHO_{98}	21.7	15.5

Source: U.S. EPA (2002d).

The CDD/CDF concentrations and congener group patterns observed in the U.S. surveys are similar to those reported for sewage sludges in several other Western countries. Stuart et al. (1993) reported mean CDD/CDF concentrations of 23.3 ng I-TEQ_{DF}/kg (dry weight) for three sludges from rural areas, 42.3 ng I-TEQ_{DF}/kg for six sludges from light industry/domestic areas, and 52.8 ng I-TEQ_{DF}/kg for six sludges from industrial/domestic areas collected during 1991–1992 in England and Wales. Näf et al. (1990) reported concentrations ranging from 31 to 40 ng I-TEQ_{DF}/kg (dry weight) in primary and digested sludges collected from the POTW in Stockholm, Sweden, during 1989. Gobran et al. (1995) reported an average concentration of 15.7 ng I-TEQ_{DF}/kg in anaerobically digested sludges from an industrial/domestic POTW in Ontario, Canada. In all three studies, the congener group concentrations increased with

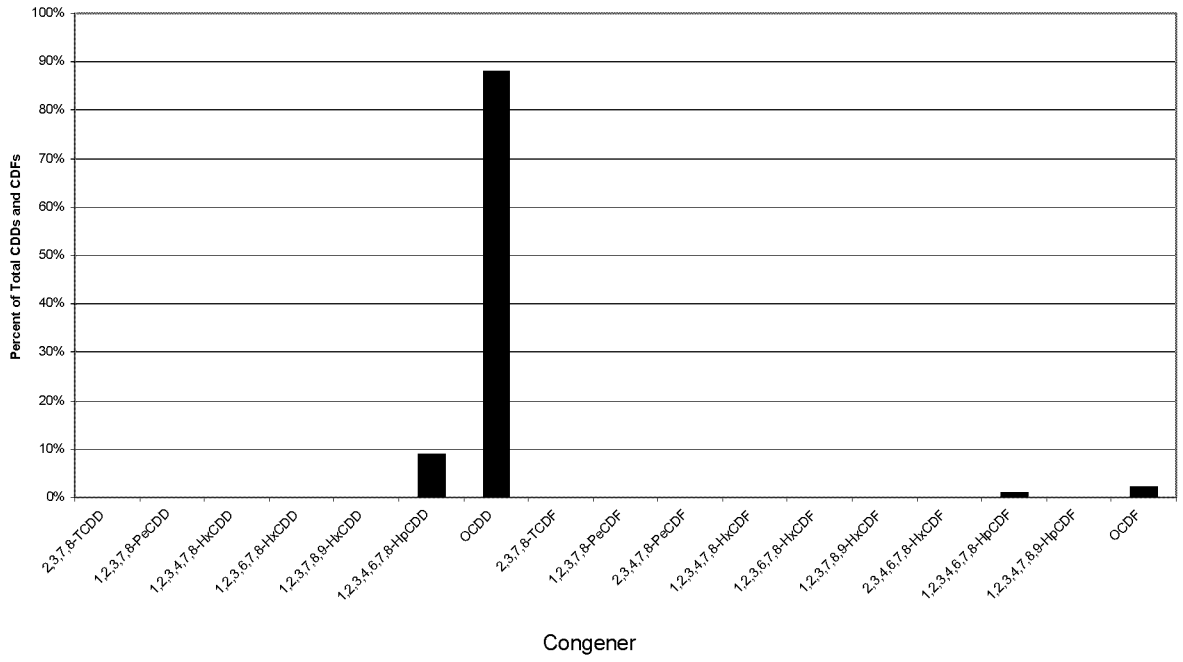


Figure 8-6. Congener profiles for sewage sludge (created from data in Table 8-38).

increasing degrees of chlorination, with OCDD the dominant congener. Figure 8-6 presents congener profiles, using the mean concentrations reported by Green et al. (1995).

Because the mean I-TEQ_{DF} concentration values reported in the 1988/1989 sewage sludge survey (U.S. EPA, 1996e) and the 1995 survey (Green et al., 1995; Cramer et al., 1995) were very similar, the estimated amounts of TEQs that may have been present in sewage sludge and released to the environment in 1987 and 1995 were assumed to be the same. These values were estimated using the average (49 ng I-TEQ_{DF}/kg) of the mean I-TEQ_{DF} concentration values (nondetects equal to DLs) reported by U.S. EPA (1996e) (50 ng I-TEQ_{DF}/kg) and by Green et al. (1995) and Cramer et al. (1995) (36.3 ng TEQ_{DF}-WHO_{98}/kg [47.7 ng I-TEQ_{DF}/kg]). Therefore, the overall average mean emission factor for reference years 1987 and 1995 is 36.3 ng TEQ_{DF}-WHO_{98}/kg (48.9 ng I-TEQ_{DF}/kg). The emission factor of 21.7 ng TEQ_{DF}-WHO_{98}/kg, as calculated from the 2001 survey, appears to be the most reasonable TEQ emission factor estimate for reference year 2000 because this estimate is nationally weighted on the basis of wastewater flow rates of POTWs operating in the United States in 2001.

8.4.1.3.2. ***Activity level information.*** According to the results of its 1988/1989 National Sewage Sludge Survey, EPA estimated that approximately 5.4 million dry metric tons of sewage

sludge were generated in 1989 (Federal Register, 1993a). EPA also used the results of the 1984 to 1996 Clean Water Needs Surveys to estimate that 6.3 million dry metric tons of sewage sludge were generated in 1998. Because estimates for reference years 1987 and 1995 are not available, the 1989 and 1998 activity level estimates were used for 1987 and 1995, respectively. Tables 8-41 and 8-42 list the volumes, by use and disposal practices, of sludge disposed of annually for reference years 1987 and 1995, respectively.

U.S. EPA (1999b) estimated that 6.6 million dry metric tons of sewage sludge would be generated in 2000. Table 8-43 lists the volumes, by use and disposal practices, of sludge disposed of annually for reference year 2000. Similarly, the National Research Council (NRC) analyzed the amount of biosolids being applied to land in 2002 (NRC, 2002). Citing 2001 data (unpublished) from the Wisconsin Department of National Resources, the NRC estimated that approximately 8,650 of the 16,000 POTWs operating in the United States generated sewage sludge requiring use or disposal. Using data from 37 states, the investigators estimated that 5,900 of these sewage sludge generators either land applied or publicly distributed more than 3.4 million dry tons of biosolids annually. The volume of biosolids, by use and disposal practices, is presented in Table 8-44. The volume of biosolids and their distribution among the various categories estimated by the NRC are very close to those estimated by EPA.

8.4.1.3.3. ***Emission estimates.*** Annual potential releases of CDDs/CDFs were determined by multiplying the mean total TEQ concentrations by the sludge volumes generated. The mean total TEQ concentrations in sewage sludges for reference years 1987, 1995, and 2000 are reported in Tables 8-41, 8-42, and 8-43, respectively. For 1987, the total annual potential release from nonincinerated sludges was 151 g TEQ_{DF}-WHO_{98}. Of this amount, 2.6 g TEQ_{DF}-WHO_{98} (3.5 g I-TEQ_{DF}) entered commerce as a product for distribution and marketing and 76.6 g TEQ_{DF}-WHO_{98} (103 g I-TEQ_{DF}) was applied to land. The remaining 71.8 g TEQ_{DF}-WHO_{98} did not result in an environmental release because it was sent to RCRA Subtitle D landfills or disposal sites. For 1995, the total annual potential release from nonincinerated sludges was 178 g TEQ_{DF}-WHO_{98}. Of this amount, 3 g TEQ_{DF}-WHO_{98} (4 g I-TEQ_{DF}) entered commerce as a product for distribution and marketing and 116.1 g TEQ_{DF}-WHO_{98} (156.5 g I-TEQ_{DF}) was applied to land. The remaining 58.9 g TEQ_{DF}-WHO_{98} did not result in an environmental release because it was sent to RCRA Subtitle D landfills or disposal sites. For 2000, the total annual release of nonincinerated sludges was 111 g TEQ_{DF}-WHO_{98}. Of this amount, 1.9 g TEQ_{DF}-WHO_{98} (1.9 g I-TEQ_{DF}) entered commerce as a product for distribution and marketing and 78.2 g TEQ_{DF}-WHO_{98} (78.2 g I-TEQ_{DF}) was applied to land. The remaining 30.9 g TEQ_{DF}-WHO_{98} did not result in an environmental release because it was sent to RCRA Subtitle D landfills or disposal sites.

Table 8-41. Quantity of sewage sludge disposed of and potential dioxin TEQ releases from primary, secondary, and advanced treatment publicly owned treatment works for reference year 1987

Use/disposal practice	Volume disposed of (1,000 dry metric tons/yr)	Percent of total volume	Potential dioxin release[a] (g TEQ/yr)	
			I-TEQ_{DF}	TEQ_{DF}-WHO_{98}
Land application	1,714	32[b]	84	62.2
Distribution and marketing	71	1.3	3.5	2.6
Surface disposal site/other	396	7.4	19.4	14.4
Sewage sludge landfill	157	2.9	7.7	5.7
Co-disposal landfills[c]	1,819	33.9	89.1	66
Sludge incinerators and co-incinerators[d]	865	16.1	[e]	[e]
Ocean disposal	(336)[f]	(6.3)[f]	[f]	[f]
TOTAL	5,358	100	203.7	150.9

[a]Potential dioxin TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (second column) by the average of the mean I-TEQ_{DF} concentrations in sludge reported by Rubin and White (1992) (i.e., 50 ng/kg dry weight) and Green et al. (1995) and Cramer et al. (1995) (47.7 ng/kg). The calculations of TEQ_{DF}-WHO_{98} used the mean concentration of 36.3 ng TEQ_{DF}-WHO_{98}/kg for the results reported by Green et al. (1995) and Cramer et al. (1995).

[b]Includes 21.9% applied to agricultural land, 2.8% applied as compost, 0.6% applied to forestry land, 3.1% applied to "public contact" land, 1.2% applied to reclamation sites, and 2.4% applied in undefined settings.

[c]Landfills used for disposal of sewage sludge and solid waste residuals.

[d]Co-incinerators treat sewage sludge in combination with other combustible waste materials.

[e]See Section 3.5 for estimates of CDD/CDF releases to air from sewage sludge incinerators.

[f]The Ocean Dumping Ban Act of 1988 generally prohibited the dumping of sewage sludge into the ocean after December 31, 1991. Ocean dumping of sewage sludge ended in June 1992 (Federal Register, 1993a). The current method of disposal of the 336,000 metric tons of sewage sludge that were disposed of in the oceans in 1988 has not been determined.

These release estimates are assigned a high confidence rating for both the production and the emission factor estimates. The high rating is based on the judgment that the 174 facilities tested as part of the 1988/1989 National Sewage Sludge Survey (U.S. EPA, 1996e), the 74 facilities tested as part of the 1994/1995 AMSA Survey (Green et al., 1995 and Cramer et al., 1995), and the 94 facilities tested as part of the 2001 National Sewage Sludge Survey (U.S. EPA, 2002d) were reasonably representative of the variability in POTW technologies and sewage characteristics nationwide.

Table 8-42. Quantity of sewage sludge disposed of and potential dioxin TEQ releases from primary, secondary, and advanced treatment publicly owned treatment works for reference year 1995

Use/disposal practice	Volume disposed of (1,000 dry metric tons/yr)	Percent of total volume	Potential dioxin release[a] (g TEQ/yr)	
			I-TEQ_{DF}	TEQ_{DF}-WHO_{98}
Land application[b]	2,500	40	122.3	90.7
Advanced treatment[c]	700	11	34.2	25.4
Other beneficial use[d]	500	8	24.5	18.2
Surface disposal/landfill	1,100	17	53.8	39.9
Incineration	1,400	22	[e]	[e]
Other disposal method	100	2	4.9	3.6
TOTAL	6,300	100	239.7	177.8

[a]Potential dioxin TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (second column) by the average of the mean I-TEQ_{DF} concentrations in sludge reported by Rubin and White (1992) (50 ng/kg dry weight) and Green et al. (1995) and Cramer et al. (1995) (47.7 ng/kg). The calculations of TEQ_{DF}-WHO_{98} used the mean concentration of 36.3 ng TEQ_{DF}-WHO_{98}/kg for the results reported by Green et al. (1995) and Cramer et al. (1995).

[b]Without further processing or stabilization, such as composting.

[c]Such as composting.

[d]EPA assumes that this category includes distribution and marketing (i.e., sale or give-away of sludge for use in home gardens). Based on the 1988 National Sewage Sludge Survey and 1988 Needs Survey, approximately 1.3% of the total volume of sewage disposed is distributed and marketed (Federal Register, 1993a). Therefore, it is estimated that 3 g TEQ_{DF}-WHO_{98} (4 g I-TEQ_{DF}) were released through distribution and marketing in 1995.

[e]See Section 3.5 for estimates of CDD/CDF releases to air from sewage sludge incinerators.

Sources: Federal Register (1990, 1993a).

8.4.2. Drinking Water Treatment Plants

There is no strong evidence that chlorination of water for drinking purposes results in the formation of CDDs/CDFs. Few surveys of CDD/CDF content in finished drinking water have been conducted. Those that have been published have only rarely reported the presence of any CDDs/CDFs, even at low picogram per liter DLs, and in those cases, CDDs/CDFs were also present in the untreated water.

Rappe et al. (1989b) reported the formation of tetra- through octa-CDFs when tap water and double-distilled water were chlorinated using chlorine gas. The CDF levels found in the single samples of tap water and double-distilled water were 35 and 7 pg I-TEQ_{DF}/L, respectively. No CDDs were detected at DLs ranging from 1 to 5 pg/L. However, the water samples were

Table 8-43. Quantity of sewage sludge disposed of and potential dioxin TEQ releases from primary, secondary, and advanced treatment publicly owned treatment works for reference year 2000

Use/disposal practice	Volume disposed of (1,000 dry metric tons/yr)	Percent of total volume	Potential dioxin release[a] (g TEQ/yr)
			TEQ_{DF}-WHO_{98}
Land application[b]	2,800	42	60.80
Advanced treatment[c]	800	12	17.40
Other beneficial use[d]	500	8	10.90
Surface disposal/landfill	900	14	19.50
Incineration	1,500	23	[e]
Other disposal method	100	2	2.17
TOTAL	6,600	100	111.00

[a]Potential dioxin TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (second column) by the average of the mean TEQ_{DF}-WHO_{98} concentrations in sludge reported in U.S. EPA (2002d).
[b]Without further processing or stabilization, such as composting.
[c]Such as composting.
[d]EPA assumes that this category includes distribution and marketing (sale or give-away of sludge for use in home gardens). Based on the 1988 National Sewage Sludge Survey and 1988 Needs Survey, approximately 1.3% of the total volume of sewage disposed is distributed and marketed (Federal Register, 1993a). Therefore, it is estimated that 1.9 g TEQ_{DF}-WHO_{98} were released through distribution and marketing in 2000.
[e]See Section 3.5 for estimates of CDD/CDF releases to air from sewage sludge incinerators.

Table 8-44. Biosolids disposal practices for reference year 2000

Use/disposal practice	Volume disposed of (1,000 dry metric tons/yr)	Percent of total volume
Land application	3,100	61
Surface disposal/landfill	940	18
Incineration	1,000	20
Other	64	1
TOTAL	5,104	100

Source: NRC (2002).

chlorinated at a dosage rate of 300 mg/L, which is considerably higher (by one to two orders of magnitude) than the range of dosage rates typically used to disinfect drinking water. The authors hypothesized that the CDFs or their precursors were present in chlorine gas.

Rappe et al. (1990c) analyzed a 1,500-L sample of drinking water from a municipal drinking water treatment plant in Sweden. Although the untreated water was not analyzed, a sludge sample from the same facility was analyzed. The large sample volume enabled DLs on the order of 0.001 pg/L. The TEQ contents of the water and the sludge were 0.0029 pg I-TEQ_{DF}/L and 1.4 ng/kg, respectively. The congener patterns of the drinking water and sludge sample were very similar, suggesting that the CDDs/CDFs detected in the finished water were present in the untreated water.

8.4.3. Soaps and Detergents

As discussed in Section 8.4.1, CDDs/CDFs were detected in nearly all sewage sludges tested, whether the sludges were obtained from industrialized areas or from rural areas. Because of the ubiquitous presence of CDDs/CDFs in sewage sludge, several studies have been conducted to determine their source(s). A logical category of products to test, because of their widespread use, is detergents, particularly those that contain or release chlorine during use (i.e., hypochlorite-containing and dichloroisocyanuric acid-containing detergents). The results of studies conducted to date, summarized below, indicate that CDDs/CDFs are not formed during use of chlorine-free detergents, chlorine-containing or chlorine-releasing detergents, or chlorine bleach during household bleaching operations.

Sweden's Office of Nature Conservancy (1991) reported that the results of a preliminary study conducted at one household indicated that CDDs/CDFs may be formed during use of dichloroisocyanurate-containing dishwasher detergents. A more extensive main study with multiple runs was then conducted using standardized food, dishes, cutlery, and other household items. Testing of laundry washing and fabric bleaching and actual testing of the CDD/CDF content of detergents was also performed. The study examined (1) hypochlorite- and dichloroisocyanurate-containing dishwasher detergents, (2) sodium hypochlorite-based bleach (4.4% NaOCl) in various combinations with and without laundry detergent, and (3) sodium hypochlorite-based bleach, used at a high enough concentration to effect bleaching of a pair of imported blue jeans.

CDDs/CDFs were not detected in either the chlorine-free detergent or the detergent with hypochlorite; 0.6 pg TEQ/g were detected in the detergent containing dichloroisocyanurate. The results of all dishwasher and laundry washing machine tests showed very low levels of CDDs/CDFs, often nondetected values. There was no significant difference between the controls and the test samples; in fact, the control samples had a higher TEQ content than did some of the test samples. The drainwater from the dishwasher tests contained <1 to <3 pg I-TEQ_{DF}/L (the water-only control sample contained <2.8 pg I-TEQ_{DF}/L). The CDD/CDF content of the laundry

drainwater samples ranged from <1.1 to <4.6 pg I-TEQ_{DF}/L (the water-only control sample contained <4.4 pg I-TEQ_{DF}/L).

Thus, under the study's test conditions, CDDs/CDFs were not formed during dishwashing or laundry washing or during bleaching with hypochlorite-containing bleach. No definitive reason could be found for the difference in results between the preliminary study and the main study for dishwashing with dichloroisocyanurate-containing detergents. The authors of the study suggested that differences in the foods used and the prewashing procedures employed in the two studies were the likely causes of the variation in the results.

Rappe et al. (1990b) analyzed a sample of a Swedish commercial soft soap, a sample of tall oil, and a sample of tall resin for CDD/CDF content. Tall oil and tall resin, by-products of the pulping industry, are the starting materials for the production of soft liquid soap. Crude tall oil, collected after the Kraft pulping process, is distilled under reduced pressure at temperatures of up to 280 to 290°C, yielding tall oil and tall resin. The measured TEQ content of the liquid soap was found to be 0.647 ng TEQ_{DF}-WHO_{98}/L (0.447 ng I-TEQ_{DF}/L). PeCDDs were the dominant congener group, followed by HpCDDs, HxCDDs, PeCDFs, and OCDD, with some tetra-CDFs and CDDs also present. The TEQ contents of the tall oil (12 ng TEQ_{DF}-WHO_{98}/kg [9.4 ng I-TEQ_{DF}/kg]) and tall resin (196 ng TEQ_{DF}-WHO_{98}/kg [200 ng I-TEF_{DF}/kg]) were significantly higher than the level found in the liquid soap. The tall oil contained primarily tetra- and penta-CDDs and CDFs, whereas the tall resin contained primarily HpCDDs, HxCDDs, and OCDD. The investigators compared the congener patterns of the three samples and noted that although the absolute values for the tetra- and penta-CDDs and CDFs differed among the tall oil, tall resin, and liquid soap samples, the same congeners were present. The congener patterns for the higher-chlorinated congeners were very similar. Table 8-45 presents the results of the study.

In 1987, 118 million L of liquid household soaps were shipped in the United States (U.S. DOC, 1990b); shipment quantity data are not available in the 1992 U.S. Economic Census (U.S. DOC, 1996). Because only one sample of liquid soap has been analyzed for CDD/CDF content (Rappe et al., 1990b), no estimate of environmental release can be made.

8.4.4. Textile Manufacturing and Dry Cleaning

As discussed in Section 8.4.1, CDDs/CDFs have been detected in almost all sewage sludges tested, whether they were obtained from industrialized areas or rural areas. To determine whether textile fabric or fabric finishing processes could account for the observed CDDs/CDFs, several studies were conducted in Germany. These studies, summarized in the following paragraphs, indicate that some finished textile products do contain detectable levels of CDDs/CDFs and that they can be released from the textile during laundering or dry cleaning;

Table 8-45. CDD/CDF concentrations in Swedish liquid soap, tall oil, and tall resin

Congener/congener group	Liquid soap (ng/L)	Tall oil (ng/kg)	Tall resin (ng/kg)
2,3,7,8-TCDD	ND (0.009)	3.6	ND (1)
1,2,3,7,8-PeCDD	0.4	5.3	3.1
1,2,3,4,7,8-HxCDD	ND (0.02)	ND (2)	ND (4)
1,2,3,6,7,8-HxCDD	0.32	ND (2)	810
1,2,3,7,8,9-HxCDD	0.18	ND (2)	500
1,2,3,4,6,7,8-HpCDD	1.9	ND (1)	5,900
OCDD	1	5.3	6,000
2,3,7,8-TCDF	0.62	17	ND (2)
1,2,3,4,8-/1,2,3,7,8-PeCDF	0.29	4.2	ND (0.4)
2,3,4,7,8-PeCDF	0.2	1.9	ND (0.5)
1,2,3,4,7,8/9-HxCDF	0.013	1.4	24
1,2,3,6,7,8-HxCDF	ND (0.004)	0.7	--
1,2,3,7,8,9-HxCDF	ND (0.004)	ND (0.7)	ND (1)
2,3,4,6,7,8-HxCDF	ND (0.004)	ND (0.5)	ND (0.7)
1,2,3,4,6,7,8-HpCDF	ND (0.005)	ND (0.8)	10
1,2,3,4,7,8,9-HpCDF	ND (0.01)	ND (2)	9.0
OCDF	NA	NA	NA
Total 2,3,7,8-CDD[a]	3.8	14.2	13,213.1
Total 2,3,7,8-CDF[a]	1.123	25.2	43
Total I-TEQ_{DF}[a]	0.447	9.4	200
Total TEQ_{DF}-WHO_{98}[a]	0.647	12	196
Total TCDD	0.12	31	ND (1)
Total PeCDD	15	380	25
Total HxCDD	3.4	3.3	6,800
Total HpCDD	3.6	ND (1)	11,000
Total OCDD	1	5.3	6,000
Total TCDF	1	26	ND (2)
Total PeCDF	1.3	41	ND (0.5)
Total HxCDF	0.15	4.9	56
Total HpCDF	ND (0.01)	ND (2)	19
Total OCDF	NA	NA	NA
Total CDD/CDF[a]	25.57	491.5	23,900

[a]Calculations assume nondetect values were zero.

NA = Not analyzed
ND = Not detected (value in parenthesis is the detection limit)
-- = No information given

Source: Rappe et al. (1990b).

however, textile finishing processes are typically not sources of CDD/CDF formation. Rather, the use of CDD/CDF-containing dyes and pigments and the use in some countries of PCP to treat unfinished cotton appear to be the sources of the detected CDDs/CDFs.

Horstmann et al. (1993b) analyzed the CDD/CDF content of eight different raw (unfinished) cotton cloths containing fiber from different countries and five different white synthetic materials (acetate, viscose, bleached polyester, polyamide, and polyacrylic). The maximum concentrations found in the textile fabrics were 30 ng/kg in the cotton products and 45 ng/kg in the synthetic materials. Also, a cotton finishing scheme was developed that subjected one of the cotton materials to a series of 16 typical cotton finishing processes; one sample was analyzed following each step. The fabric finishing processes showing the greatest effect on CDD/CDF concentration were the application of an indanthrene dye and the "wash and wear" finishing process, which together resulted in a CDD/CDF concentration of about 100 ng/kg. On the basis of the concentrations found, the authors concluded that neither unfinished new fabrics nor common cotton finishing processes could explain the CDD/CDF levels found in laundry wastewater.

Fuchs et al. (1990) reported that the dry-cleaning solvent redistillation residues collected from 12 commercial and industrial dry-cleaning operations contained considerable amounts of CDDs/CDFs. The reported I-TEQ_{DF} content ranged from 131 to 2,834 ng/kg, with the dominant congeners being OCDD and HpCDD. Towara et al. (1992) demonstrated that neither the use of chlorine-free solvents nor variation of the dry-cleaning process parameters lowered the CDD/CDF content of the residues.

Umlauf et al. (1993) conducted a study to characterize the mass balance of CDDs/CDFs in the dry-cleaning process. The soiled clothes (containing 16 pg total CDDs/CDFs per kg) accounted for 99.996% of the CDD/CDF input. Input of CDDs/CDFs from indoor air containing 0.194 pg/m^3 accounted for the remainder (0.004%). The dry-cleaning process removed 82.435% of the CDDs/CDFs in the soiled clothing. Most of the input CDDs/CDFs (82.264%) were found in the solvent distillation residues. Air emissions (at 0.041 pg/m^3) accounted for 0.0008% of the total input, which was less than the input from indoor air. The fluff (at a concentration of 36 ng/kg) accounted for 0.1697%, and water effluent (at a concentration of 0.07 pg/L) accounted for 0.0000054%.

Horstmann and McLachlan (1994a, b, 1995) analyzed 35 new textile samples (primarily cotton products) obtained in Germany for CDDs/CDFs. Low levels were found in most cases (total CDD/CDF <50 ng/kg). The dominant congeners were OCDD and HpCDD. However, several colored T-shirts from a number of clothing producers had extremely high levels, with concentrations up to 290,000 ng/kg. Because the concentrations in identical T-shirts purchased at the same store varied by up to a factor of 20, the authors concluded that the source of

CDDs/CDFs was not a textile finishing process, because a process source would have resulted in a more consistent level of contamination. Klasmeier and McLachlan (1995) subsequently analyzed 68 new textile products obtained in Germany for OCDD and OCDF. Most samples had nondetectable levels (42 samples <60 ng/kg). Only four samples had levels exceeding 500 ng/kg.

Horstmann and McLachlan (1994a, b) reported finding two different congener group patterns in the more contaminated of the 35 textile products. One pattern agreed with the congener pattern for PCP reported by Hagenmaier and Brunner (1987), whereas the other pattern was similar to that reported by Remmers et al. (1992) for chloranil-based dyes. The authors hypothesized that the use of PCP to preserve cotton, particularly when it is randomly strewn on bales of cotton as a preservative during sea transport, was the likely source of the high levels occasionally observed. Although the use of PCP for nonwood uses was prohibited in the United States in 1987 (see Section 8.3.8), PCP is still used in developing countries, especially to preserve cotton during sea transport (Horstmann and McLachlan, 1994a).

Horstmann and McLachlan (1994a, b) conducted additional experiments that demonstrated that the small percentage of clothing items with high CDD/CDF levels could be responsible for the quantity of CDDs/CDFs observed in household wastewater (see Section 8.4.1.1).

9. INDICATIONS OF POSSIBLE NATURAL SOURCES OF CDDs/CDFs

Numerous laboratory and field research studies have demonstrated that biochemical and photolytic formation of CDDs/CDFs from chlorophenol precursors is possible. In addition, under certain conditions, some CDDs/CDFs can be biodegraded to form less chlorinated (and possibly more toxic) CDDs/CDFs. Both of these mechanisms are discussed in this chapter; however, the extent to which CDDs/CDFs are formed by either mechanism in the environment is not known at present. The potential for releases of CDDs/CDFs from the application of animal manure to farmland and the mining and use of ball clay is also discussed.

9.1. BIOLOGICAL SOURCES OF CDDs/CDFs

9.1.1. Biotransformation of Chlorophenols

Biochemical formation of CDDs/CDFs—particularly the higher-chlorinated congeners—from chlorophenol precursors is possible, as indicated in laboratory studies with solutions of trichlorophenols and pentachlorophenol (PCP) in the presence of peroxidase enzymes and hydrogen peroxide (Svenson et al., 1989; Oberg et al., 1990; Wagner et al., 1990; Oberg and Rappe, 1992; Morimoto and Kenji, 1995) and with sewage sludge spiked with PCP (Oberg et al., 1992). However, the extent to which CDDs/CDFs are formed in the environment via this mechanism cannot be estimated at this time.

In 1991, Lahl et al. (1991) reported finding CDDs/CDFs in all 22 samples of the various types of composts analyzed. The hepta- and octa-substituted CDDs/CDFs were typically the dominant congener groups found. The I-TEQ_{DF} content of the composts ranged from 0.8 to 35.7 ng I-TEQ_{DF}/kg. The CDDs/CDFs found in compost may primarily result from atmospheric deposition onto plants that are subsequently composted, but they may also be caused by uptake of CDDs/CDFs from air by the active compost (Krauss et al., 1994). CDDs/CDFs are also frequently detected in sewage sludges, and they may come primarily from the sources identified in Section 8.4.1.

Peroxidases are common enzymes in nature. For example, the initial degradation of the lignin polymer by white- and brown-rot fungi is peroxidase catalyzed (Wagner et al., 1990). The conversion efficiency of chlorinated phenols to CDDs/CDFs that has been observed is low. In the solution studies, Oberg and Rappe (1992) and Morimoto and Kenji (1995) reported conversion efficiencies of PCP to OCDD of about 0.01% and 0.8%, respectively, and Wagner et al. (1990) reported a conversion efficiency of trichlorophenol to HpCDD of about 0.001%. Oberg et al. (1990) reported a conversion efficiency of trichlorophenols to CDDs/CDFs of about 0.001%. In their sewage sludge study, Oberg et al. (1992) reported a conversion efficiency of PCP to total CDDs of 0.0002 to 0.0004%.

Several researchers have conducted both laboratory and field studies in an attempt to better understand the extent of, and factors affecting, the fate or formation of CDDs/CDFs in composts and sewage sludges. The findings of several of these studies are discussed in the following paragraphs. These findings are not always consistent because the congener profiles and patterns detected—and the extent of CDD/CDF formation, if any—may vary with compost materials studied, differences in experimental or field composting design, and duration of the studies.

Harrad et al. (1991) analyzed finished composts and active compost windrows from a municipally operated yard waste composting facility in Long Island, NY. Concentrations measured in 12 finished composts ranged from 14 to 41 ng I-TEQ_{DF}/kg (mean, 3 ng I-TEQ_{DF}/kg). The concentrations in the five active compost samples (1 to 30 days in age) ranged from 7.7 to 54 ng I-TEQ_{DF}/kg (mean, 21 ng I-TEQ_{DF}/kg). The authors observed that CDD/CDF concentrations measured in two soil samples from the immediate vicinity of the composting facility were significantly lower (1 and 1.3 ng I-TEQ_{DF}/kg) than the levels found in the composts, suggesting that the source(s) of CDDs/CDFs in the composts was different from the source(s) affecting local soils.

Harrad et al. (1991) also noted a strong similarity between the congener profiles observed in the composts and the congener profile of a PCP formulation (i.e., predominance of 1,2,4,6,8,9-HxCDF and 1,2,3,4,6,8,9-HpCDF in their respective congener groups), which seemed to indicate that leaching of CDDs/CDFs from PCP-treated wood in the compost piles was the likely source of the observed CDDs/CDFs. The levels of PCP in the 12 finished composts ranged from 7 to 190 µg/kg (mean, 33 µg/kg), and the PCP levels in the active compost samples ranged from 17 to 210 µg/kg (mean, 68 µg/kg). The PCP level in both soil samples was 1.5 µg/kg.

Goldfarb et al. (1992) and Malloy et al. (1993) reported the results of testing composts at three municipal yard waste composting facilities (5 to 91 ng I-TEQ_{DF}/kg; mean, 30 ng I-TEQ_{DF}/kg), two municipal solid waste composting facilities (19 to 96 ng I-TEQ_{DF}/kg; mean, 48 ng I-TEQ_{DF}/kg), and one municipal facility composting solid waste and dewatered sewage sludge (37 to 87 ng I-TEQ_{DF}/kg; mean, 56 ng I-TEQ_{DF}/kg). All facilities were located in the United States. Two general trends were observed for the three types of composts: a progressive increase in analyte levels, with an increasing degree of chlorination for each compound type (CDDs, CDFs, chlorophenols, and chlorobenzenes), and a progressive increase in concentration of each congener or homologue group from yard waste to solid waste to solid waste/sewage sludge composts. As noted above, the mean TEQ concentrations showed this same trend, which was primarily due to increasing levels of 1,2,3,4,6,7,8-HpCDD and OCDD. The mean PCP concentrations in the three compost types were 20 µg/kg (yard waste), 215 µg/kg (solid waste), and 615 µg/kg (solid waste/sewage sludge).

Comparison of congener profiles by the authors indicated that the CDD/CDF residue in PCP-treated wood in the compost feedstock was a major but not exclusive contributor of the observed CDDs/CDFs. The authors postulated that biological formation of HxCDDs, HpCDDs, and OCDD from chlorophenols (tri, tetra, and penta) in the compost could be responsible for the elevated levels of these congener groups relative to their presence in PCP.

Oberg et al. (1993) measured the extent of CDD/CDF formation in three conventional garden composts; two were spiked with PCP and one was spiked with hexachlorobenzene. One PCP-spiked compost was monitored for 55 days and the other for 286 days. A significant increase in the concentrations of the more highly chlorinated congeners, particularly the HpCDDs, OCDD, and, to a lesser extent, OCDF, were observed. Similar results were reported for the hexachlorobenzene-spiked compost, which was monitored for 49 days. Oberg et al. stated that for a "typical" composting event, a two- to threefold increase in TEQ content corresponded with an elevation of 0.2 to 0.5 ng I-TEQ_{DF}/kg dry weight.

Weber et al. (1995) subjected sewage sludges from two German communities to anaerobic digestion in laboratory reactors for 60 days. The two sludges were spiked with 2,3,5-trichlorophenol (10 to 25 mg/kg), a mixture of 2,3,5-trichlorophenol and dichlorophenols (2.5 to 25 mg/kg), or a mixture of di-, tri-, and tetrachlorobenzenes (4 to 40 mg/kg). The initial CDD/CDF concentrations in the two sludges were 9 and 20 ng I-TEQ_{DF}/kg. In nearly all of the digestion experiments, the addition of the precursors did not lead to any significant changes in concentrations. The only exceptions were increased 2,3,7,8-TCDF concentrations in the mixed chlorophenol experiments and decreased 2,3,7,8-TCDF concentrations in the mixed chlorobenzene experiments. However, the same increases or decreases for this congener were also observed in the controls (i.e., no precursors added).

Researchers at the U.S. Department of Agriculture (USDA) (Fries et al., 1997) reported that dairy cows that were fed PCP-treated wood excreted amounts of OCDD almost four times greater than the amounts ingested. Feil and Tiernan (1997) reported that rats fed technical PCP had liver concentrations of HxCDD, HpCDD, HpCDF, OCDD, and OCDF two to three orders of magnitude higher than those of rats fed purified PCP. These results suggest the in vivo formation of CDDs/CDFs from pre-dioxins (i.e., chlorinated phenoxy phenols present as contaminants in the PCP). A follow-up USDA study (Huwe et al., 1998) investigated the metabolic conversion of a pre-dioxin (monochloro-2-phenoxyphenol) to OCDD in a feeding study with rats. The results of the study demonstrated the formation of OCDD from the pre-dioxin, although the conversion was estimated to be less than 2%. Interestingly, the study noted that the presence of added OCDD in the feed material increased the percentage of pre-dioxin conversion.

Wittsiepe et al. (1998) demonstrated that CDDs/CDFs can be formed through reaction of chlorophenols with myeloperoxidase (a component of neutrophile granulocytes, a subgroup of human leucocytes). The CDDs/CDFs formed showed different homologue patterns and formation rates depending on the degree of chlorination of the chlorophenol substrate. The formation rates ranged from 1 to 16 µmol of CDD/CDF per mol of chlorophenol substrate.

9.1.2. Biotransformation of Higher CDDs/CDFs

Results of several studies that examined the fate of a range of CDD/CDF congeners in pure cultures, sediments, and sludges indicate that under certain conditions some CDD/CDF congeners will undergo biodegradation to form lower-chlorinated (and possibly more toxic) CDDs/CDFs. However, the extent to which more toxic CDDs/CDFs are formed in the environment via this mechanism cannot be estimated at this time.

Several reports indicate that CDDs and CDFs may undergo microbial dechlorination in anaerobic sediments. Adriaens and Grbic-Galic (1992, 1993) and Adriaens et al. (1995) reported the results of a series of microcosm studies using Hudson River sediment (contaminated with Aroclor 1242) and aquifer material (contaminated with CDDs) from Pensacola, FL. Both types of substrates were spiked with several CDDs (1,2,3,4,6,7,8-HpCDD; 1,2,3,4,7,8-HxCDD; and 1,2,4,6,8,9-/1,2,4,6,7,9-HxCDD) and CDFs (1,2,3,4,6,7,8-HpCDF and 1,2,4,6,8-PeCDF) and monitored over a 16-month period at an incubation temperature of 30°C. The Hudson River sediment was spiked with 144 µg/kg of each congener, and the Pensacola aquifer material was spiked with 63 µg/kg of each congener.

All of the congeners, with the exception of 1,2,3,4,6,7,8-HpCDF, showed a slow decrease in concentration over time, which was attributed to biologically mediated reductive dechlorination, with net disappearance rates ranging from 0.0031 wk^{-1} to 0.0175 wk^{-1} (i.e., half-lives of approximately 1 to 4 yr). However, Adriaens et al. concluded that actual half-lives may be orders of magnitude higher. The experiment with 1,2,3,4,6,7,8-HpCDD yielded formation of 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD. Thus, removal of the peri-substituted (1,4,6,9) chlorines was favored, with enrichment of 2,3,7,8-substituted congeners. No lower-chlorinated congeners were identified from incubation with the other tested congeners. 1,2,4,6,8-PeCDF was also examined in dichlorophenol-enriched cultures. After 6 months of incubation, several TCDFs were identified, which also indicated that peri-dechlorination was the preferred route of reduction.

Barkovskii and Adriaens (1995, 1996) reported that 2,3,7,8-TCDD extracted from Passaic River sediments was susceptible to reductive dechlorination when incubated at 30°C under methanogenic conditions in a mixture of aliphatic and organic acids inoculated with microorganisms obtained from the sediments. The initial concentration of 2,3,7,8-TCDD (20 ± 4

μg/L) decreased by 30% to 14 ± 2 μg/L over a period of 7 months, with the consecutive appearance and disappearance of tri-, di-, and mono-CDDs. Experiments were also conducted by spiking the sediment with HxCDDs, HpCDDs, and OCDD. Up to 10% of the spiked OCDD was converted to hepta-, hexa-, penta-, tetra-, tri-, di-, and mono-chlorinated isomers, but the reaction stoichiometry was not determined. Two distinct pathways of dechlorination were observed: the peri-dechlorination pathway of 2,3,7,8-substituted hepta- to penta-CDDs, resulting in the production of 2,3,7,8-TCDD, and the peri-lateral dechlorination pathway of non-2,3,7,8-substituted congeners.

Several studies have reported that CDDs/CDFs can be formed during composting operations through biological action on chlorophenols present in the compost feed material. The results of studies that specify likely involvement of chlorophenols are described in Section 9.1. Another possible formation mechanism was suggested by Vikelsoe et al. (1994), who reported that higher-chlorinated CDD/CDF congeners are formed when humic acid is reacted with a peroxidase enzyme, hydrogen peroxide, and sodium chloride. It is expected that some organic material in compost and sewage sludge has a humic-like structure. Several additional studies are described below in which the potential involvement of chlorophenols could not be assessed because chlorophenol concentrations in the composts were not reported.

Schäfer et al. (1993) monitored the seasonal changes in the CDD/CDF content, as well as the extent of CDD/CDF formation, in composts from a vegetable and garden waste composting operation in Germany. Finished compost samples were collected and analyzed every 2 months for 1 yr. An annual cycle was observed in TEQ concentrations, with peak concentrations in the summer (approximately 8.5 ng I-TEQ_{DF}/kg) being 2.5 times higher than the lowest concentrations observed in the winter (approximately 3.5 ng I-TEQ_{DF}/kg). No seasonal source was apparent that could explain the observed differences in seasonal levels.

The CDD/CDF content of the starting waste materials for two compost cycles (March and September) was measured to monitor the extent of CDD/CDF formation during composting. For the March cycle sample, most 2,3,7,8-substituted CDD/CDF congeners decreased in concentration during composting. Four CDF congeners showed a slight increase in concentration (less than 10%). For the September cycle sample, OCDD and HpCDD concentrations increased 300% during composting. Increases of less than 10% were observed for HxCDDs and OCDF; all other 2,3,7,8-substituted CDD/CDF congeners showed decreases in concentrations during composting.

Krauss et al. (1994) measured the extent of CDD/CDF formation during the composting of household waste using a laboratory compost reactor. After 11 wk, the TEQ content of the compost increased from 3 to 4.5 ng. The largest increases in mass content were observed for HpCDD (primarily 1,2,3,4,6,7,8-HpCDD) and OCDD. TCDD, PeCDD, and HxCDD showed no

change in mass content. All CDF congener groups showed decreases in mass content; however, the concentrations in both the starting and the finished compost were close to the analytical detection limits.

Oberg et al. (1994) reported the results of monitoring two household waste composts and two garden composts. The total CDD/CDF content of both household waste composts decreased over the 12-wk test period. Total CDD content and PCB content decreased, but total CDF content increased, in contrast to the findings of Krauss et al. (1994). However, a small increase in OCDD content in both composts was observed. The two garden composts were monitored for a 60-wk period. Total CDD/CDF concentration increased, with the largest increases observed for OCDD and HpCDDs. The lower-chlorinated CDFs decreased in concentration.

As a follow-up to a preliminary study (Hengstmann et al., 1990) that indicated CDD/CDF concentrations may increase and congener profiles may change during anaerobic digestion of sewage sludge, Weber et al. (1995) subjected sewage sludges from two German communities to anaerobic digestion and aerobic digestion in laboratory reactors for 60 days and 20 days, respectively. The initial average I-TEQ_{DF} concentrations in the raw sludges were 20 and 200 ng I-TEQ_{DF}/kg. No significant increase or decrease in total CDD/CDF content or congener group content was observed with either sludge. In contrast, a significant decrease in CDD/CDF content was observed in the aerobic digestion experiments with both sludges. The greatest percentage decreases in congener group concentrations (greater than 40%) were observed for TCDF, PeCDF, HxCDF, TCDD, and PeCDD in the sludge initially containing 20 ng I-TEQ_{DF}/kg and for TCDF, TCDD, HpCDD, and OCDD in the initially high-content sludge. The greatest percentage decreases in congener concentrations (greater than 40%) were observed for non-2,3,7,8-substituted congeners.

The data presented in this section and in Section 9.1.1 do not provide a basis for making a release estimate via biotransformation; therefore, biotransformation releases are classified as Category E (not quantifiable).

9.1.3. Dioxin-Like Compounds in Animal Manure

In 2000, approximately 9 billion individual livestock and poultry animals were raised on commercial farms in the United States (U.S. Census Bureau, 2001). It is estimated that beef animals, dairy cows, chickens, turkeys, and pigs, combined, produced in excess of 190 billion kg (dry weight) of manure in 2000 (Table 9-1). Because livestock and poultry manure can provide valuable organic material and nutrients for crop and pasture growth, most of the animal manure generated at commercial farms and animal feed lots is applied to farmland as fertilizer. To the extent dioxin-like compounds may contaminate animal manures, the practice of land-spreading animal waste may result in releases of CDDs/CDFs to the open and circulating environment.

Table 9-1. Estimated quantity of animal manure produced in the United States in 2000

Species	Numbers of individuals on farms in 2000[a]	Average weight of animal (lbs)[b]	Total live weight on farms (lbs)	Manure generation rate factor (dry weight lb/lb live unit weight/day)[c]	Manure generated (lb/yr dry weight)	Manure produced (kg/yr dry weight)
Swine	6.73e+07	135	9.09e+09	8.2e-03	2.72e+10	1.23e+10
Layer	4.35e+08	4	1.74e+09	1.6e-02	1.02e+10	4.61e+09
Broiler	8.26e+09	2	1.65e+10	2.1e-02	1.27e+11	5.74e+10
Turkey	2.7e+08	15	4.05e+09	1.2e-02	1.77e+10	8.04e+09
Beef	9.73e+07	800	7.78e+10	6.9e-03	1.96e+11	8.89e+10
Dairy cow	9.21e+06	1,400	1.29e+10	1e-02	4.71e+10	2.13e+10
Total					4.25e+11	1.93e+11

[a]Source: U.S. Census Bureau (2001).
[b]Source: U.S. EPA (2001d).
[c]Source: Stevens and Jones (2003).

Stevens and Jones (2003) published results of CDD and CDF detection in animal manure applied to farmland in the United Kingdom. Manure from six milking dairy cows was sampled at six farms in the northern United Kingdom. In addition, single samples of sheep, chicken, and pig manure were collected from other farms in the region. The samples were shipped to a laboratory for trace chemical analysis. Samples were analyzed using high-resolution gas chromatography coupled with high-resolution mass spectrometry and a capillary column for the identification of CDD/CDF congeners. Recoveries of the internal standard ranged from 51 to 94%, with a mean of 74% for CDD/CDF congeners. Table 9-2 summarizes the results of the study. The pig and chicken manure contained approximately 0.2 ng WHO-TEQ/kg, and the cow manure averaged 3.6 ng WHO-TEQ/kg in concentration.

This study provides extremely limited data on the possible levels and occurrences of dioxin-like compounds in farm animal manure, and, therefore, these data are clearly not representative of national releases of dioxin-like compounds from the land application of all farm animal manure in the United States. Accordingly, EPA currently considers this source to be unquantifiable (Category E) in terms of dioxin emissions.

Table 9-2. CDD and CDF concentrations (ng/kg dry weight) in samples of animal manure in the United Kingdom

Congener	Cows (n = 6) (mean)	Sheep (n = 1)	Pig (n = 1)	Chicken (n = 1)
2,3,7,8-TCDD	0.17	0.11	0.01	0.01
1,2,3,7,8-PeCDD	0.46	0.41	0.07	0.04
1,2,3,4,7,8-HxCDD	2.4	0.9	0.26	0.03
1,2,3,6,7,8-HxCDD	4.5	0.86	0.1	0.09
1,2,3,7,8,9-HxCDD	2.6	0.56	0.07	0.12
1,2,3,4,6,7,8-HpCDD	120	9.4	0.8	1.4
OCDD	460	53	11	14
Total 2,3,7,8-CDD	590.1	65.2	12.3	15.7
2,3,7,8-TCDF	0.3	1.2	0.03	0.03
1,2,3,7,8-PeCDF	0.3	1.1	0.04	0.09
2,3,4,7,8-PeCDF	0.28	1.2	0.06	0.12
1,2,3,4,7,8-HxCDF	0.6	1.4	0.05	0.15
1,2,3,6,7,8-HxCDF	0.51	1.1	0.06	0.07
1,2,3,7,8,9-HxCDF	1.9	0.15	0.04	0.05
2,3,4,6,7,8-HxCDF	0.4	1.4	0.06	0.14
1,2,3,4,6,7,8-HpCDF	7.6	5.2	0.48	0.37
1,2,3,4,7,8,9-HpCDF	12	0.56	0.04	0.09
OCDF	35	5	0.73	0.8
Total 2,3,7,8-CDF	58.9	18.3	1.6	1.9
Total CDD/CDF	649	83.5	13.9	17.6
WHO-TEQ	3.6	2.1	0.2	0.2

Source: Stevens and Jones (2003).

9.2. PHOTOTRANSFORMATION OF CHLOROPHENOLS

Several researchers have demonstrated that CDDs/CDFs can be formed via photolysis of PCP under laboratory conditions. However, the extent to which CDDs/CDFs are formed in the environment via this mechanism cannot be estimated at this time.

Lamparski et al. (1980) conducted laboratory studies to determine the effect of simulated summer sunlight on the formation of OCDD, HpCDDs, and HxCDDs in wood pressure-treated in the laboratory with PCP. In the first set of experiments, wood veneers (southern pine) treated with purified PCP or Dowicide EC-7, using methylene chloride as the PCP carrier, were exposed to light for 70 days. The PCP concentration in the treated wood was 5% by weight, which approximates the concentration in the outer layer of PCP-treated wood utility poles. Photolytic condensation of PCP to form OCDD was observed, with the OCDD concentration increasing by a maximum factor of 3,000 for the purified PCP and by a factor of 20 for EC-7 at about day 20

before leveling off. HpCDD and HxCDD were also formed, apparently by photolytic degradation of OCDD rather than by condensation of PCP and tetrachlorophenols. The HxCDD concentration increased by a factor of 760 for the purified PCP and by a factor of 50 for EC-7 over the 70-day exposure period. The predominant HpCDD congener formed was 1,2,3,4,6,7,8-HpCDD as a result of an apparently preferential loss of chlorine at the peri position (positions 1, 4, 6, and 9).

In a second set of experiments conducted by Lamparski et al. (1980), a hydrocarbon oil (P-9 oil) was used as the carrier to treat the wood. The increases observed in the OCDD, HpCDD, and HxCDD were reported to be much lower relative to the increases observed in the first set of experiments, which used methylene chloride as the carrier. Results were reported only for OCDD. The OCDD concentration increased by a maximum factor of 1.5 for both EC-7 and technical PCP and by a factor of 88 for purified PCP. The authors concluded that the oil either reduced condensation of PCP to OCDD or accelerated degradation to other species by providing a hydrocarbon trap for free-radical species.

Vollmuth et al. (1994) studied the effect of irradiating laboratory water and landfill seepage water that contained PCP under conditions simulating those used to purify water with ultraviolet (UV) radiation (5-hr exposure to 254 nm radiation from low-pressure mercury lamps). Before irradiation, the three solutions tested contained approximately 1 mg/L of PCP or PCP-Na, but the CDD/CDF content of one solution varied dramatically from those of the other two (1.5 vs. 2,066 and 2,071 pg I-TEQ_{DF}/L). Irradiation resulted in nearly total destruction of PCP (greater than 99% loss) in all three experiments. An overall net increase in I-TEQ_{DF}-content was observed in the initially low I-TEQ_{DF}-content water, but a net decrease was observed for the two initially high I-TEQ_{DF}-content waters.

Irradiation of laboratory water containing purified PCP showed an increase in I-TEQ_{DF} concentration from 1.5 pg/L to 214.5 pg/L. The increase was due entirely to the formation of 1,2,3,4,6,7,8-HpCDD, OCDD, and 1,2,3,4,6,7,8-HpCDF. Formation of non-2,3,7,8-substituted HpCDDs and HpCDFs was also observed. The ratios of the concentrations of these non-2,3,7,8-congeners to the concentrations of the 2,3,7,8-congeners were 0.6 for HpCDDs and 5 for HpCDFs. The HpCDD and HpCDF congeners formed indicate that the operative mechanism was photoinduced dechlorination of OCDD at a peri position and dechlorination of OCDF at only the 1 and 9 peri positions.

Irradiation of water containing technical PCP-Na (Dowicide-G) resulted in a net loss in I-TEQ_{DF} content, from 2,065.5 pg/L to 112.7 pg/L. The only 2,3,7,8-substituted congener showing an increased concentration was 1,2,3,6,7,8-HxCDD. The other congeners originally present in the technical PCP-Na showed reductions of 80.6 to 100%.

The I-TEQ_{DF} content of seepage water from a landfill (2,071 pg I-TEQ_{DF}/L) was reduced by a factor of 2, to 1,088 pg I-TEQ_{DF}/L. However, several 2,3,7,8-substituted congeners did increase in concentration (1,2,3,6,7,8-HxCDD; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,8-HpCDF; and OCDF).

Waddell et al. (1995) also studied the effect of irradiating distilled laboratory water containing PCP under conditions simulating those used to purify water with UV radiation. The results obtained were similar to those of Vollmuth et al. (1994). Analytical-grade PCP at a concentration of 10 mg/L was exposed for 12 min to 200 to 300 nm radiation from a medium-pressure mercury lamp. All CDD/CDF congener groups increased in concentration over the 12-min exposure period, with the greatest increases observed for OCDD (75-fold increase) and HpCDDs (34-fold increase). The I-TEQ_{DF} content of the solution increased from 4.2 pg I-TEQ_{DF}/L to 137 pg I-TEQ_{DF}/L over the 12-min period. The dominant congeners formed, in terms of both concentration and contribution to I-TEQ_{DF}, were 1,2,3,4,6,7,8-HpCDD, OCDD, and 1,2,3,7,8,9-HxCDD.

9.2.1. Photolysis of Higher CDDs/CDFs

Photolysis appears to be one of the few environmentally significant degradation mechanisms for CDDs/CDFs in water, air, and soil. Although good mass balances were not obtained and the photolytic pathways for CDDs/CDFs were not fully identified in most studies, a major photolysis pathway appears to be photodechlorination, resulting in formation of lower-chlorinated CDDs/CDFs. A preferential loss of chlorines from the peri positions (1, 4, 6, and 9) rather than from the lateral positions (2, 3, 7, and 8) was reported for some congener groups when irradiated as dry films and sorbed to soil and in gas-phase CDDs/CDFs (Choudhry and Webster, 1989; Kieatiwong et al., 1990; Sivils et al., 1994, 1995; Tysklind et al., 1992). Several researchers reported that carbon-oxygen cleavage and other mechanisms may be similarly or more important pathways for CDDs/CDFs containing four or fewer chlorines.

Because of the difficulties inherent in controlling experimental variables for nonvolatile and highly lipophilic compounds such as CDDs/CDFs, few photolysis studies have been performed on natural waters, soils, atmospheric particulates, and atmospheric gases to examine the rates and products of photolysis under environmentally relevant conditions. Thus, it is not possible at this time to quantitatively estimate the mass of various CDD/CDF congeners formed in the environment annually via photolytic mechanisms. The following sections summarize the key findings of environmentally significant studies for water, soil, vegetation, and air.

9.2.2. Photolysis in Water

Numerous studies have demonstrated that CDDs/CDFs will undergo photodechlorination following first-order kinetics in organic solution, with preferential loss of chlorine from the lateral positions. Photolysis is slow in pure water, but it increases dramatically when solvents serving as hydrogen donors such as hexane, benzene, methanol, acetonitrile, hexadecane, ethyl oleate, dioxane, and isooctane are present. However, only a few studies have examined the photolysis of CDDs/CDFs using natural waters and sunlight.

Choudhry and Webster (1989) experimentally determined the sunlight photolysis half-life of 1,3,6,8-TCDD in pond water to be 3.5 days (more than 10 times greater than the half-life predicted by laboratory experiments using a water/acetonitrile solution). The authors attributed this significant difference in photolysis rates to the light screening/quenching effects of dissolved organic matter.

Friesen et al. (1990) examined the photolytic behavior of 1,2,3,4,7-PeCDD and 1,2,3,4,6,7,8-HpCDD in water:acetonitrile (2:3, v/v) and in pond water under sunlight at 50 degrees North latitude. The observed half-lives of these two compounds in the water:acetonitrile solution were 12 and 37 days, respectively, but were much shorter in pond water, 0.94 and 2.5 days, respectively. Similarly, Friesen et al. (1993) studied the photodegradation of 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF by sunlight using water:acetonitrile (2:3, v/v) and lake water. The observed half-lives were 6.5 and 46 days, respectively, in the water:acetonitrile solution and 1.2 and 0.19 days, respectively, in lake water. The significant differences between the natural water and the water:acetonitrile solution results were attributed to indirect or sensitized photolysis due to the presence of naturally occurring components in the lake and pond water.

Dung and O'Keefe (1992), in an investigation of aqueous photolysis of 2,3,7,8-TCDF and 1,2,7,8-TCDF, reported findings similar to those of Friesen et al. (1993). The photolysis rates of the two TCDF congeners observed in river and lake water (half-lives of about 4 to 6 hr) were double those observed in pure water (half-lives of about 8 to 11 hr). The authors attributed the difference in rates to the presence of natural organics in the river and lake water that may act as sensitizers.

9.2.3. Photolysis on Soil

Photolysis of CDDs/CDFs on soil has not been well characterized. According to the data generated to date, however, photolysis is an operative degradation process only in the near-surface soil where UV light penetrates (the top few millimeters or less of soil), and dechlorination of peri-substituted chlorines appears to occur preferentially.

Miller et al. (1989) studied the CDD degradation products resulting from irradiation of ^{13}C-labeled OCDD on two soil types using sunlamps. Approximately 38 to 42% of the OCDD

was degraded by day 5 of the experiment; no significant further loss of OCDD was observed over the following 10 days. Although the authors determined that photodechlorination was not the dominant photolysis pathway, it was observed in both soils; approximately 10 to 30% of the lower-chlorinated congeners were produced from the immediate higher-chlorinated congeners. The HpCDD and HxCDD congeners observed as degradation products were present in proportions similar to the number of congeners in each congener group. However, the investigators observed greater yields of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD than would be expected on the basis of the number of potential TCDD and PeCDD congeners. One-fifth to one-third of the total yield of PeCDDs was 1,2,3,7,8-PeCDD, and one-half of the total yield of TCDDs was 2,3,7,8-TCDD.

Kieatiwong et al. (1990) performed experiments similar to those of Miller et al. (1989) using natural sunlight rather than sunlamps for irradiation of ^{13}C-labeled OCDD on soils. Photodechlorination was estimated to account for approximately 10% of the loss of OCDD. One-third to one-half of the total yield of PeCDDs was 1,2,3,7,8-PeCDD, and one-half of the total yield of TCDDs was 2,3,7,8-TCDD. These findings, along with those of Miller et al., indicate that the 2,3,7,8-substituted TCDD and PeCDD congeners were either preferentially formed or were photochemically less reactive than the other congeners that were formed.

Tysklind et al. (1992) studied the sunlight photolysis of OCDD on soil and reported results similar to those of Miller et al. (1989) and Kieatiwong et al. (1990). Photodechlorination was observed with production of HpCDDs, HxCDDs, PeCDDs, and TCDDs over the 16-day irradiation period. Photodechlorination at the peri-substituted positions was the preferred photodechlorination mechanism; the proportions of 2,3,7,8-substituted congeners present in the soils after 16 days for each congener group were as follows: HxCDD, 65%; PeCDD, 40%; and TCDD, 75%. Tysklind et al. (1992) also studied the sunlight photolysis of OCDF on soil. Photodechlorination was observed; however, unlike the case with OCDD, photodechlorination of the lateral-substituted positions was found to be the dominant photodechlorination mechanism, resulting in a relative decreasing proportion of 2,3,7,8-substituted congeners during the irradiation period. 2,3,7,8-TCDF was not observed in any of the irradiated samples.

9.2.4. Photolysis on Vegetation

Photolysis of CDDs/CDFs sorbed on the surface of vegetation has not been well characterized, and the findings to date are somewhat contradictory. McCrady and Maggard (1993) reported that 2,3,7,8-TCDD sorbed on the surface of reed canary grass (*Phalaris arundinacea L.*) underwent photolytic degradation, with a half-life of 44 hr in natural sunlight. In contrast, Welsch-Pausch et al. (1995) found little difference in the CDD/CDF congener

patterns between grass (*Lolium multiflorum*) grown on an outdoor plot and grass grown in a greenhouse (i.e., UV light transmission blocked).

In an attempt to clarify this contradiction, Welsch-Pausch and McLachlan (1995) studied the photodegradation of CDDs/CDFs on pasture grass (*Arrhenatherion elatioris*) during two growing cycles (summer and autumn) using two greenhouses. One greenhouse was constructed of glass that blocks UV transmission and the other was constructed of plexiglass (4 mm) with a UV light transmission of greater than 50% in the 280 to 320 nm range. In both the summer and the autumn exposure periods, the concentrations of CDDs/CDFs (on a congener-group basis) were similar in the grass exposed to UV light and the grass that was not exposed. The authors concluded that if photodegradation was occurring, it was a relatively insignificant factor in the accumulation of CDDs/CDFs in pasture grass.

9.2.5. Photolysis in Air

Photolysis of CDDs/CDFs in the atmosphere has not been well characterized. On the basis of data generated to date, however, photolysis appears to be a significant mechanism for degradation (principally, dechlorination of the peri-substituted chlorines) of those CDDs/CDFs present in the atmosphere in the gas phase. For airborne CDDs/CDFs sorbed to particulates, photolysis appears to proceed very slowly, if at all. Because of the low volatility of CDDs/CDFs, few studies have been attempted to measure actual rates of photodegradation of gas-phase CDD/CDF, and only recently have studies examined the relative importance of photolysis to particulate-bound CDDs/CDFs.

Sivils et al. (1994, 1995) studied the gas-phase photolysis of several CDDs (2,3,7-TrCDD; 2,3,7,8-TCDD; 1,2,3,4-TCDD; 1,2,3,7,8-PeCDD, and 1,2,4,7,8-PeCDD) by irradiating the effluent from a gas chromatograph with broadband radiation in the UV/visible region for periods of up to 20 min. The irradiated sample was then introduced into a second gas chromatograph to measure the extent of dechlorination. The results showed that degradation followed first-order kinetics and that an inverse relationship existed between the degree of chlorination and the rate of disappearance. Although the lack of photoproducts prevented an independent confirmation of the preferential loss mechanism, the results indicate that laterally substituted congeners (chlorines at the 2, 3, 7, and 8 positions) degrade at a slower rate than do the peri-substituted congeners (chlorines at the 1, 4, 6, and 9 positions). Although Sivils et al. (1994) did not present the rate constants, the degradation rate for 2,3,7,8-TCDD (30% loss in 20 min) was reported to be slower than the rates for all other tested CDDs. Also, 1,2,4,7,8-PeCDD (with two perichlorines) degraded significantly faster than did 1,2,3,7,8-PeCDD (with only one perichlorine).

Mill et al. (1987) studied the photolysis of 2,3,7,8-TCDD sorbed onto small-diameter fly ash particulates suspended in air. The results indicated that fly ash confers photostability on 2,3,7,8-TCDD. Little (8%) to no loss was observed on the two fly ash samples after 40 hr of illumination. Tysklind and Rappe (1991) and Koester and Hites (1992) reported similar results of photolysis studies with fly ash. Tysklind and Rappe subjected fly ash from two German incinerators to various simulated environmental conditions. The fraction of photolytically degradable CDD/CDF after 288 hr of exposure was in the range of 20 to 40% of the extractable CDD/CDF. However, a 10 to 20% reduction was also observed in the darkened control samples. With the exception of HpCDD and HpCDF, the concentration of all other congener groups either increased or stayed the same during the exposure period from hour 144 to hour 288.

Koester and Hites (1992) studied the photodegradation of CDDs/CDFs naturally adsorbed to fly ash collected from five electrostatic precipitators. They observed no significant degradation in 11 photodegradation experiments performed on the ash for periods ranging from 2 to 6 days. The authors concluded that (a) the absence of photodegradation was not due to the absence of a hydrogen-donor organic substance; (b) other molecules on the ash, as determined by a photolysis experiment with an ash extract, inhibited photodegradation, either by absorbing light and dissipating energy or by quenching the excited states of the CDDs/CDFs; and (c) the surface of the ash itself may have hindered photolysis by shielding the CDDs/CDFs from light.

9.3. CDDs/CDFs IN BALL CLAY

9.3.1. Initial Discovery of CDD/CDF Contamination of Ball Clay

The presence of dioxin-like compounds in ball clay was discovered in 1996 as a result of an investigation to determine the sources of relatively high levels of dioxin found in two chicken fat samples during a national survey of poultry. The survey was conducted jointly by USDA, the U.S. Food and Drug Administration (FDA), and EPA to assess the national prevalence and concentrations of CDDs, CDFs, and coplanar PCBs in poultry (Ferrario et al., 1997).

The results of the investigation indicated that soybean meal added to chicken feed was the source of dioxin contamination (Ferrario et al., 2000). Further investigation showed that the CDD contamination came from the ball clay added to the soymeal as an anticaking agent. The ball clay was added at approximately 0.3 to 0.5% of the soybean meal. Samples of raw ball clay were subsequently taken at the mine of origin in Mississippi. Analysis of the samples showed elevated levels of CDDs with a congener profile similar to the CDD profiles found in the soymeal, chicken feed, and immature chickens.

9.3.2. Characteristics of Mississippi Embayment Ball Clays

The ball clays from the mine discussed above are part of a larger ball clay resource that spans portions of western Kentucky, Tennessee, and Mississippi. These clays were deposited along the shores of the Mississippi embayment during the early to middle Eocene epoch, which occurred approximately 40 to 45 million years ago. The Mississippi embayment ball clays are secondary clays composed mainly of poorly defined crystalline kaolinite. Other minerals present include illite, smectite, and chlorite. Quartz sand is the major nonclay mineral. These deposits of ball clay occur in lenses surrounded by layers of sand, silt, and lignite. The clays can have a gray appearance caused by the presence of finely divided carbonaceous particles. It is not uncommon to find black carbonized imprints of fossil leaves and other plant debris in the clay (Patterson and Murray, 1984).

The plasticity of ball clay makes it an important natural resource for the ceramic industry. The breakdown of the ceramic uses of ball clay is 33% for floor and wall tile, 24% for sanitary ware, 11% for pottery, and 32% for other industrial and commercial uses (Virta, 2000). A minor use of ball clay was as an anticaking agent in animal feeds, but this use has been banned by the FDA (Headrick et al., 1999). Total mining of ball clay in 1999 was 1.14 million metric tons (Virta, 2000).

9.3.3. Levels of Dioxin-Like Compounds in Ball Clay

The joint EPA/FDA and USDA investigation of ball clay as a source of dioxin contamination in animal feeds resulted in sampling the clay at an operational mine in western Mississippi. Eight samples of raw (unprocessed) ball clay were collected from an open mining pit at a depth of about 10 to 15 m. Samples were prepared and analyzed by EPA using EPA Method 1613 (Ferrario et al., 2000). The concentrations of the CDDs/CDFs present in the raw ball clay samples from the one mine are shown in Table 9-3. The ratio of the limits of detection to the limits of quantification for the CDDs/CDFs in the clay samples were 0.5:1 pg/g (ppt, dry weight) for the tetras; 1:2 pg/g for the pentas, hexas, and heptas; and 5:10 pg/g for the octas. The mean concentrations of all of the CDDs exceeded 100 ppt (dry weight).

OCDD was found at the highest concentration in all of the samples, followed by either 1,2,3,4,6,7,8-HpCDD or 1,2,3,7,8,9-HxCDD. The maximum OCDD concentration in the eight samples was approximately 59,000 pg/g. The most toxic tetra and penta congeners were present at unusually high concentrations in all of the samples, with average concentrations of 711 pg/g and 508 pg/g for 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, respectively. Although the ball clays showed elevated levels of 2,3,7,8-substituted CDDs, they showed very low levels of 2,3,7,8-substituted CDFs. In addition, there was a consistent ratio within the HxCDD congener

Table 9-3. Concentrations of CDDs (pg/g, dry weight) in eight ball clay samples in the United States

Congener	Mean	Median	Minimum	Maximum	TEQ_{DF}-WHO_{98}
2,3,7,8-TCDD	711	617	253	1,259	711
1,2,3,7,8-PeCDD	508	492	254	924	508
1,2,3,4,7,8-HxCDD	131	134	62	193	13
1,2,3,6,7,8-HxCDD	456	421	254	752	46
1,2,3,7,8,9-HxCDD	2,093	1,880	1,252	3,683	209
1,2,3,4,6,7,8-HpCDD	2,383	2,073	1,493	3,346	24
OCDD	20,640	4,099	8,076	58,766	2
Total TEQ					1,513

Source: Ferrario et al. (2000).

distribution across all samples (1,2,3,7,8,9-HxCDD was present at higher concentrations than the other 2,3,7,8-substituted HxCDD congeners). The average percent distribution of the three individual 2,3,7,8-hexa congeners was 5, 17, and 78%, respectively. This congener pattern was observed in all the raw ball clay samples analyzed.

The mean total TEQ_{DF}-WHO_{98} for the raw ball clay was determined to be 1,513 pg/g dry weight; 2,3,7,8-TCDD accounted for 47% of the TEQ_{DF}-WHO_{98}, followed by 1,2,3,7,8-PeCDD at 34%. As expected, even though present at the highest concentration, OCDD contributed less than 1% percent of the total TEQ_{DF}-WHO_{98} due to its relatively small WHO-TEF. In comparison, the typical ranges of background TEQ_{DF}-WHO_{98} concentrations in North American urban and rural surface soil samples were found to be 2 to 21 pg/g and 0.1 to 6 pg/g, respectively (U.S. EPA, 2000c). In soil samples, all 2,3,7,8-CDD/CDF congeners were detected, and 2,3,7,8-TCDD represented less than 1% of total CDD/CDF present. The most prevalent congeners in soils were OCDD, followed by OCDF. Table 9-4 compares the mean CDD/CDF congener group concentrations in ball clay with those in rural and urban background soils. This comparison indicates there are few similarities between the ball clay and soils in the congener group distributions.

9.3.4. Evidence for Ball Clay as a Natural Source

Several lines of evidence suggest that dioxin-like compounds in ball clay are of natural origin. The clay samples were obtained from undisturbed deposits. It is unknown how human activity could have contaminated these deposits without disturbing them. The EPA laboratory in Athens, GA, analyzed the Mississippi mine clays using a broad screen for anthropogenic contaminants and no compounds were found outside of the normal range (Ferrario et al., 2000).

Table 9-4. Comparison of the mean CDD/CDF congener group concentrations in ball clay with those in urban and rural soils in North America (pg/g, dry weight)

Congener group	Mean concentration		
	Raw ball clay	Urban background soil	Rural background soil
TCDD	3,729	36.1	2.3
TCDF	6	23.5	6.8
PeCDD	4,798	18.1	4.1
PeCDF	2	40.8	12.7
HxCDD	6,609	31.7	22.7
HxCDF	6	23.5	21.9
HpCDD	6,194	194.4	114.7
HpCDF	9	46.4	37.3
OCDD	11,222	2,596	565.1
OCDF	11	40.2	33.5
Total CDD/CDF	32,586	3,050.7	821.1

Sources: Adapted from U.S. EPA (2000c); Ferrario et al. (2000)

All known anthropogenic sources of dioxin have associated with them a wide variety of other contaminants. The absence of elevated levels of other compounds is strong evidence that the dioxins found in the clay were not the result of waste disposal.

The congener profiles of ball clay do not match those of known anthropogenic sources. Cleverly et al. (1997) reported on the congener profiles that are typical of known anthropogenic sources of dioxin-like compounds in the United States. The results of this study, presented below, were used as a basis of comparison for the profiles of raw ball clay.

The congener pattern characteristic of waste combustion sources differs significantly from the ball clay profile in several aspects. In combustion source emissions, all 2,3,7,8-substituted CDD and CDF congeners are measured, and 2,3,7,8-TCDD is usually 0.1 to 1% of total CDD/CDF mass emitted. In ball clay, 2,3,7,8-TCDD is approximately 5% of total mass of dioxins present. As with the ball clay, the most prevalent 2,3,7,8-Cl-substituted CDD congeners in most incinerator emissions are OCDD and 1,2,3,4,6,7,8-HpCDD; however, combustion emissions contain appreciable amounts of CDFs, of which the 1,2,3,4,6,7,8-HpCDF, OCDF, 1,2,3,4,7,8-HxCDF, 2,3,7,8-TCDF, and 2,3,4,6,7,8-HxCDF congeners dominate.

The combustion of wood generates a congener profile not unlike that of waste combustion (i.e., the ratio of CDD:CDF is <1), and all laterally substituted congeners can be detected in emissions. The combustion of tree bark produces a congener profile in which the

CDD:CDF ratio is >1, showing only minimal and barely detectable levels of CDFs in the smoke, the exception being that 2,3,7,8-TCDF is present at approximately 2% of total mass. The dominant congener in tree bark combustion emissions is OCDD (>30% total CDD/CDF mass), followed by 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8,9-HxCDD.

The congener profile of 2,4-D salts and esters seems to mimic a combustion source profile in the number of congeners represented and in the minimal amount of 2,3,7,8-TCDD relative to all 2,3,7,8-Cl-substituted congeners. Nevertheless, unlike the combustion source profile, the 1,2,3,7,8-PeCDD and the 1,2,3,4,6,7,8-HpCDF constitute major fractions of total CDD/CDF contamination present in 2,4-D. The congener profile of technical-grade PCP is clearly dominated by OCDD and 1,2,3,4,6,7,8-HpCDD; however, only trace amounts of 2,3,7,8-TCDD are detected in PCP, and 1,2,3,4,6,7,8-HpCDF and OCDF constitute roughly 15% of typical formulations.

Metal smelting and refining processes, such as secondary aluminum, copper, and lead smelting, also have all the 2,3,7,8-Cl-substituted CDD/CDF congeners in stack emissions. In secondary aluminum smelting, 2,3,7,8-TCDD is less than 0.1% of total CDDs/CDFs, whereas PeCDF is nearly 25% of total emissions of dioxin-like compounds, and the CDD/CDF ratio is <1. Secondary copper operations show a similar pattern of CDD/CDF emissions, but with six compounds dominating emissions: 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDF; 1,2,3,4,6,7,8-HpCDF; OCDF; OCDD; and 1,2,3,4,6,7,8-HpCDD. In iron ore sintering, the dominant congener in emissions of 2,3,7,8-Cl-substituted compounds is 2,3,7,8-TCDF.

A number of studies have shown that natural processes can produce chlorinated aromatic compounds, including dioxin-like compounds. Gribble (1994) reviewed the biological production of a wide variety of halogenated organic compounds in nature. The Mississippi salt marsh grass "needlerush" (*Juncus roemerianus*) contains the aromatic compound 1,2,3,4-tetrachlorobenzene, and the blue-green alga *Anacystis marina* naturally contains chlorophenol. The soil fungus *Penicillium sp.* produces 2,4-dichlorophenol, and the common grasshopper is known to secrete 2,5-dichlorophenol.

Urhahn and Ballschmiter (1998) also provide a good review of the chemistry of the biosynthesis of chlorinated organic compounds under natural conditions. It has been hypothesized that CDDs, CDFs, and other chlorinated aromatic compounds can be naturally formed from halogenated humic substances, and halomethanes can be formed through chloroperoxidase-mediated reactions in undisturbed peat bogs (Silk et al., 1997). A similar chloroperoxidase-mediated biochemical formation of CDDs/CDFs from chlorophenols was achieved under laboratory conditions by Oberg and Rappe (1992).

It has been observed that chlorophenols can be biosynthesized (Gribble, 1994; Silk et al., 1997), and that chorophenols are readily adsorbed into peat-bentonite mixtures (Viraraghavan

and Slough, 1999). Hoekstra et al. (1999) offers the hypothesis that 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, and 1,2,3,7,8,9-HxCDD can be naturally formed in soils of coniferous forests from chlorinated phenol. These same congeners are also the predominant congeners in the ball clay from the Mississippi embayment. Although none of these natural processes can be directly connected with the presence of dioxin in ball clay, the existence of such mechanisms lends plausibility to a hypothesis that they are of natural origin.

CDDs/CDFs have been found in other clays quite distant from Mississippi embayment ball clay deposits. No evidence of anthropogenic sources have been discovered in these areas either. The presence of CDDs has been discovered in kaolinitic clay mined in Germany (Jobst and Aldag, 2000). Because no anthropogenic source could be determined to explain the presence and levels of CDDs in the ball clay, the authors speculated that they were the result of an unknown geologic process. In addition, the German clay also has a congener profile similar to that observed in the Mississippi ball clay, with an absence of CDFs at comparable concentrations and the predominance of 1,2,3,7,8,9-HxCDD among the toxic hexa-CDDs. The similarity in the congener profiles in ball clay mined in the United States and Germany suggests a common origin to the CDDs present in these clays (Ferrario et al., 2000).

In summary, no anthropogenic sources have been identified that explain the levels and profiles of CDDs/CDFs present in ball clay. On the other hand, no definitive scientific evidence has been brought forward that identifies the principal chemical and physical mechanism involved in the selective chemical synthesis of CDDs under the conditions inherent in the formation of ball clays some 40 million years ago.

9.3.5. Environmental Releases of Dioxin-Like Compounds from the Mining and Processing of Ball Clay

In 1995, approximately 993 million kg of ball clay was mined in the United States (Virta, 2000). Multiplication of the mean TEQ_{DF}-WHO_{98} concentration in mined ball clay by the total amount of ball clay mined in 1995 gives an estimate of 1,502 g TEQ_{DF}-WHO_{98} contained in all the ball clay mined in 1995. It is unknown whether any of these CDDs are released to the environment during the mining, initial refining, and product handling. As discussed above, most ball clay is used to produce ceramics through a process of high-temperature vitrification. The temperatures found in ceramic kilns are well above the levels needed for both volatilization and destruction of CDDs. Despite these high temperatures, it is unclear whether some release occurs, and no stack measurements have yet been made. Therefore, insufficient evidence is available to make even a preliminary estimate of releases, and this activity is classified as a Category E source.

10. SOURCES OF DIOXIN-LIKE POLYCHLORINATED BIPHENYLS (PCBs)

The purpose of this chapter is twofold: (1) to identify sources that release dioxin-like PCB congeners into the environment and (2) to derive national estimates for releases from these sources in the United States. PCBs have been found in all media and in all parts of the world. PCBs were manufactured in relatively large quantities for use in commercial products such as dielectrics, hydraulic fluids, plastics, coatings and paints, and although PCBs are no longer commercially produced in the United States, they continue to be released to the environment through the use and disposal of these products. PCBs may also be inadvertently produced as by-products during the manufacture of certain organic chemicals and also as products of the incomplete combustion of some waste materials.

10.1. GENERAL FINDINGS OF THE EMISSIONS INVENTORY

Table 10-1 provides a compilation of known or suspected dioxin-like PCB-emitting source categories in the United States for which emission measurements of dioxin-like PCB congeners, Aroclors, or PCB congener groups have been reported in government, industry, and trade association reports; conference proceedings and journal articles; and comments submitted to EPA on previous versions of this document. The intent of Table 10-1 is to clearly identify those source categories and media (air, water, land, and products) for which the available data are adequate for reliably quantifying emissions of dioxin-like PCBs and those for which the data are inadequate.

Nationwide emission estimates for the United States inventory are presented in Table 10-2 (emissions to air, water, land, and product) for those source categories for which estimates can be reliably quantified (the category has been assigned a confidence rating of A, B, or C) (see Section 1.2.3 for details on confidence ratings). Table 10-2 also lists preliminary estimates of the potential magnitude of emissions from "unquantified" sources (i.e., sources assigned a confidence rating of D) in reference year 2000. Because of large uncertainties for these Category D estimates, they are not included in the quantitative inventory.

Currently, no significant releases of newly formed dioxin-like PCBs are occurring in the United States. Unlike CDDs/CDFs, PCBs were intentionally manufactured in the United States in large quantities from 1929 until production was banned in 1977. Releases to the environment of "old" dioxin-like PCBs (dioxin-like PCBs manufactured prior to the production ban) can occur from ongoing use and disposal practices. Prior to regulations enacted beginning in the late 1970s that limited the manufacture/use/disposal of PCBs, significant quantities were released to the environment in association with (a) the manufacture of PCBs, (b) the manufacture of products containing PCBs, and (c) the use and disposal of products containing PCBs as well as

Table 10-1. Confidence rating classes for 2000 for releases from all known and suspected source categories of dioxin-like PCBs[a]

Source category	Air	Land	Water
Approved PCB disposal	E		
Accidental PCB releasees	E	E	E
Municipal wastewater treatment sludge		A	
Municipal waste combustion	E		
Industrial wood combustion	E		
Medical waste incineration	E		
Tire combustion	E		
Cigarette combustion	D		
Sewage sludge incineration	C		
Backyard barrel burning	E		
Petroleum refining catalyst regeneration	E		

[a] Blank cells mean not applicable or no data.

A= Characterization of the source category judged to be adequate for quantitative estimation with high confidence in the emission factor and high confidence in the activity level.
C= Characterization of the source category judged to be adequate for quantitative estimation with low confidence in the emission factor and/or the activity level.
D= These are preliminary indications of the potential magnitude of emissions from "unquantified" sources in Reference Year 1995. These estimates were assigned a "confidence category" rating of D and are not included in the Inventory.
E= Not quantifiable.

materials that may have been contaminated with trace levels of PCBs from prior PCB use or disposal. Following the ban on PCB production, releases from these first two categories ceased. The third type of releases, those associated with product use and disposal, will continue in at least four ways:

1. Disposal of products containing greater than 2 lb of PCBs (e.g., dielectric fluids in transformers and large capacitors), which is controlled by disposal regulations that have minimized environmental releases;

2. Disposal of products containing small quantities of PCBs (e.g., small capacitors, fluorescent lighting fixtures) or trace quantities of PCBs (e.g., wastepapers), which is subject to disposal as municipal solid waste but which may result in some release to the general environment;

Table 10-2. Inventory of contemporary releases of dioxin-like PCBs in the United States for 1987, 1995, and 2000 and preliminary release estimates of dioxin-like PCBs for 2000 (g TEQ_p-WHO_{98}/yr)

Emissions source category	2000 Inventory			1995 Inventory			1987 Inventory			Preliminary estimate for 2000
	A	B	C	A	B	C	A	B	C	D
Releases to air										
Combustion sources										
Cigarettes										0.01
Sewage sludge incineration			0.7			1.1			0.4	
Total quantified releases to air			0.7			1.1			0.4	0.01
Releases to land										
Municipal sludge (land application and farming)	18.8				77.4			51.1		
Total quantified releases to land	18.8				77.4			51.1		
Releases to products										
Municipal sludge as soil ammendment	0.5				2.0			1.7		
Total quantified releases to products	0.5				2.0			1.7		

A= Characterization of the source category judged to be adequate for quantitative estimation with high confidence in the emission factor and high confidence in the activity level.

C= Characterization of the source category judged to be adequate for quantitative estimation with low confidence in the emission factor and/or the activity level.

D= These are preliminary indications of the potential magnitude of emissions from "unquantified" sources in Reference Year 1995. These estimates were assigned a "confidence category" rating of D and are not included in the Inventory.

E= Not quantifiable.

3. Leaks and spills of still-in-service PCBs; and

4. Illegal disposal of PCBs.

Although it has been demonstrated that small quantities of dioxin-like PCBs can be emitted into the air during waste combustion, no strong evidence exists that they are emitted in significant quantities as by-products during combustion. The widespread occurrence of dioxin-like PCBs in the U.S. environment most likely reflects past releases associated with PCB production, use, and disposal. Further support for this finding is based on observations of reductions since the 1980s in PCB concentrations in Great Lakes sediment and in other areas.

10.2. RELEASES OF COMMERCIAL PCBs

PCBs were commercially manufactured by the direct batch chlorination of molten biphenyl with anhydrous chlorine in the presence of a catalyst, followed by separation and purification of the desired chlorinated biphenyl fractions. The degree of chlorination was controlled by the chlorine contact time in the reactor. Commercial PCB production is believed to have been confined to 10 countries. Total PCBs produced worldwide since 1929 (the first year of known production) has been estimated at 1.5 million metric tons.

Initially, PCBs were used primarily as dielectric fluids in transformers. After World War II, PCBs found steadily increasing use as dielectric fluids in capacitors, as heat-conducting fluids in heat exchangers, and as heat-resistant hydraulic fluids in mining equipment and vacuum pumps. PCBs also were used in a variety of "open" applications (i.e, uses from which PCBs cannot be recollected), including plasticizers, carbonless copy paper, lubricants, inks, laminating agents, impregnating agents, paints, adhesives, waxes, additives in cement and plaster, casting agents, dedusting agents, sealing liquids, fire retardants, immersion oils, and pesticides (DeVoogt and Brinkman, 1989).

U.S. production peaked in 1970, with a volume of 39,000 metric tons. In 1971, Monsanto Corporation, the major U.S. producer, voluntarily restricted the sale of PCBs for all applications, with the exception of "closed electrical systems." Annual production fell to 18,000 metric tons in 1974. Monsanto ceased PCB manufacture in mid-1977 and shipped the last inventory in October of that year. Regulations issued by EPA beginning in 1977, principally under the Toxic Substances Control Act (TSCA) (40 CFR 761), have strictly limited the production, import, use, and disposal of PCBs. The estimated cumulative production and consumption volumes of PCBs in the United States from 1930 to 1975 were 635.03 million kg produced, 1.36 million kg imported (primarily from Japan, Italy, and France), 568.35 million kg

sold in the United States, and 68.04 million kg exported (ATSDR, 1993; DeVoogt and Brinkman, 1989). The reliability of these values is +5% and –20% (Versar, Inc., 1976).

Monsanto Corporation marketed technical-grade mixtures of PCBs primarily under the trade name Aroclor. The Aroclor mixtures are identified by a four-digit numbering code in which the last two digits indicate the chlorine content by weight percent. The exception to this coding scheme is Aroclor 1016, which contains only mono- through hexachlorinated congeners with an average chlorine content of 41%. From 1957 until 1972, Monsanto also manufactured several blends of PCBs and polychlorinated terphenyls (PCTs) under the trade names Aroclor 2565 and Aroclor 4465; manufacture and sales volumes are not available for these blends. Listed below are the percentages of total Aroclor production during the years 1957 to 1977 by Aroclor mixture, as reported by Brown (1994).

Aroclor	1957–1977 U.S. production (%)
1016	12.88
1221	0.96
1232	0.24
1242	51.76
1248	6.76
1254	15.73
1260	10.61
1262	0.83
1268	0.33

The trade names of the major commercial PCB technical-grade mixtures manufactured in other countries included Clophen (Germany), Fenclor and Apirolio (Italy), Kanechlor (Japan), Phenoclor and Pyralene (France), Sovtel (USSR), Delor and Delorene (Czechoslovakia), and Orophene (German Democratic Republic) (DeVoogt and Brinkman, 1989). The mixtures marketed under these trade names had similar chlorine content (by weight percent and average number of chlorines per molecule) to those of various Aroclor mixtures. Listed below are comparable mixtures in terms of chlorine content marketed under several trade names.

Aroclor	Clophen	Pyralene	Phenoclor	Fenclor	Kanechlor
1232		2000			200
1242	A-30	3000	DP-3	42	300
1248	A-40		DP-4		400
1254	A-50		DP-5	54	500
1260	A-60		DP-6	64	600

Major advances in analytical separation and resolution techniques beginning in the 1970s enabled various researchers to identify and quantify PCB congeners present in Aroclors, Clophens, and Kanechlors (Jensen et al., 1974; Albro and Parker, 1979; Huckins et al., 1980; Albro et al., 1981; Duinker and Hillebrand, 1983; Kannan et al., 1987; Tanabe et al., 1987; Duinker et al., 1988; Schulz et al., 1989; Himberg and Sippola, 1990; Larsen et al., 1992; deBoer et al., 1993; Schwartz et al., 1993; Frame et al., 1996a, b; Frame, 1997). Schulz et al. (1989) were the first to identify and quantify all PCB congeners present in a series of Aroclors and Clophens. Frame (1995) reported preliminary results of a nearly completed round robin study, one goal of which was to determine the distribution of all PCB congeners above 0.05 weight percent in various Aroclors (1221, 1016, 1242, 1260, and 1262) using 18 state-of-the-art gas chromatography/mass spectrometry (GC/MS) or electron capture detector (GC/ECD) systems.

Table 10-3 presents mean summary statistics on the concentrations of the dioxin-like PCBs in each mixture group (e.g., Aroclor 1248, Clophen A-40, and Kanechlor 400 are in one mixture group) reported by these researchers. Table 10-3 also presents the mean TEQ concentration of each congener in each mixture group as well as the total mean TEQ concentration in the mixture group. Because of the wide variability in the reported results, the uncertainty associated with these mean concentrations is very large.

For each mixture group, the congeners detected were generally similar. There was, however, wide variability in the concentrations reported by some researchers for some congeners. Brown et al. (1995) compiled similar statistics using a somewhat different set of studies and derived significantly lower mean concentrations of some congeners in several Aroclors. Frame (1995) and Larsen (1995) attributed such differences to either potential limitations in the GC columns used by various researchers to separate similar eluting congeners or actual differences in the congener concentrations in the Aroclor, Clophen, and Kanechlor lots analyzed by various research groups.

The congener distributions also vary among the different mixtures. Therefore, the calculated TEQs also vary. The congener distributions for various lots of Aroclor 1254, and the corresponding TEQs, are presented in another study (Frame, 1999) in which the relative TEQs for late production lots were reported to be much higher than those for the earlier production lots; however, the late production lots were estimated to account for only about 1% of the total production volume of Aroclor 1254. Therefore, the data for the later production lots were not included in the average TEQ calculation for Aroclor 1254 in Table 10-3.

In the environment, PCBs also occur as mixtures of congeners, but their composition differs from those of the commercial mixtures because after release to the environment the mixtures change over time through partitioning, chemical transformation, and preferential bioaccumulation (U.S. EPA, 1996f). Dioxin-like PCB congeners differ by up to one to two

Table 10-3. Weight percent concentrations of dioxin-like PCBs in Aroclors, Clophens, and Kanechlors

Dioxin-like PCB congener	IUPAC number	No. of samples analyzed	No. of detections	Mean conc. (nondetect set to zero) (g/kg)	TEQ_P-WHO_{98} conc. (nondetect set to zero) (mg/kg)	Mean conc.[a] (nondetect set to ½ detection limit) (g/kg)	TEQ_P-WHO_{98} conc.[a] (nondetect set to ½ detection limit) (mg/kg)
Aroclor 1016							
3,3',4,4'-TCB	77	5	0	0	0	0	0
3,4,4',5-TCB	81	3	0	0	0	0	0
2,3,3',4,4'-PeCB	105	4	1	0.0375	0.00375	0.109	0.011
2,3,4,4',5-PeCB	114	4	0	0	0	0	0
2,3',4,4',5-PeCB	118	4	1	0.0125	0.00125	0.091	0.009
2',3,4,4',5-PeCB	123	4	0	0	0	0	0
3,3',4,4',5-PeCB	126	4	0	0	0	0	0
2,3,3',4,4',5-HxCB	156	4	0	0	0	0	0
2,3,3',4,4',5'-HxCB	157	4	0	0	0	0	0
2,3',4,4',5,5'-HxCB	167	4	0	0	0	0	0
3,3',4,4',5,5'-HxCB	169	5	0	0	0	0	0
2,2',3,3',4,4',5-HpCB	170	4	0	0	0	0	0
2,2',3,4,4',5,5'-HpCB	180	4	0	0	0	0	0
2,3,3',4,4',5,5'-HpCB	189	4	0	0	0	0	0
Total TEQ_P-WHO_{98}					0.005		0.0200
Total TEQ_P-WHO_{94}					0.005		0.0200
Aroclor 1221							
3,3',4,4'-TCB	77	4	4	1.075	0.1075	1.078	0.108
3,4,4',5-TCB	81	4	1	0.0875	0.00875	0.116	0.012
2,3,3',4,4'-PeCB	105	4	3	0.3875	0.03875	0.4	0.04
2,3,4,4',5-PeCB	114	4	0	0	0	0	0
2,3',4,4',5-PeCB	118	4	4	1.725	0.1725	1.725	0.173
2',3,4,4',5-PeCB	123	4	0	0	0	0	0
3,3',4,4',5-PeCB	126	4	0	0	0	0	0
2,3,3',4,4',5-HxCB	156	4	0	0	0	0	0
2,3,3',4,4',5'-HxCB	157	4	0	0	0	0	0
2,3',4,4',5,5'-HxCB	167	4	0	0	0	0	0
3,3',4,4',5,5'-HxCB	169	4	0	0	0	0	0
2,2',3,3',4,4',5-HpCB	170	3	0	0	0	0	0
2,2',3,4,4',5,5'-HpCB	180	3	0	0	0	0	0
2,3,3',4,4',5,5'-HpCB	189	4	0	0	0	0	0
Total TEQ_P-WHO_{98}					0.328		0.333
Total TEQ_P-WHO_{94}					0.749		0.752

Table 10-3. Weight percent concentrations of dioxin-like PCBs in Aroclors, Clophens, and Kanechlors (continued)

Dioxin-like PCB congener	IUPAC number	No. of samples analyzed	No. of detections	Mean conc. (nondetect set to zero) (g/kg)	TEQ_P-WHO_{98} conc. (nondetect set to zero) (mg/kg)	Mean conc.[a] (nondetect set to ½ detection limit) (g/kg)	TEQ_P-WHO_{98} conc.[a] (nondetect set to ½ detection limit) (mg/kg)
Aroclor 1242, Clophen A-30, and Kanechlor 300							
3,3',4,4'-TCB	77	15	15	3.3	0.33	3.301	0.33
3,4,4',5-TCB	8	7	6	1.09	0.11	1.089	0.109
2,3,3',4,4'-PeCB	105	11	11	4.02	0.4	4.024	0.402
2,3,4,4',5-PeCB	114	8	5	1.13	0.57	1.201	0.601
2,3',4,4',5-PeCB	118	9	9	8.04	0.8	8.044	0.804
2',3,4,4',5-PeCB	123	9	7	1.12	0.11	1.157	0.116
3,3',4,4',5-PeCB	126	14	8	0.049	4.94	0.094	9.404
2,3,3',4,4',5-HxCB	156	9	8	0.39	0.2	0.424	0.212
2,3,3',4,4',5'-HxCB	157	8	2	0.021	0.011	0.096	0.048
2,3',4,4',5,5'-HxCB	167	8	2	0.021	0.00021	0.096	0.001
3,3',4,4',5,5'-HxCB	169	14	2	0.000013	0.00013	0.048	0.476
2,2',3,3',4,4',5-HpCB	170	6	2	0.19	0	0.244	0
2,2',3,4,4',5,5'-HpCB	180	5	2	0.16	0	0.218	0
2,3,3',4,4',5,5'-HpCB	189	7	0	0	0	0	0
Total TEQ_P-WHO_{98}					7.47		12.5
Total TEQ_P-WHO_{94}					8.70		13.74
Aroclor 1248, Clophen A-40, and Kanechlor 400				4.36	0.44	4.36	0.44
3,3',4,4'-TCB	77	13	13	1.76	0.18	1.77	0.18
3,4,4',5-TCB	81	6	4	10.12	1.01	10.12	1.01
2,3,3',4,4'-PeCB	105	9	8	3.39	1.69	3.4	1.7
2,3,4,4',5-PeCB	114	7	6	20.98	2.1	20.98	2.1
2,3',4,4',5-PeCB	118	8	8	1.48	0.15	1.48	0.15
2',3,4,4',5-PeCB	123	7	7	0.11	10.55	0.14	13.51
3,3',4,4',5-PeCB	126	11	6	1.13	0.56	1.13	0.56
2,3,3',4,4',5-HxCB	156	8	8	0.19	0.09	0.2	0.1
2,3,3',4,4',5'-HxCB	157	7	3	0.16	0.0016	0.16	0.0016
2,3',4,4',5,5'-HxCB	167	7	3	0.01	0.1006	0.041	0.41
3,3',4,4',5,5'-HxCB	169	12	3	0.96	0	0.97	0
2,2',3,3',4,4',5-HpCB	170	5	4	1.24	0	1.24	0
2,2',3,4,4',5,5'-HpCB	180	4	4	0.0018	0.0001833	0.06	0.006
2,3,3',4,4',5,5'-HpCB	189	6	1				
Total TEQ_P-WHO_{98}					16.87		20.16
Total TEQ_P-WHO_{94}					18.55		21.83

Table 10-3. Weight percent concentrations of dioxin-like PCBs in Aroclors, Clophens, and Kanechlors (continued)

Dioxin-like PCB congener	IUPAC number	No. of samples analyzed	No. of detections	Mean conc. (nondetect set to zero) (g/kg)	TEQ_P-WHO_{98} conc. (nondetect set to zero) (mg/kg)	Mean conc.[a] (nondetect set to ½ detection limit) (g/kg)	TEQ_P-WHO_{98} conc.[a] (nondetect set to ½ detection limit) (mg/kg)
Aroclor 1254, Clophen A-50, and Kanechlor 500				0.8	0.0795	0.83	0.08
3,3',4,4'-TCB	77	15	12	7.85	0.79	7.86	0.79
3,4,4',5-TCB	81	6	1	35.83	3.58	35.83	3.58
2,3,3',4,4'-PeCB	105	12	11	12.17	6.08	12.23	6.11
2,3,4,4',5-PeCB	114	9	6	81.65	8.17	81.65	8.17
2,3',4,4',5-PeCB	118	11	11	4.59	0.46	4.59	0.46
2',3,4,4',5-PeCB	123	8	8	0.99	99.46	1.02	101.7
3,3',4,4',5-PeCB	126	14	12	11.08	5.54	11.08	5.54
2,3,3',4,4',5-HxCB	156	10	10	1.91	0.95	1.93	0.97
2,3,3',4,4',5'-HxCB	157	9	8	2.74	0.0274	2.74	0.03
2,3',4,4',5,5'-HxCB	167	10	9	0.08	0.8	0.12	1.23
3,3',4,4',5,5'-HxCB	169	14	6	5.06	0	5.06	0
2,2',3,3',4,4',5-HpCB	170	8	8	5.79	0	5.79	0
2,2',3,4,4',5,5'-HpCB	180	7	7	0.045	0.0045429	0.13	0.013
2,3,3',4,4',5,5'-HpCB	189	7	2				
Total TEQ_P-WHO_{98}				125.94			128.67
Total TEQ_P-WHO_{94}				126.04			128.78
Aroclor 1260, Clophen A-60, and Kanechlor 600							
3,3',4,4'-TCB	77	15	6	0.13	0.01256	0.17	0.017
3,4,4',5-TCB	81	6	1	0.08	0.0075	0.1	0.01
2,3,3',4,4'-PeCB	105	11	10	1.59	0.16	1.59	0.16
2,3,4,4',5-PeCB	114	9	4	0.71	0.35	0.77	0.39
2,3',4,4',5-PeCB	118	11	10	9.51	0.95	9.51	0.95
2',3,4,4',5-PeCB	123	8	1	0.0005	0.00005	0.08	0.008
3,3',4,4',5-PeCB	126	14	7	1.81	180.89	1.84	183.82
2,3,3',4,4',5-HxCB	156	11	11	6.89	3.45	6.89	3.45
2,3,3',4,4',5'-HxCB	157	8	8	1.59	0.79	1.59	0.79
2,3',4,4',5,5'-HxCB	167	10	9	2.87	0.03	2.87	0.03
3,3',4,4',5,5'-HxCB	169	14	5	0.16	1.64	0.19	1.92
2,2',3,3',4,4',5-HpCB	170	8	8	32.94	0	32.94	0
2,2',3,4,4',5,5'-HpCB	180	7	7	82.61	0	82.61	0
2,3,3',4,4',5,5'-HpCB	189	8	8	1.74	0.1739792	1.74	0.17
Total TEQ_P-WHO_{98}					188.45		191.71
Total TEQ_P-WHO_{94}					192.62		195.89

Table 10-3. Weight percent concentrations of dioxin-like PCBs in Aroclors, Clophens, and Kanechlors (continued)

[a]Calculated for a congener only when at least one sample contained detectable levels of that congener.

Sources: Adapted from Schulz et al. (1989); Duinker and Hillebrand (1983; deBoer et al. (1993); Schwartz et al. (1993); Larsen, et al. (1992); Kannan et al. (1987); Huckins et al. (1980); Albro and Parker (1979; Jensen et al. (1974); Albro et al. (1981); Duinker et al. (1988); Tanabe et al. (1987); Himberg and Sippola (1990); Frame et al. (1996a, b); Frame (1997).

orders of magnitude in their water solubility, vapor pressure, K_{ow} value, and Henry's Law constant. Thus, although all the dioxin-like PCB congeners are poorly soluble in water and have very low vapor pressures, they will volatilize and leach at different rates. Similarly, because the congeners differ somewhat in their rates of biodegradation, bioaccumulation, and photodegradation, the congener patterns found in environmental media and biota will vary from those found in commercial mixtures.

Although environmental mixtures are often characterized in terms of Aroclors, this characterization can be both imprecise and inappropriate. Qualitative and quantitative errors can arise from judgements in comparing GC/MS peaks for a sample with the characteristic peak patterns for different Aroclors, particularly for environmentally altered patterns (U.S. EPA, 1996f). For the same reason, it can be both imprecise and inappropriate to infer concentrations of dioxin-like PCB congeners in an environmental sample on the basis of characterization of the sample's Aroclor content and knowledge of the dioxin-like congener content in the commercial Aroclor. Safe (1994) wrote, "Regulatory agencies and environmental scientists have recognized that the composition of PCBs in most environmental extracts does not resemble the compositions of the commercial product." Similarly, ATSDR (1993) stated, "It is important to recognize that the PCBs to which people may be exposed are likely to be different from the original PCB source because of changes in congener and impurity composition resulting from differential partitioning and transformation in the environment and differential metabolism and retention."

10.2.1. Approved PCB Disposal/Destruction Methods

In 1978, EPA began regulating the disposal of PCBs and PCB-contaminated waste under TSCA, PL 94-469. The disposal regulations, published in the Code of Federal Regulations, 40 CFR, Part 761, state that the preferred disposal method is incineration at 1,200°C or higher. If the waste contains material that cannot be destroyed by incineration, EPA clearance must be obtained to dispose of the waste in a chemical waste landfill or by another approved manner.

The PCB disposal regulations describe disposal of three distinct types of PCB waste: PCBs, PCB articles (items containing PCBs), and PCB containers. Within these categories, further distinctions are made on the basis of the PCB concentration in the waste, with the acceptable disposal methods being based on the concentrations in the specific waste to be destroyed. The acceptable disposal methods are Annex I incinerators, high-efficiency boilers, Annex II chemical waste landfills, and other approved methods. The following paragraphs and Table 10-4 provide brief descriptions of these disposal methods. More complete descriptions of the specific methodologies are provided in 40 CFR, Part 761.

Table 10-4. Disposal requirements for PCBs and PCB items

PCBs/items	Waste characterization		Disposal requirements
PCBs	Mineral oil dielectric fluids from PCB transformers	Those analyzing >500 ppm PCB	Annex I incinerator[a]
	Mineral oil dielectric fluids from PCB-contaminated transformers	Those analyzing 50–500 ppm PCB	Annex I incinerator High-efficiency boiler (40 CFR 761.10(a)(2)(iii)) Other approved incinerator[b] Annex II chemical waste landfill[c]
	PCB liquid wastes other than mineral oil dielectric fluid	Those analyzing >500 ppm PCB Those analyzing 50–500 ppm PCB	Annex I incinerator Annex I incinerator High-efficiency boiler (40 CFR 761.10(a)(2)(iii)) Other approved incinerator[b] Annex II chemical waste landfill[c]
	Nonliquid PCB wastes (e.g., contaminated materials from spills)		Annex I incinerator Annex II chemical waste landfill
	Dredged materials and municipal sewage treatment sludges containing PCBs		Annex I incinerator Annex II chemical waste landfill Other approved disposal method, 40 CFR 761.10(a)(5)(iii)
PCB articles	Transformers	PCB transformers PCB contaminated transformers	Annex I incinerator Drained and rinsed transformers may be disposed of in Annex II chemical waste landfill Disposal of drained transformers is not regulated
	PCB capacitors[d]		Annex I incinerator
	PCB hydraulic machines	Those containing >1,000 ppm PCB Those containing <1,000 ppm PCB	Drained and rinsed machines may be disposed of as municipal solid waste or salvaged Drained machines may be disposed of as municipal solid waste or salvaged

Table 10-4. Disposal requirements for PCBs and PCB items (continued)

PCBs/items	Waste characterization		Disposal requirements
	Other PCB articles	Those containing PCB fluids	Drained machines may be disposed of by Annex I or Annex II
		Those not containing PCB fluids	Annex I incinerator or Annex II chemical waste landfill
PCB containers	Those used to contain only PCBs at a concentration <500 ppm		As municipal solid waste provided any liquid PCBs are drained prior to disposal
	Other PCB containers		Annex I incinerator Annex II, provided any liquid PCBs are drained prior to disposal Decontaminate per Annex IV

[a]Annex I incinerator is defined in 40 CFR 761.40.
[b]Requirements for other approved incinerators are defined in 40 CFR 761.10(e).
[c]Annex II chemical waste landfills are described in 40 CFR 761.41. Annex II disposal is permitted if the PCB waste contains less than 500 ppm PCB and is not ignitable as per 40 CFR Part 761.41(b)(8)(iii).
[d]Disposal of containerized capacitors in Annex II landfills was permitted until March 1, 1981; thereafter, only Annex I incineration has been permitted.

Source: U.S. EPA (1987d).

10.2.1.1. *Approved Incinerators/High-Efficiency Boilers*

PCB Annex I incinerators must meet the specific technical standards and criteria listed in Annex I of EPA's PCB regulations. The minimum operating requirements for disposal of liquid wastes are 2 sec at 1,200°C with 3% excess oxygen (measured in the stack gas) or 1.5 sec at 1,600°C with 2% excess oxygen (measured in the stack gas). Monitoring requirements, approval conditions, and trial burn requirements are prescribed in Annex I. Operators of commercial or industrial incinerators who intend to destroy liquid PCB wastes must demonstrate the incineration's compliance with the Annex I requirements through a comprehensive trial burn program. Annex I incinerators operating at optimum performance level should destroy 99.997% of liquid PCB waste, with a resulting maximum emission factor of 0.03 g/kg.

Criteria for Annex I incinerators were established for the destruction of liquid PCB wastes; however, these incinerators also may be used for disposal of nonliquid PCB items (such as capacitors), provided that a destruction and removal efficiency of 99.9999% and a maximum emission factor of 0.001 g/kg are met.

High-efficiency boilers may be used to destroy PCBs and PCB-contaminated waste with PCB concentrations not exceeding 500 ppm. Conventional industrial and utility boilers may be designated as high-efficiency boilers if they are operated under the prescribed combustion conditions defined in the PCB disposal regulations. The PCB regulations do not specify a minimum destruction efficiency for high-efficiency boilers; however, EPA-approved boilers operated according to the regulations have reported destruction efficiencies in excess of 99.99%, with a corresponding maximum emission factor of 0.1 g/kg (U.S. EPA, 1987d).

10.2.1.2. *Approved Chemical Waste Landfills*

Approved chemical waste landfills can be used for the disposal of some but not all PCB wastes. PCB-contaminated materials acceptable for land disposal in an approved landfill include PCB mixtures (e.g., certain PCB-contaminated soil/solid debris, PCB-contaminated dredged materials, and PCB-contaminated municipal sewage sludge), PCB articles that cannot feasibly be incinerated (e.g., drained and flushed transformers), and drained PCB containers. Written approval must be obtained from EPA in order to landfill PCB articles other than transformers. PCB-contaminated materials not acceptable for land disposal in an approved landfill include nonliquid PCB mixtures in the form of contaminated soil, rags, or other solid debris, and sealed capacitors. Typically, PCBs disposed of in these landfills are placed in sealed containers, thereby minimizing any PCB emissions.

10.2.1.3. *Other Approved Disposal Methods*

Other thermal and nonthermal destruction techniques may be approved by EPA Regional Administrators if these processes can effect a level of destruction of PCBs equivalent to that of incinerators or boilers. After April 29, 1983, all other PCB disposal technologies (thermal and nonthermal) used in more than one EPA Region had to be approved by EPA Headquarters. Examples of thermal technologies approved for commercial-scale use or for research and development projects include a pyrolysis process to treat contaminated soils, a fluid wall reactor, a cement kiln, a diesel engine, a steam-stripping operation, an aluminum melting furnace, and a molten salt process. Examples of approved nonthermal processes include chemical dechlorination processes, physical/chemical extraction techniques, and biological reduction methods. The physical/chemical techniques extract the PCBs from transformers or capacitors and concentrate them for disposal; they do not destroy the PCBs.

10.2.2. Emission Estimates

Tables 10-5 and 10-6 list the amounts of PCBs reported in EPA's Toxics Release Inventory (TRI) as transferred off site for treatment, energy recovery, or disposal and the amounts released between 1988 and 2000, respectively. These quantities do not necessarily represent entry of PCBs into the environment. If it is assumed that all transferred PCBs are incinerated in high-efficiency boilers with a destruction and removal efficiency of 99.99%, then annual emissions of PCBs to air during 1988, 1995, and 2000 could have been as high as 264 kg, 31 kg, and 15 kg, respectively. Because no stack testing data are available for dioxin-like PCBs, it is not possible to estimate what fraction of these potential PCB releases would have been dioxin-like congeners.

10.2.3. Accidental Releases of Still-in-Service PCBs

After the 1977 ban on production of PCBs, releases of commercially produced PCBs to the environment (aside from minimal releases occurring during approved disposal or destruction) have been limited to accidental release of in-service PCBs (U.S. EPA, 1987d). Accidental releases are the result of leaks or spills during failure/breakage of an existing piece of PCB-containing equipment or of incomplete combustion during accidental fires involving PCB-containing equipment. These two types of accidental releases are discussed in the following sections.

Table 10-5. Off-site transfers of PCBs reported in the Toxics Release Inventory (TRI) (1988–2000)

Year	No. of TRI forms filed	Reported transfers (kg)		
		Transfers to POTWs	Transfers for treatment/disposal	Total transfers
2000	NA	102	150,888	150,990
1999	NA	0	434,666	434,666
1998	NA	0	386,903	386,903
1997	NA	[a]	471,319	471,319
1996	NA	0	160,802	160,802
1995	NA	0	308,347	308,347
1994	NA	0	466,948	466,948
1993	16	120	463,385	463,505
1992	20	0	766,638	766,638
1991	26	0	402,535	402,535
1990	NA	0	1,181,961	1,181,961
1989	NA	0.5	2,002,237	2,002,237
1988	122	113	2,642,133	2,642,246

[a]Facilities left that particular cell blank on the Form R submissions.

NA = Not available
POTWs = Publicly owned treatment works

Sources: U.S. EPA (1993f, 1995h, 1998b, 2003c).

10.2.3.1. *Leaks and Spills*

PCBs that remain in active service at this time are those contained in "closed systems" (i.e., those pieces of electrical equipment that completely enclose the PCBs and do not provide direct atmospheric access for the PCBs during normal use). This equipment includes PCB transformers, capacitors, voltage regulators, circuit breakers, and reclosures. With the exception of PCB transformers—and probably small PCB capacitors—the majority of the PCB-containing electrical equipment in service during 1981 was owned by the electrical utility industry. Approximately 70% of the estimated 140,000 PCB transformers in service in 1981 were owned by nonutilities. No information was available on the relative distribution of small PCB capacitors (Versar, Inc., 1988).

Table 10-6. Releases of PCBs reported in the Toxics Release Inventory (TRI) (1988–2000)

Year	No. of TRI forms filed	Reported releases (kg)					
		Fugitive or nonpoint air emissions	Stack or point air emissions	Surface water discharges	Underground injection	On-site releases to land	Total on-site Releases
2000	NA	158	2,497	13	0.5	648,128	650,796.5
1999	NA	0	0	[a]	[a]		0.0
1998	NA	0	0	0	[a]	60,854	60,854.0
1997	NA	0	0	0	[a]	3,081	3,081.0
1996	NA	2.3	114	0	0	4,179	4,295.3
1995	NA	0	0	0	0	0	0.0
1994	NA	0	0	0	0	0	0.0
1993	16	0	0	0	0	120	120.0
1992	20	0	0	0	0	0.5	0.5
1991	26	0	0	0	0	0	0.0
1990	NA	2.3	0	0	0	32,372	32,374.3
1989	NA	0	0	120	0	453	573.0
1988	122	2.7	0	4.5	0	341	348.2

[a]Facilities left that particular cell blank on the Form R submissions.

NA = Not available

Sources: U.S. EPA (1993f, 1995h, 1998b, 2003c).

The number of each of these items owned by the utility industry, the quantity of PCBs contained in each, and an estimate of the annual quantity of PCBs leaked and/or spilled were investigated by the Edison Electric Institute and the Utility Solid Wastes Activity Group (EEI/USWAG) for EPA in 1981. The findings of this investigation, which were reported in a proposed modification to the PCB regulations (Federal Register, 1982a), indicated that more than 99% of the total quantity of PCBs contained in utility-owned electrical equipment in 1981 (73,700 metric tons) was in 40,000 PCB transformers (those containing >500 ppm of PCBs) and large PCB capacitors (those containing >3 lb of PCBs). An upper-bound estimate of the mass of PCBs that leached or spilled from this equipment in 1981 was 177 metric tons. Approximately 95% of the estimated releases were the result of leaks from large PCB capacitors (Federal Register, 1982a). Leaks/spills typically occur in transformers when the gasket joining the top to the body corrodes, tears, or physically fails. PCBs can then leak past this failed section and potentially spill onto the surrounding ground. PCB capacitors typically fail by rupturing, exposing the contained PCBs to the environment. Failure is caused by environmental and weathering effects (e.g., lightning) or material failures (e.g., metal fatigue).

As of mid-1988, the total population of in-service PCB transformers and large PCB capacitors was estimated to have decreased from 140,000 to 110,000 and from 3.3 million to 1.9 million, respectively (Versar, Inc., 1988). PCB transformers have normal operating lifetimes of 30 years and 40 years, respectively. EPA's PCB Electrical Use Rule (Federal Register, 1982b) required the removal of 950 food/feed industry transformers by 1985 and 1.1 million unrestricted-access large PCB capacitors by October 1988. In addition, EPA's PCB Transformer Fires Rule (Federal Register, 1985b) required the removal by 1990 of 7,600 480-volt network transformers.

More recent inventories of PCB-containing electrical equipment are not available. However, an Information Collection Request submitted by EPA to the Office of Management and Budget for information on uses, locations, and conditions of PCB electrical equipment estimated that there may be 150,000 owners of PCB-containing transformers used in industry, utilities, government buildings, and private buildings (Federal Register, 1997b). It is expected, and is demonstrated by the reported PCB transfers in the EPA's TRI (see Table 10-5), that many owners of PCB electrical equipment have removed PCB-containing equipment to eliminate potential liability.

10.2.3.2. *Accidental Fires*

The available information is not adequate to support an estimate of potential annual releases of dioxin-like PCBs from accidental electrical equipment fires. For fires involving PCB transformers or capacitors, the amount of PCBs released is dependent on the extensiveness of the

fire and the speed at which it is extinguished. A number of these fires are documented. A New York fire involving 200 gal of transformer fluid containing some 65% by weight PCBs resulted in a release of up to 1,300 lb of PCBs. A capacitor fire that burned uncontrolled for 2 hr in Sweden resulted in the destruction of 12 large utility capacitors containing an estimated 25 pounds each of PCBs, for a total potential release of 300 lb. However, data are incomplete on the exact amount of PCBs released as a result of these two fires.

EPA has imposed reporting requirements to ensure that the National Response Center is informed immediately of fires involving PCB transformers (40 CFR 761). The recordkeeping requirements are used to document the use, location, and condition of PCB equipment. Responses are mandatory, but the submitter may claim them to be confidential information. The number of PCB transformer fires is estimated to be approximately 20 per year; the number of PCB capacitor fires is unknown (U.S. EPA, 1987d). As these PCB-containing items reach the end of their useful lives and are retired, their susceptibility to fires will be eliminated, and the overall number of PCB transformer and capacitor fires will be reduced.

10.2.4. Municipal Wastewater Treatment

EPA conducted the National Sewage Sludge Survey in 1988 and 1989 to obtain national data on sewage sludge quality and management. As part of this survey, EPA tested for more than 400 analytes, including seven of the Aroclors, in sludges from 175 publicly owned treatment works (POTWs) that employed at least secondary wastewater treatment. Sludges from 19% of the POTWs had detectable levels of at least one of the following Aroclors: 1248, 1254, or 1260; none of the other Aroclors were detected in any sample (the detection limit [DL] was typically about 200 µg/kg dry weight) (U.S. EPA, 1996e). Analyses were not performed for dioxin-like PCB congeners. The Aroclor-specific results of the survey are presented in Table 10-7.

Gutenmann et al. (1994) reported similar results in a survey of sludges from 16 large U.S. cities for Aroclor 1260 content. At a DL of 250 µg/kg (dry weight), the investigators detected Aroclor 1260 (4,600 µg/kg) at only one facility. These results indicate that PCBs are not likely to be formed at POTWs, but rather are present because of disposal of PCB products or recirculation of previously disposed of PCBs.

Although PCBs, measured as Aroclors, were not commonly detected in sewage sludge at microgram-per-kilogram levels in studies by EPA (U.S. EPA, 1996e) and Gutenmann et al. (1994), the presence of dioxin-like PCB congeners at lower concentrations may be more common. Green et al. (1995) and Cramer et al. (1995) reported the results of analyses of 99 samples of sewage sludge for PCB congener numbers 77, 81, 126, and 169. The sludge samples were collected from 74 wastewater treatment plants across the United States during the summer

Table 10-7. Aroclor concentrations (ng/kg) measured in EPA's National Sewage Sludge Survey[a]

Aroclor	Percent detected	Maximum concentration	Median concentration	
			Nondetects set to detection limit	Nondetects set to zero
1016	0	--	--	0
1221	0	--	--	0
1232	0	--	--	0
1242	0	--	--	0
1248	9	5.2	0.209	0
1254	8	9.35	0.209	0
1260	10	4.01	0.209	0
Any Aroclor (total)	19	14.7	1.49	0

[a]For publicly owned treatment works with multiple samples, the pollutant concentrations were averaged before the summary statistics presented in the table were calculated.

-- = No information given

Source: U.S. EPA (1996e).

of 1994. These data are summarized in Table 10-8. Results from all samples collected from the same facility were averaged by Green et al. and Cramer et al. to ensure that results were not biased toward the concentrations found at facilities from which more than one sample was collected. If all nondetect values were assumed to be zero, then the POTW mean TEQ_P-WHO_{94} and TEQ_P-WHO_{98} concentrations were 25.1 and 24.2 ng TEQ/kg (dry-weight basis), respectively. If the nondetect values were set equal to the DLs, then the POTW mean TEQ_P-WHO_{94} and TEQ_P-WHO_{98} concentrations were 25.2 and 24.3 ng TEQ/kg, respectively.

In 1999, sewage sludge samples from a POTW in Ohio were collected and analyzed for PCBs (U.S. EPA, 2000b). The facility, which accepts both domestic and industrial wastewater, employs secondary wastewater technology. Assuming nondects were zero, the mean TEQ emission factor was 141 ng TEQ_P-WHO_{98}/kg. These results are presented in Table 10-9.

In 2000 and 2001, the Association of Metropolitan Sewage Agencies conducted a survey of dioxin-like PCB compounds in sewage sludge (Alvarado et al., 2001). A total of 200 sewage sludge samples were collected from 171 POTWs located in 31 states. Assuming nondetects were zero, the mean and median TEQ emission factors were reported as 8.3 and 3.37 ng TEQ_P-WHO_{98}/kg, respectively.

Table 10-8. Dioxin-like PCB concentrations measured in sludges collected from 74 U.S. publicly owned treatment works (POTWs) during 1994[a,b]

Congener	IUPAC number	Percent detected	Maximum concentration (ng/kg)	Median concentration (ng/kg)		Mean concentration (ng/kg)	
				Nondetect set to ½ detection limit	Nondetect set to zero	Nondetect set to ½ detection limit	Nondetect set to zero
3,3',4,4'-TCB	77	100	22,900	783	783	2,243	2,243
3,4,4',5-TCB	81	86	1,250	27.3	27	65.2	63.5
2,3,3',4,4'-PeCB	105						
2,3,4,4',5-PeCB	114						
2,3',4,4',5-PeCB	118						
2',3,4,4',5-PeCB	123						
3,3',4,4',5-PeCB	126	99	3,020	91.6	91.6	237	237
2,3,3',4,4',5-HxCB	156						
2,3,3',4,4',5'-HxCB	157						
2,3',4,4',5,5'-HxCB	167						
3,3',4,4',5,5'-HxCB	169	22	1,470	8.5	0	32.5	26.2
2,2',3,3',4,4',5-HpCB	170						
2,2',3,4,4',5,5'-HpCB	180						
2,3,3',4,4',5,5'-HpCB	189						
Total TEQ_P-WHO_{98}				9.3	9.2	24.3	24.2

[a]For POTWs with multiple samples, the sample concentrations were averaged by Cramer et al. (1995) to POTW averages before calculation of the total TEQ mean and median values presented in the table. The TEQ_P-WHO_{94} and TEQ_P-WHO_{98} values were calculated on a facility-level basis.
[b]Blank cells indicate that no measurements of these congeners were made.

Source: Green et al. (1995); Cramer et al. (1995).

Table 10-9. Dioxin-like PCB concentrations in sewage sludge collected from U.S. publicly owned treatment works during 1999

Congener	IUPAC number	Mean emission factor (ng/kg)	
		Nondetect set to ½ detection limit	Nondetect set to zero
3,3',4,4'-TCB	77	42,467	42,467
2,3,3',4,4'-PeCB	105	7,230	7,230
2,3,4,4',5-PeCB	114	701	701
2',3,4,4',5-PeCB	123	249	249
2,3',4,4',5-PeCB	118	12,867	12,867
3,3',4,4',5-PeCB	126	1,270	1,270
2,3,3',4,4',5-HxCB	156	1,843	1,843
2,3,3',4,4',5'-HxCB	157	524	524
2,3',4,4',5,5'-HxCB	167	935	935
3,3',4,4',5,5'-HxCB	169	570	570
2,2',3,3',4,4',5-HpCB	170	2,627	2,627
2,2',3,4,4',5,5'-HpCB	180	6,497	6,497
2,3,3',4,4',5,5'-HpCB	189	199	199
Total TEQ_P-WHO_{98}		141	141

Source: U.S. EPA (2000b).

For 2001, EPA conducted another National Sewage Sludge Survey to characterize the dioxin and dioxin-like equivalence levels in biosolids produced by the 6,857 POTWs operating in the United States in 2001 (U.S. EPA, 2002d). Sewage sludge samples were collected from 94 POTWs that used secondary or higher treatment practices. All the facilities had been sampled as part of the 1988/1989 National Sewage Sludge Survey. To determine the mean and median TEQ emission estimates of the dioxin-like PCBs, EPA weighted the values on the basis of wastewater flow rates of all POTWs in the United States (i.e., number of facilities with wastewater flow rate >100 mg/day, >10 but ≤100 mg/day, >1 but ≤10 mg/day, and ≤1 mg/day). The weighted mean and median TEQ_P-WHO_{98} concentrations of the dioxin-like PCB congeners were 5.22 and 2.05 ng/kg, respectively.

According to the results of its 1988/1989 National Sewage Sludge Survey, EPA estimated that approximately 5.4 million dry metric tons of sewage sludge were generated in 1989 (Federal Register, 1993a). EPA also used the results of the 1984 to 1996 Clean Water Needs Surveys to

estimate that 6.3 million dry metric tons of sewage sludge were generated in 1998 and 6.6 million dry metric tons were generated in 2000 (U.S. EPA, 1999b). Because estimates for 1987 and 1995 are not available, the 1989 and 1998 activity level estimates are used for reference years 1987 and 1995, respectively. Tables 10-10, 10-11, and 10-12 list the volume, by use and disposal practices, of sludge disposed of annually for reference years 1989, 1995, and 2000.

Table 10-10. Quantity of sewage sludge disposed of annually in 1989 by primary, secondary, or advanced treatment publicly owned treatment works (POTWs) and potential dioxin-like PCB TEQ releases

Use/disposal practice	Volume disposed of (1,000 dry metric tons/yr)	Percent of total volume	Potential TEQ_P-WHO_{98} release[a] (g of TEQ/yr)	Potential TEQ_P-WHO_{94} release[a] (g of TEQ/yr)
Land application	1,714	32[b]	41.5	43
Distribution and marketing	71	1.3	1.7	1.8
Surface disposal site/other	396	7.4	9.6	9.9
Sewage sludge landfill	157	2.9	4.2	3.9
Co-disposal landfills[c]	1,819	33.9	44	45.6
Sludge incinerators and co-incinerators[d]	865	16.1	e	e
Ocean disposal[f]	336	6.3	0	0
TOTAL	5,358	100	101	104.2

[a]Potential TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (column 2) by the mean dioxin-like PCB TEQ concentration in 74 POTW sludges reported by Green et al. (1995) and Cramer et al. (1995) (i.e., 24.2 ng TEQ_P-WHO_{98}/kg and 25.1 ng TEQ_P-WHO_{94}/kg).
[b]Includes 21.9% applied to agricultural land, 2.8% applied as compost, 0.6% applied to forestry land, 3.1% applied to "public contact" land, 1.2% applied to reclamation sites, and 2.4% applied in undefined settings.
[c]Landfills used for disposal of sewage sludge and solid waste residuals.
[d]Co-incinerators treat sewage sludge in combination with other combustible waste materials.
[e]See Section 10.4.6 for a discussion of dioxin-like PCB releases to air from sewage sludge incinerators.
[f]The Ocean Dumping Ban Act of 1988 generally prohibited the dumping of sewage sludge into the ocean after December 31, 1991. Ocean dumping of sewage sludge ended in June 1992 (Federal Register, 1993a). The current method of disposal of the 336,000 metric tons of sewage sludge that were disposed of in the oceans in 1988 has not been determined.

Sources: Federal Register (1990, 1993a); Green et al. (1995); Cramer et al. (1995).

Table 10-11. Quantity of sewage sludge disposed of annually in 1995 by primary, secondary, or advanced treatment publicly owned treatment works (POTWs) and potential dioxin-like PCB TEQ releases

Use/disposal practice	Volume disposed of (1,000 dry metric tons/yr)	Percent of total volume	Potential dioxin release[a] (g TEQ/yr)	
			TEQ_P-WHO_{98}	TEQ_P-WHO_{94}
Land application[b]	2,500	39.7	60.5	62.8
Advanced treatment[c]	700	11.1	16.9	17.6
Other beneficial use[d]	500	7.9	12.1	12.6
Surface disposal/Landfill	1,100	17.5	26.6	27.6
Incineration	1,400	22.2	e	e
Other disposal method	100	1.6	2.4	2.5
TOTAL	6,300	100	118.5	123.1

[a]Potential TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (column 2) by the mean dioxin-like PCB TEQ concentration in 74 POTW sludges reported by Green et al. (1995) and Cramer et al. (1995) (i.e., 24.2 ng TEQ_P- WHO_{98}/kg and 25.1 ng TEQ_P-WHO_{94}/kg).
[b]Without further processing or stabilization, such as composting.
[c]Such as composting.
[d]EPA assumed that this category includes distribution and marketing (i.e., sale or give-away of sludge for use in home gardens). Based on the 1988 National Sewage Sludge Survey and 1988 Needs Survey, approximately 1.3% of the total volume of sewage disposed was distributed and marketed (Federal Register, 1993a). Therefore, it is estimated that 2 g (TEQ_P-WHO_{98} and TEQ_P-WHO_{94}) were released through distribution and marketing in 1995.
[e]See Section 3.5 for estimates of CDD/CDF releases to air from sewage sludge incinerators.

Sources: U.S. EPA (1999b); Green et al. (1995); Cramer et al. (1995).

These tables also list the estimated amount of dioxin-like PCB TEQs that may be present in sewage sludge and potentially released to the environment. For reference years 1987 and 1995, these values were estimated using the POTW mean TEQ_P-WHO_{98} concentration calculated from the results reported by Green et al. (1995) and Cramer et al. (1995). For reference year 2000, they were estimated using the POTW mean TEQ_P-WHO_{98} concentration reported by EPA (U.S. EPA, 2002d) as part of the 2001 National Sewage Sludge Survey. Multiplying these TEQ concentrations by the sludge volumes generated yields annual potential total releases of 101 g TEQ_P-WHO_{98} (104.2 g TEQ_P-WHO_{94}) in 1987, 118.5 g TEQ_P-WHO_{98} (123.1 g TEQ_P-WHO_{94}) in 1995, and 26.6 g TEQ_P-WHO_{98} in 2000 for nonincinerated sludges.

Table 10-12. Quantity of sewage sludge disposed of annually in 2000 by primary, secondary, or advanced treatment publicly owned treatment works (POTWs) and potential dioxin-like PCB TEQ releases

Use/disposal practice	Volume disposed of (1,000 dry metric tons/yr)	Percent of total volume	Potential TEQ_{DF}-WHO_{98} release[a] (g TEQ/yr)
Land application[b]	2,800	42.4	14.6
Advanced treatment[c]	800	12.1	4.2
Other beneficial use[d]	500	7.6	2.6
Surface disposal/landfill	900	13.6	4.7
Incineration	1,500	22.7	e
Other disposal method	100	1.5	0.5
TOTAL	6,600	100	26.6

[a]Potential dioxin TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (column 2) by the average of the mean TEQ_{DF}-WHO_{98} concentrations in sludge reported by U.S. EPA (2002c) (i.e., 5.22 ng TEQ_{DF}-WHO_{98}/kg).
[b]Without further processing or stabilization, such as composting.
[c]Such as composting.
[d]EPA assumed that this category includes distribution and marketing (i.e., sale or give-away of sludge for use in home gardens). Based on the 1988 National Sewage Sludge Survey and 1988 Needs Survey, approximately 1.3% of the total volume of sewage disposed of was distributed and marketed (Federal Register, 1993a). Therefore, it is estimated that 0.5 g TEQ_{DF}-WHO_{98} were released through distribution and marketing in 2000.
[e]See Section 3.5 for estimates of CDD/CDF releases to air from sewage sludge incinerators.

Sources: U.S. EPA (1999b, 2002d).

Of the 101 g TEQ_P-WHO_{98} released in 1987, 1.7 g entered commerce as a product for distribution and marketing and the remainder was applied to land (41.5 g to land application and 9.6 g to surface disposal sites) or landfilled (48.2 g). Of the 118.5 g TEQ_P-WHO_{98} released in 1995, 60.5 g were applied to land without further processing or stabilization, 16.9 g underwent advanced treatment such as composting, 26.6 g were disposed of on the surface or landfilled, and the remainder was either used or disposed of in other ways. Of the 26.6 g TEQ_P-WHO_{98} released in 2000, 14.6 g were applied to land without further processing or stabilization, 4.2 g underwent advanced treatment such as composting, 4.7 g were disposed of on the surface or landfilled, and the remainder was either used or disposed of in other ways. The PCBs in landfilled sludge were not considered releases to the environment under the definition established in this document. The other disposal practices were considered releases and were summed to get total land releases, as shown in Table 10-2 (above).

The 1987 and 1995 release estimates are assigned a confidence rating of B, indicating high confidence in the production estimate and medium confidence in the emission factor estimates. The medium rating was based on the judgment that, although the 74 facilities tested by Green et al. (1995) and Cramer et al. (1995) may be reasonably representative of the variability in POTW technologies and sewage characteristics nationwide, the sample size was still relatively small, and not all dioxin-like PCB congeners were monitored. The 2000 release estimates are assigned a confidence rating of A, indicating high confidence in both the production estimate and the emission factor estimates. High confidence was placed in the emission factors estimated because they were weighted on the basis of wastewater flow rates of all POTWs in the United States.

10.3. CHEMICAL MANUFACTURING AND PROCESSING SOURCES

In the early 1980s, EPA investigated the extent of inadvertent generation of PCBs during the manufacture of synthetic organic chemicals (Hammerstrom et al., 1985). For example, phthalocyanine dyes and diarylide pigments were reported to contain PCBs in the milligram-per-kilogram range. EPA subsequently issued regulations under TSCA (40 CFR 761.3) that ban the distribution in commerce of any products containing an annual average PCB concentration of 25 mg/kg (50 mg/kg maximum concentration at any time). In addition, EPA requires manufacturers with processes that inadvertently generate PCBs and importers of products that contain inadvertently generated PCBs to report to EPA any process or import for which the PCB concentration is greater than 2 mg/kg for any resolvable PCB gas chromatographic peak.

10.4. COMBUSTION SOURCES

10.4.1. Municipal Waste Combustors

Municipal waste combustors (MWCs) have long been identified as potential PCB air emission sources. Stack gas concentrations of PCBs for three MWCs were reported (U.S. EPA, 1987d); the average test results yielded an emission factor of 18 µg/kg refuse. Stack gas emissions of PCBs from the three MWCs were quantified without determining the MWCs' PCB destruction efficiency.

EPA also analyzed the PCB content of various consumer paper products (U.S. EPA, 1987d). The results indicated that paper products such as magazine covers and paper towels contained up to 139 µg/kg paper. These levels, which were reported in 1981, were attributed to the repeated recycling of waste paper containing PCBs. For example, carbonless copy paper manufactured prior to 1971 contained PCB levels as high as 7%. This copy paper then became a component of waste paper, which was recycled. The PCBs were inevitably introduced into other paper products, resulting in continued measurable levels in municipal refuse some four years

after the PCB manufacturing ban was imposed. Refuse-derived fuel manufactured from these paper products had PCB levels of 8,500 µg/kg, indicating that this fuel could be a source of atmospheric PCBs. Therefore, it was assumed that municipal refuse does contain detectable levels of PCBs and that some of these PCBs may enter the atmosphere when the refuse is incinerated (U.S. EPA, 1987d).

Shane et al. (1990) analyzed fly ash from five MWCs for PCB congener group content. Total PCB levels ranged from 99 to 322 µg/kg in the ash, with the tri, tetra, and penta congener groups occurring in the highest concentrations. The investigators also analyzed seven bottom ash and eight bottom ash/fly ash mixtures for total PCB measured as Aroclor 1254. The DL for this Aroclor analysis was 5 µg/kg. Aroclor 1254 was detected in two of the seven bottom ash samples (26 and 8 µg/kg) and in five of the eight fly ash/bottom ash mixtures (range, 6 to 33 µg/kg).

Sakai et al. (2001) analyzed the PCB levels in fly ash and bottom ash from a newly constructed MWC in Japan. The I-TEQ values derived from the data give a total TEQ value of 31.6 ng/kg for fly ash and 0.85 ng/kg for bottom ash.

The development of more sensitive analytical methodologies has enabled researchers in recent years to detect dioxin-like PCB congeners in the stack gases and fly ash from full-scale and pilot-scale MWCs (Sakai et al., 1993a, b, 1994, 2001; Boers et al., 1993; Schoonenboom et al., 1993). Similarly, the advances in analytical techniques have enabled researchers to determine that dioxin-like PCBs can be formed during the oxidative solid combustion phase of incineration, presumably due to dimerization of chlorobenzenes. Laboratory-scale studies have also demonstrated that dioxin-like PCBs can be formed from heat treatment of fly ash in air (Schoonenboom et al., 1993; Sakai et al., 1994); however, the available data are not adequate to support development of a quantitative estimate of a dioxin-like PCB emission factor for this source category. MWCs are designated as a Category E source.

10.4.2. Industrial Wood Combustion

Emissions of PCB congener groups (but not individual congeners) were measured during stack testing at two industrial wood-burning facilities (CARB, 1990d, e). Table 10-13 presents the average of the congener group (monochlorobiphenyl [MCB] through decachlorobiphenyl [DCB]) emission factors for these two facilities. No tetra- or higher-chlorinated congeners (the congener groups containing the dioxin-like PCBs) were detected at either facility at DLs corresponding to emission factors in the low range of nanogram per kilogram of wood combusted.

Table 10-13. PCB congener group emission factors for industrial wood combustors[a]

Congener group	Number of detections	Maximum concentration detected (ng/kg wood)	Mean concentration (ng/kg)	
			Nondetect set to detection limit	Nondetect set to zero
Monochlorobiphenyls	1	32.1	39.4	16
Dichlorobiphenyls	1	23	50.9	11.5
Trichlorobiphenyls	1	19.7	42.3	9.8
Tetrachlorobiphenyls	0	--	22.7	--
Pentachlorobiphenyls	0	--	17.6	--
Hexachlorobiphenyls	0	--	17	--
Heptachlorobiphenyls	0	--	17.9	--
Octachlorobiphenyls	0	--	15.8	--
Nonachlorobiphenyls	0	--	25	--
Decachlorobiphenyls	0	--	36.3	--

[a]Two sites for each congener group.

-- = No information given

Source: CARB (1990d, e).

In CARB (1990d), PCBs were measured in the emissions from two spreader stoker wood-fired boilers operated in parallel by an electric utility for generating electricity. The exhaust gas stream from each boiler was passed through a dedicated electrostatic precipitator (ESP), after which the gas streams were combined and emitted to the atmosphere through a common stack. Stack tests were conducted both when the facility burned fuels allowed by existing permits and when the facility burned a mixture of permitted fuel supplemented by urban wood waste at a ratio of 70:30.

In CARB (1990e), PCBs were measured in the emissions from twin fluidized-bed combustors designed to burn wood chips to generate electricity. The air pollution control device (APCD) system consisted of ammonia injection for controlling nitrogen oxides and a multiclone and an ESP for controlling PM. During testing, the facility burned wood wastes and agricultural wastes allowed by existing permits. The available data are not adequate to support development of a quantitative estimate of dioxin-like PCB emissions from this source. Industrial wood combustion is designated as a Category E source.

10.4.3. Medical Waste Incineration

As discussed in Chapter 3, Section 3.3, EPA has issued nationally applicable emission standards and guidelines that address CDD/CDF emissions from medical waste incinerators (MWIs). Although PCBs are not addressed in these regulations, the database of stack test results at MWIs compiled for this rulemaking does contain limited data on PCB congener group emission factors. Data are available for two MWIs lacking add-on APCD equipment and for two MWIs with add-on APCD equipment in place. The average congener group emission factors derived from these test data are presented in Table 10-14. Because data are available for only 4 of the estimated 1,065 facilities that make up this industry, and because these data do not provide congener-specific emission factors, no national estimates of total PCB or dioxin-like PCB emissions are being made at this time. Medical waste incineration is designated as a Category E source.

Table 10-14. PCB congener group emission factors for medical waste incinerators (MWIs)[a]

Congener group	Mean emission factor (ng/kg) (2 MWIs without APCD)		Mean emission factor (ng/kg) (2 MWIs with APCD)	
	Nondetects set to detection limit	Nondetects set to zero	Nondetects set to detection limit	Nondetects set to zero
Monochlorobiphenyls	0.059	0.059	0.311	0
Dichlorobiphenyls	0.083	0.083	0.34	0
Trichlorobiphenyls	0.155	0.155	0.348	0
Tetrachlorobiphenyls	4.377	4.377	1.171	0
Pentachlorobiphenyls	2.938	2.938	17.096	9.996
Hexachlorobiphenyls	0.238	0.238	1.286	1.078
Heptachlorobiphenyls	0.155	0.155	0.902	0
Octachlorobiphenyls	0.238	0.238	0.205	0
Nonachlorobiphenyls	0.155	0.155	--	--
Decachlorobiphenyls	0.155	0.155	0.117	0

[a]See Section 3.3 for details on tested facilities.

APCD = Air pollution control device
-- = No information given

10.4.4. Tire Combustion

As discussed in Chapter 3, Section 3.6, tires are burned in a variety of facilities, including dedicated tire burners, cement kilns, industrial boilers, and pulp and paper combustion facilities. Emissions of PCB congener groups (but not individual congeners) were measured during stack testing of a tire incinerator (CARB, 1991). The facility consisted of two excess air furnaces equipped with steam boilers to recover the energy from the heat of combustion. Discarded whole tires were fed to the incineration units at rates ranging from 2,800 to 5,700 kg/hr during the three testing days. The furnaces were equipped to burn natural gas as auxiliary fuel. The steam produced from the boilers drove electrical turbine generators that produced 14.4 megawatts of electricity. The facility was equipped with a dry acid gas scrubber and a fabric filter for the control of emissions prior to exiting the stack. Table 10-15 presents the congener group (MCB through DCB) emission factors for this facility. The emission factor for the total of the tetra- through heptachlorinated congener groups was about 1.2 µg/kg tire processed. Because these data do not provide PCB congener-specific emission factors, no estimates of emissions of dioxin-like PCBs can be made. Tire combustion is designated as a Category E source.

Table 10-15. PCB congener group emission factors for a tire combustor[a]

Congener group	Number of detections	Maximum emission factor (ng/kg)	Mean emission factor (ng/kg)	
			Nondetect set to detection limit	Nondetect set to zero
Monochlorobiphenyls	0	--	0.04	--
Dichlorobiphenyls	1	34.8	11.7	11.6
Trichlorobiphenyls	1	29.5	11.8	9.8
Tetrachlorobiphenyls	0	--	10	--
Pentachlorobiphenyls	2	2,724	1,092	1,092
Hexachlorobiphenyls	1	106.5	55.9	35.5
Heptachlorobiphenyls	1	298.6	107.7	99.5
Octachlorobiphenyls	0	--	20.9	--
Nonachlorobiphenyls	0	--	17.7	--
Decachlorobiphenyls	0	--	41.9	--

[a]Three samples for each congener group.

-- = No information given

Source: CARB (1991).

10.4.5. Cigarette Smoking

Using high-resolution mass spectrometry, Matsueda et al. (1994) analyzed tobacco from 20 brands of commercially available cigarettes collected in 1992 from Japan, the United States, Taiwan, China, the United Kingdom, Germany, and Denmark for the PCB congeners 77, 126, and 169. Table 10-16 presents the results of the study. However, no studies examining tobacco smoke for the presence of these congeners have been reported. Thus, it is not known whether the PCBs present in the tobacco are destroyed or volatilized during combustion or whether PCBs are formed during combustion. At least 1,200 tobacco constituents (e.g., nicotine, n-paraffin, some terpenes) are transferred intact from the tobacco into the smoke stream by distillation in this area, and it is plausible that PCBs present in the unburned tobacco would be subject to similar distillation.

Cigarette consumption and the combustion processes operating during cigarette smoking are discussed in Chapter 5, Section 5.5.

A preliminary rough estimate of potential emissions of dioxin-like PCBs can be made using the following assumptions: (a) the average TEQ_P-WHO_{98} content of seven brands of U.S. cigarettes reported by Matsueda et al. (1994), 0.64 pg/pack (0.032 pg/cigarette), is representative of cigarettes smoked in the United States; (b) dioxin-like PCBs are neither formed nor destroyed, and the congener profile reported by Matsueda et al. (1994) is not altered during combustion of cigarettes; and (c) all dioxin-like PCBs contributing to the TEQ are released from the tobacco during smoking. On the basis of these assumptions, the calculated annual emissions would be 0.018 g TEQ_P-WHO_{98}, 0.016 g TEQ_P-WHO_{98}, and 0.014 g TEQ_P-WHO_{98} for reference years 1987, 1995, and 2000, respectively. These estimates are assigned a confidence rating of D because the emission factor is clearly not representative of cigarette smoke.

10.4.6. Sewage Sludge Incineration

EPA (U.S. EPA, 1996g) derived an emission factor of 5.4 µg PCBs/kg dry sewage sludge incinerated. This emission factor was based on measurements conducted at five multiple-hearth incinerators controlled with wet scrubbers. However, it is not known what fraction of the emissions was dioxin-like PCBs.

In 1999, stack tests were conducted at a multiple-hearth incinerator in Ohio equipped with a venturi scrubber and a three-tray impingement conditioning tower (U.S. EPA, 2000b). Of the four test runs conducted, the first test run was aborted and the results from the fourth test run were determined to be statistical outliers ($p>0.05$). The back-half CDD/CDF concentrations for test run 4 were 50 to 60% lower than back-half emission concentrations for test runs 2 and 3. Because of the problems associated with test run 4, the results were not used to calculate an emission factor for dioxin-like PCBs. The average TEQ emission factor (excluding test run 4)

Table 10-16. Dioxin-like PCB concentrations in cigarette tobacco in brands from various countries (pg/pack)[a]

Congener	IUPAC number	U.S. (avg. of 7 brands)	Japan (avg. of 6 brands)	United Kingdom (avg. of 3 brands)	Taiwan (1 brand)	China (1 brand)	Denmark (1 brand)	Germany (1 brand)
3,3',4,4'-TCB	77	105.7	70.2	53	133.9	12.6	21.7	39.3
3,4,4',5-TCB	81							
2,3,3',4,4'-PeCB	105							
2,3,4,4',5-PeCB	114							
2,3',4,4',5-PeCB	118							
2',3,4,4',5-PeCB	123							
3,3',4,4',5-PeCB	126	6.2	7.8	6.1	14.5	2.4	2.2	7.3
2,3,3',4,4',5-HxCB	156							
2,3,3',4,4',5'-HxCB	157							
2,3',4,4',5,5'-HxCB	167							
3,3',4,4',5,5'-HxCB	169	0.9	0.9	0.9	2.4	0.4	0.5	1.6
2,2',3,3',4,4',5-HpCB	170							
2,2',3,4,4',5,5'-HpCB	180							
2,3,3',4,4',5,5'-HpCB	189							
Total TEQ_P-WHO_{98}		0.64	0.8	0.62	1.49	0.24	0.23	0.75

[a]Blank cells indicate that no measurements of these congeners were made.

Source: Matsueda et al. (1994).

was 0.51 ng TEQ_P-WHO_{98}/kg (see Table 10-17). This emission factor was assigned a low confidence rating because it is based on limited surveys that are judged to be possibly nonrepresentative.

Table 10-17. Dioxin-like PCB concentrations in stack gas collected from a U.S. sewage sludge incinerator

Congener	IUPAC number	Mean emission factor (ng/kg)	
		Nondetect set to ½ detection limit	Nondetect set to zero
3,3',4,4'-TCB	77	92.37	92.37
2,3,3',4,4'-PeCB	105	18	18
2,3,4,4',5-PeCB	114	2.56	2.56
2',3,4,4',5-PeCB	123	0.82	0.82
2,3',4,4',5-PeCB	118	38.65	38.65
3,3',4,4',5-PeCB	126	4.51	4.51
2,3,3',4,4',5-HxCB	156	4.25	4.25
2,3,3',4,4',5'-HxCB	157	1.41	1.41
2,3',4,4',5,5'-HxCB	167	2.55	2.55
3,3',4,4',5,5'-HxCB	169	3.61	3.61
2,2',3,3',4,4',5-HpCB	170	7.19	7.19
2,2',3,4,4',5,5'-HpCB	180	17.79	17.79
2,3,3',4,4',5,5'-HpCB	189	0.6	0.6
Total TEQ_P-WHO_{98}		0.51	0.51

Source: U.S. EPA (2000b).

Approximately 0.865 million dry metric tons of sewage sludge were incinerated in 1988 (Federal Register, 1993a), approximately 2.11 million dry metric tons in 1995 (e-mail dated July 13, 1998, from K. Maw, Pacific Environmental Services, to G. Schweer, Versar, Inc.), and an estimated 1.42 million dry metric tons in 2000 (U.S. EPA, 1999b). Using the above estimated amounts of sewage sludge incinerated per year and the average TEQ emission factor of 0.51 ng TEQ_P-WHO_{98}/kg, the estimated annual releases of total PCBs to air were 0.44 g TEQ_P-WHO_{98} in 1987, 1.1 g TEQ_P-WHO_{98} in 1995, and 0.72 g TEQ_P-WHO_{98} in 2000. These emissions were assigned a low confidence rating (Category C) because the emission factor was given a low rating.

10.4.7. Backyard Barrel Burning

The low combustion temperatures and oxygen-starved conditions associated with backyard barrel burning may result in incomplete combustion and increased pollutant emissions (Lemieux, 1997). EPA's Control Technology Center, in cooperation with New York State's departments of health and environmental conservation, conducted a study to examine, characterize, and quantify emissions from the simulated open burning of household waste materials in barrels (Lemieux, 1997). A representative waste to be burned was prepared on the basis of the typical percentages of various waste materials disposed of by New York State residents (i.e., nonavid recyclers); hazardous wastes such as chemicals, paints, and oils were not included in the test waste. A variety of compounds, including dioxin-like PCBs, were measured in the emissions from the simulated open burning. The measured TEQ emission factors for waste that had not been separated for recycling purposes were 1.02×10^{-2} µg TEQ_P-WHO_{94}/kg and 5.26×10^{-3} µg TEQ_P-WHO_{98}/kg waste burned (see Table 10-18). These limited emissions data were judged to be inadequate for estimating national emissions (a Category E source). The activity level for backyard barrel burning is discussed in Section 6.5.2.

10.4.8. Petroleum Refining Catalyst Regeneration

As discussed in Section 5.4, regeneration of spent catalyst used in catalytic reforming to produce high-octane reformates is a potential source of CDD/CDF air emissions. In 1998, emissions from the caustic scrubber used to treat gases from the external catalyst regeneration unit of a refinery in California were tested for CDDs/CDFs as well as PCB congener groups (CARB, 1999) (see Chapter 5, Section 5.4 for details).

All PCB congener groups were detected in each of the three samples collected. The average congener group emission factors in units of nanograms per barrel of reformer feed are presented in Table 10-19. The total PCB emission factor was 118 ng/barrel. This emission factor assumes that emissions are proportional to reforming capacity; emission factors may be more related to the amount of coke burned, APCD equipment present, and/or other process parameters.

Because emissions data are available for only one U.S. petroleum refinery (which represents less than 1% of the catalytic reforming capacity at U.S. refineries), and because these data do not provide congener-specific emission factors, no national estimates of total PCB or dioxin-like PCB emissions are being made at this time. This is a Category E source.

Table 10-18. Dioxin-like PCB emission factors from backyard barrel burning[a]

Congener	IUPAC number	Emission factors (µg/kg)		
		Test 1	Test 2	Average
3,3',4,4'-TCB	77	9.3	15.2	12.3
3,4,4',5-TCB	81			
2,3,3',4,4'-PeCB	105	5.9	4.9	5.4
2,3,4,4',5-PeCB	114			
2,3',4,4',5-PeCB	118	8.3	14.3	11.3
2',3,4,4',5-PeCB	123	18.6	28.7	23.7
3,3',4,4',5-PeCB	126			
2,3,3',4,4',5-HxCB	156			
2,3,3',4,4',5'-HxCB	157			
2,3',4,4',5,5'-HxCB	167			
3,3',4,4',5,5'-HxCB	169			
2,2',3,3',4,4',5-HpCB	170			
2,2',3,4,4',5,5'-HpCB	180			
2,3,3',4,4',5,5'-HpCB	189			
Total TEQ_P-WHO_{98}		4.21e-03	6.31e-03	5.26e-03

[a]Blank cells indicate that the congener was not detected in either of the two duplicate samples.

Source: Lemieux (1997).

Table 10-19. PCB congener group emission factors for a petroleum catalytic reforming unit[a]

Congener group	Mean concentration (ng/dscm) (at 12% O_2)	Mean emission rate (lb/hr)	Mean emission factor (lb/1000 bbl)	Mean emission factor (ng/barrel)
Monochlorobiphenyls	166	5.51e-08	7.11e-09	3.23e+00
Dichlorobiphenyls	355	1.17e-07	1.52e-08	6.89e+00
Trichlorobiphenyls	743	2.45e-07	3.17e-08	1.44e+01
Tetrachlorobiphenyls	849	2.81e-07	3.62e-08	1.64e+01
Pentachlorobiphenyls	914	3.02e-07	3.88e-08	1.76e+01
Hexachlorobiphenyls	780	2.57e-07	3.30e-08	1.50e+01
Heptachlorobiphenyls	1,430	4.73e-07	6.01e-08	2.73e+01
Octachlorobiphenyls	698	2.32e-07	2.95e-08	1.34e+01
Nonachlorobiphenyls	179	5.99e-08	7.59e-09	3.44e+00
Decachlorobiphenyls	41.3	1.39e-08	1.76e-09	7.98e-01
Total PCBs	6,155.3	2.04e-06	2.61e-07	1.18e+02

[a]Three samples and three detections for each congener group.

Source: CARB (1999).

10.5. NATURAL SOURCES

This section discusses biotransformation and photochemical transformation of other PCBs. Although there is some evidence that these processes occur, the data were considered insufficient for developing release estimates.

10.5.1. Biotransformation of Other PCBs

Studies show that under anaerobic conditions, biologically mediated reductive dechlorination to lower-chlorinated congeners, followed by slow anaerobic and/or aerobic biodegradation, is a major pathway for destruction of PCBs in the environment. Research reported to date and summarized below indicates that biodegradation should result in a net decrease rather than a net increase in the environmental load of dioxin-like PCBs.

Laboratory studies (e.g., Bedard et al., 1986; Pardue et al., 1988; Larsson and Lemkemeier, 1989; Hickey, 1995; Schreiner et al., 1995) have revealed that more than two dozen strains of aerobic bacteria and fungi that are capable of degrading most PCB congeners with five or fewer chlorines are widely distributed in the environment. Many of these organisms are of the genus *Pseudomonas* or *Alcaligenes*. The major metabolic pathway involves addition of oxygen at the 2,3-position by a dioxygenase enzyme, with subsequent dehydrogenation to the catechol followed by ring cleavage. Several bacterial strains have been shown to possess a dioxygenase enzyme that attacks the 3,4-position.

Only a few strains have demonstrated the ability to degrade hexachlorobiphenyl (HxCB) and the higher-chlorinated biphenyls. The rate of aerobic biodegradation decreases with increasing chlorination. The half-lives for biodegradation of tetrachlorobiphenyls (TCBs) in fresh surface water and soil are 7 to 60+ days and 12 to 30 days, respectively. For pentachlorobiphenyls (PeCBs) and the higher-chlorinated PCBs, the half-lives in fresh surface water and soil are likely to exceed 1 year. PCBs with all or most chlorines on one ring and PCBs with fewer than two chlorines in the ortho position tend to degrade more rapidly. For example, Gan and Berthouex (1994) monitored over a 5-yr period the disappearance of PCB congeners applied to soil with sewage sludge. Three of the tetra- and pentachlorinated dioxin-like PCBs (IUPAC Nos. 77, 105, and 118) followed a first-order disappearance model, with half-lives ranging from 43 to 69 months. A hexa-substituted congener (IUPAC No. 167) and a hepta-substituted congener (IUPAC No. 180) showed no significant loss over the 5-yr period.

Prior to the early 1990s, little investigation focused on anaerobic microbial dechlorination or degradation of PCBs, even though most PCBs eventually accumulate in anaerobic sediments (Abramowicz, 1990; Risatti, 1992). Environmental dechlorination of PCBs via losses of meta and para chlorines has been reported in field studies for freshwater, estuarine, and marine anaerobic sediments, including those from the Acushnet Estuary, the Hudson River, the

Sheboygan River, New Bedford Harbor, Escambia Bay, Waukegan Harbor, the Housatonic River, and Woods Pond (Brown et al., 1987; Rhee et al., 1989; Van Dort and Bedard, 1991; Abramowicz, 1990; Bedard et al., 1995; Bedard and May, 1996). The altered PCB congener distribution patterns found in these sediments (i.e., different patterns with increasing depth or distance from known sources of PCBs) have been interpreted as evidence that bacteria may dechlorinate PCBs in anaerobic sediment.

Reported results of laboratory studies confirm anaerobic degradation of PCBs. Chen et al. (1988) found that "PCB-degrading" bacteria from the Hudson River could significantly degrade the MCB, dichlorobipheyl (DiCB), and trichlorobiphenyl (TrCB) components of a 20 ppm Aroclor 1221 solution within 105 days. These congener groups make up 95% of Aroclor 1221. No degradation of higher-chlorinated congeners (present at 30 ppb or less) was observed, and a separate 40-day experiment with TCB also showed no degradation.

Rhee et al. (1989) reported degradation of mono- to penta-substituted PCBs in contaminated Hudson River sediments held under anaerobic conditions in the laboratory (N_2 atmosphere) for 6 months at 25°C. Amendment of the test samples with biphenyl resulted in greater loss of PCBs. No significant decreases in the concentrations of the higher-chlorinated congeners (more than five chlorines) were observed. No evidence of degradation was observed in samples incubated in CO_2/H_2 atmospheres. Abramowicz (1990) hypothesized that this result could be an indication that, in the absence of CO_2, a selection is imposed favoring organisms capable of degrading PCBs to obtain CO_2 and/or low-molecular-weight metabolites as electron receptors.

Risatti (1992) examined the degradation of PCBs at varying concentrations (10,000 ppm, 1,500 ppm, and 500 ppm) in the laboratory with "PCB-degrading" bacteria from Waukegan Harbor. After nine months of incubation at 22°C, the 500 ppm and 1,500 ppm samples showed no change in PCB congener distributions or concentrations, thus indicating a lack of degradation. Significant degradation was observed in the 10,000 ppm sediment, with at least 20 congeners ranging from the TrCBs through the PeCBs showing decreases.

Quensen et al. (1988) also demonstrated that microorganisms from PCB-contaminated sediments (Hudson River) dechlorinated most TrCBs through HxCBs in Aroclor 1242 under anaerobic laboratory conditions. The Aroclor 1242 used to spike the sediment contained predominantly TrCBs and TCBs (85 mol percent). Three concentrations of the Aroclor, corresponding to 14, 140, and 700 ppm on a sediment dry-weight basis, were used. Dechlorination was most extensive at the 700 ppm test concentration: 53% of the total chlorine was removed in 16 weeks, and the proportion of TCBs through HxCBs decreased from 42 to 4%. Much less degradation was observed in the 140 ppm sediment, and no observable degradation was found in the 14ppm sediment. These results and those of Risatti (1992) suggest that the

organism(s) responsible for this dechlorination may require relatively high levels of PCBs as a terminal electron acceptor to maintain a growing population.

Quensen et al. (1990) reported that dechlorination of 500 ppm spike concentrations of Aroclor 1242, 1248, 1254, and 1260 by microorganisms from PCB-contaminated sediments in the Hudson River and Silver Lake occurred primarily at the meta and para positions; ortho-substituted MCBs and DiCBs increased in concentration. Significant decreases over the incubation period (up to 50 weeks) were reported for dioxin-like PCBs 156, 167, 170, 180, and 189. Of the four dioxin-like TCBs and PeCBs detected in the Aroclor spikes (IUPAC Nos. 77, 105, 114, and 118), all decreased significantly in concentration, with the possible exception of PeCB 114 in the Aroclor 1260-spiked sediment.

Nies and Vogel (1990) reported similar results with Hudson River sediments incubated anaerobically and enriched with acetone, methanol, or glucose. Approximately 300 ppm of Aroclor 1242 (31 mol percent TCBs, 7 mol percent PeCBs, and 1 mol percent HxCBs) were added to the sediments prior to incubation for 22 weeks under an N_2 atmosphere. Significant dechlorination was observed, primarily at the meta and para positions on the higher-chlorinated congeners (TCBs, PeCBs, and HxCBs), resulting in the accumulation of lower-chlorinated, primarily ortho-substituted mono- through tri-substituted congeners. No significant dechlorination was observed in the control samples (samples containing no added organic chemical substrate and samples that were autoclaved).

Bedard and May (1996) also reported similar findings in the sediments of Woods Pond, which was believed to be contaminated with Aroclor 1260. Significant decreases in the sediment concentrations of PCBs 118, 156, 170, and 180 (relative to their concentrations in Aroclor 1260) were observed. No increases or decreases were reported for the other dioxin-like PCBs.

Bedard et al. (1995) demonstrated that it is possible to stimulate substantial microbial dechlorination of the highly chlorinated PCB mixture Aroclor 1260 in situ with a single addition of 2,6-dibromobiphenyl. The investigators added 365 g of 2,6-dibromobiphenyl to 6-ft-diameter submerged caissons containing 400 kg sediment (dry weight) and monitored the change in PCB congener concentrations for a period of one year. At the end of the observation period, the MCBs through HxCBs decreased by 74% in the top of the sediment and by 69% in the bottom. The average number of chlorines per molecule dropped 21%, from 5.83 to 4.61, with the largest reduction observed in meta chlorines (54% reduction) followed by para chlorines (6%). The dechlorination stimulated by 2,6-dibromobiphenyl selectively removed meta-chlorines positioned next to other chlorines.

The findings of these latter studies are significant, because removal of meta and para chlorines from the dioxin-like PCBs should reduce their toxicity and bioaccumulative potential

and also lead to the formation of lower-chlorinated congeners that are more amenable to aerobic biodegradation.

Van Dort and Bedard (1991) reported the first experimental demonstration of biologically mediated ortho-dechlorination of a PCB and stoichiometric conversion of that PCB congener (2,3,5,6-TCB) to lower-chlorinated forms. In that study, 2,3,5,6-TCB was incubated under anaerobic conditions with unacclimated methanogenic pond sediment for 37 weeks, with reported dechlorination to 2,5-DiCB (21%); 2,6-DiCB (63%); and 2,3,6-TrCB (16%).

10.5.2. Photochemical Transformation of Other PCBs

Photolysis and photo-oxidation may be major pathways for destruction of PCBs in the environment. Research reported to date and summarized below indicates that ortho-substituted chlorines are more susceptible to photolysis than are meta- and para-substituted congeners; thus, photolytic formation of more toxic dioxin-like PCBs may occur. Oxidation by hydroxyl radicals, however, apparently occurs preferentially at the meta and para positions, resulting in a net decrease rather than a net increase in the environmental load of dioxin-like PCBs.

On the basis of the data available in 1983, Leifer et al. (1983) concluded that all PCBs, especially the higher-chlorinated congeners and those that contain two or more chlorines in the ortho position, photodechlorinate. In general, as the chlorine content increases, the photolysis rate increases. More recently, Lepine et al. (1992) exposed dilute solutions (4 ppm) of Aroclor 1254 in cyclohexane to sunlight for 55 days in December and January. Congener-specific analysis indicated that the amounts of many higher-chlorinated congeners, particularly mono-ortho-substituted congeners, decreased, whereas those of some lower-chlorinated congeners increased. The results for the dioxin-like PCBs indicated a 43.5% decrease in the amount of PeCB 114, a 73.5% decrease in the amount of HxCB 156, and a 24.4% decrease in the amount of HxCB 157. However, TCB 77 and PeCB 126 (the most toxic of the dioxin-like PCB congeners), which were not detected in unirradiated Aroclor 1254, represented 2.5% and 0.43%, respectively, of the irradiated mixture.

With regard to photo-oxidation, Atkinson (1987) and Leifer et al. (1983), using assumed steady-state atmospheric OH concentrations and measured oxidation rate constants for biphenyl and MCB, estimated atmospheric decay rates and half-lives for gas-phase PCBs. Atmospheric transformation was estimated to proceed most rapidly for those PCB congeners containing either a small number of chlorines or those containing all or most of the chlorines on one ring. Kwok et al. (1995) extended the work of Atkinson (1987) by measuring the OH radical reaction rate constants for 2,2'-, 3,3'-, and 3,5-DiCB. These reaction rate constants, when taken together with Atkinson's measurements for biphenyl and MCB and the estimation method described in Atkinson (1991), were used to generate more reliable estimates of the gas-phase OH radical

reaction rate constants for the dioxin-like PCBs. The persistence of the PCB congeners increased with increasing degree of chlorination. Table 10-20 presents these estimated rate constants and the corresponding tropospheric lifetimes and half-lives.

Table 10-20. Estimated tropospheric half-lives of dioxin-like PCBs with respect to gas-phase reaction with the OH radical

Congener group	Dioxin-like congener	Estimated OH reaction rate constant (10^{-12} cm^3/ molecule-sec)	Estimated tropospheric lifetime (days)[a]	Estimated tropospheric half-life (days)[a]
Tetrachlorobiphenyls	3,3',4,4'-TCB	0.583	20	14
	3,4,4',5-TCB	0.71	17	12
Pentachlorophenyls	2,3,3',4,4'-PeCB	0.299	40	28
	2,3,4,4',5-PeCB	0.383	31	22
	2,3',4,4',5-PeCB	0.299	40	28
	2',3,4,4',5-PeCB	0.482	25	17
	3,3',4,4',5-PeCB	0.395	30	21
Hexachlorobiphenyls	2,3,3',4,4',5-HxCB	0.183	65	45
	2,3,3',4,4',5'-HxCB	0.214	56	39
	2,3',4,4',5,5'-HxCB	0.214	56	39
	3,3',4,4',5,5'-HxCB	0.266	45	31
Heptachlorobiphenyls	2,2',3,3',4,4',5-HpCB	0.099	121	84
	2,2',3,4,4',5,5'-HpCB	0.099	121	84
	2,3,3',4,4',5,5'-HpCB	0.125	95	66

[a]Calculated using a 24-hr, seasonal, annual, and global tropospheric average OH radical concentration of 9.7×10^5 molecule/cm^3 (Prinn et al., 1995).

Source: Telephone conversation on November 16, 1995, between Roger Atkinson, Air Pollution Research Center, University of California, and Greg Schweer, Versar, Inc. (based on Atkinson, 1991, and Kwok et al., 1995).

Sedlak and Andren (1991) demonstrated in laboratory studies that OH radicals generated with Fenton's reagent rapidly oxidized PCBs (2-MCB and the DiCBs through PeCBs present in Aroclor 1242) in aqueous solutions. The results indicated that the reaction occurs via addition of a hydroxyl group to one nonhalogenated site; reaction rates are inversely related to the degree of chlorination of the biphenyl. The results also indicated that meta and para sites are more reactive than ortho sites due to stearic hindrance effects. On the basis of their kinetic measurements and reported steady-state aqueous system OH concentrations or estimates of OH radical production rates, the authors estimated environmental half-lives for dissolved PCBs (MCB through

octachlorobiphenyl) in fresh surface water and in cloud water to be 4 to 11 days and 0.1 to 10 days, respectively.

10.6. PAST USE OF COMMERCIAL PCBs

An estimated total of 1.5 million metric tons of PCBs were produced worldwide (DeVoogt and Brinkman, 1989). Slightly more than one-third of these PCBs (568,000 metric tons) were used in the United States (Versar, Inc., 1976). Although the focus of this section is on past uses of PCBs within the United States, it is necessary to note that the use and disposal of PCBs in many countries, coupled with the persistent nature of PCBs, have resulted in their movement and presence throughout the global environment. The ultimate sink of most PCBs released to the environment is aquatic sediments. Currently, however, large quantities of PCBs are estimated to be circulating between the air and water environments or are present in landfills and dumps, some of which may offer the potential for re-release of PCBs into the air. Tanabe (1988) presented a global mass balance for PCBs that indicated that as of 1985, 20% of the total PCBs produced were present in seawater, whereas only 11% were present in sediments (see Table 10-21). Nearly two-thirds of total global PCB production was estimated by Tanabe to still be in use in electrical equipment or to be present in landfills and dumps.

As discussed in Section 10.2, an estimated 568,000 metric tons of PCBs were sold in the United States between 1930 and 1975 (Versar, Inc., 1976). Table 10-22 presents annual estimates of domestic sales by year for each Aroclor from 1957 to 1974. Estimates of PCB usage in the United States by usage category from 1930 to 1975 are presented in Table 10-23. Prior to voluntary restrictions by Monsanto Corporation in 1972 on sales for uses other than "closed electrical systems," approximately 13% of the PCBs were used in "semi-closed applications," and 26% were used in "open-end applications." Most of the usage for semi-closed and open-end applications occurred between 1960 and 1972 (Versar, Inc., 1976).

Table 10-24 presents estimates of the amounts of individual Aroclors that were directly released to the environment (water, air, or soil) between 1930 and 1974. Because detailed usage data were not available for the period 1930 to 1957, Versar, Inc. (1976) assumed that the usage pattern for this period followed the average pattern for the period of 1957 to 1959. The basic assumption used by Versar in deriving these estimates was that PCBs were released on the order of 5% of those used in closed electrical systems, 60% of those used in semi-closed applications, and 25% of those used for plasticizers and that 90% of PCBs used for miscellaneous industrial uses had escaped. The reliability of these release estimates was assumed to be ±30%.

Versar, Inc. (1976) also estimated that 132,000 metric tons of PCBs were landfilled. This total comprised 50,000 metric tons from capacitor and transformer production wastes, 36,000 metric tons from disposal of obsolete electrical equipment, and 46,000 metric tons from disposal

Table 10-21. Estimated PCB loads in the global environment as of 1985

Environment	PCB load (metric tons)	Percentage of PCB load	Percentage of world production
Terrestrial and coastal			
Air	500	0.13	
River and lake water	3,500	0.94	
Seawater	2,400	0.64	
Soil	2,400	0.64	
Sediment	130,000	35	
Biota	4,300	1.1	
Total	143,100	39	
Open ocean			
Air	790	0.21	
Seawater	230,000	61	
Sediment	110	0.03	
Biota	270	0.07	
Total	231,170	61	
Total load in environment	374,000	100	31
Degraded and incinerated	43,000		4
Land-stocked[a]	783,000		65
World production	1,200,000[b]		100

[a]Still in use in electrical equipment and other products, and deposited in landfills and dumps.
[b]This value is from Tanabe (1988). DeVoogt and Brinkman (1989) estimated worldwide production to have been 1,500,000 metric tons.

Source: Tanabe (1988).

of material from open-end applications. An estimated additional 14,000 metric tons of PCBs, although still "in service" in various semi-closed and open-end applications in 1976, were ultimately destined for disposal in landfills.

An estimated 3,702 kg of TEQ_P-WHO_{98} were released directly to the U.S. environment between 1930 and 1977 (see Table 10-25). These estimates are based on the Aroclor release estimates presented in Table 10-22 and the mean TEQ_P-WHO_{98} concentrations in Aroclors presented in Table 10-3.

Table 10-22. Estimated domestic sales of aroclors and releases of PCBs, 1957–1974 (metric tons)

Year	Estimated domestic sales									Total PCB releases
	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Aroclor 1268	
1957	0	10	89	8,265	807	2,023	3,441	14	0	14,649
1958	0	7	51	4,737	1,161	3,035	2,713	83	33	11,820
1959	0	115	109	6,168	1,535	3,064	3,002	163	46	14,202
1960	0	47	70	8,254	1,282	2,761	3,325	148	86	15,973
1961	0	43	109	8,993	1,825	2,855	2,966	164	72	17,027
1962	0	64	102	9,368	1,571	2,869	2,991	196	95	17,256
1963	0	164	6	8,396	2,274	2,681	3,459	188	129	17,297
1964	0	270	6	10,692	2,376	2,849	3,871	202	86	20,352
1965	0	167	3	14,303	2,524	3,509	2,645	253	89	23,493
1966	0	239	7	17,943	2,275	3,191	2,665	348	129	26,797
1967	0	200	11	19,529	2,134	3,037	2,911	381	130	28,333
1968	0	62	41	20,345	2,220	4,033	2,382	327	127	29,537
1969	0	230	124	20,634	2,563	4,455	2,013	323	136	30,478
1970	0	670	118	22,039	1,847	5,634	2,218	464	150	33,140
1971	1,512	1,005	78	9,970	97	2,114	782	0	0	15,558
1972	9,481	78	0	330	366	1,585	138	0	0	11,978
1973	10,673	16	0	2,812	0	3,618	0	0	0	17,119
1974	9,959	26	0	2,815	0	2,805	0	0	0	15,605
TOTAL	31,625	3,413	924	195,593	26,857	56,118	41,522	3,254	1,308	360,614
% of Total	8.8	0.9	0.3	54.2	7.4	15.6	11.5	0.9	0.4	100

Source: Versar, Inc. (1976).

Table 10-23. Estimated U.S. usage of PCBs by use category, 1930–1975

Use class	Use category	Amount used (1,000 metric tons)	Percent of total usage	Reliability of estimate (%)
Closed electrical systems	Capacitors	286	50.3	±20
	Transformers	152	26.8	±20
Semi-closed applications	Heat transfer fluids	9	1.6	±10
	Hydraulics and lubricants	36	6.3	±10
Open-end applications	Plasticizer uses	52	9.2	±15
	Carbonless copy paper	20	3.5	±5
	Misc. industrial	12	2.1	±15
	Petroleum additives	1	<1	±50
TOTAL		568	100	

Source: Versar, Inc. (1976).

Table 10-24. Estimated direct releases of Aroclors to the U.S. environment, 1930–1974[a] (metric tons)

Year	Estimated environmental releases					Total PCB releases
	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	
1930–56	0	8,486	2,447	2,269	1,614	14,816
1957	0	903	319	307	423	1,952
1958	0	649	483	416	355	1,903
1959	0	1,042	724	518	507	2,791
1960	0	1,340	556	449	540	2,885
1961	0	1,852	792	587	611	3,842
1962	0	1,811	659	554	571	3,595
1963	0	1,655	935	529	682	3,801
1964	0	2,085	980	555	755	4,375
1965	0	2,689	1,025	660	497	4,871
1966	0	3,180	876	566	472	5,094
1967	0	3,376	814	525	504	5,219
1968	0	3,533	853	733	433	5,552
1969	0	4,165	993	985	452	6,595
1970	0	4,569	697	1,168	474	6,908
1971	76	1,466	51	325	121	2,039
1972	474	22	0	104	9	609
1973	534	141	0	181	0	856
1974	498	141	0	140	0	779
TOTAL	1,582	43,105	13,204	11,571	9,020	78,482
% of Total	2.0	54.9	16.8	14.7	11.5	100

[a]Does not include an additional 132,000 metric tons estimated to have been landfilled during this period.

Source: Versar, Inc. (1976).

Table 10-25. Estimated releases of dioxin-like PCB TEQs to the U.S. environment, 1930–1977

Aroclor	Percent of U.S. sales[a] (1957–1974)	Estimated PCB releases (1930–1974)[b] (metric tons)	Estimated mean TEQ_P-WHO_{98} concentration[c] (mg/kg)	Estimated total TEQ_P-WHO_{98} released (kg)
1016	12.88	1,582	[d]	[d]
1221	0.96	--	0.328	--
1232	0.24	--	--	--
1242	51.76	43,103	7.47	322
1248	6.76	13,205	16.87	223
1254	15.73	11,572	125.94	1,457
1260	10.61	9,019	188.45	1,700
1262	0.83	--	--	--
1268	0.33	--	--	--
TOTAL				3,702

[a]Sales during the period 1957–1974 constituted 63% of all PCB sales during 1930–1977. Sales data for individual Aroclors are not available for years prior to 1957; however, sales of Aroclors 1221, 1232, 1262, and 1268 were minor even prior to 1957.

[b]From Table 10-24.

[c]From Table 10-3 (assumes nondetect values are zero).

[d]Data are available for only a few samples of Aroclor 1016 where only two dioxin-like PCB congeners were detected. The total TEQ_P-WHO_{98} released is less than 0.01 kg.

-- = Indicates that release estimates were not made because of relatively low usage amounts

Source: Versar, Inc. (1976).

11. RESERVOIR SOURCES OF CDDs/CDFs AND DIOXIN-LIKE PCBs

National CDD/CDF source inventories have been conducted in several nations, including the United Kingdom (U.K.), the Netherlands, Germany, Austria, and Sweden, to characterize emissions from various source categories and estimate annual CDD/CDF emissions to air (and sometimes other media). These inventories focused mainly on emissions from primary sources (i.e., emissions from the site or process where the CDDs/CDFs are formed).

The authors of these inventories (Rappe, 1991; Harrad and Jones, 1992; Bremmer et al., 1994; Thomas and Spiro, 1995, 1996; Eduljee and Dyke, 1996; Jones and Alcock, 1996; Duarte-Davidson et al., 1997) indicated that the annual estimates of releases to air provided in these inventories may, for several reasons, be underestimates of actual emissions. First, on an empirical basis, estimates of the amounts of CDDs/CDFs deposited annually from the atmosphere were greater than the estimates of annual CDD/CDF emissions to the atmosphere. Second, because the emission test data were limited, the inventories may have underestimated releases from known sources or may not have identified all primary sources. Third, the investigators were not able to reliably quantify emissions from potential reservoir (secondary) sources, including volatilization of CDDs/CDFs from PCP-treated wood, volatilization from soil, and resuspension of soil particles. Relatively little research of either a monitoring or a theoretical nature has been performed to identify reservoir sources and to quantify the magnitude of current or potential future releases from these sources.

This chapter presents background information on the major reservoir sources of CDDs/CDFs and PCBs, including the potential magnitude (mass) of CDDs/CDFs and PCBs in each reservoir, the chemical/physical mechanisms responsible for releases of these compounds, and estimates of potential annual releases from each reservoir, if such estimates are feasible.

11.1. POTENTIAL RESERVOIRS

Chapters 2 through 10 of this document discuss both known and suspected sources of releases of newly formed dioxin-like compounds to the environment in the United States. Once released into the open environment, CDDs, CDFs, and PCBs partition to air, soils, water, sediments, and biota according to both the nature of the release and the contaminant's chemical and physical properties.

For this analysis, reservoirs are defined as materials or places that contain previously formed CDDs/CDFs or dioxin-like PCBs and have the potential for redistributing and circulating these compounds into the environment. Potential reservoirs include soils, sediments, biota, water, and some anthropogenic materials. The atmosphere is not considered a reservoir, but serves as a medium for transporting and distributing CDDs and CDFs over large geographical

areas. Atmospheric deposition of CDDs/CDFs to the earth's surface results in an exchange of CDDs/CDFs from the atmosphere to surface waters and soils.

Dioxin-like compounds are sequestered by a reservoir only until physical processes cause these contaminants to become released into the open environment over a defined time and space. When this occurs, reservoirs become sources of dioxin-like compounds in the circulating environment. Reservoir sources are not included in the quantitative inventory of contemporary sources because they do not involve original releases but rather the re-circulation of past releases from anthropogenic sources. They can, however, contribute to human exposure and, therefore, are important to consider.

The rate of movement from one environmental medium to another is termed "flux," and it refers to the direction and magnitude of flow and exchange over a reference time period and space. Figure 11-1 presents a conceptual diagram of flux and exchange of dioxin-like compounds to multiple environmental compartments such as soils, water, air, sediments, and biota. This dynamic system consists of fluxes in and out of the atmosphere as well as other exchanges between reservoirs and the atmosphere (recall that the atmosphere is not formally considered an environmental reservoir, rather it is a transport media for dioxin-like compounds). Movement of dioxin-like compounds between media can be induced by the physical processes of volatilization, wet and dry atmospheric particle and vapor deposition, adsorption, erosion and runoff, resuspension of soils into air, and resuspension of sediments into water.

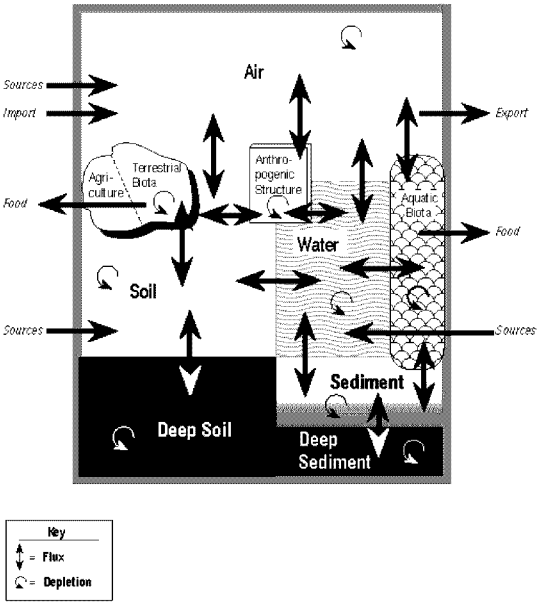


Figure 11-1. Fluxes among environmental reservoirs.

11.2. CHARACTERIZATION OF RESERVOIR SOURCES

This section is organized according to each principle reservoir, i.e., soil, water, sediment, and biota. The discussion of each environmental reservoir provides information in three parts: (1) the potential amount or mass of dioxin-like compounds contained within the reservoir, (2) the chemical/physical mechanisms responsible for releases of these compounds back into the open and circulating environment, and (3) estimates of potential annual releases from the reservoir if such estimates are feasible, given the available state of knowledge. Although anthropogenic structures (e.g., PCP-treated fenceposts, telephone poles) are potential reservoir sources, they are not discussed here because they are covered in Chapter 8 (the most detailed discussion is on PCP, Section 8.3.8).

11.2.1. Soil

11.2.1.1. *Potential Mass of Dioxin-Like Compounds Present*

In estimating burdens for the U.K., Harrad and Jones (1992) and Duarte-Davidson et al. (1997) assumed that the majority of CDDs/CDFs in soil is present in the top 5 cm (except possibly in cropland, where they may be present at greater depths due to plowing) and that the soil density is 1,000 kg/m^3. Coupling these assumptions with the rural and urban U.S. surface areas and TEQ concentrations yielded soil burden estimates of 1,350 kg TEQ_{DF}-WHO_{98} (1,530 kg I-TEQ_{DF}) in rural soils and 220 kg TEQ_{DF}-WHO_{98} (250 kg I-TEQ_{DF}) in urban soils in the United States. These calculations are not definitive, and only serve to indicate approximate amounts of CDDs/CDFs that may be contained in soils in rural and urban areas of the United States.

Higher concentrations of CDDs/CDFs for background urban and rural soils may be present in soils underlain by municipal and industrial waste and in soils at contaminated industrial sites. Higher concentrations may also be present in the soils of areas that have been treated with pesticides contaminated with CDDs/CDFs. The lack of comprehensive data on CDD/CDF concentrations in these soils, as well as the lack of data on the mass of these soils nationwide, precludes estimating total national soil burdens of CDDs/CDFs. Because of the lack of data, it is not possible to estimate current soil burdens of CDDs/CDFs associated with past pesticide use; however, estimates can be made of the total mass of CDD/CDF TEQs that have been applied to soil from past use of the pesticides 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T).

2,4-D (and its salts and esters) are widely used as post-emergence herbicides in agricultural and nonagricultural settings in the United States for control of broadleaf weeds and brush. Commercial production of 2,4-D in the United States started in 1944 (Esposito et al., 1980), and it has been in large-scale, large-volume commercial use for many years (U.S. EPA, 1975). In terms of annual volume, 2,4-D ranks among the top 10 pesticides used in the United

States (U.S. EPA, 1994d, 1997e). Table 11-1 presents a compilation of domestic production, sales, and usage volumes for 2,4-D and its salts and esters.

Table 11-1. Historical production, sales, and usage of 2,4-dichlorophenoxy-acetic acid (2,4-D) (metric tons)[a]

Year	2,4-D, acid			2,4-D, esters and salts (as reported)[b]	
	Production volume	Sales volume	Domestic usage/ disappearance	Production volume	Sales volume
2000	—	—	23,600–28,100[c]	—	—
1998/99	—	—	23,600–28,100[d]	—	—
1996/97	—	—	23,600–27,200[d]	—	—
1994/95	—	—	21,800–26,300[e]	—	—
1993	—	—	16,800–20,400[f]	—	—
1992	—	—	16,800–20,400[f]	—	—
1991	—	—	18,100–29,500[g]	—	—
1990	—	—	18,100–29,500[g]	—	—
1989	—	—	18,100–29,500[h]	—	—
1988	—	—	23,600–30,400[i]	—	—
1987	—	—	23,600–30,400[j]	—	—
1986	—	—	--	8,618	12,150
1985	—	—	--	—	0
1984	—	—	--	—	0
1983	—	—	--	7,702	8,234
1982	—	—	--	8,762	8,400
1981	5,859	3,275	--	8,987	8,002
1980	6,164	3,137	--	11,313	11,147
1979	5,763	6,187	--	11,874	13,453
1978	—	—	--	8,958	9,256
1977	—	—	--	12,552	10,196
1976	—	—	17,418[k]	10,913	7,813
1975	—	—	--	16,134	13,414
1974	—	—	--	6,558	5,991
1973	—	—	--	13,400	13,698
1972	24,948[b]	—	21,772[k]	10,192	10,899
1971	—	5,619	15,700[k]	—	18,654
1970	19,766	7,159	--	—	19,920
1969	21,354	8,521	--	25,854	20,891
1968	35,953	10,352	--	42,690	30,164
1967	34,990	15,432	--	37,988	29,300
1966	30,927	12,710	28,985[l]	32,895	25,075

Table 11-1. Historical production, sales, and usage of 2,4-dichlorophenoxy-acetic acid (2,4-D) (metric tons)[a] (continued)

Year	2,4-D, acid			2,4-D, esters and salts (as reported)[b]	
	Production volume	Sales volume	Domestic usage/ disappearance	Production volume	Sales volume
1965	28,721	11,816	22,906[l]	28,740	21,454
1964	24,364	11,343	19,958[l]	24,660	18,263
1963	21,007	9,446	15,059[l]	20,178	16,333
1962	19,503	7,716	16,284[l]	16,831	13,075
1961	19,682	7,591	14,107[l]	16,683	12,533
1960	16,413	—	14,107[l]	15,436	13,661
1959	13,282	7,240	15,468[l]	12,438	7,070
1958	14,036	6,234	9,662[l]	11,295	5,649
1957	15,536	6,871	--	12,392	7,125
1956	13,079	6,465	--	9,635	7,294
1955	15,656	5,924	--	13,390	8,121
1954	—	4,838	--	10,268	6,886
1953	11,761	—	--	10,733	8,855
1952	13,933	—	--	11,358	9,637
1951	—	—	--	—	—
1950	6,421	4,301	--	5,274	3,219
1949	6,852	2,991	--	5,829	3,211
1948	9,929	4,152	--	2,458	1,598
1947	2,553	2,320	--	1,468	1,108
1946	2,479	2,330	--	515	81
1945	416	286	--	—	—

[a]All values are from USITC (1946–1994) unless footnoted otherwise.
[b]No data were reported for domestic usage/disappearance of 2,4-D esters and salts.
[c]Source: U.S. EPA (1991c).
[d]Source: U.S. EPA (2000a).
[e]Source: U.S. EPA (1997e).
[f]Source: U.S. EPA (1994d).
[g]Source: U.S. EPA (1992g).
[h]Source: U.S. EPA (1991d).
[i]Source: U.S. EPA (1990c).
[j]Source: U.S. EPA (1988d).
[k]Source: U.S. EPA (1975).
[l]Source: USDA (1970).

— = Not reported to avoid disclosure of proprietary data
-- = No information given

As described in Section 8.3.8, CDDs/CDFs were detected in several formulations of 2,4-D and its derivatives during analyses performed to comply with EPA's 1987 Data Call-In (DCI) for CDDs/CDFs. Although the analytical results of these tests indicated that CDDs/CDFs were seldom above the regulatory limits of quantification (LOQs) established by EPA for the DCI, several registrants detected and quantified CDDs/CDFs at lower LOQs. The results of these tests are summarized in Table 8-28 (Chapter 8). The average TEQ in these tests was 1.1 μg TEQ_{DF}-WHO_{98}/kg (0.7 μg I-TEQ_{DF}/kg). Schecter et al. (1997) reported similar concentrations in 2,4-D samples manufactured in Europe and Russia; lower levels were observed in U.S. products. Some of the results from Schecter et al. are presented in Table 8-34 (Chapter 8).

If it is assumed that the EPA DCI results are typical of CDD/CDF levels in 2,4-D pesticides over the past 20 yr and that the average annual use of these pesticides in the United States has been approximately 25,000 metric tons, then the estimated CDD/CDF TEQ released to the environment from 2,4-D use during the period of 1975 to 1995 was 550 g TEQ_{DF}-WHO_{98} (350 g I-TEQ_{DF}).

2,4,5-T was used in the United States for a variety of herbicidal applications until the late 1970s to early 1980s. The major use of 2,4,5-T (about 41% of annual usage) was for control of woody and herbaceous weed pests on rights-of-way. The other major herbicidal uses were forestry (28% of usage), rangeland (20% of usage), and pasture (5% of usage). Uses of 2,4,5-T for home or recreation areas and for lakes, ponds, and ditches were suspended by EPA in 1970; rights-of-way, forestry, and pasture uses were suspended by EPA in 1979; and all uses were canceled in 1983.

Table 11-2 presents a compilation of domestic production, sales, and usage volumes for 2,4,5-T and its salts and esters. As shown in Table 11-2, production and use of 2,4,5-T generally increased each year following its introduction in the 1940s until the late 1960s. Production, sales, and usage information for the 1970s are generally not available but are reported to have steadily declined during that decade (Federal Register, 1979; Esposito et al., 1980).

Some information is available on the 2,3,7,8-TCDD content of 2,4,5-T, but little information is available on the concentrations of the other 2,3,7,8-substituted CDD/CDFs that may have been present. Plimmer (1980) reported that 2,3,7,8-TCDD concentrations as high as 70,000 μg/kg were detected in 2,4,5-T during the late 1950s. In a study of 42 samples of 2,4,5-T manufactured before 1970, Woolson et al. (1972) found 500 to 10,000 μg/kg of TCDDs in 7 samples, and another 13 samples contained 10,000 to 100,000 μg/kg of TCDDs. HxCDDs were found in 4 samples at levels between 500 and 10,000 μg/kg and in 1 sample at a concentration exceeding 10,000 μg/kg but less than 100,000 μg/kg. The detection limit in the study was 500 μg/kg.

Table 11-2. Historical production, sales, and usage of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) (metric tons)[a]

Year	2,4,5-T			2,4,5-T, esters and salts (as reported)[b]	
	Production volume	Sales volume	Domestic usage/ disappearance	Production volume	Sales volume
1993	—	—	--	—	—
1992	—	—	--	—	—
1991	—	—	--	—	—
1990	—	—	--	—	—
1989	—	—	--	—	—
1988	—	—	--	—	—
1987	—	—	--	—	—
1986	—	—	--	—	—
1985	—	—	--	—	—
1984	—	—	--	—	—
1983	—	—	--	—	—
1982	—	—	--	—	—
1981	—	—	--	—	—
1980	—	—	900[c]	—	—
1979	3,200–4,100[d]	—	--	—	—
1978	—	—	3,200[e]	—	—
1977	—	—	4,100[d]	—	—
1976	—	—	--	—	—
1975	—	—	3,200[e]	—	—
1974	—	—	900[f]	—	—
1973	—	—	--	—	—
1972	—	—	--	—	—
1971	—	—	694[g]	—	1,675
1970	—	—	3,200[e]	5,595	3,272
1969	2,268	—	--	5,273	2,576
1968	7,951	1,329	~7,000[h,i]	19,297	15,021
1967	6,601	757	~7,000[h,i]	12,333	11,657
1966	7,026	2,312	7,756[h]	8,191	4,553
1965	5,262	—	3,266[h]	6,131	5,977
1964	5,186	1,691	4,037[h]	5,880	3,128
1963	4,123	1,928	3,266[h]	4,543	2,585
1962	3,796	1,021	3,674[h]	4,765	2,543

Table 11-2. Historical production, sales, and usage of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) (metric tons)[a] (continued)

Year	2,4,5-T			2,4,5-T, esters and salts (as reported)[b]	
	Production volume	Sales volume	Domestic usage/ disappearance	Production volume	Sales volume
1961	3,134	1,196	2,449[h]	3,536	2,372
1960	2,874	—	2,676[h]	3,594	1,891
1959	2,516	1,039	2,495[h]	3,644	1,843
1958	1,668	692	1,724[h]	2,372	1,151
1957	2,419	—	--	3,098	1,337
1956	2,345	816	--	3,196	1,473
1955	1,327	662	1,300[e]	1,720	1,077
1954	1,223	639	--	1,761	615
1953	2,395	—	--	2,443	1,817
1952	1,583	—	--	1,423	569
1951	—	—	1,100[e]	—	—
1950	852	297	--	—	—
1949	—	—	--	—	—
1948	—	—	--	—	—
1947	—	—	--	—	—
1946	—	—	--	—	—
1945	—	—	--	—	—

[a]All values are from USITC (1946–1994) unless footnoted otherwise.
[b]No data were reported for domestic usage/disappearance of 2,4,5-T esters and salts.
[c]Source: Esposito et al. (1980).
[d]Source: Federal Register (1979).
[e]Source: Thomas and Spiro (1995).
[f]Source: U.S. EPA (1977).
[g]Source: USDA (1971); reflects farm usage only.
[h]Source: USDA (1970); values include military shipments abroad.
[i]Source: Kearney et al. (1973) reports slightly lower domestic consumption for the years 1967 and 1968 than for 1966.

— = Not reported to avoid disclosure of proprietary data
-- = No information given

The average 2,3,7,8-TCDD concentration in 200 samples of Agent Orange, a defoliant containing about a 50/50 mixture of the butyl esters of 2,4,5-T and 2,4-D that was used by the U.S. Air Force in Vietnam, was 1,910 µg/kg (Kearney et al., 1973). Of the 200 samples, 64 (32%) contained more than 500 µg/kg of 2,3,7,8-TCDD, with the highest concentration reported to be 47,000 µg/kg. Storherr et al. (1971) reported detecting 2,3,7,8-TCDD at concentrations

ranging from 100 to 55,000 μg/kg in five samples of 2,4,5-T. Kearney et al. (1973) reported that production samples of 2,4,5-T obtained from the three principal 2,4,5-T manufacturers in 1971 contained 2,3,7,8-TCDD at levels of <100 μg/kg, 100 μg/kg, and 2,300 μg/kg.

A 1975 survey of 10 lots of a commercial formulation containing 2,4,5-T showed 2,3,7,8-TCDD concentrations ranging from 10 to 40 μg/kg (Lewert, 1976). Analyses by EPA of 16 technical-grade 2,4,5-T samples from five different manufacturers revealed 2,3,7,8-TCDD contents ranging from <10 to 25 μg/kg (Federal Register, 1979). Schecter et al. (1997) reported the analytical results of one sample of 2,4,5-T purchased from Sigma Chemical Co. (product number T-5785, lot number 16H3625). The results, presented in Table 11-3, indicate a total TEQ_{DF}-WHO_{98} concentration of 3.26 μg/kg (2.88 μg I-TEQ_{DF}/kg).

Because of the wide variability (three orders of magnitude) in the limited available information on the 2,3,7,8-TCDD content of 2,4,5-T (particularly the 2,4,5-T used in the 1950s) and incomplete information on domestic usage, it is difficult to reliably estimate the amount of 2,3,7,8-TCDD that was released to the U.S. environment as a result of 2,4,5-T use. A very uncertain estimate can be made using the following assumptions: (1) average annual consumption during the 1950s, 1960s, and 1970s was 2,000, 4,000, and 1,500 metric tons/yr, respectively; and (2) the average 2,3,7,8-TCDD concentration in 2,4,5-T used over these three decades was 10,000 μg/kg in the 1950s, 4,000 μg/kg in the 1960s, and 100 μg/kg in the 1970s. Based on these assumptions, the very uncertain estimate of 2,3,7,8-TCDD input from 2,4,5-T use over the period of 1950 to 1979 was 36,000 g.

Another contributing source to the soil reservoir is CDD/CDF in sewage sludge applied to land (i.e., surface disposal or land farming), estimated to have been 75 g TEQ_{DF}-WHO_{98} (103 g I-TEQ_{DF}) in 1995 (see Section 8.4.1 for details). If this same amount of TEQ had been applied each year during the period of 1975 to 1995, the total amount applied would have been 1,500 g TEQ_{DF}-WHO_{98} (2,000 g I-TEQ_{DF}).

11.2.1.2. *Mechanisms Responsible for Releases from Surface Soils*

The atmospheric deposition of dioxin-like compounds is believed to be the primary means whereby surface soils, in general, become contaminated with dioxin-like compounds. CDDs/CDFs and PCBs are highly lipid soluble and have low volatility, and they tend to partition to soil rather than into air or water. Once present in or on soils, physical/chemical and biological mechanisms (photolysis and biodegradation) can slowly alter the composition and amount of compound present. Studies indicate that the dioxin-like compounds (particularly the higher-chlorinated CDDs/CDFs) exhibit little downward mobility to lower soil depths after they are deposited in or on soil (Puri et al. 1989; Freeman and Schroy, 1985; Orazio et al., 1992; Paustenbach et al., 1992). However, re-mobilization of the contaminants to the atmosphere is possible through volatilization and resuspension of soil particles.

Table 11-3. CDD/CDF concentrations (μg/kg) in recent sample of 2,4,5-trichloro-phenoxyacetic acid (2,4,5-T)

Congener/congener group	2,4,5-T sample
2,3,7,8-TCDD	1.69
1,2,3,7,8-PeCDD	0.412
1,2,3,4,7,8-HxCDD	0.465
1,2,3,6,7,8-HxCDD	2.28
1,2,3,7,8,9-HxCDD	1.35
1,2,3,4,6,7,8-HpCDD	18.1
OCDD	33.9
2,3,7,8-TCDF	0.087
1,2,3,7,8-PeCDF	0.102
2,3,4,7,8-PeCDF	0.183
1,2,3,4,7,8-HxCDF	1.72
1,2,3,6,7,8-HxCDF	0.356
1,2,3,7,8,9-HxCDF	ND (0.012)
2,3,4,6,7,8-HxCDF	0.126
1,2,3,4,6,7,8-HpCDF	2.9
1,2,3,4,7,8,9-HpCDF	0.103
OCDF	3.01
Total 2,3,7,8-CDD[a]	58.2
Total 2,3,7,8-CDF[a]	8.59
Total I-TEQ_{DF}[a]	2.88
Total TEQ_{DF}-WHO_{98}[a]	3.05
Total TCDD	--
Total PeCDD	--
Total HxCDD	--
Total HpCDD	--
Total OCDD	--
Total TCDF	--
Total PeCDF	--
Total HxCDF	--
Total HpCDF	--
Total OCDF	--
Total CDD/CDF	--

[a] Calculated assuming nondetect values were zero.

ND = Not detected (value in parenthesis is the detection limit)
-- = No information given

Source: Schecter et al. (1997).

Young (1983) conducted field studies on the persistence and movement of 2,3,7,8-TCDD from 1973 to 1979 on a military test area that had been aerially sprayed with 73,000 kg of 2,4,5-T from 1962 to 1970. TCDD levels of 10 to 1,500 ng/kg were found in the top 15 cm of soil 14 yr after the last application of herbicide at the site. Although actual data were not available on the amount of 2,3,7,8-TCDD originally applied as a contaminant of the 2,4,5-T, best estimates indicated that less than 1% of the applied 2,3,7,8-TCDD remained in the soil after 14 yr. Young suggested that photodegradation at the time of and immediately after aerial application was responsible for most of the disappearance; however, once incorporated into the soil, the data indicated a half-life of 10 to 12 yr. Similarly, Paustenbach et al. (1992) concluded that the half-life of 2,3,7,8-TCDD in soils at the surface might be 9 to 15 yr and the half-life below the surface could be 25 to 100 yr.

Ayris and Harrad (1997) studied the mechanisms affecting volatilization fluxes of several PCB congeners (PCB 28, 52, 101, 138, and 180) from soil and found positive correlations between flux and soil temperature, soil moisture content, and soil PCB concentration. For PCBs, secondary releases from soils (primarily via volatilization) are believed to currently exceed primary emissions in the U.K. (Harner et al., 1995; Jones and Alcock, 1996). Lee et al. (1998) quantified PCBs in air samples taken every 6 hr over a 7-day period in the summer at a rural site in England and found a strong correlation between air temperature and PCB congener concentrations. The concentrations followed a clear diurnal cycle, thus providing some evidence that rapid, temperature-controlled soil-to-air exchange of PCBs influences air concentrations and enables regional/global scale cycling of these compounds.

CDDs/CDFs and PCBs sorbed to soil and urban dust particles can also be moved from the terrestrial environment to the aquatic environment through contaminated storm water runoff and surface erosion of contaminated soils. Results of recent research indicate that, for at least some water bodies, soil erosion and storm water runoff can be an important way of transporting CDDs/CDFs into the surface water. This is especially true for water bodies lacking nonpoint sources of dioxin-like compounds. Smith et al. (1995) analyzed CDD/CDF concentrations in sediment cores, air, precipitation, soil, and storm water runoff in an effort to determine the contributing sources of these compounds to the lower Hudson River. The mass balance estimates developed from these data for 1990 to 1993 are as follows: stormwater runoff entering tributaries (76% of total CDD/CDF input), anthropogenic wastes (19%), atmospheric deposition (4%), and shoreline erosion (less than 1%). The authors projected the percent contribution of these same sources for 1970 as anthropogenic wastes (70%), stormwater runoff into tributaries (15%), atmospheric deposition (15%), and shoreline erosion (0.1%).

Studies conducted by Paustenbach et al. (1996), Mathur et al. (1997) and Fisher et al. (1999) discerned the relative concentrations of CDDs and CDFs in storm water. Paustenbach et al. and Mathur et al. reported that stormwater runoff from 15 sites in the San Francisco area

contained CDD/CDF TEQ at levels ranging from 0.01 to 65 pg I-TEQ_{DF}/L; most samples contained less than 15 pg I-TEQ_{DF}/L. The sites differed widely in land use; the highest levels measured were obtained from an urban but nonindustrialized area. A distinct variability was noted in the results obtained at the same sampling location during different rain events. The profiles of CDDs/CDFs in the urban stormwater samples were similar, particularly in samples collected at the onset of rain events. Stowe (1996) reported similar findings from analyses of sediments from three stormwater basins collecting runoff from a military base, a city street, and parking lots.

Fisher et al. (1999) reported that urban runoff samples from eight sites (15 samples) in the Santa Monica Bay watershed contained CDD/CDF TEQ at levels ranging from 0.7 to 53 pg I-TEQ_{DF}/L (all but one sample were in the range of 0.7 to 10 pg I-TEQ_{DF}/L). The samples were collected in 1988/1989 from continuously flowing storm drains during both dry and storm periods. The mean concentration measured during storm events, 18 pg I-TEQ_{DF}/L, was higher than concentration observed during dry periods, 1 pg I-TEQ_{DF}/L.

Atmospheric deposition of CDDs and CDFs to lakes and the watershed area of water bodies is another important means of contaminating bottom sediments. For example, Lebeuf et al. (1996) analyzed sediment cores from different locations in the lower St. Lawrence River Estuary and the Gulf of St. Lawrence. The congener group profiles found in the samples indicated that the input of CDDs/CDFs was primarily from the atmosphere. Comparison of the CDD/CDF concentrations in sediments collected from areas where sediment accumulation is due primarily to fluvial transport with sediments from areas where sediment accumulation is due primarily to direct atmospheric deposition onto the water indicates that the contribution of CDDs/CDFs from direct atmospheric deposition represents less than 35% of the sediment burden. Thus, the primary source of CDDs/CDFs is emissions to the atmosphere upwind of the estuary that are deposited within the watershed and subsequently transported downstream by fluvial waters.

11.2.1.3. *Estimated Annual Releases from Soil to Water*

Nonpoint sources of CDDs/CDFs to waterways include stormwater runoff from urban areas and soil erosion in rural areas during storms. Approaches for estimating national loadings to water for both of these sources are described below. The estimate derived for the potential annual national loading of CDDs/CDFs in urban runoff to waterways is uncertain, but it suggests that the loading may be comparable to the contribution from known industrial point sources (at least 20 g I-TEQ_{DF} in 1995). Similarly, the estimate derived for the potential annual national loading of CDDs/CDFs in rural eroded soils to waterways is uncertain, but it has a stronger analytical base than does the urban runoff estimate. This loading estimate, however, is significantly higher than the contribution from known industrial point sources.

Urban runoff. Few data on CDD/CDF concentrations in urban runoff have been reported. The most recent and largest data sets were reported in studies conducted in the San Francisco Bay and Santa Monica Bay regions (Mathur et al., 1997; Fisher et al., 1999). These studies found a wide range of CDD/CDF levels in samples of stormwater runoff from 23 sites, varying from 0.01 to 83 pg I-TEQ_{DF}/L. The wide variability and limited geographic coverage of these data preclude derivation of a national emissions estimate at this time. However, by making a number of assumptions, a preliminary estimate of the potential CDD/CDF magnitude from this source can be made.

In order to estimate the amount of rainfall in urbanized areas of the conterminous United States, a Geographic Information System (GIS) analysis was performed to determine the total area of every U.S. Census urbanized area and the 30-yr annual average rainfall for each of those areas and to calculate the product of the total areas of urbanized areas with the annual average rainfall (Lockheed Martin Corp., 1998). This approach yields an estimate of 1.9×10^{14} L/yr. If it is assumed that urban runoff in the United States averages 1 pg TEQ_{DF}-WHO_{98}/L (1 pg I-TEQ_{DF}/L) (i.e., approximately the midpoint of the range reported by Mathur et al., 1997, and Fisher et al., 1999), this source could contribute a total of 190 g TEQ_{DF}-WHO_{98} or I-TEQ_{DF}/yr to U.S. waterways. No data were available to make similar estimates for PCBs.

A similar analysis was conducted using historical precipitation data from the National Oceanic and Atmospheric Administration (NOAA, 2004) and metropolitan/urban area statistics from the 1990 and 2000 census. The 30-year annual average rainfall for each state was calculated for 1987, 1995, and 2000. An approximation of the urban area for each state was estimated by summing the acreage for each metropolitan area identified in the 1990 census. Assuming that the amount of land classified as urban did not change significantly from 1987 to 1990, the urban areas for each state in 1990 were assumed to be equal to those in 1987. Similarly, an approximation for urban area for each state was estimated by summing the urban area acreage available from the 2000 census. An approximation of the 1995 urban area for each State was estimated by taking the average of the 1990 and 2000 estimates. Multiplying the 30-year average rainfall by the urban area for each state and summing the results provides an estimated amount of urban runoff for the conterminous United States. The urban runoff was 1.24×10^{14}, 1.33×10^{14}, and 1.42×10^{14} L/year for 1987, 1995, and 2000, respectively. Applying the emission factors generated above, urban runoff contributed 124, 133, and 142 g I-TEQ_{DF} or TEQ_{DF}-WHO_{98} to U.S. waterways in 1987, 1995, and 2000, respectively. These numbers are in agreement with the estimate developed using Lockheed Martin Corp. (1998) data.

Rural soil erosion. Using acreage and erosion factors for cropland provided in the 2001 Annual National Resources Inventory (USDA, 2003), 1.36, 1.07, 0.96, and 0.91 billion metric tons of soil and rill erosion were generated in 1987, 1992, 1997, and 2001, respectively.

Likewise, using acreage data for rangeland from USDA (2003) and a soil and rill erosion factor of 4.2 tons/acre/yr (USDA, 1995), approximately 1.55 billion metric tons of soil and rill erosion were generated in 1987, 1992, 1997, and 2001. For purposes of estimating values for reference years 1995 and 2000, it was assumed that the 1995 erosion estimate was the average of soil and rill erosion estimates developed for 1992 and 1997, and that the 2001 numbers approximated those generated in 2000. The total amount of eroded soil entering waterways was greater than this value, because this value did not include soil erosion from construction areas, forests, and other non-croplands and non-rangelands.

The data summarized in U.S. EPA (2000c) suggest that typical concentrations of CDDs/CDFs in soils in rural areas is about 2.8 ng TEQ_{DF}-WHO_{98}/kg. It is not known how well this estimate represents eroded soil from cropland and rangeland. If these soils contain an average of 1 ng TEQ_{DF}/kg (i.e., a lower value than the background value for all types of rural soil), they would have contributed 2,900, 2,600, and 2,500 g TEQ_{DF}-WHO_{98} to the nation's waterways in 1987, 1995, and 2000, respectively. Given the uncertainties in both the amount of eroded soil and dioxin levels, these estimates are considered preliminary (i.e., Category D). As with urban runoff, no data were available to make similar estimates for PCBs.

11.2.1.4. *Estimated Annual Releases from Soil to Air*

No quantitative estimates of the mass of dioxin-like compounds that may be released to the atmosphere annually from U.S. soils have been published in the literature and none were developed for this report. As noted above, the vapor flux of these compounds from soil to air is dependent on the soil and air concentrations of dioxin-like compounds and the temperature, moisture content, and organic carbon content of the soil. Most of these parameters are not characterized well enough for the United States as a whole to enable a reliable estimate to be made at present. Particle flux is dependent on many factors, including wind speed, vegetative cover, activity level, particle size, soil type/conditions, moisture content, and particle density. Through use of models and various assumptions, Kao and Venkataraman (1995) estimated the fraction of ambient air CDD/CDF concentrations in the upper midwestern section of the United States that may be the result of atmospheric re-entrainment of soil particles. Similarly, through use of models and various assumptions, Jones and Alcock (1996) and Harner et al. (1995) reached tentative conclusions about the relative importance of volatilization of dioxin-like compounds from soils in the U.K.

Modeling re-entrainment of soil to the atmosphere was conducted by Kao and Venkataraman (1995). Their model incorporated information on particle sizes, deposition velocities, and concentrations of CDDs/CDFs in soils. Smaller particulates, with median diameters ranging from about 0.01 μm to 0.3 μm, are primarily formed from combustion sources when hot vapors condense and through accumulation of secondary reaction products on smaller

nuclei. Particles at the upper end of this size range will deposit to the ground in several days. Large or coarse particles, having median diameters of about 8 μm, are generated from wind-blown dust, sea spray, and mechanically generated particles. CDDs/CDFs absorbed onto re-entrained soil would be included in this larger particle size. These larger particles have a lifetime in the atmosphere from a few to many hours.

The fraction of ambient air concentration of CDDs/CDFs that results from soil re-entrainment was established on the basis of the contribution of crustal sources to the ambient aerosol. Data on typical crustal soil concentrations in air (15 to 50 $\mu g/m^3$ for rural areas and 5 to 25 $\mu g/m^3$ for urban areas) were combined with data on the average concentrations of CDDs/CDFs in soils (73 ng/kg for rural, 2,075 ng/kg for urban, and 8,314 ng/kg for industrial soils) published by Birmingham (1990) for Ontario, Canada, and several U.S. midwestern states. This analysis estimated the concentrations of CDDs/CDFs in the ambient aerosol that originate from soils to be 1×10^{-3} to 4×10^{-3} pg/m^3 in rural areas and 0.01 to 0.05 pg/m^3 in urban areas. These particulate dioxin concentrations were compared with average total particulate dioxin levels of 1.36 pg/m^3 in Eitzer and Hites (1989) to arrive at the conclusion that soil re-entrainment could account for only 1 to 4% of the particulate dioxins in the atmosphere in urban areas and 0.1 to 0.3% of those in rural regions (Kao and Venkataraman, 1995).

This information on the size distribution of ambient aerosols and relative CDD/CDF concentrations in different particle size fractions was integrated with particle size deposition velocities to estimate the relative contribution to the total mass deposition flux for small and large particle sizes. Even though re-entrained soil may constitute only a small fraction of the atmospheric levels of CDDs/CDFs, the contribution of dioxins in re-entrained surface soil to the total deposition flux could be significant because coarse particles dominate in dry deposition. Soil re-entrainment could possibly account for as much as 70 to 90% of the total dry deposition of CDDs/CDFs in urban areas and 20 to 40% in rural regions (Kao and Venkataraman, 1995).

Two approaches were used by Jones and Alcock (1996) to assess the potential significance of CDD/CDF volatilization from soils: the fugacity quotient concept and a simple equilibrium partitioning model. The fugacity quotient model compares the fugacity (the tendency of a chemical to escape from a phase) of individual CDD/CDF compounds in different environmental media to determine the tendency for these compounds to accumulate in particular environmental compartments (McLachlan, 1996). Fugacities for individual compounds, by media, were estimated by Jones and Alcock on the basis of physical/chemical properties of the compounds as well as the concentrations in the media. In this instance, fugacity quotients were calculated for air and soil by dividing each compound's fugacity for air by that of soil. Quotients near 1 indicate equilibrium conditions between media; values greater than 1 represent a tendency for flux (volatilization) from soil to air, and values less than 1 indicate a net flux to the soil from the air. The equilibrium partitioning model used by Jones and Alcock predicts the

maximum (possible "worst case") flux of CDDs/CDFs from soil to the atmosphere. Air phase-to-soil partition coefficients were calculated using the ratios of soil and air fugacity capacities. Equilibrium air concentrations were then calculated using typical U.K. soil concentrations for both urban and rural settings.

From the fugacity quotient model, Jones and Alcock (1996) concluded that the lower-chlorinated CDDs/CDFs may be close to soil-air equilibrium in the U.K., whereas for other congeners, soil is a sink rather than a source to the atmosphere. The authors reported that the equilibrium partitioning model predicted that 0.15 kg I-TEQ volatilizes annually from soil in the U.K. However, they discounted this estimate and concluded that soil volatilization is unlikely to be a significant contributor to emissions. The likelihood that these estimates were high was attributed to the fact that assumptions were made that the concentrations of CDDs/CDFs in air were zero and the model does not consider the resistance of CDDs/CDFs to volatilize from soil.

Harner et al. (1995) developed a model to predict the long-term fate of PCBs in soils, with emphasis on soil-to-air exchanges. Using data on levels of PCBs in air, soil, and vegetation in the U.K., the investigators developed a mass balance model to simulate the fate of PCBs in U.K. soils from 1935 to 1994. Specifically, monitoring data and physical/chemical property data were compiled to calculate fugacities for PCB congeners 28, 52, 138, and 153. The model was designed to provide an order-of-magnitude level of accuracy, due in part to the inherent variability in the input data. The mass balance equations in the model included a bell-shaped function for rates of emissions of PCBs, with the maximum emission rate occurring in 1967. From these emissions rates, fluxes between air and soil over several decades were estimated. Table 11-4 summarizes the calculated fluxes.

Table 11-4. PCB 138 fluxes predicted by Harner et al. (1995)

Year	Concentration in air (pg/m^3)	Fugacity in air (Pascals × 10^{-9})	Fugacity in soil (Pascals × 10^{-9})	Concentration in soil (ng/g)	Net flux/direction
1950	4	0.24	1.1	--	air → soil (444 kg/yr)
1965	280	1.5	12	--	air → soil (1,000 kg/yr)
1975	--	--	16	--	
1980	49	--	--	--	soil → air (820 kg/yr)
1994	6	--	8.3	--	soil → air (700 kg/yr)

-- = No information given

During the 1960s and 1970s, levels of total PCBs in U.K. soils reached average levels of approximately 300 μg/kg as a result of atmospheric deposition. Because of restrictions on PCB

use during the last two decades, air concentrations have fallen, and the primary source to the atmosphere is now believed to be volatilization from soils. The mass balance model estimated a net flux of 700 kg/yr of total PCBs from soils to the atmosphere in 1994. However, this estimate is presented with the caveat that the model tends to underestimate the rate of reduction of PCB concentrations in recent years, which could be attributed to other mechanisms such as biodegradation, photolysis, and other degradation processes.

11.2.2. Water

11.2.2.1. *Potential Mass of Dioxin-Like Compounds Present*

The surface area of inland waters (including the Great Lakes) in the United States is about 359,000 km^2 (U.S. DOC, 1995b). Assuming that the mean depth of inland water is 10 m (Duarte-Davidson et al., 1997), the total inland water volume is approximately 3,600 billion m^3. No compilation of CDD/CDF measurements in inland surface waters was made for this report; however, if it is assumed that the "typical" value used by Duarte-Davidson et al. for rivers in the U.K., 38 pg I-TEQ_{DF}/m^3, is representative of U.S. waters, then the burden is calculated to be 137 g I-TEQ_{DF}.

11.2.2.2. *Mechanisms Responsible for Supply to and Releases from Water*

As discussed in Section 11.2.1.2, dioxin-like compounds enter surface water from atmospheric deposition, stormwater runoff erosion, and discharges of anthropogenic wastes. Volatilization is the primary mechanism for release of dioxin-like compounds from the water column to the atmosphere. Several studies have addressed the water-air exchange of dioxin-like PCBs through volatilization in the Great Lakes (Achman et al., 1993; Hornbuckle et al., 1993; Swackhamer and Armstrong, 1986; Baker and Eisenreich, 1990). No similar body of literature has been developed to address volatilization of CDDs/CDFs from water.

Most studies that have addressed PCB water-air exchange have used the two-film model developed by Whitman (1927) and made popular by Liss and Slater (1974). When assessing gas exchange between air and water, the interface between the two phases can be considered as a two-layer (film) system consisting of well-mixed gas and liquid films adjacent to the interface; the rate of transfer is controlled by molecular diffusion through the stagnant boundary layer (Achman et al., 1993). Liss and Slater (1974) applied the model to assess the flux of various gases, specifically in the air-sea systems, and indicated the possibility of its use at any air-water interface in the environment if the necessary data are available. Hornbuckle et al. (1993) concluded that the two-film model is the best available tool for estimating regional and local flux of PCBs from natural waters. The following paragraph, from Achman et al. (1993), succinctly summarizes the model.

The basic equation used to describe the rate of transfer across the interface is

$$F = K_{ol}(C_w - C^*) \quad (11\text{-}1)$$

where F is the flux (mol/m^2-day), C_w (mol/m^3) is the dissolved PCB concentration in the bulk water, and C* is the air concentration expressed as a water concentration in equilibrium with the air (P/H, mol/m^3). The variable P is the vapor-phase air concentration measured (mol/m^3) and converted to units of pressure using the ideal gas law; H is Henry's Law constant (atm-m^3/mol). The overall mass-transfer coefficient, K_{ol}, has units of velocity (m/day). The concentration gradient determines the direction of flux and drives the mass transfer, whereas K_{ol} is a kinetic parameter that quantifies the rate of transfer. The value of K_{ol} is dependent on the physical and chemical properties of the compound as well as environmental conditions. The reciprocal of K_{ol} is the total resistance to transfer expressed on a gas (RT/Hk_a)- and liquid ($1/k_w$)-phase basis:

$$1/K_{ol} = 1/k_w + RT/Hk_a \quad (11\text{-}2)$$

where k_w is the water-side mass transfer coefficient (m/day) and k_a is the air-side mass transfer coefficient (m/day). R is the universal gas constant (8.2057×10^{-5} atm-m^3/mol K), T is the absolute temperature, and H is Henry's Law constant.

Achman et al. (1993) and Hornbuckle et al. (1993) calculated the volatilization rates of PCBs from Green Bay on Lake Michigan on the basis of air and water samples simultaneously collected over a 14-day period above and below the air-water interphase and analyzed for 85 PCB congeners. Air samples collected over nearby land were also analyzed for the 85 PCB congeners. The direction and magnitude of flux for each congener were then calculated using Henry's Law and meteorological and hydrological parameters in the "two-film" model (see eq 11-1).

The net total PCB transfer rate (i.e., the sum of all congener transfer rates) was found to be from water to air (i.e., volatilization). However, during cool water temperature periods (October), the direction of transfer reversed for many congeners. Calculated transfer rates to air ranged from 15 to 300 ng/m^2/day at low wind speeds (1 to 3 m/sec) to 50 to 1,300 ng/m^2/day at higher wind speeds (4 to 6 m/sec). On a congener basis, the lower-chlorinated congeners dominated total fluxes. The summary of flux calculations is presented in Table 11-5. The most important factors influencing the magnitude of volatilization were the water concentration of PCBs, wind speed, and water temperature. In addition, Achman et al. (1993) and Hornbuckle et al. (1993) found that atmospheric PCB concentrations were higher over contaminated water than over nearby land, atmospheric PCBs over water tended to increase with increasing dissolved

Table 11-5. Summary of flux calculations for total PCBs in Green Bay

Date	Site	Flux[a] (ng/m^2-day)
6-4	18	40
6-5	18	40
6-6	10	95
6-7	10	155
6-10	4	325
6-11	10	13
7-28	18	330
7-29	21	70
7-30	14	225
7-31	10	90
8-1	4	800
10-21	14	555
10-22	10	1,300
10-23	4	30

[a]Numbers indicate water-to-air transfer of total PCBs. They represent the sum of individual PCB congener fluxes and are described as "daily" fluxes because they correspond to air samples collected over 5–10 hr and water samples collected over ~1 hr.

Source: Achman et al. (1993).

PCB concentrations, and the congener distribution in the atmosphere correlated linearly with the congener distributions in the adjacent water.

Achman et al. (1993) also summarized the PCB volatilization rates reported by other researchers (Baker and Eisenreich, 1990; Swackhamer and Armstrong, 1986; Strachan and Eisenreich, 1988; Swackhamer et al., 1988) for Great Lakes water bodies. The results of these other studies, presented below, also show net flux of PCBs from water to air.

Water body	Total PCB volatilization rate (ng/m^2/day)	Reference
Lake Superior	141	Baker and Eisenreich (1990)
Lake Michigan	240	Strachan and Eisenreich (1988)
Lake Superior	63	Strachan and Eisenreich (1988)
Siskiwit Lake	23	Swackhamer et al. (1988)
Lake Michigan	15	Swackhamer and Armstrong (1986)

11.2.3. Sediment

11.2.3.1. *Potential Mass of Dioxin-Like Compounds Present*

EPA conducted congener-specific measurements of CDDs/CDFs in the sediments from 11 U.S. lakes located in areas relatively unimpacted by nearby industrial activity. The mean TEQ concentration in the uppermost sediment layers from these 11 lakes was 5.3 ng TEQ_{DF}-WHO_{98}/kg (5.3 ng I-TEQ_{DF}/kg) dry weight. For most of the lakes, the uppermost layer represents about 10 years worth of sedimentation. CDD/CDF concentrations in lakes impacted by industrial activity may have higher concentrations. For example, Duarte-Davidson et al. (1997) reported a TEQ concentration of 54 ng I-TEQ_{DF}/kg for urban sediments in the U.K.

As noted above, the surface area of inland waters in the United States is approximately 359,000 km^2 (U.S. DOC, 1995b). In their calculations of sediment burdens in the U.K., Duarte-Davidson et al. (1997) assumed that (1) the sediment surface area equals the water surface area, (2) the majority of CDDs/CDFs were located in the top 5 cm of sediment, and (3) sediment density was 0.13 g dry weight/cm^3. Applying these assumptions to the water surface area and background TEQ concentration for U.S. sediments yields a burden of at least 120 kg TEQ_{DF}-WHO_{98} (120 kg I-TEQ_{DF}).

11.2.3.2. *Mechanisms Responsible for Supply to and Releases from Sediment*

Because sediment is closely connected to the water column above it, evaluating the potential for sediment to act as a reservoir of dioxin-like compounds is complex and likely to be more difficult than studying dioxin-like compounds in a single medium, such as water or soil. Volatilization and sedimentation are two mechanisms whereby persistent chemicals such as CDDs/CDFs and PCBs are lost from water bodies/columns. Numerous authors (Swackhamer and Armstrong, 1986; Muir et al., 1985; Ling et al., 1993) have noted that sediments are a likely sink for persistent hydrophobic organic compounds because these compounds are likely to be strongly bound to organic particles in the sediment.

For example, Muir et al. (1985) radiolabeled 2,3,7,8-TCDD and studied its dissipation from sediments (collected from a farm pond and a lake) to the water column in laboratory studies under static aerobic conditions at 10EC. After 675 days, more than 80% of the labeled TCDD was still present in the pond sediment and 87% was still present in the lake sediment. Aeration had little effect on the dissipation rates.

The concept of fugacity is a useful way to estimate the behavior of dioxin-like compounds in sediments. Fugacity is expressed in units of pressure (pascals, or Pa) and is the partial pressure exerted by the chemical in each medium. Fugacity models estimate equilibrium concentrations in specific media at given chemical concentrations in the environment. Clark et al. (1988) suggested evaluating contaminant concentrations in multiple environmental media by comparing fugacity of adjoining media (e.g., comparing sediment fugacity with water column

fugacity to determine a chemical's tendency to move from one to the other). The authors evaluated fugacities of certain organochlorine compounds, including PCBs, in air, water, sediment, fish, and fish-eating birds and their eggs. The authors presented PCBs fugacities developed from data collected in a study of the Lake Ontario region. The fugacities of PCBs in various media can be ranked as birds>fish>water>bottom sediment, indicating that PCBs and other similar chemicals are likely to remain in bottom sediment and are less likely to re-enter the water column.

11.2.3.3. *Releases from Sediment to Water*

Given the lack of data, no quantitative estimates of annual releases can be made. Ling et al. (1993) evaluated the fate of various chemicals, including PCBs, in Hamilton Harbour, located in Ontario, Canada, using a modified version of the Quantitative Water Air Sediment Interaction (QWASI) fugacity model. Among the processes evaluated were diffusion between air and water and sediment and water; sediment deposition, resuspension, and burial; and sediment transformation. Three primary compartments were studied: air, water, and bottom sediments. The sediment was treated as a simple, well-mixed surface layer of active sediment and the buried sediment underneath. Chemicals in the active sediment were assumed to be able to exchange with the overlying water; chemicals in the buried sediment were assumed to be isolated from the sediment-water exchange. Sediment was assumed to be homogenous rather than heterogenous. The epi- and hypolimnetic compartments of the water column were defined on the basis of a thermocline, and the atmosphere was defined as a semi-infinite medium of constant, defined composition.

Ling et al. estimated rates of PCB movement on the basis of 1987 loadings using two models: one with a thermocline and one without a thermocline. The results for the water-sediment transfer using the model with a thermocline were ~32 kg/yr entering the hypolimnion from the epilimnion, ~27 kg/yr entering the surface sediment from the hypolimnion, and ~18 kg/yr (>50%) going to burial. For sediment-to-water transfer, ~7 kg/yr transferred to the hypolimnion and then 12.5 kg/yr transferred to the epilimnion. Similar numbers were found in the single water column model (the model without a thermocline).

Both the model with a thermocline and the model without a thermocline predicted volatilization from the water to the atmosphere—1.6 kg/yr and 1.8 kg/yr, respectively. However, the actual contribution of PCBs from sediment to air was not determined. A comparison of estimated concentrations with observed values are presented in Table 11-6. For PCBs, 68% were buried in the sediment, 20% were exported to Lake Ontario, 5.4% degraded in the water and sediment, and 6% volatilized. The authors noted that these percentages were uncertain. At the sediment-water exchange, more than 90% of each chemical was contained in the sediment because of particle deposition and the high affinity of the chemical for sediment.

Table 11-6. Comparison of model-estimated PCB concentrations with observed values

Variable	PCBs
Observed concentration	
Sediment	0.23–1.04 μg/g
Water	<20 μg/m^3
Estimated concentration from model without thermocline	
Sediment	0.518 μg/g
Water	8.33 μg/m^3
Amount in sediment	74.9 kg
Amount in water	2.33 kg
Total mass	77.2 kg
Estimated concentration from model with thermocline	
Sediment	0.527 μg/g
Hypolimnion	8.48 μg/m^3
Epilimnion	7.93 μg/m^3
Amount in sediment	76.3 kg
Amount in hypolimnion	1.28 kg
Amount in epilimnion	1.02 kg
Total mass	78.6 kg

Source: Ling et al. (1993).

There was no indication that contaminants buried in the bottom sediments are transferred through diffusion mechanisms back to the surface sediments; however, episodic release of these chemicals from surface sediments can occur through mechanisms such as resuspension during flooding or lake inversions and uptake/ingestion by benthic biota.

11.2.4. Biota

11.2.4.1. *Potential Mass of Dioxin-Like Compounds Present*

The mass of CDDs/CDFs in biota in the United States was not estimated as part of this report. However, to place perspective on the potential magnitude of this reservoir, 82 g I-TEQ$_{DF}$ have been estimated to be present in biota in the U.K. (50 g in humans and 32 g in vegetation), which is about three orders of magnitude less than the mass estimated to be present in U.K. surface soils (Duarte-Davidson et al., 1997; Eduljee and Dyke, 1996). No data are available to estimate the biota burden in the United States.

11.2.4.2. *Mechanisms Responsible for Supply to and Releases from Biota*

Apparently, very little of the dioxin-like compounds contained in contaminated soil is ultimately taken up by the vegetation growing in the soil. Kjeller et al. (1991) analyzed

concentrations of CDDs/CDFs in archived soil and grass samples collected from the mid-1840s to 1989 at an English experimental station and found that only 0.006 to 0.02% of the soil burden of CDDs/CDFs was taken up by the grass. In addition, scientists generally agree that, once taken up by plant tissue, CDDs/CDFs are not translocated to other parts of the plant (e.g., fruits or shoots) (Bacci and Gaggi, 1985; Hülster and Marschner, 1993, 1994; Nakamura et al., 1994).

Researchers have found that the concentration of dioxin-like compounds in a plant should reach equilibrium with the vapor phase concentrations of dioxin-like compounds in the surrounding air (Bacci et al., 1990a, b; Frank and Frank, 1989; Horstmann and McLachlan, 1992; McCrady and Maggard, 1993; McLachlan et al., 1995; Paterson et al., 1991; Simonich and Hites, 1994; Tolls and McLachlan, 1994; Welsch-Pausch et al., 1995). Horstmann and McLachlan (1992) stated that the leaf-air transfer of volatile compounds is a reversible process governed by concentration gradients. If CDD/CDF concentrations are higher in the surrounding air than they are in the air spaces within plant tissue, CDDs/CDFs should diffuse into the plant. Once equilibrium is reached and CDD/CDF concentrations in the plant equal that of surrounding air, no more CDDs/CDFs should be taken into the plant. When CDD/CDF concentrations in surrounding air begin to decrease, CDDs/CDFs should diffuse (probably at a slow rate) out of the plant tissue. Apparently, CDDs/CDFs are not bioconcentrated to a significant extent in the lipid portion of the leaf cuticle (Gaggi et al., 1985). The CDDs/CDFs present in the leaf tissue are predominantly released from the plant through leaf fall onto soil. Therefore, vegetation is not likely to be a long-term reservoir of dioxin-like compounds.

Research suggests that dioxin-like compounds in animal tissue, unlike in vegetation, seldom, if ever, reach equilibrium with vapor phase concentrations in the surrounding atmosphere (or water column concentrations in the case of aquatic life). Rather, animals exposed to dioxin-like compounds are known to bioaccumulate these compounds, primarily in body fat (U.S. EPA, 1993g, h). Nonetheless, animals, unlike plants, can metabolize certain chlorinated hydrocarbons after they enter the body (Carlberg et al., 1983). Dioxin-like compounds can be released from an animal's body (at congener-specific rates) through metabolic processes or through weight loss, breast-feeding, or sweating. McLachlan (1996) reported the half-life for the clearance of 2,3,7,8-TCDD from humans to be 7 yr. As a result, animal life has a greater potential than does vegetation for being a long-term reservoir source of CDDs/CDFs. The majority of the dioxin-like compounds released by animals in the form of waste materials will be released to water or soil. Similarly, upon death, the dioxin-like compounds remaining in the body will be deposited onto soil or aquatic sediments or will be ingested by other animals.

11.2.4.3. *Approaches for Measuring and Estimating Releases from Biota*

Researchers have investigated the uptake and release of CDDs/CDFs by vegetation through measurement of actual concentrations during uptake and release by vegetation grown in closed systems (greenhouses). Bacci et al. (1992) conducted uptake and release studies of 1,2,3,4-TCDD by plant foliage in a closed system (a specially constructed greenhouse). Concentrations of TCDD vapor in the greenhouse air were maintained during the 370-hr uptake phase at a mean concentration of 0.0062 ng/L (air concentration varied slightly from 0.005 to 0.0075 ng/L). To begin the release phase, the TCDD vapor source (amended sand) as well as the greenhouse walls were removed, and release of CDDs/CDFs from the leaves was measured for 500 hr. The authors concluded that, during uptake, TCDD concentration in the leaves varied as a function of time and was dependent on the concentration of vapor-phase TCDD in the surrounding air. They estimated the release of TCDD from the vegetation to be relatively slow, with a half-life of TCDD of 3,300 hr.

McCrady and Maggard (1993) conducted a mass balance study of uptake and release of dioxin in grass foliage. The results indicated a half-life of dioxin in grass of 128 hr. These researchers also noted that, in addition to volatilization, photodegradation of dioxins on the foliage appeared to be a significant removal mechanism. They calculated the photodegradation half-life to be 44 hr.

Interpretation of uptake and release data over variable exposure times and contaminant concentrations has led to the development of models describing air-to-vegetation equilibrium and kinetics controlling the behavior of dioxin in vegetation. Some earlier fugacity modeling attempts described the leaf of a plant as behaving as a single compartment. One-compartment models were described by Bacci et al. (1990a, b), Trapp et al. (1990), Schramm et al. (1987), and Tolls and McLachlan (1994). Researchers presenting most of the recently developed models claim that the available data better support the concept of a leaf behaving as two compartments (Riederer, 1990; Paterson et al., 1991; Horstmann and McLachlan, 1992; McCrady and Maggard, 1993; Tolls and McLachlan, 1994; McLachlan et al., 1995). Input parameters considered by most models include critical chemical characteristics of the contaminant, characteristics of the plant, exposure times, and contaminant concentrations measured within the plant. Riederer (1990) suggested treating a leaf as multiple compartments having different accessibilities to the atmosphere and different diffusion resistances.

Input parameters for the two-compartment model are octanol-water coefficients, cuticle-water partition coefficients, aqueous solubility, and saturation vapor pressure of the chemical of concern. Outputs of the model are prediction of equilibrium concentration in different leaf tissues, estimates of air-to-vegetation bioconcentration equilibria, and identification of leaf compartments in which compounds are likely to accumulate. Riederer (1990) also presented an

approach for using the model to semiquantitatively assess the potential for revolatilization of dioxins from vegetation.

One advantage of the model presented by Riederer (1990) is that it considers critical plant characteristics in the release of dioxins. A plant is an active organism, responding to changes in its environment and acting accordingly to ensure its survival. Certain plant characteristics, such as the action of stomata (specialized cells usually on the lower leaf surface that open and close to control passage of vapors into and out of the leaf interior) and total leaf volume, are important factors that affect the release rates of vapor phase contaminants from vegetation.

Paterson et al. (1991) also presented a two-compartment model for release of dioxin-like compounds from vegetation. This model describes a plant as being made up of compartments in terms of volume fractions of air, water, and nonpolar (lipid-soluble, or octanol-equivalent) organic matter. Paterson et al. attempted to show that leaf-air equilibrium and kinetics can be correlated with chemical properties of the contaminant and properties of the leaf. The authors suggested that the clearance rate constant (k_2) can be correlated with the bioconcentration factor. This model does not consider critical plant characteristics, such as action of the stomata, and for this reason it may be less reliable than models that do consider plant characteristics, such as the model presented by Riederer (1990).

Horstmann and McLachlan (1992) developed a fugacity model to describe release of semivolatile organic compounds from the surface of a solid (spruce needles). Their approach was slightly different in that their goal was instrument/method development, but their data supported the behavior of a leaf as a two-compartment system.

McCrady and Maggard (1993) also collected data supporting the importance of viewing a leaf as a two-compartment system. They used a two-compartment model similar to the one described by Paterson et al. (1991) that also does not consider critical plant characteristics and thus may be less reliable than models that do (e.g., Reiderer, 1990).

Tolls and McLachlan (1994) exposed grass cultures for up to 240 hr to several semivolatile organic compounds and then measured the release of contaminants from the grass. They developed a two-compartment partitioning model based on the data they collected. The model consists of a small surface compartment (the leaf cuticle) and a large interior reservoir (air spaces within the leaf). Their model assumes that the flux of a chemical is the product of the fugacity difference (surface fugacity minus reservoir fugacity) and the conductance between the leaf compartments.

In an attempt to validate this model, McLachlan et al. (1995) compared concentrations of semivolatile organic compounds measured in grass grown under field conditions with concentrations predicted by their previous laboratory work with a fugacity meter. The

concentrations measured in the grass cultures agreed with results predicted by the mathematical model described by Tolls and McLachlan (1994).

11.3. SUMMARY AND CONCLUSIONS

As depicted in Figure 11-1 a set of complex relationships exists among reservoirs and between reservoirs and contemporary formation sources. The significance of reservoirs for human exposure is more dependent on their ability to affect the concentration of dioxin-like compounds in other media than on their size or net release rate. This section first summarizes and draws conclusions from the limited information available regarding the character and magnitude of reservoir sources. This information is then used to discuss the implications of reservoir sources to human exposure.

11.3.1. Reservoir Sources

The following are summary statements about soil reservoir sources.

- Soil is likely to be the reservoir source with the greatest potential for release of CDDs/CDFs to other environmental media, particularly to water. This is due in part to its relatively large mass of stored CDDs/CDFs, but more importantly, it is due to the existence of demonstrated transport mechanisms for intermedia exchange, e.g., soil erosion to surface waters and particle resuspension to air.

- The preliminary estimates of CDD/CDF runoff from urban areas to waterways is comparable to known industrial point source releases, and runoff from agricultural areas to surface waters is more than 100 times greater. It is unclear how much of the soil erosion and runoff represents recently deposited CDDs/CDFs from primary sources or longer-term accumulation. Much of the eroded soil comes from tilled agricultural lands, which would include a mix of CDDs/CDFs from various deposition times. The age of CDDs/CDFs in urban runoff is less clear.

- Based on the limited information currently available (i.e., primarily fugacity modeling), volatilization of CDDs/CDFs from soils is not believed to significantly alter ambient air concentrations. However, volatilization of PCBs from soil may be a significant process.

- Based on the limited information currently available, resuspension of soil may account for a small fraction (~4%) of CDD/CDF concentrations in air. This resuspended soil may, however, constitute a more significant portion of dry deposition.

The following are summary statements about water reservoir sources.

- It is unclear whether volatilization of CDDs/CDFs from water can significantly alter air concentrations. For PCBs, however, the water-air exchange appears to be significant, and for some water bodies results in a net transfer from water to air.

- Water is the major media contributing CDDs/CDFs and PCBs to sediment. Note that most of the CDDs/CDFs in sediments originally came from soils. For specific water bodies, however, the CDDs/CDFs and PCBs in sediments may have been dominated by local industrial discharges to water.

The following are summary statements about sediment reservoir sources.

- It is important to distinguish between surface and deep sediments. Surface sediments are commonly resuspended and introduced back into the water; deep sediments generally do not interact with the water column. Surface sediments can contribute significantly to the CDD/CDF and PCB concentrations in water, whereas deep sediments do not.

- There is little, if any, movement of dioxin-like compounds once they are buried in the bottom sediments. Bottom sediments may be considered as sinks.

The following are summary statements about biota reservoir sources.

- The mass of CDDs/CDFs in vegetation at any given time is likely to be small when compared with the mass in soil. Vegetation does play an important role in transferring CDDs/CDFs from the air to the soil via the decay of plant biomass.

- Release by volatilization from vegetation has been studied and modeled using the fugacity approach, and half-lives have been estimated. Based on these results, volatilization is not believed to be a significant mechanism for release of CDDs/CDFs and PCBs except possibly during forest/brush fires.

- The mass of CDDs/CDFs in animals at any given time is likely to be small when compared with the mass in soil. Similarly, releases are small and occur primarily by excretion and decomposition of dead biomass.

11.3.2. Implications for Human Exposure

Although, the ability to make quantitative estimates of releases from reservoir sources is limited at present, it is reasonable to conclude that the contribution of reservoir sources to human exposure may be significant. Diet accounts for more than 95% of human exposure. Although the size of the biota reservoir is small when compared with the soil and sediment reservoirs, it is clearly the key contributor to human exposure. The potential contribution of the other reservoirs to human exposure is discussed below.

PCB reservoir releases. Because current sources of newly formed PCBs are most likely negligible, human exposure to the dioxin-like PCBs is thought to be derived almost completely from current releases of old PCBs stored in reservoir sources. Key pathways involve releases from both soils and sediments to both aquatic and terrestrial food chains. One-third of general population TEQ_{DFP} exposure is due to PCBs. Thus, at least one-third of the overall risk to the general population from dioxin-like compounds comes from reservoir sources.

CDD/CDF releases from soil and sediments to water and exposure via the aquatic pathway. The earlier discussion has shown that soils can have significant inputs to waterways via soil erosion and runoff. Similarly, the sediment reservoir contributes significantly to CDD/CDF concentrations in water. These releases appear to be greater than those from the primary sources included in the inventory. Dioxins in waterways bioaccumulate in fish, and fish consumption causes human exposure. Fish consumption makes up about one-third of the total general population CDD/CDF TEQ exposure. This suggests that a significant portion of the CDD/CDF TEQ exposure could be due to releases from the soil and sediment reservoir.

CDD/CDF releases from soil to air and exposure via the terrestrial pathway. Potentially, soil reservoirs could have vapor and particulate releases that deposit on plants and enter the terrestrial food chain. The magnitude of this contribution, however, is unknown. EPA plans future studies in agricultural areas that will compare modeled air concentrations from primary sources with measured levels as a way to gain further insight into this issue.

REFERENCES

Abad, E; Adrados, A; Caixach, J; et al. (2002) Dioxin abatement strategies and mass balance at a municipal waste management plant. Environ Sci Technol 36:92-99.

Abramowicz, D. (1990) Aerobic and anaerobic biodegradation of PCBs: a review. Crit Rev Biotech 10(3):241-251.

Achman, DA; Hornbuckle, KC; Eisenreich, SJ. (1993) Volatilization of polychlorinated biphenyls from Green Bay, Lake Michigan. Environ Sci Technol 27(1):75-87.

Addink R; Altwicker, ER. (1999) Formation experiments of polychlorinated dibenzo-p-dioxins/dibenzofurans with Na ^{37}Cl. Organohalogen Compounds 4:69-72.

Addink, R; Olie, K. (1995) Mechanisms of formation and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans in heterogeneous systems. Environ Sci Technol 29:1425-1435.

Addink, R; Van Bavel, B; Visser, R; et al. (1990) Surface catalyzed formation of polychlorinated dibenzo-p-dioxins/dibenzofurans during municipal waste incineration. Chemosphere 20(10-12):1929-1934.

Addink, R; Drijver, DJ; Olie, K. (1991) Formation of polychlorinated dibenzo-p-dioxins/dibenzofurans in the carbon/fly ash system. Chemosphere 23(8-1):1205-1211.

Addink, R; Bakker, WCM; Olie, K. (1995) Influence of HCl and Cl_2 on the formation of polychlorinated dibenzo-p-dioxins/dibenzofurans in a carbon/fly ash mixture. Environ Sci Technol 29:2055-2058.

Adriaens, P; Grbic-Galic, D. (1992) Effect of cocontaminants and concentration on the anaerobic biotransformation of PCDD/F in methanogenic river sediments. Organohalogen Compounds 8:209-212.

Adriaens, P; Grbic-Galic, D. (1993) Reductive dechlorination of PCDD/F by anaerobic cultures and sediments. Organohalogen Compounds 12:107-110.

Adriaens, P; Fu, Q; Grbic-Galic, D. (1995) Bioavailability and transformation of highly chlorinated dibenzo-p-dioxins and dibenzofurans in anaerobic soils and sediments. Environ Sci Technol 29(9):2252-2260.

Advanced Technology Systems, Inc. (1995) Report on measurement of hazardous air pollutants from aluminum melt furnace operations at Ravenswood Aluminum Corporation. Monroeville, PA.

AGES (Applied Geotechnical and Environmental Services Corp). (1992) Source sampling report: comprehensive emissions testing; blast furnace. May/June 1992, Franklin Smelting and Refining Corp, Valley Forge, PA. Report No. 42614.01-01.

AHA (American Hospital Association). (1995) Comments by the American Hospital Association in review of EPA's external review draft Estimating Exposures to Dioxin-Like Compounds (EPA/600/688/005Ca-c). Public Comment Number EXP-48-A1, received January 17, 1995.

Ahlborg, VG; Becking, GC; Birnbaum, LS; et al. (1994) Toxic equivalency factors for dioxin-like PCBs. Chemosphere 28(6):1049-1067.

Ahling, B; Lindskog, A. (1982) Emission of chlorinated organic substances from combustion. In: Hutzinger, O; Safe, S, eds. Chlorinated dioxins and related compounds, impact on the environment. New York, NY: Pergamon Press.

Ahling, B; Bjorseth, A; Lunde, G. (1978) Formation of chlorinated hydrocarbons during combustion of polyvinyl chloride. Chemosphere 7:799-806.

AISI (American Iron and Steel Institute). (1990) Annual statistical report, 1989. Washington, DC.

Aittola, JP. (1993) Environmental emissions from landfill fires, preliminary investigation. Viatek Topiola Og, Espoo, Finland.

Aittola, J; Paasivirta, J; Vattulainen, A. (1992) Measurements of organochloro compounds at a metal reclamation plant. Organohalogen Compounds 9:9-12.

Albro, PW; Parker, CE. (1979) Comparison of the compositions of Aroclor 1242 and Aroclor 1016. J Chromatog 169:161-166.

Albro, PW; Corbett, JT; Schroeder, JL. (1981) Quantitative characterization of polychlorinated biphenyl mixtures (Aroclors 1248, 1254, and 1260) by gas chromatography using capillary columns. J Chromatog 205:103-111.

Altwicker, ER; Milligan, MS. (1993) Formation of dioxins: competing rates between chemically similar precursors and de novo reactions. Chemosphere 27(1-3):301-307.

Altwicker, ER; Konduri, R; Lin C; et al. (1993) Formation of precursors to chlorinated dioxin/furans under heterogeneous conditions. Combust Sci Tech 88:349-368.

Alvarado, MJ; Armstrong, BS; Crouch, E. (2001) The AMSA 2000/2001 survey of dioxin-like compounds in biosolids: statistical analysis. Cambridge, MA: Cambridge Environmental Inc.

Amendola, GA; Barna, DR. (1989) U.S. EPA petroleum refinery dioxin screening survey: BP Oil-Lima, Ohio refinery. U.S. Environmental Protection Agency, Region 5, Environmental Sciences Division, Westlake, OH.

American Forest and Paper Association. (1997) Paper, paperboard, and wood pulp statistics: data through 1996. Washington, DC.

American Paper Institute. (1992) Statistics of paper, paperboard, and wood pulp: data through 1991. New York, NY.

American Wood Preservers Institute. (1977) Pentachlorophenol: a wood preservative. McLean, VA.

American Wood Preservers Institute. (1995) 1994 Wood preserving industry production statistical report. McLean, VA.

ASME (American Society of Mechanical Engineer). (1995) The relationship between chlorine in waste streams and dioxin emissions from waste combustor stacks. Vol 36. New York, NY: Report number CRTD.

Atkinson, R. (1987) Estimation of OH radical reaction rate constants and atmospheric lifetimes for polychlorobiphenyls, dibenzo-p-dioxins, and dibenzofurans. Environ Sci Technol 21:305-307.

Atkinson, R. (1991) Atmospheric lifetimes of dibenzo-p-dioxins and dibenzofurans. Sci Total Environ 104:17-33.

ATSDR (Agency for Toxic Substances and Disease Registry). (1993) Toxicological profile for selected PCBs (Aroclor-1260, -1254, -1248, -1242, -1232, -1221, and -1016). Atlanta, GA. Available from the National Technical Information Service, Springfield, VA; PB93-182517.

Ayris, S; Harrad, S. (1997) Factors affecting the volatilization of PCBs from soil. Organohalogen Compounds 33:250-254.

BAAQMD (Bay Area Air Quality Management District). (1996) Air emissions of dioxins in the Bay area. San Francisco, CA.

Bacci, E; Gaggi, C. (1985) Polychlorinated biphenyls in plant foliage: translocation or volatilization from contaminated soils? Bull Environ Contam Toxicol 35:673-681.

Bacci, E; Calamari, D; Gaggi, C; et al. (1990a) Bioconcentration of organic chemical vapors in plant leaves: experiments, measurements and correlation. Environ Sci Technol 24(6):885-889.

Bacci, E; Calamari, D; Gaggi, C; et al. (1990b) Bioconcentration of organic chemical vapors in plant leaves: the azalea model. Chemosphere 21(4-5):525-535.

Bacci, E; Cerejeira, MJ; Gaggi, C; et al. (1992) Chlorinated dioxins: volatilization from soils and bioconcentration in plant leaves. Bull Environ Contam Toxicol 48:401-408.

Bacher, R; Swerev, M; Ballschmiter, K. (1992) Profile and pattern of monochloro-through octachlorodibenzodioxins and dibenzofurans in chimney deposits from wood burning. Environ Sci Technol 26(8):1649-1655.

Baker, JE; Eisenreich, SJ. (1990) Concentrations and fluxes of polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air-water interface of Lake Superior. Environ Sci Technol 24(3):342-352.

Ball, M; Päpke, O; Lis, A. (1990) Polychloridibenzodioxine und polychlordibenzofurane in cigaretterauch. Beiträge zur Tabakforschung International 14(6):393-402.

Ballschmiter, K; Buchert, H; Niemczyk, R; et al. (1986) Automobile exhausts versus municipal waste incineration as sources of the polychloro-dibenzodioxins (PCDD) and -furans (PCDF) found in the environment. Chemosphere 15(7):901-915.

Barkovskii, AL; Adriaens, P. (1995) Reductive dechlorination of tetrachloro-dibenzo-p-dioxin partitioned from Passaic River sediments in an autochthonous microbial community. Organohalogen Compounds 24:17-21.

Barkovskii, AL; Adriaens, P. (1996) Microbial dechlorination of historically present and freshly spiked chlorinated dioxins and diversity of dioxin-dechlorinating populations. App Environ Microbiol 62(12):4556-4562.

Beard, A; Krishnat, PN; Karasek, FW. (1993) Formation of polychlorinated dibenzofurans by chlorination and de novo reactions with $FeCl_3$ in petroleum refining processes. Environ Sci Technol 27(8):1505-1511.

Bedard, DL; May, RJ. (1996) Characterization of the polychlorinated biphenyls in the sediments of Woods Pond: evidence for microbial dechlorination of Aroclor 1260 in situ. Environ Sci Technol 30(1):237-245.

Bedard, DL; Unterman, R; Bopp, LH; et al. (1986) Rapid assay for screening and characterizing microorganisms for the ability to degrade polychlorinated biphenyls. Appl Environ Microbiol 51(4):761-768.

Bedard, DL; Smullen, LA; DeWeerd, KA; et al. (1995) Chemical activation of microbially-mediated PCB dechlorination: a field study. Organohalogen Compounds 24:23-28.

Behrooz, GS; Altwicker, ER. (1995) Formation of polychlorinated dioxins, furans, benzenes and phenols in the post-combustion region of a heterogeneous combustor: effect of bed material and post-combustion temperature. Environ Sci Technol 29:1156-1162.

Behrooz, GS; Altwicker, ER. (1996) Rapid formation of polychlorinated dioxins/furans during the heterogeneous combustion of 1,2-dichlorobenzene and 2,4-dichlorophenol. Chemosphere 32(1):133-144.

Bell, A. (1999) AB2588 emissions testing at California Portland Cement Company's Colton Plant; coal firing and coal with tires firing. Prepared by Delta Air Quality Services, Inc., California Portland Cement Company, Glendora, CA.

Bergström, J; Björner, B. (1992) Dioxiner ock bränder vid ovfallsuplag. Mamo, Miljökonsulterna i Studsvik AB. Stiftelsen reforsk. FoU nr 68. 94p. [Dioxins and fires at landfills. The Reforsk Foundation, Studsvik, Sweden. Report No. 68, p. 94].

Bingham, AG; Edmunds, CJ; Graham, BW; et al. (1989) Determination of PCDDs and PCDFs in car exhaust. Chemosphere 19(1-6):669-673.

Birmingham, B. (1990) Analysis of PCDD and PCDF patterns in soil samples: use in the estimation of the risk of exposure. Chemosphere 20(7-9):807-814.

Blumenstock, M; Zimmermann, R; Schraumm, L-W; et al. (1998) Presence of polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDFs), biphenyls (PCB), chlorinated benzenes (PCBz) and polycyclic aromatic hydrocarbons (PAH) under various combustion conditions in a post combustion chamber. Organohalogen Compounds 36:59-63.

Boers, JP; de Leer, EWB; Gramberg, L; et al. (1993) Levels of coplanar PCBs in flue gases of high temperature processes and their occurrence in environmental samples. Organohalogen Compounds 11:233-236.

Born, JGP; Mulder, P; Louw, R. (1993) Fly ash mediated reactions of phenol and monochlorophenols: oxychlorination, deep oxidation, and condensation. Environ Sci Technol 27:1849-1863.

Bowes, GW; Mulvihill, MJ; Simoneit, BRT; et al. (1975a) Identification of chlorinated dibenzofurans in American polychlorinated biphenyls. Nature 256:305-307.

Bowes, GW; Mulvihill, MJ; DeCamp, MR; et al. (1975b) Gas chromatographic characteristics of authentic chlorinated dibenzofurans; identification of two isomers in American and Japanese polychlorinated biphenyls. J Agric Food Chem 23(6):1222-1223.

Bramley, MJ. (1998) Dioxin and hexachlorobenzene releases from magnesium production in North America: lessons from Noranda's project in Asbestos, Quebec. Greenpeace Canada, Toronto.

Bremmer, HJ; Troost, LM; Kuipers, G; et al. (1994) Emissions of dioxins in The Netherlands. National Institute of Public Health and Environmental Protection (RIVM) and Netherlands Organization for Applied Scientific Research (TNO). Report No. 770501018.

Bröker, G; Geueke, KJ; Hiester, E; et al. (1992) Emission polychloierter dibenzo-p-dioxins und -furane aus hausbrand-feuerungen. Essen, Germany: Landesanstalt Für Immissionsschutz Nordhein-Westfalen. ISSN 0720-8499.

Brown, JF. (1994) Determination of PCB metabolic, excretion, and accumulation rates for use as indicators of biological response and relative risk. Environ Sci Technol 28(13):2295-2305.

Brown, A. (2002) 2002 North Carolina flue-cured tobacco production guide. Environ Sci Technol 29:2090-2098.

Brown, JF; Bedard, DL; Brennan, MJ; et al. (1987) Polychlorinated biphenyl dechlorination in aquatic sediments. Science 236:709-712.

Brown, JF; Carnahan, JC; Dorn, SB; et al. (1988) Levels of bioactive PCDF congeners in PCB dielectric fluids from capacitors and transformers. Chemosphere 17(9):1697-1702.

Brown, JF; Frame, GM; Olson, DR; et al. (1995) The sources of the coplanar PCBs. Organohalogen Compounds 26:427-430.

Bruce, KR; Beach, LO; Gullet, RK. (1991) The role of gas-phase Cl_2 in the formation of PCDD/PCDF during waste combustion. Waste Management 11:97-102.

Brunner, CR. (1984) Incineration systems, selection and design. New York, NY: Van Nostrand Reinhold; pp. 56-99.

Brunner, CR. (1992) Sewage sludge. In: Buonicore, AJ; Davis, WT; eds. Air pollution engineering manual. Air and Waste Management Association. New York, NY: Van Nostrand Reinhold; pp. 296-311.

Bryant, JG. (1993) Chlorinated benzenes. In: Kirk-Othmer encyclopedia of chemical technology. 4th ed. Vol. 6. pp. 87-100.

Buckland, SJ; Dye, EA; Leathem, SV; et al. (1994) The levels of PCDDs and PCDFs in soil samples collected from conservation areas following brush fires. Organohalogen Compounds 20:85-89.

Buekens, A; Stieglitz, L; Huang, H; et al. (1997) Preliminary investigation of formation mechanism of chlorinated dioxins and furans in industrial and metallurgical processes. Organohalogen Compounds 31:516-520.

Bumb, RR; Crummett, WB; Cutie, SS; et al. (1980) Trace chemistries of fire: a source of chlorinated dioxins. Science 210(4468):385-390.

Buonicore, AJ. (1992a) Control of gaseous pollutants. In: Buonicore, AJ; Davis, WT; eds. Air pollution engineering manual. New York, NY: Van Nostrand Reinhold. pp. 46-201.

Buonicore, AJ. (1992b) Medical waste incineration. In: Buonicore, AJ; Davis, WT; eds. Air pollution engineering manual. New York, NY: Van Nostrand Reinhold; pp.27-49.

Buser, HR. (1979) Formation of polychlorinated dibenzofurans (PCDFs) and dibenzo-p-dioxins (PCDDs) from the pyrolysis of chlorobenzenes. Chemosphere 8:415-424.

Buser, HR; Bosshardt, HP. (1976) Determination of polychlorinated dibenzo-p-dioxins and dibenzofurans in commercial pentachlorophenols by combined gas chromatography-mass spectrometry. Journal of the AOAC 59(3):562-569.

Cains, PW; Dyke, P. (1994) Emissions of chlorinated dibenzodioxins and dibenzofurans from waste combustion plants in the UK. Organohalogen Compounds 20:271-276.

Calcagni, J; Ciolek, M; Mulrine, P. (1998) Dioxin emissions from U.S. sinter plants. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC.

CANA (Cremation Association of North America). (2002) Confirmed 2000 statistics: 2000-2025. Available online at http://www.cremationassociation.org/docs/Web00Confirmed.pdf.

CANA (Cremation Association of North America). (2006) Historical statistics (provides data for 1876–2005, based on the number of deaths, the number of crematories, and the number of cremations for both the United States and Canada). Available online at http://www.cremationassociation.org/html/statistics.html.

Capes, CE. (1983) Size enlargement. In: Kirk-Othmer encyclopedia of chemical technology. 3rd ed. New York, NY: John Wiley and Sons; pp. 21:77-105.

CARB (California Air Resources Board). (1987) Determination of PCDD and PCDF emissions from motor vehicles [Draft]. State of California Air Resource Board, Sacramento, CA. Test Report No. C-86-029.

CARB (California Air Resources Board). (1990a) Evaluation test on two propane fired crematories at Camellia Memorial Lawn Cemetery. Engineering Evaluation Branch, Monitoring and Laboratory Division, Sacramento, CA. Test Report No. C-90-004.

CARB (California Air Resources Board). (1990b) Evaluation on a woodwaste fired incinerator at Koppers Company, Oroville, California. Engineering Evaluation Branch, Monitoring and Laboratory Division, Sacramento, CA. Test Report No. C-88-065.

CARB (California Air Resources Board). (1990c) Compliance testing for non-criteria pollutants at a landfill flare. Engineering Evaluation Branch, Monitoring and Laboratory Division, Sacramento, CA. Confidential Report No. ERC-2.

CARB (California Air Resources Board). (1990d) Evaluation test on a wood waste fired incinerator at Pacific Oroville Power Inc. Engineering Evaluation Branch, Monitoring and Laboratory Division, Sacramento, CA. Test Report No. C-88-050.

CARB (California Air Resources Board). (1990e) Evaluation test on twin fluidized bed wood waste fueled combustors located in Cental California. Engineering Evaluation Branch, Monitoring and Laboratory Division, Sacramento, CA. Test Report No. C-87-042.

CARB (California Air Resources Board). (1990f) Evaluation test on a wood waste fired incinerator at Louisiana Pacific Hardboard Plant, Oroville, CA. Engineering Evaluation Branch, Monitoring and Laboratory Division, Sacramento, CA. Test Report No. C-88-066.

CARB (California Air Resources Board). (1991) Emissions test of the Modesto Energy Project tires-to-energy facility. Engineering Evaluation Branch, Monitoring and Laboratory Division, Sacramento, CA. Project No. C-87-072.

CARB (California Air Resources Board). (1992a) Dioxin/furan estimates from a secondary aluminum facility. Engineering Evaluation Branch, Monitoring and Laboratory Division, Sacramento, CA. Confidential Report No. ERC-9.

CARB (California Air Resources Board). (1992b) Emission measurements on delacquering system. Engineering Evaluation Branch, Monitoring and Laboratory Division, Sacramento, CA. Confidential Report No. ERC-32.

CARB (California Air Resources Board). (1993) Emissions measurement of toxic compounds from a cupola baghouse at a steel foundry. Engineering Evaluation Branch, Monitoring and Laboratory Division, Sacramento, CA. Confidential Report No. ERC-61.

CARB (California Air Resources Board). (1999) Determination of emissions from the no. 3 reformer as Tosco Refining Company San Francisco Area Refinery at Avon. Engineering and Laboratory Branch, Monitoring and Laboratory Division, Sacramento, CA. Project No. C-96-0396.

CARB (California Air Resources Board). (2002) Staff report: initial statement of reasons for the proposed airborne toxic control measure to reduce emissions of toxic air contaminants from outdoor residential waste burning. State of California Air Resource Board, Sacramento, CA.

Carlberg, GE; Ofstad, EB; Drangsholt, H. (1983) Atmospheric deposition of organic micropollutants in Norway studied by means of moss and lichen analysis. Chemosphere 12(3):341-356.

Carpenter, C; Schweer, G; Stinnett, G; et al. (1986) Exposure assessment for hexachlorobenzene. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC; EPA 560/5-86-019.

Carroll, WF. (1996) Is PVC in house fires the great unknown source of dioxin? Fire and Materials 20:161-166.

CCC (Chlorine Chemistry Council). (2003a) CDD/CDF data validation project. CDD/CDF release estimates for Dupont: Midland, MI; Plaquemine, LA, Texas Operations, Freeport, TX. Prepared by Amendola Engineering, Inc., Westlake, OH, and PD Consulting, Herefordshire, U.K.

CCC (Chlorine Chemistry Council). (2003b) CDD/CDF data validation project. CDD/CDF release estimates for PPG Industries, Inc.: Lake Charles, LA; Natrium, WV. Prepared by Amendola Engineering, Inc., Westlake, OH, and PD Consulting, Herefordshire, U.K.

CCC (Chlorine Chemistry Council). (2003c) CDD/CDF data validation project. CDD/CDF release estimates for The Georgia Gulf Corporation: Plaquemine, LA. Prepared by Amendola Engineering, Inc., Westlake, OH, and PD Consulting, Herefordshire, U.K.

CCC (Chlorine Chemistry Council). (2003d) CDD/CDF data validation project. CDD/CDF release estimates for Occidental Chemical Corporation: Convent, LA; Deer Park (VCM PLANT), TX; Ingleside, TX; Laporte, TX; Mobile, AL. Prepared by Amendola Engineering, Inc., Westlake, OH, and PD Consulting, Herefordshire, U.K.

CCC (Chlorine Chemistry Council). (2004) CDD/CDF data validation project. CDD/CDF release estimates for occidental chemical corporation: Convent, LA; Deer Park (VCM Plant), TX; Ingleside, TX; LaPorte, TX; Mobile, AL.

CCC (Chlorine Chemistry Council). (2005) CDD/CDF data validation project. CDD/CDF release estimates for Dupont: Delisle, MS; Edge Moor, DE; Johnsonville, TN. Prepared by Amendola Engineering, Inc., Westlake, OH, and PD Consulting, Herefordshire, U.K.

C&EN (Chemical & Engineering News). (2002) Production: down but not out. June 24, 2002. Available online at http://pubs.acs.org/cen.

CEQ (Council on Environmental Quality). (1997) Environmental quality 1990. 25th Annual Report. Council on Environmental Quality, Executive Office of the President of the United States, Washington, DC.

ChemRisk. (1993) Critique of dioxin factories. Prepared for The Vinyl Institute.

Chen, YR; Chen, CJ; Lee, CC; et al. (1986) Reproductive effects of emissions from waste electrical products combustion. Presented at Dioxin '86, 6th International Symposium on Chlorinated Dioxins and Related Compounds; September, Fukuoka University, Fukuoka, Japan.

Chen, M; Hong, CS; Bush, B; et al. (1988) Anaerobic biodegradation of polychlorinated biphenyls by bacteria from Hudson River sediments. Ecotoxicol and Environ Safety 16:95-105.

Chinkin, LR; Weir, BR; Latimer, DA. (1987) Inventory of chlorophenol use in the forest products industry and investigation of related emissions of chlorinated dibenzodioxins and dibenzofurans. California Air Resources Board, Sacramento, CA. Contract No. A5-125-32.

Choudhry, GG; Hutzinger, O. (1983) Mechanistic aspects of the thermal formation of halogenated organic compounds including polychlorinated dibenzo-p-dioxins. New York, NY: Gordon and Breach.

Choudhry, GG; Webster, GRB. (1989) Environmental photochemistry of PCDDs. 2. Quantum yields of direct phototransformation of 1,2,3,7-tetra-, 1,3,6,8-tetra-, 1,2,3,4,6,7,8-hepta-, and 1,2,3,4,6,7,8,9-octachlorodibenzo-p-dioxin in aqueous acetonitrile and their sunlight half-lives. J Agric Food Chem 37:254-261.

Christmann, W; Kasiske, D; Klöppel, KD; et al. (1989a) Combustion of polyvinyl chloride: an important source for the formation of PCDD/PCDF. Chemosphere 19(1-6):387-392.

Christmann, W; Klöppel, KD; Partscht, H; et al. (1989b) Tetrachlorobenzoquinones, a source of PCDD/PCDF. Chemosphere 18(1-6):789-792.

Cianciarelli, D. (2000) Measurement of PCDD/PCDF and hexachlorobenzene emissions from an electric arc furnace shop, Dofasco Inc., Hamilton, Ontario. Emissions Research Advancement Division, Environment Canada. Report ERMD 99-08.

Cianciarelli, D. (2001) Characterization of organic emissions from an electric arc furnace, Gerdau Courtice Steel Inc., Cambridge, Ontario. Emissions Research and Measurement Division, Environmental Technology Advancement Directorate, Environment Canada. Report ERMD 2000-05.

Charles E. Napier Company, Ltd. (2000) Draft: background technical discussion paper on the release and control of dioxins/furans from the steel sector. Prepared for Environment Canada, Minerals and Metals Division.

Charles E. Napier Company, Ltd. (2002) Final: generic dioxin/furan emission testing protocol for the base metals smelting sector. Prepared for Environment Canada.

Clark, T; Clark, K; Paterson, S; et al. (1988) Wildlife monitoring, modeling, and fugacity. Environ Sci Technol 22(2):120-127.

Clement, RE; Tashiro, C. (1991) Forest fires as a source of PCDD and PCDF. Presented at Dioxin '91, 11th International Symposium on Chlorinated Dioxins and Related Compounds; Research Triangle Park, NC; September 1991.

Clement, RE; Tosine, HM; Ali, B. (1985) Levels of polychlorinated dibenzo-p-dioxins and dibenzofurans in wood burning stoves and fireplaces. Chemosphere 14:815-819.

Clement, RE; Tosine, HM; Osborne, J; et al. (1988) Gas chromatographic/mass spectrometric determination of chlorinated dibenzo-p-dioxins and dibenzofurans in incinerator stack emissions and fly-ash: a 13-test study. Biomedical and Environmental Mass Spectrometry 17:81-96.

Cleverly, DH; Morrison, RM; Riddle, BL; et al. (1991) Regulatory analysis of pollutant emissions, including polychlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs), from municipal waste combustors. In: Hattemer-Frey, HA; Travis, C; eds. Health effects of municipal waste incineration. Boca Raton, FL: CRC Press; pp. 47-65.

Cleverly, D; Schaum, J; Schweer, G; et al. (1997) The congener profiles of anthropogenic sources of chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans in the United states. Organohalogen Compounds 32:430-435.

Commoner, B; McNamara, M; Shapiro, K; et al. (1984) Environmental and economic analysis of alternative municipal solid waste disposal technologies, part II: the origins of chlorinated dioxins and dibenzofurans emitted by incinerators that burn unseparated municipal solid waste, and an assessment of methods of controlling them. Center for the Biology of Natural Systems, Queens College, CUNY, Flushing, New York.

Commoner, B; Webster, T, Shapiro, K; et al. (1985) The origins and methods of controlling polychlorinated dibenzo-p-dioxin and dibenzofuran emissions from MSW incinerators. Presented at the 78th Annual Meeting of the Air Pollution Control Association; Detroit, MI; June 1985.

Commoner, B; Shapiro, K; Webster, T. (1987) The origin and health risks of PCDD and PCDF. Waste Management and Research 5:327-346.

Commonwealth Aluminum Corp (1995). Item II-D-64 in USEPA secondary aluminum MACT air docket number A-92-61; letter and attachment, S. Bruntz, Commonwealth Aluminum Corp., July 5, 1995, enclosing test report and discussion of test report results, test report entitled MACT emission testing of the 'B' rotary kiln at Commonwealth Aluminum Corporation, Lewisport, Kentucky (9 volumes total).

Costner, PK. (1998) Correlation of chlorine input and PCDD/PCDF emissions at a full-scale hazardous waste incinerator. Organohalogen Compounds 36:147-151.

Council of Great Lakes Industries. (1999) Octachlorostyrene and suggested industrial sources. A report to the Great Lakes Binational Toxics Strategy OCS Workgroup. Council of Great Lakes Industries, Ann Arbor, MI.

Cramer, PH; Heiman, J; Horrigan, M; et al. (1995) Results of a national survey for polychlorinated dibenzo-p-dioxins, dibenzofurans, and coplanar polychlorinated biphenyls in municipal biosolids. Organohalogen Compounds 24:305-308.

CRE (Coal Research Establishment). (1994) Emissions of environmental concern from coal utilization. Coal Research Establishment, National Coal Board, Stoke Orchard, United Kingdom. Report number ECSC 7220-EC/011.

Cull, MR; Dobbs, AJ; Goudot, M; et al. (1984) Polychlorodibenzo-p-dioxins and dibenzofurans in technical pentachlorophenol-results of a collaborative analytical exercise. Chemosphere 13(10):1157-1165.

Curlin, LC; Bommaraju, TV. (1991) Alkali and chlorine products. In: Kirk-Othmer encyclopedia of chemical technology. 4th ed. pp. 938-1025.

deBoer, J.; Stronck, CJN; Traag, WA; et al. (1993) Non-ortho and mono-ortho substituted chlorobiphenyls and chlorinated dibenzo-p-dioxins, and dibenzofurans in marine and freshwater fish and shellfish from The Netherlands. Chemosphere 26(10):1832-1842.

De Fre, R; Rymen, R. (1989) PCDD and PCDF formation from hydrocarbon combustion in the presence of hydrogen chloride. Chemosphere 19(1-9):331-336.

Dempsey, CR; Oppelt, ET. (1993) Incineration of hazardous waste: a critical review update. Air and Waste 43:25-73.

Deutsch, DG; Goldfarb, TD. (1988) PCDD/PCDF contamination following a plastic fire in a university lecture hall building. Chemosphere 17(12):2423-2431.

DeVoogt, P; Brinkman, UA. (1989) Production, properties and usage of polychlorinated biphenyls. In: Kimbrough, R; Jensen, AA, eds. Halogenated biphenyls, terphenyls, napthalenes, dibenzodioxins and related products. New York, NY: Elsevier Science Publishers.

Dickson, LC; Karasek, FW. (1987) Mechanism of formation of polychlorinated dibenzo-p-dioxins produced on municipal incinerator flyash from reactions of chlorinated phenols. J Chromatography 389:127-137.

Dickson, LC; Lenoir, D; Hutzinger, O. (1992) Quantitative comparison of de novo and precursor formation of polychlorinated dibenzo-p-dioxins under simulated municipal solid waste incinerator post combustion conditions. Environ Sci Technol 26:1822-1828.

Domalski, ES; Churney, KL; Ledford, AE; et al. (1986) Monitoring the fate of chlorine from MSW sampling through combustion, part 1: analysis of the waste stream for chlorine. Chemosphere 15(9-12):1339-1354.

Donnelly, JR. (1992) Waste incineration sources: refuse. In: Buonicore, AJ; Davis, WT; eds. Air pollution engineering manual. Air and Waste Management Association. New York, NY: Van Nostrand Reinhold. pp. 263-275.

Douben, PET; Eduljee, GH; Dyke, P. (1995) A review of potential PCDD and PCDF emission sources in the UK. Organohalogen Compounds 24:131-136.

Duarte-Davidson, R; Sewart, A; Alcock, RE; et al. (1997) Exploring the balance between sources, deposition and the environmental burden of PCDD/Fs in the U.K. terrestrial environment: an aid to identifying uncertainties and research needs. Environ Sci Technol 31(1):1-11.

Duinker, JC; Hillebrand, MTJ. (1983) Characterization of PCB components in Clophen formulations by capillary GC-MS and GC-ECD techniques. Environ Sci Technol 17(8):449-456.

Duinker, JC; Schulz, DE; Petrick, G. (1988) Multidimensional gas chromatography with electron capture detection for the determination of toxic congeners of polychlorinated biphenyl mixtures. Analytical Chemistry 60:478-482.

Dumler-Gradl, R; Thoma, H; Vierle, O. (1995) Research program on dioxin/furan concentration in chimney soot from house heating systems in the Bavarian area. Organohalogen Compounds 24:115-118.

Dung, M; O'Keefe, PW. (1992) Comparative rates of photolysis of polychlorinated dibenzofurans in organic solvents and in aqueous solutions. Organohalogen Compounds 8:233-236.

Dyke, P; Coleman, P. (1995) Dioxins in ambient air, Bonfire Night 1994. Organohalogen Compounds 24:213-216.

Edelstein, DL. (1995) Minerals yearbook: copper. U.S. Geological Survey, Geologic Division, Reston, VA.

Edelstein, DL. (2000) Minerals yearbook: copper. U.S. Geological Survey, Geologic Division, Reston, VA.

Edelstein, DL. (2001) Minerals yearbook: copper. U.S. Geological Survey, Geologic Division, Reston, VA.

Eduljee, GH; Dyke, P. (1996) An updated inventory of potential PCDD and PCDF emission sources in the UK. The Science of the Total Environment 177:303-321.

EIA (Energy Information Administration). (1991) Estimates of U.S. biofuels consumption in 1990. U.S. Department of Energy, Office of Coal, Nuclear, Electric and Alternate Fuels, Washington, DC; DOE/EIA-0548(90).

EIA (Energy Information Administration). (1992) Fuel oil and kerosene sales 1991. U.S. Department of Energy, Office of Oil and Gas, Washington, DC; DOE/EIA-0535(91).

EIA (Energy Information Administration). (1993) Petroleum supply annual 1992. Vol. 1. U.S. Department of Energy, Office of Oil and Gas, Washington, DC; DOE/EIA-0340(92)/1.

EIA (Energy Information Administration). (1994) Estimates of U.S. biomass energy consumption 1992. U.S. Department of Energy, Office of Coal, Nuclear, Electric, and Alternative Fuels, Washington, DC; DOE/EIA-0548(92).

EIA (Energy Information Administration). (1995) Annual energy review 1994. U.S. Department of Energy, Office of Energy Markets and End Use, Washington, DC; DOE/EIA-0884(94).

EIA (Energy Information Administration). (1997a) Fuel oil and kerosene sales 1996. U.S. Department of Energy, Office of Oil and Gas, Washington, DC; DOE/EIA-0535(96).

EIA (Energy Information Administration). (1997b) Annual energy review 1996. U.S. Department of Energy, Office of Energy Markets and End Use, Washington, DC; DOE/EIA-0384(96).

EIA (Energy Information Administration). (1999) State energy data report 1996, consumption estimates. U.S. Department of Energy, Office of Energy Markets and End Use, Washington, DC; DOE/EIA-0214(96).

EIA (Energy Information Administration). (2002) Annual energy review 2000. Available online at www.eia.doe.gov.

EIA (Energy Information Administration). (2003a) 2000 State energy data. Available online at http://www.eia.doe.gov/emeu/states/sep_fuel/html/pdf/fuel_all.pdf).

EIA (Energy Information Administration). (2003b) Monthly energy review, energy consumption by sector for the year 2000. Available online at www.eia.doe.gov/mer/consump.html.

Eitzer, BD; Hites, RA. (1987) Reply to comment on "Airborne dioxins and dibenzofurans: sources and fate." Environ Sci Technol 21:924.

Eitzer, BD; Hites, RA. (1989) Dioxins and furans in the ambient atmosphere: A baseline study. Chemosphere 18(1-6):593-598.

Eklund, G; Pedersen, JR; Stromberg, B. (1986) Phenol and HCl at 550°C yield a large variety of chlorinated toxic compounds. Nature 320:155-156.

Eklund, G; Pedersen, JR; Stromberg, B. (1988) Methane, hydrogen chloride and oxygen form a wide range of chlorinated organic species in the temperature range 400°C-959°C. Chemosphere 17(3):575-586.

Environics Research Group. (2001) Household garbage disposal and burning: Ontario survey. Prepared for Environment Canada.

Environment Canada. (1985) The national incineration testing and evaluation program: two-stage combustion (Prince Edward Island). Environment Canada, Ottawa, Ontario, Canada. Report EPS 3/UP/1.

Environment Canada. (2000) Characterization of organic compounds from selected residential wood stoves and fuels. Environment Canada, Emissions Research and Measurement Division, Ottawa, Canada. Report ERMD 2000-01.

Environmental Risk Sciences, Inc. (1995) An analysis of the potential for dioxin emissions in the primary copper smelting industry. Prepared for the National Mining Association.

EPRI (Electric Power Research Institute). (1994) Electric utility trace substances synthesis report. Palo Alto, CA; EPRI TR-104614.

EPRI (Electric Power Research Institute). (1995) Pentachlorophenol (PCP) in soils adjacent to in-service utility poles in New York State. Palo Alto, CA; EPRI TR-104893.

ERG (Eastern Research Group, Inc.) (1998) Report of the meeting to peer review inventory of sources of dioxin in the United States. Prepared for the U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC. EPA Contract No. 68-D5-0028, Work Assignment No. 98-05.

Erickson, M. (1986) Analytical chemistry of PCBs. Boston, MA: Butterworth Publishers.

Erickson, MD; Cole, CJ; Flora, JD; et al. (1984) Thermal degradation products from dielectric fluids. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC; EPA-560/5-84-009.

Esposito, MP; Tiernan, TO; Drydent, FE. (1980) Dioxins. Prepared for the U.S. Environmental Protection Agency, Cincinnati, OH; EPA-600/2-80-197.

Fangmark, I; Stomberg, G; Berge, N; et al. (1994) Influence of postcombustion temperature profiles on the formation of PCDDs, PCDFs, PCBzs, and PCBs in a pilot incinerator. Environ Sci Technol 28:624-629.

Federal Register. (1979) Decision and emergency order suspending registrations for certain uses of 2,4,5-T and Silvex. FR (March 15) 44:15874-15920.

Federal Register. (1982a) Polychlorinated biphenyls (PCBs) use in electrical equipment. FR (April 22) 47:17426.

Federal Register. (1982b) Polychlorinated biphenyls (PCBs) manufacturing, processing, distribution in commerce and use prohibitions; use in electrical equipment. FR (August 25) 47:37342.

Federal Register. (1984) Pentachlorophenol, and inorganic arsenicals; intent to cancel registrations of pesticide products containing creosote, pentachlorophenol (including its salts) and the inorganic arsenicals; determination concluding the rebuttal presumption against registration of the wood preservative uses of pesticide products; availability of position document. FR (July 13) 49:28666-28689.

Federal Register. (1985a) Regulation of fuels and fuel additives; gasoline lead content: final rule and supplemental notice of proposed rulemaking. FR (March 7) 50:9386-9408.

Federal Register. (1985b) Polychlorinated biphenyls in electrical transformers. FR (July 17) 50:29170.

Federal Register. (1986) Creosote, pentachlorophenol, and inorganic arsenicals; amendment of notice of intent to cancel registrations. FR (January 10) 51:1334-1348.

Federal Register. (1987a) Polyhalogenated dibenzo-p-dioxins/dibenzofurans; testing and reporting requirements; final rule. FR (June 5) 52:21412-21452.

Federal Register. (1987b) Pentachlorophenol; amendment of notice of intent to cancel registrations. FR (January 2) 52:140-148.

Federal Register. (1987c) Final determination and intent to cancel and deny applications for registrations of pesticide products containing pentachlorophenol (including but not limited to its salts and esters) for non-wood uses. FR (January 21) 52:2282-2293.

Federal Register. (1990) National sewage sludge survey: availability of information and data, and anticipated impacts on proposed regulation. FR (November 9) 55:47210-47283.

Federal Register. (1991a) Standards of performance for new stationary sources and final guidelines for municipal waste combustors. FR (February 11) 56:5488-5527.

Federal Register. (1991b) Burning of hazardous waste in boilers and industrial furnaces–final rule. FR (February 21) 56:7134.

Federal Register. (1991c) Standards of performance for new stationary sources and guidelines for control of existing sources: municipal solid waste landfills: proposed rule and guideline. FR (May 30) 56:24468.

Federal Register. (1993a) Standards for the use or disposal of sewage sludge; final rules. FR (February 19) 58:9248-9404.

Federal Register. (1993b) Standards of performance for new stationary sources and guidelines for control of existing sources: municipal solid waste landfills: notice of availability. FR (June 21) 58:33790-33792.

Federal Register. (1993c) Chemicals; toxic chemical release reporting; community right-to-know; significant new use rule. FR (December 1) 58:63500-63518.

Federal Register. (1993d) 2,3,5,6-Tetrachloro-2,5-cyclohexadiene-1,4-dione; proposed significant new use of a chemical substance. FR (May 12) 58:27980-27986.

Federal Register. (1995a) Standards of performance for new stationary sources and emission guidelines for existing sources: municipal waste combustors, final rule. FR (December 19) 60:65387-65436.

Federal Register. (1995b) Hazardous waste management system; identification and listing of hazardous waste: petroleum refining process wastes; land disposal restrictions for newly identified wastes; and CERCLA hazardous substance designation and reportable quantities. FR (November 20) 60:57747-57800.

Federal Register. (1996a) Revised standards for hazardous waste combustors: proposed rule. FR (April 19) 61:17357-17536.

Federal Register. (1996b) Standards of performance for new stationary sources and guidelines for control of existing sources: municipal solid waste landfills: final rule and guideline. FR (March 12) 61:9905-9944.

Federal Register. (1997a) Standards of performance for new stationary sources and emission guidelines for existing sources: hospital/medical/infectious waste incinerators; final rule. FR (September 15) 62:48347-48391.

Federal Register. (1997b) Toxic chemicals; PCBs; submission of IRC No. 1000 to OMB; information collection activities. FR (January 21) 62:3035-3036.

Federal Register. (1998a) Source category listing for Section 112(d)(2) rulemaking pursuant to Section 112(c)(6) requirements. FR (April 10) 63:17838-17855.

Federal Register. (1998b) Hazardous waste management system; identification and listing of hazardous waste; petroleum refining process wastes; land disposal restrictions for newly identified wastes; and CERCLA hazardous substance designation and reportable quantities. FR (August 8) 63:42110-42189.

Federal Register. (1998c) National emission standards for hazardous air pollutants for source category: pulp and paper production; effluent limitations guidelines, pretreatment standards, and new source performance standards: pulp, paper, and paperboard category. FR (April 15) 63:18504-18751.

Federal Register. (1999a) NESHAPS: final standards for hazardous air pollutants for hazardous waste combustors. FR (September 30) 64:52828-53077.

Federal Register. (1999b) National emission standards for hazardous air pollutants for source categories; Portland Cement manufacturing industry. FR (June 14) 64:31897-31962.

Federal Register. (1999c) Standards for the management of cement kiln dust; proposed rule. FR (August 20) 64:161.

Federal Register. (2003) Federal plan requirements for small municipal waste combustion units constructed on or before August 30, 1999. F.R. (January 31) 68:5144-5187.

Federal Register. (2004) National emission standards for hazardous air pollutants: proposed standards for hazardous air pollutants for hazardous waste combustors (phase 1 final replacement standards and phase II): proposed rule. FR (April 20) 69:21347-21385.

Feil, VJ; Tiernan, T. (1997) Pentachlorophenol as a source of dioxins and furans. Organohalogen Compounds 33:353-354.

FEMA (Federal Emergency Management Agency). (1997) Fire in the United States. United States Fire Administration, Washington, DC. FA-173.

FEMA (Federal Emergency Management Agency). (2001) The national fire problem. United States Fire Administration, Washington, DC. Available online at http://www.usfa.fema.gov/nfdc/national.htm.

Fenton, M. (1996) Minerals yearbook: iron and steel. U.S. Department of the Interior, U.S. Geological Survey, Washington, DC.

Fenton, M. (2001) Minerals yearbook: iron and steel. U.S. Department of the Interior, U.S. Geological Survey, Washington, DC.

Ferrario, J; Byrne, C; Lorber, M; et al. (1997) A statistical survey of dioxin-like compounds in United States poultry fat. Organohalogen Compounds 32:245-251.

Ferrario, J; Byrne, C; Cleverly, D. (2000) 2,3,7,8-Dibenzo-p-dioxins in mined clay products from the United States: evidence for possible natural formation. Environ Sci Technol 34:4524-4532.

Fiedler, H; Hutzinger, O. (1992) Sources and sinks of dioxins: Germany. Chemosphere 25:1487-1491.

Fiedler, H; Lindert, M. (1998) Düsseldorf Airport fire 1996: results and comparison with accidental fires. Organohalogen Compounds 36:69-72.

Fiedler, H; Hutzinger, O; Hosseinpour, J. (1993) Analyses and remedial actions following an accidental fire in a kindergarten. Organohalogen Compounds 14:19-22.

Firestone, D; Ress, J; Brown, NL; et al. (1972) Determination of polychlorodibenzo-p-dioxins and related compounds in commercial chlorophenols. J Assoc Off Anal Chem 55(1):85-92.

Fisher, TS; Hayward, DG; Stephens, RD; et al. (1999) Dioxins and furans in Los Angeles urban runoff. J Environ Engineering 125:185–191.

Fleischer, O; Wichmann, H; Lorenz, W. (1999) Release of polychlorinated dibenzo-p-dioxins and dibenzofurans by setting off fireworks. Chemosphere 39:925-932.

Frame, GM. (1995) A comprehensive, multicenter study of PCB elution on capillary GC columns. Pittcon '95. Sponsored by the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Inc. New Orleans, LA; March 8, 1995; Paper 717.

Frame, GM. (1997) A collaborative study of 209 PCB congeners and 6 aroclors on 20 different HRGC columns. Fresenius Journal of Analytical Chemistry 357(6):714-722.

Frame, GM. (1999) Improved procedure for single DB-XLB column GC MS-SIM quantitation of PCB congener distributions and characterization of two different preparations sold as "Aroclor 1254". J High Resol Chromatogr 22(10):533-540.

Frame, GM; Cochran, JW; Bowadt, SS. (1996a) Complete PCB congener distributions for 17 aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. J High Resol Chromatogr 19(12):657-668.

Frame, GM; Wagner, RE; Carnahan, JC; et al. (1996b) Comprehensive, quantitative, congener-specific analyses of eight aroclors and complete PCB congener assignments on DB-1 capillary GC columns. Chemosphere 33(4):603-623.

Frank, H; Frank, W. (1989) Uptake of airborne tetrachloroethane by spruce needles. Environ Sci Technol 23(3):365-367.

Freeman, RA; Schroy, J.M. (1985) Environmental mobility of dioxins. Aquatic Toxicology and Hazard Assessment: Eighth Symposium, ASTM STP 891, Bahner, RC; Hansen, DJ; eds. American Society for Testing and Materials, Philadelphia, PA; pp. 422-439.

Fries, GF; Dawson, TE; Paustenbach, DJ; et al. (1997) Biosynthesis of hepta- and octa-chlorodioxins in cattle and evidence for lack of involvement by rumen microorganisms. Organohalogen Compounds 33:296-301.

Friesen, JK; Muir, DCG; Webster, GRB. (1990) Evidence of sensitized photolysis of polychlorinated dibenzo-p-dioxins in natural waters under sunlight conditions. Environ Sci Technol 24(11):1739-1744.

Friesen, KJ; Loewen, MD; Foga, MM. (1993) Environmental aquatic photodegradation of chlorinated dibenzofurans and their photoproducts. Organohalogen Compounds 12:135-137.

Froese, KL; Hutzinger, O. (1994) The formation of chlorinated benzenes and phenols in fly ash catalyzed reactions of trichloroethylene. Chemosphere 28 (11):1977-1987.

Froese, KL; Hutzinger, O. (1996a) Polychlorinated benzene and polychlorinated phenol in heterogeneous combustion reactions of ethylene and ethane. Environ Sci Technol 30:1009-1013.

Froese, KL; Hutzinger, O. (1996b) Polychlorinated benzene, phenol, dibenzo-p-dioxin, and dibenzofuran in heterogeneous combustion reactions of acetylene. Environ Sci Technol 30: 998-1008.

Froese, K; Hutzinger, O. (1997) Mechanisms of formation of polychlorinated benzenes and phenols from heterogeneous reactions of C_s aliphatics. Environ Sci Technol 31:542-547.

Fuchs, R; Towara, J; Hutzinger, O. (1990) PCDD/F in the dry-cleaning process. Organohalogen Compounds 3:441-444.

Funcke, W; Theisen, J; Balfanz, E; Konig, J. (1988) Polychlorierte dibenzofurane (PCDF) und polychlorierte dibenzo(p)dioxine (PCDD) in Ruckstanden und emissionen eines Brandes in Anwesenheit von PBC-haltigen materialien. Staub-Reinhaltung der Luft 48:393-396.

Gaggi, C; Bacci, E; Calamari, D; et al. (1985) Chlorinated hydrocarbons in plant foliage: an indication of the tropospheric contamination level. Chemosphere 14(11-12):1673-1686.

Galson Corporation. (1995) Source test report: source emission testing at Roth Brothers Smelting Corporation. Galson Corporation, East Syracuse, NY.

Gambogi, J. (1996) Minerals yearbook: titanium. U.S. Geological Survey, Geologic Division, Reston, VA.

Gan, DR; Berthouex, PM. (1994) Disappearance and crop uptake of PCBs from sludge-amended farmland. Water Environment Research 66(1):54-69.

Gertler, AW; Sagebiel, JC; Dippel, WA; et al. (1996) A study to quantify on-road emissions of dioxins and furans from mobile sources: phase 2. Desert Research Institute, Reno, NV.

Gertler, A; Sagebiel, J; Dippel, W; et al. (1998) Measurement of dioxin and furan emissions factors from heavy duty diesel vehicles. J of the Air and Waste Mgmt Assoc 48:276-278.

Geueke, K; Gessner, A; Quass, U; et al. (1999) PCDD/F emissions from heavy duty vehicle diesel engines. Chemosphere 38:2791-2806.

Gillespie, WJ. (1994) A summary of data reflective of U.S. pulp and paper industry progress in reducing the TCDD/TCDF content of effluents, pulps and wastewater treatment sludges. Organohalogen Compounds 20:255-260.

Gillespie, WJ. (1995) Progress in reducing the TCDD/TCDF content of effluents, pulps and wastewater treatment sludges from the manufacturing of bleached chemical pulp. National Council of the Paper Industry for Air and Stream Improvement, Inc., Research Triangle Part, NC.

Gilman, AP; Douglas, VM; Newhook, RC; et al. (1988) Chlorophenols and their impurities: a health hazard evaluation. Health and Welfare Canada. Document No. H46-2/88-110E.

Gobran, T; Khurana, V; MacPherson, K; et al. (1995) PCDD/PCDF levels in raw sewage, final effluent, sludge, and ash samples from an Ontario wastewater treatment plant. Organohalogen Compounds 24:75-80.

Goldfarb, TD; Malloy, TA; Surico, M. (1992) PCDDs, PCDFs, PCBs, chlorophenols (CPs) and chlorobenzenes (CBzs) in samples from various types of composting facilities in the United States. Organohalogen Compounds 8:253-256.

Green, LC; Lester, RL; Armstrong, SR. (1995) Comments on EPA's external review draft Estimating Exposures to Dioxin-Like Compounds. Cambridge Environmental Inc., Cambridge, MA. Dated January 12, 1995, and May 11, 1995.

Greenpeace. (1993) Dioxin factories: a study of the creation and discharge of dioxins and other organochlorines from the production of PVC. Greenpeace International, Amsterdam, The Netherlands.

Greer, WL; Johnson, MD; Raught, EC; et al. (1992) Portland cement. In: Buonicore, AJ; Davis, WT; eds. Air pollution engineering manual. Air and Waste Management Association. New York, NY: Van Nostrand Reinhold.

Gribble, GW. (1994) The natural production of chlorinated compounds. Environ Sci Technol 28(7):310A-319A.

Guerin, MR; Jenkins, RA; Tomkins, BA. (1992) The chemistry of environmental tobacco smoke: composition and measurement. Chelsea, MI: Lewis Publishers.

Gullett, BK; Lemieux, PM. (1994) Role of combustion and sorbent parameters in prevention of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran formation during waste combustion. Environ Sci Technol 28(1):107-118.

Gullett, BK; Ryan, JV. (1997) On-road sampling of diesel engine emissions of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran. Organohalogen Compounds 32:451-456.

Gullett, B; Touati, A. (2003) PCDD/F emissions from forest fire simulations. Atmospheric Environment 37:803-813.

Gullett, BK; Bruce, KR; Beach, LO. (1990a) Formation of chlorinated organics during solid waste combustion. Waste Management and Research 8:203-214.

Gullett, BK; Bruce, KR; Beach, LO. (1990b) The effect of metal catalysts on the formation of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran precursors. Chemosphere 20:1945-1952.

Gullett, BK; Bruce, KR; Beach, LO. (1991a) The effect of sulfur compounds on the formation mechanism of PCDD and PCDF in municipal waste combustors. U.S. EPA, Research Triangle Park,NC; Acurex Corp., Research Triangle Park,NC. In: Conference papers from the second international conference on municipal waste combustion, April 15-19, 1991, Tampa, FL. Air and Waste Management Association, Pittsburgh, PA; pp.16-34.

Gullett, BK; Bruce, KR; Beach, LO; et al. (1991b) Mechanistic steps in the production of PCDD and PCDF during waste combustion. Presented at Dioxin '91, 11th International Symposium on Chlorinated Dioxins and Related Compounds; Research Triangle Park, NC; September 1991.

Gullett, B; Bruce, K; Beach, L. (1992) Mechanistic steps in the production of PCDD and PCDF during waste combustion. Chemosphere 25(7-10):1387-1392.

Gullett, BK; Lemieux, PM; Lutes, CC; et al. (1999) PCDD/F emissions from uncontrolled, domestic waste burning. Organohalogen Compounds 41:27-30.

Gullett, BK; Lemieux, PM; Winterrowd, CK; et al. (2000) PCDD/F emissions from uncontrolled, domestic waste burning. Organohalogen Compounds 46:193-196.

Gullett, BK; Lemieux, PM; Lutes, CC; et al. (2001) Emissions of PCDD/F from uncontrolled, domestic waste burning. Chemosphere 43:721–725.

Gurprasad, N; Constable, M; Haidar, N; et al. (1995) Polychlorinated dibenzo-p-dioxins (PCDDs) leaching from pentachlorophenol-treated utility poles. Organohalogen Compounds 24:501-504.

Gutenmann, WH; Rutzke, M; Kuntz, HT; et al. (1994) Elements and polychlorinated biphenyls in sewage sludges of large cities in the United States. Chemosphere 28(4):725-728.

Hagenmaier, H. (1986) Determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin in commercial chlorophenols and related products. Fresenius Z Anal Chem 325:603-606.

Hagenmaier, H. (1987) Belastung der umwelt mit dioxinen [Environmental loading with dioxins]. Institut für Organische Chemie der Universität Tübingen.

Hagenmaier, H. (1994) Contributions of diesel-powered vehicles and wood burning to overall PCDD/PCDF emissions. Organohalogen Compounds 20:267-270.

Hagenmaier, H; Brunner, H. (1987) Isomer-specific analysis of pentachlorophenol and sodium pentachlorophenate for 2,3,7,8-substituted PCDD and PCDF at sub-ppb levels. Chemosphere 16:1759-1764.

Hagenmaier, H; Dawidowsky, V; Weber, UB; et al. (1990) Emission of polyhalogenated dibenzodioxins and dibenzofurans from combustion-engines. Organohalogen Compounds 2:329-334.

Hagenmaier, H; Lindig, C; She, J. (1994) Correlation of environmental occurrence of polychlorinated dibenzo-p-dioxins and dibenzofurans with possible sources. Chemosphere 29(9-11):2163-2174.

Haglund, P; Egeback, K-E; Jansson, B. (1988) Analysis of PBDD/F in vehicle exhaust. Presented at: Dioxin '88, 8th International Symposium on Chlorinated Dioxins and Related Compounds; Umea, Sweden; August 1988.

Halonen, L; Tarhanen, J; Ollikainen, S; et al. (1994) The effect of inorganic and organic chlorine on formation of highly chlorinated organic compounds during incineration: laboratory pilot study. Chemosphere 28(12):2129-2138.

Hammerstrom, K; Schweer, G; Adkins, L; et al. (1985) Exposure assessment for polychlorinated biphenyls (PCBs): incidental production, recycling, and selected authorized uses. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC. EPA Contract No. 68-01-6271, Task No. 21.

Harner, T; Mackay, D; Jones, KC. (1995) Model of the long-term exchange of PCBs between soil and the atmosphere in the southern U.K. Environ Sci Technol 29(5):1200-1209.

Harnly, M; Stephens, R; McLaughlin, C; et al. (1995) Polychlorinated dibenzo-p-dioxin and dibenzofuran contamination at metal recovery facilities, open burn sites, and a railroad car incineration facility. Environ Sci Technol 29(3):677-684.

Harrad, SJ; Jones, KC. (1992) A source inventory and budget for chlorinated dioxins and furans in the United Kingdom environment. The Science of the Total Environment 126:89-107.

Harrad, SJ; Malloy, TA; Khan, MA; et al. (1991) Levels and sources of PCDDs, PCDFs, chlorophenols (CPs) and chlorobenzenes (CBzs) in composts from a municipal yard waste composting facility. Chemosphere 23(2):181-191.

Hay, DJ; Finkelstein, A; Klicius, R. (1986) The national incineration testing and evaluation program: an assessment of two-stage incineration and pilot scale emission control. Paper presented to the U.S. EPA Science Advisory Board, Washington, DC. Environment Canada, Ottawa, Ontario, Canada.

Headrick, M; Hollinger, K; Lovell, R; et al. (1999) PBBs, PCBs, and dioxins in food animals, their public health implications. Vet Clin North Am Food Anim Pract 15(1):109-131.

Heindl, A; Hutzinger, O. (1987) Search for industrial sources of PCDD/PCDF, III. short-chain chlorinated hydrocarbons. Chemosphere 16(8/9):1949-1957.

Helble, JJ. (1993) Analysis of dioxin emissions from the incineration of hazardous waste. U.S. Environmental Protection Agency, Office of Solid Waste, Permits and State Programs Division, Washington, DC.

Hengstmann, R; Hamann, R; Weber, H; et al. (1990) Impact of sewage sludge and sewer slimes by polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Organohalogen Compounds 4:407-412.

Hickey, WJ. (1995) Enhancing PCB biodegradatin in soil with chlorobenzoate-degrading inoculants. Organohalogen Compounds 24:29-32.

Himberg, K; Sippola, E. (1990) Multidimensional gas chromatography: mass spectrometry as a method for the determination of coplanar PCB congeners. Organohalogen Compounds 4:183-186.

HMIP. (1995) A review of dioxin emissions in the UK. Her Majesty's Inspectorate of Pollution. HMIP/CPR2/41/1/38.

Ho, AKW; Clement, RE. (1990) Chlorinated dioxins/furans in sewage and sludge of municipal water pollution control plants. Chemosphere 20(10-12):1549-1552.

Hoekstra, EJ; De Leer, WB; Brinkman, UT. (1999) Natural formation of chlorinated phenols, dibenzo-p-dioxins, and dibenzofurans in soil of a Douglas fir forest. Environ Sci and Technol 33:2543-2549.

Holderman, TS; Cramer, PH. (1995) Updated results of polyhalogenated dibenzo-p-dioxin/dibenzofuran testing and reporting under the Toxic Substances Control Act (TSCA). Organohalogen Compounds 24:137-140.

Hornbuckle, KC; Achman, DR; Eisnreich, SJ. (1993) Over-water and over-land, polychlorinated biphenyls in Green Bay, Lake Michigan. Environ Sci Technol 27(1):87-97.

Horstmann, M; McLachlan, MS. (1992) Initial development of a solid-phase fugacity meter for semivolatile organic compounds. Environ Sci Technol 26(8):1643-1649.

Horstmann, M; McLachlan, MS. (1994a) Textiles as a source of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/CDF) in human skin and sewage sludge. Environ Sci and Pollut Res 1(1):15-20.

Horstmann, M; McLachlan, MS. (1994b) Polychlorinated dibenzo-p-dioxins and dibenzofurans in textiles and their transfer to human skin, sewage sludge and other matrices. Organohalogen Compounds 20:251-254.

Horstmann, M; McLachlan, MS. (1995) Concentrations of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in urban runoff and household wastewaters. Chemosphere 31(3):2887-2896.

Horstmann, M; McLachlan, M; Reissinger, M. (1992) Investigation of the origin of PCDD/CDF in municipal sewage. Organohalogen Compounds 9:97-100.

Horstmann, M; McLachlan, M; Reissinger, M. (1993a) Further investigations of the sources of PCDD/CDF in municipal sewage sludge. Organohalogen Compounds 11:293-296.

Horstmann, M; McLachlan, M; Reissinger, M; et al. (1993b) An investigation of PCDD/CDF formation during textile production and finishing. Organohalogen Compounds 11:417-420.

Houck, G. (1991) Minerals yearbook: iron and steel. U.S. Geological Survey, Geologic Division, Reston, VA.

Huang, H; Buekens, A. (1995) On the mechanisms of dioxin formation in combustion processes. Chemosphere 31 (9):4099-4117.

Huang, CW; Miyata, H; Lu, J; et al. (1992) Levels of PCBs, PCDDs and PCDFs in soil samples from incineration sites for metal reclamation in Taiwan. Chemosphere 24(11):1669-1676.

Huang, H; Biesemans, M, Buekens, A. (1999) Characterization of the nature of de novo synthesis by ^{13}C NMR. Organohalogen Compounds 41:105-108.

Huckins, JN; Stalling, DL; Petty, JD. (1980) Carbon-foam chromatographic separation of non-*o*-*o'*-chlorine substituted PCBs from Aroclor mixtures. J Assoc Off Anal Chem 63(4):750-755.

Hülster, A; Marschner, H. (1993) Soil-plant transfer of CDD/PCDF to vegetables of the cucumber family (*Cucurbitaceae*). Environ Sci Technol 28(6):1110-1115.

Hülster, A; Marschner, H. (1994) The influence of root exudates on the uptake of CDD/PCDF by plants. Organohalogen Compounds 20:31-34.

Hutzinger, O; Fiedler, H. (1991a) Formation of dioxins and related compounds from combustion and incineration processes. In: Bretthauer, EW; Kraus, HW; di Domenico, A; eds. Dioxin perspectives. A pilot study on international information exchange on dioxins and related compounds. New York, NY: Plenum Press.

Hutzinger, O; Fiedler, H. (1991b) Formation of dioxins and related compounds in industrial processes. In: Bretthauer, EW; Kraus, HW; di Domenico, A; eds. Dioxin perspectives. A pilot study on international information exchange on dioxins and related compounds. New York, NY: Plenum Press.

Hutzinger, O; Essers, U; Hagenmaier, H. (1992) Untersuchungen zur emission halogenierter dibenzodioxine und dibenzofurane aus verbrennungsmortoren beim betrieb mit handelsüblichen betriebsstoffen. Universities of Bayreuth, Stuttgart and Tübingen, Germany. GSF-Forschungszentrum, Munich, Germany, ISSN 0937-9932.

Huwe, JK; Feil, VJ; Tiernan, TO. (1998) In vivo formation of octachlorodibenzo-p-dioxin from a predioxin. Organohalogen Compounds 36:93-95.

Imagawa, T; Lee, C. (2001) Correlation of polychlorinated naphthalenes with polychlorinated dibenzofurans formed from waste incineration. Chemosphere 44:1151-1520.

Jager, J; Wilken, M; Zeschmar-Lahl, B. (1992) Dioxin und furan emissionen in Berlin eine hochrechnung [Dioxin and furan emissions in Berlin, a computer forecast]. Staub-Reinhaltung der Luft 52:99-106.

Jansson, B; Sundstrom, G; Ahling, B. (1977) Formation of polychlorinated dibenzo-p-dioxins during combustion of chlorophenol formulations. Science in the Total Environment 10:209-217.

Jarmohamed, W; Mulder, P. (1994) Oxychlorination and combustion of propene on fly-ash formation of chlorinated benzenes, dibenzodioxins and mono- and dibenzofurans. Chemosphere 29 (9-11): 1911-1917.

Jensen, S; Sundström, G; Frescati, L. (1974) Structures and levels of most chlorobiphenyls in two technical PCB products and in human adipose tissue. Ambio 3(2):70-76.

Jobst, H; Aldag, R. (2000) Dioxine In Lagersttatten-Tonen. UWSF-Zeitschrift furUmweltchem. Okotoxikologie 12(1):2–4.

Jones, KC; Alcock, RE. (1996) Dioxin inputs to the environment: a review of temporal trend data and proposals for a monitoring programme to detect past and future change in the U.K. Department of Environment report.

Kannan, N; Tanabe, S; Wakimoto, T; et al. (1987) Coplanar polychlorinated biphenyls in Aroclor and Kanechlor mixtures. J Assoc Off Anal Chem 70(3):451-454.

Kanters, J; Louw, R. (1994) Chlorine input and output in combustion of municipal solid waste in a lab-scale mini-reactor system. Chemosphere 29 (9-11):1919-1925.

Kao, AS; Venkataraman, C. (1995) Estimating the contribution of reentrainment to the atmospheric deposition of dioxin. Chemosphere 31(10):4317-4331.

Katami, T; Yasuhara, A; Okuda, T; et al. (2002) Formation of PCDDs, PCDFs, and coplanar PCBs from polyvinylchloride during combustion in an incinerator. Environ Sci Technol 36:1320-1324.

Kearney, PC; Woolson, EA; Isensee, AR; et al. (1973) Tetrachlorodibenzodioxin in the environment: sources, fate, and decontamination. Environ Health Perspect 5:273-277.

Kieatiwong, S; Nguyen, LV; Hebert, VR; et al. (1990) Photolysis of chlorinated dioxins in organic solvents and on soils. Environ Sci Technol 24(10):1575-1580.

Kim, K-S; Hong, K-H; Ko, Y-H (2004) Emission characteristics of PCDD/Fs, PCBs, chlorobenzenes, chlorophenols, and PAHs from polyvinylchloride bomustion at various temperatures. J Air Waste Manage Assoc 54:555-562.

Kirby, R. (1994) Petroleum refining industry: presence of dioxins and furans in wastewater generated by reforming operations. U.S. Environmental Protection Agency, Office of Water, Engineering and Analysis Division, Washington, DC.

Kjeller, L; Jones, KC; Johnston, AE; et al. (1991) Increases in the polychlorinated dibenzo-p-dioxin and -furan content of soils and vegetation since the 1840s. Environ Sci Technol 25(9):1619-1627.

Klasmeier, J; McLachlan, MS. (1995) A screening method for detection of OCDD/F in textiles. Organohalogen Compounds 23:131-134.

Knepper, WA. (1981) Iron. In: Kirk-Othmer encyclopedia of chemical technology. 3rd ed. 13:735-753. New York, NY: John Wiley and Sons.

Knittel, D. (1983) Titanium and titanium alloys. In: Kirk-Othmer encyclopedia of chemical technology. 3rd ed. 23:98-130. New York, NY: John Wiley and Sons.

Kobylecki, R; Ohira, K; Ito, I; et al. (2001) Dioxin and fly ash free incineration by ash pelletization and reburning. Environ Sci Technol 35:4313-4319.

Koester, CJ; Hites, RA. (1992) Photodegradation of polychlorinated dioxins and dibenzofurans adsorbed to fly ash. Environ Sci Technol 26(3):502-507.

Konduri, R; Altwicker, E. (1994) The effect of the electric field on the formation of PCDD in electrostatic precipitators. Hazardous Waste and Hazardous Materials 11(1):145-156.

Kramer, DA. (1995) Minerals yearbook : magnesium. U.S. Geological Survey, Geologic Division, Reston, VA.

Krauss, T; Krauss, P; Hagenmaier, H. (1994) Formation of PCDD/PCDF during composting? Chemosphere 28(1):155-158.

Kuck, PH. (1995) Minerals yearbook: nickel. U.S. Geological Survey, Geologic Division, Reston, VA.

Kwok, ESC; Atkinson, R; Arey, J. (1995) Rate constants for the gas-phase reactions of the OH radical with dichlorobiphenyls, 1-chlorodibenzo-p-dioxin, 1,2-dimethoxybenzene, and diphenyl ether: estimation of OH radical reaction rate constants for PCBs, PCDDs, and PCDFs. Environ Sci Technol 29(6):1591-1598.

Lahl, U. (1993) Sintering plants of steel industry: the most important thermical PCDD/CDF source in industrialized regions. Organohalogen Compounds 11:311-314.

Lahl, U. (1994) Sintering plants of steel industry: PCDD/F emission status and perspectives. Chemosphere 29(9-11):1939-1945.

Lahl, U; Wilken, M; Zeschmar-Lahl, B; Jager, J. (1991) PCDD/PCDF balance of different municipal waste management methods. Chemosphere 23(8-10):1481-1489.

Lamparski, LL; Stehl, RH; Johnson, RL. (1980) Photolysis of pentachlorophenol-treated wood. Chlorinated dibenzo-p-dioxin formation. Environ Sci Technol 14(2):196-200.

Lamparski, LL; Nestrick, TJ; Cutie, SS. (1990) The impact on the environment of airborne particulate matter from the eruption of Mount Saint Helens in May 1980. In: Clement, R; Kogel, R; eds. Emissions from combustion processes: origin, measurement, control. Chelsea, MI: Lewis Publishers.

Larsen, BR. (1995) HRGC separation of PCB congeners. J High Res Chromatogr 18:141-151.

Larsen, B; Bøwadt, S; Facchetti, S. (1992) Separation of toxic congeners from PCB mixtures on two series coupled narrow-bore columns (50 m SIL-8 and 25 m HT-5). International Journal of Environmental Analytical Chemistry (47):147-166.

Larssen, S; Brevick, EM; Oehme, M. (1990) Emission factors of PCDD and PCDF for road vehicles obtained by a tunnel experiment. Organohalogen Compounds 1:453-456.

Larsson, P; Lemkemeier, K. (1989) Microbial mineralization of chlorinated phenols and biphenyls in sediment-water systems from humic and clear-water lake. Water Research 23(9):1081-1085.

Lasagni, M; Collina, E; Tettamanti, M; et al. (2000) Kinetics of MSWI fly ash thermal degradation, 1. Empirical rate equation for native carbon gasification. Environ Sci Technol 34:130-136.

Launhardt, T; Thoma, H. (2000) Investigation on organic pollutants from a domestic heating system using various solid biofuels. Chemosphere 40:1149-1157.

Lebeuf, M; Gobeil, C; Brochu, C; et al. (1996) Direct atmospheric deposition versus fluvial inputs of PCDD/Fs to the sediments of the Lower St. Lawrence Estuary. Organohalogen Compounds 28:20-24.

Lee, RG; Hung, H; Mackay, D; et al. (1998) Measurement and modeling of the diurnal cycling of atmospheric PCBs and PAHs. Environ Sci Technol 32(14):2172-2179.

Leifer, A; Brink, RH; Thom, GC; et al. (1983) Environmental transport and transformation of polychlorinated biphenyls. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC; EPA-56 0/5-83-025.

Lemieux, PM. (1997) Evaluation of emissions from the open burning of household waste in barrels, U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Research Triangle Park, NC; EPA-600/R-97-134a.

Lemieux, PM; Gullett, BK; Lutes, CC; et al. (2000) Parameters influencing emissions of PCDDs/Fs from open burning of household waste in barrels. Presented at AWMA/Environment Canada Specialty Conference "Recent Advances in the Science and Management of Air Toxics," April 10-12, 2000, Banff, Alberta, Canada.

Lepine, F; Milot, S; Vincent, N. (1992) Formation of toxic PCB congeners and PCB-solvent adducts in a sunlight irradiated cyclohexane solution of Aroclor 1254. Bull Environ Contam Toxicol 48:152-156.

Lewert, HV; ed. (1976) A closer look at the pesticide question for those who want the facts. Dow Chemical Company, Midland, Michigan. Report No. 41.

Lexen, K; De Wit, C; Jansson, B; et al. (1993) Polychlorinated dibenzo-p-dioxin and dibenzofuran levels and patterns in samples from different Swedish industries analyzed within the Swedish dioxin survey. Chemosphere 27(1-3):163-170.

Liberson, GL; Belanger, WD. (1995) An analysis of dioxin production as a function of chlorine feed. In: Kilgroe, J, ed. Solid waste management: thermal treatment & waste-to-energy technologies. Proceedings of an interantional specialty conference sponsored by the Air and Waste Management Association, Washington, DC, April 18-21, 1995; pp. 425-432.

Liberti, A; Brocco, D. (1982) Formation of polychlorodibenzodioxins and polychlorodibenzofurans in urban incinerator emissions. In: Hutzinger, O; Frei, RW; Merian, E; et al; eds. Chlorinated dioxins and related compounds. New York, NY: Pergamon Press.

Ling, H; Diamond, M; Mackay, D. (1993) Application of the QWASI fugacity/aquivalence model to assessing sources and fate of contaminants in Hamilton Harbour. Journal of Great Lakes Research 19(3):582-602.

Liss, PS; Slater, PG. (1974) Flux of gases across the air-sea interface. Nature 247:181-184.

Lockheed Martin Corp. (1998) Urbanized areas rainfall. EPA Contract No. 68-C5-0091.

Lockwood, LF; Ansel, G; Haddad, PO. (1981) Magnesium and magnesium alloys. In: Kirk-Othmer encyclopedia of chemical technology. 3rd ed. New York, NY: John Wiley and Sons; pp. 570-615.

Löfroth, G; Zebühr, Y. (1992) Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDFs) in mainstream and sidestream cigarette smoke. Bull Environ Contam Toxicol 48:789-794.

Lorang, PA. (1996) Comments on the API document: a study to quantify on-road emissions of dioxins and furans from mobile sources: phase 2. Memorandum dated December 1996. U.S. Environmental Protection Agency, National Vehicle and Fuel Emissions Laboratory, Ann Arbor, MI.

Lorber, M; Braverman, C; Gehring, P; et al. (1996) Soil and air monitoring in the vicinity of a municipal solid waste incinerator, part I: soil monitoring. Organohalogenhalogen Compounds 28:255-261.

Lorenz, W; Wichmann, H; Bahadir, M. (1996) Balancing of the release of polychlorinated dibenzo-p-dioxins and dibenzofurans in fire accidents: a contribution to the discussion. Reinhaltung der Luft. 56:49-53.

LUA (Landesumweltamt Nordrhein-Westfalen). (1997) Identification of relevant industrial sources of dioxins and furans in Europe. Materialien No. 43. North Rhine-Westphalia State Environment Agency, Essen, Germany. ISSN 0947-5206.

Luijk, R; Govers, HA; Neilssen, L. (1992) Formation of polybrominated dibenzofurans during extrusion of high impact polystyrene/decabromodiphenyl ether/antimony (III) oxide. Environ Sci Technol 26(11):2191-2198.

Luijk, R; Akkerman, DM; Slot, P; et al. (1994) Mechanism of formation of polychlorinated dibenzo-p-dioxins and dibenzofurans in the catalyzed combustion of carbon. Environ Sci Technol 28:312-321.

Lustenhouwer, JA; Olie, K; Hutzinger, O. (1980) Chlorinated dibenzo-p-dioxins and related compounds in incinerator effluents: a review of measurements and mechanisms of formation. Chemosphere 9:501-522.

Luthe, C; Karidio, I; Uloth, V. (1996) Controlling dioxins emissions in coastal power boilers: a status report. Pulp and Paper Canada 97(9):76-82.

Luthe, C; Karidio, I; Uloth, V. (1998) Dioxins formation in salt-laden power boilers: a mass balance. Chemosphere 36(2):231-249.

Lykins, BW; Clark, R; Cleverly, DH. (1987) Polychlorinated dioxin and furan discharge during carbon reactivation. Journal of Environmental Engineering 114(2): 330-316.

Malisch, R. (1994) Determination of PCDD/PCDF in PCB products and milk samples; correlation between PCB- and PCDD/PCDF-contamination of milk samples. Organohalogen Compounds 20:209-214.

Malloy, TA; Goldfarb, TD; Surico, MTJ. (1993) PCDDs, PCDFs, PCBs, chlorophenols (CPs) and chlorobenzenes (CBzs) in samples from various types of composting facilities in the United States. Chemosphere 27(1-3):325-334.

Maniff, K; Lewis, M. (1988) MISA monitoring discovers dioxins and furans in wastewater stream of petroleum refinery. Ontario Ministry of the Environment Communique, Ontario, Canada.

Mannsville. (1983) Mannsville chemical products synopsis. Cortland, NY: Mannsville Chemical Products Corp. December 1983.

Marklund, S; Rappe, C; Tysklind, M; et al. (1987) Identification of polychlorinated dibenzofurans and dioxins in exhausts from cars run on leaded gasoine. Chemosphere 16(1):29-36.

Marklund, S; Andersson, R; Tysklind, M; et al. (1989) Emissions of PCDDs and PCDFs from a PVC-fire in Holmsund, Sweden. Chemosphere 18(1-6):1031-1038.

Marklund, S; Andersson, R; Tysklind, M; et al. (1990) Emissions of PCDDs and PCDFs in gasoline and diesel fueled cars. Chemosphere 20(5):553-561.

Masunaga, S; Takasuga, T; Nakanishi, J. (2001) Dioxin and dioxin-like PCB impurities in some Japanese agrochemical formulations. Chemosphere 44:873-885.

Mathur, DB; Stephenson, MJ; Wenning, RJ; et al. (1997) PCDD/PCDFs in storm water outfalls adjacent to urban areas and petroleum refineries in San Francisco Bay, California, USA. Organohalogen Compounds 32:1-5.

Matsueda, T; Kurokawa, Y; Nakamura, M; et al. (1994) Concentrations of PCDDs, PCDFs and coplanar PCBs in cigarettes from various countries. Organohalogen Compounds 20:331-334.

McAloon, K. (2003) Memorandum: 2000 medical waste incinerator (MWI) update for sources and environmental releases of dioxin-like compounds in the United States: year 2000 update. Versar, Inc., Springfield, VA.

McCord, AT. (1981) A study of the emission rate of volatile compounds from lagoons.
Presented at the 5th National Conference on Management of Uncontrolled Hazardous Waste Sites, Washington, DC, October 28–30.

McCrady, JK; Maggard, SP. (1993) Uptake and photodegradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin sorbed to grass foliage. Environ Sci Technol 27:343-350.

McLachlan, M. (1996) Bioaccumulation of hydrophobic chemicals in agricultural food chains. Environ Sci Technol 30:252-259.

McLachlan, MS; Welsch-Pausch, K; Tolls, J. (1995) Field validation of a model of the uptake of gaseous SOC in *Lolium multiflorum* (rye grass). Environ Sci Technol 29(8):1998-2004.

Merk, M; Schramm, KW; Lenoir, D; et al. (1995) Determination of the PCDD/F concentration in the fumes from a PVC fire. Organohalogen Compounds 23:491-494.

Metal Producing. (1991) Sinter plant roundup. 33 Metal Producing 29(5):24.

Metal Producing. (1996) Census of the North American steel industry. 33 Metal Producing 34(3):40-52.

Mill, T; Rossi, M; McMillen, D; et al. (1987) Photolysis of tetrachlorodioxin and PCBs under atmospheric conditions. Internal report prepared by SRI International for U.S. Environmental Protection Agency, Office of Health and Environmental Assessment, Washington, DC.

Miller, A. (1993) Dioxin emissions from EDC/VCM plants. Environ Sci Technol 27:1014-1015.

Miller, GC; Hebert, VR; Miille, MJ; et al. (1989) Photolysis of octachlorodibenzo-p-dioxin on soils: production of 2,3,7,8-TCDD. Chemosphere 18:1265-1274.

Milligan, MS; Altwicker, ER. (1995) Mechanistic aspects of the de novo synthesis of polychlorinated dibenzo-p-dioxins and furans in fly ash from experiments using isotopically labeled reagents. Environ Sci Technol 29:1353-1358.

Milligan, MS; Altwicker, ER. (1996) Chlorophenol reactions on fly ash. Equilibrium surface coverage and global kinetics. Environ Sci Technol 30:230-236.

Mitchell, D; Loader, A. (1993) Investigation of pollutant emissions from crematoria. United Kingdom. Warren Spring Laboratory. Report No. LR908(PA).

Mitchell, W; Suggs, J. (1998) Emission factors for the disposal of energetic materials by open burning and open detonation (OB/OD). National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC; EPA/600/R-98/103.

Miyabara, Y; Hashimoto, S; Sagai, M; et al. (1999) PCDDs and PCDFs in vehicle exhaust particles in Japan. Chemosphere 39:143-150.

Morimoto, K; Kenji, T. (1995) Effect of humic substances on the enzymatic formation of OCDD from PCP. Organohalogen Compounds 23:387-392.

Muir, CG; Yarechewski, AL.; Corbet, RL; et al. (1985) Laboratory and field studies on the fate of 1,3,6,8 - tetrachlorodibenzo-p-dioxin in soil and sediments. J Agric Food Chem 33:518-523.

Musdalslien, VI; Nokleby, PH; Wallevik, O. (1998) Formation of dioxins from carbonaceous materials in production of anhydrous magnesium chloride. Organohalogen Compounds 36:81-84.

Muto, H; Takizawa, Y. (1989) Dioxins in cigarette smoke. Archives of Environmental Health 44(3):171-174.

Muto, H; Takizawa, Y. (1992) Potential health risk via inhalation/ingestion exposure to polychlorinated dibenzo-p-dioxins and dibenzofurans. Bull Environ Contam Toxicol 49:701-707.

Näf, C; Broman, D; Ishaq, R; et al. (1990) PCDDs and PCDFs in water, sludge and air samples from various levels in a waste water treatment plant with respect to composition changes and total flux. Chemosphere 20(10-12):1503-1510.

Naikwadi, KP; Karasek, FW. (1989) Prevention of PCDD formation in MSW incinerators by inhibition of catalytic activity of fly ash produced. Chemosphere 19(1-6):299-304.

Nakamura, M; Matsueda, T; Kurokawa, Y; et al. (1994) Levels and profiles of CDDs and PCDFs in soils and plants. Organohalogen Compounds 20:103-106.

NATO (North Atlantic Treaty Organization). (1988) Pilot study on international information

exchange on dioxins and related compounds: emissions of dioxins and related compounds from combustion and incineration sources. North Atlantic Treaty Organization, Committee on the Challenges of Modern Society. Report #172.

NCASI (National Council of the Paper Industry for Air and Stream Improvement). (1993) Summary of data reflective of pulp and paper industry progress in reducing the TCDD/TCDF content of effluents, pulps and wastewater treatment sludges. New York, NY.

NCASI (National Council of the Paper Industry for Air and Stream Improvement). (1995) NCASI summary of PCDD/F emission from wood residue and black liquor combustion. Attachment 2 to comments on EPA's external review draft Estimating Exposures to Dioxin-Like Compounds. Submitted January 13, 1995, New York, NY.

Nestrick, TJ; Lamparski, LL. (1982) Isomer-specific determination of chlorinated dioxins for assessment of formation and potential environmental emission from wood combustion. Anal Chem 54(13):2292-2299.

Nestrick, TJ; Lamparski, LL. (1983) Assessment of chlorinated dibenzo-p-dioxin formation and potential emission to the environment from wood combustion. Chemosphere 12(4/5):617-626.

Nestrick, TJ; Lamparski, LL, Crummett, WB. (1987) Thermolytic surface-reaction of benzene and iron (III) chloride to form chlorinated dibenzo-p-dioxins and dibenzofurnas. Chemosphere 16(4):777-790.

Nies, L; Vogel, TM. (1990) Effects of organic substrates on dechlorination of Aroclor 1242 in anaerobic sediments. Applied and Environmental Microbiology 56(9):2612-2617.

Nito, SN; Akimoto, Y; Imagawa,T; et al. (1997) Comparative study on formations of polychlorinated dibenzo-p-dioxin, chlorinated dibenzofuran and related compounds by pyrolysis of some precursors on unused sand for fluidized bed incinerator and long term used sand. Chemosphere 35:1717-1727.

NOAA (2004) Data retrieval from National Climatic Data Center. Available online at http//www1.ncdc.noaa.gov/drd964x.pcp.txt.

NRC (National Research Council). (2000) Waste incineration and public health. Committee on Health Effects of Waste Incineration, Board of Environmental Studies and Toxicology, Commission on Life Sciences. Washington DC: National Academy Press.

NRC (National Research Council). (2002) Biosolids applied to land. Advancing standards and practices. Committee on Toxicants and Pathogens in Biosolids Applied to Land, Board on Environmental Studies and Toxicology, Division on Earth and Life Sciences. Washington, DC: National Academies Press.

Oberg, LG; Rappe, C. (1992) Biochemical formation of PCDD/Fs from chlorophenols. Chemosphere 25(1-2):49-52.

Oberg, T; Warman, K; Berstrom, J. (1989) Production of chlorinated aromatics in the post-combustion zone and boiler. Chemosphere 19(1-6):317-322.

Oberg, LG; Glas, B; Swanson, SE; et al. (1990) Peroxidase-catalyzed oxidation of chlorophenols to polychlorinated dibenzo-p-dioxins and dibenzofurans. Arch Environ Contam Toxicol 19:930-938.

Oberg, LG; Andersson, R; Rappe, C. (1992) De novo formation of hepta- and octachlorodibenzo-p-dioxins from pentachlorophenol in municipal sewage sludge. Organohalogen Compounds 9:351-354.

Oberg, LG; Wagman, N; Andersson, R; et al. (1993) De novo formation of PCDD/Fs in compost and sewage sludge: a status report. Organohalogen Compounds 11:297-302.

Oberg, LG, Wagman, N; Koch, M; et al. (1994) Polychlorinated dibenzo-p-dioxins, dibenzofurans and non-ortho PCBs in household organic-waste compost and mature garden waste compost. Organohalogen Compounds 20:245-250.

Oehme, M; Mano, S; Bjerke, B. (1989) Formation of polychlorinated dibenzofurans and dibenzo-p-dioxins by production processes for magnesium and refined nickel. Chemosphere 18(7-8):1379-1389.

Oehme, M; Larssen,S; Brevik, EM. (1991) Emission factors of PCDD/CDF for road vehicles obtained by a tunnel experiment. Chemosphere 23:1699-1708.

O'Keefe, PW; Smith, RM. (1989) PCB capacitor/transformer accidents. In: Kimbrough, RD; Jensen, AA; eds. Halogenated biphenyls, terphenyls, napthalenes, dibenzodioxins and related products. New York, NY: Elsevier Science Publishers.

Opatick, RE. (1995) Chlorobenzene Producers Association comments on EPA's external review draft Estimating Exposures to Dioxin-Like Compounds. Chlorobenzene Producers Association, Washington, DC. January 10.

Orazio, CE; Kapila, S; Puri, RK; et al. (1992) Persistence of chlorinated dioxins and furans in the soil environment. Chemosphere 25(7-10):1469-1474.

Ozvacic, V. (1985) A review of stack sampling methodology for PCDDs/PCDFs. Chemosphere 15(9-12):1173-1178.

Paciorek, KL; Kratzer, RH; Kaufman, J; et al. (1974) Oxidative thermal decomposition of poly (vinyl chloride) compositions. J Appl Polym Sci 18:3723-3729.

Palmer, FH; Sapudar, RA; Heath, JA; et al. (1988) Chlorinated dibenzo-p-dioxin and dibenzofuran contamination in California from chlorophenol wood preservative use. California State Water Resources Control Board. Report No. 88-5WQ.

Papke, O; Ball, M; Lis, ZA; et al. (1989) PCDD and PCDF in indoor air in kindergartens in Northern W. Germany. Chemosphere 18:617-626.

Pardue, JH; Delaune, RD; Patrick, WH. (1988) Effect of sediment pH and oxidation-reduction potential on PCB mineralization. Water, Air and Soil Pollution 37:439-447.

Paterson, S; Mackay, D; Bacci, E; et al. (1991) Correlation of the equilibrium and kinetics of leaf-air exchange of hydrophobic organic chemicals. Environ Sci Technol 25(5):866-871.

Patterson, SH; Murray, HH. (1984) Kaolin, refractory clay, ball clay, and halloysite in North America, Hawaii, and the Caribbean region. U.S. Geological Survey. Professional Paper No. 1306.

Paustenbach, D; Wenning, RJ; Lau, V; et al. (1992) Recent developments on the hazards posed by 2,3,7,8-TCDD in soil: implications for setting risk-based cleanup levels at residential and industrial sites. Journal of Toxicology and Environmental Health 36:103-149.

Paustenbach, DJ; Wenning, RJ; Mathur, D; et al. (1996) PCDD/PCDFs in urban stormwater discharged to San Francisco Bay, California, USA. Organohalogen Compounds 28:111-116.

PCA (Portland Cement Association). (2001) U.S. and Canadian Portland Cement Industry: plant information summary. Skokie, Illinois.

Pechan and Associates. (2002) Draft technical memorandum no. 1: Survey results for open burning activity and rule effectiveness in the MANE-VU region. Prepared for Mid-Atlantic Regional Air Management Association.

Pechan and Associates. (2004) Final technical memorandum numbers 1: A survey results for open burning activity and rule effectiveness in the MANE-VU Region, and 2: Activity data and emission estimates for residential open burning in the MANE-VU Region.

Persson, PE; Bergström, J. (1991) Emission of chlorinated dioxins from landfill fires. In: Proceedings of the Sardinia 91: Third International Landfill Symposium. Vol. 1:1635-1645.

Peters, A. (1988) Minerals yearbook: iron and steel. U.S. Geological Survey, Geologic Division, Reston, VA.

Plimmer, JR. (1980) Herbicides. In: Kirk-Othmer encyclopedia of chemical technology. 3rd ed. Vol. 12. pp. 297-351.

Pohlandt, K; Marutzky, R. (1994) Concentration and distribution of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in wood ash. Chemosphere 28(7):1311-1314.

Prinn, RG; Weiss, RF; Miller, BR; et al. (1995) Atmospheric trends and lifetime of CH_3CCl_3 and global OH concentrations. Science 269:187–192.

Procaccini, C; Bozzelle, JW; Longwell, JP; et al. (2003) Formation of chlorinated aromatics by reactions of Cl*, Cl_2 and Hcl with benzene in the cool-down zone of a combuster. Environ Sci Technol 37:1684-1689.

Puri, RK; Clevenger, TE; Kapila, S; et al. (1989) Studies of parameters affecting translocation of tetrachlorodibenzo-p-dioxin in soil. Chemosphere 18(1-6):1291-1296.

Quab, U; Fermann, M. (1997) Identification of relevant industrial sources of dioxins and furans in Europe. North Rhine-Westphalia State Environment Agency. Report No. 43.

Quensen, JF; Tiedje, JM; Boyd, SA. (1988) Reductive dechlorination of polychlorinated biphenyls by anaerobic microorganisms from sediment. Science 242:752-754.

Quensen, JF; Boyd, SA; Tiedje, JM. (1990) Dechlorination of four commercial polychlorinated biphenyl mixtures (Aroclors) by anaerobic microorganisms from sediments. Appl Environ Microbiol 56(1):2360-2369.

Radian Corporation. (1991) Results of dioxin testing on the catalytic reformer unit #1 exhaust Texas Refinery; Bakersfield, California. Sacramento, CA.

Raghunathan, K; Gullett, BK (1996) Role of sulfur in reducing PCDD and PCDF formation. Environ Sci Technol 30(6):1827-1834.

Randall, D. (1995) Memorandum dated April 8, 1995, from David Randall and Brian Hardee, Midwest Research Institute, Cary, North Carolina, to Richard Copland, Combustion Group, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC. Subject: Emission factors for medical waste incinerators (MWIs), EPA Contract No. 68-01-0115. EPA Docket Number A-91-61; IV B 042.

Rappe, C. (1991) Sources of human exposure to CDDs and PCDFs. In: Gallo, M; Scheuplein, R; van der Heiden, K; eds. Biological basis for risk assessment of dioxin and related compounds. Plainview, NY: Cold Spring Harbor Laboratory Press. Banbury Report No. 35.

Rappe, C. (1992a) Sources of exposure, environmental levels and exposure assessment of PCDDs and PCDFs. Organohalogen Compounds 9:5-8.

Rappe, C. (1992b) Sources of PCDDs and PCDFs. Introduction. Reactions, levels, patterns, profiles and trends. Chemosphere 25(1-2):41-44.

Rappe, C. (1993) Sources of exposure, environmental concentrations and exposure assessment of PCDDs and PCDFs. Chemosphere 27(1-3):211-225.

Rappe, C. (1995) Comments on EPA's external review draft Estimating Exposures to Dioxin-Like Compounds. Comments submitted to EPA by the Integrated Waste Services Association; Washington, DC.

Rappe, C; Marklund, S; Buser, HR; et al. (1978a) Formation of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) by burning or heating chlorophenates. Chemosphere 3:269-281.

Rappe, C; Gara, A; Buser, HR. (1978b) Identification of polychlorinated dibenzofurans (PCDFs) in commercial chlorophenol formulations. Chemosphere 12:981-991.

Rappe, C; Kjeller, LO; Bruckmann, P; et al. (1988) Identification and quantification of PCDD/CDFs in urban air. Chemosphere 17(1):3-20.

Rappe, C; Kjeller, LO; Andersson, R. (1989a) Analyses of PCDDs and PCDFs in sludge and water samples. Chemosphere 19(1-6):13-20.

Rappe, C; Swanson, S; Gals, B; et al. (1989b) Formation of PCDDs and PCDFs by the chlorination of water. Chemosphere 19(12):1875-1880.

Rappe, C; Glas, B; Kjeller, LO; et al. (1990a) Levels of PCDDs and PCDFs in products and effluent from the Swedish pulp and paper industry and chloralkali process. Chemosphere 20(10-12):1701-1706.

Rappe, C; Andersson, R; Lundström, K; et al. (1990b) Levels of polychlorinated dioxins and dibenzofurans in commercial detergents and related products. Chemosphere 21(1-2):43-50.

Rappe, C; Kjeller, LO; Kulp, SE. (1990c) Sampling and analysis of PCDDs and PCDFs in surface water and drinking water at 0.001 ppq levels. Organohalogen Compounds 2:207-210.

Rappe, C; Kjeller, L; Kulp, S; et al. (1991) Levels, profile and pattern of PCDDs and PCDFs in samples related to the production and use of chlorine. Chemosphere 23(11-12):1629-1636.

Rappe, C; Anderson, R; Karlaganis, G; et al. (1994) PCDDs and PCDFs in samples of sewage sludge from various areas in Switzerland. Organohalogen Compounds 20:79-84.

Rappe, C; Anderson, R; Bonner, M; et al. (1998) PCDDs and PCDFs in municipal sewage sludge and effluent from POTW in the State of Mississippi, USA. Chemosphere 36:315-328.

Ree, KC; Evers, EHG; Van Der Berg, M. (1988) Mechanism of formation of polychlorinated dibenzo(p)dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from potential industrial sources. Toxicological and Environmental Chemistry 17:171-195.

Remmers, J; Dupuy, A; McDaniel, D; et al. (1992) Polychlorinated dibenzo-p-dioxin and dibenzofuran contamination in chloranil and carbazole violet. Chemosphere 25(7-10):1505-1508.

Rhee, GY; Bush, B; Brown, MP; et al. (1989) Anaerobic biodegradation of polychlorinated biphenyls in Hudson River sediments and dredged sediments in clay encapsulation. Water Research 23(8):957-964.

Riederer, M. (1990) Estimating partitioning and transport of organic chemicals in the foliage/atmosphere system: discussion of a fugacity-based model. Environ Sci Technol 24(6):829-837.

Rieger, R; Ballschmiter, K. (1992) Search for sources of CLxDD/CLxDF in sewage sludge of mixed industrial/domestic origin. Organohalogen Compounds 9:203-206.

Riggs, KB; Brown, TD; Schrock, ME. (1995) PCDD/PCDF emissions from coal-fired power plants. Organohalogen Compounds 24:51-54.

Rigo, H.G. (1998) Dioxin and chlorine: new evidence of no material relationship in a commercial scale system. Organohalogen Compounds 36:261-264.

Rigo, GH; Chandler, JA; Lanier, SW. (1995) The relationship between chlorine and dioxin emissions from waste combustors. In: Kilgroe, J; ed. Solid waste management: thermal treatment & waste-to-energy technologies. Proceedings of an international specialty conference sponsored by the Air and Waste Management Association, Washington, DC. April 18-21, 1995. ASME/CRTD. Vol. 36.

RIPA (Reusable Industrial Packaging Association). (1997) 1997 Statistics as found on the Reusable Industrial Packaging Association (RIPA) webpage. Available online at http://www.reusablepackaging.org/Stats.html.

Risatti, JB. (1992) Rates of microbial dechlorination of polychlorinated biphenyls (PCBs) in anaerobic sediments from Waukegan Harbor. The Illinois Hazardous Waste Research and Information Center, Champaign, IL. HWRIC RR-061.

Rotard, W. (1993) Fires. In: Current views on the impact of dioxins and furans on human health and the environment. Toxicology Forum, Inc., Washington, DC.

Rubber Manufacturers Association. (2002) Statistical report on scrap tire markets. Rubber Manufacturers Association, Washington, DC. Available online at http://www.rma.org/scrap_tires/.

Rubin, A; White, C. (1992) Computer printout from National Sewage Sludge Survey Data Base. U.S. Environmental Protection Agency, Office of Science and Technology, Health and Ecological Criteria Division, Sludge Risk Assessment Branch. December 21, 1992.

Ruokojärvi, P; Ettala, M; Rahkonen, P; et al. (1995) Polychlorinated dibenzo-p-dioxins and -furans (PCDDs and PCDFs) in municipal waste landfill fires. Chemosphere 30(9):1697-1708.

Safe, S. (1994) Polychlorinated biphenyls (PCBs): environmental impact, biochemical and toxic responses, and implications for risk assessment. Crit Rev Toxicol 21(1):51-88.

SAIC (Science Applications International Corporation). (1994) Identification of sources of dioxin in catalytic reformers and potential mitigation. U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH. EPA Contract No. 68-C0-0044.

Sakai, S; Hiraoka, M; Takeda, N; et al. (1993a) Coplanar PCBs and PCDD/PCDFs in municipal waste incineration. Chemosphere 27(1-3):233-240.

Sakai, S; Hiraoka, M; Takeda, N; et al. (1993b) On emission and formation of non-ortho CBs and mono-ortho CBs in municipal waste incineration. Organohalogen Compounds 11:245-248.

Sakai, S; Hiraoka, M; Takeda, N; et al. (1994) Behavior of coplanar PCBs in oxidative condition of municipal waste incineration. Organohalogen Compounds 20:309-313.

Sakai, S; Hayakawa, K; Takatsuki, H; et al. (2001) Dioxin-like PCBs released from waste incineration and their deposition flux. Environ Sci Technol 35:3601-3607.

Santl, H; Gruber, L; Stöhrer, E. (1994) Some new sources of polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) in waste papers and recycled pulps. Chemosphere 29(9-11):1995-2003.

Schäfer, K; McLachlan, MS; Reissinger, M; et al. (1993) An investigation of PCDD/F in a composting operation. Organohalogen Compounds 11:425-428.

Schatowitz, B; Brandt, G; Gafner, F; et al. (1993) Dioxin emissions from wood combustion. Organohalogen Compounds 11:307-310.

Schaub, WM; Tsang, W. (1983) Physical and chemical properties of dioxins in relation to their disposal. In: Tucker, RE; Young, AL, Gray, A.P; eds. Human and environmental risks of chlorinated dioxins and related compounds. New York, NY: Plenum Press.

Schecter, A; Papke, O; Isaac, J; et al. (1997) 2,3,7,8 Chlorine substituted dioxin and dibenzofuran congeners in 2,4-D, 2,4,5-T and pentachlorophenol. Organohalogen Compounds 32:51-55.

Schoonenboom, MH; Tromp, PC; Olie, K. (1993) The formation of coplanar PCBs, PCDDs and PCDFs in a fly-ash model system. Organohalogen Compounds 11:277-280.

Schramm, K; Reischl, A; Hutzinger, O. (1987) UNITTree: A multimedia compartment model to estimate the fate of lipophilic compounds in plants. Chemosphere 16:2653-2663.

Schreiner, M; Reifenhäuser, W; Vierle, O. (1992) Measurements of the emission concentrations of PCDD/PCDF in a digester-torch of a municipal sewage plant. Organohalogen Compunds 9:255-257.

Schreiner, G; Schimmel, H; Ballschmiter, K. (1995) Influence of the substitution pattern on the microbial degradation of mono- to tetrachlorinated dibenzofurans and dibenzodioxins. Organohalogen Compounds 24:43-46.

Schulz, DE; Petrick, G; Duinker, JC. (1989) Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. Environ Sci Technol 23:852-859.

Schwartz, TR; Tillitt, DE; Feltz, KP; et al. (1993) Determination of mono- and non--*o-o'*-chlorine substituted polychlorinated biphenyls in Aroclors and environmental samples. Chemosphere 26(8):1443-1460.

Schwind, K-H; Thoma, H; Hutzinger, O; et al. (1991) Emission halogenierter dibenzodioxine (PXDD) und dibenzofurane (PXDF) aus verbrennungsmotoren [Emission of halogenated dibenzo-p-dioxins (PCDD) and dibenzofurans(PCDF) from combustion engines]. UWSF-Z. Umweltchem. Oekotox. 3, 291-298. [English translation]

Schwind, KH; Hosseinpour, J; Fiedler, H; et al. (1995) Human exposure to consumer products: analysis of chlorinated organic compounds in candles and their exhaust fumes. Organohalogen Compounds 26:113-116.

Secor International, Inc. (1995a) Emission measurement results for furans and dioxins from the main stack at the Phelps Dodge-Hidalgo Smelter, Playos, New Mexico. Prepared for the Phelps Dodge Mining Company by Secor International, Inc., Redmond, WA.

Secor International, Inc. (1995b) Furans and dioxins emission measurement results for Cyprus Miami Mining Corporation. Prepared for the Cypress Amax Minerals Company by Secor International, Inc., Redmond, WA.

Sedlak, DL; Andren, AW. (1991) Aqueous-phase oxidation of polychlorinated biphenyls by hydroxyl radicals. Environ Sci Technol 25(8):1419-1427.

Sewart, A; Harrad, SJ; McLachlan, MS; et al. (1995) PCDD/Fs and non-o-PCBs in digested U.K. sewage sludges. Chemosphere 30(1):51-67.

Shane, BS; Henry, CB; Hotchkiss, JH; et al. (1990) Organic toxicants and mutagens in ashes from eighteen municipal refuse incinerators. Arch Environ Contam Toxicol 19:665-673.

Shaub, WM; Tsang, W. (1983) Dioxin formation in incinerators. Envrion Sci Technol 17:721-730.

Shibata, E; Yamamoto, S; Kasai, E; Nakamura, E. (2003) Formation behavior of PCDD/Fs in PVC pyrolysis with copper oxide. Chemosphere 50:1235-1242.

Shin, K-J; Chang, Y-S. (1999) Characterization of polychlorinated dibenzo-p-dioxins, dibenzofurans, biphenyls, and heavy metals in fly ash produced from Korean municipal solid waste incinerators. Chemosphere 38:2655-2666.

Sidhu, S. (1999) Role of aliphatic precursors in the formation mechanism of PCDD/F, PCB, and PCN. Organohalogen Compounds 41:59-62.

Silk, PJ; Lonergan, GC; Arsenault, TL; et al. (1997) Evidence of natural organochlorine formation in peat bogs. Chemosphere 35:2865-2880.

Simonich, SL; Hites, RA. (1994) Vegetation-atmosphere partitioning of polycyclic aromatic hydrocarbons. Environ Sci Technol 28(5):939-943.

Sivils, LD; Kapila, S; Yan, Q; et al. (1994) Studies on gas-phase phototransformation of polychlorinated dibenzo-p-dioxins. Organohalogen Compounds 19:349-353.

Sivils, LD; Kapila, S; Yan, Q; et al. (1995) Studies on vapor phase phototransformation of polychlorinated dibenzo-p-dioxins (PCDDs): effect of environmental parameters. Organohalogen Compounds 24:167-172.

Smith, RM; O'Keefe, PW; Hilker, D; et al. (1995) Direct and indirect contribution of atmospheric PCDDs and PCDFs to Hudson River National Estuarine Research Reserve sediment cores. Organohalogen Compounds 24:141-145.

Solid Waste Technologies. (1994) A comprehensive status report on MSW waste-to-energy facilities, incinerators refuse-derived-fuel, and tire processing facilities throughout North America. Kansas City, MO: HCI Publications.

Someshwar, AV; Pinkerton, JE. (1992) Wood processing industry. In: Buonicore, AJ; Davis, WT; eds. Air pollution engineering manual. Air and Waste Management Association. New York, NY: Van Nostrand Reinhold. pp. 835-847.

St. Lawrence County. (1993) Legal open burning and on-premises burial of solid waste in St. Lawrence County, NY: The environmental impacts. St. Lawrence County Planning Office, Canton, NY.

Stanmore, BR. (2004) The formation of dioxins in combustion systems. Combustion and Flame 136:398-427.

Stehl, RH; Lamparski, LL. (1977) Combustion of several 2,4,5-trichlorophenoxy compounds: formation of 2,3,7,8-tetrachlorodibenzo-p-dioxin. Science 197:1008-1009.

Stehl, RH; Papenfuss, RR; Bredeweg, RA; et al. (1973) The stability of pentachlorophenol and chlorinated dioxins to sunlight, heat, and combustion. In: Blair, EH; ed. Chlorodioxins: origin and fate. American Chemical Society, Washington, DC.

Stevens, JL; Jones, KC. (2003) Quantification of PCDD/F concentrations in animal manure and comparison of the effects of the application of cattle manure and sewage sludge to agricultural land on human exposure to PCDD/F. Chemosphere 50:1183-1191.

Stieglitz, L; Zwick, G; Beck, J; et al. (1989) Carbonaceous particles in fly ash: a source for the de novo synthesis of organochlorocompounds. Chemosphere 19(1-6):283-290.

Stieglitz, L; Vogg, H; Zwick, G; et al. (1991) On formation conditions of organohalogen compounds from particulate carbon of fly ash. Chemosphere 23(8-10):1255-1264.

Storherr, RW; Watts, RR; Gardner, AM; et al. (1971) Steam distillation technique for the analysis of 2,3,7,8-tetrachlorodibenzo-p-dioxin in technical 2,4,5-T. Journal of the AOAC 54(1):218-219.

Stowe, RA. (1996) A needle in a haystack. Environmental Protection. August 1996. pp. 22-25.

Strachan, WMJ; Eisenreich, SJ. (1988) Mass balancing of toxic chemicals in the Great Lakes: the role of atmospheric deposition. International Joint Commission, Windsor, Ontario.

Strandell, ME; Lexen, KM; deWit, CA; et al. (1994) The Swedish dioxin survey: summary of results from PCDD/F and coplanar PCB analyses in source-related samples. Organohalogen Compounds 20:363-366.

Stringer, RL; Costner, P; Johnston, PA. (1995) PVC manufacture as a source of PCCD/Fs. Organohalogen Compounds 24:119-123.

Strong, B; Hanks, K. (1999) Memorandum "Emissions inventory for hospital, medical, infectious waste incinerators covered by the proposed Section 11(d)/129 Federal Plan." EPA Docket number A-98-24, item II-B-1.

Stuart, B; Carter, D; Hoodless, RA. (1993) Report on the examination of sewage sludges for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Laboratory of the Government Chemist, London, England.

Svenson, A; Kjeller, LO; Rappe, C. (1989) Enzyme-mediated formation of 2,3,7,8-tetrasubstituted chlorinated dibenzodioxins and dibenzofurans. Environ Sci Technol 23(7):900-902.

Sverdrup Corp. (1991) Chemetco, Inc., compliance testing, final report. Sverdrup Corp., St. Louis, MO.

Swackhamer, DL; Armstrong, DE. (1986) Estimation of the atmospheric and nonatmospheric contributions and losses of polychlorinated biphenyls for Lake Michigan on the basis of sediment records of remote lakes. Environ Sci Technol 20(9):879-883.

Swackhamer, DL; McVeety, BD; Hites, RA. (1988) Deposition and evaporation of polychlorobiphenyl congeners to and from Siskiwit Lake, Isle Royale, Lake Superior. Environ Sci Technol 22(6):664-672.

Sweden's Office of Nature Conservancy. (1991) Organochlorine compounds from dishwashing detergents and bleach? Sweden Office of Nature Conservancy, Solna, Sweden. Report No. 4009.

Takeda, N; Takaoka, M; Fujiwara, T; et al. (1998) Research on PCDDs/DFs emissions from crematories in Japan. Organohalogen Compounds 36:167-170.

Takeda, N; Takaoka, M; Fujiwara, T; et al. (2001) Measures to prevent emissions of PCDDs/DFs and coplanar PCBs from crematories in Japan. Chemosphere 43:763-771.

Takizawa, Y; Asada, S; Muto, H. (1994) Dioxins in dust fall and volcanic ash from the active volcanos Fugendake and Sakurajima. Organohalogen Compounds 20:359-362.

Tanabe, S. (1988) PCB problems in the future: foresight from current knowledge. Environ Pollut 50:5-28.

Tanabe, S; Kannan, N; Wakimoto, T; et al. (1987) Method for the determination of three toxic non-orthochlorine substituted coplanar PCBs in environmental samples at part-per-trillion levels. Intern J Environ Anal Chem 29:199-213.

Tashiro, C; Clement, RE; Stocks, BJ; et al. (1990) Preliminary report: dioxins and furans in prescribed burns. Chemosphere 20:1533-1536.

Taylor, A; Zannes, M. (1996) The 1996 IWSA municipal waste combustion directory of United States facilities. Integrated Waste Services Association, Washington, DC.

The Aluminum Association, Inc. (1997) U.S. aluminum industry plant directory, November 1997. The Aluminum Association, Washington, DC.

The Tobacco Institute. (1995) Tobacco industry profile 1995. The Tobacco Institute, Washington, DC.

The Vinyl Institute. (1998) Dioxin characterization program. Phase I Report. The Vinyl Institute, Morristown, NJ.

Thiesen, J; Funcke, W; Balfanz, E; et al. (1989) Determination of PCDFs and PCDDs in fire accidents and laboratory combustion tests involving PVC-containing materials. Chemosphere 19(1-6):423-428.

Thoma, H; Hutzinger, O. (1989) Content and formation of toxic products in flame retardants. Presented at the Workshop on Brominated Aromatic Flame Retardants. Slokloster, Sweden; October 24-26, 1989. Sponsored by the Swedish Environmental Protection Agency.

Thomas, VM; Spiro, TG. (1995) An estimation of dioxin emissions in the United States. Toxicological and Environmental Chemistry 50:1-37.

Thomas, VM; Spiro, TG. (1996) The U.S. dioxin inventory: are there missing sources? Environ Sci Technol 30(2):82A-85A.

Thompson, TS; Clement, RE; Thornton, N; et al. (1990) Formation and emission of PCDDs/PCDFs in the petroleum refining industry. Chemosphere 20(10-12):1525-1532.

Thub, U; Popp, P; Ehrlich, C; et al. (1995) Domestic lignite combustion as source of polychlorodibenzodioxins and furans (PCDD/F). Chemosphere 31(2):2591-2604.

Tolls, J; McLachlan, MS. (1994) Partitioning of semivolatile organic compounds between air and *Lolium multiflorum* (Welsh rye grass). Environ Sci Technol 28(1):159-166.

Tosine, H; Clement, R; Osvacic, V; et al. (1983) Levels of chlorinated organics in a municipal incinerator. Presented at the 186th National Meeting of the American Chemical Society; August 28–September 2, Washington, DC. September, 1, 1983.

Towara, J; Hiller, B; Hutzinger, O; et al. (1992) PCDD/F in distillation residues from dry cleaning machines. Chemosphere 25:1509.

Trapp, S; Matthies, M; Scheunert, I.; et al. (1990) Modeling the bioconcentration of organic chemicals in plants. Environ Sci Technol 24:1246-1252.

TRRCPO (Two Rivers Region Council of Public Officials and Patrick Engineering, Inc.) (1994) Emission characteristics of burn barrels. Prepared for U.S. Environmental Protection Agency, Region V, Chicago, IL.

Tysklind, M; Rappe, C. (1991) Photolytic transformation of polychlorinated dioxins and dibenzofurans in fly ash. Chemosphere 23(8-10):1365-1375.

Tysklind, M; Söderström; Rappe, C; et al. (1989) PCDD and PCDF emissions from scrap metal melting processes at a steel mill. Chemosphere 19(1-6):705-710.

Tysklind, M; Carey, AE; Rappe, C; et al. (1992) Photolysis of OCDF and OCDD on soil. Organohalogen Compounds 8:293-296.

U.K. Department of the Environment. (1995). Comments on EPA's external review draft Estimating Exposures to Dioxin-Like Compounds. Submitted by the Department of the Environment, Food, and Rural Affaires, London, England.

Umlauf, G; Horstmann, M; Klein, P; et al. (1993) Mass balance of PCDD/F in a dry cleaning machine. Organohalogen Compounds 11:413-416.

Umweltbundesamt. (1996) Determination of requirements to limit emissions of dioxins and furans. Report from the Working Group of the Subcommittee Air/Technology of the Federal Government/Federal States Emission Control Committee. Berlin, Germany.

Urhahn, T; Ballschmiter, K. (1998) Chemistry of the biosynthesis of halogenated methanes: Cl-organohalogens as pre-industrial chemical stressors in the environment. Chemosphere 37:1017-1032.

U.S. Census Bureau. (2000) Census 2000. Washington, DC.

U.S. Census Bureau. (2001) Statistical abstract of the United States: 2001. Washington, DC.

USDA (U.S. Department of Agriculture). (1970) Restricting the use of phenoxy herbicides: costs to farmers. Economic Research Service and Agricultural Research Service, Washington, DC. Agricultural Economic Report No. 194.

USDA (U.S. Department of Agriculture). (1971) Farmer's use of pesticides in 1971 and quantities. Economics Research Service, Washington, DC. Agricultural Economic Report No. 252.

USDA (U.S. Department of Agriculture). (1995) Graphic highlights of natural resource trends in the United States between 1982 and 1992. U.S. Department of Agriculture, Natural Resources Conservation Service, National Resources Inventory, Washington, DC.

USDA (U.S. Department of Agriculture). (1997) Tobacco leaf and products statistics and analysis. U.S. Department of Agriculture, Economic Research Service, Washington, DC.

USDA (U.S. Department of Agriculture). (2003) National Resources Inventory 2001 Annual Report. Natural Resources Conservation Service, U.S. Department of Agriculture, Washington, DC.

U.S. Department of Health and Human Services. (1989) Toxicology and carcinogenesis studies of two pentachlorophenol technical-grade mixtures in B6C3F1 mice (feed studies). U.S. Department of Health and Human Services, National Toxicology Program, Research Triangle Park, NC. NIH Publication No. 89-2804.

U.S. DOC (U.S. Department of Commerce). (1990a) 1987 Census of manufactures. Smelting and refining of nonferrous metals and alloys. U.S. Bureau of the Census, Washington, DC. Report No. 33C-18.

U.S. DOC (U.S. Department of Commerce). (1990b) 1987 Census of manufacturers. Soap, cleaners, and toilet goods. U.S. Bureau of the Census, Washington, DC. Report No. MC-87-I-28D.

U.S. DOC (U.S. Department of Commerce). (1990c) 1987 Census of manufactures. Industrial inorganic chemicals. Bureau of the Census, Washington, DC. Report No. MC87-I-28A.

U.S. DOC (U.S. Department of Commerce). (1995a) 1992 Census of transportation. Truck inventory and use survey. U.S. Bureau of the Census, Washington, DC. Report No. TC92-T-52.

U.S. DOC (U.S. Department of Commerce). (1995b) Statistical abstract of the United States, 1995. 118th ed. Washington, DC.

U.S. DOC (U.S. Department of Commerce). (1995c) 1992 Census of manufactures. Smelting and refining of nonferrous metals and alloys. U.S. Bureau of the Census, Washington, DC. Report No. MC92-I-33C.

U.S. DOC (U.S. Department of Commerce). (1996) 1992 Economic census report series, disc 1G. U.S. Bureau of the Census, Washington, DC. Report No. CD-EC92-1G.

U.S. DOC (U.S. Department of Commerce). (1997) Statistical abstract of the United States, 1997. 117th ed. U.S. Bureau of the Census, Washington, DC.

U.S. DOC (U.S. Department of Commerce). (2002) International data base. U.S. Bureau of the Census. Available online at http://blue.census.gov/cgi-bin/ipc/idbagg.

U.S. DOC (U.S. Department of Commerce). (2003) Census 2000 Summary File 1 (SF 1) 100-Percent Data. U.S. Bureau of the Census, Washington DC.. Available online at http://factfinder.census.gov/servlet/DTTable?_ts=64261331968.

U.S. DOT (Department of Transportation) (2002) 2002 Status of the nation's highways, bridges, and transit: conditions and performance report to Congress. Federal Highway Administration, Federal Transit Administration, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1975) Production, distribution, use and environmental impact potential of selected pesticides. Office of Pesticide Programs and Office of Water and Hazardous Materials, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1977) Pesticide usage survey of agricultural, governmental, and industrial sectors in the United States, 1974. Office of Pesticide Programs, Washington, DC; EPA-540/9-78-007.

U.S. EPA (Environmental Protection Agency). (1980) Materials balance for chlorophenols. Level I-preliminary. Office of Toxic Substances, Washington, DC; EPA-560/13-80-004.

U.S. EPA (Environmental Protection Agency). (1982a) Development document for effluent limitations guidelines and standards for the iron and steel manufacturing point source category. Vol. II. Office of Water, Washington, DC; EPA-440/1-82/024.

U.S. EPA (Environmental Protection Agency). (1982b) Development document for effluent limitations guidelines and standards for the inorganic chemicals manufacturing point source category. Office of Water Regulations and Standards, Washington, DC; EPA 440/1-82/007.

U.S. EPA (Environmental Protection Agency). (1984) Thermal degradation products from dielectric fluids. Office of Toxic Substances, Washington, DC; EPA-560/5-84-009.

U.S. EPA (Environmental Protection Agency). (1987a) National dioxin study Tier 4: combustion sources. Engineering analysis report. Office of Air Quality Planning and Standards, Research Triangle Park, NC; EPA-450/4-84-014h.

U.S. EPA (Environmental Protection Agency). (1987b) Municipal waste combustion study. Characterization of the municipal waste combustion industry. Office of Air and Radiation, Washington, DC; EPA/530-SW-87-021b.

U.S. EPA (Environmental Protection Agency). (1987c) Hospital waste combustion study: Data gathering phase. Office of Air Quality Planning and Standards, Research Triangle Park, NC; EPA-450/3-88-017.

U.S. EPA (Environmental Protection Agency). (1987d) Locating and estimating air emissions from sources of polychlorinated biphenyls (PCB). Office of Air Quality Planning and Standards, Research Triangle Park, NC; EPA-450/4-84-007n.

U.S. EPA (Environmental Protection Agency). (1988a) Estimating exposure to 2,3,7,8-TCDD. Office of Health and Environmental Assessment, Washington, DC; EPA/600/6-88/005A.

U.S. EPA (Environmental Protection Agency). (1988b) U.S. EPA cooperative dioxin screening study. Office of Water Regulations and Standards, Washington, DC; EPA-440/1-88-025.

U.S. EPA (Environmental Protection Agency). (1988c) Pesticide assessment guidelines, subdivision D: product chemistry. Series 61-4, addendum 1 on data reporting. Office of Pesticide Programs, Washington, DC. Available from the National Technical Information Service, Springfield, VA; PB88-191705.

U.S. EPA (Environmental Protection Agency). (1988d) Pesticide industry sales and usage: 1987 market estimates. Office of Pesticide Programs, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1989) Interim procedures for estimating risks associated with exposures to mixtures of chlorinated dibenzo-p-dioxins and -dibenzofurans (CDDs and CDFs) and 1989 update. Risk Assessment Forum, Washington, DC; EPA/625/3-89/016.

U.S. EPA (Environmental Protection Agency). (1990a) Characterization of municipal waste combustion ash, ash extracts, and leachates. Office of Solid Waste and Emergency Response, Washington, DC; EPA 530-SW-90-029A.

U.S. EPA (Environmental Protection Agency). (1990b) Operation and maintenance of hospital medical waste incinerators. Office of Air Quality Planning and Standards, Research Triangle Park, NC; EPA/625/6-89/024.

U.S. EPA (Environmental Protection Agency). (1990c) Pesticides industry sales and usage: 1988 market estimates. Office of Pesticides and Toxic Substances, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1990d) Emissions of metals, chromium and nickel species, and organics from municipal wastewater sludge incinerators. Office of Research and Development, Risk Reduction Engineering Laboratory, Cincinnati, OH. EPA Contract No. 68-C0-0027, Work Assignment No. 0-5.

U.S. EPA (Environmental Protection Agency). (1990e) Summary report on USEPA/industry cooperative dioxin study. "The 104 Mill Study." Office of Water Regulations and Standards, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1991a) Methodology for assessing environmental releases of and exposure to municipal solid waste combustor residuals. Office of Research and Development, Washington, DC; EPA/600/8-91/031.

U.S. EPA (Environmental Protection Agency). (1991b) Medical and institutional waste incineration: regulations, management, technology, emissions, and operations. Center for Environmental Research Information, Cincinnati, OH; EPA/625/4-91/030.

U.S. EPA (Environmental Protection Agency). (1991c) Workshop report on toxicity equivalency factors for polychlorinated biphenyls congeners. Risk Assessment Forum, Washington, DC; EPA/625/3-91/020.

U.S. EPA (Environmental Protection Agency). (1991d) Pesticides industry sales and usage: 1989 market estimates. Office of Pesticides and Toxic Substances, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1992a) Economic impact and preliminary regulatory impact analysis for proposed MACT-based emission standards and guidelines for municipal waste combustors. Office of Air Quality Planning and Standards, Research Triangle Park, NC; EPA-450/3-91-029.

U.S. EPA (Environmental Protection Agency). (1992b) Markets for scrap tires. Office of Solid Waste and Emergency Response, Washington, DC; EPA/530-SW-90-074A.

U.S. EPA (Environmental Protection Agency). (1992c) Secondary lead smelter emission test report, East Penn Manufacturing, Lyon Station, Pennsylvania. Office of Air Quality Planning and Standards, Emission Measurement Branch, Research Triangle Park, NC. EMB Report No. 92-SLS-3.

U.S. EPA (Environmental Protection Agency). (1992d) Industry agrees to switch to low-dioxin chloranil from contaminated chloranil. Chemicals in Progress Bulletin 12(2):23.

U.S. EPA (Environmental Protection Agency). (1992e) Pesticides industry sales and usage: 1990 and 1991 market estimates. Office of Prevention, Pesticides and Toxic Substances, Washington, DC; 733-K-92-001.

U.S. EPA (Environmental Protection Agency). (1993a) Report to Congress on cement kiln dust. Office of Solid Waste, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1993b) Development document for proposed effluent limitations guidelines and standards for the pulp, paper and paperboard point source category. Office of Water, Washington, DC; EPA-821-R-93-019.

U.S. EPA (Environmental Protection Agency). (1993c) Economic analysis of impacts of integrated air/water regulations for the pulp and paper industry on disposal of wastewater sludge. Office of Pollution Prevention and Toxics, Regulatory Impacts Branch, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1993d) EPA publishes proposed rule for chloranil. Chemicals in Progress Bulletin 14(2):26.

U.S. EPA (Environmental Protection Agency). (1993e) Press advisory: EPA terminates special review of non-wood pesticide uses of pentachlorophenol. Office of Pesticide Programs, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1993f) 1991 Toxics release inventory: public data release. Office of Pollution Prevention and Toxics, Washington, DC. EPA-745-R-93-003.

U.S. EPA (Environmental Protection Agency). (1993g) Interim report on data and methods for assessment of 2,3,7,8-tetrachlorodibenzo-p-dioxin risks to aquatic life and associated wildlife. Office of Research and Development, Washington, DC; EPA/600/R-93/055.

U.S. EPA (Environmental Protection Agency). (1993h) Wildlife exposure factors. Vol. I. Office of Health and Environmental Assessment, Office of Research and Development, Washington, DC; EPA/600/R-93/187a.

U.S. EPA (Environmental Protection Agency). (1994a) Combustion emissions technical resource document (CETRED). Draft Report. Office of Solid Waste and Emergency Response, Washington, DC; EPA/530-R-94-014.

U.S. EPA (Environmental Protection Agency). (1994b) Preliminary source assessment for the secondary copper smelting industry. Draft report. Office of Air Quality Planning and Standards, Research Triangle Park, NC. EPA Contract No. 68-D1-118, Work Assignment Nos. 25, 40, and 46.

U.S. EPA (Environmental Protection Agency). (1994c) Secondary lead smelting industry: background information document for proposed standards. Final report. Office of Air Quality Planning and Standards, Research Triangle Park, NC; EPA-450/R-94-024.

U.S. EPA (Environmental Protection Agency). (1994d) Pesticide industry sales and usage: 1992 and 1993 market estimates. Office of Prevention, Pesticides and Toxic Substances, Washington, DC; EPA 733-K-94-001.

U.S. EPA (Environmental Protection Agency). (1995a) Compilation of air pollutant emission factors. 5th ed. Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U.S. EPA (Environmental Protection Agency). (1995b) Locating and estimating air emissions from sources of dioxins and furans. Draft final report. Office of Air Quality Planning and Standards, Research Triangle Park, NC. Contract No. 68-D2-0160.

U.S. EPA (Environmental Protection Agency). (1995c) Secondary aluminum plant emission test report: Rochester Aluminum Smelting Corporation. Office of Air Quality Planning and Standards, Research Triangle Park, NC. EMC Report 95-SAL-01.

U.S. EPA (Environmental Protection Agency). (1995d) Final emission test report, HAP emission testing on selected sources at a secondary lead smelter, Schuylkill Metals Corporation, Forest City, Missouri. Office of Air Quality Planning and Standards, Emission Measurement Branch, Research Triangle Park, NC. EMB Report No. 93-SLS-2.

U.S. EPA (Environmental Protection Agency). (1995e) Final emission test report, HAP emission testing on selected sources at a secondary lead smelter, Tejas Resources, Inc., Terrell, Texas. Office of Air Quality Planning and Standards, Emission Measurement Branch, Research Triangle Park, NC. EMB Report No. 93-SLS-1.

U.S. EPA (Environmental Protection Agency). (1995f) SRRD's dioxin/furan status report. Office of Pesticide Programs, Special Review and Reregistration Division, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1995g) An SAB report: A second look at dioxin. Review of the Office of Research and Development's reassessment of dioxin and dioxin-like compounds by the Dioxin Reassessment Review Committee. Science Advisory Board, Washington, DC; EPA-SAB-EC-95-021.

U.S. EPA (Environmental Protection Agency). (1995h) 1993 Toxics release inventory: public data release. Office of Pollution Prevention and Toxics, Washington, DC; EPA-745-R-95-010.

U.S. EPA (Environmental Protection Agency). (1996a) Draft technical support document for hazardous waste combustor MACT standards. Volume I: Description of source categories. Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1996b) EPA OSW hazardous waste combustion data base. Office of Solid Waste, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1996c) EIIP. Vol. II, Chapter 3, Preferred and alternative methods for estimating air emissions from hot-mix asphalt plants. Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U.S. EPA (Environmental Protection Agency). (1996d) Municipal solid waste factbook, version 3.0. Office of Solid Waste, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1996e) Percentile estimates used to develop the list of pollutants for round two of the Part 503 Regulation. Office of Science and Technology, Washington, DC. EPA Contract No. 68-C4-0046.

U.S. EPA (Environmental Protection Agency). (1996f) PCBs: Cancer dose-response assessment and application to environmental mixtures. Office of Research and Development, Washington, DC; EPA/600/P-96/001.

U.S. EPA (Environmental Protection Agency). (1996g) Emissions inventory of Section 112(c)(6) pollutants: polycyclic organic matter (POM), 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)/2,3,7,8-tetrachlorodibenzofuran (TCDF), polychlorinated biphenyl compounds (PCBs), hexachlorobenzene, mercury, and alkylated lead. Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U.S. EPA (Environmental Protection Agency). (1997a) Locating and estimating air emissions from sources of dioxins and furans. Office of Air Quality Planning and Standards, Research Triangle Park, NC. DCN No. 95-298-130-54-01.

U.S. EPA (Environmental Protection Agency). (1997b) 1996 Clean Water Needs Survey Report to Congress. Office of Water, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1997c) Draft technical support document for hazardous waste combustors MACT standards (NODA). Vol. I. MACT evaluations based on revised database. Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1997d) Supplemental technical development document for effluent limitations guidelines and standards for the pulp, paper, and paperboard category. Office of Water, Washington, DC; EPA-821-R-97-011.

U.S. EPA (Environmental Protection Agency). (1997e) Pesticide industry sales and usage: 1994 and 1995 market estimates. Office of Prevention, Pesticides and Toxic Substances, Washington, DC; EPA-733-R-97-002.

U.S. EPA (Environmental Protection Agency). (1998a) Inventory of sources of dioxin in the United States. Workshop Review Draft. National Center for Environmental Assessment, Office of Research and Development, Washington, DC; EPA/600/P-98/002Aa.

U.S. EPA (Environmental Protection Agency). (1998b) 1996 Toxics release inventory--public data release. Office of Pollution Prevention and Toxics, Washington, DC; EPA 745-R-98-005.

U.S. EPA (Environmental Protection Agency). (1998c) AP-42: compilation of air pollutant emissions factors. Volume I: stationary point and area sources. Supplement D to the 5th edition. Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U.S. EPA (Environmental Protection Agency). (1999a) Emission test evaluation of a crematory at Woodlawn Cemetery in the Bronx, NY. Office of Air Quality Planning and Standards, Washington, DC; EPA-454/R-99-049

U.S. EPA (Environmental Protection Agency). (1999b) Biosolids generation, use, and disposal in the United States. Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1999c) Technical background document for the Report to Congress on remaining wastes from fossil fuel combustion: waste characterization. Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1999d) Technical background document for the Report to Congress on remaining wastes from fuel combustion: industry statistics and waste management practices. Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1999e) EPA OSWER hazardous waste combustor emissions data base. Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA (Environmental Protection Agency). (1999f) Monthly reporting of CDD/CDF content in technical pentachlorophenol manufactured by KMG-Bermuth, Inc. and Vulcan Chemicals, 1987 to 1999. Office of Pesticide Programs, Washington, DC.

U.S. EPA (Environmental Protection Agency). (2000a) Emission test evaluation of a pathological waste incinerator at the University of Georgia. Office of Air Quality Planning and Standards, Research Triangle Park, NC; EPA-456/R-00-004.

U.S. EPA (Environmental Protection Agency). (2000b) Source characterization for sewage sludge incinerators. Office of Air Quality Planning and Standards, Washington, DC; EPA-454/R-00-038a.

U.S. EPA (Environmental Protection Agency). (2000c) Exposure and human health reassessment of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and related compounds. Part 1: Estimating exposure to dioxin-like compounds. National Center for Environmental Assessment, Office of Research and Development, Washington, DC; EPA/600/P-00/001B(b-d).

U.S. EPA (Environmental Protection Agency). (2001a) Documentation report for national and county-level emission estimates for residential wood combustion. Prepared by Eastern Research Group, Inc., for Emission Inventory and Analysis Group, Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U.S. EPA (Environmental Protection Agency). (2001b) Municipal solid waste in the United States: 1999 facts and figures. Office of Solid Waste and Emergency Response, Washington, DC; EPA530-R-01-014.

U.S. EPA (Environmental Protection Agency). (2001c) Final titanium dioxide listing background document for the inorganic chemical listing determination. Office of Solid Waste, Washington, DC.

U.S. EPA (Environmental Protection Agency). (2001d) Environmental assessment of proposed revisions to the national pollutant discharge elimination system regulation and the effluent guidelines for concentrated animal feeding operations. Office of Water Regulations and Standards, Washington DC; EPA-821-B-01-001.

U.S. EPA (Environmental Protection Agency). (2002a) Hazardous waste MACT database. Office of Solid Waste. Available at: http://www.epa.gov/epaoswer/hazwaste/combust/ph2noda1/page2-3.htm#Words. Accessed February 25, 2003.

U.S. EPA (Environmental Protection Agency) . (2002b) Documentation for version 2 of the 1999 NEI for criteria air pollutants, area sources. Office of Air Quality Planning and Standards, Emission Factor and Inventory Group, Research Triangle Park, NC.

U.S. EPA (Environmental Protection Agency). (2002c) Municipal solid waste in the United States: 2000 facts and figures. Office of Solid Waste and Emergency Response, Washington, DC; EPA530-R-02-001.

U.S. EPA (Environmental Protection Agency). (2002d) Statistical support document for the development of round 2 biosolids use or disposal regulations. Office of Science and Technology, Washington, DC; EPA-822-R-02-034.

U.S. EPA (Environmental Protection Agency). (2003a) EPA TRI Explorer (Ver 4.01). Office of Environmental Information. Available online at http://www.epa.gov/triexplorer.

U.S. EPA (Environmental Protection Agency). (2003b) Documentation of emission estimation methods for year 2000 and 2001 mobile and nonpoint source dioxin inventories. Prepared for the Office of Air Quality Planning and Standards, Washington, DC, by E.H. Pechan & Associates, Inc.

U.S. EPA (Environmental Protection Agency). (2003c) Chemical information collection and data development (testing) web site. Office of Prevention, Pesticides and Toxic Substances, Washington, DC. Available online at http://www.epa.gov/opptintr/chemtest/polyha.pdf.

U.S. EPA (Environmental Protection Agency). (2004) Clean water needs survey 2000, discharge report. Office of Water, Office of Wastewater Management, Washington, DC. Available online at http://cfpub.epa.gov/cwns/rpt_discharge1_00.cfm.

USGS (U.S. Geological Survey). (1997a) Statistical compendium: copper. U.S. Department of the Interior, U.S. Geological Survey, Washington, DC.

USGS (U.S. Geological Survey). (1997b) Statistical compendium: aluminum. U.S. Geological Survey, Geologic Division, Reston, VA.

USGS (U.S. Geological Survey). (1997c) Mineral commodities summary: aluminum. U.S. Geological Survey, Geologic Division, Reston, VA.

USGS (U.S. Geological Survey). (1997d) Statistical compendium: titanium. U.S. Geological Survey, Geologic Division, Reston, VA.

USGS (U.S. Geological Survey). (1997e) Minerals yearbook: recycling: nonferrous metals. U.S Geological Survey, Geologic Division, Reston, VA.

USGS (U.S. Geological Survey). (1997f) Mineral commodity survey: iron and steel scrap. U.S. Department of the Interior, U.S. Geological Survey, Washington, DC.

USGS (U.S. Geological Survey). (2000) Mineral commodity summaries for 2000: iron and steel. U.S. Geological Survey, Reston, VA.

USGS (U.S. Geological Survey). (2001) Mineral commodity summaries for 2001: iron and steel. U.S. Geological Survey, Reston, VA.

USGS (U.S. Geological Survey). (2002) Mineral commodity summaries for 2002. U.S. Geological Survey, Geologic Division, Reston, VA.

U.S. ITC (International Trade Commission). (1946 through 1994) Synthetic organic chemicals: United States production and sales. U.S. International Trade Commission, Washington, DC.

U.S. ITC (International Trade Commission). (1984) Imports of benzenoid chemicals and products 1983; investigation no. 332-135. U.S. International Trade Commission, Washington, DC. USITC Publication No. 1548.

Van den Berg, M; Birnbaum, L; Bosveld, ATC; et al. (1998) Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. Environ Health Perspect 106:775-792.

Van Dort, HM; Bedard, DL. (1991) Reductive ortho and meta dechlorination of a polychlorinated biphenyl congener by anaerobic microorganisms. Appl Environ Microbiol 57:1576-1578.

Van Oostdam, JC; Ward, JEH. (1995) Dioxins and furans in the British Columbia environment. BC Environment, Environmental Protection Department, Victoria, British Columbia.

Van Wijnen, JH; Liem, AKD; Olie, K; et al. (1992) Soil contamination with PCDDs and PCDFs of small (illegal) scrap wire and scrap car incineration sites. Chemosphere 24(2):127-134.

Versar, Inc. (1976) PCBs in the United States: industrial use and environmental distribution. Prepared for the U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC; EPA Contract No. 68-01-3259, Task I.

Versar, Inc. (1985) List of chemicals contaminated or precursors to contamination with incidentally generated polychlorinated and polybrominated dibenzodioxins and dibenzofurans. Prepared for the U.S. Environmental Protection Agency; EPA Contract No. 68-02-3968, Task No. 48.

Versar, Inc. (1988) PCB exposure assessment of scrap/salvage facilities. Prepared for the U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC; EPA Contract No. 68-02-4254, Task No. 136.

Vikelsoe, J; Madsen, H; Hansen, K. (1993) Emission of dioxins from Danish wood-stoves. Organohalogen Compounds 11:405-408.

Vickelsoe, J; Lassen, P; Johansen, E; et al. (1994) Formation of PCDD/PCDFs via an enzymatically mediated chlorination of humic acids. Organohalogen Compounds 20:351-354.

Villanueva, EC; Jennings, RW; Burse, VW; et al. (1974) Evidence of chlorodibenzo-p-dioxin and chlorodibenzofuran in hexachlorobenzene. J Agr Food Chem 22(5):916-917.

Viraraghavan, T; Slough, K. (1999) Sorption of pentachlorophenol on peat-bentonite mixtures. Chemosphere 39:1487-1496.

Virta, RL. (2000) Clays. U.S. Geological Survey mineral commodity summaries. February 2000. Available online at http://www.usgs.gov/.

Vogg, H; Metzger, M; Steiglitz, L. (1987) Recent findings on the formation and decomposition of PCDD/PCDF in municipal solid waste incineration. Waste Management and Research 5(3):285-294.

Vogg, H; Nunsinger, H, Merz, A; et al. (1992) Influencing the production of dioxin/furan in solid waste incineration plants by measures affecting the combustion as well as the flue gas cleaning systems. Chemosphere 25(1-2):149-152.

Vollmuth, S; Zajc, A; Niessner, R. (1994) Formation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans during the photolysis of pentachlorophenol-containing water. Environ Sci Technol 28(6):1145-1149.

Waddell, DS; Boneck-Ociesa, H; Gobran, T; et al. (1995) PCDD/PCDF formation by UV photolysis of pentachlorophenol with and without the addition of hydrogen peroxide. Organohalogen Compounds 23:407-412.

Wagner, JC; Green, AES. (1993) Correlation of chlorinated organic compound emissions from incineration with chlorinated organic input. Chemosphere 26(11):2039-2054.

Wagner, HC; Schramm, KW; Hutzinger, O. (1990) Biogenic polychlorinated dioxin and furan from trichlorophenol. Organohalogen Compounds 3:453-456.

Walsh, PJJ; Brimblecombe, P; Creaser, CS; et al. (1994) Biomass burning and polychlorinated dibenzo-p-dioxins & furans in soil. Organohalogen Compounds (20):283-287.

Wan, MT. (1995) Treated wood as a source of dioxin/furan releases. Organohalogen Compounds 24:109-114.

Wan, MT; Van Oostdam, J. (1995) Utility and railway rights-of-way contaminants: dioxins and furans. J Environ Qual 24:257-265.

Wang, LC; Lee, WJ; Lee, WS; et al. (2003) Effect of chlorine content in feeding wastes of incineration on the emission of polychlorinated dibenzo-p-dioxins/dibenzofurans. The Science of the Total Environment 302:185-198.

Ward, DE; McMahon, CK; Johansen, RW. (1976) An update on particulate emissions from forest fires. Presented at 69th Annual Meeting of the Air Pollution Control Association. Portland, OR; June 27-July 1.

Ward, DE; Peterson, J; Hao, W.M. (1993) An inventory of particulate matter and air toxic emissions from prescribed fires in the USA for 1989. Presented at 86th Annual Meeting & Exhibition, Air & Waste Management Association; Denver, Colorado; June.

Washington State Department of Ecology. (1998) Washington State dioxin source assessment. Washington State Department of Ecology, Olympia, Washington. Publication No. 98-320.

Watanabe, I; Tatsukawa, R. (1987) Formation of brominated dibenzofurans from the photolysis of flame retardant decabromobiphenyl ether in hexane solution by UV and sun light. Bull Environ Contam Toxicol 39:953-959.

Water Pollution Control Federation. (1990) Operation of municipal wastewater treatment plants. Manual of practice No. 11. Water Pollution Control Federation, Alexandria, VA.

Weber, R; Hagenmaier, H. (1999) Mechanism of formation of polychlorinated dibenzo-p-dioxins and dibenzofurans from chlorophenols in gas phase reactions. Chemosphere 38:529-549.

Weber, H; Disse, G; Hamann, R; et al. (1995) Influence of the aerobic and anaerobic digestion on the levels of chlorinated dibenzofurans and dibenzodioxins in sewage sludge. Organohalogen Compounds 24:81-85.

Weber, P; Altwicker, E; Dinjus, E; et al. (1999) The role of aliphatic organic chlorine in the formation of PCDD/PCDF on fly ash in comparison to inorganic chlorine. Organohalogen Compounds 41:11-14.

Welsch-Pausch, K; McLachlan, MS. (1995) Photodegradation of PCDD/Fs on pasture grass. Organohalogen Compounds 24:509-512.

Welsch-Pausch, K; McLachlan, MS; Umlauf, G. (1995) Determination of the principal pathways of polychlorinated dibenzo-p-dioxins and dibenzofurans to *Lolium multiflorum* (Welsh Ray Grass). Environ Sci Technol 29:1090-1098.

Western Environmental Services and Testing, Inc. (2000) Magnesium Corporation of America, Rowley, Utah. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Melt reactor and cathode stacks. File Number 00-1043.

Weston, R. (1996). Item II-D-82 in USEPA secondary aluminum MACT air docket number A-92-61: scrap dryer and reverberatory furnace emission test report, Wabash, Indiana. Prepared for Wabash Alloys, Work Order No. 11590-001-001.

Wevers, M; De Fre, R. (1995) Estimated evolution of dioxin emissions in Belgium from 1988 to 1995. Organohalogen Compounds 24:105-108.

Wevers, M; De Fre, R; Rymen, T. (1992) Dioxins and dibenzofurans in tunnel air. Vol. 9 (sources of exposure) of extended abstracts. Organohalogen Compounds 9:321-324.

Whitman, WG. (1927) The two-film theory of gas absorption. Chemical and Metallurgical Engineering 29(4):146-148.

WHO (World Health Organization). (1991) IARC monographs on the evaluation of carcinogenic risks to humans: occupational exposures in insecticide application, and some pesticides. World Health Organization, International Agency for Research on Cancer, Geneva, Switzerland.

Wichmann, H; Zelinski, V; Scholz-Böttcher, B; et al. (1993) Sampling strategy to investigate the distribution behavior of low volatile pollutants like "dioxins" during vehicle fires in traffic tunnels. Chemosphere 26(6):1159-1166.

Wichmann, H; Lorenz, W; Bahadir, M. (1995) Release of PCDD/F and PAH during vehicle fires in traffic tunnels. Chemosphere 31(2):2755-2766.

Wienecke, J; Kruse, H; Wassermann, O. (1992) Organic compounds in the flue gas from a power station with circulatory fluid bed combustion of coal. Chemosphere 25(12):1889-1895.

Wikstrom, E; Lofvenius, G; Rappe, C; et al. (1996) Influence of level and form of chlorine on the formation of chlorinated dioxins, dibenzofurans, and benzenes during combustion of an artificial fuel in a laboratory reactor. Environ Sci Technol 30:1637-1644.

Wikstrom, E; Ryan, S; Touati, A; et al. (2003) Importance of chlorine speciation on de Novo formation of polychlorinated dibenzo-p-dioxins and polychlorinated dibanzofurans. Environ Sci Technol 37:1108-1113.

Wikstrom, E; Persson, A; Marklund, S. (1998) Secondary formation of PCDDs, PCDFs, PCBs, PCBzs, PHPhs and PAHs during MSW combustion. Organohalogen Compounds 36:65-68.

Wikstrom, E; Ryan, S; Touati, A; Telfer; M; et al. (2003) Importance of chlorine speciation on de Novo formation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Environ Sci Technol 37:1108-1113.

Williams, CH; Prescott, CL; Stewart, PB; et al. (1985) Formation of polychlorinated dibenzofurans and other potentially toxic chlorinated pyrolysis products in PCB fires. In: Keith, LH; Rappe, C; Choudhary, G; eds. Chlorinated dioxins and dibenzofurans in the total environment II. Boston, MA: Butterworth Publishers.

Williams, DT; LeBel, GL; Benoit, FM. (1992) Polychlorodibenzodioxins and polychlorodibenzofurans in dioxazine dyes and pigments. Chemosphere 24(2):169-180.

Wittsiepe, J; Kullmann, Y; Schrey, P; et al. (1998) Myeloperoxidase: catalyzed formation of PCDD/F from chlorophenols. Organohalogen Compounds 36:351-356.

Woolson, EA; Thomas, RF; Ensor, PDJ. (1972) Survey of polychlorodibenzo-p-dioxin content in selected pesticides. J Agr Food Chem 20(2):351-354.

Young, AL. (1983) Long-term studies on the persistence and movement of TCDD in a natural ecosystem. In: Tucker, RE; Young, AL; Gray, AP; eds. Human and environmental risks of chlorinated dibenzodioxins and related compounds. New York, NY: Plenum Press.

Zenith Research Group, Inc. (2000) Summary report on burn barrels. Prepared for the Western Lake Superior Sanitary District, Duluth, MN.

Zenith Research Group, Inc. (2001) A survey of residents of Northeast Minnesota & Northwest Wisconsin. Prepared for the Western Lake Superior Sanitation District, Duluth, MN.

Zheng, M-H; Liu, P-Y; Xu, X-B. (1999) Mechanism of formation of polychlorinated biphenyls from the pyrolysis of chlorobenzenes. Organohalogen Compounds 41:15-18.