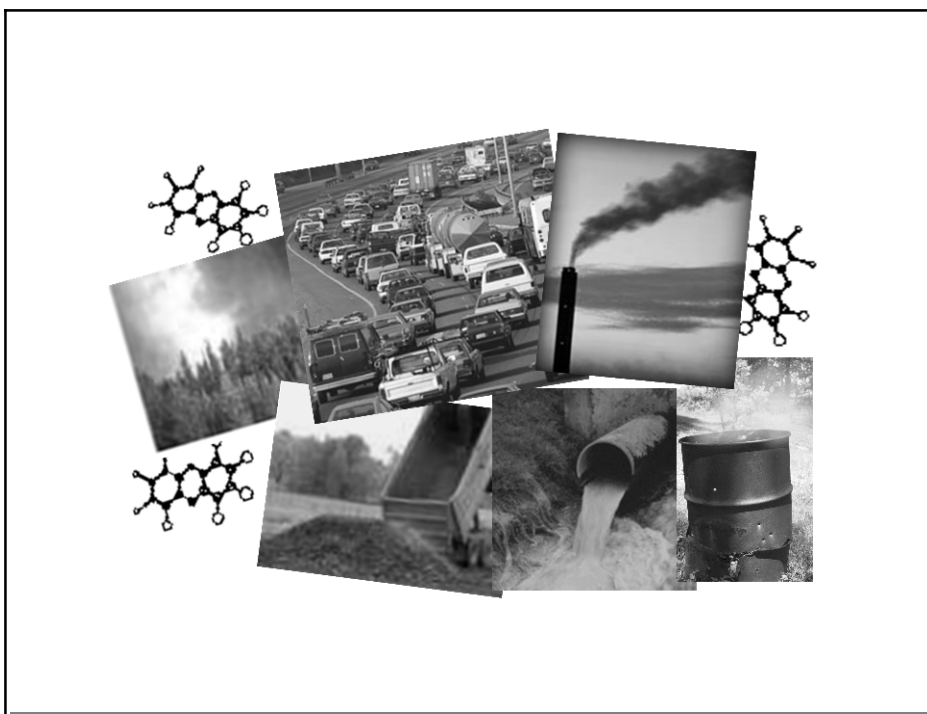




United States  
Environmental Protection  
Agency

# The Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States: The Year 2000 Update



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# **The Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States: The Year 2000 Update**

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

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## ABSTRACT

The purpose of this report 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, biological and photochemical processes 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 equivalent (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. Using this WHO procedure, the annual releases of TEQ<sub>DF</sub>-WHO<sub>98</sub> to the U.S. environment over the three reference years are 13,962 g in 1987, 3,280 g in 1995, and 1,529 g in 2000. This analysis indicates that between reference years 1987 and 2000, there was approximately 89% 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 third 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.

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## LIST OF ABBREVIATIONS AND ACRONYMS

AHA	American Hospital Association
AMSA	Association of Metropolitan Sewerage Agencies
APCD	Air pollution control device
BDDs	Polybrominated dibenzo- <i>p</i> -dioxins
BDFs	Polybrominated dibenzofurans
Btu	British thermal unit
CaCl <sub>2</sub>	Calcium chloride
CARB	California Air Resources Board
CBI	Confidential business information
CDD	Polychlorinated dibenzo- <i>p</i> -dioxin
CDF	Polychlorinated dibenzofuran
CFR	Code of Federal Regulations
CSF	Confidential Statement of Formula
CKD	Cement Kiln Dust
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
CuCl	Copper (I) chloride
CuCl <sub>2</sub>	Copper (II) chloride
D	Symbol for Congener Class: Dibenzo- <i>p</i> -dioxin
D	Symbol for di (i.e., Two Halogen Substitution)
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

## LIST OF ABBREVIATIONS AND ACRONYMS (continued)

EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	Electrostatic precipitator
FF	Fabric filter
FCEM	Field Chemical Emissions Measurement
FeCl <sub>3</sub>	Ferric (iron) chloride
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- <i>p</i> -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 <sub>2</sub>	Magnesium chloride
MgO	Magnesium oxide
MSW	Municipal solid waste
MWI	Medical waste incinerator
NaCl	Sodium chloride
NaOCl	Sodium hypochlorite
NCASI	National Council of the Paper Industry for Air and Stream Improvement
NiCl <sub>2</sub>	Nickel chloride
NiO	Nickel oxide

## LIST OF ABBREVIATIONS AND ACRONYMS (continued)

Nm <sup>3</sup>	Standard cubic meter
NMOC	Nonmethane organic compound
OAQPS	Office of Air Quality Planning and Standards
O <sub>2</sub>	Molecular oxygen
OH	Hydroxide ion
OPP	Office of Pesticide Programs
ORD	Office of Research and Development
OSW	Office of Solid Waste
Pb	Lead
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
SNUR	Significant New Use Rule
SO <sub>2</sub>	Sulfur dioxide
TCBz	Trichlorobenzene
TCDD	2,3,7,8-tetrachlorobidibenzo- <i>p</i> -dioxin

## **LIST OF ABBREVIATIONS AND ACRONYMS (continued)**

TCDF	2,3,7,8-tetrachlorobenzofuran
TeCB	Tetrachlorobiphenyl
TeCP	Tetrachlorophenol
TEF	Toxicity equivalency factor
TEQ	Toxicity equivalent
TEQ/yr	Toxicity equivalents per year
TiCl <sub>4</sub>	Titanium tetrachloride
TrCB	Trichlorobiphenyl
TrCP	Trichlorophenol
TRI	Toxics Release Inventory
TSCA	Toxic Substances Control Act
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 report 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 battery of 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.

This current inventory is an update of an external review draft report entitled, *The Inventory of Sources of Dioxin in the United States* (EPA/600/P-98/002Aa), dated April 1998. The 1998 draft inventory presented annual estimates of environmental releases for reference years 1987 and 1995. A meeting of scientific and engineering experts was convened June 3-4, 1998, to review the scientific soundness of EPA’s dioxin inventory. Overall, the reviewers found the inventory report to be comprehensive and well documented and the “emission factor approach” that was used to develop the inventory to be scientifically defensible. The review committee recommended that EPA (a) take a less conservative approach for including data on emissions of dioxin-like compounds from sources, especially data from foreign countries and those found in the nonpeer-reviewed literature; (b) adopt a qualitative ranking system that clearly indicates the relative amount of uncertainty behind the calculations of annual releases of dioxin-like compounds; (c) present the inventory of sources and environmental releases specific

to the reference years, because technologies and emissions of dioxin from sources changes over time; and (d) present the dioxin inventory as a summary table of sources and estimated annual releases, including quantifiable as well as poorly understood sources. The current inventory reflects comments made by the review committee and also represents an update with the inclusion of a third reference year, 2000.

This updated inventory of sources and environmental releases of dioxin-like compounds concludes that, between 1987 and 2000, there was an approximately 89% 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 1,529 g in reference year 2000; 3,280 g in reference year 1995; and 13,962 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.

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## **PREFACE**

This external review draft report presents an inventory of all known sources and environmental releases of dioxin-like compounds in the United States associated with reference years 1987, 1995, and 2000. This perspective allows for the observation of time trends of releases of dioxin-like compounds to the open and circulating environment from industrial, combustion, chemical, and ferrous and nonferrous metal smelting processes as they are configured and operated in the United States. The assessment was prepared by the National Center for Environmental Assessment, which is the health risk assessment program in the Office of Research and Development.



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## EXECUTIVE SUMMARY

### Background

*The Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States: The Year 2000 Update* presents estimates of annual releases of dioxin-like compounds specific to three reference 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 circulating environment, that is, to air, water, and land.

The primary purposes of the report are to:

1. Document and describe sources in the United States which release dioxin-like compounds into the circulating environment.
2. Quantify annual releases to the environment of the United States from known sources in a scientific and transparent manner.
3. Provide a reliable basis for time-trends analyses.

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

### Approach

Only sources judged to have a reasonable likelihood for releases to the “open and circulating environment” were addressed in this document. The document discusses both contemporary formation sources and reservoir sources. Reservoirs are materials or places that contain previously formed CDDs/CDFs or dioxin-like PCBs that have the potential for redistribution and circulation in the environment. Potential reservoirs include soils, sediments, biota, water, and some anthropogenic materials. Reservoirs become sources when they release compounds to the circulating environment. While reservoir sources are discussed in the

document, they are not counted as part of the national inventory because they are not original releases.

The emissions were computed on the basis of an emission factor and activity level. The emission factor is the amount of dioxin emitted per unit of activity and is determined via sampling and analyzing the environmental releases from the source. The activity level reflects how much action is associated with a release and can take several forms such as kilograms of material processed per year by an industrial facility, vehicle miles traveled per year by trucks and automobiles, and liters of wastewater discharged into surface water from industrial sources. These factors are multiplied to arrive at an estimate of total environmental releases for a given year. The confidence in the accuracy of both the emission factor and activity level are rated as low, medium, or high based on the quality and representativeness of the data. The overall estimate of environmental release is also rated as low, medium, or high based on the lowest rating assigned to either the emission factor or activity level. In some cases, the data were not adequate to support even a low confidence rating. These cases were treated in two ways. If the data were sufficient to make an approximate, but clearly nonrepresentative estimate of releases, these were labeled as preliminary and not included in the national quantitative inventory. If the limited data suggested that dioxin releases were possible from a source, but were not adequate to support emission calculations, the source was labeled as unquantifiable. This approach resulted in the following classification scheme:

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 toxic equivalents (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 (see Section 1.1.4 for details). 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. 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.

## **Results - Total Environmental Releases**

Tables 1-6 and 1-7 in Chapter 1 show the emission estimates for all sources that could be quantified, i.e., Categories A, B, C, and D. The Category D estimates are clearly labeled as outside the national inventory. Category E sources are shown in Table 1-5.

For the year 2000, EPA makes the following conclusions:

- The total releases in the inventory (Categories A, B, and C) were 1,529 g TEQ<sub>DF</sub>-WHO<sub>98</sub>/yr. Releases to the air accounted for 92% of the total releases. The top three sources were backyard barrel burning of refuse (32%), medical waste incinerators (MWIs) (24%), and municipal waste combustors (MWCs) (5%).
- The contemporary formation sources included Category D air releases totaling 6,777 g TEQ<sub>DF</sub>-WHO<sub>98</sub>/yr. Forest fires accounted for 72% of the total releases.
- A total of 18 contemporary formation sources were identified as Category E.
- Releases from only two reservoir sources could be estimated for 2000: urban runoff to surface water 142 g TEQ<sub>DF</sub>-WHO<sub>98</sub> and rural soil erosion to surface water 2,500 g TEQ<sub>DF</sub>-WHO<sub>98</sub>. Both of these estimates are preliminary (i.e., Category D). Releases from the other reservoirs (air, sediment, water, and biota) could not be quantified (i.e., Category E).

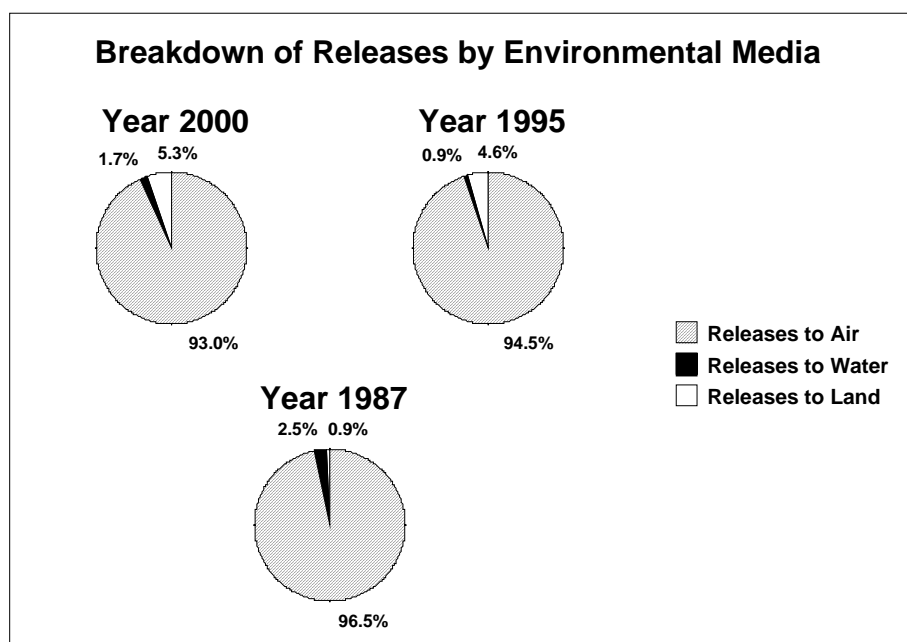
The following table summarizes the environmental releases of dioxin from all sources in the inventory for years 2000, 1995, and 1987. It shows the sources in ranked order from highest to lowest and also shows the percent contribution of each source to the total emissions. In 1987 and 1995, the leading source of dioxin emissions to the U.S. environment was municipal waste combustion; however, because of reductions in dioxin emissions from MWCs, it dropped to the third 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.

### Top ten dioxin emitting sources for the years 2000, 1995, and 1987

Ranking of the year 2000 sources	Year 2000 Grams	Percent of Total	Ranking of the year 1995 sources	Year 1995 Grams	Percent of Total	Ranking of the year 1987 sources	Year 1987 Grams	Percent of Total
Backyard barrel burning of refuse	498.53	32.59%	Municipal waste combustion	1,250.00	38.11%	Municipal waste combustion	8,877.00	63.58%
Medical waste/pathological incineration	378.00	24.71%	Backyard barrel burning of refuse	628.00	19.15%	Medical waste/pathological incineration	2,590.00	18.55%
Municipal waste combustion	78.90	5.16%	Medical waste/pathological incineration	488.00	14.88%	Secondary copper smelters	983.00	7.04%
Municipal wastewater treatment sludge	78.20	5.11%	Secondary copper smelters	271.00	8.26%	Backyard barrel burning of refuse	604.00	4.33%
Coal fired-utility boilers	69.50	4.54%	Cement kilns (hazardous waste burning)	156.10	4.76%	Bleached chemical wood pulp and paper mills	356.00	2.55%
Cement kilns (hazardous waste burning)	68.40	4.47%	Municipal wastewater treatment sludge	116.10	3.54%	Cement kilns (hazardous waste burning)	117.80	0.84%
Diesel heavy duty trucks	65.40	4.28%	Coal fired-utility boilers	60.10	1.83%	Municipal wastewater treatment sludge	76.60	0.55%
Primary Magnesium production	42.00	2.75%	Diesel heavy duty trucks	33.30	1.02%	Coal fired-utility boilers	50.80	0.36%
Industrial wood combustion	41.50	2.71%	Secondary aluminum smelters	29.10	0.89%	Automobiles using leaded gasoline	37.50	0.27%
Secondary aluminum smelting	35.90	2.35%	2,4-Dichlorophenoxy acetic acid	28.90	0.88%	2,4-Dichlorophenoxy acetic acid	33.40	0.24%
Other	173.16	11.32%	Other	219.33	6.69%	Other	236.29	1.69%
<i>Total Environmental Releases</i>	<i>1529.49</i>	<i>100.00%</i>	<i>Total Environmental Releases</i>	<i>3,279.93</i>	<i>100.00%</i>	<i>Total Environmental Releases</i>	<i>13,962.39</i>	<i>100.00%</i>

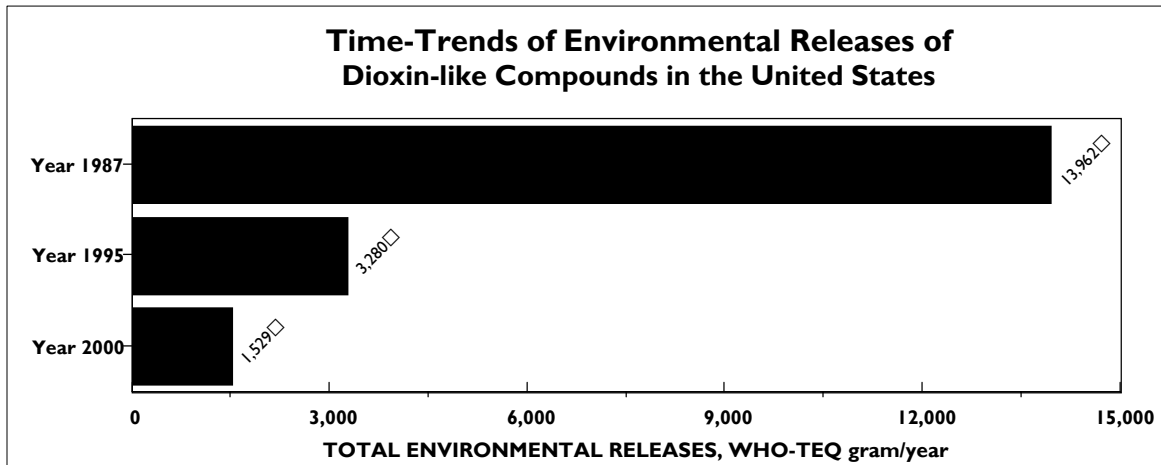


Environmental releases of CDDs/CDFs in the United States occur from a wide variety of sources but are dominated by releases to the air from combustion sources. The following pie charts summarize the breakdown of CDD/CDF releases to air, water, and land for each of the reference years.



### Results - 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) are approximately 1,529 g TEQ<sub>DF</sub>-WHO<sub>98</sub> in reference year 2000; 3,280 g TEQ<sub>DF</sub>-WHO<sub>98</sub> in reference year 1995; and 13,962 g TEQ<sub>DF</sub>-WHO<sub>98</sub> in reference year 1987 (see the following figure). From 1987 to 2000 there was approximately an 89% reduction in releases to all media. Most of the reduction in dioxin releases (77%) occurred in the time period from 1987 to 1995.



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 from wastewater discharged into surface waters from pulp and paper mills using chlorine. These reductions have occurred from a combination of regulatory activities, improved emission controls, voluntary actions on the part of industry, and the closing of a number of facilities. The following table shows the reductions made among the largest sources.

Source category	Media release	Reference year 2000 (g TEQ <sub>DF</sub> -WHO <sub>98</sub> )	Reference year 1987 (g TEQ <sub>DF</sub> -WHO <sub>98</sub> )	Percent reduction in environmental releases
Municipal waste combustion	Air	78.9	8877	>99
Medical waste incineration	Air	378	2590	85
Cement kilns burning hazardous waste	Air	68.4	117.8	42
Bleached chemical wood pulp and paper mills	Surface water	1	356	>99

## **Results - Sources Not Considered in the Inventory**

Significant amounts of the dioxin-like compounds produced annually in the United States are not considered releases to the open 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 landfills.

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

# 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. It is a detailed review and description of all known sources and their associated activities that cause these compounds to be released into the circulating environment, that is, to air, water, and land.

The primary purposes of this report are to

- Document and describe sources in the United States of releases of dioxin-like compounds into the circulating environment.
- 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 with the passage of time. Time-trend analyses provide a quantitative indication of the achievements made in reducing environmental releases of dioxin-like compounds from known sources in the United States.

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

The primary technical resource supporting the inventory of sources of dioxin-like compounds is the U.S. Environmental Protection Agency's (EPA's) *Database of Sources of Environmental Releases of Dioxin-Like Compounds in the United States* (U.S. EPA, 2001a). This database includes congener-specific chlorinated dibenzo-*p*-dioxin (CDD) and chlorinated dibenzofuran (CDF) emissions data extracted from original engineering test reports. After the 2000 update has been reviewed, an updated database will be made available to the public that reflects the years 1987, 1995, and 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.

#### **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. The selection and use of three reference years provides a basis for comparing environmental releases of dioxin-like compounds 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 chlorinated dibenzo-*p*-dioxin (CDD) and chlorinated dibenzofuran (CDF) congeners in environmental samples. Soon after this time, a number of facilities began upgrades

1 specifically intended to reduce CDD/CDF emissions. Consequently, 1987 emissions are  
2 representative of levels of emissions that occurred before the widespread installation of dioxin-  
3 specific emission controls.

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

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

#### 14 15 **1.1.2. Regulatory Summary**

16 The following is a synopsis of EPA regulatory activities addressing releases of dioxin-like  
17 compounds. As discussed in Section 1.3.2, these regulations (along with other factors)  
18 contributed to the reductions in dioxin emissions observed over time.

#### 19 20 Municipal Waste Combustors (MWCs)

21 In 1987, MWCs were the largest source of dioxin releases to the environment, amounting  
22 to an estimated 64% of dioxin releases. In July 1987, as a result of these findings, EPA  
23 announced plans to set regulatory standards for the control of dioxin and other pollutant  
24 emissions to the air from MWCs. The Agency issued guidance to the states to ensure that best  
25 available control technologies (BACT) were used on new facilities even before the development  
26 of the upcoming regulations. BACT for dioxin control was identified as dry scrubbers (DSs)  
27 combined with fabric filters (FFs) (52 FR 25399, July 7, 1987). EPA took the following  
28 regulatory actions to reduce dioxin releases from MWCs:  
29

- December 20, 1989, EPA proposed dioxin standards for new MWCs and guidelines for existing MWCs (54 FR 52251 and 54 FR 52209, respectively).
- November 15, 1990, Amendments to the Clean Air Act (CAA) were enacted and Section 129 was added which specifies that revised standards and guidelines must be developed for both large and small MWC plants and they must reflect more restrictive performance levels. Section 129 includes a schedule for revising the 1991 standards and guidelines.
- February 11, 1991, EPA promulgated final maximum achievable control technology (MACT) dioxin standards and guidelines (56 FR 5488 and 56 FR 5514, respectively) only on large MWCs (capacities above 250 tons per day).
- The Sierra Club, the Natural Resources Defense Council, and the Integrated Waste Services Association filed complaints with the U.S. District Court for the Eastern District of New York to require dioxin standards for small MWCs. The proposal notice for the standards and guidelines was signed as scheduled and published on September 20, 1994 (59 FR 48198 and 59 FR 48228, respectively).
- October 31, 1995, EPA issued final standards and guidelines on revised MACT standards and guidelines to MWC units with aggregate plant capacity above 40 tons per day.

#### Hazardous Waste Incinerators

- July 16, 1992, EPA issued proposed dioxin regulations (57 FR 31576) for hazardous waste incinerators, hazardous waste burning cement kilns, and hazardous waste burning lightweight aggregate kilns.
- May 18, 1993, EPA issued a Hazardous Waste Minimization and Combustion Strategy. This required tighter permitting requirements for dioxin emissions from Hazardous Waste Incinerators.
- September 30, 1999, EPA promulgated dioxin standards (under the CAA) for hazardous waste incinerators, hazardous waste burning cement kilns, and hazardous waste burning lightweight aggregate kilns.

#### Medical Waste Incinerators (MWIs)

- Feb 27, 1995, EPA proposed dioxin standards for MWIs under the CAA (60 FR 10654).
- August 15, 2000, EPA promulgated dioxin emission standards (65 FR 49739).

#### Pulp and Paper Mills

- December 17, 1993, EPA proposed dioxin effluent standards under the CWA.
- April 15, 1998, EPA promulgated dioxin effluent standards under the CWA.

### 1.1.3. Definition of Dioxin-Like Compounds

This inventory of sources and environmental releases addresses specific compounds in the following chemical classes: polychlorinated dibenzo-*p*-dioxins (CDDs), polychlorinated dibenzofurans (CDFs), and polychlorinated biphenyls (PCBs); it describes this subset of chemicals 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), are thought to have dioxin-like toxicity; these are 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; these also are ones with substitutions in the 2, 3, 7, and 8 positions. This suggests that 17 individual CDDs/CDFs exhibit dioxin-like toxicity.

There are 209 PCB congeners, of which only 13 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.

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 equivalency (TEQ) is discussed below.



#### 1.1.4. Toxicity Equivalency Factors (TEFs)

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 TEQ has been considered and discussed by the scientific community, and 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 along with considerations of chemical structure, persistence, and resistance to metabolism and 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).

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

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 1-1.
- TEQ-WHO<sub>94</sub> 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 1-2.
- TEQ-WHO<sub>98</sub> 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 1-3.

The nomenclature also uses subscripts to indicate which family of compounds is included in any specific TEQ calculation. Under this convention, the subscript D is used to designate dioxins, the subscript F to designate furans, and the subscript P to designate PCBs. As an example, “TEQ<sub>DF</sub>-WHO<sub>98</sub>” 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<sub>98</sub> scheme. If PCBs had also been determined, the nomenclature would be “TEQ<sub>DFP</sub>-WHO<sub>98</sub>.” Note that the designations TEQ<sub>DF</sub>-WHO<sub>94</sub> and I-TEQ<sub>DF</sub> 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 and F subscripts. This indicates that the TEQ calculation includes both dioxins and furans. A complete listing of the nomenclature used in this report is depicted in Table 1-4. This document emphasizes the WHO<sub>98</sub> TEF scheme as the preferred scheme to be used to assign TEQ 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

1 or earlier. Some 2004 documents are cited, primarily in Chapter 2 on Formation Theory, but a  
2 thorough literature review has not been extended past 2003.

3 EPA's Toxic Release Inventory (TRI) began collecting data on PCBs in 1988 and on  
4 CDD/CDFs in 2000 (U.S. EPA, 2003c). These data have been considered in this report for  
5 purposes of identifying possible sources but were not used for making quantitative release  
6 estimates because of the following:

- 7  
8 • With respect to PCBs, the TRI data are reported as total PCBs and not on a congener-  
9 specific basis. Thus, it is unknown what portion of these releases are dioxin-like  
10 PCBs and, therefore, TEQs cannot be calculated. In this present format, the PCB TRI  
11 data is not readily usable within the structure of this dioxin inventory.
- 12  
13 • With respect to CDDs/CDFs, the reporting format under TRI is the sum quantity of  
14 the 17 toxic CDDs and CDFs that are emitted in a given year (i.e., the sum of the  
15 2,3,7,8-chlorine substituted compounds). Neither the releases of the individual  
16 CDD/CDF congeners nor the TEQS must be reported, therefore, the dioxin TRI data  
17 is not readily usable within the structure of this dioxin inventory.
- 18  
19 • The accuracy of the TRI data are unknown because they are self-reported and are not  
20 required to be based on measurements.
- 21  
22 • The TRI reports lack specific details and descriptions of the reporting industries.  
23 This information is needed for the dioxin inventory, because the calculation of source-  
24 specific emission factors (representative of industrial source categories) strongly  
25 depends on closely matching facilities in terms of similarity of process, production,  
26 and pollution control.
- 27  
28 • The TRI reporting format does not include information on the strengths/weaknesses  
29 of the data, and therefore, it would be difficult to evaluate these data in terms of the  
30 confidence rating scheme developed for this inventory.

## 31 32 33 **1.2. APPROACH**

34 Only sources judged to have a reasonable likelihood for releases to the “circulating  
35 environment” were addressed in this document. Examples of the circulating environment system  
36 boundary are

- 37  
38 • CDDs/CDFs and dioxin-like PCBs in air emissions and wastewater discharges are  
39 included, whereas CDDs/CDFs and dioxin-like PCBs in intermediate products or  
40 internal wastestreams are not included. For example, the CDDs/CDFs in a  
41 wastestream going to an on-site incinerator are not addressed in this document, but  
42 any CDDs/CDFs in the stack emissions from the incinerator are included.
- 43  
44 • 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

In the United States, the major identified sources of environmental releases of dioxin-like compounds have been grouped into five broad categories:

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

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

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

*Biological and photochemical processes.* Recent studies suggest that CDDs/CDFs can be formed under certain environmental conditions (e.g., composting) from the action of microorganisms on chlorinated phenolic compounds. Similarly, CDDs/CDFs have been reported to be formed during photolysis of highly chlorinated phenols.

*Reservoirs.* Reservoirs are materials or places that contain previously formed CDDs/CDFs or dioxin-like PCBs, which have the potential for redistribution and circulation in the environment. Potential reservoirs include soils, sediments, biota, water, and some anthropogenic materials. Reservoirs become sources when they have releases to the circulating environment.

Sources can also be divided 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 11 and the reservoir sources are discussed in Chapter 12. The presence of CDDs/CDFs in ball clay is discussed in Chapter 13. Table 1-5 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 1-5 and release estimates are shown in Tables 1-6 and 1-7.
2. *Contemporary formation sources with preliminary release estimates*. These sources are listed in Table 1-5 and release estimates for 2000 are shown in Tables 1-6 and 1-7.
3. *Contemporary formation sources without quantified release estimates*. These sources are listed in Table 1-5.
4. *Reservoir sources with reasonably well-quantified releases*. These sources would have been listed in Table 1-5 and release estimates would have been shown in Table 1-13, but none have yet been identified.
5. *Reservoir sources with preliminary release estimates*. These sources are listed in Table 1-5 and release estimates are shown in Table 1-13.
6. *Reservoir sources without quantified releases*. These sources are listed in Table 1-5.

Only contemporary formation sources (numbers 1-3 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.

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. These products have been classified into one of the above six groups. 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 Tables 1-8 and 1-9.

### 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, cement kilns that burn hazardous waste, effluent from chlorine-bleached pulp and paper mills, and sewage sludge (biosolids) that are applied to farm lands and grazing lands. Other source categories, have relatively few tested facilities. In these cases, EPA relies on the use of emission factors to estimate CDD/CDF releases from the untested facilities. This provides a method of extrapolation from tested facilities 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 configuration, fuel type, air pollution control equipment, etc.). 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, etc.). It was developed by averaging the emission factors for the tested facilities in the class. This average emission factor was 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 were summed for the tested facilities and nontested facilities. In summary, this procedure can be represented by the following equations:

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

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

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 along with their emission factors, activity levels, and annual emissions for the reference years 1987,

1 1995, and 2000 in I-TEQ and WHO-TEQ units. Figures 1-5 and 1-9 depict comparisons of the  
2 estimated I-TEQ and WHO-TEQ air emissions for the reference years 1987, 1995, and 2000.

3 Some source categories are made up of facilities that vary widely in terms of design and  
4 operating conditions. For these sources, as explained above, an attempt was made to create  
5 subcategories that grouped facilities with common features and then to develop separate emission  
6 factors for each subcategory. Implicit in this procedure is the assumption that facilities with  
7 similar design and operating conditions should have similar CDD/CDF release potential. For  
8 most source categories, however, the specific combination of features that contributes most to  
9 CDD/CDF or dioxin-like PCB release is not well understood. Therefore, how to best  
10 subcategorize a source category was often problematic. For each subcategorized source category  
11 in this document, a discussion is presented about the variability in design and operating  
12 conditions, what is known about how these features contribute to CDD/CDF or dioxin-like PCB  
13 release, and the rationale for subcategorizing the category.

14 The emission factors developed for the inventory are intended to be used for estimating  
15 total emissions for a source category rather than emissions from individual facilities. EPA has  
16 made uncertainty determinations for each of these emission factors based, in part, on the  
17 assumption that by applying them to a group of facilities, the potential for overestimating or  
18 underestimating individual facilities will, to some extent, be self-compensating. This means that  
19 in using these emission factors one can place significantly greater confidence in an emission  
20 estimate for a class than in an estimate for any individual facility. Given the limited amount of  
21 data available for deriving emission factors and the limitations of our understanding about  
22 facility-specific conditions that determine formation and control of dioxin-like compounds, the  
23 current state of knowledge cannot support the development of emission factors that can be used  
24 to accurately estimate emissions on an individual facility-specific basis. The emission factors  
25 developed for each of the categories discussed in this national emissions inventory are listed in  
26 Tables 1-11 and 1-12.

### 27 28 **1.2.3. Confidence Ratings**

29 As discussed above, each source emission calculation required estimates of an “emission  
30 factor” and an “activity level.” For each emission source, the quantity and quality of the  
31 available information for both terms vary considerably. Consequently, it is important that  
32 emission estimates be accompanied by some indicator of the uncertainties associated with their  
33 development. For this reason, a qualitative confidence rating scheme was developed as an  
34 integral part of the emission estimate in consideration of the following factors:

- *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 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.
- *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 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.

The confidence rating scheme in Table 1-10, presents the qualitative criteria used to assign a high, medium, or low confidence rating to the emission factor and activity level terms for those source categories for which emission estimates can be reliably quantified. The overall “confidence rating” assigned to an emission estimate was determined by the confidence ratings assigned to the corresponding “activity level” term and “emission factor” term. If the lowest rating assigned to either the activity level or the emission factor term is “high,” then the category rating assigned to the emission estimate is high (also referred to as “A”). If the lowest rating assigned to either the activity level or the emission factor term is “medium,” then the category rating assigned to the emission estimate is medium (also referred to as “B”). If the lowest rating assigned to either the activity level or the emission factor term is “low,” then the category rating assigned to the emission estimate is low (also referred to as “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 cannot



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 class rating of D (Tables 1-6 and 1-7 show preliminary release estimates for the year 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 emission estimate. These source categories were assigned a confidence category rating of “E” and also were not included in the national inventory (see listings in Table 1-5 under the “Not quantifiable” column).

### 1.3. CONCLUSIONS

#### 1.3.1. Total Environmental Releases

Nationwide emission estimates of I-TEQ<sub>DF</sub> and TEQ<sub>DF</sub>-WHO<sub>98</sub> for the United States are presented in Tables 1-6 and 1-7, respectively. For the year 2000, EPA makes the following conclusions:

- The total releases in the inventory (Categories A, B, and C) were 1,529 g TEQ<sub>DF</sub>-WHO<sub>98</sub>/yr. These were dominated by releases to the air (92%). Most of the air releases were from combustion sources. The top three sources were backyard barrel burning of refuse (32%), MWIs (24%), and MWCs (5%).
- The contemporary formation sources included Category D air releases totaling 6,777 g TEQ<sub>DF</sub>-WHO<sub>98</sub>/yr. These were dominated by forest fires (72%) .
- A total of 18 contemporary formation sources were identified as Category E.
- Releases from only two reservoir sources could be estimated for 2000: urban runoff to surface water 142 g TEQ<sub>DF</sub>-WHO<sub>98</sub> and rural soil erosion to surface water 2,500 g TEQ<sub>DF</sub>-WHO<sub>98</sub>. Both of these estimates are preliminary (i.e., category D). Releases from the other reservoirs (air, sediment, water, and biota) could not be quantified (i.e., Category E).

### 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 1,529 g TEQ<sub>DF</sub>-WHO<sub>98</sub> in reference year 2000; 3,280 g in reference year 1995; and 13,962 g in reference year 1987. From 1987 to 2000 there was approximately an 89% reduction in releases to all media. Most of the reduction in dioxin releases (77%) occurred in the time period from 1987 to 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 third 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. A complete listing of all sources in the inventory ranked in order of releases is provided in Table 1-14.

Reductions in environmental releases of dioxin-like compounds are attributed primarily to reductions in air emissions from MWCs, MWIs, cement kilns burning hazardous waste, and 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, voluntary actions on the part of industry, and the closing of a number of 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 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 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 the following: bleached pulp, ethylene dichloride/vinyl chloride, pentachlorophenol-treated wood, and dioxazine dyes and pigments. None of these, however, were considered to have release potential and were not included in the inventory.

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

6 The possibility remains that truly undiscovered sources exist. Many of the sources that  
7 are well accepted today were discovered only in the past 20 years. For example, CDDs/CDFs in  
8 stack emissions from MWCs were not detected until the late 1970s; CDDs/CDFs in the  
9 wastewater effluent from bleached pulp and paper mills were found unexpectedly in the mid-  
10 1980s; iron ore was not recognized as a source until the early 1990s.

#### 11 12 **1.3.4. Formation Theory**

13 Current theory proposes that CDDs/CDFs are formed within the cool-down region of  
14 combustion processes, either *de novo* or from dioxin precursors. *De novo* synthesis involves  
15 solid phase reactions with carbon, chlorine, and oxygen, on combustion generated particles  
16 promoted by copper chloride as a catalyst. A less efficient, but plausible, formation process is  
17 the gas phase formation from precursors catalyzed by the presence of a transition metal such as  
18 copper chloride. The temperatures ideal for *de novo* dioxin formation are from 200 to 400° C.  
19 Reducing temperatures to below 200° C, especially at the air pollution control device, will  
20 minimize dioxin formation and releases from combustion sources. Chlorine sources present in  
21 feeds are necessary for dioxin formation. Experiments suggest that chlorine content of 1% in the  
22 feed/fuel is the threshold for a direct relationship to dioxin formation from combustion sources,  
23 i.e.,  $\text{Cl}_2 \geq 1\%$  is strongly correlated to the amount of dioxin formed, but  $\text{Cl}_2 \leq 1\%$  is not.  
24 However, in well designed, controlled, and operated full-scale combustion systems there doesn't  
25 appear to be a direct relationship with the amount of chlorine present in the waste or the amount  
26 of dioxin emissions from the stack.

27 Controversy exists regarding PVC's role in the formation of CDDs/CDFs during  
28 municipal waste combustion. Experimental evidence suggests that PVC combustion generates  
29 hydrogen chloride gas (HCl) and dioxin precursors such as chlorobenzenes and chlorophenols,  
30 both of which may contribute to dioxin formation. HCl is a progenitor of chlorine radicals that  
31 then participate in the dioxin formation chemistry. Precursors are foundation molecules to dioxin  
32 formation. If PVC was the only source of chlorine and dioxin precursors during the combustion  
33 of MSW, then the removal of PVC may reduce the amount of dioxin formed and emitted.  
34 However, the complex mixture of materials comprising MSW provides sufficient chlorine for *de*

1 *novo* synthesis, and dioxin precursors are formed as products of the incomplete combustion of  
2 the waste constituents. Therefore, the elimination of PVC from the waste prior to combustion  
3 doesn't necessarily eliminate the formation and emissions of CDDs/CDFs from municipal waste  
4 combustion.

5 Current information strongly suggests that releases of CDDs/CDFs to the U.S.  
6 environment occur principally from anthropogenic activities. However, scientific studies have  
7 identified the possibility of natural formation of some CDDs/CDFs (e.g., ball clay).  
8

### 9 **1.3.5. Congener Profiles of CDD/CDF Sources**

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

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

25 On the basis of inspection and comparisons of the average CDD/CDF congener profiles  
26 across combustion and noncombustion sources, the following observations were made (Cleverly  
27 et al., 1997) (these generalizations are derived from this data set, and their application beyond  
28 these data is uncertain):  
29

- 30 • It appears that combustion sources emit all 2,3,7,8-substituted CDDs/CDFs, although  
31 in varying percentages of total CDDs/CDFs.  
32
- 33 • In combustion source emissions, 2,3,7,8-TCDD is usually 0.1 to 1% of total  
34 CDDs/CDFs. The exception is stack emissions from industrial oil-fired boilers,  
35 where the available, but limited, data indicate that 2,3,7,8-TCDD constitutes an  
36 average of 7% of total CDD/CDF emissions.  
37

- It cannot be concluded that octa-CDD (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.
- 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-HpCDF; OCDD; 1,2,3,4,6,7,8-HpCDD/1,2,3,4,7,8-HxCDF; 2,3,4,6,7,8-HxCDF/octa-CDF (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 burning and not burning hazardous waste. 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-HxCDF; 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 sources 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 air measurements from a tunnel study of diesel traffic are quite similar.

**Table 1-1. The TEF scheme for I-TEQ<sub>DF</sub>**

<b>Dioxin congeners</b>	<b>TEF</b>	<b>Furan congeners</b>	<b>TEF</b>
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 1-2. 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'-TeCB	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 1-3. The TEF scheme for TEQ<sub>DFP</sub>-WHO<sub>98</sub>**

Dioxin congeners	TEF	Furan congeners	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'-TeCB	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



**Table 1-4. Nomenclature for dioxin-like compounds**

<b>Term/ symbol</b>	<b>Definition</b>
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 8 congener groups of CDDs, monochlorinated through octochlorinated).
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).
D	Symbol for congener class: dibenzo- <i>p</i> -dioxin
F	Symbol for congener class: dibenzofuran
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)
CDD	Chlorinated dibenzo- <i>p</i> -dioxin, halogens substituted in any position
CDF	Chlorinated dibenzofuran, halogens substituted in any position
PCB	Polychlorinated biphenyl
2,3,7,8	Halogen substitutions in the 2,3,7,8 positions

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

**Table 1-5. Known and suspected sources of CDDs/CDFs**

Emission source category	Contemporary formation sources			Reservoir sources		
	Quantifiable Categories A,B & C	Preliminary estimate Category D	Not quantifiable Category E	Quantifiable Categories A,B & C	Preliminary estimate Category D	Not quantifiable Category E
<b>I. COMBUSTION SOURCES</b>						
<b>Waste incineration</b>						
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		✓				
<b>Power/energy generation</b>						
Vehicle fuel combustion - leaded <sup>a</sup>	✓					
- unleaded	✓					
- diesel	✓					
Wood combustion - residential	✓					
- industrial	✓					
Coal combustion - residential		✓				
- industrial/utility	✓					
Oil combustion - residential		✓				
- industrial/utility	✓					

**Table 1-5. Known and suspected CDD/CDF sources (continued)**

Emission source category	Contemporary formation sources			Reservoir sources		
	Quantifiable Categories A,B & C	Preliminary estimate Category D	Not quantifiable Category E	Quantifiable Categories A,B & C	Preliminary estimate Category D	Not quantifiable Category E
<b>Other high-temperature sources</b>						
Cement kilns (hazardous waste burning)	✓					
Cement kilns (nonhazardous waste burning)	✓					
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			✓			
<b>Minimally controlled or uncontrolled combustion</b>						
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			✓			
<b>II. METAL SMELTING/REFINING</b>						
<b>Ferrous metal smelting/refining</b>						
Sintering plants	✓					
Coke production		✓				
Electric arc furnaces		✓				
Ferrous foundries		✓				

**Table 1-5. Known and suspected CDD/CDF sources (continued)**

Emission source category	Contemporary formation sources			Reservoir sources		
	Quantifiable Categories A,B & C	Preliminary estimate Category D	Not quantifiable Category E	Quantifiable Categories A,B & C	Preliminary estimate Category D	Not quantifiable Category E
<b>Nonferrous metal smelting/refining</b>						
Primary aluminum			✓			
Primary copper	✓					
Primary magnesium		✓				
Primary nickel			✓			
Secondary aluminum	✓					
Secondary copper	✓					
Secondary lead	✓					
<b>Scrap electric wire recovery</b>			✓			
<b>Drum and barrel reclamation</b>	✓					
<b>III. CHEMICAL MANUFACTURING (releases to the environment)</b>						
Bleached chemical wood pulp and paper mills	✓					
Mono- to 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			✓			
<b>IV. BIOLOGICAL AND PHOTOCHEMICAL PROCESSES</b>			✓			✓
<b>V. RESERVOIR SOURCES</b>						

**Table 1-5. Known and suspected CDD/CDF sources (continued)**

Emission source category	Contemporary formation sources			Reservoir sources		
	Quantifiable Categories A,B & C	Preliminary estimate Category D	Not quantifiable Category E	Quantifiable Categories A,B & C	Preliminary estimate Category D	Not quantifiable Category E
Land Air Water Sediments					✓	✓ ✓ ✓
<b>Anthropogenic structures</b> PCP-treated wood						✓

<sup>a</sup>Leaded fuel production and the manufacture of motor vehicle engines requiring leaded fuel for highway use have been prohibited in the United States.  
(See Section 4.1 for details.)

**Table 1-6. Inventory of contemporary releases (g TEQ/yr) of I-TEQ<sub>DF</sub> from known sources in the United States for reference years 2000, 1995, and 1987 (Columns A, B & C) and preliminary release estimates for 2000 (Column D)**

Emission source category	Confidence rating <sup>a</sup>									
	2000 Inventory			2000 Preliminary	1995 Inventory			1987 Inventory		
	A	B	C	D	A	B	C	A	B	C
RELEASES TO AIR										
WASTE INCINERATION										
Municipal waste combustion	78.9			0.01		1,100			7,915	
Hazardous waste incineration		3.18				5.7			5	
Boilers/industrial furnaces			1.82				0.38			0.77
Halogen acid furnaces			0.3							
Medical waste/pathological incineration			378				461			2,440
Crematoria - human			0.26				0.2			0.14
- animal										
Sewage sludge incineration		9.4				14			5.8	
Tire combustion			0.51				0.11			0.11
Pulp and paper mill sludge incinerators <sup>b</sup>										
Biogas combustion				0.22						
POWER/ENERGY GENERATION										
Vehicle fuel combustion										
- leaded gasoline <sup>c</sup>							1.3			31.9
- unleaded gasoline on-road			6.7				4.4			3.3
- unleaded gasoline off-road			0.35							
- diesel on-road			61.7				31.5			26.3
- diesel off-road										
- equipment			21				11			8.8
- railroad			6.4				6.6			5.5
- commercial marine vessel			4				4.5			3.6
Wood combustion										
- residential			11.3			15.7			22	

**Table 1-6. Inventory of contemporary releases (g TEQ/yr) of I-TEQ<sub>DF</sub> from known sources in the United States for reference years 2000, 1995, and 1987 (Columns A, B & C) and preliminary release estimates for 2000 (Column D) (continued)**

Emission source category	Confidence rating <sup>a</sup>									
	2000 Inventory			2000 Preliminary	1995 Inventory			1987 Inventory		
	A	B	C	D	A	B	C	A	B	C
- industrial			39.4				24.9			25.2
Coal combustion										
- utility boilers		70.4		2.7		60.9			51.4	
- residential <sup>d</sup>				35.4						
- commercial/industrial										
Oil combustion										
- industrial/utility (residual oil)			1.47				9.3			15.5
- industrial/utility (distillate oil)			6.3				6.4			7.2
- institutional/commercial heating (residual oil)			0.56				0.73			1.34
- institutional/commercial heating (distillate oil)			2.53				2.7			3.24
- residential (distillate oil)			3.59				3.93			4.22
OTHER HIGH-TEMPERATURE SOURCES										
Cement kilns (hazardous waste burning)			63.3				145.3			109.6
Lightweight aggregate kilns burning hazardous waste			1.79				2.4			3.3
Cement kilns (nonhazardous waste burning)			16.6				15.9			12.3
Asphalt mixing plants				0.55						7
Petroleum refining catalyst regeneration			2.09				2.14			2.11
Cigarette combustion			0.4				0.8			1
Carbon reactivation furnaces			0.08				0.08			0.06
Kraft recovery boilers	0.75 <sup>e</sup>					2.3			2	

**Table 1-6. Inventory of contemporary releases (g TEQ/yr) of I-TEQ<sub>DF</sub> from known sources in the United States for reference years 2000, 1995, and 1987 (Columns A, B & C) and preliminary release estimates for 2000 (Column D) (continued)**

Emission source category	Confidence rating <sup>a</sup>									
	2000 Inventory			2000 Preliminary	1995 Inventory			1987 Inventory		
	A	B	C	D	A	B	C	A	B	C
MINIMALLY CONTROLLED OR UNCONTROLLED COMBUSTION <sup>f</sup>										
Combustion of landfill gas				22						
Landfill fires				1,126 <sup>g</sup>						
Accidental fires - structural				16						
Accidental fires - vehicles				23.8						
Forest and brush fires <sup>h</sup>				4,538						
Backyard barrel burning <sup>i</sup>			472.6				595			573
Residential yard waste burning <sup>j</sup>				9.5						
Land clearing debris burning				528						
METALLURGICAL PROCESSES										
Ferrous metal smelting/refining	24.4			6.03		25.1				29.3
- sintering plants										
- coke production										
- electric arc furnaces										
- foundries				13.9						
Nonferrous metal smelting/refining	0.29		33.8			<0.5	27.4		<0.5	15.3
- primary copper										
- secondary aluminum										
- secondary copper										
- secondary lead										
- primary magnesium	42	2.35	0.85			1.63		1.22		
Drum and barrel reclamation			0.58				0.08			0.08
CHEMICAL MANUFACTURE/PROCESSING SOURCES										
Ethylene dichloride/vinyl chloride		5.51				11.2				
Akalies/chlorine manufacturing		0.08								



**Table 1-6. Inventory of contemporary releases (g TEQ/yr) of I-TEQ<sub>DF</sub> from known sources in the United States for reference years 2000, 1995, and 1987 (Columns A, B & C) and preliminary release estimates for 2000 (Column D) (continued)**

Emission source category	Confidence rating <sup>a</sup>									
	2000 Inventory			2000 Preliminary	1995 Inventory			1987 Inventory		
	A	B	C	D	A	B	C	A	B	C
TOTAL RELEASES TO AIR <sup>k</sup>	1,375.54			6381.4	2,861.08			12,291.95		
RELEASES TO WATER										
CHEMICAL MANUFACTURE/PROCESSING SOURCES										
Bleached chemical wood pulp and paper mills	1.02			15.7	28			356		
POTW (municipal) wastewater										
Ethylene dichloride/vinyl chloride		23.8				0.043				
Akalies/chlorine manufacturing		1.85								
TOTAL RELEASES TO WATER <sup>k</sup>	26.67			15.7	28.04			356		
RELEASES TO LAND										
CHEMICAL MANUFACTURING/PROCESSING SOURCES										
Bleached chemical wood pulp and paper mill sludge	0.08				2			14.1		
Ethylene dichloride/vinyl chloride		1.45				0.73				
Municipal wastewater treatment sludge	78.2				156.5			103		
Commercially marketed sewage sludge	1.9				4			3.5		
2,4-Dichlorophenoxy acetic acid					18.4			21.3		
TOTAL RELEASES TO LAND <sup>k</sup>	81.63				181.63			141.9		
OVERALL RELEASES TO OPEN AND CIRCULATING ENVIRONMENT	1,483.84			6,397.0	3,070.75			12,788.85		
	(SUM OF COLUMNS A, B, C)				(SUM OF COLUMNS A, B, C)			(SUM OF COLUMNS A, B, C)		

**Table 1-6. Inventory of contemporary releases (g TEQ/yr) of I-TEQ<sub>DF</sub> from known sources in the United States for reference years 2000, 1995, and 1987 (Columns A, B & C) and preliminary release estimates for 2000 (Column D) (continued)**

<sup>a</sup>The most reliable estimates of environmental releases are those sources in categories A, B, and C.

<sup>b</sup>Included in estimate for Wood combustion - industrial.

<sup>c</sup>Leaded fuel production and the manufacture of motor vehicle engines requiring leaded fuel for highway use have been prohibited in the United States. (See Section 4.1 for details.)

<sup>d</sup>Includes combustion of bituminous/subbituminous coal and anthracite coal.

<sup>e</sup>This estimate is based on a TEQ<sub>DF</sub>-WHO<sub>98</sub> emissions estimate.

<sup>f</sup>This refers to conventional pollutant control, not dioxin emissions control. Very few of the sources listed in this inventory control specifically for CDD/CDF emissions.

<sup>g</sup>Congener-specific emissions data were not available; the Nordic TEQ estimate was used as a surrogate for the I-TEQ<sub>DF</sub> emissions estimate.

<sup>h</sup>Includes forest wildfires and prescribed burning for forest management.

<sup>i</sup>This term refers to the burning of residential waste in barrels.

<sup>j</sup>Includes burning of brush and leaves.

<sup>k</sup>Total reflects only the total of the estimates made in this report.

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 I-TEQ<sub>DF</sub> emissions from “Unquantified” (Category D) sources; **based on extremely limited data, judged to be clearly nonrepresentative**.

POTW = Publicly owned treatment works

**Table 1-7. Inventory of contemporary releases (g TEQ/yr) of TEQ<sub>DF</sub>-WHO<sub>98</sub> from known sources in the United States for reference years 2000, 1995, and 1987 (Columns A, B & C) and preliminary release estimates for 2000 (Column D)**

Emission source category	Confidence rating <sup>a</sup>									
	2000 Inventory			2000 Preliminary	1995 Inventory			1987 Inventory		
	A	B	C	D	A	B	C	A	B	C
RELEASES TO AIR										
WASTE INCINERATION										
Municipal waste combustion	78.9 <sup>b</sup>			0.01		1,250			8,877	
Hazardous waste incineration		3.2				5.8			5	
Boilers/industrial furnaces			1.82				0.39			0.78
Halogen acid furnaces			0.31							
Medical waste/pathological incineration			378				488			2,590
Crematoria - human			0.27				0.21			0.14
- animal										
Sewage sludge incineration		9.6				14.2			5.8	
Tire combustion			0.51				0.11			0.11
Pulp and paper mill sludge incinerators <sup>c</sup>										
Biogas combustion				0.22						
POWER/ENERGY GENERATION										
Vehicle fuel combustion										
- leaded gasoline <sup>d</sup>							1.6			37.5
- unleaded gasoline on-road			7				4.7			3.6
- unleaded gasoline off-road			0.36							
- diesel on-road			65.4				33.3			27.8
- diesel off-road										
- equipment			22				12			9.4
- railroad			6.8				7			5.8
- commercial marine vessel			4.3				4.8			3.8
Wood combustion										
- residential			11.3 <sup>b</sup>			15.7 <sup>b</sup>			22 <sup>b</sup>	
- industrial			41.5			26.2			26.5	

**Table 1-7. Inventory of contemporary releases (g TEQ/yr) of TEQ<sub>DF</sub>-WHO<sub>98</sub> from known sources in the United States for reference years 2000, 1995, and 1987 (Columns A, B & C) and preliminary release estimates for 2000 (Column D) (continued)**

Emission source category	Confidence rating <sup>a</sup>									
	2000 Inventory			2000 Preliminary	1995 Inventory			1987 Inventory		
	A	B	C	D	A	B	C	A	B	C
Coal combustion										
- utility boilers		69.5		2.7 <sup>b</sup>		60.1			50.8	
- residential <sup>c</sup>				35.4 <sup>b</sup>						
- commercial/industrial										
Oil combustion										
- industrial/utility (residual oil)			1.69				10.7			17.8
- industrial/utility (distillate oil)			7.25				7.3			8.3
- institutional/commercial heating (residual oil)			0.65				0.84			1.54
- institutional/commercial heating (distillate oil)			2.92				3.11			3.73
- residential (distillate oil)			4.54				4.98			5.35
<b>OTHER HIGH-TEMPERATURE SOURCES</b>										
Cement kilns (hazardous waste burning)			68.4				156.1			117.8
Lightweight aggregate kilns burning hazardous waste			1.86				2.4 <sup>b</sup>			3.3 <sup>b</sup>
Cement kilns (nonhazardous waste burning)			17.2				16.6			12.7
Asphalt mixing plants				0.55 <sup>b</sup>						
Petroleum refining catalyst Regeneration			2.19				2.24			2.21
Cigarette combustion			0.4				0.8			1
Carbon reactivation furnaces			0.08 <sup>b</sup>				0.08 <sup>b</sup>			0.06 <sup>b</sup>
Kraft recovery boilers	0.75					2.3			2	

**Table 1-7. Inventory of contemporary releases (g TEQ/yr) of TEQ<sub>DF</sub>-WHO<sub>98</sub> from known sources in the United States for reference years 2000, 1995, and 1987 (Columns A, B & C) and preliminary release estimates for 2000 (Column D) (continued)**

[illegible]

**Table 1-7. Inventory of contemporary releases (g TEQ/yr) of TEQ<sub>DF</sub>-WHO<sub>98</sub> from known sources in the United States for reference years 2000, 1995, and 1987 (Columns A, B & C) and preliminary release estimates for 2000 (Column D) (continued)**

Emission source category	Confidence rating <sup>a</sup>									
	2000 Inventory			2000 Preliminary	1995 Inventory			1987 Inventory		
	A	B	C	D	A	B	C	A	B	C
TOTAL RELEASES TO AIR <sup>k</sup>	1,422.51			6,764.11	3,101.16			13,479.69		
RELEASES TO WATER										
CHEMICAL MANUFACTURE/PROCESSING SOURCES										
Bleached chemical wood pulp and paper mills	1.02			13	28			356		
POTW (municipal) wastewater										
Ethylene dichloride/vinyl chloride		22.6 <sup>b</sup>				0.043 <sup>b</sup>				
Akalies/chlorine manufacturing		1.82 <sup>b</sup>								
TOTAL RELEASES TO WATER <sup>k</sup>	25.44			13	28.04			356		
RELEASES TO LAND										
CHEMICAL MANUFACTURING/PROCESSING SOURCES										
Bleached chemical wood pulp and paper mill sludge	0.08				2			14.1		
Ethlyene dichloride/vinyl chloride		1.36				0.73 <sup>b</sup>				
Municipal wastewater treatment sludge	78.2				116.1			76.6		
Commercially marketed sewage sludge	1.9				3			2.6		
2,4-Dichlorophenoxy acetic acid					28.9			33.4		
TOTAL RELEASES TO LAND <sup>j</sup>	81.54				150.73			126.7		
OVERALL RELEASES TO OPEN AND CIRCULATING ENVIRONMENT	1,529.49			6777.1	3,279.93			13,962.39		
	(SUM OF COLUMNS A, B, C)				(SUM OF COLUMNS A, B, C)			(SUM OF COLUMNS A, B, C)		

<sup>a</sup>The most reliable estimates of environmental releases are those sources in categories A, B, and C.

<sup>b</sup>This estimate is based on a TEQ<sub>DF</sub>-WHO<sub>98</sub> emissions estimate.

<sup>c</sup>Included in estimate for Wood combustion - industrial.

<sup>d</sup>Leaded fuel production and the manufacture of motor vehicle engines requiring leaded fuel for highway use have been prohibited in the United States. (See Section 4.1 for details.)

<sup>e</sup>Includes combustion of bituminous/subbituminous coal and anthracite coal.

**Table 1-7. Inventory of contemporary releases (g TEQ/yr) of TEQ<sub>DF</sub>-WHO<sub>98</sub> from known sources in the United States for reference years 2000, 1995, and 1987 (Columns A, B & C) and preliminary release estimates for 2000 (Column D) (continued)**

<sup>f</sup>This refers to conventional pollutant control, not dioxin emissions control.

Very few of the sources listed in this inventory control specifically for CDD/CDF emissions.

<sup>g</sup>Congener-specific emissions data were not available; the Nordic TEQ estimate was used as a surrogate for the I-TEQ<sub>DF</sub> emissions estimate.

<sup>h</sup>Includes forest wildfires and prescribed burning for forest management.

<sup>i</sup>This term refers to the burning of residential waste in barrels.

<sup>j</sup>Includes burning of brush and leaves.

<sup>k</sup>Total reflects only the total of the estimates made in this report.

- 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 I-TEQ<sub>DF</sub> emissions from “Unquantified” (Category D) sources; **based on extremely limited data, judged to be clearly nonrepresentative**.

POTW = Publicly owned treatment works

**Table 1-8. Identification of products containing CDDs/CDFs (g I-TEQ<sub>DF</sub>/yr)**

<b>Product</b>	<b>2000</b>	<b>1995</b>	<b>1987</b>
Bleached chemical wood pulp	0.58	40	505
Ethylene dichloride/vinyl chloride	0.02	0.02	NA
Chloaranil	1.16	50.6	NA
Pentachlorophenol	7,325	8,400	36,000
2,4 -Dichlorophenoxy acetic acid	NA	18.4	21.3
<b>TOTAL AMOUNT IN PRODUCTS</b>	<b>7,327</b>	<b>8,509</b>	<b>36,526</b>

NA = Information not available

Only 2,4-D is considered an environmental release.



**Table 1-9. Identification of products containing CDDs/CDFs (g TEQ<sub>DF</sub>-WHO<sub>98</sub>/yr)**

<b>Product</b>	<b>2000</b>	<b>1995</b>	<b>1987</b>
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	NA	28.9	33.4
<b>TOTAL AMOUNT IN PRODUCTS</b>	<b>4,397</b>	<b>4,933</b>	<b>20,538</b>

NA = Information not available

Only 2,4-D is considered an environmental release.

**Table 1-10. Confidence rating scheme for U.S. emission estimates**

<b>Confidence rating</b>	<b>Activity level estimate</b>	<b>Emission factor estimate</b>
<b>Categories/media for which releases can be reasonably quantified</b>		
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
<b>Categories/media for which releases cannot be reasonably quantified</b>		
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

**Table 1-11. I-TEQ<sub>DF</sub> emission factors used to develop national emission inventory estimates of releases to air**

Emission source category	I-TEQ <sub>DF</sub> emission factor			Emission factor units
	2000	1995	1987	
WASTE INCINERATION				
Municipal waste combustion	2.82	38.2 <sup>a</sup>	573 <sup>a</sup>	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	0.64	ng TEQ/kg waste combusted
Halogen acid furnaces	0.803			ng TEQ/kg waste feed
Medical waste/pathological incineration	630 <sup>a</sup>	598 <sup>a</sup>	1,706 <sup>a</sup>	ng TEQ/kg waste combusted
Crematoria - human	410	17,000	17,000	ng TEQ/body
- animal	0.11			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 <sup>b</sup>				
POWER/ENERGY GENERATION				
Vehicle fuel combustion - leaded <sup>c</sup>	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 <sup>d</sup>	0.56–13.2 <sup>d</sup>	0.56–13.2 <sup>d</sup>	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	1.04–28.58 <sup>e</sup>	1.04–28.58 <sup>e</sup>	1.04–28.58 <sup>e</sup>	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
MINIMALLY CONTROLLED OR UNCONTROLLED COMBUSTION				
Backyard barrel burning <sup>f</sup>	72.8	72.8	72.8	ng TEQ/kg waste combusted

**Table 1-11. I-TEQ<sub>DF</sub> emission factors used to develop national emission inventory estimates of releases to air (continued)**

Emission source category	I-TEQ <sub>DF</sub> emission factor			Emission factor units
	2000	1995	1987	
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	21.1	21.1	21.1	ng TEQ/kg scrap feed
- secondary copper smelting <sup>g</sup>				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 <sup>a</sup>		ng TEQ/kg EDC produced

<sup>a</sup>Different emission factors were derived for various subcategories within this industry; the value listed is a weighted average.

<sup>b</sup>Included in total for Wood combustion - industrial.

<sup>c</sup>Leaded fuel production and the manufacture of motor vehicle engines requiring leaded fuel for highway use have been prohibited in the United States. (See Section 4.1 for details.)

<sup>d</sup>Emission factor of 0.56 ng I-TEQ<sub>DF</sub>/kg used for nonsalt-laden wood; emission factor of 13.2 ng I-TEQ<sub>DF</sub>/kg used for salt-laden wood.

<sup>e</sup>Emission factor of 1.04 ng I-TEQ<sub>DF</sub>/kg used for kilns with air pollution control device inlet temperatures less than 232 °C; emission factor of 28.58 ng I-TEQ<sub>DF</sub>/kg used for kilns with APCD inlet temperatures greater than 232 °C.

<sup>f</sup>Includes the burning of brush and leaf residential yard waste.

<sup>g</sup>Facility-specific emission factors were used ranging from 3.6 to 16,600 ng I-TEQ<sub>DF</sub>/kg scrap consumed.

**Table 1-12. TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factors used to develop national emission inventory estimates of releases to air**

Emission source category	TEQ <sub>DF</sub> -WHO <sub>98</sub> emission factor			Emission factor units
	2000	1995	1987	
WASTE INCINERATION				
Municipal waste combustion	2.82	43.4 <sup>a</sup>	644 <sup>a</sup>	ng TEQ/kg waste combusted
Hazardous waste incineration	2.13	3.88	3.88	ng TEQ/kg waste combusted
Boilers/industrial furnaces	1.21	0.65	0.65	ng TEQ/kg waste combusted
Halogen acid furnaces	0.836			ng TEQ/kg waste feed
Medical waste/pathological incineration	630 <sup>a</sup>	633 <sup>a</sup>	1,811 <sup>a</sup>	ng TEQ/kg waste combusted
Crematoria - human <sup>b</sup>	434	17,000	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 <sup>c</sup>				
POWER/ENERGY GENERATION				
Vehicle fuel combustion - leaded <sup>d</sup>	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	2 <sup>b</sup>	2 <sup>b</sup>	2 <sup>b</sup>	ng TEQ/kg wood combusted
- industrial <sup>e</sup>	0.6–13.2	0.6–13.2	0.6–13.2	ng TEQ/kg wood combusted
Coal combustion - utility	0.78	0.078	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	1.11–30.7 <sup>f</sup>	1.11–30.7 <sup>f</sup>	1.11–30.7 <sup>f</sup>	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 <sup>b</sup>	1.2 <sup>b</sup>	1.2 <sup>b</sup>	ng TEQ/kg of reactivated carbon
Kraft recovery boilers	0.028	0.028	0.028	ng TEQ/kg solids combusted

**Table 1-12. TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factors used to develop national emission inventory estimates of releases to air (continued)**

Emission source category	TEQ <sub>DF</sub> -WHO <sub>98</sub> emission factor			Emission factor units
	2000	1995	1987	
MINIMALLY CONTROLLED OR UNCONTROLLED COMBUSTION				
Backyard barrel burning <sup>g</sup>	76.8 <sup>b</sup>	76.8 <sup>b</sup>	76.8 <sup>b</sup>	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 <sup>b</sup>	<0.31	<0.31	<0.31	ng TEQ/kg copper produced
- secondary aluminum smelting	22.4	22.4	22.4	ng TEQ/kg scrap feed
- secondary copper smelting <sup>h</sup>				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 <sup>a, b</sup>		ng TEQ/kg EDC produced

<sup>a</sup>Different emission factors were derived for various subcategories within this industry; the value listed is a weighted average.

<sup>b</sup>Congener-specific data were not available; the TEQ<sub>DF</sub> emission factor was used as a surrogate for the TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factor.

<sup>c</sup>Included in total for Wood combustion - industrial.

<sup>d</sup>Leaded fuel production and the manufacture of motor vehicle engines requiring leaded fuel for highway use have been prohibited in the United States. (See Section 4.1 for details).

<sup>e</sup>Emission factor of 0.6 ng I-TEQ<sub>DF</sub>/kg used for non-salt-laden wood; emission factor of 13.2 ng I-TEQ<sub>DF</sub>/kg used for salt-laden wood.

<sup>f</sup>Emission factor of 1.11 ng I-TEQ<sub>DF</sub>/kg used for kilns with air pollution control device inlet temperatures less than 232 °C; emission factor of 28.58 ng I-TEQ<sub>DF</sub>/kg used for kilns with APCD inlet temperatures greater than 232 °C.

<sup>g</sup>This term refers to the burning of residential waste in barrels.

<sup>h</sup>Facility-specific emission factors were used ranging from 3.6 to 16,600 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg scrap consumed.

**Table 1-13. Releases (g TEQ<sub>DF</sub>-WHO<sub>98</sub>) to the open environment from reservoir sources**

	<b>Reference year 2000</b>	<b>Reference year 1995</b>	<b>Reference year 1987</b>
Urban runoff to surface water	142 (D)	133 (D)	124 (D)
Rural soil erosion to surface water	2,500 (D)	2,600 (D)	2,900 (D)

Letter in parenthesis shows the confidence rating for these releases.

**Table 1-14. Sources in quantitative inventory ranked by releases to all media**

Ranking of the year 2000 sources	Yr 2000 (grams)	Percent of Total	Ranking of the year 1995 sources	Yr 1995 (grams)	Percent of Total	Ranking of the year 1987 sources	Yr 1987 (grams)	Percent of Total
Backyard barrel burning of refuse (Air)	498.53	32.59%	Municipal waste combustion (Air)	1250	38.11%	Municipal waste combustion (Air)	8877	63.58%
Medical waste/pathological incineration (Air)	378	24.71%	Backyard barrel burning of refuse (Air)	628	19.15%	Medical waste/pathological incineration (Air)	2590	18.55%
Municipal waste combustion (Air)	78.9	5.16%	Medical waste/pathological incineration (Air)	488	14.88%	Secondary copper smelters (Air)	983	7.04%
Municipal wastewater treatment sludge (Land)	78.2	5.11%	Secondary copper smelters (Air)	271	8.26%	Backyard barrel burning of refuse (Air)	604	4.33%
Coal fired-utility boilers (Air)	69.5	4.54%	Cement kilns (hazardous waste burning) (Air)	156.1	4.76%	Bleached chemical wood pulp and paper mills (Water + Land)	370.1	2.65%
Cement kilns (hazardous waste burning) (Air)	68.4	4.47%	Municipal wastewater treatment sludge (Land)	116.1	3.54%	Cement kilns (hazardous waste burning) (Air)	117.8	0.84%
Diesel heavy duty trucks (Air)	65.4	4.28%	Coal fired-utility boilers (Air)	60.1	1.83%	Municipal wastewater treatment sludge (Land)	76.6	0.55%
Primary Magnesium production (Air)	42	2.75%	Diesel heavy duty trucks (Air)	33.3	1.02%	Coal fired-utility boilers (Air)	50.8	0.36%
Industrial wood combustion (Air)	41.5	2.71%	Bleached chemical wood pulp and paper mills (Water + Land)	30	0.91%	Automobiles using leaded gasoline (Air)	37.5	0.27%
Secondary aluminum smelting (Air)	35.9	2.35%	Secondary aluminum smelting (Air)	29.1	0.89%	2,4-Dichlorophenoxy acetic acid (Land)	33.4	0.24%
Ethylene dichloride/vinyl chloride production (Water + Land + Air)	29.42	1.92%	2,4-Dichlorophenoxy acetic acid (Land)	28.9	0.88%	Sintering plants (Air)	32.7	0.23%
Sintering plants (Air)	27.6	1.80%	Sintering plants (Air)	28	0.85%	Diesel heavy duty trucks (Air)	27.8	0.20%
Diesel off road equipment (Air)	22	1.44%	Industrial wood combustion (Air)	26.2	0.80%	Industrial wood combustion (Air)	26.5	0.19%



**Table 1-14. Sources in quantitative inventory ranked by releases to all media (continued)**

Ranking of the year 2000 sources	Yr 2000 (grams)	Percent of Total	Ranking of the year 1995 sources	Yr 1995 (grams)	Percent of Total	Ranking of the year 1987 sources	Yr 1987 (grams)	Percent of Total
Cement kilns (nonhazardous waste burning) (Air)	17.2	1.12%	Cement kilns (nonhazardous waste burning) (Air)	16.6	0.51%	Residential wood combustion (Air)	22	0.16%
Residential wood combustion (Air)	11.3	0.74%	Residential wood combustion (Air)	15.7	0.48%	Industrial/utility oil combustion (residual oil) (Air)	17.8	0.13%
Sewage sludge incineration (Air)	9.6	0.63%	Sewage sludge incineration (Air)	14.2	0.43%	Secondary aluminum smelting (Air)	16.3	0.12%
Industrial/utility oil combustion (distillate oil) (Air)	7.25	0.47%	Diesel off road equipment (Air)	12	0.37%	Cement kilns (nonhazardous waste burning) (Air)	12.7	0.09%
Automobiles using unleaded gasoline (Air)	7	0.46%	Ethylene dichloride/vinyl chloride production (Water + Land + Air)	11.97	0.36%	Diesel off road equipment (Air)	9.4	0.07%
Diesel railroad locomotives (Air)	6.8	0.44%	Industrial/utility oil combustion (residual oil) (Air)	10.7	.33%	Industrial/utility oil combustion (distillate oil) (Air)	8.3	0.06%
Residential heating (distillate oil) (Air)	4.54	0.30%	Industrial/utility oil combustion (distillate oil) (Air)	7.3	0.22%	Diesel railroad locomotives (Air)	5.8	0.04%
Diesel commercial marine vessel (Air)	4.3	0.28%	Diesel railroad locomotives (Air)	7	0.21%	Sewage sludge incineration (Air)	5.8	0.04%
Hazardous waste incineration (Air)	3.2	0.21%	Hazardous waste incineration (Air)	5.8	0.18%	Residential heating (distillate oil) (Air)	5.35	0.04%
Institutional/commercial heating (distillate oil) (Air)	2.92	0.19%	Residential heating (distillate oil) (Air)	4.98	0.15%	Hazardous waste incineration (Air)	5	0.04%
Secondary lead smelting (Air)	2.48	0.16%	Diesel commercial marine vessel (Air)	4.8	0.15%	Diesel commercial marine vessel (Air)	3.8	0.03%
Petroleum Refining Catalyst Regeneration (Air)	2.19	0.14%	Automobiles using unleaded gasoline (Air)	4.7	0.14%	Institutional/commercial heating (distillate oil) (Air)	3.73	0.03%
Commercially marketed sewage sludge (Land)	1.9	0.12%	Institutional/commercial heating (distillate oil) (Air)	3.11	0.09%	Automobiles using unleaded gasoline (Air)	3.6	0.03%

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**Table 1-14. Sources in quantitative inventory ranked by releases to all media (continued)**

Ranking of the year 2000 sources	Yr 2000 (grams)	Percent of Total	Ranking of the year 1995 sources	Yr 1995 (grams)	Percent of Total	Ranking of the year 1987 sources	Yr 1987 (grams)	Percent of Total
Akalies/chlorine manufacturing (Water + Air)	1.9	0.12%	Commercially marketed sewage sludge (Land)	3	0.09%	Lightweight aggregate kilns burning hazardous waste (Air)	3.3	0.02%
Lightweight aggregate kilns burning hazardous waste (Air)	1.86	0.12%	Lightweight aggregate kilns burning hazardous waste (Air)	2.4	0.07%	Commercially marketed sewage sludge (Land)	2.6	0.02%
Boilers/industrial furnaces (Air)	1.82	0.12%	Kraft recovery boilers (Air)	2.3	0.07%	Petroleum Refining Catalyst Regeneration (Air)	2.21	0.02%
Industrial/utility oil combustion (residual oil) (Air)	1.69	0.11%	Petroleum Refining Catalyst Regeneration (Air)	2.24	0.07%	Kraft recovery boilers (Air)	2	0.01%
Bleached chemical wood pulp and paper mills (Water + Land)	1.1	0.07%	Secondary lead smelting (Air)	1.72	0.05%	Industrial/utility oil combustion (residual oil) (Air)	1.54	0.01%
Secondary copper smelting (Air)	0.86	0.06%	Automobiles using leaded gasoline (Air)	1.6	0.05%	Secondary lead smelting (Air)	1.29	0.01%
Kraft recovery boilers (Air)	0.75	0.05%	Industrial/utility oil combustion (residual oil) (Air)	0.84	0.03%	Cigarette combustion (Air)	1	0.01%
Institutional/commercial heating (residual oil) (Air)	0.65	0.04%	Cigarette combustion (Air)	0.8	0.02%	Boilers/industrial furnaces (Air)	0.78	0.01%
Drum and barrel reclamation (Air)	0.61	0.04%	Primary copper smelting (Air)	0.5	0.02%	Primary copper smelting (Air)	0.5	0.004%
Tire incineration (Air)	0.51	0.03%	Boilers/industrial furnaces (Air)	0.39	0.01%	Crematoria - human (Air)	0.14	0.001%
Cigarette combustion (Air)	0.4	0.03%	Crematoria - human (Air)	0.21	0.01%	Tire incineration (Air)	0.11	0.001%
Unleaded gasoline off-road equipment (Air)	0.36	0.02%	Tire incineration (Air)	0.11	0.003%	Drum and barrel reclamation (Air)	0.08	0.001%
Halogen acid furnaces (Air)	0.31	0.02%	Drum and barrel reclamation (Air)	0.08	0.002%	Carbon reactivation furnaces (Air)	0.06	<b>0.000%</b>
Primary copper smelting (Air)	0.29	0.02%	Carbon reactivation furnaces (Air)	0.08	0.002%			
Crematoria - human (Air)	0.27	0.02%						
Automobiles using leaded gasoline (Air)	0	0.00%						

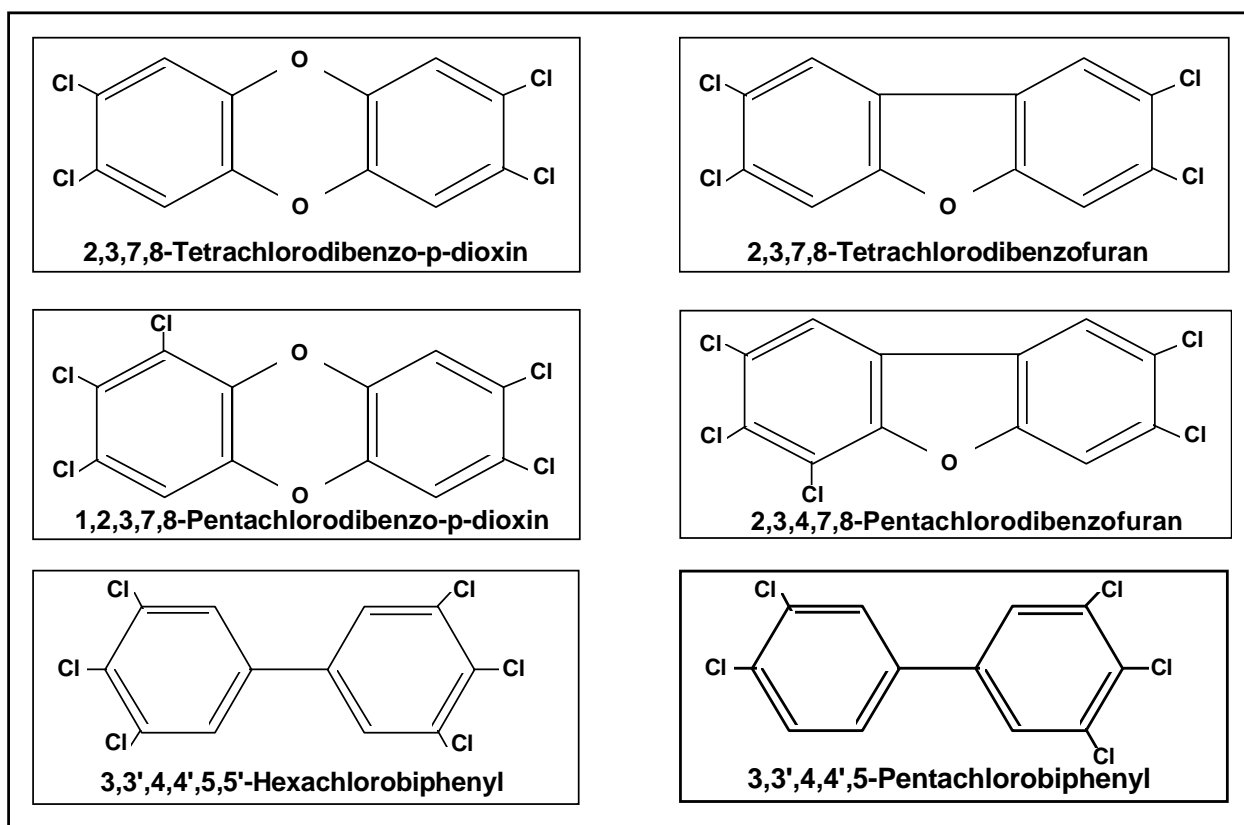
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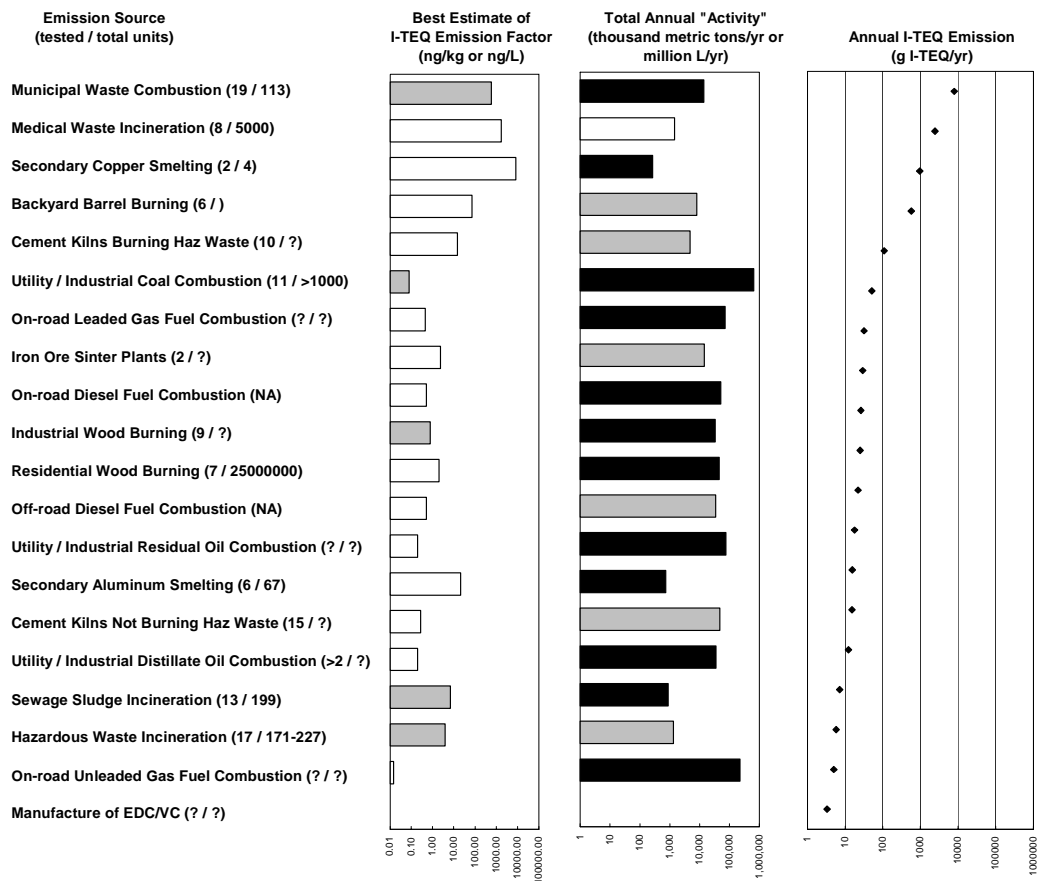
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Table 1-14. Sources in quantitative inventory ranked by releases to all media (continued)

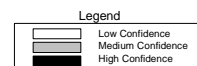
Ranking of the year 2000 sources	Yr 2000 (grams)	Percent of Total	Ranking of the year 1995 sources	Yr 1995 (grams)	Percent of Total	Ranking of the year 1987 sources	Yr 1987 (grams)	Percent of Total
TOTAL	1529.49	100%		3279.93	100%		13962.39	100%



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

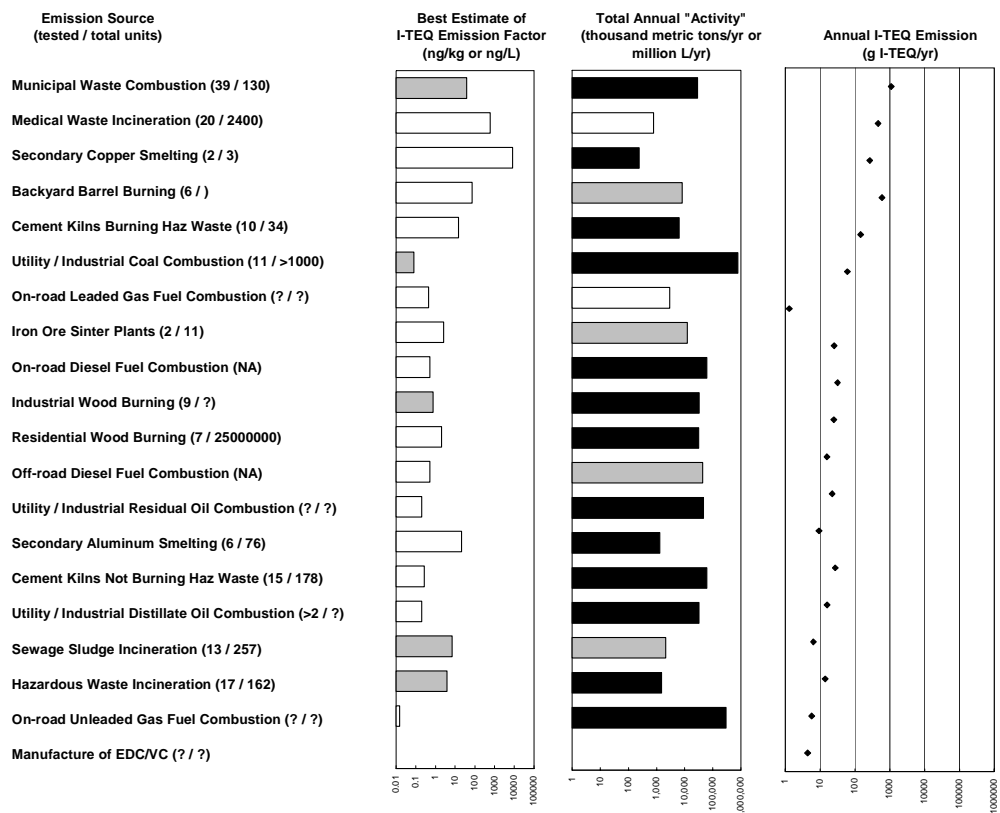


The figures include sources with annual I-TEQ emission estimates greater than 5 g I-TEQ/yr in one or both of the Reference Years 1987 or 1995. Derivation of the emission factors and annual "Activity" estimates (e.g., kg of waste incinerated) are presented in the following chapters of this report. The 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.

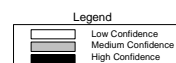


**Figure 1-2. Estimated CDD/CDF I-TEQ emissions to air from combustion sources in the United States (reference year: 1987).**

Note: Municipal solid waste incineration is currently referred to as municipal waste combustion.

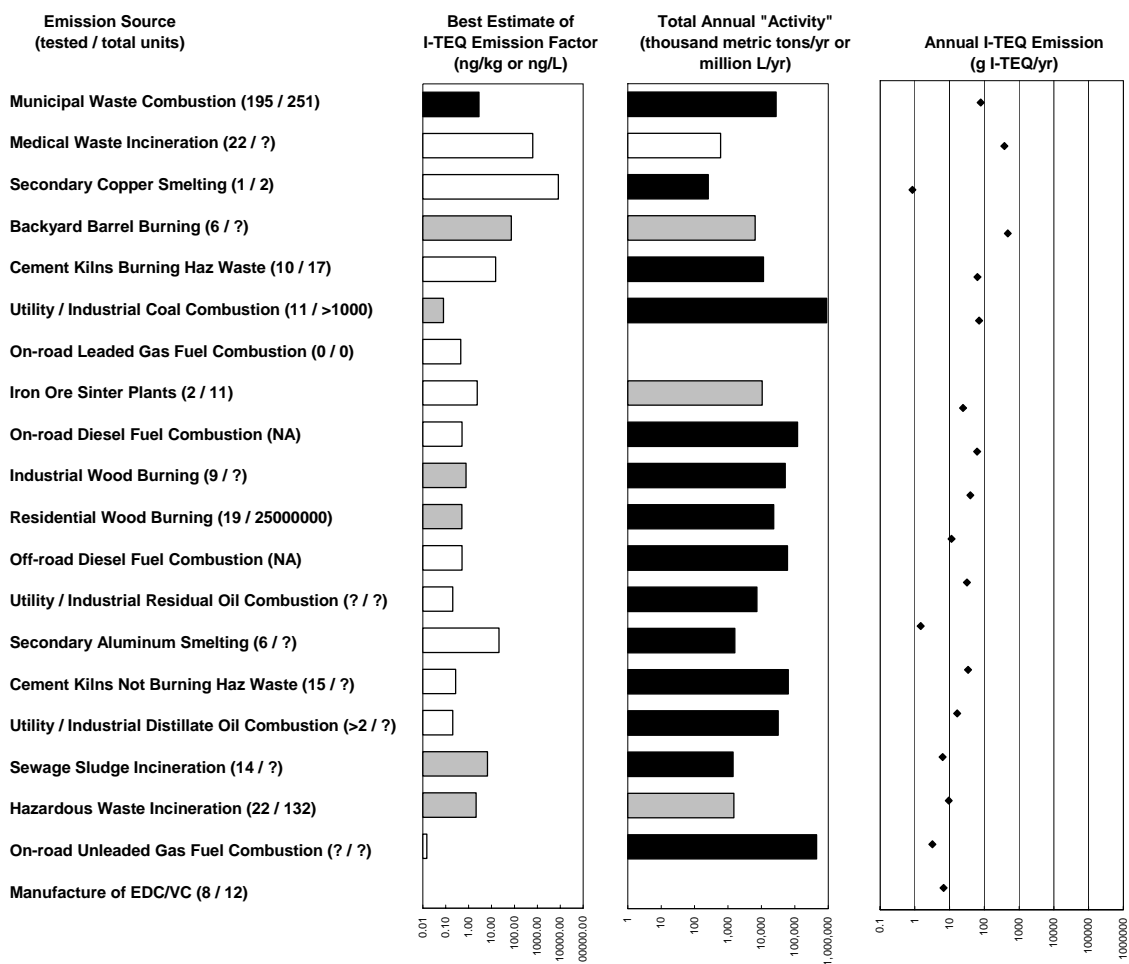


The figures include sources with annual I-TEQ emission estimates greater than 5 g I-TEQ/yr in one or both of the Reference Years 1987 or 1995. Derivation of the emission factors and annual "Activity" estimates (e.g., kg of waste incinerated) are presented in the following chapters of this report. The 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.

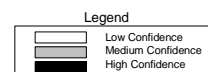


**Figure 1-3. Estimated CDD/CDF I-TEQ emissions to air from combustion sources in the United States (reference year: 1995).**

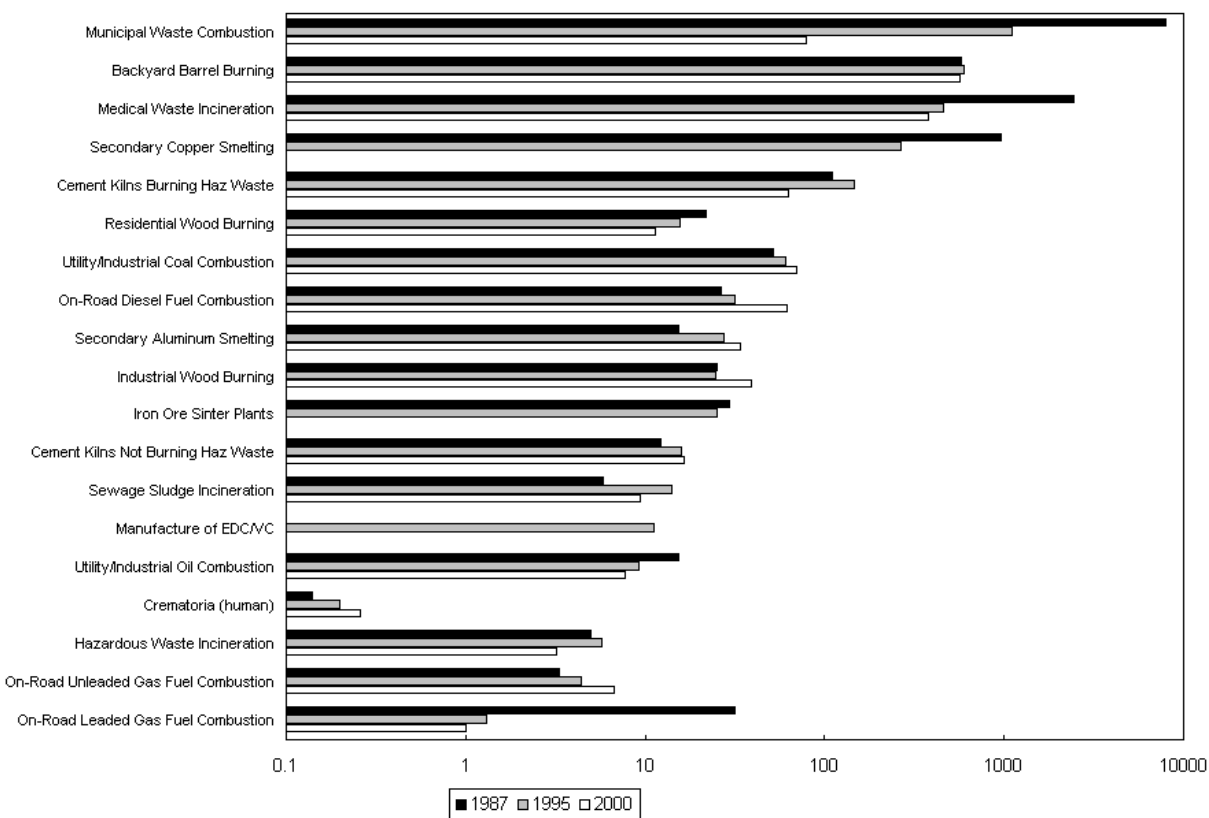
Note: Municipal solid waste incineration is currently referred to as municipal waste combustion.



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.

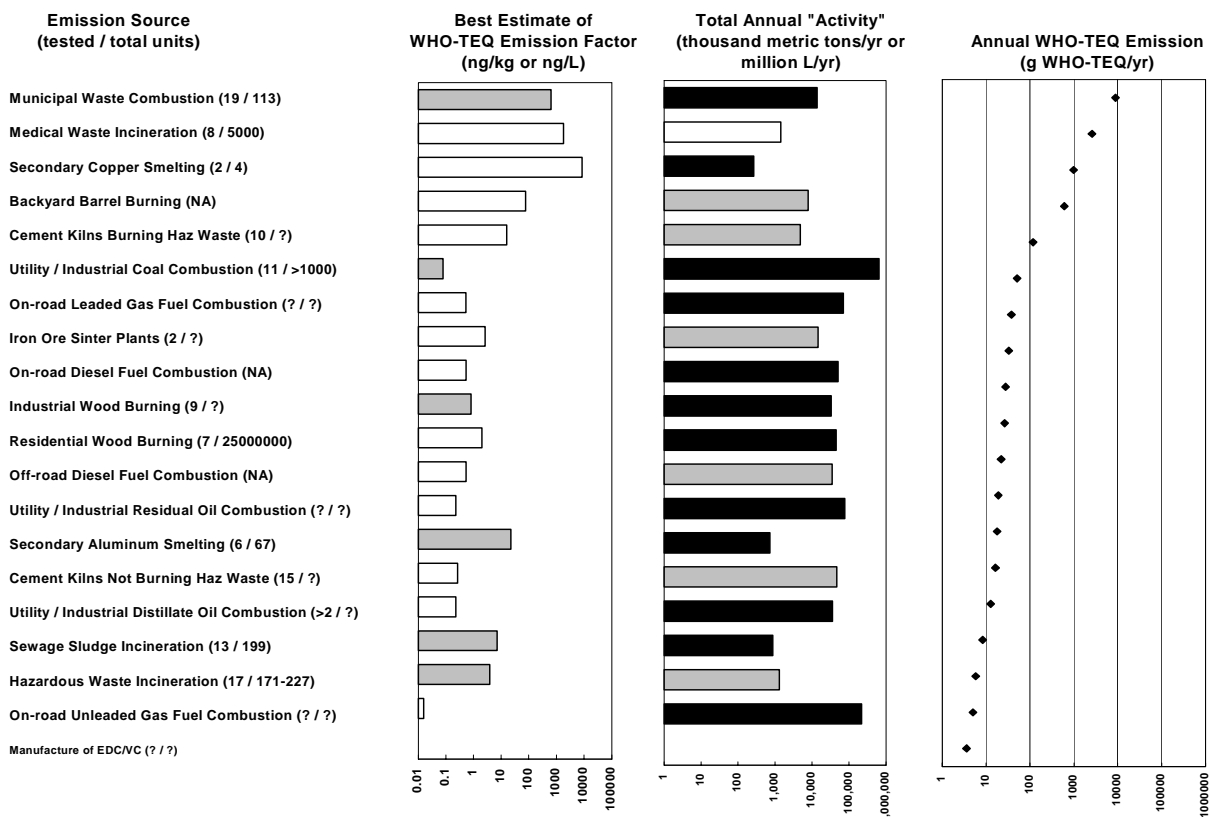


**Figure 1-4. Estimated CDD/CDF I-TEQ emissions to air from combustion sources in the United States (reference year: 2000).**



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



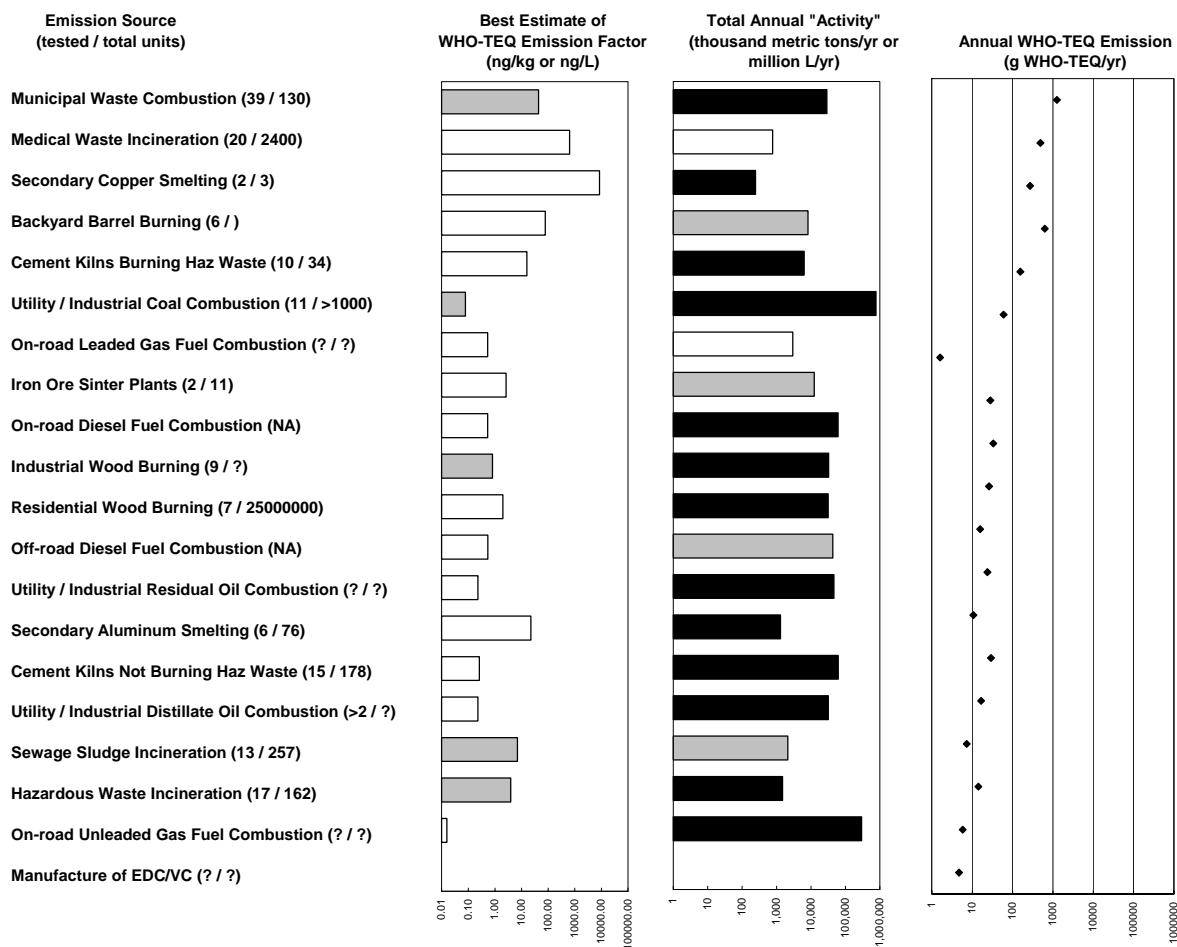


The figures include sources with annual WHO-TEQ emission estimates greater than 5 g WHO-TEQ/yr in one or both of the Reference Years 1987 or 1995. Derivation of the emission factors and annual "Activity" estimates (e.g., kg of waste incinerated) are presented in the following chapters of this report. 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.

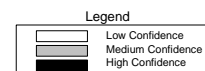


**Figure 1-6. Estimated CDD/CDF WHO-TEQ emissions to air from combustion sources in the United States (reference year: 1987).**

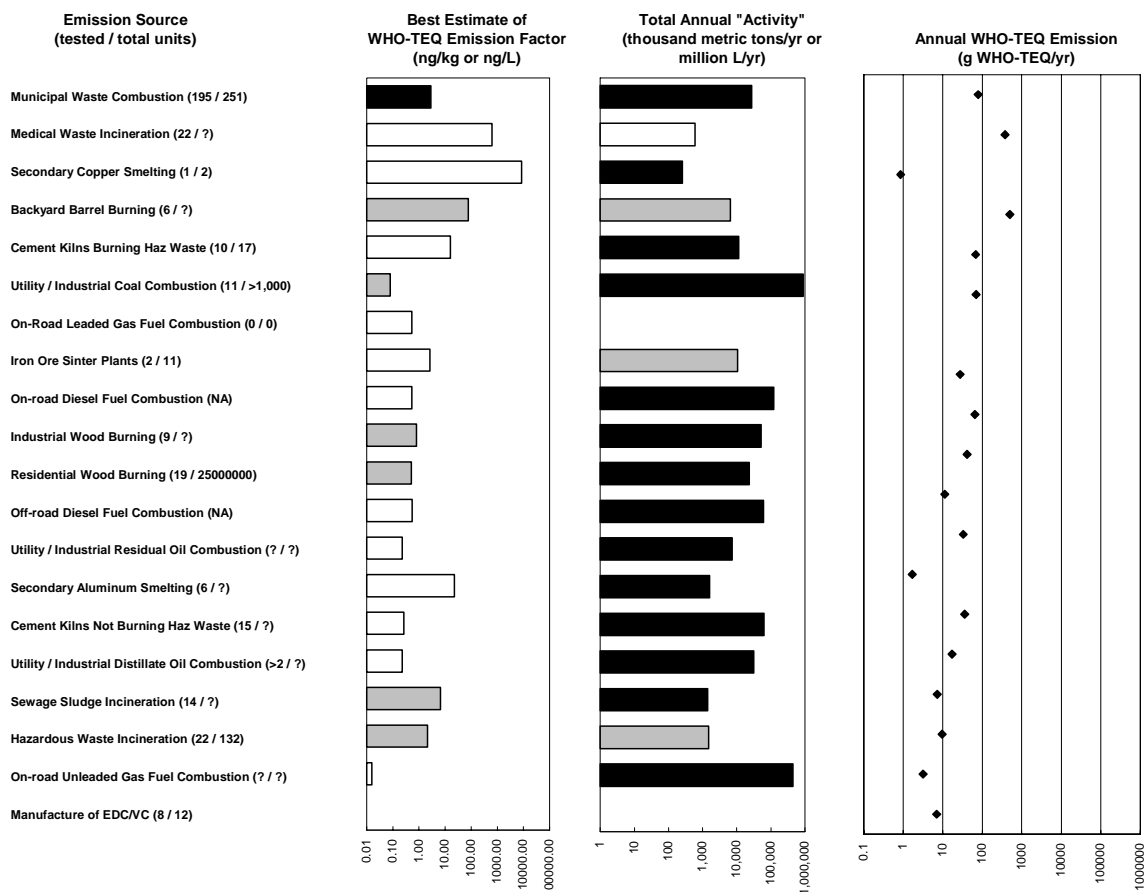
Note: Municipal solid waste incineration is currently referred to as municipal waste combustion.



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.



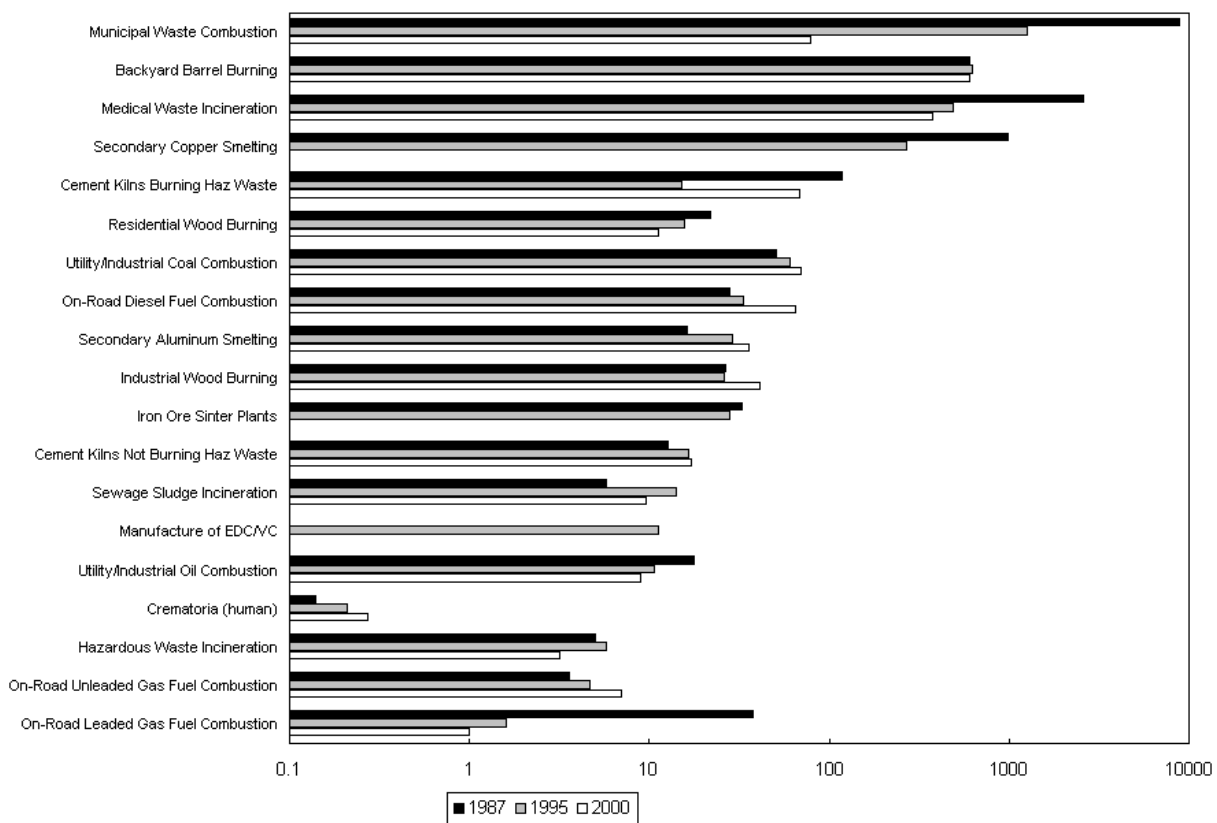
**Figure 1-7. Estimated CDD/CDF WHO-TEQ emissions to air from combustion sources in the United States (reference year: 1995).**



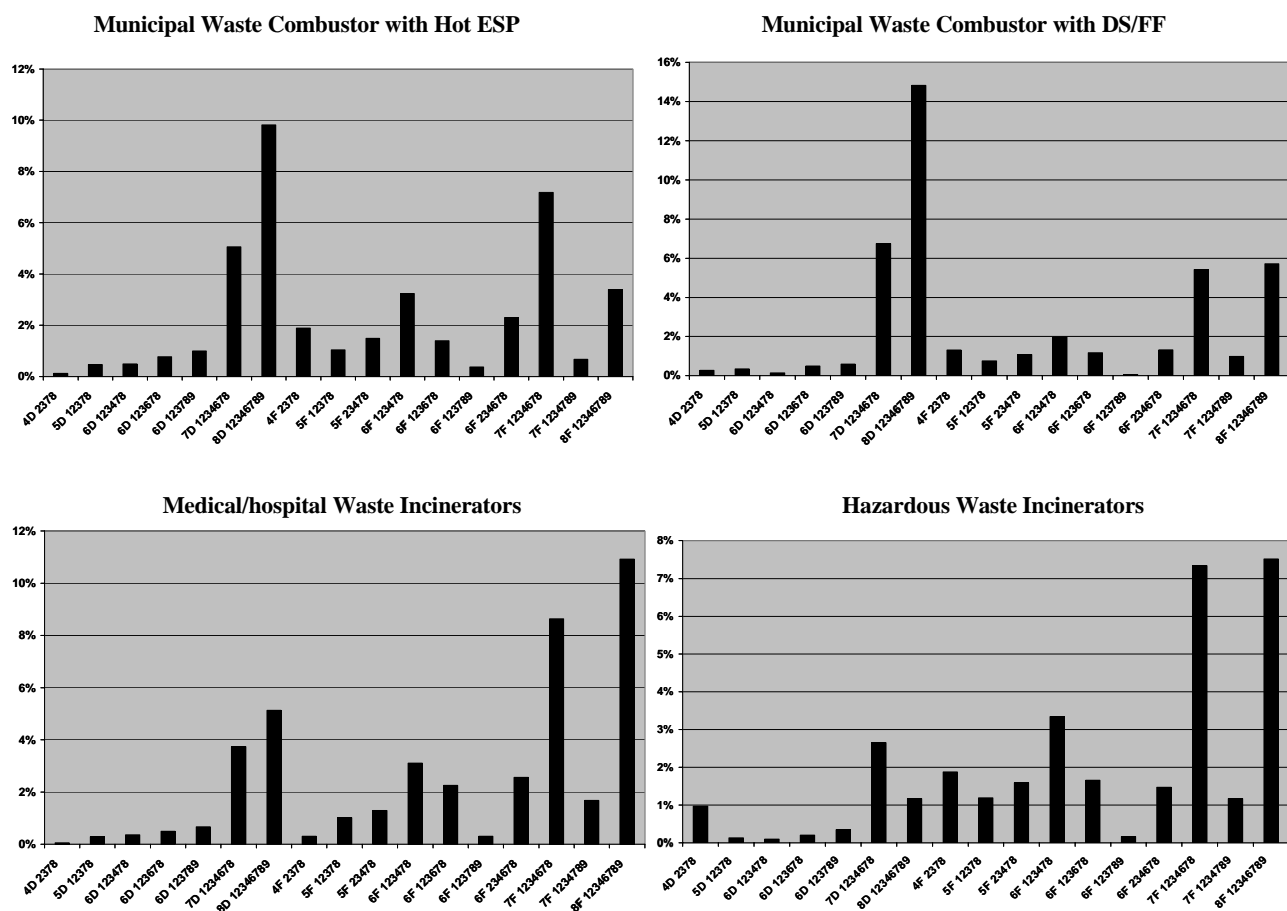
The figures include sources with annual WHO-TEQ emission estimates greater than 5 g WHO-TEQ/yr in one or both of reference years 1995 and 1987. Derivations of emission factors and annual "activity" estimates (e.g., kg of waste incinerated) are presented in this report. The difference in bar shading indicates 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.



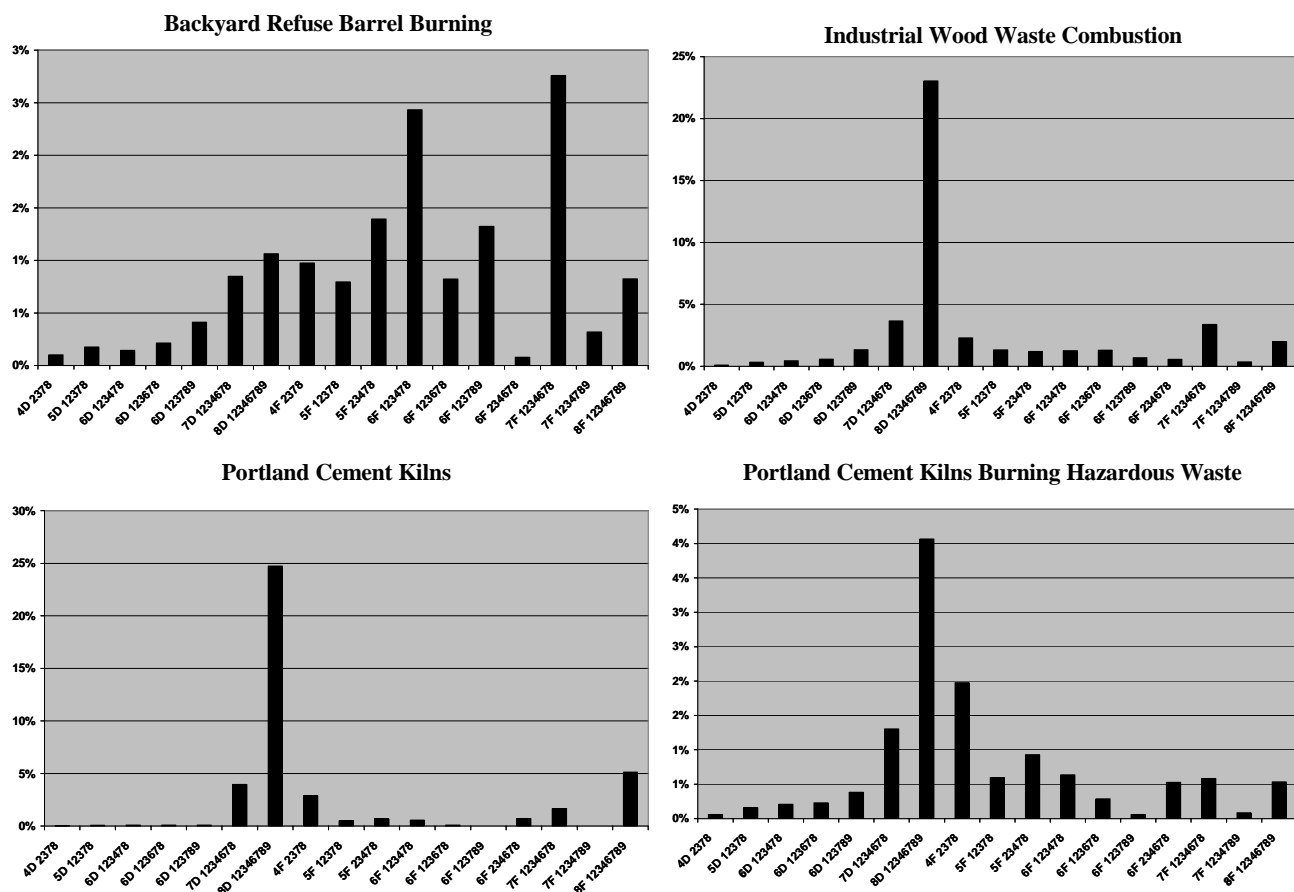
**Figure 1-8. Estimated CDD/CDF WHO-TEQ emissions to air from combustion sources in the United States (reference year: 2000).**



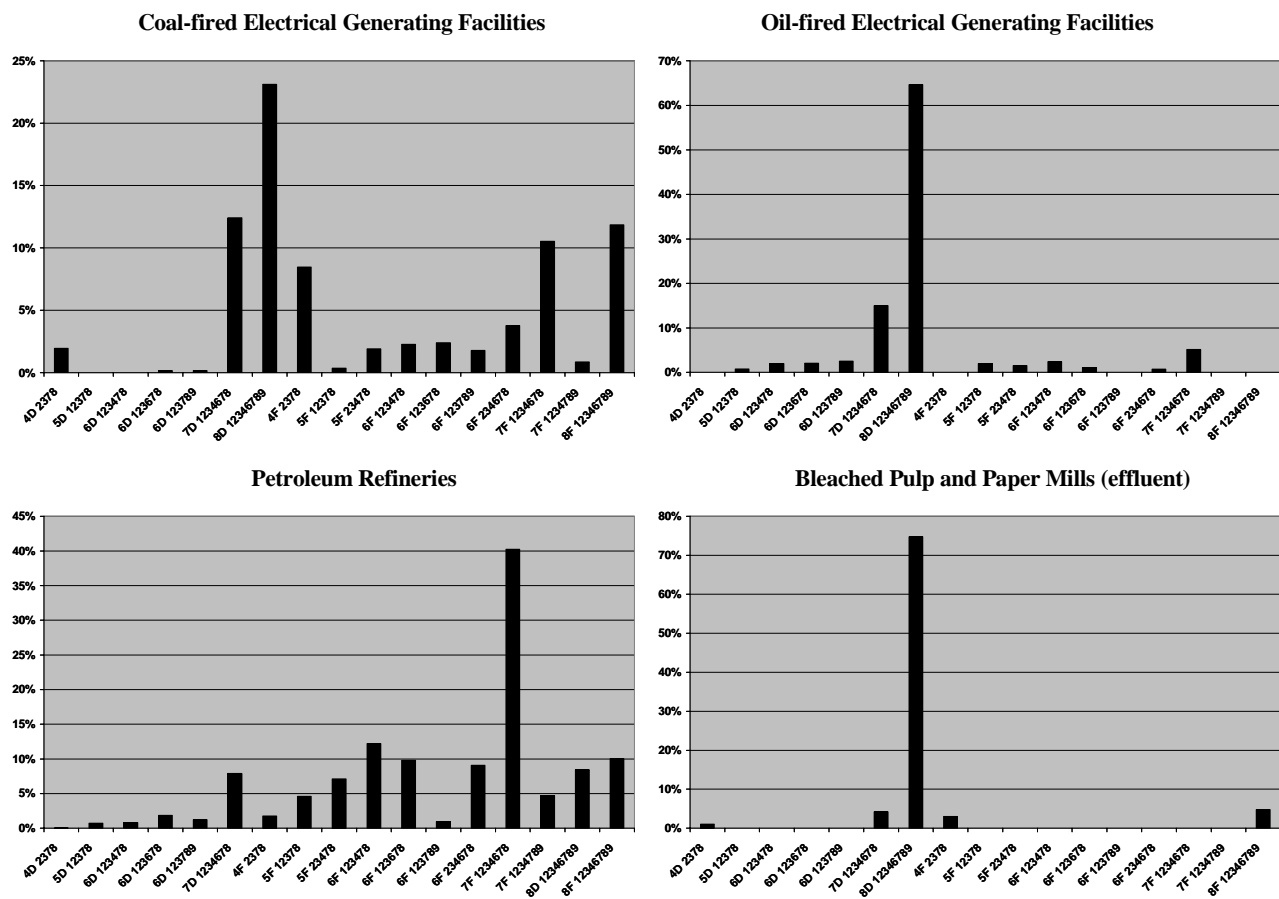
**Figure 1-9. Comparison of estimates of annual WHO-TEQ emissions to air (g WHO-TEQ/yr) for reference years 1987, 1995, and 2000.**



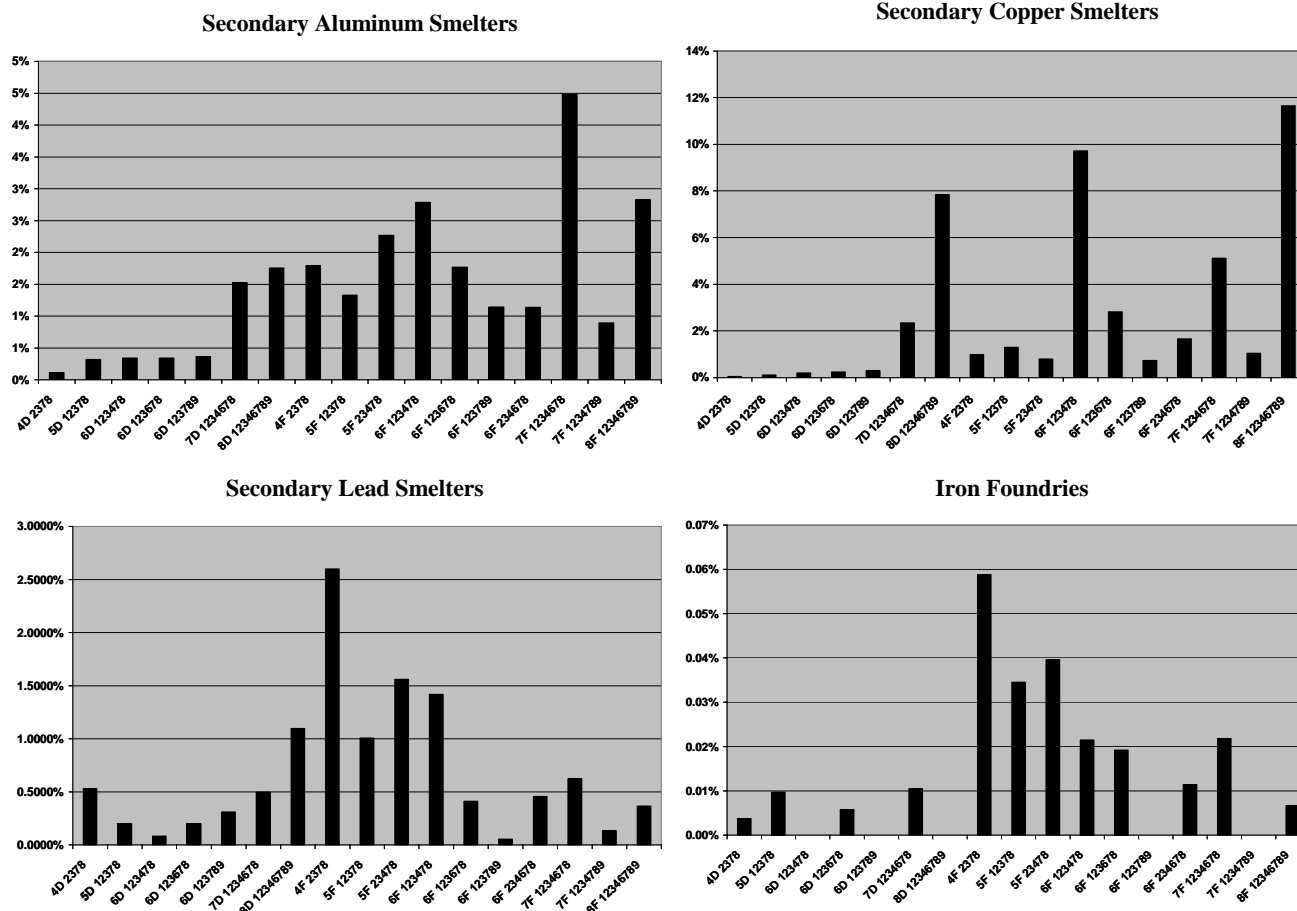
**Figure 1-10. The Congener Profiles (as percent distributions to the sum of CDD + CDF) of Anthropogenic Sources of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans in the United States.**



**Figure 1-10. The Congener Profiles (as percent distributions to the sum of CDD + CDF) of Anthropogenic Sources of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans in the United States (continued).**

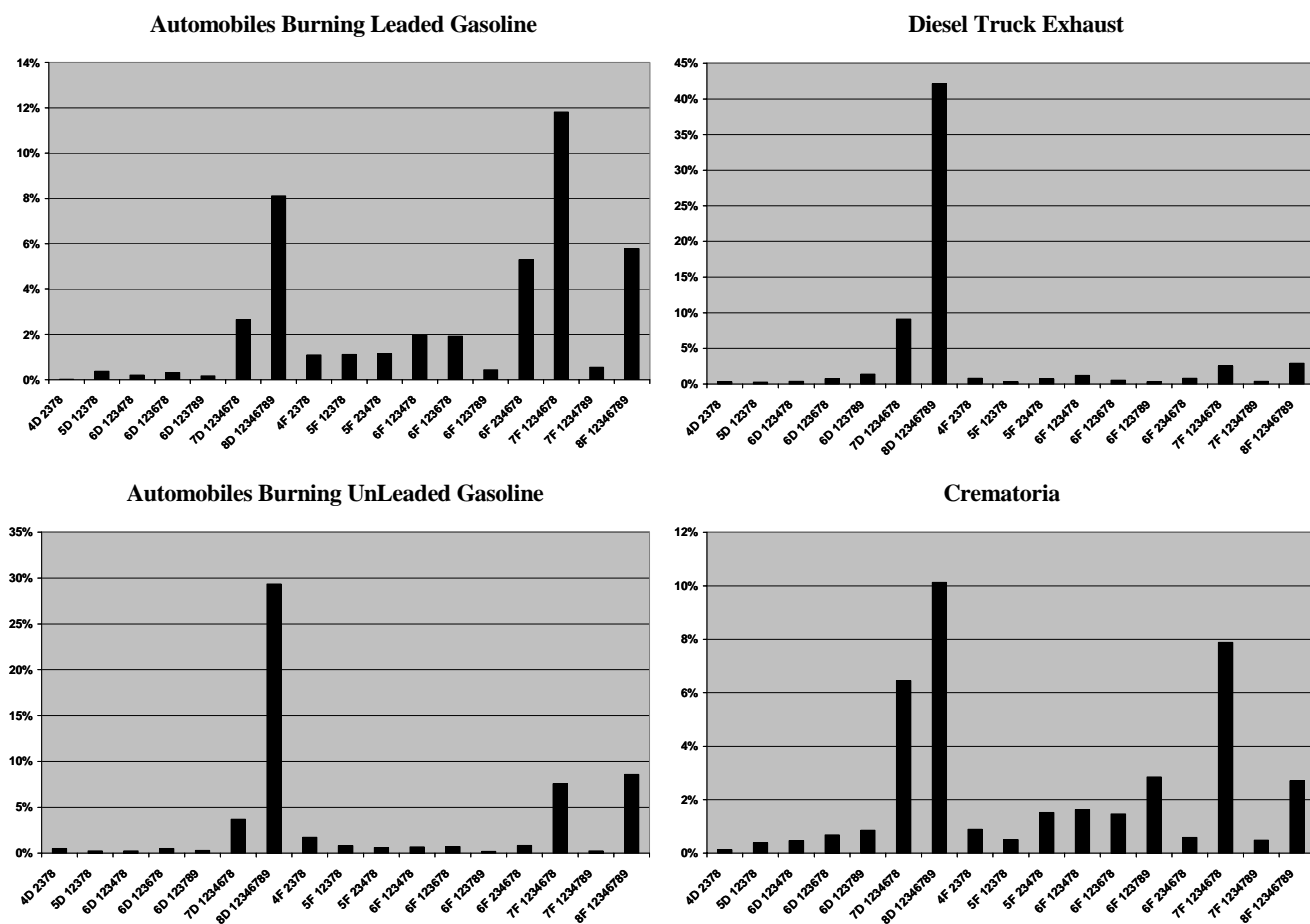


**Figure 1-10. The Congener Profiles (as percent distributions to the sum of CDD + CDF) of Anthropogenic Sources of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans in the United States (continued).**

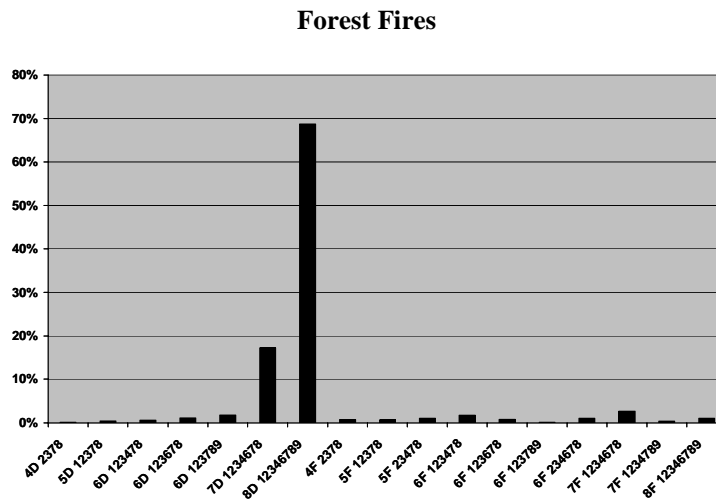


**Figure 1-10. The Congener Profiles (as percent distributions to the sum of CDD + CDF) of Anthropogenic Sources of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans in the United States (continued).**





**Figure 1-10. The Congener Profiles (as percent distributions to the sum of CDD + CDF) of Anthropogenic Sources of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans in the United States (continued).**



**Figure 1-10. The Congener Profiles (as percent distributions to the sum of CDD + CDF) 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 primarily derived from studies of full-scale municipal waste combustors (MWCs), augmented with observations involving the experimental combustion of synthetic fuels and feeds within 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 variable temperatures, residence times, and oxygen requirements adds to this complex problem. However, central chemical events that participate in the formation of CDDs/CDFs can be identified by evaluating emission test results from MWCs in combination with 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 2.5 discusses the generation and formation of coplanar 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 temperature.

1 The temperature of the combustion gases (i.e., flue gases) is perhaps the single most important  
2 factor in forming dioxin-like compounds. Temperatures between 200 and 450 °C are most  
3 conducive to the formation of CDDs/CDFs, with maximum formation occurring at around  
4 350 °C. If the temperature falls outside this range, the amount of CDDs/CDFs formed is  
5 minimized.

## 6 7 **2.1. MECHANISM 1 (PASS THROUGH): CDD/CDF CONTAMINATION IN FUEL AS** 8 **A SOURCE OF COMBUSTION STACK EMISSIONS**

9 The first mechanism involved in stack emissions of CDDs/CDFs is the incomplete  
10 destruction of CDD/CDF contaminants present in the fuel or feeds delivered to the combustion  
11 chamber. Not all of these molecules are destroyed by the combustion system, thus allowing trace  
12 amounts to be emitted from the stack. Most work in this area has involved the study of  
13 incineration of municipal solid waste (MSW), where CDDs/CDFs were analytically measured in  
14 the raw refuse fed into the incinerator. CDDs/CDFs are ubiquitous in the environment (air,  
15 water, and soil) and in foods and paper; therefore, they clearly are present in municipal waste  
16 (Tosine et al., 1983; Ozvacic, 1985; Clement et al., 1988; Federal Register, 1991a; Abad et al.,  
17 2002).

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

25 A number of studies have provided evidence that most of the CDDs/CDFs present in the  
26 MSW are destroyed during combustion (Abad et al., 2002; Clement et al., 1988; Commoner et  
27 al., 1984, 1985, 1987; Hay et al., 1986; Environment Canada, 1985). These studies have  
28 involved a mass balance of the input versus output of CDDs/CDFs at two operational MWCs.  
29 The mass of CDDs/CDFs outside the incinerator furnace was found to be much greater than the  
30 mass of CDDs/CDFs in the raw MSW fed into the incinerator, and the profiles of the  
31 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- to octa-CDDs/CDFs could be detected in the stack gases. Moreover, the ratio of the total concentration of CDDs in the MSW in relation to the total CDF concentration was greater than 1, whereas in typical incinerator stack emissions, this ratio is less than 1 (meaning more dibenzofurans are emitted than dioxins). Such evidence gives the conclusion that CDDs/CDFs are being synthesized after the contaminated feed has been combusted (Abad et al., 2002). Moreover, it is 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 (Schaub 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 ( $\text{Cl}_2$ ), and chlorine radicals ( $\text{Cl}\cdot$ ) 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 are 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 ( $\text{CuCl}_2$ ) 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 (2,4,5-T) in a bench-scale furnace at 600 to 800 °C and generated ppm<sub>v</sub> 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 byproducts; Buser (1979) 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 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



1 °C. Table 2-1 summarizes these data. Because the relative concentration of CDDs/CDFs  
2 increased while exposed to varying temperatures, it was concluded that the temperature of the  
3 combustion gas is crucial to promoting the formation of CDDs/CDFs on the surface of fly ash.  
4 Within a temperature range of 200 to 450 °C, the concentration of CDDs/CDFs increases to some  
5 maxima; outside this range, the concentration diminishes.

6 The region of cooler gas temperature is often referred to as the “post-combustion zone.”  
7 The heat loss may be inherent to the conduction and transfer through the combustion gas metal  
8 ducting system or related to adsorbing/exchanging heat to water in boiler tubes. This region  
9 extends from near the exit of the furnace to the point of release of the combustion gases at stack  
10 tip.

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

17 Oberg et al. (1989) examined the role of temperature in the formation kinetics using a full-  
18 scale hazardous waste incinerator (HWI) operating in Sweden. The investigators observed that  
19 maximum CDD/CDF formation transpired in the boiler used to extract heat for cogeneration of  
20 energy. In this study, significant increases in total concentration of I-TEQ<sub>DF</sub> occurred between 280  
21 and 400 °C, and concentrations declined at temperatures above 400 °C. Weber and Hagenmaier  
22 (1999) showed that in gas-phase reactions, chlorophenols react in the presence of oxygen at  
23 temperatures above 340 °C to form CDDs/CDFs. Phenoxyradicals were formed, which in turn  
24 caused the formation of CDDs. Polychlorinated dihydroxybiphenyls were identified as reaction  
25 intermediates in the gas-phase dimerization of chlorophenols, and these intermediates could form  
26 CDFs.

27 Konduri and Altwicker (1994) proposed that rate-limiting factors were the nature and the  
28 concentrations of the precursors, the reactivity and availability of the fly ash surface, and the  
29 residence time in the post-combustion zone. Dickson and Karasek (1987) investigated fly ash  
30 reactivity with <sup>13</sup>C<sub>6</sub>-chlorophenol compounds. Several samples of fly ash from MWCs, copper  
31 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 ashes included a sample from a poorly operated mass burn refractory incinerator and a sample from a well-operated fluidized-bed combustor. The MWC fly ashes proved to be the most active catalytic medium, despite similarities with respect to specific surface area and average pore diameters. The fly ash from the refractory MWC generated about seven times more mass of dioxin-like compounds than 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.  $^{13}\text{C}_{12}$ -labeled PCP and two trichlorophenol isotopes ( $^{13}\text{C}_{12}$ -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.

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

6 Dickson and Karasek (1987) proposed that CDDs on fly ash surfaces may result from  
7 chlorophenol undergoing molecular rearrangement or isomerization as a result of dechlorination,  
8 dehydrogenation, and transchlorination before condensation occurs. These reactions were  
9 proposed as controlling the types and amounts of CDDs that are ultimately formed. Born et al.  
10 (1993) conducted experiments on the oxidation of chlorophenols with fly ash in a quartz tube  
11 reactor heated to about 300 °C. The MWC fly ash mediated the oxidation of chlorophenols to  
12 produce carbon dioxide ( $\text{CO}_2$ ) and carbon monoxide (CO) as major products and polychlorinated  
13 benzenes, monobenzofurans, and nonhalogenated dibenzo-*p*-dioxins as trace species. Formation  
14 of these trace aromatic species occurred after residence times of only 7 to 8 sec, which was  
15 consistent with the later experimental result of Behrooz and Altwicker (1995), which showed the  
16 potential for rapid formation from a precursor.

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

28 Experimental evidence suggests that condensation to CDD of chlorophenol compounds  
29 via isomerization and the "Smiles" rearrangement on reactive MWC fly ash surfaces is a proven  
30 pathway for the formation of dioxins from a precursor compound (Addink and Olie, 1995).

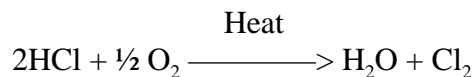
1 However, no detailed mechanisms have been presented for CDD/CDF formation from other  
2 precursors such as chlorobenzenes under conditions simulating incineration.

3 A condition in the synthesis of CDDs/CDFs from aromatic precursor compounds is that  
4 the presence of a transition metal catalyst promotes the chemical reaction on the surface of fly ash.  
5 Copper chloride ( $\text{CuCl}_2$ ) is a strong catalyst for promoting surface reactions on particulate matter  
6 to convert aromatic precursor compounds to CDDs/CDFs (Vogg et al., 1987).  $\text{CuCl}_2$  promotes  
7 ring condensation reactions (of the chlorophenols) on fly ash to form CDDs/CDFs (Addink and  
8 Olie, 1995) via the Ullman reaction (Born et al., 1993). In the Ullman reaction, copper catalyzes  
9 the formation of diphenyl ethers by the reaction of halogenated benzenes with alkali metal  
10 phenolates (Born et al., 1993), with copper participating in a nucleophilic aromatic substitution  
11 reaction. Thus, Born et al. (1993) proposed a similar mechanism in catalyzing the formation of  
12 dioxin-like compounds. Using the Ullman reaction as a model, the authors proposed that the  
13 copper-catalyzed condensation of two ortho-substituted chlorophenol molecules form chlorine-  
14 free dibenzo-*p*-dioxins.

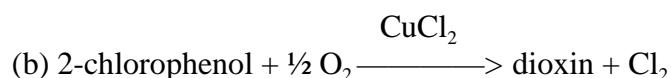
15 Vogg et al. (1987) proposed an oxidation reaction pathway, giving rise to the formation of  
16 CDDs/CDFs in the post-furnace regions of the incinerator in the following order: (1) HCl is  
17 thermolytically derived as a product of the combustion of heterogeneous fuels containing  
18 abundant chlorinated organic chemicals and chlorides; (2) oxidation of HCl, with  $\text{CuCl}_2$  as a  
19 catalyst, yields free gaseous chlorine via the Deacon reaction; (3) phenolic compounds (present  
20 from combustion of lignin in the waste or other sources) entrained in the combustion plasma are  
21 substituted on the ring structure by contact with the free chlorine; and (4) a chlorinated precursor  
22 to dioxin (e.g., chlorophenol) is further oxidized (with  $\text{CuCl}_2$  as a catalyst) to yield CDDs/CDFs  
23 and chlorine.

24 Gullett et al. (1990a, b, 1991a, b, 1992) studied the formation mechanisms through  
25 extensive combustion research at EPA and verified the observations of Vogg et al. (1987). It was  
26 proven that CDDs/CDFs could ultimately be produced from low-temperature (i.e., 350 °C)  
27 reactions between dichloride ( $\text{Cl}_2$ ) and a phenolic precursor combining to form a chlorinated  
28 precursor, followed by oxidation of the chlorinated precursors (catalyzed by a copper catalyst such  
29 as  $\text{CuCl}_2$ ), as shown below.

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



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 from the breakdown and molecular rearrangement of the precursor. The reaction is promoted by  $\text{CuCl}_2$  acting as a catalyst (Vogg et al., 1987; Dickson and Karasek, 1987; Gullett et al., 1992):



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, tetrachlorodibenzofuran, trichlorodibenzo-*p*-dioxin, tetrachlorodibenzo-*p*-dioxin, hexachlorodibenzo-*p*-dioxin, hexachlorodibenzofuran, pentachlorobenzene, pentachlorobiphenyl, and pentachlorodihydroxycyclohexane were observed as minor products. Trace species formed included monochlorodibenzofuran, pentachlorodibenzofuran, pentachlorodibenzo-*p*-dioxin, octachlorodibenzofuran, and octachlorodibenzo-*p*-dioxin.

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  $\geq 150$  °C. The experimental protocol introduced 100 to 700 mg benzene and  $^{13}\text{C}_6$ -

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 byproduct 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 ( $\text{FeCl}_3$ ) was added to form an  $\text{FeCl}_3$ /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.

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

The third mechanism, *de novo* synthesis, 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  $\text{m}^2/\text{kg}$  (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*

1 *de novo* synthesis over the precursor synthesis is the oxidation of carbon in particulate at the start of  
2 the process to yield precursor compounds. In mechanism 2, the precursor compound is the  
3 starting molecule of the condensation reactions forming CDDs/CDFs (Dickson et al., 1992). By  
4 this distinction, however, one could argue that mechanism 3 is really an augmentation of  
5 mechanism 2 because the production of CDDs/CDFs may still require the formation of a  
6 CDD/CDF precursor as an intermediate species. Nevertheless, a distinction is presented here to  
7 describe additional pathways suggested for the thermal formation of these compounds.

8 To delineate the *de novo* synthesis of CDDs/CDFs, Stieglitz et al. (1989a) conducted  
9 experiments that involved heating particulate carbon containing adsorbed mixtures of magnesium-  
10 aluminum (Mg-Al) silicate in the presence of CuCl<sub>2</sub> (as a catalyst to the reaction). The authors  
11 described heating mixtures of Mg-Al silicate with activated charcoal (4% by weight), chloride as  
12 potassium chloride (7% by weight), and CuCl<sub>2</sub> (1% in water) in a quartz flow tube reactor at 300  
13 °C. The retention time was varied at 15 min, 30 min, and 1, 2, and 4 hr to obtain differences in  
14 the amounts of CDDs/CDFs that could be formed. The results are summarized in Table 2-3. In  
15 addition to the CDDs/CDFs formed as primary products of the *de novo* synthesis, the investigators  
16 observed precursors formed at the varying retention times during the experiment. In particular,  
17 similar yields of tri- through hexachlorobenzenes, tri- through heptachloronaphthalenes, and tetra-  
18 through heptachlorobiphenyls were quantified; this was seen as highly suggestive of the role these  
19 compounds may play as intermediates in the continued formation of CDDs/CDFs.

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

- 21  
22 • The *de novo* synthesis of CDDs/CDFs via the oxidation of carbonaceous particulate  
23 matter occurred at a temperature of 300 °C. Additionally, the experiment yielded  
24 parts-per-billion to parts-per-million concentrations of chlorinated benzenes,  
25 chlorinated biphenyls, and chlorinated naphthalenes through a similar mechanism.  
26 When potassium bromide was substituted for potassium chloride as a source of  
27 halogen for the organic compounds in the reaction, polybrominated dibenzo-*p*-dioxins  
28 and dibenzofurans formed as reaction products.
- 29  
30 • The transition metal compound CuCl<sub>2</sub> catalyzed the *de novo* synthesis of CDDs/CDFs  
31 on the surface of particulate carbon in the presence of oxygen, yielding CO<sub>2</sub> and  
32 chlorinated/brominated aromatic compounds.
- 33  
34 • Particulate carbon, which is characteristic of combustion processes, may act as the  
35 source for the direct formation of CDDs/CDFs, as well as other chlorinated organics.

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

11 Addink et al. (1991) conducted a series of experiments to observe the *de novo* synthesis of  
12 CDDs/CDFs in a carbon fly ash system. In this experiment, 4 g of carbon-free MWC fly ash were  
13 combined with 0.1 g of activated carbon and placed into a glass tube between two glass wool  
14 plugs. The glass tube was then placed into a furnace at specific temperatures ranging from 200 to  
15 400 °C. This protocol was repeated for a series of retention times and temperatures. The  
16 investigators observed that CDD/CDF formation was optimized at 300 °C and at the furnace  
17 retention times of 4 to 6 hr. Figure 2-2 displays the relationship between retention time,  
18 temperature, and CDD/CDF production from the heating of carbon particulate.

19 Addink et al. (1991) also investigated the relationship between furnace temperature and  
20 CDD/CDF production from the heating of carbonaceous fly ash. Figure 2-3 displays this  
21 relationship. In general, the concentration began to increase at 250 °C and crested at 350 °C, with  
22 a sharp decrease in concentration above 350 °C. The authors also noted a relationship between  
23 temperature and the CDD/CDF congener profile: at 300 to 350 °C, the less chlorinated tetra- and  
24 penta-CDD/CDF congeners increased in concentration, whereas hexa-, hepta-, and octa-  
25 CDD/CDF congeners either remained the same or decreased in concentration. The congener  
26 profile of the original MWC fly ash (not subject to *de novo* experimentation) was investigated  
27 with respect to changes caused by either temperature or residence time in the furnace. No  
28 significant changes occurred, leading the authors to propose an interesting hypothesis for further  
29 testing: after formation of CDDs/CDFs occurs on the surface of fly ash, the congener profile  
30 remains fixed and insensitive to changes in temperature or residence time, indicating that some  
31 form of equilibrium is reached in the formation kinetics.



1 Gullett et al. (1994) used a pilot-scale combustor to study the effect of varying combustion  
2 gas composition, temperature, residence time, quench rate, and sorbent (Ca[OH]<sub>2</sub>) injection on  
3 CDD/CDF formation. The fly ash loading was simulated by injecting fly ash collected from a  
4 full-scale MWC. Sampling and analysis indicated that CDDs/CDFs formed on the injected fly ash  
5 at levels representative of those observed at full-scale MWCs. A statistical analysis of the results  
6 showed that, although the effect of combustor operating parameters on CDD/CDF formation is  
7 interactive and very complicated, substantial reduction in CDD/CDF formation can be realized  
8 with high-temperature sorbent injection to reduce HCl or Cl<sub>2</sub> concentrations, control of excess air  
9 (also affects the ratio of CDDs to CDFs formed), and increased quench rate.

10 Milligan and Altwicker (1995) found that increases in the carbon gasification rate caused  
11 increases in the amounts of CDDs/CDFs formed and gave further evidence linking the oxidation  
12 of carbon to the formation of CDDs/CDFs. Neither the gas-phase CO<sub>2</sub> or CO (products of carbon  
13 oxidation) act as precursors to chlorobenzenes or CDDs/CDFs from reactions with carbon  
14 particulate (Milligan and Altwicker, 1995). Activated carbon, with its high surface area and  
15 excellent adsorptive characteristics, also has the highest gasification rate of all residual carbon  
16 (Addink and Olie, 1995).

17 Experimental evidence suggests the following factors for the *de novo* synthesis of  
18 CDDs/CDFs from carbon: (a) carbon consisting of imperfect and degenerated layers of graphite,  
19 (b) the presence of oxygen, (c) the presence of chlorine, (d) catalyzed reactions by CuCl<sub>2</sub>  
20 or some other transition metal, and (e) temperatures in the range of 200 to 350 °C (Huang and  
21 Buekens, 1995). The oxidation of carbon in fly ash is apparently inhibited at temperatures below  
22 200 °C, thus indicating the lower temperature limit for the thermal inertization of *de novo*  
23 synthesis (Lasagni et al., 2000).

24 Lasagni et al. (2000) determined that at a temperature of 250 °C, the primary product of  
25 the gasification of carbon in fly ash is CO<sub>2</sub>, but in a temperature range of 250 to 325 °C, organic  
26 compounds are formed as products of the oxidation of the carbon. Addink and Olie (1995) raised  
27 the possibility that the molecular backbone of CDDs/CDFs may be present in carbon. If this is the  
28 case, the generation of dioxins and furans from the oxidation of carbon would not require the  
29 formation of intermediate aromatic ring structures. More work is needed to confirm these  
30 possibilities.

1           The *de novo* synthesis of CDDs/CDFs also involves the possibility that aromatic  
2 precursors are formed within the post-combustion zone in the following manner: (1) fuel  
3 molecules are broken down into smaller molecular species (e.g., C<sub>1</sub> and C<sub>2</sub> molecules) during  
4 primary combustion, and (2) these simple molecules recombine in the post-combustion zone to  
5 form larger-molecular aromatic species (i.e., chlorobenzenes and chlorophenols) (Altwicker et al.,  
6 1993). Thus, small molecular products that evolve in the hot zone of the furnace as a  
7 consequence of incomplete fuel or feed material combustion may be important foundation  
8 molecules to the subsequent formation of precursor compounds in the cooler, post-combustion  
9 region.

10           Eklund et al. (1988) reported formation of a wide range of chlorinated organic compounds,  
11 including CDDs, CDFs, and PCBs, from the oxidation of methane with HCl at temperatures of  
12 400 to 950 °C in a quartz flow tube reactor. No active catalysts or reactive fly ashes were added  
13 to the combustion system. From these experimental results, the authors hypothesized that  
14 chlorocarbons, including CDDs/CDFs, are formed at high temperatures via a series of reversible  
15 reactions starting with chloromethyl radicals. The chloromethyl radicals can be formed from the  
16 reaction of methyl radicals and HCl in a sooting flame. Methane is chlorinated by HCl in the  
17 presence of oxygen at high temperatures, forming chlorinated methanes, which react with methyl  
18 radicals at higher temperatures (e.g., 800 °C) to form aromatic compounds. In an oxidative  
19 atmosphere, chlorinated phenols are formed, but alkanes and alkenes are the primary products.  
20 The chlorinated phenols then act as precursors for the subsequent formation of CDDs/CDFs.

21           Aliphatic compounds are common products of incomplete combustion, and they may be  
22 critical to the formation of simple ring structures in the post-combustion zone (Weber et al., 1999;  
23 Sidhu, 1999; Froese and Hutzinger, 1996a, b; Jarmohamed and Mulder, 1994). The aromatic  
24 precursor compounds may be formed in a potentially rich reaction environment of aliphatic  
25 compounds, reactive fly ash particles, HCl, and oxygen. Sidhu (1999) noted that combustion of  
26 acetylene on carbon (a common combustion effluent) in the presence of gaseous HCl and CuCl<sub>2</sub>  
27 (as a catalyst) at 300 °C led to the formation of intermediate precursors and, subsequently,  
28 CDDs/CDFs.

29           Propene oxidized at 350 to 550 °C when in contact with reactive MWC fly ash in a flow  
30 tube reactor formed a wide range of chlorinated aromatic compounds when the resulting  
31 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<sub>2</sub> 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 (SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and 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.

Chorobenzenes 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<sub>2</sub> 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-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 tetrachlorodibenzofurans occurred at 500 °C. Froese and Hutzinger (1996a) noted a 100-fold increase in tetrachlorodibenzofuran formation at 500 °C when compared with formation at 400 °C. An

1 explanation for this increase is that the higher temperature maximized the formation of the  
2 CDD/CDF precursor (chlorophenol) from the aliphatic starting compound.

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

11 Froese and Hutzinger (1996b) also investigated the effects of elemental catalysts on  
12 potentiating the heterogeneous combustion reactions by measuring the amount of chlorobenzene  
13 and chlorophenol product formed from the reactions of ethylene/HCl over each catalyst at  
14 600 °C. The reaction with SiO<sub>2</sub> did not have a catalytic effect. Al<sub>2</sub>O<sub>3</sub> catalytic action showed  
15 high intensity for the dichlorobenzene isomers and decreasing intensity for the higher chlorinated  
16 isomers. Comparison of the amount of dichlorobenzene product formed indicated that an equal  
17 quantity was produced with either Al<sub>2</sub>O<sub>3</sub> or fly ash; however, Al<sub>2</sub>O<sub>3</sub> formed four to five times  
18 more product than did the CuO catalyst. For tri- to hexachlorobenzene congeners, MWC fly ash  
19 reactions produced 5 to 10 times more product than did the metal catalysts. However, the  
20 presence of the CuO catalyst in these reactions produced a chlorobenzene congener pattern  
21 comparable to the fly ash reactions. With regard to chlorophenol production, Al<sub>2</sub>O<sub>3</sub> also produced  
22 a unique dichlorophenol pattern, suggesting that Al<sub>2</sub>O<sub>3</sub> has a unique catalytic effect in the high-  
23 temperature reactions of C<sub>2</sub> aliphatic compounds.

24 Reactions with CuO produced additional products, including chlorinated methyl  
25 compounds, chlorinated C<sub>2</sub> aliphatics, and perchlorinated C<sub>3</sub>–C<sub>5</sub> alkyl compounds. The authors  
26 noted that these perchlorinated alkyl groups, formed by reacting ethylene and ethane over fly ash  
27 in the presence of the CuO catalyst, are key intermediate compounds to the formation of first  
28 aromatic rings in typical combustion systems. This emphasizes the importance of copper's  
29 catalytic effects in a combustion fly ash system. Al<sub>2</sub>O<sub>3</sub> catalyzed reactions produced  
30 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<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>) 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 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., 2004 ). Chlorine concentration in this region is related somehow 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 or not 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: the transfer of chlorine to residual carbon particulate with subsequent formation of carbon-chlorine bonds and the oxidation of this macromolecular complex to yield CO<sub>2</sub> and volatile and semivolatile organic compounds as side products (Weber et al., 1999). Transition metal compounds, such as CuCl<sub>2</sub>, catalyze these reactions. Gaseous HCl, Cl<sub>2</sub>, and chlorine radicals are the most abundant sources of chlorine available for participating in the formation of CDDs/CDFs and 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 average 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 reacting with hydrocarbons present in the fuel (Wikstrom et al., 2003). HCl may oxidize to yield free chlorine gas by the Deacon process, and the free chlorine 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<sub>2</sub> 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 in the Deacon process temperature (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. Bruce et al. (1991) verified a dependence of the formation of CDDs/CDFs in the post-combustion

1 zone on the concentration and availability of gaseous chlorine. This finding is in agreement with  
2 a simple experiment by Eklund et al. (1986) in which unsubstituted phenol was mixed with HCl at  
3 550 °C in a quartz tube reactor. A wide range of toxic chlorinated hydrocarbons was formed,  
4 including CDDs/CDFs. Eklund et al. (1988) also found a dependence of the amounts of  
5 chlorinated phenol product formed from the nonchlorinated starting material on the increased  
6 amount of HCl introduced into the reaction. Under the conditions of this experiment, no  
7 chlorinated compounds were formed at an HCl concentration of less than  $10^{-3}$  mol, and maximum  
8 chlorophenol concentration occurred at around  $10^8$  mol.

9 Born et al. (1993) also observed that increasing levels of HCl gave rise to increasing rates  
10 of oxychlorination of precursors, with increasing chances for the post-combustion formation of  
11 CDDs/CDFs. However, Addink et al. (1995) observed that an HCl atmosphere and/or chlorine  
12 produced approximately equal quantities of CDDs/CDFs during the *de novo* synthesis from  
13 oxidation of particulate carbon. Such results suggest that chlorine production via the Deacon  
14 process reaction in the *de novo* synthesis may not be the only chlorination pathway and may  
15 indicate that the HCl molecule can be a direct chlorinating agent. In addition, some chlorine is  
16 expected to be formed from the oxidation of metal chlorides (e.g.,  $\text{CuCl}_2$ ), but  $\text{Cl}_2$  formation from  
17 the Deacon process is greater because of the continuous supply of HCl delivered from the  
18 combustion chamber (Bruce et al., 1991). In this case, a first-order dependence of HCl to  $\text{Cl}_2$  is  
19 observed.

20 More recently, however, Wikstrom et al. (2003) have reported on the importance of  
21 chlorine species on the *de novo* formation of CDDs/CDFs. HCl can react with oxidizing radicals  
22 (e.g., hydroxyl radical or OH) to produce chlorine radicals ( $\text{Cl}\cdot$ ).  $\text{Cl}\cdot$  are highly reactive and can  
23 replace hydrogen atoms with chlorine atoms in the H-C bond of the aromatic structure. Thus, HCl  
24 is most likely an indirect chlorinating agent via the formation of chlorine radicals.

25 Experimentally, about 18% of the total chlorine content in fuels can be thermally  
26 converted to chlorine radicals in the post-combustion zone (Procaccini et al., 2003). Although  
27 HCl is the primary chlorine-containing product formed from the combustion of chlorine rich fuels,  
28 HCl may not be the major chlorinating agent in the formation of chloro-organics in the cooled  
29 down region of the combustor. The experiments of Procaccini et al. (2003) indicate that the major  
30 role of HCl in the formation of chloro-organic compounds at cooler temperatures may be that of a  
31 chemical progenitor of chlorine radicals. HCl reacts with the oxidizing radicals OH and O

1 abundantly present in combustion off-gases to reform  $\text{Cl}\cdot$ . Chlorine radicals readily abstract  
2 hydrogen atoms from the H-C bond of aromatic compounds formed as combustion by-products of  
3 organic fuels. By this means, unsubstituted aromatic compounds, e.g., benzene, undergo oxy-  
4 chlorination reactions with the  $\text{Cl}\cdot$  to form chlorobenzenes and chlorophenols. These products are  
5 well defined precursor compounds for the synthesis of CDDs/CDFs.

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

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

26 In a similar experiment, Wikstrom et al. (1996) investigated the influence of chlorine in  
27 feed materials in the formation of CDDs/CDFs and benzenes in a laboratory-scale fluidized bed  
28 reactor. Seven artificial fuels (composed of 34% paper, 30% wheat flour, 14% saw dust, 7%  
29 polyethylene, and 2% metals), to which varying amounts of organic chlorine and inorganic  
30 chlorine ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ) were added, were combusted. The chlorine content of these fuels varied  
31 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<sub>DF</sub>). Moreover, a correlation was found between I-TEQ<sub>DF</sub> and PCB levels in the flue gases and the chlorine content of the fuel. A fivefold increase in both I-TEQ<sub>DF</sub> 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 or lower (0.5%). 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 forming 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 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 1,130 °C. These data indicated that significant quantities of various isomers of dichloro-,  
2 trichloro-, tetrachloro-, and hexachlorobenzenes could be produced. Choudhry and Hutzinger  
3 (1983) proposed that the radical species  $\text{Cl}\cdot$  and  $\text{H}\cdot$  generated in the incineration process may  
4 attack the chlorinated benzenes and abstract hydrogen atoms to produce orthochlorine-substituted  
5 chlorophenol radicals. These intermediate radical species then react with molecular oxygen to  
6 yield ortho-substituted chlorophenols. As a final step, the ortho-substituted chlorophenols act as  
7 ideal precursors to yield CDDs/CDFs with heat and oxygen. The chlorine in aliphatic compounds  
8 has been observed as both yielding high amounts of HCl during combustion and acting as a direct  
9 chlorine source for the *de novo* synthesis of CDDs/CDFs (Weber et al., 1999).

10 In addition to HCl as a by-product of PVC combustion, Kim et al. (2004) determined that  
11 the combustion of pure PVC yielded appreciable amounts of PAHs, PCBs, chlorobenzenes, and  
12 chlorophenols. They suggested that the gas-phase production of PCBs and chlorobenzenes  
13 contributed to the gas-phase formation of CDDs/CDFs through the precursor mechanism.  
14 Chlorophenols, however, contributed to the *de novo* formation. Kim et al. (2004) reported that the  
15 *de novo* synthesis of CDDs/CDFs from chlorophenols was approximately 100 times greater than  
16 formation from PCB and chlorobenzene precursors.

17 Takeo et al. (2002) found a clear correlation between dioxin formation and the chlorine  
18 content of mixed plastics combusted in a laboratory scale incinerator. PVC, polyethylene (PE),  
19 polystyrene (PS), and polyethylene terephthalate (PET) and their various mixtures were burned at  
20 temperatures greater than 600 °C. Average CO concentrations in the exhaust gases were varied  
21 from 2 to 880 ppm as a general indication of the quality of the fire in the combustion chamber.  
22 When incinerated, each type of plastic formed CDDs/CDFs in the exhaust gases. Of the total  
23 CDDs formed, hexa-CDD and tetra-CDD formed in the greatest amounts when PE was  
24 combusted. Mono-CDF was the most abundant CDF formed from PE combustion. Mono-ortho  
25 coplanar PCBs were preferentially formed over nonortho-PCBs. The combustion of PS caused  
26 tetra-CDD to be formed in the greatest abundance of all possible CDDs whereas tetra-CDF was  
27 the most abundant dibenzofuran. Mono-ortho PCBs formed more than nonortho coplanar PCBs  
28 when PS was combusted. The combustion of PET mostly formed mono-CDD and mono-CDF  
29 among the CDDs/CDFs formed. When PVC was combusted with the conditions of high  
30 temperature and low CO (good combustion), a total of 53.5 ng/g of total CDD was formed, with  
31 the hexa-CDD predominating. In addition, good combustion conditions formed a total of 771

1 ng/g of CDFs, with Cl<sub>2</sub> and Cl<sub>3</sub> CDF congeners dominating. When PVC was combusted with the  
2 conditions of low temperature and high CO (poor combustion), the total CDDs and CDFs formed  
3 increased significantly to 429 ng/g and 8,492 ng/g, respectively. Tri-CDD and di-CDF dominated  
4 the congener distributions suggesting that poor combustion of PVC tends to form high levels of  
5 lower chlorinated CDDs/CDFs. The investigators observed that maintaining good combustion  
6 tended to minimize the formation of CDDs/CDFs from the combustion of chlorinated plastics.

7 Shibata et al. (2003) reported on forming CDDs/CDFs from the combustion of PVC in  
8 quartz ampules. Synthesis of CDDs/CDFs proceeded *de novo* in a temperature range of 200 to  
9 400 °C and catalyzed by copper oxide (CuO). Maximum formation occurred at 300 °C. Hepa-  
10 and Octa-CDD were the dominant CDDs observed in the flue gases whereas tetra-, penta-and  
11 hexa-CDFs dominated the CDFs. The ratio of CDFs to CDDs from PVC combustion was greater  
12 than 1, which is typical of MSW combustion (Shabata et al., 2003).

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

19 De Fre and Rymen (1989) reported on the formation of CDDs/CDFs from hydrocarbon  
20 combustion in a domestic gas/oil burner in the presence of 15 and 300 ppm concentrations of HCl.  
21 More than 100 chlorinated organic compounds were detected in the flue gases whenever HCl was  
22 injected into the system. The investigators observed formation of CDDs and CDFs in all  
23 experiments where HCl was injected in a hydrocarbon flame. In this case, CDFs were always  
24 more abundant than CDDs. It was concluded that the relationship between the HCl concentration  
25 and the emitted concentration of CDDs/CDFs under fixed combustion conditions appeared to be  
26 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 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 tend 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 operational 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 (i.e., MWCs, hospital waste incinerators, HWIs, biomass combustors, laboratory combustors, and bench-scale combustors) to 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. AMSE (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 (i.e., 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<sub>2</sub>). 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 to the formation of CDDs/CDFs, i.e., association with the magnitude of CDDs/CDFs formed occurred only when chlorine content in the feed was  $\geq 1\%$ . Wang et al (2003) confirmed the apparent existence of a chlorine threshold to the 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. Rayhunathan 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<sub>2</sub>, thereby neutralizing the catalyzing agent and reducing the formation of CDDs/CDFs. The Deacon reaction, which forms free chlorine in the combustion plasma, is seen as occurring only in the presence of a catalyst. Thus,

the sulfur dioxide (SO<sub>2</sub>) 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<sub>2</sub> formed. The authors observed that the principal action of sulfur in inhibiting the formation of CDDs/CDFs in combustion systems is through SO<sub>2</sub> depletion of Cl<sub>2</sub>, as follows:



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 <sup>13</sup>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 per 100 µg <sup>13</sup>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 an 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):

$$DRE = \frac{W_I - W_O}{W_I} \times 100\% \quad (2-1)$$

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 PCBs/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 zone, either from *de novo* synthesis or from precursor compounds. Zheng et al. (1999) observed the formation of PCBs in the post-combustion zone 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<sub>2</sub>. 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 zone similar to the *de novo* synthesis of CDDs/CDFs, albeit PCBs were formed in only small amounts relative to CDDs/CDFs.

Fangmark and coworkers (1994) postulated that formation of PCBs and CDDs/CDFs in the post-combustion zone 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 zone (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 CDFs and CDDs 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 or not 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

1 residence times should result in the destruction of most CDDs/CDFs in the feed. Second, mass  
2 balance studies of a number of combustion systems show that more CDDs/CDFs can be detected  
3 in the cool down region downstream of the furnace than in the feed. Third, the CDD/CDF  
4 congener profile in the feed differs from the congener profile in the stack emissions.  
5 Consequently, synthesis appears to be a more important mechanism than pass through. The  
6 concentration of CDDs/CDFs in the flue gases of any particular combustion system will  
7 ultimately be derived as a result of the balance between reactions leading to formation and  
8 reactions leading to destruction of these compounds.

9 **Mechanism 2 (precursor).** This mechanism involves the formation of CDDs/CDFs from  
10 the thermal breakdown and molecular rearrangement of aromatic precursors either originating in  
11 the feed or forming as a product of incomplete combustion. Actual synthesis of CDDs/CDFs  
12 occurs in the post-combustor environment. Gaseous benzene is the most abundant aromatic  
13 compound associated with products of incomplete combustion of waste. Benzene reacts with  
14 chlorine radicals within the combustion gas plasma causing aromatic H abstraction and the  
15 subsequent formation of chlorobenzenes and chlorophenols. Homogeneous gas-phase formation  
16 of CDDs/CDFs occurs from these precursor compounds at temperatures >500 °C, catalyzed by the  
17 presence of copper compounds. In addition, the CDDs/CDFs can form from gas-phase  
18 precursors as heterogeneous, catalytic reactions with reactive fly ash surfaces. This reaction has  
19 been observed to be catalyzed by the presence of a transition metal sorbed to the fly ash. The  
20 most potent catalyst is CuCl<sub>2</sub>. Relatively low temperatures in the range of 200 to 450 °C has been  
21 identified as a necessary condition for these heterogeneous reactions to occur, with either lower or  
22 higher temperatures inhibiting the process. Because these reactions involve homogeneous gas-  
23 phase and heterogeneous solid-phase chemistry, the rate of emissions is less dependent on reactant  
24 concentration than on conditions that are favorable to formation, such as temperature, retention  
25 time, source and species of chlorine, and the presence of a catalyst.

26 **Mechanism 3 (*de novo* synthesis).** This mechanism involves the heterogeneous solid-  
27 phase formation of CDDs/CDFs in the post-combustion environment on the surface of fly ash.  
28 Such heterogeneous chemistry occurs in two ways: (1) Directly from the oxidation of carbon  
29 within the fly ash and subsequent reactions with organic and inorganic chlorine, and (2) The  
30 oxidative breakdown of macromolecular carbon structures (e.g., graphite), and oxychlorination  
31 reactions of aromatic precursors (such as chlorobenzenes and chlorophenols) on fly ash surfaces

1 leading to CDD/CDF formation. In either case, formation kinetics is most favored at temperatures  
2 in the range of 200 to 450 °C and is promoted by the catalytic properties of either the fly ash or  
3 the presence of a transition metal compound. Mechanisms 2 and 3 can occur simultaneously,  
4 share a number of common reaction pathways, and occur in the same physical environment, and  
5 they are controlled by many of the same physical conditions. In well-designed and well-operated  
6 combustion systems, the precursor species needed for mechanism 2 are reduced; consequently *de*  
7 *novo* synthesis can become the dominant pathway for formation. In systems with incomplete  
8 combustion, it is difficult to sort out the relative contribution of these two mechanisms to total  
9 emissions. Both mechanisms, however, can be curtailed if steps are taken to minimize the  
10 physical conditions needed to support formation (i.e., time, temperature, and reactive surface).

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

### 16 17 **2.7.2. Role of Chlorine**

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

20 1. Although chlorine is an essential component in the formation of CDDs/CDFs in  
21 combustion systems, the empirical evidence indicates that, for commercial-scale incinerators,  
22 chlorine levels in feed are not the dominant controlling factor for the amount of CDDs/CDFs  
23 released in stack emissions. Important factors that can affect the rate of CDD/CDF formation  
24 include overall combustion efficiency, post-combustion flue gas temperatures and residence  
25 times, and the types and designs of air pollution control devices employed on combustion  
26 systems. Data from bench-, pilot-, and commercial-scale combustors indicate that CDD/CDF  
27 formation can occur by three principal mechanisms. Some of these data, primarily from bench-  
28 and pilot-scale combustors, have shown direct correlation between chlorine content in fuels and  
29 rates of CDD/CDF formation. Other data, primarily from commercial-scale combustors, show a  
30 weaker relationship between the presence of chlorine in feed and fuels and rates of CDD/CDF  
31 released from the stacks of combustion systems. The conclusion that the amount of chlorine in

1 feed is not a strong determinant of the magnitude of CDD/CDF stack emissions applies to the  
2 overall population of commercial-scale combustors. For any individual commercial-scale  
3 combustor, circumstances may exist in which changes in chlorine content in feed could affect  
4 CDD/CDF emissions. For uncontrolled combustion, such as open burning of household waste,  
5 chlorine content of wastes may play a more significant role in levels of CDD/CDF emissions than  
6 the one observed in commercial-scale combustors.

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

16 3. Laboratory-scale experiments have examined correlations between chlorine content of  
17 feeds and total CDDs/CDFs formed in combustion systems. These experiments suggested that for  
18 feeds containing <1% chlorine, the amount of CDDs/CDFs formed is independent of the chlorine  
19 content of the feed. For feeds with a chlorine content >1%, a direct correlation is observed. The  
20 existence of an apparent threshold to the chlorine content of waste has been verified in full-scale  
21 combustion systems. It has not been determined, however, whether these relationships are  
22 relevant to poorly controlled combustion of wastes and biomass such as backyard barrel burning,  
23 landfill fires, and agricultural burning.

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

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

### 7 8 **2.7.3. General Conclusion**

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

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

Congener	CDD/CDF concentration on fly ash (ng/g)				
	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).

**Table 2-2. CDDs/CDFs formed from the thermolytic reaction of 690 mg benzene + FeCl<sub>3</sub> silica complex**

<b>Congener</b>	<b>Mass produced (ng)</b>	<b>Number of mols produced</b>	<b>Percent yield<sup>a</sup></b>
DiCDD	4.9	0.019	4.3 e-7
TriCDD	54	0.019	4.3 e-6
TCDD	130	0.4	9.0 e-6
PeCDD	220	0.62	1.4 e-5
HxCDD	170	0.44	9.9 e-6
HpCDD	98	0.23	5.2 e-6
OCDD	20	0.04	9.0 e-7
Total CDDs	696.9	1.94	4.4 e-5
DiCDF	990	4.2	9.5 e-5
TriCDF	7,800	29	6.6 e-4
TCDF	12,000	39	8.8 e-4
PeCDF	20,000	59	1.3 e-3
HxCDF	33,000	88	2.0 e-3
HpCDF	40,000	98	1.1 e-3
OCDF	74,000	167	3.8 e-3
Total CDFs	187,000	484.2	1.1 e-2

percent yield = (number of mols of CDD or CDF/mols benzene) x 100.

Source: Nestrick et al. (1987).

**Table 2-3. *De novo* formation of CDDs/CDFs after heating Mg-Al silicate, 4% charcoal, 7% Cl, 1% CuCl<sub>2</sub> in H<sub>2</sub>O at 300 °C**

Congener	Concentration of CDD/CDF (ng/g)				
	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

Source: Stieglitz et al. (1989a).



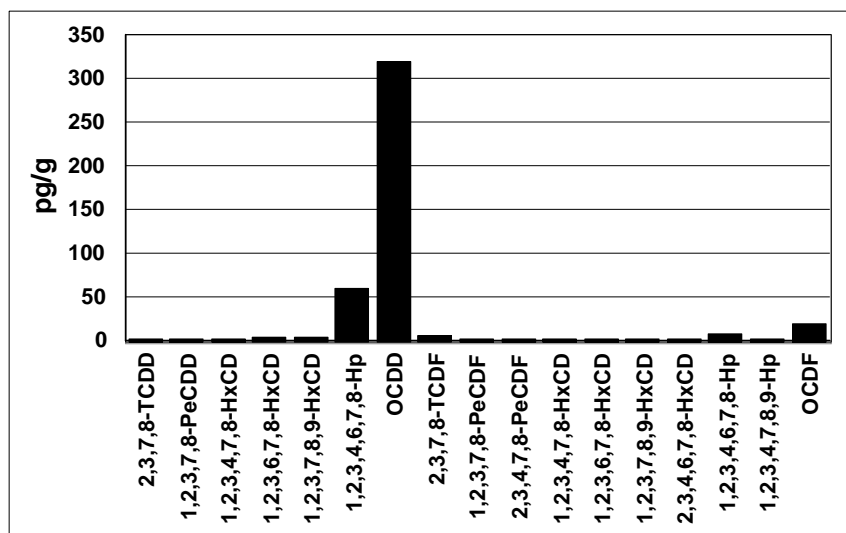
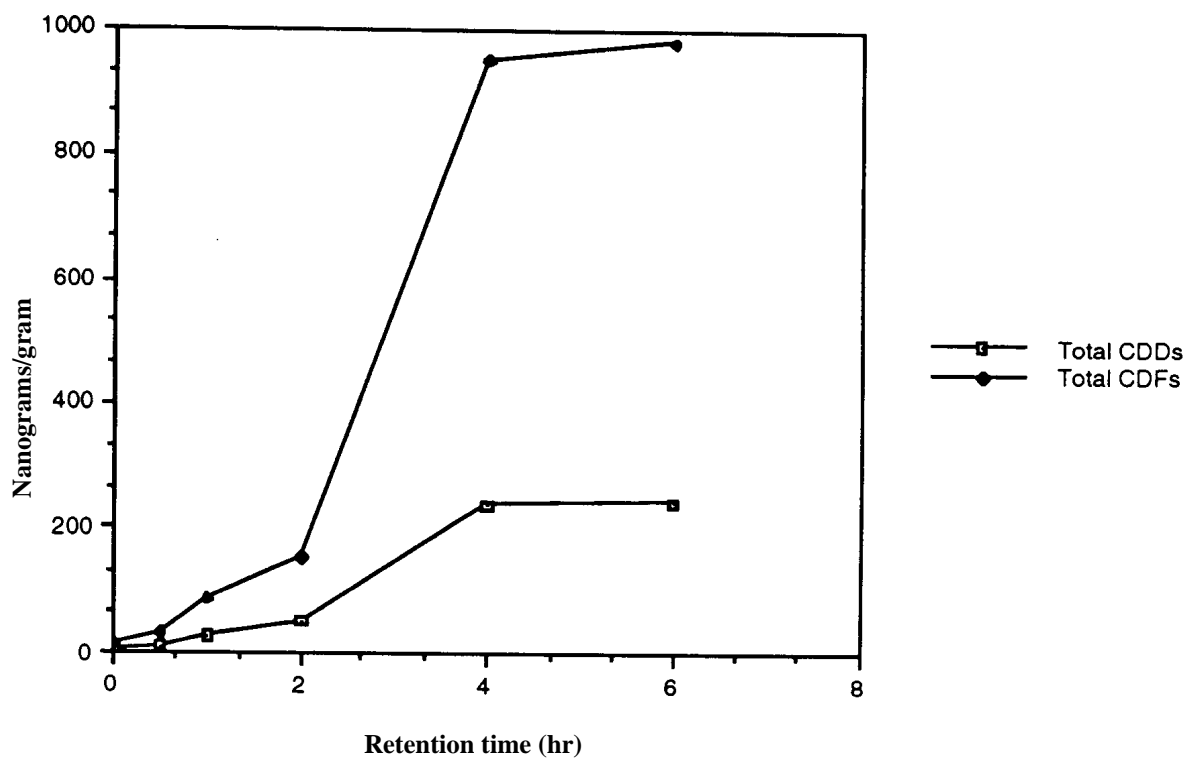


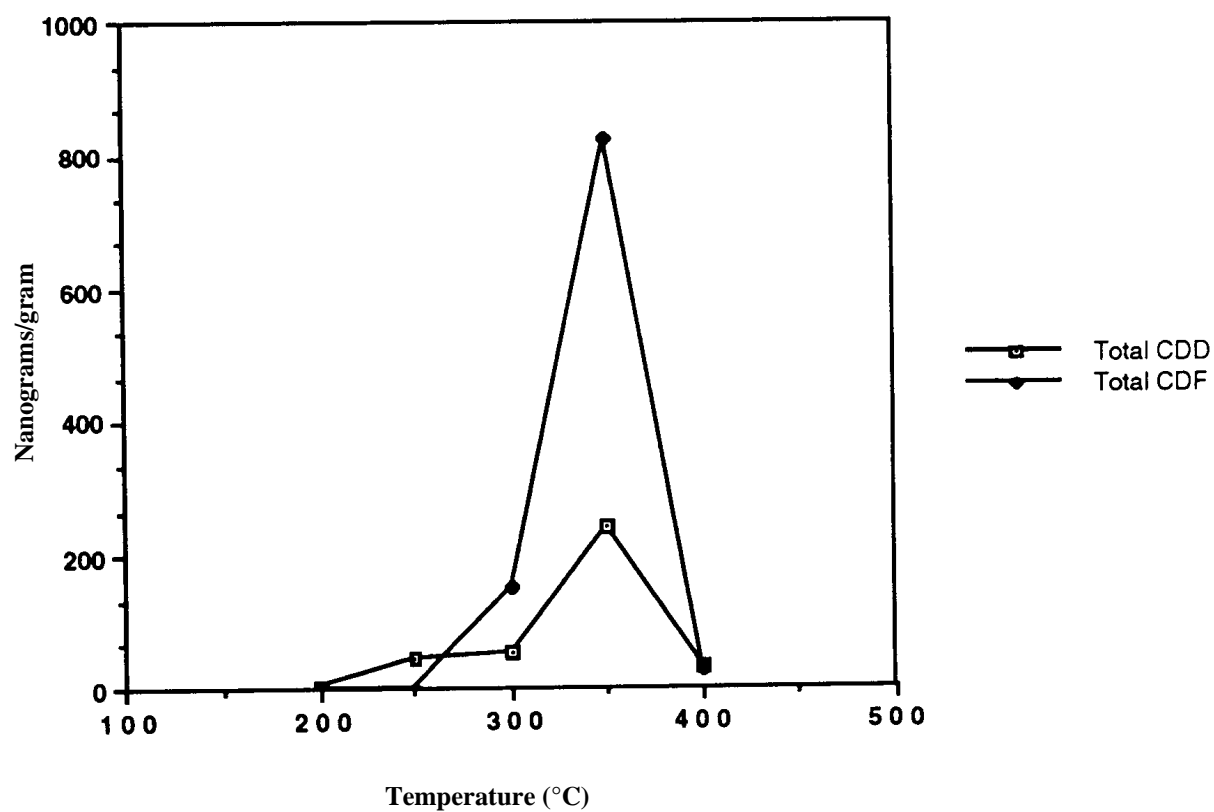
Figure 2-1. Typical CDD and CDF congener distribution in contemporary municipal solid waste (MSW).

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



**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).



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

Source: Addink et al. (1991).

### 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 noted in Chapter 2, combustion research has developed three theories on the mechanisms involved in the emission of CDDs and CDFs from combustion systems: (1) CDDs/CDFs can be introduced into the combustor with the feed and pass through the system unchanged (pass through), (2) CDDs/CDFs can be formed during combustion (precursor), and/or (3) CDDs/CDFs can be formed via chemical reactions in the post-combustion portion of the system (*de novo* synthesis). The 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 furnace design, composition of the waste feed, temperature in the post-combustion zone of the system, and 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 zone 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 on the basis of 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 refused-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 dominate 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. The 1995 inventory indicated that the combustion capacities of mass burn facilities range from 90 to 2,700 metric tons of MSW per day. 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 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.

**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 secondary chamber). In the 1995 inventory, the combustion capacity of modular combustors ranged from 4 to 270 metric tons per day, that is, 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 excess-air MWC.

- 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 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 starved-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, 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 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 RDFs burn either RDF or normal MSW, along with another fuel.
- The fluidized-bed RDF 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 RDFs typically operate at 30 to 100% excess air levels and at bed temperatures around 815 °C. A typical fluidized-bed RDF is represented in Figure 3-6. The technology has two basic designs: (1) a bubbling-bed incineration unit and (2) 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.

### **3.1.1.2. Air Pollution Control Devices**

MWCs are commonly equipped with one or more post-combustion APCDs to remove various pollutants prior to release from the stack, such as PM, heavy metals, acid gases, and organic contaminants (U.S. EPA, 1992d). 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 in 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, 1994f). 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 occurs 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.



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

8       **Spray dry scrubbing system (SDSS).** Spray dry scrubbing, also called spray dryer  
9 adsorption, involves the removal of both acid gas and PM from the post-combustion gases. By  
10 themselves, the units probably have little effect on dioxin emissions. In a typical SDSS, hot  
11 combustion gases enter a scrubber reactor vessel. An atomized hydrated lime slurry (water plus  
12 lime) is injected into the reactor at a controlled velocity (Donnelly, 1992). The slurry rapidly  
13 mixes with the combustion gases within the reactor. The water in the slurry quickly evaporates,  
14 and the heat of evaporation causes the combustion gas temperature to rapidly decrease. The  
15 neutralizing capacity of hydrated lime reduces the acid gas constituents of the combustion gas  
16 (e.g., HCl and  $\text{SO}_2$ ) by greater than 70%. A dry product consisting of PM and hydrated lime  
17 settles to the bottom of the reactor vessel.

18       SDSS technology is used in combination with ESPs or FFs. SDSSs reduce ESP inlet  
19 temperatures to make a cold-sided ESP. In addition to acid gas, particulate, and metals control,  
20 SDSSs with FFs or ESPs achieve greater than 90% dioxin control (U.S. EPA, 1992d), and they  
21 typically achieve greater than 90%  $\text{SO}_2$  and HCl control.

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

27       **Wet scrubber (WS).** WS devices are designed for acid gas removal and are more  
28 common to MWC facilities in Europe than in the United States. They should help reduce  
29 emissions of dioxin in both vapor and particle forms. The devices consist of two-stage  
30 scrubbers. The first stage removes HCl, and the second stage removes  $\text{SO}_2$  (Donnelly, 1992).

Water is used to remove HCl and caustic or hydrated lime is added to remove SO<sub>2</sub> 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 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 emission, the MWCs operating in 1987 and 1995 were divided into categories according to the eight furnace types and seven 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. This information was derived from five reports: U.S. EPA, 1987b; SAIC, 1994; Taylor and Zannes, 1996; Solid Waste Technologies, 1994; and Huckaby, 2003. In general, the information was collected via telephone interviews with the plant operators.

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 (113 in 1987, 130 in 1995, and 104 facilities in 2000), but the amount of MSW incinerated more than doubled from 1987 to 1995 (13.8 billion kg in 1987 and 28.8 billion kg in 1995) and remained constant from 1995 to 2000 (27.7 billion kg in 2000).
- The dominant furnace technology shifted from modular in 1987 (57 units and 1.4 billion kg) to MB-WW facilities in 1995 (57 units and 17 billion kg) and 2000 (142 units and 19 billion kg).
- The dominant APCD technology shifted from hot-sided ESPs in 1987 (54 units and 11 billion kg) to FFs in 1995 (55 units and 16 billion kg) and spray dryer with FF, CI, and selective noncatalytic reduction (88 large MSW units) and ESPs (28 small MWCs) in 2000.
- The use of hot-sided ESPs dropped from 54 facilities in 1987 (11 billion kg) to 16 facilities in 1995 (2.2 billion kg).
- The number of uncontrolled facilities dropped from 38 in 1987 (0.6 billion kg) to 10 in 1995 (0.2 billion kg) and 8 in 2000 (0.1 billion kg).

### **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***

OAQPS has obtained dioxin test reports for all 167 large MWCs following emission control retrofits and used these data to calculate emissions for large MWCs for reference year 2000. Test reports for small MWCs will not be obtained until retrofits are completed in 2005. Emissions for small MWCs for 2000 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 167 MWC units (Huckaby, 2003). The calculations were based on the individual 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 congener concentration with three different 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 lists the national dioxin/furan TEQ emissions for large MWCs.

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

Within the context of this report, adequate emission 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 of combustion gas [ng/dscm]) 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, 1995b). 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:

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

where:

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

C = combustion flue gas TEQ concentration (ng/dscm) (20 °C, 1 atm; adjusted to 7% O<sub>2</sub>)

V = volumetric flow rate of combustion flue gas (dscm/hr) (20 °C, 1 atm; adjusted to 7% O<sub>2</sub>)

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 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:

$$EF_{MWC} = \frac{C \times F_v}{I_w} \quad (3-2)$$

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<sub>2</sub>)

$F_v$  = volumetric flue gas flow rate (dscm/hr) (20 °C, 1 atm; adjusted to 7% O<sub>2</sub>)

$I_w$  = average waste incineration rate (kg/hr)

**Example:** An MB-WW MWC equipped with a cold-sided ESP.

Given:

$C = 10 \text{ ng TEQ/dscm}$  (20 °C, 1 atm; adjusted to 7% O<sub>2</sub>)

$F_v = 40,000 \text{ dscm/hr}$  (20 °C, 1 atm; adjusted to 7% O<sub>2</sub>)

$I_w = 10,000 \text{ kg MSW/hr}$

$$\begin{aligned} EF_{MB-WW} &= \frac{10 \text{ ng}}{\text{dscm}} \times \frac{40,000 \text{ dscm}}{\text{hr}} \times \frac{\text{hr}}{10,000 \text{ kg}} \\ &= \frac{40 \text{ ng TEQ}}{\text{kg MSW burned}} \end{aligned}$$

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. Sum 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 (13.8 billion kg of waste), 1995 (28.8 billion kg of waste), and 2000 (27.7 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; Huckaby, 2003).

The emission factor estimates are given a high confidence rating for 2000 and a medium confidence rating for both 1995 and 1987. All 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 113 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 occur during other conditions (e.g., upset conditions, start up, and shut down).

These confidence ratings produce an overall high confidence rating in the annual emission estimates of 78.9 g I-TEQ<sub>DF</sub> in 2000 (13.7 g TEQ<sub>DF</sub>-WHO<sub>98</sub> [15.3 g I-TEQ<sub>DF</sub>] for large MWC units and 63.6 g I-TEQ<sub>DF</sub> for small MWC units). A medium confidence rating is assigned to the annual emission estimates of 1,250 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (1,100 g I-TEQ<sub>DF</sub>) in 1995 and 8,877 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (7,915 g I-TEQ<sub>DF</sub>) in 1987.

### **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 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 Huckaby (2003), 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<sub>DF</sub> 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.

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, 1991b).

EPA reported the results of analyses of MWC ash samples for CDDs/CDFs (U.S. EPA, 1990c). 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<sub>DF</sub>/kg, with a mean value of 258 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub>/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:

<u>Location</u>	<u>Type of Residual</u>	<u>I-TEQ (µg/kg)</u>	<u>I-TEQ (mg/day)</u>
Ft. Lewis	Bottom ash	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
	Fly ash	0.51	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 than those reported by EPA (U.S. EPA, 1990c).

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, 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 multiple fashions. 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 only landfilled. 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 (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.

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 et al. (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<sub>DF</sub>/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<sub>DF</sub>/kg for fly ash and 10.5 ng I-TEQ<sub>DF</sub>/kg for bottom ash for dioxins and 31.6 ng I-TEQ<sub>DF</sub>/kg for fly ash and 0.85 ng I-TEQ<sub>DF</sub>/kg for bottom ash for PCBs.

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, 1990c). 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<sub>DF</sub>/L); the only detectable congeners were HpCDDs, OCDD, and HpCDFs.

### 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, 1995e). 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, 1995e). 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 for large MWCs

(ng total CDD/CDF/dscm)

60

30

13

Facility age, size, and APCD

Existing; >225 metric tons/day; ESP-based APCD

Existing; >225 metric tons/day; non-ESP-based APCD

New; >225 metric tons/day

EPA reestablished emission standards for small MWCs (MWC units between 35 and 225 tons/day combustion capacity) in December 2000. These standards contain two different 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 limit for the Class I MWCs is the same as the 1995 limits for large MWCs. The limit for the smaller Class II MWCs is 125 ng/dscm. These small MWCs are 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 (U.S. EPA, 2003e).

### 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 technology used to manage hazardous waste under RCRA and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, or Superfund) programs.

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 to 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 subsections 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, 1996h). 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 semi-solid 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, 1996h). 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 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

1 evaporates, leaving a highly combustible mix of waste fumes and combustion air (U.S. EPA,  
2 1996h). Secondary air is added to the combustion chamber to complete the oxidation of the  
3 fume and air mixture.

4 **Fixed-hearth.** Fixed-hearth incinerators are starved-air or pyrolytic incinerators. Waste  
5 is ram-fed into the primary chamber and incinerated at about 50 to 80% of stoichiometric  
6 requirements. The resulting smoke and pyrolytic combustion products are then passed through a  
7 secondary combustion chamber where relatively high temperatures are maintained by the  
8 combustion of auxiliary fuel. Oxygen is introduced into the secondary chamber to promote  
9 complete thermal oxidation of the organic molecules entrained in the gases. Other types of  
10 hearths include roller hearths and rotary hearths. Roller hearths use a conveyor system to move  
11 waste from the kiln entrance to the exit. In rotary hearths, waste enters and exits through the  
12 same gate, and the hearth rotates inside a circular tunnel kiln.

13 **Fluidized-bed.** The fluidized-bed incinerator is similar in design to the incinerators used  
14 in MSW incineration (see Section 3.1). In fluidized-bed HWIs, a layer of sand is placed on the  
15 bottom of the combustion chamber. The bed is preheated by underfire auxiliary fuel at startup.  
16 The hot gases channel through the sand at relatively high velocity, and the turbulent mixing of  
17 combustion gases and combustion air causes the sand to become suspended (Buonicore, 1992a)  
18 and take on the appearance of a fluid medium; hence the term “fluidized-bed” combustor. The  
19 incinerator is operated at temperatures below the melting point of the bed material (typical  
20 temperatures are within a range of 650 to 940 °C). A constraint on the types of waste burned is  
21 that the solid waste particles must be capable of being suspended within a furnace. When the  
22 liquid or solid waste is combusted in the fluid medium, the exothermic reaction causes heat to be  
23 released into the upper portion of the combustion chamber. The upper portion typically has  
24 much larger volume than the lower portion, and temperatures can reach 1,000 °C (Buonicore,  
25 1992a). This high temperature is sufficient to combust volatilized pollutants emanating from the  
26 combustion bed.

### 28 3.2.2. APCDs for HWIs

29 Most HWIs use APCDs to remove undesirable components from the flue gases that  
30 evolve during the combustion of the hazardous waste. These unwanted pollutants include  
31 suspended ash particles (PM), acid gases, metals, and organic pollutants. The APCD controls

1 collect these pollutants and reduce the amount discharged from the incinerator stack to the  
2 atmosphere. The levels and types of these combustion byproducts are highly site-specific,  
3 depending on factors such as waste composition and incinerator system design and operating  
4 parameters (e.g., temperature and exhaust gas velocity). The APCD typically comprises a series  
5 of different devices that work together to clean the combustion exhaust flue gas. Unit operations  
6 usually include exhaust gas cooling followed by PM and acid gas control.

7 Exhaust gas cooling may be achieved using a waste heat boiler or heat exchanger, by  
8 mixing with cool ambient air, or by injecting a water spray into the exhaust gas. A variety of  
9 types of APCDs are used to remove PM and acid gases. Such devices include WSs (such as  
10 venturi, packed bed, and ionizing systems), ESPs, and FFs (sometimes used in combination with  
11 dry acid gas scrubbing). In general, the control systems can be grouped into the following three  
12 categories: wet, dry, and hybrid wet/dry systems. The controls for acid gases (either dry or wet  
13 systems) cause temperatures to be reduced preceding the control device. This impedes the  
14 formation of CDDs/CDFs in the post-combustion area of the typical HWI. It is not unusual for  
15 stack concentrations of CDDs/CDFs at a particular HWI to be in the range of 1 to 100 ng/dscm  
16 (Helble, 1993), which is low when compared with those of other waste incineration systems.  
17 However, the range of total CDD/CDF flue gas concentrations measured in the stack emissions  
18 of HWIs during trial burns across the class of HWI facilities spans four orders of magnitude,  
19 ranging from 0.1 to 1,600 ng/dscm (Helble).

20 The three categories of APCD systems are described below:

- 21  
22 • **Wet system.** A WS is used for both particulate and acid gas control. Typically, a  
23 venturi scrubber and a packed-bed scrubber are used in a back-to-back arrangement.  
24 Ionizing WSs, wet ESPs, and innovative venturi-type scrubbers may be used for more  
25 efficient particulate control. WSs generate a wet effluent liquid wastestream  
26 (scrubber blowdown). They are relatively inefficient at fine particulate control when  
27 compared with dry control techniques and have equipment corrosion concerns.  
28 However, WSs provide efficient control of acid gases and have lower operating  
29 temperatures (compared with dry systems), which may help control the emissions of  
30 volatile metals and organic pollutants.
- 31  
32 • **Dry system.** In SDSSs, an FF or ESP is used for particulate control, frequently in  
33 combination with dry scrubbing for acid gas control. Compared with WSs, SDSSs  
34 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 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 furnace types and numbers 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.

$$EF_{HWI} = \frac{C \times F_v}{I_w} \quad (3-3)$$

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 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.

$$EF_{avgHWI_{n=1-17}} = (EF_{HWI_1} + EF_{HWI_2} + EF_{HWI_3} + ..... + EF_{HWI_{17}}) / N \quad (3-4)$$

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 through 1996 are presented in Figure 3-13. The average emission factor for the 17 HWIs was 3.88 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (3.83 ng I-TEQ<sub>DF</sub>/kg) of waste feed (assuming nondetect values are zero). The average emission factor for the 22 HWIs tested in 2000 was 2.13 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (2.12 ng I-TEQ<sub>DF</sub>/kg) of waste feed (assuming nondetect values are 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 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, 1996b). The activity level estimate for 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.

$$E_{HWI} = EF_{HWI} \times A_{HWI} \quad (3-5)$$

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<sub>DF</sub>-WHO<sub>98</sub>/kg waste [3.83 ng I-TEQ<sub>DF</sub>/kg waste]) to these production estimates yields estimated emissions of 5 g TEQ (TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub>) in 1987 and 5.8 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (5.7 g I-TEQ<sub>DF</sub>) in 1995. For 2000, applying the average TEQ emission factors for dedicated HWIs (2.13

1 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg waste [2.12 ng I-TEQ<sub>DF</sub>/kg waste]) to a production estimate of 1.5 million  
2 metric tons yields estimated emissions of 3.2 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (3.18 g I-TEQ<sub>DF</sub>). Medium  
3 confidence rating is assigned to these estimates because the emission factor was given a medium  
4 confidence rating.

### 6 **3.2.5. Recent EPA Regulatory Activities**

7 The EPA regulated CDD/CDF emissions from HWIs (Federal Register, 1999b, 2004).  
8 The regulations are specific to the I-TEQ concentration in the combustion gases leaving the  
9 stack. Existing HWIs equipped with waste heat boilers and dry scrubbers (as air pollution  
10 control devices) cannot emit more than 0.28 ng I-TEQ/dscm. All other existing HWIs are limited  
11 to 0.4 ng I-TEQ/dscm of stack gas. Regulatory requirements are more strict for newly built  
12 HWIs. Newly built HWIs equipped with waste heat boilers and dry scrubbers (as air pollution  
13 control devices) cannot emit more than 0.11 ng I-TEQ/dscm. All other newly built HWIs are  
14 limited to 0.2 ng I-TEQ/dscm of stack gas.

### 16 **3.2.6. Industrial Boilers and Furnaces Burning Hazardous Waste**

17 In 1991, EPA established rules that allow the combustion of some liquid hazardous waste  
18 in industrial boilers and furnaces (Federal Register, 1991c). These facilities typically burn oil or  
19 coal for the primary purpose of generating electricity. Liquid hazardous waste can only be  
20 burned as supplemental (auxiliary) fuel, and the rule limits use to no more than 5% of the  
21 primary fuels. These facilities typically use an atomizer to inject the waste as droplets into the  
22 combustion chamber. They are equipped with particulate and acid gas emission controls and in  
23 general are sophisticated, well-controlled facilities that achieve good combustion.

24 The national OSW database contains congener-specific emission concentrations for two  
25 boilers burning liquid hazardous waste as supplemental fuel tested from 1993 to 1996. The  
26 average congener and congener group emission profiles for the industrial boiler data set are  
27 presented in Figure 3-14. The database also contains congener-specific emission concentrations  
28 for four boilers tested in 2000. Of the boilers tested in 2000, sufficient data to calculate average  
29 TEQ emissions were available for only one boiler. The average congener and TEQ emission  
30 factors are presented in Tables 3-14a and 3-14b. The limited set of emissions data prevented  
31 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 TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (0.64 ng I-TEQ<sub>DF</sub>/kg) of waste feed for 1993 to 1996 and 1.212 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (1.214 ng I-TEQ<sub>DF</sub>/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, 1996b). 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<sub>DF</sub>-WHO<sub>98</sub> (0.77 g I-TEQ<sub>DF</sub>) in 1987, 0.39 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (0.38 g I-TEQ<sub>DF</sub>) in 1995, and 1.82 g TEQ (TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub>) 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, 1991b).

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 above. The average TEQ emission factor for HAFs is  $0.836 \text{ ng TEQ}_{\text{DF}}\text{-WHO}_{98}/\text{kg}$  ( $0.803 \text{ ng I-TEQ}_{\text{DF}}/\text{kg}$ ) 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).

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 for dedicated HWIs, was also used to calculate annual TEQ emissions for HAFs. Multiplying the average TEQ emission factors by the total estimated kg of liquid hazardous waste burned in 2000 yields annual emissions in  $\text{g I-TEQ}_{\text{DF}}$ . From this procedure, the emissions from all industrial boilers/furnaces burning hazardous waste as supplemental fuel are estimated as  $0.31 \text{ g TEQ}_{\text{DF}}\text{-WHO}_{98}$  ( $0.3 \text{ g I-TEQ}_{\text{DF}}$ ). 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. EPA indicated that 538 µg/kg and 2,853 µg/kg were the mean concentrations of CDDs and CDFs, respectively, from a hazardous waste incinerator with an afterburner (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, 1997b). 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 subsections 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, 1997b).

**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, 1991d, 1997b; 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, 1990d, 1991d; 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, 1990d, 1991d; 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



1 automated charging systems can be used, but the incinerator must be shut down for ash removal.  
2 Continuous incinerators are operated 24 hr/day and use automatic charging systems to charge  
3 waste into the unit in small, frequent batches. All continuous incinerators operate using a  
4 mechanism to automatically remove the ash from the incinerator (U.S. EPA, 1990d, 1991d).

### 6 **3.3.2. Characterization of MWIs for Reference Years 1987, 1995, and 2000**

7 Medical waste incineration remains a poorly characterized industry in the United States in  
8 terms of knowing the exact number of facilities in operation over time, the types of APCDs  
9 installed on these units, and the aggregate volume and weight of medical waste that is combusted  
10 in any given year (U.S. EPA, 1997b). The primary reason for this lack of information is that  
11 permits were not generally required for the control of pollutant stack emissions from MWIs until  
12 the early 1990s, when state regulatory agencies began setting limits on emissions of PM and  
13 other contaminants (Federal Register, 1997b). Prior to that, only opacity was controlled.

14 The information available to characterize MWIs from 1987 and 1995 comes from  
15 national telephone surveys, stack emission permits, and data gathered by EPA during public  
16 hearings (Federal Register, 1997b). For 2000, information was also provided by a memorandum  
17 on emissions from MWIs (Strong and Hanks, 1999) and a limited telephone survey conducted by  
18 Versar, Inc. (McAloon, 2003). Strong and Hanks provided information on MWIs in the United  
19 States, including the APCD being used by each facility.

20 In 2003, Versar used the Strong and Hanks memorandum to identify six states as having a  
21 large number of medical waste facilities operating in 1999. A telephone survey was conducted  
22 with the state agencies in each of these six states to obtain the number of MWIs that were  
23 operating in 2000. Versar was able to obtain an updated list from four of the six states, which are  
24 listed below, along with the dates they were contacted, the number of MWIs operating in 1999,  
25 the updated number of MWIs for that state in 2000, and the percent of facilities closed over this  
26 time period for each state.

<u>State</u>	<u>Date contacted</u>	<u>No. of MWIs</u>		<u>Percent of facilities</u>
		<u>1999</u>	<u>2000</u>	<u>closed from 1999 to 2000</u>
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, 1987d), 2,375 in 1995 (Federal Register, 1997b), 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, 1987d) and 0.77 billion kg in 1995 (Federal Register, 1997b).

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 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

1 they submit the state plan to EPA within 1 year of EPA's promulgation of the guidelines (i.e., by  
2 September 15, 1998). The compliance schedule, however, allows up to three years from EPA  
3 approval of the state plan for MWIs to comply, provided the plan includes enforceable  
4 increments of progress. All MWIs were required to be in compliance within three years of  
5 approval of their state plan or by September 15, 2002, whichever was earlier.

6 Compliance is stated to be either completion of retrofit of air pollution controls or  
7 shutdown of the facility. As a result, many facilities have closed down and hospitals have  
8 switched to less expensive medical waste treatment technologies such as autoclaving (Federal  
9 Register, 1997b). Autoclaving, or steam sterilization, is one of the most common waste  
10 management practices used today. This process involves placing bags of infectious waste into a  
11 sealed chamber, sometimes pressurized, and then heating it by direct contact with steam to  
12 sterilize the waste.

13 The actual controls used on MWIs on a facility-by-facility basis in 1987 are unknown,  
14 and EPA generally assumes that MWIs were mostly uncontrolled (U.S. EPA, 1987d). However,  
15 the modular design does cause some destruction of organic pollutants within the secondary  
16 combustion chamber. Residence time within the secondary chamber is key to inducing the  
17 thermal destruction of the organic compounds. Residence time is the time that the organic  
18 compounds entrained within the flue gases are exposed to elevated temperatures in the secondary  
19 chamber. EPA has demonstrated with full-scale MWIs that increasing residence time from 1/4  
20 sec to 2 sec in the secondary chamber can reduce organic pollutant emissions, including  
21 CDDs/CDFs, by up to 90% (Federal Register, 1997b). In this regard, residence time can be  
22 viewed as a method of air pollution control.

23 EPA estimates that about two-thirds of the medical waste burned in MWIs in 1995 went  
24 to facilities that had some method of air pollution control (Federal Register, 1997b). The types  
25 of APCDs installed and the methods used on MWIs include DSI, FFs, ESPs, WSs, and FFs  
26 combined with packed-bed scrubbers (composed of granular activated carbon). Some organic  
27 constituents in the flue gases can be adsorbed by the packed bed. Within the uncontrolled class  
28 of MWIs, about 12% of the waste was combusted in facilities with design capacities of less than  
29 200 lb/hr, with the majority of waste burned at facilities with capacities greater than 200 lb/hr. In  
30 controlled facilities, an estimated 70% of the aggregate activity level is associated with facilities  
31 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, 1997b).

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 spray dryer 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. These data limitations have lead to a variety of approaches for estimating CDD/CDF emissions from MWIs:

1. **OAQPS approach** (Federal Register, 1997b). EPA's OAQPS used this approach in support of the promulgation of final air emission standards for hospital/medical/infectious waste incinerators.
2. **American Hospital Association (AHA) approach** (AHA, 1995). The AHA proposed an approach in its comments on drafts of this document and on the proposed MWI emissions regulations.
3. **ORD approach**. In the preparation of this document, EPA's ORD developed a third approach.

Given the limitations of existing information, both the OAQPS and the AHA approaches are reasonable methods for calculating annual releases of CDDs/CDFs from MWIs. Both methods relied heavily on a series of assumptions to account for missing information. In developing a third approach, ORD built upon the other two approaches by using the most logical features of each. Because of the uncertainties about the existing data, it is currently not known

which approach gives the most accurate estimate of CDD/CDF air emissions from all MWIs nationwide. The three approaches yield different air emission estimates, but the estimates all agree within a factor of 4.

### **3.3.4. OAQPS Approach for Estimating CDD/CDF Emissions from MWIs**

As stated in Section 3.3.2, EPA promulgated final standards of performance for new and existing MWIs under the Clean Air Act Amendments on September 15, 1997 (Federal Register, 1997b). CDD/CDF stack emission limits for existing MWIs were established as follows: 125 ng/dscm of total CDD/CDF (at 7%t oxygen, 1 atm), equivalent to 2.3 ng/dscm TEQ. In order to evaluate emissions reductions that will be achieved by the standard, OAQPS estimated, as a baseline for comparison, nationwide annual CDD/CDF emissions from all MWIs operating in 1995.

#### **3.3.4.1. OAQPS Approach for Estimating Activity Level**

As a starting point for deriving national estimates, OAQPS constructed an inventory of the numbers and types of MWIs believed to be operating in 1995. The inventory was based on an inventory of 2,233 MWIs prepared by the AHA (AHA, 1995), supplemented with additional information compiled by EPA. This created a listing of 2,375 MWIs in the United States. The following assumptions were then used to derive activity level estimates:

1. 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 units were assumed to be batch operations, and the others were classified as either intermittent or continuous, assuming a ratio of 3 to 1.
2. 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 OAQPS estimated annual operating hours for each MWI design type.

#### 3.3.4.2. *OAQPS Approach for Estimating CDD/CDF Emission Factors*

On the basis of information obtained from the AHA and state regulatory agencies, one-third of the population of MWIs operating in 1995 was estimated to have had no APCD (i.e., they were uncontrolled), and two-thirds had some type of APCD. CDD/CDF TEQ emission factors were then developed for uncontrolled and controlled MWIs as shown below.

**Estimating TEQ emission factors for uncontrolled facilities.** The uncontrolled category of facilities was subdivided by residence time of the secondary combustion chamber. On the basis of tests at three MWIs, OAQPS concluded that stack emissions of CDDs/CDFs from uncontrolled facilities were dependent on the residence time (i.e., the amount of time the compounds are exposed to elevated temperatures within the secondary combustion chamber) (Strong, 1996). The tests demonstrated that when the residence time in the secondary chamber was short (<1 sec), the stack emissions of CDDs/CDFs would increase; conversely, the longer the residence time (>1 sec), the greater the decrease in CDD/CDF emissions. The emissions testing at these MWIs provided the basis for the derivation of I-TEQ<sub>DF</sub> emission factors for residence times of 1/4 sec, 1 sec, and 2 sec. Table 3-18 summarizes the emission factors developed for each MWI type as a function of residence time.

The OAQPS inventory of MWIs in 1995 did not provide residence times for each facility. OAQPS overcame this data gap by assuming that residence time in the secondary combustion chamber corresponded approximately with the PM stack emission limits established in state air permits. This approach assumed that the more stringent PM emission limits would require longer residence times in the secondary chamber in order to further oxidize carbonaceous soot particles and reduce PM emissions. Table 3-19 lists the assumed residence times in the secondary chamber corresponding to various state PM emission limits. State implementation plans (SIPs) were reviewed to determine the PM emission limits for incinerators, and from this review both a residence time and an I-TEQ<sub>DF</sub> emission factor were assigned to each uncontrolled MWI on the inventory.

**Estimating TEQ emission factors for controlled MWIs.** Two-thirds of the MWI population were assumed to have some form of APCD. As discussed in Section 3.3.2, APCDs typically used by MWIs consist of one or more of the following: WS, SDSS, and FF combined with a packed bed. The OAQPS approach also included the addition of activated carbon to the flue gases as a means of emissions control (i.e., SDSSs combined with CI). TEQ emission

factors were developed for these control systems on the basis of incinerator emissions testing data gathered in support of the regulations (U.S. EPA, 1997b). Because the inventory did not list the APCDs for all MWIs, state requirements for PM control were used to make assumptions about the type of APCD installed on each facility in the inventory. These assumptions are summarized in Table 3-19.

### 3.3.4.3. *OAQPS Approach for Estimating Nationwide CDD/CDF TEQ Air Emissions*

Annual TEQ emissions for each MWI facility were calculated as a function of the design capacity of the incinerator, the annual waste charging hours, the capacity factor, and the TEQ emission factor as shown in eq 3-6.

$$E_{MWI} = (C \times H \times C_1) \times F_{TEQ} \quad (3-6)$$

where:

$E_{MWI}$  = annual MWI CDD/F TEQ stack emissions (g/yr)

$C$  = MWI design capacity (kg/hr)

$H$  = annual medical waste charging hours (hr/yr)

$C_1$  = capacity factor (unitless)

$F_{TEQ}$  = CDD/CDF TEQ emission factor (g TEQ/kg)

The annual TEQ air emission of all MWIs operating in 1995 is the sum of the annual emissions of each individual MWI. The following equation is applied to estimate annual TEQ emissions from all MWIs.

$$E_{MWI} (nationwide) = (Em_{MWI_1} + Em_{MWI_2} + Em_{MWI_3} + ..... + Em_{MWI_{2375}}) \quad (3-7)$$

where:

$E_{MWI} (nationwide)$  = nationwide MWI TEQ emissions (g/yr)

Table 3-18 summarizes estimated I-TEQ<sub>DF</sub> emissions for 1995 using the OAQPS approach.

### 3.3.5. AHA Approach for Estimating CDD/CDF Emissions from MWIs

In 1995, the AHA responded to EPA's request for public comment on the 1994 draft public release of this document. As part of its comments (AHA, 1995), the AHA attached an analysis of CDD/CDF emissions from MWIs prepared by Doucet (1995) for the AHA. Doucet estimated the total number of MWIs operating in 1995, the distribution of APCDs, CDD/CDF TEQ emission factors, and nationwide TEQ emissions. The following is a brief discussion of the AHA inventory and the Doucet analysis.

From a national telephone survey of member hospitals conducted between September and November 1994, the AHA developed what is generally considered to be the first attempt to systematically inventory MWIs in the United States. Approximately 6% of the hospitals with MWIs were contacted (AHA, 1997). The AHA survey showed that, as of December 1994, 2,233 facilities were in operation. Doucet (1995) subdivided the AHA MWI inventory into two uncontrolled categories on the basis of combustor design-rated capacity and two controlled categories on the basis of APCD equipment. Doucet then developed CDD/CDF emission factors for each MWI category. Test reports of 19 MWIs were collected and evaluated. Average CDD/CDF TEQ flue gas concentrations (ng/dscm at 7% oxygen) were derived by combining tests from several MWIs in each capacity range category and APCD. The average TEQ flue gas concentrations were then converted to average TEQ emission factors, which were in units of lb TEQ/10<sup>6</sup> lb of medical waste incinerated (equation for conversion not given). Table 3-20 lists the I-TEQ<sub>DF</sub> emission factors calculated by Doucet for each level of assumed APCDs on MWIs.

As in the OAQPS approach (Section 3.3.4), the distribution of the APCD categories was derived by assuming that state PM limits would indicate the APCD on any individual MWI (Doucet, 1995). Table 3-21 displays the AHA assumptions of air pollution control used on MWIs on the basis of PM emission limits.

With the activity levels, the percent distribution of levels of controls, and the CDD/CDF TEQ emission factors having been calculated with existing data, the final step of the AHA approach was the estimation of annual I-TEQ<sub>DF</sub> emissions (g/yr) from MWIs nationwide. Although no equation was given, it is presumed that the emissions were estimated by multiplying the activity level for each MWI size and APCD category by the associated I-TEQ<sub>DF</sub> emission factor. The sum of these calculations for each designated class yields the estimated annual I-TEQ<sub>DF</sub> emissions for all MWIs nationwide. Doucet (1995) indicated that these computations



were appropriate for I-TEQ<sub>DF</sub> emissions in 1995. Table 3-22 summarizes the nationwide annual I-TEQ<sub>DF</sub> emissions from MWIs using the AHA approach.

### **3.3.6. ORD Approach for Estimating CDD/CDF Emissions from MWIs**

Because of the limitations of the emissions data and activity levels, the ORD approach used many of the logical assumptions developed in the OAQPS and AHA approaches. The discussion below describes the rationale for how these decisions were made and presents the resulting emission estimates.

#### **3.3.6.1. *ORD Approach for Classifying MWIs and Estimating Activity Levels***

As with the OAQPS and AHA approaches, the ORD approach divided the MWIs into controlled and uncontrolled classes. The rationale for further dividing these two classes is discussed below.

**Uncontrolled MWIs.** For purposes of assigning CDD/CDF emission factors and activity levels to the uncontrolled class of MWIs, the OAQPS approach divided this class on the basis of residence time within the secondary combustion chamber. This approach has theoretical appeal, because it is logical to expect more complete combustion of CDDs/CDFs with longer residence times at high temperatures. Unfortunately, the residence times on a facility-by-facility basis are not known, making it difficult to assign emission factors and activity levels on this basis. As discussed earlier, the OAQPS approach assumed that residence time would strongly correlate with state PM stack emission requirements (i.e., the more stringent the PM requirements, the longer the residence time required to meet the standard).

This PM method for estimating residence time resulted in the following distribution of residence times: 6% of the waste incinerated at MWIs with 1/4-sec residence time, 26% of the waste incinerated at MWIs with 1-sec residence time, and 68% of the waste incinerated at MWIs with 2-sec residence time. Thus, about two-thirds of the activity level within the uncontrolled class was assumed in the OAQPS approach to be associated with facilities with the longest residence time and the lowest CDD/CDF emission factor.

The AHA approach subcategorized the uncontrolled class on the basis of design-rated capacity. There is also theoretical support for this approach. Smaller-capacity operations (<200 lb/hr) are likely to have higher emissions because they are more likely to be operating in a batch

1 mode. The batch mode results in infrequent operation with more start up and shut down cycles.  
2 Thus, the batch-operated MWI usually spends more time outside of the ideal range of operating  
3 conditions. In support of this approach, the AHA presented limited empirical evidence indicating  
4 that CDD/CDF emission factors calculated from emission test reports for the low-capacity units  
5 were about a factor of 2 higher than the emission factors for the high-capacity units (>200 lb/hr)  
6 (Doucet, 1995).

7 Thus, both the OAQPS and the AHA approaches have a sound theoretical basis but lack  
8 strong supporting data. In order to decide which of the two approaches to use, ORD first tested  
9 the assumption that there is a strong relationship between state PM requirements and residence  
10 time. ORD conducted a limited telephone survey of regulatory agencies in four states where a  
11 large number of MWI facilities were in operation: Michigan, Massachusetts, New Jersey, and  
12 Virginia (O'Rourke, 1996). The results of the limited survey, summarized in Table 3-23, did not  
13 verify the existence of a strong relationship between PM emission limits and residence time in  
14 the secondary chamber at MWIs.

15 Next, the available emission testing data for low- and high-capacity units were evaluated  
16 to determine whether, as posited in the AHA approach, smaller-capacity units have greater  
17 emission factors than do larger-capacity units. This evaluation indicated a distinct difference in  
18 the emission factors between the two capacity categories, although the difference in the set of  
19 data evaluated was not as great as the difference observed in the data set evaluated in the AHA  
20 approach. The ORD approach, therefore, adopted the subcategorization scheme used in the AHA  
21 approach.

22 **Controlled MWIs.** Both the OAQPS approach and the AHA approach subcategorized  
23 the controlled MWIs on the basis of APCD equipment. However, the two approaches differed in  
24 the subcategories developed. The AHA approach divided the controlled class into two groups:  
25 facilities equipped with WSs (alone, with an ESP, or with an FF) and facilities equipped with  
26 DSI and an FF (Doucet, 1995). The OAQPS approach divided the controlled class into three  
27 groups: facilities equipped with WSs, facilities equipped with SDSSs (with or without CI), and  
28 facilities equipped with FFs and packed bed scrubbers. This third category comprises a few  
29 facilities located primarily in the northeastern United States (O'Rourke, 1996). The ORD  
30 approach adopted the two subcategories of the AHA approach and the third subcategory of the  
31 OAQPS approach.

For 1987, the ORD approach 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, 1987d). 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 3-24). For 1995, ORD used the activity levels for each facility as reported in the OAQPS inventory; the activity levels were then summed across facilities for each APCD subclass (see Table 3-25).

In 1997, the amount of waste combusted by MWIs was estimated to be 0.8 million tons/yr (0.7 billion kg/yr) (National Research Council, 2000). This number represents a 9% decrease from 1995. If we assume that this decrease occurred every 2 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 3-26. For all years, these activity levels were assigned a rating of low confidence because the data were judged to be possibly nonrepresentative.

### **3.3.6.2. ORD Approach for Estimating CDD/CDF Emission Factors**

ORD collected the engineering reports of 24 tested MWIs to calculate 1987 and 1995 emission estimates. After reviewing these test reports, ORD 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.

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, 1995b). 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:

$$EF_{MWI} = \frac{C \times F_v}{I_w} \quad (3-8)$$

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<sub>2</sub>)

$F_v$  = average volumetric flue gas flow rate (dscm/hr) (20 °C, 1 atm; adjusted to 7% O<sub>2</sub>)

$I_w$  = average medical waste incineration rate of the tested MWI (kg/hr)

The emission factor estimate for each design class for 1995 and the number of stack tests used to derive the estimate are shown in Table 3-25. Table 3-26 provides the updated emission factor estimates for 2000. Figures 3-15 and 3-16 present congener and congener group profiles for air emissions from MWIs lacking APCDs and for MWIs equipped with a WS/FF APCD system, respectively.

### 3.3.7. Summary of CDD/CDF Emissions from MWIs

Because the stack emissions from so few facilities have been tested relative to the number of facilities in this industry and because several tested facilities are no longer in operation or installed new APCD after testing, the ORD approach did not calculate nationwide CDD/CDF emissions by calculating emissions from the tested facilities and adding those to calculated emissions for the nontested facilities. Rather, the ORD approach (as well as the OAQPS and

1 AHA approaches) multiplied the emission factor and activity level developed for each design  
2 class and then summed the calculated emissions for all classes. Tables 3-24, 3-25, and 3-26  
3 summarize the resulting national TEQ air emissions for reference years 1987, 1995, and 2000,  
4 respectively. These tables also indicate the activity level and the TEQ emission factor used in  
5 estimating annual TEQ emissions.

6 In estimating annual TEQ emissions for each reference year, a low confidence rating was  
7 assigned to the estimate of the activity level. The primary reason for the low confidence rating is  
8 that very limited information is available on a facility-level basis for characterizing MWIs in  
9 terms of the frequency and duration of operation, the actual waste volume handled, and the level  
10 of pollution control. The 1987 inventory of facilities was based on very limited information.  
11 Although the 1995 OAQPS inventory was more comprehensive than the 1987 inventory, it was  
12 still based on a fairly limited survey of operating facilities (approximately 6%). The 2000  
13 inventory included only two additional facilities and estimated an activity level based on a 1997  
14 value and the distribution among APCDs from the 1995 estimates.

15 The emission factor estimates were given a low confidence rating because the reports of  
16 only 20 tested MWI facilities could be used to derive emission factors representing the 2,375  
17 facilities operating in 1995 (i.e., less than 1% of the estimated number of operating facilities) and  
18 only two additional test reports were obtained for 2000. Even fewer tested facilities could be  
19 used to represent the larger number of facilities operating in 1987 (8 tested facilities were used to  
20 represent 5,000 facilities). The limited emission tests available cover all design categories used  
21 here to develop emission factors. However, because of the large number of facilities in each of  
22 these classes, it is very uncertain whether the few tested facilities in each class capture the true  
23 variability in emissions.

24 Table 3-26 shows the year 2000 emissions estimate as being 378 g TEQ<sub>DF</sub>-WHO<sub>98</sub>. The  
25 TEQ emissions are estimated to have been 488 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (461 g I-TEQ<sub>DF</sub>) in 1995 (Table  
26 3-25) and 2,590 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (2,440 g I-TEQ<sub>DF</sub>) in 1987 (Table 3-24). Since the activity  
27 level and emission factors had low confidence ratings, the emission estimates for all years were  
28 assigned a low confidence rating.

29 As explained above, the ORD approach to estimating national CDD/CDF TEQ emissions  
30 is a “hybridization” of the OAQPS and AHA approaches. Table 3-27 compares the main features  
31 of each of the three approaches. The 1995 TEQ emissions estimated here (461 g I-TEQ<sub>DF</sub>/yr) are

about 3.5 times higher than those of OAQPS and AHA (141 and 138 g I-TEQ<sub>DF</sub>/yr, respectively). Most of this difference is due to differences in the emission estimates for the uncontrolled facilities (ORD: 432 g I-TEQ<sub>DF</sub>/yr; OAQPS: 136 g I-TEQ<sub>DF</sub>/yr; AHA: 120 g I-TEQ<sub>DF</sub>/yr). An explication of the differences in how these groups estimated emissions from the uncontrolled facilities is presented below:

- **Differences between the ORD and AHA approaches.** The ORD approach adopted the classification scheme of the AHA approach for the uncontrolled class and assumed similar activity levels. Thus, the difference in emission estimates is primarily due to differences in the emission factors used. Both groups used similar emission factors for facilities with design capacities less than or equal to 200 lb/hr, but the emission factor for MWIs greater than 200 lb/hr used in the ORD approach was higher than the one used in the AHA approach by a factor of 3. The factors differ because the two approaches used different sets of emission tests to derive their emission factors.
- **Differences between the ORD and OAQPS approaches.** Because the two approaches subcategorized the uncontrolled facilities into different classes, the activity levels and emission factors cannot be directly compared. Considering the class as a whole, however, both approaches used essentially identical activity levels. The OAQPS approach assigned 68% of the total activity to the class with the lowest emission factor (i.e., those with greater than 2-sec residence time). The emission factor for this class, 74 ng I-TEQ<sub>DF</sub>/kg, is considerably lower than either emission factor used in the ORD approach (1,680 and 1,860 ng I-TEQ<sub>DF</sub>/kg).

Given the uncertain database available for making these estimates, it is difficult to know which of the three estimation approaches yields the most accurate annual TEQ estimate. However, despite the differences in methodologies and assumptions used, the three approaches yielded annual TEQ estimates that are not fundamentally different; the estimates differ from each other by a factor of 4 or less. Because the ORD approach was the last of the three to be developed, it had the benefit of being able to use the most logical and supportable features of the previously developed OAQPS and AHA approaches.

### 3.3.8. Recent EPA Regulatory Activities

In September 1997, the EPA promulgated final regulations under the Clean Air Act Amendments limiting CDD/CDF stack emissions from MWIs (Federal Register, 1997b). 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 wet scrubbers, dry sorbent injection of activated carbon combined with fabric filters and/or spray dryers and fabric filters. EPA expects that many facilities which currently operate onsite 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<sub>DF</sub>/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<sub>DF</sub> 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<sub>DF</sub> 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 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<sub>DF</sub> 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<sub>DF</sub>/m<sup>3</sup> (at 11% oxygen) at the first facility and from 25.4 to 45.5 ng I-TEQ<sub>DF</sub>/m<sup>3</sup> (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<sub>DF</sub>/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<sub>DF</sub>/body (mean of 9,200 ng I-TEQ<sub>DF</sub>/body). When nondetect values were treated as one-half the DL, the range was 450 to 63,000 ng I-TEQ<sub>DF</sub>/body (mean of 11,000 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub>/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, 1990c) and one at Woodlawn Cemetery in New York (U.S. EPA, 1999f). Additionally, EPA obtained test data from one crematorium for



1 animals operating in the United States: University of Georgia Veterinary School (U.S. EPA,  
2 2000e); however, it is not appropriate to use the emission factors from this facility to characterize  
3 emissions associated with human cremation.

4 Testing at the Camellia Memorial Lawn crematorium, which is classified as a warm-type  
5 facility using the criteria of Bremmer et al. (1994), was conducted in 1990 (CARB, 1990c). The  
6 combusted material at this facility consisted of the body, as well as 4 pounds of cardboard, up to  
7 6 pounds of wood, and an unquantified amount of unspecified plastic wrapping. The three  
8 emission tests conducted at this facility, which operates using an afterburner, yielded an average  
9 emission factor of 543 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/body (501 ng I-TEQ<sub>DF</sub>/body). Table 3-28 presents the  
10 congener-specific emission factors for this facility.

11 Testing at Woodlawn Cemetery, which has a crematorium with a primary combustion  
12 chamber, a secondary combustion chamber, and a scrubber APCD, was conducted in 1995. Tests  
13 were run at three secondary combustion chamber temperatures: 675, 870, and 980 °C (U.S. EPA,  
14 1999f). The combusted material consisted of the body, as well as a 10- to 100-pound casket  
15 constructed of fiberboard, particle board, or wood and various body wrappings and articles such  
16 as a plastic sheet, a cloth sheet, or clothes. For this facility, average emission factors of 325 and  
17 961 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/body cremated (310 and 780 ng I-TEQ<sub>DF</sub>/body cremated) were calculated,  
18 based on emissions collected at the scrubber inlet and outlet, respectively. The congener-specific  
19 emission factors for this facility are shown in Table 3-29.

20 In 1995, 1,155 crematoria were reported to be operating in the United States; this number  
21 had decreased to approximately 1,060 by 2000. To determine whether the emissions data  
22 collected at the Woodlawn Cemetery facility are representative of a typical crematorium  
23 operating in the United States, representatives from the Cremation Association of North America  
24 (CANA) were contacted to identify the typical operating conditions at U.S. crematoria.  
25 According to the CANA representatives, all crematoria operating in the United States have  
26 primary and secondary combustion chambers. Additionally, crematoria with operating  
27 conditions that indicate the presence of an afterburner are considered to contain secondary  
28 combustion chambers. The primary and secondary combustion chambers at U.S. crematoria  
29 typically operate at between 675 and 870 °C, but many operate at 980 °C, as required by their  
30 respective states.

1 Only one or two facilities in the United States incorporate the use of an APCD, such as a  
2 scrubber. Therefore, the inlet dioxin emission factors rather than the outlet dioxin emission  
3 factors at the Woodlawn crematorium would be representative of a typical crematorium operating  
4 in the United States (telephone conversation between Allen Kroboth, CANA, and K. Riley,  
5 Versar, Inc., February 12, 2003, and telephone conversation between Dale Walter, Mathews  
6 Cremation, and K. Riley, Versar Inc., February 13, 2003).

7 In the previous inventory, an average emission factor of 17,000 ng I-TEQ<sub>DF</sub>/body  
8 (assuming nondetect values are zero) was developed, based on emission factors measured for 16  
9 of the tested facilities, including the one at Camellia Memorial Lawn (CARB, 1990c), the 10  
10 Japanese facilities (Takeda et al., 1998), the two Dutch facilities (Bremmer et al., 1994), the one  
11 German facility (Jager et al., 1992), and the two British facilities (Mitchell and Loader, 1993).  
12 The more recent data provided by Takeda et al. (2001) for the 17 Japanese facilities support the  
13 emission factor of 17,000 ng I-TEQ<sub>DF</sub>/body. However, an average emission factor developed  
14 using the data reported for the two U.S. crematoria (i.e., the outlet values for the Camellia  
15 Memorial Lawn facility and the inlet values for the Woodlawn Cemetery facility) is 434 ng  
16 TEQ<sub>DF</sub>-WHO<sub>98</sub>/body (410 I-TEQ<sub>DF</sub>/body cremated), assuming nondetect values are zero. These  
17 values are two orders of magnitude less than the overall average calculated above. An  
18 examination of the differences in U.S. and foreign operating practices may provide a rationale for  
19 the large discrepancies.

20 Bremmer et al. (1994) reported an emission factor of 2,400 ng I-TEQ<sub>DF</sub>/body for a Dutch  
21 facility with a cold-type furnace and an emission factor of 4,900 ng I-TEQ<sub>DF</sub>/body for another  
22 Dutch facility with a warm-type furnace where flue gases were cooled to 220 °C. Neither of the  
23 U.S. facilities are considered to have cold-type furnaces. Additionally, the flue gases at the  
24 Camellia Memorial Lawn crematorium were not cooled prior to exiting the furnace. At the  
25 Woodlawn Cemetery facility, the flue gases were cooled from 681 to 860 °C prior to entering the  
26 scrubber to 271 to 354 °C by the time they exited the scrubber and the furnace. The emissions  
27 were higher at the scrubber outlet than at the inlet (961 vs. 325 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/body [780 vs.  
28 319 I-TEF/body]); however, the emissions were not on the same magnitude as reported by  
29 Bremmer for the warm-type facility (4,900 ng I-TEQ<sub>DF</sub>/body). The Jager et al. (1992) report did  
30 not include operating process information; therefore the German facility could not be compared  
31 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<sub>DF</sub>/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<sub>DF</sub>-WHO<sub>98</sub>/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 3-30). The data also indicate that oxygen levels decreased as the temperature increased (U.S. EPA, 1999). Given these data, one could speculate that as the temperature increased, incomplete combustion conditions arose, leading to an increase in dioxin formation.

Using data from U.S. crematoria, EPA recommends an average emission factor of 434 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/body (410 ng I-TEQ<sub>DF</sub>/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 3-31, 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, 2002; Springer, 1997).

#### **3.4.1.3. Emission Estimates**

Combining the average emission rate of 434 ng WHO-TEQ<sub>98</sub>/body (410 ng I-TEQ<sub>DF</sub>/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 0.14 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (0.14 g I-TEQ<sub>DF</sub>) in 1987, 0.21 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (0.2 g I-TEQ<sub>DF</sub>) in 1995, and 0.27 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (0.26 g I-TEQ<sub>DF</sub>) in 2000. An overall confidence rating of low was assigned to the emissions, since 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 were measured from a newly installed animal incineration unit located at the University of Georgia Veterinary School (U.S. EPA, 2000e). 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<sub>DF</sub>-WHO<sub>98</sub>/kg (0.11 ng I-TEQ<sub>DF</sub>/kg) of animal cremated. The average emission factors for these test runs are provided in Table 3-32 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 National Emissions 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 the 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<sub>DF</sub>-WHO<sub>98</sub>/kg (0.11 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub>-WHO<sub>98</sub> (0.009 g I-TEQ<sub>DF</sub>) 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.

## 3.5. SEWAGE SLUDGE INCINERATION

The three principal combustion technologies used to incinerate sewage sludge in the United States are the multiple-hearth incineration, fluidized-bed incineration, and electric furnace incineration (Brunner, 1992; U.S. EPA, 1995b). 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, 1997b; Maw, 1998).

**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

1 the furnace. Moisture is evaporated from the sludge cake in the upper hearths. The center  
2 hearths are the burning zone, where gas temperatures reach 871 °C. The bottom hearths are the  
3 burn-out zone, where the sludge solids become ash. A waste-heat boiler is usually included in  
4 the burning zone, where steam is produced to provide supplemental energy at the sewage  
5 treatment plant. Air pollution control measures typically include a venturi scrubber, an  
6 impingement tray scrubber, or a combination of both. Wet cyclones and dry cyclones are also  
7 used (U.S. EPA, 1995b).

8 **Fluidized-bed incinerators.** A fluidized-bed incinerator is a cylindrical refractory-lined  
9 shell with a steel plate structure that supports a sand bed near the bottom of the furnace (Brunner,  
10 1992). Air is introduced through openings in the bed plate supporting the sand. This causes the  
11 sand bed to undulate in a turbulent air flow; hence, the sand appears to have a fluid motion when  
12 observed through furnace portals. Sludge cake is added to the furnace at a position just above  
13 this fluid motion of the sand bed. The fluid motion promotes mixing in the combustion zone.  
14 Sludge ash exits the furnace with the combustion gases; therefore, air pollution control systems  
15 typically consist of high-energy venturi scrubbers or venturi/impingement tray combinations  
16 (U.S. EPA, 1995b).

17 **Electric furnaces.** Also called infrared furnaces, these consist of a long rectangular  
18 refractory-lined chamber. A belt conveyer system moves the sludge cake through the length of  
19 the furnace. To promote combustion of the sludge, supplemental heat is added by electric  
20 infrared heating elements located just above the traveling belt within the furnace. Electric power  
21 is required to initiate and sustain combustion. Emissions are usually controlled with a venturi  
22 scrubber or some other WS (Brunner, 1992; U.S. EPA, 1995b).

### 24 **3.5.1. Emission Estimates from Sewage Sludge Incinerators**

25 EPA measured CDD/CDF emissions at three multiple-hearth incinerators as part of Tier 4  
26 of the National Dioxin Survey (U.S. EPA, 1987a). During the pretest surveys, two of the  
27 facilities were judged to have “average” potential and one facility was judged to have “high”  
28 potential for CDD/CDF emissions with respect to other sewage sludge incinerators. The results  
29 of these tests include congener group concentrations in stack gas but lack measurement results  
30 for specific congeners other than 2,3,7,8-TCDD and 2,3,7,8-TCDF. The results show a wide  
31 variability in the emission factors at these three facilities; total CDD/CDF emission factors

1 ranged from 90 to 3,400 ng/kg (average of 1,266 ng/kg). Total TEQ emissions could not be  
2 determined for these facilities because of the lack of congener-specific data.

3 In 1990, EPA measured CDD/CDF emissions (including all 17 toxic congeners) at  
4 another multiple-hearth incinerator and also at a fluidized-bed incinerator (U.S. EPA, 1990f).  
5 Assuming nondetects are zero, the total CDD/CDF emission factors for these two facilities were  
6 79 and 846 ng/kg, and the total average TEQ emission factors were 3.6 and 43.2 ng TEQ<sub>DF</sub>-  
7 WHO<sub>98</sub>/kg (2.4 and 43.3 ng I-TEQ<sub>DF</sub>/kg) of dry sludge. In 1995, the Association of Metropolitan  
8 Sewerage Agencies (AMSA) submitted to EPA the results of stack tests conducted at an  
9 additional 13 sewage sludge incinerators (Green et al., 1995). Two of these data sets were  
10 considered not usable by EPA because either DLs or feed rates and stack flow rates were not  
11 provided. As with the EPA-tested facilities (U.S. EPA, 1987a, 1990f), wide variability was  
12 observed in the emission factors for the 11 AMSA facilities. Assuming nondetects are zero, total  
13 CDD/CDF emission factors ranged from 0 to 1,392 ng/kg (average of 217 ng/kg), and total  
14 average TEQ emission factors ranged from 0 to 16 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (average, 3.47 ng) (3.46  
15 ng I-TEQ<sub>DF</sub>/kg) of dry sludge.

16 In 1999, stack tests were conducted at a multiple hearth-incinerator equipped with a  
17 venturi scrubber and a three-tray impingement conditioning tower (U.S. EPA, 2000f). Four test  
18 runs were conducted; however, the first test run was aborted, and the CDD/CDF results from the  
19 fourth test run were determined to be statistical outliers ( $p < 0.05$ ). The back-half emission  
20 concentrations for test run 4 were 50 to 60% lower than those for test runs 2 and 3. Overall, total  
21 CDD/CDF emissions measured during test run 4 were 48 ng/kg, whereas total CDD/CDF  
22 emissions measured during test runs 2 and 3 were 120 and 116 ng/kg, respectively. It could not  
23 be determined whether the lower concentrations associated with test run 4 were due to analyte  
24 loss or whether they represented an accurate reflection of a change in incinerator emission  
25 releases.

26 The average TEQ emission factor, excluding test run 4, was 3.28 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg  
27 (3.23 ng I-TEQ<sub>DF</sub>/kg). The average TEQ emission factor based on the data for the 11 AMSA  
28 facilities (Green et al., 1995) and the three facilities reported by EPA (U.S. EPA, 2000f, 1990f) is  
29 6.74 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (6.65 ng I-TEQ<sub>DF</sub>/kg) of dry sludge, assuming nondetect values are  
30 zero. Figure 3-19 presents the average congener and congener group profiles based on these  
31 data. Additionally, Table 3-33 presents the average congener and congener-specific group

1 emission factors and the average TEQ emission factors for these facilities. Table 3-33 also  
2 presents 2,3,7,8-TCDD, 2,3,7,8-TCDF, and congener-specific group emission factors for the  
3 three facilities reported by EPA (1987a).

4 Other countries have reported similar results. Bremmer et al. (1994) reported an emission  
5 rate of 5 ng I-TEQ<sub>DF</sub>/kg for a fluidized-bed sewage sludge incinerator in the Netherlands that was  
6 equipped with a cyclone and a WS. Cains and Dyke (1994) measured CDD/CDF emissions at  
7 two sewage sludge incinerators in the United Kingdom. The emission rate at an incinerator  
8 equipped with an ESP and a WS ranged from 2.75 to 28 ng I-TEQ<sub>DF</sub>/kg. The emission rate  
9 measured at a facility equipped with only an ESP was 43 ng I-TEQ<sub>DF</sub>/kg.

10 In 1988, approximately 199 sewage sludge incineration facilities combusted about 0.865  
11 million metric tons of dry sewage sludge (Federal Register, 1993b). In 1995, approximately 257  
12 sewage sludge incinerators (some of which were backup or alternate incinerators) combusted  
13 about 2.11 million dry metric tons of sewage sludge (Maw, 1998). Using trends in wastewater  
14 flow rates from the 1988 National Sewage Sludge Survey and from the 1984 to 1996 Needs  
15 Surveys, EPA estimated that in 2000 approximately 6.4 million metric tons of dry sewage sludge  
16 would be generated (U.S. EPA, 1999e). Of this amount, EPA projected that 22% (1.42 million  
17 metric tons) would be incinerated.

18 According to EPA, sewage sludge generation will increase to 6.9 million dry tons in 2005  
19 and 7.4 million dry tons in 2010; however, the percentage of sewage sludge incinerated will  
20 decrease slightly, to 20% in 2005 and 19% in 2010. EPA estimates that approximately 1.38  
21 million metric tons of dry sewage sludge will be incinerated in 2005 and 1.41 million metric tons  
22 will be incinerated in 2010. EPA believes that incineration as a disposal method for sewage  
23 sludge will decrease as a result of increasing costs and public concerns about the environmental  
24 and health impacts associated with incineration.

25 A medium confidence rating is assigned to the average TEQ emission factor because it  
26 was derived from stack testing at 14 U.S. sewage sludge incinerators. The 1988 activity level  
27 estimate (used as a surrogate for the 1987 activity level) and the 2000 activity level estimate are  
28 assigned a high confidence rating because they are based on extensive EPA surveys to support  
29 rule-making activities. The 1995 activity level estimate is assigned a medium confidence rating  
30 because assumptions were made for numerous facilities concerning hours of operation, operating  
31 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<sub>DF</sub>-WHO<sub>98</sub>/kg (6.65 ng I-TEQ<sub>DF</sub>/kg), the estimate of TEQ emissions to air is 5.8 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (5.8 g I-TEQ<sub>DF</sub>) in 1987, 14.2 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (14 g I-TEQ<sub>DF</sub>) in 1995, and 9.6 g TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (9.4 g I-TEQ<sub>DF</sub>/kg) in 2000. Since 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 nondetected, 20 ng/kg, 10 ng/kg, and 0.3 ng/kg, respectively. For total CDFs, the respective values were nondetected, 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 from one dedicated tire incinerator tested by the California Air Resources Board (CARB, 1991a). 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 3-34 presents the congener-specific emission factors for this facility. Figure 3-20 presents CDD/CDF congener and congener group profiles based on these TEQ emission factors. From these data, the average

1 emission factor is estimated to be 0.281 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (0.282 ng I-TEQ<sub>DF</sub>/kg) of tires  
2 incinerated (when all nondetect values are treated as zero). This emission factor is used to  
3 estimate annual TEQ releases from the tire combustion source category for the years 1987, 1995,  
4 and 2000. EPA assigned a low confidence rating to the estimated TEQ emission factor because it  
5 is possible that it is not representative of TEQ emissions from all tire combustion facilities. It is  
6 also possible that this emission factor is an underestimation of emissions from this source  
7 category, because it was derived from the emissions of a facility equipped with very advanced air  
8 pollution control technology specific for the control of dioxin emissions. These devices (DS/FF)  
9 are capable of greater than 95% reduction and control of dioxin-like compounds prior to  
10 discharge from the stack into the air. Because other facilities may not be equipped with similar  
11 air pollution control systems, the TEQ emissions could be higher than the estimates developed  
12 above. For example, Cains and Dyke (1994) reported much higher emission rates for two tire  
13 incinerators in the United Kingdom that were equipped with only simple grit arrestors. These  
14 emissions produced emission factors of 188 and 228 ng I-TEQ<sub>DF</sub>/kg of tires combusted.

15 EPA estimated that approximately 500 million kg of tires were combusted in 1990  
16 (U.S. EPA, 1992a). Of this total, 23% (115 million kg) were combusted in cement kilns, and it is  
17 assumed that the remaining 385 million kg were combusted in dedicated tire combustion  
18 facilities, industrial boilers, and pulp and paper mill combustion facilities. This activity level  
19 was adopted for the years 1987 and 1995 and is assigned a medium confidence rating.

20 The Rubber Manufacturers Association (2002) reported that 281 million scrap tires,  
21 weighing approximately 5.68 million metric tons, were generated in the United States in 2001.  
22 Approximately 115 million of these scrap tires were combusted as tire-derived fuel, or roughly  
23 2.32 million metric tons (2.32 billion kg) of tires. Subtracting the 23% of the tires burned in  
24 cement kilns yields a total of 1.8 billion kg of tires estimated to have been combusted in facilities  
25 other than cement kilns in 2001. This figure is used to represent the activity level for tire  
26 combustion in the year 2000. This activity level is assigned a medium confidence rating.

27 Annual emissions for the reference years is estimated by multiplying the activity level  
28 times the TEQ emission factor. The TEQ emission factor of 0.281 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (0.282  
29 ng I-TEQ<sub>DF</sub>/kg) of tires combusted was used to estimate annual emissions for all years.  
30 Multiplying the emission factor by the activity level (385 million kg of tires) yields an estimate  
31 of 0.11 g TEQ<sub>DF</sub>-WHO<sub>98</sub>/yr (0.11 g I-TEQ<sub>DF</sub>/yr) emitted to the air in 1987 and 1995. Using the

1 same emission factor multiplied by the estimated activity level of 1.8 billion kg tires combusted  
2 in 2000 gives an estimate of 0.51 g TEQ<sub>DF</sub>-WHO<sub>98</sub>/yr (0.51 g I-TEQ<sub>DF</sub>/yr). The estimated TEQ  
3 emissions to air from tire combustion for the years 1987, 1995, and 2000 are given a low  
4 confidence rating because of the low confidence rating of the emission factor.

### 5 6 **3.7. COMBUSTION OF WASTEWATER SLUDGE AT BLEACHED CHEMICAL PULP** 7 **MILLS**

8 Approximately 20.5% of the wastewater sludges generated at bleached chemical pulp  
9 mills are dewatered and burned in bark boilers at the mills. These sludges can contain  
10 CDDs/CDFs and elevated levels of chloride. However, the level of heat input from sludge in the  
11 mixed feed to bark boilers rarely exceeds 10% (NCASI, 1995).

12 NCASI (1995) provided congener-specific test results for four wood residue/sludge  
13 boilers tested between 1987 and 1993. Sludge comprised 6 to 10% of the solids in the feed. The  
14 average congener-specific emission factors derived from the stack test results obtained from  
15 these facilities are presented in Table 3-35. The average TEQ emission factor derived from the  
16 test results is 0.062 ng I-TEQ<sub>DF</sub>-WHO<sub>98</sub> (0.061 ng I-TEQ<sub>DF</sub>/kg) of feed (i.e., sludge and wood  
17 residue), assuming nondetect values are zero. The range in facility-specific emission factors was  
18 wide (0.0004 to 0.118 ng I-TEQ<sub>DF</sub>/kg, assuming nondetect values are zero).

19 NCASI (1995) also presented stack emission test results for five other bark boilers.  
20 These boilers combusted only bark during the tests even though the boilers normally fire bark in  
21 combination with sludge and coal. These boilers are discussed in Section 4.2.2 as industrial  
22 facilities burning wood scrap/residues. The average TEQ emission factor for these facilities was  
23 0.4 ng I-TEQ<sub>DF</sub>/kg of feed. The emissions test data presented in NCASI (1995), and discussed  
24 above, indicate that the CDD/CDF emission factors for bark/sludge combustors are similar to the  
25 emission factor developed in Section 4.2.2 for industrial facilities burning only wood  
26 residues/scrap. Based on the fact that wood residues comprise a far greater fraction of the feed to  
27 these bark/sludge burners than does sludge, the national TEQ emission estimates derived in  
28 Section 4.2.2 of this report for industrial wood-burning facilities are assumed to include  
29 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 sludge digester 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<sub>DF</sub>/ standard cubic meter (Nm<sup>3</sup>) at the bottom of the flare, 3.3. pg I-TEQ<sub>DF</sub>/Nm<sup>3</sup> at the top of the flare, and 13.1 pg I-TEQ<sub>DF</sub>/Nm<sup>3</sup> in the middle of the flare. Congener-specific results were not reported. Using the theoretical ratio of flare gas volume to digester gas volume combusted, 78.6:1, and the average CDD/CDF content of the three measurements, 5.9 pg I-TEQ<sub>DF</sub>/Nm<sup>3</sup>, yields an emission rate of 0.46 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup> of digester gas combusted.

During 1996, publicly owned treatment works (POTWs) in the United States treated approximately 122 billion L of wastewater daily (U.S. EPA, 1997c). 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 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 digester gas combusted in flares annually can be estimated using operation parameters for a “typical” anaerobic digester 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 digester gas volume of 467-million Nm<sup>3</sup>:

- Fraction of total solids that are volatile solids = 75%;
- Reduction of volatile solids during digestion = 50%;
- Specific gas production = 0.94 m<sup>3</sup>/kg volatile solids reduced; and
- Fraction of produced gas that is flared = 66%.

1           Because there are no direct measurements of CDD/CDF emissions from U.S. anaerobic  
2   sludge digester flares and because of uncertainties about the activity level for biogas combustion,  
3   no national emission estimate has been developed for inclusion in the national inventory.  
4   However, a preliminary estimate of the potential annual TEQ emissions from this source can be  
5   obtained by multiplying the emission factor of 0.46 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup> of digester gas flared by the  
6   estimated volume of gas flared annually in the United States, 467 million Nm<sup>3</sup>. This calculation  
7   yields an annual potential release in 2000 of 0.22 g. This estimate should be regarded as a  
8   preliminary indication of possible emissions from this source category; further testing is needed  
9   to confirm the true magnitude of these emissions.

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

APCD <sup>b</sup>	MWC type																			
	MB/RC		MB		MB/WW/RC		MB/REF		MB/WW		MOD/EA				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 <sup>c</sup>	S(4)	2.52e+08							S(2)	5.69e+08	S(3)	1.03e+08	S	4.27e+07	S(2)	8.45e+07	L(2)	1.65e+08	S(14) L(2)	5.40e+08 1.65e+08
DSI/ESP							S(2)	1.14e+08					S	1.35e+08					S(9)	2.49e+08
DSI/FF/ H <sub>2</sub> O/SNCR																	L(2)	4.03e+07	L(2)	4.03e+07
ESP	S(4)	1.96e+08							S(8)	2.96e+08	S(3)	8.37e+07	S	1.04e+08			S(2)	1.42e+08	S(28)	8.22e+08
FF					S(1)	1.59e+07							S	2.85e+07					S(3)	4.44e+07
WS													S	4.95e+07					S(4)	4.95e+07
WS/ESP											S(3)	1.03e+08								
SD <sup>d</sup> /FF/CI/ SNCR									L(6)	8.17e+08									L(6)	8.17e+08
SD/ESP																	L(4)	9.78e+08	L(4)	9.78e+08
SD/ESP/CI									L(4)	3.39e+08									L(4)	3.39e+08
SD/ESP/ CI/SNCR									L(15)	2.54e+09									L(15)	2.54e+09
SD/ESP/ FF <sup>e</sup> /CI																	L(2)	6.72e+08	L(2)	6.72e+08
SD/FF	L(6)	1.01e+09	S(2)	5.69e+07					S(4)	1.14e+08	S(3)	1.20e+08					L(12)	1.53e+09	S(9) L(18)	2.90e+08 2.54e+09
SD/FFe/ SNCR																	L(1)	3.31e+08	L(1)	3.31e+08
SD/FF/CI									S(2) L(5)	1.14e+08 8.63e+08			S	5.69e+07					S(6) L(5)	1.71e+08 8.63e+08
SD/FF/ CI/SNCR	L(3)	3.6e+08							L(81)	1.13e+10							L(4)	6.06e+08	L(88)	1.23e+10

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

APCD <sup>b</sup>	MWC type																			
	MB/RC		MB		MB/WW/RC		MB/REF		MB/WW		MOD/EA				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
SD/FF/SNCR									L(13)	2.72e+09							L(7)	1.09e+09	L(20)	3.8e+09
Unc									S(2)	2.85e+07			S	6.75e+07					S(8)	9.6e+07
TOTAL	L(9)	1.37e+09							L(124)	1.86e+10							L(34)	5.41e+09	L(167)	2.54e+10

<sup>a</sup>For size, S = small; L = large.

<sup>b</sup>Slash(es) indicates devices used in conjunction.

<sup>c</sup>Also equipped with flue gas cooling (138 to 143 °C).

<sup>d</sup>Also equipped with furnace dry sorbent injection system.

<sup>e</sup>Also equipped with compact hybrid particulate collector system.

**APCD:**

CI = Carbon injection

DSI = Dry sorbent injection

ESP = Electrostatic precipitator

FF = Fabric filter

H<sub>2</sub>O = 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 <sup>a</sup>	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	1.29e+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	5.19e+09
DSI/H-ESP					1	4.22e+08			1	2.00e+08			1	1.41e+07	3	6.37e+08
DS/FF	2	1.14e+090	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	4.49e+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	2.53e+08
TOTAL	12	2.10e+09	7	1.18e+09	57	1.68e+10	3	3.66e+08	19	7.30e+09	23	6.80e+07	9	4.18e+08	130	2.88e+10

<sup>a</sup>Slash(es) indicates devices used in conjunction.



**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)**

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 <sup>a</sup>	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			54	1.12e+10
DS/FF			1	1.41e+07	1	1.55e+08									2	2.96e+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	1.425e+09
TOTAL	4	4.10e+08	20	3.04e+09	20	5.35e+09	9	3.35e+09	3	2.53e+08	53	1.15e+09	4	2.36e+08	113	1.38e+10

<sup>a</sup>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-derive fuel/cofired

RDF/ded = Refuse-derived fuel/dedicated

**Table 3-4. National average dioxin/furan congener concentrations for large municipal waste combustors (ng/dscm @ 7%O<sub>2</sub>)**

Congener	Nondetect set to zero <sup>a</sup>	Nondetect set to ½ detection limit <sup>a</sup>	Nondetect set to detection limit <sup>a</sup>
TrCDD	0.0305	0.0305	0.0305
2,3,7,8-TCDD	0.0054	0.0058	0.0061
1,2,3,7,8-PeCDD	0.0159	0.0163	0.0167
1,2,3,4,7,8-HxCDD	0.016	0.0162	0.0164
1,2,3,6,7,8-HxCDD	0.0371	0.0364	0.0374
1,2,3,7,8,9-HxCDD	0.0318	0.0319	0.032
1,2,3,4,6,7,8-HpCDD	0.2185	0.2187	0.2187
OCDD	0.3452	0.3452	0.3452
Other TCDD	0.2319	0.2389	0.2459
Other PeCDD	0.3232	0.3336	0.344
Other HxCDD	0.4936	0.5016	0.5096
Other HpCDD	0.2198	0.2198	0.2198
TrCDF	0.037	0.037	0.037
2,3,7,8-TCDF	0.0721	0.0723	0.0725
1,2,3,7,8-PeCDF	0.0503	0.051	0.0516
2,3,4,7,8-PeCDF	0.0687	0.0687	0.0688
1,2,3,4,7,8-HxCDF	0.0824	0.0825	0.0825
1,2,3,6,7,8-HxCDF	0.0587	0.0593	0.0599
1,2,3,7,8,9-HxCDF	0.0131	0.0134	0.0137
2,3,4,6,7,8-HxCDF	0.0656	0.0663	0.0669
1,2,3,4,6,7,8-HpCDF	0.1555	0.1572	0.1589
1,2,3,4,7,8,9-HpCDF	0.0237	0.024	0.0242
OCDF	0.0904	0.0922	0.0939
Other TCDF	1.0805	1.0828	1.085
Other PeCDF	0.7466	0.7584	0.7702
Other HxCDF	0.3256	0.3287	0.3318
Other HpCDF	0.0787	0.0787	0.0787
TOTAL	4.7851	4.8337	4.8836

<sup>a</sup>Values incorporating use of the detection limit when the laboratory report indicated “not detected” for individual CDD/CDF congeners.

Source: Huckaby (2003).

**Table 3-5. National dioxin/furan TEQ emissions (g/yr) for large municipal waste combustors**

<b>Basis</b>	<b>Nondetect set to zero</b>	<b>Nondetect set to ½ detection limit</b>	<b>Nondetect set to detection limit</b>
TEQ (1989 NATO) <sup>a</sup>	15.3	15.4	15.5
TEQ (1997 WHO) <sup>b</sup>	13.7	13.8	14
Total mass basis	665	671	678

<sup>a</sup>TEQ (1989 NATO) = I-TEQ<sub>DF</sub>

<sup>b</sup>TEQ (1997 WHO) = TEQ<sub>DF</sub>-WHO<sub>98</sub>

Source: Huckaby (2003).

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

<b>Incinerator design</b>	<b>Air pollution control device (APCD)<sup>a</sup></b>	<b>Average I-TEQ<sub>DF</sub> emission factor</b>	<b>Average TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factor</b>	<b>Basis and rationale</b>
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

<sup>a</sup>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

**Incinerator design:**

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<sub>DF</sub> emissions from municipal waste combustors (MWCs) operating in 1995**

<b>MWC type</b>	<b>Air pollution control device (APCD)<sup>a</sup></b>	<b>I-TEQ<sub>DF</sub> emissions from tested facilities (g TEQ/yr)</b>	<b>Average I-TEQ<sub>DF</sub> emission factor (ng/kg)</b>	<b>Activity level nontested facilities (kg/yr)</b>	<b>I-TEQ<sub>DF</sub> emissions from nontested facilities (g TEQ/yr)</b>	<b>Total I-TEQ<sub>DF</sub> emissions from all facilities (g TEQ/yr)</b>
MB/WW	C-ESP	0	6.1	2.81e+09	17.1	17.1
	DS/C-ESP		6.1	1.88e+09		
	DS/CI/FF		1.5	7.44e+08		
	DS/FF		0.63	5.98e+09		
	DSI/CI/H-ESP		—	0		
	DSI/FF		—	0		
	DSI/H-ESP		7.74	4.22e+08		
	H-ESP		473	1.79e+08		
	Subtotal	170			121	291
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	0.168	0.168
	DSI/FF	0	1.91	1.13e+08	0.216	0.216
	WS	0	236	2.04e+08	48.1	48.1
	Subtotal	61.4			48.5	110
MB/RC	C-ESP	0	470.646475	2.00e+08	9.4	9.4
	DS/FF			7.57e+08		
	DSI/C-ESP			5.07e+08		
	DSI/FF			1.46e+08		
	Subtotal	5.54			40.6	46.1
RDF/ded	C-ESP	32.5	231	1.67e+09	385	418
	DS/C-ESP		0.53	1.14e+09		
	DS/FF		0.24	1.58e+09		
	DSI/FF		231	4.22e+08		
	DSI/H-ESP		231	2.00e+08		
	H-ESP		1492	4.22e+07		
	DS/FF/C-ESP		0.24	5.63e+08		
	Subtotal	33			593	626
MOD/SA	C-ESP	0	16.2	1.25e+08	2	2
	DSI/FF		—	0		
	H-ESP		79	8.03e+07		
	Unc		0.025	1.87e+08		
	WS		16.2	4.90e+07		
	WS/FF		16.2	2.82e+07		
	DS/DSI/C-ESP		16.2	7.60e+07		
	Subtotal	8.01			10.8	18.8

**Table 3-7a. Annual I-TEQ<sub>DF</sub> emissions from municipal waste combustors (MWCs) operating in 1995 (continued)**

MWC type	Air pollution control device (APCD) <sup>a</sup>	I-TEQ <sub>DF</sub> emissions from tested facilities (g TEQ/yr)	Average I-TEQ <sub>DF</sub> emission factor (ng/kg)	Activity level nontested facilities (kg/yr)	I-TEQ <sub>DF</sub> emissions from nontested facilities (g TEQ/yr)	Total I-TEQ <sub>DF</sub> emissions from all facilities (g TEQ/yr)
MOD/EA	C-ESP	0.0643	16.2	6.25e+07	1	1.07
	DS/FF		16.2	1.18e+08		
	DSI/FF		0.025	1.01e+08		
	DSI/H-ESP		118	1.41e+07		
	H-ESP		<sup>b</sup>	0		
	Unc		0.025	1.41e+07		
	WS/C-ESP		16.2	6.76e+07		
	Subtotal	2.39			5.64	8.03
FB/RDF	DS/FF	0	0.63	1.69e+08	0.106	0.106
	DSI/EGB			1.13e+08		0.0709
	DSI/FF			8.45e+07		0.0532
	Subtotal	0			0.231	0.231
TOTAL		280			820	1,100

<sup>a</sup>Slash indicates devices used in conjunction.

<sup>b</sup>Value could not be calculated.

**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<sub>DF</sub>-WHO<sub>98</sub> emissions from municipal waste combustors (MWCs) operating in 1995**

MWC type	Air pollution control device (APCD) <sup>a</sup>	TEQ <sub>DF</sub> -WHO <sub>98</sub> emissions from tested facilities (g TEQ/yr)	Average TEQ <sub>DF</sub> -WHO <sub>98</sub> emission factor (ng/kg)	Activity level nontested facilities (kg/yr)	TEQ <sub>DF</sub> -WHO <sub>98</sub> emissions from nontested facilities (g TEQ/yr)	Total TEQ <sub>DF</sub> -WHO <sub>98</sub> 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	4.04	6.14
	DSI/CI/H-ESP	2.26	—	0	0	2.26
	DSI/FF	0.3	—	0	0	0.3
	DSI/H-ESP	0	8.22	4.22e+08	3.47	3.47
	H-ESP	183	535	1.79e+08	94.7	278
	Subtotal	191			134	325
MB/REF	C-ESP	43	—	0	0	43
	DS/C-ESP	22.5	—	0	0	22.5
	DS/FF	0	0.72	2.68e+08	0.181	0.181
	DSI/FF	0	2.07	1.13e+08	0.234	0.234
	WS	0	254	2.04e+08	51.9	51.9
	Subtotal	65.4			52.3	117.8
MB/RC	C-ESP	0	93.1	2.00e+08	18.6	18.6
	DS/FF	0.265	0.68	7.57e+08	0.53	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			80	90.8
RDF/ded	C-ESP	35.6	253	1.67e+09	422	458
	DS/C-ESP	0.34	0.56	1.14e+09	0.638	0.98
	DS/FF	0.1	0.26	1.58e+09	0.405	0.5
	DSI/FF	0	253	4.22e+08	107	107
	DSI/H-ESP	0	253	2.00e+08	50.6	50.6
	H-ESP	0	1679	4.22e+07	70.9	70.9
	DS/FF/C-ESP	0	253	5.63e+08	0.144	0.144
	Subtotal	36.1			651	687
MOD/SA	C-ESP	0	17	1.25e+08	2.12	2.12
	DSI/FF	0.0008	—	0	0	0.0008
	H-ESP	8.69	85.7	8.03e+07	6.88	15.57
	Unc	0	0.024	1.87e+08	0.005	0.005
	WS	0	17	4.90e+07	0.832	0.832
	WS/FF	0	17	2.82e+07	0.478	0.478
	DS/DSI/C-ESP	0	17	7.60e+07	1.29	1.29
	Subtotal	8.69			11.6	20.3



**Table 3-7b. Annual TEQ<sub>DF</sub>-WHO<sub>98</sub> emissions from municipal waste combustors (MWCs) operating in 1995 (continued)**

<b>MWC type</b>	<b>Air pollution control device (APCD)<sup>a</sup></b>	<b>TEQ<sub>DF</sub>-WHO<sub>98</sub> emissions from tested facilities (g TEQ/yr)</b>	<b>Average TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factor (ng/kg)</b>	<b>Activity level nontested facilities (kg/yr)</b>	<b>TEQ<sub>DF</sub>-WHO<sub>98</sub> emissions from nontested facilities (g TEQ/yr)</b>	<b>Total TEQ<sub>DF</sub>-WHO<sub>98</sub> emissions from all facilities (g TEQ/yr)</b>
MOD/EA	C-ESP	0.068	17	6.25e+07	1.06	1.13
	DS/FF	0	17	1.18e+08	2.01	2.01
	DSI/FF	0	0.024	1.01e+08	0.002	0.002
	DSI/H-ESP	0	119	1.41e+07	1.68	1.68
	H-ESP	2.35	—	0	0	2.35
	Unc	0	0.024	1.41e+07	0.003	0.003
	WS/C-ESP	0	17	6.76e+07	1.15	1.15
	Subtotal	2.42			5.9	8.32
FB/RDF	DS/FF	0	0.72	1.69e+08	0.114	0.114
	DSI/EGB	0	0.72	1.13e+08	0.076	0.076
	DSI/FF	0	0.72	8.45e+07	0.057	0.057
	Subtotal	0			0.247	0.247
<b>TOTAL</b>		<b>315</b>		<b>935</b>		<b>1,250</b>

<sup>a</sup>Slash 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  
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<sub>DF</sub> emissions to the air from municipal waste combustors (MWCs) operating in 1987**

MWC type	Air pollution control device (APCD) <sup>a</sup>	I-TEQ <sub>DF</sub> emissions from tested facilities (g TEQ/yr)	Average I-TEQ <sub>DF</sub> emission factor (ng/kg)	Activity level nontested facilities (kg/yr)	I-TEQ <sub>DF</sub> emissions from nontested facilities (g TEQ/yr)	Total I-TEQ <sub>DF</sub> emissions from all facilities (g TEQ/yr)
MB/WW	DS/FF	0.0373	—	3.3e+09	0	0.0373
	H-ESP	433	473		1,550	1,980
	Subtotal	433			1,550	1,980
MB/REF	DS/FF	0	0.63	1.41e+08	0.0887	0.0887
	H-ESP	0	473	2.00e+09	944	944
	WS	0	236	9.01e+08	212	212
	Subtotal	0			1160	1,160
MB/RC	FF	0	47.0	1.58e+07	0.741	0.741
	H-ESP	48.2	285	2.25e+08	64.2	112
	Subtotal	48.2			65	113
RDF/ded	H-ESP	840	1492	2.45e+09	3,660	4,500
	WS	0	231	3.38e+08	78.1	78.1
	Subtotal	840			3,730	4,570
RDF/cofired	H-ESP	0	231	2.53e+08	58.6	58.6
MOD/SA	FF	0	16.2	1.43e+08	2.29	2.29
	H-ESP	0.0643	79.0	3.61e+08	28.5	28.5
	Unc	0	0.025	5.73e+08	0.0142	0.0142
	WS	0	16.2	5.30e+07	0.848	0.848
	Subtotal	0.0643			31.6	31.7
MOD/EA	EGB	0	0.025	6.76e+07	0.0017	0.0017
	Unc	0	0.025	4.17e+07	0.0010	0.001
	WS	0	16.2	1.27e+08	2.03	2.03
	Subtotal	0			2.03	2.03
TOTAL		1,320			6,590	7,915

<sup>a</sup>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<sub>DF</sub>-WHO<sub>98</sub> emissions to the air from municipal waste combustors (MWCs) operating in 1987**

MWC type	Air pollution control device (APCD) <sup>a</sup>	TEQ <sub>DF</sub> -WHO <sub>98</sub> emissions from tested facilities (g TEQ/yr)	Average TEQ <sub>DF</sub> -WHO <sub>98</sub> emission factor (ng/kg)	Activity level nontested facilities (kg/yr)	TEQ <sub>DF</sub> -WHO <sub>98</sub> emissions from nontested facilities (g TEQ/yr)	Total TEQ <sub>DF</sub> -WHO <sub>98</sub> emissions from all facilities (g TEQ/yr)
MB/WW	DS/FF	0.039	—	0	0	0.039
	H-ESP	485	535	3.27e+09	1,732	2,218
	Subtotal	485			1,732	2,218
MB/REF	DS/FF	0	0.72	1.41e+08	0.095	0.095
	H-ESP	0	535	2.00e+09	1,058	1,058
	WS	0	254	9.01e+08	229	229
	Subtotal	0			1,287	1,287
MB/RC	FF	0	93.1	1.58e+07	1.47	1.47
	H-ESP	53.4	316	2.25e+08	71.2	124.6
	Subtotal	53.4			72.7	126.1
RDF/ded	H-ESP	946	1,679	2.45e+09	4,114	5,060
	WS	0	253	3.38e+08	85.5	85.5
	Subtotal	946			4,200	5,146
RDF/cofired	H-ESP	0	253	2.53e+08	64.1	64.1
MOD/SA	FF	0	17	1.43e+08	2.43	2.43
	H-ESP	0.068	85.7	3.61e+08	30.9	31
	Unc	0	0.024	5.73e+08	0.014	0.014
	WS	0	17	5.30e+07	0.898	0.898
	Subtotal	0.068			34.2	34.3
MOD/EA	EGB	0	0.024	6.76e+07	0.0016	0.0016
	Unc	0	0.024	4.17e+07	0.001	0.001
	WS	0	17	1.27e+08	2.15	2.15
	Subtotal	0			2.15	2.15
TOTAL		1,485			7,392	8,877

<sup>a</sup>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 3-9. Fly ash from a municipal incinerator (µg/kg)**

<b>Congener group</b>	<b>Average concentration</b>	<b>Concentration range</b>
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	6.2–94
TCDF	12	5.1–36
PeCDF	17	8.3–40
HxCDF	14	3.9–40
HpCDF	2.9	0.8–9.2
OCDF	1.2	ND–2.1
TOTAL CDFs	47	22–110

Source: Clement et al. (1988).

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

<b>Data source</b>	<b>Type of ash</b>	<b>Mean total CDD/CDF concentration (ng/kg)</b>	<b>Mean I-TEQ<sub>DF</sub> (ng/kg)</b>	<b>Annual TEQ amount 1995 value<sup>a</sup> (g I-TEQ<sub>DF</sub>/yr)</b>	<b>Annual TEQ amount 1987 value<sup>a</sup> (g I-TEQ<sub>DF</sub>/yr)</b>
U.S. EPA, 1990c	Mixed	12383	258	1806	1290
Washington State Department of Ecology (1998)	Bottom	0	0	0	0
Ft. Lewis	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)	Fly	1,286,000	—	—	—
North America	Fly	876,000	—	—	—
Europe	Fly	2,600	—	—	—
Japan	Fly	12,010	—	—	—
Wire reclamation	Fly	1,310	—	—	—
	Bottom		—	—	—
Lahl et al. (1991)	Mixed	177,640	—	—	—

<sup>a</sup>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

**Table 3-11. Concentration of dioxin in fly ash samples from combustion of municipal solid waste (ng/kg)**

Congener	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

Source: Imagawa et al. (2000) (numbers estimated from Figure 2 of report).

**Table 3-12. Concentration of dioxin in fly ash samples from municipal solid waste**

<b>Congener</b>	<b>Concentration (ng/kg)</b>	<b>TEQ (ng/kg)</b>
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
<b>TOTAL</b>	<b>119,800</b>	<b>862</b>

Source: Kobylecki et al. (2001) (values estimated from values in Figure 4 of “Before Incineration”).

**Table 3-13. Dioxin and furan concentrations in municipal solid waste ash**

Congener	Concentrations (ng/kg)		I-TEQs (ng/kg)	
	Fly ash	Bottom ash	Fly ash	Bottom ash
2,3,7,8-TCDD	19	1.6	19	1.6
1,2,3,7,8-PeCD	78	3.1	39	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	0.56
1,2,3,7,8,9-HxCDD	130	3.6	13	0.36
1,2,3,4,6,7,8-HpCDD	1,300	33	13	0.33
OCDD	2,800	110	2.8	0.11
2,3,7,8-TCDF	150	4.8	15	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	2.95
1,2,3,4,7,8-HxCDF	310	4.4	31	0.44
1,2,3,6,7,8-HxCDF	310	4.9	31	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	0.67
1,2,3,4,6,7,8-HpCDF	1,100	23	11	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	8,250	226	423	10.5

Source: Sakai et al. (2001).



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

Congener/congener group	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
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 <sub>DF</sub>	4.22	3.83	0.78	0.64
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	4.29	3.88	0.83	0.65
Total TCDD	NR	NR	0.77	0.77
Total PeCDD	NR	NR	1.15	0.77
Total HxCDD	NR	NR	1.67	1.62
Total HpCDD	NR	NR	2.34	2.34
Total OCDD	4.13	3.74	5.24	5.24
Total TCDF	NR	NR	5.47	5.47
Total PeCDF	NR	NR	5.51	5.51
Total HxCDF	NR	NR	4.04	4.04
Total HpCDF	NR	NR	1.94	1.94
Total OCDF	13.78	13.46	0.7	0.7
Total CDD/CDF	153	153	28.83	28.39

ESP = Electrostatic precipitator

NR = Not reported

**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) <sup>a</sup>		Hot-sided ESP boilers mean emission factor (1 facility) (ng/kg feed) <sup>a</sup>	
	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
1,2,3,7,8-PeCDD	0.6141	0.0907	0.0488	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
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	36.27	36.23	0.7841	0.7841
Total I-TEQ <sub>DF</sub>	2.54	2.119	1.313	1.214
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	2.809	2.127	1.335	1.212
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	5.211	5.17	1.554	1.554
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	36.27	36.23	0.7841	0.7841
Total CDD/CDF	195.7	194.1	17.24	16.66

<sup>a</sup>Values incorporating use of the detection limit when the laboratory report indicated “not detected” for individual CDD/CDF congeners.

NR = Not reported

Source: U.S. EPA (2002b).

**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 $\frac{1}{2}$ 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	0.5830	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 <sub>DF</sub>	0.8176	0.8034
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	0.8519	0.8356
Total TCDD	NR	NR
Total PeCDD	NR	NR
Total HxCDD	NR	NR
Total HpCDD	NR	NR
Total OCDD	1.4944	1.4944
Total TCDF	NR	NR
Total PeCDF	NR	NR
Total HxCDF	NR	NR
Total HpCDF	NR	NR
Total OCDF	25.015	25.015
Total CDD/CDF	62.4773	62.4607

NR = Not reported

Source: U.S. EPA (2002b).

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

<b>APCD</b>	<b>Number of facilities</b>	<b>Percent of total</b>
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).

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

<b>MWI</b>	<b>Capacity range (lb/hr)</b>	<b>Annual charging hours (hr/yr)</b>	<b>Maximum annual charging hours (hr/yr)</b>	<b>Capacity factor</b>
Continuous commercial	>1,000	7,776	8,760	0.89
Continuous onsite	501–1,000	1,826	5,475	0.33
	>1,000	2,174		0.40
Intermittent	≤500	1,250	4,380	0.29
Batch	Case by case	Case by case		Case by case

Source: U.S. EPA (1990e).

**Table 3-18. Office of Air Quality Planning and Standards approach:  
estimated nationwide I-TEQ<sub>DF</sub> emissions for 1995**

Medical waste incinerator type	Residence time (sec) or air pollution control device	CDD/CDF emission factor (ng/kg)	I-TEQ <sub>DF</sub> emission factor (ng/kg)	Activity level (kg/yr)	CDD/CDF emissions (g/yr)	I-TEQ <sub>DF</sub> emissions (g/yr)
Batch	0.25	193,997	3,960	5.95e+06	1.15e+03	2.36e+01
	1	44,500	909	4.20e+05	1.87e+01	3.82e-01
	2	3,650	74	2.14e+05	7.81e-01	1.58e-02
Continuous	0.25	193,997	3,960	1.20e+06	2.33e+02	4.75e+00
	1	44,500	909	5.10e+06	2.27e+02	4.64e+00
	2	3,650	74	3.01e+07	1.10e+02	2.23e+00
Continuous/ intermittent	0.25	193,997	3,960	4.54e+06	8.81e+02	1.80e+01
	1	44,500	909	5.10e+06	2.27e+02	4.64e+00
	2	3,650	74	9.79e+07	3.57e+02	7.24e+00
Intermittent	0.25	193,997	3,960	4.18e+06	8.11e+02	1.66e+01
	1	44,500	909	5.57e+07	2.48e+03	5.06e+01
	2	3,650	74	4.31e+07	1.57e+02	3.19e+00
	Subtotal: uncontrolled			2.54e+08	6.66e+03	1.36e+02
Batch	Wet scrubber	426	10	2.42e+04	1.03e-02	2.42e-04
Continuous	Wet scrubber	426	10	1.88e+08	8.01e+01	1.88e+00
Continuous/ intermittent	Wet scrubber	426	10	1.22e+08	5.20e+01	1.22e+00
Intermittent	Wet scrubber	426	10	6.04e+07	2.57e+01	6.04e-01
	Subtotal: controlled w/wet scrubber			3.70e+08	1.58e+02	3.70e+00
Continuous	Dry scrubber, no carbon	365	7	9.94e+07	3.63e+01	6.96e-01
Continuous/ intermittent	Dry scrubber, no carbon	365	7	7.86e+06	2.87e+00	5.50e-02
Intermittent	Dry scrubber, no carbon	365	7	2.07e+07	7.56e+00	1.45e-01
Continuous	Dry scrubber, with carbon	70	2	1.43e+07	1.00e+00	2.86e-02
Continuous/ intermittent	Dry scrubber, with carbon	70	2	3.70e+06	2.59e-01	7.40e-03
	Subtotal: controlled w/dry scrubber			1.46e+08	4.80e+01	9.32e-01
Intermittent	Fabric filter/ packed bed	33,400	681	6.99e+05	2.34e+01	4.76e-01
TOTAL				7.71e+08	6.88e+03	1.41e+02

NA = Not applicable

**Table 3-19. Office of Air Quality Planning and Standards approach:  
particulate matter emission limits for medical waste incinerator (MWI) types  
and corresponding residence times in the secondary combustion chamber**

<b>MWI type</b>	<b>Particulate matter emission limit (gr/dscf)</b>	<b>Residence time in secondary chamber (sec)</b>	<b>I-TEQ<sub>DF</sub> emission factor (kg I-TEQ<sub>DF</sub>/kg waste)</b>
Intermittent and continuous	≥0.3	0.25	3.96e-9
	0.16 to < 0.3	1	9.09e-10
	0.1 to ≤0.16	2	7.44e-11
Batch	≥0.079	0.25	3.96e-9
	0.042 to <0.079	1	9.09e-10
	0.026 to <0.042	2	7.44e-11

**Table 3-20. American Hospital Association approach: I-TEQ<sub>DF</sub> emission factors calculated for air pollution control device (APCD)**

<b>APCD<sup>a</sup></b>	<b>I-TEQ<sub>DF</sub> emission factor (lb/10<sup>6</sup> lb of waste)</b>	<b>Number of medical waste incinerators (MWIs) test reports used<sup>b</sup></b>
Uncontrolled MWIs up to 200 lb/hr MWIs >200 lb/hr	1.53e-03 5.51e-04	413
WS/FF/ESP	4.49e-05	11
DSI/FF	6.95e-05	8

<sup>a</sup>Slash(es) indicates devices used in conjunction.

<sup>b</sup>The same MWI may have been used more than once in deriving emission factors.

DSI = Dry sorbent injection

ESP = Electrostatic precipitator

FF = Fabric filter

WS = Wet scrubber

Source: Doucet (1995).



**Table 3-21. American Hospital Association assumptions of the percent distribution of air pollution control on medical waste incinerators (MWIs) based on particulate matter (PM) emission limits**

<b>PM emission limits<sup>a</sup> (gr/dscf)</b>	<b>Percent MWIs uncontrolled<sup>b</sup></b>	<b>Percent MWIs with WSs/ FFs/ESPs</b>	<b>Percent MWIs with DSI/FF</b>
≥0.10	50	50	0
0.08 to <0.10	25	75	0
0.03 to <0.08	0	98	2
<0.03	0	30	70

<sup>a</sup>PM emission limits at the stack.

<sup>b</sup>No air pollution control device installed on the MWI.

DSI = Dry sorbent injection

ESP = Electrostatic precipitator

FF = Fabric filter

WS = Wet scrubber

**Table 3-22. American Hospital Association approach: estimated annual nationwide I-TEQ<sub>DF</sub> emissions**

<b>Air pollution control device (APCD)<sup>a</sup></b>	<b>Medical waste incinerator<sup>b</sup> (lb/hr)</b>	<b>I-TEQ<sub>DF</sub> emission factor<sup>c</sup> (g/kg waste)</b>	<b>Medical waste incinerator<sup>d</sup> (kg/yr)</b>	<b>Annual I-TEQ<sub>DF</sub> emissions (g/yr)</b>
Uncontrolled	≤ 200	1.54e-06	2.28e+07	3.51e+01
	> 200	5.51e-07	1.54e+08	8.48e+01
	Subtotal uncontrolled		1.77e+08	1.20e+02
WS/FF/ESP	>200	4.49e-08	3.51e+08	15.8e+01
DI/FF	>200	6.95e-08	2.60e+07	1.81
	Subtotal controlled		3.77e+08	1.76e+01
<b>TOTAL</b>			<b>5.54+08</b>	<b>1.38e+02</b>

<sup>a</sup>Slash(es) indicates devices used in conjunction.

<sup>b</sup>Design capacity of the primary combustion chamber.

<sup>c</sup>Derived from tested facilities.

<sup>d</sup>Annual amount of medical waste incinerated by each APCD class.

APCD:

DI = Dry sorbent injection

ESP = Electrostatic precipitator

FF = Fabric filter

MWI = Medical waste incinerator

WS = Wet scrubbers

**Table 3-23. Comparison between predicted residence times at medical waste incinerators (MWIs) and residence times confirmed by state agencies in the Office of Research and Development telephone survey**

<b>State</b>	<b>Residence time categories (sec)</b>	<b>Percentage of uncontrolled MWIs predicted by particulate matter method (no. of MWIs)</b>	<b>Percentage of uncontrolled MWIs confirmed by state agency (no. of MWIs)</b>
Michigan	1/4	2 (6/280)	96 (269/280)
	1	2 (5/280)	3 (9/280)
	2	96 (269/280)	1 (1/280)
Massachusetts	1/4	6 (6/94)	Unknown
	1	0 (0/94)	Unknown
	2	94 (88/94)	4 (2/50)
Virginia	1/4	11 (6/56)	4.5 (1/22)
	1	0 (0/50)	91 (20/22)
	2	89 (50/56)	4.5 (1/22)
New Jersey	1/4	0 (0/53)	Unknown
	1	0 (0/53)	Unknown
	2	100 (53/53)	Unknown

Source: O'Rourke (1996).

**Table 3-24. Summary of annual TEQ emissions from medical waste incinerators (MWIs) for reference year 1987 (ORD approach)**

<b>MWI class<sup>a</sup></b>	<b>No. of tested facilities</b>	<b>Activity level (kg/yr)</b>	<b>Total CDD/CDF emission factor<sup>b</sup> (g/kg)</b>	<b>I-TEQ<sub>DF</sub> emission factor (g/kg)</b>	<b>TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factor (g/kg)</b>	<b>Annual CDD/CDF emissions (g/yr)</b>	<b>Annual I-TEQ<sub>DF</sub> emissions (g/yr)</b>	<b>Annual TEQ<sub>DF</sub>-WHO<sub>98</sub> emissions (g/yr)</b>
≤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	2.03+03	2.14e+03
<b>TOTAL</b>	<b>8</b>	<b>1.43e+09</b>				<b>9.34e+04</b>	<b>2.44+03</b>	<b>2.59e+03</b>

<sup>a</sup>Categorization scheme of the American Hospital Association approach (Doucet, 1995).

**Table 3-25. Office of Research and Development approach: TEQ emissions from medical waste incinerators (MWIs) for reference year 1995**

MWI class (air pollution control device [APCD])	MWI subclass (capacity or APCD <sup>a</sup> )	No. of tested facilities	Total CDD/CDF emission factor (ng/kg)	I-TEQ <sub>DF</sub> emission factor (ng/kg)	TEQ <sub>DF</sub> -WHO <sub>98</sub> emission factor (ng/kg)	Activity level (kg/yr)	Annual CDD/CDF emissions (g/yr)	Annual I-TEQ <sub>DF</sub> emissions (g/yr)	Annual TEQ <sub>DF</sub> -WHO <sub>98</sub> 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	3.98e+02
Controlled	WS/FF/ESP	9	4.67e+04	7.22e+01	7.43e+01	3.71e+08	1.73e+03	2.68e+01	2.76e+01
	DSI/FF	2	2.85e+02	6.78	6.86	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	4.61e+02	4.88e+02

<sup>a</sup>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

**Table 3-26. Office of Research and Development approach: TEQ emissions from medical waste incinerators (MWIs) for reference year 2000**

<b>MWI class (air pollution control device [APCD])</b>	<b>MWI subclass (capacity or APCD<sup>a</sup>)</b>	<b>No. of tested facilities</b>	<b>Total CDD/CDF emission factor (ng/kg)</b>	<b>TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factor (ng/kg)</b>	<b>Activity level (kg/yr)</b>	<b>Annual CDD/CDF emissions (g/yr)</b>	<b>Annual TEQ<sub>DF</sub>- WHO<sub>98</sub> emissions (g/yr)</b>
Uncontrolled	≤200 lb/hr	3	9.25e+04	1.98e+03	2.40e+07	2.22e+03	4.75e+01
	>200 lb/hr	5	6.05e+04	1.78e+03	1.74e+08	1.05e+04	3.10e+02
Controlled	WS/FF/ ESP	10	4.55e+03	6.63e+01	2.88e+08	1.31e+03	1.91e+01
	DSI/FF	3	2.67e+02	4.61	1.14e+08	3.04e+01	5.26e-01
	FF/PBS	1	1.11e+05	1.49e+03	5.40e+05	5.99e+01	8.05e-01
<b>TOTAL</b>			3.77e+04	7.57e+02	6.00e+08	1.28e+04	3.78e+02

<sup>a</sup>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

**Table 3-27. Comparison of basic assumptions used in the ORD, OAQPS, and AHA approaches to estimating nationwide CDD/CDF TEQ emissions from medical waste incinerators (MWIs) for reference year 1995**

Assumption	ORD approach	OAQPS approach	AHA approach
Number of MWIs	2,375	2,375	2,233
Estimated activity level	7.71e+08 kg/yr	7.71e+08 kg/yr	5.54e+08 kg/yr
Percent of activity level at uncontrolled MWIs	33	33	32
Percent of activity level at controlled MWIs	67	67	68
Subclassification of uncontrolled class	Same as AHA assumption	By residence times in secondary chamber	By design capacity
Assumed distribution of uncontrolled class	Same as AHA assumption	By residence times of 0.25, 1, and 2 sec by state PM emission limits	By estimated annual hrs of operation of <200 lb/hr and >200 lb/hr design capacity
Air pollution control devices (APCDs) assumed for controlled class	WS/FF/ESP DSI/FF FF/PBS	WS DS no carbon DS carbon FF/PBS	WS/FF/ESP DSI/FF
Assumed distribution of controls	Yes/analogous to AHA method	Yes/analogous to AHA method	Yes/based on survey and state PM emission limits
Emission factor approach used	Yes	Yes	Yes
No. of tested MWIs used to develop emission factors	Uncontrolled: 8 Controlled: 11	Uncontrolled: 10 Controlled: 23	Uncontrolled: 13 Controlled: 12
Uncontrolled I-TEQ <sub>DF</sub> emission factors (ng/kg)	1,865 = ≤200 lb/hr 1,680 = >200 lb/hr	3,960 = 0.25 sec RT <sup>a</sup> 909 = 1 sec RT <sup>b</sup> 74 = 2 sec RT <sup>c</sup>	1,540 = ≤200 lb/hr <sup>d</sup> 551 = >200 lb/hr <sup>e</sup>
Controlled I-TEQ <sub>DF</sub> emission factors (ng/kg) <sup>f</sup>	WS/FF/ESP: 72.2 DSI/FF: 6.8 FF/PBS: 1350	WS: 10 DS no carbon: 7 DS with carbon: 2 FF/PBS: 681	WS/FF/ESP: 44.9 DSI/FF: 69.5

<sup>a</sup>0.25 seconds residence time in the secondary chamber.

<sup>b</sup>1 second residence time in the secondary chamber.

<sup>c</sup>2 seconds residence time in the secondary chamber.

<sup>d</sup>Design capacities less than or equal to 200 lb/hr.

<sup>e</sup>Design capacities greater than 200 lb/hr.

<sup>f</sup>Emission factors as reported in Tables 3-9, 3-12, and 3-14.

AHA = American Hospital Association

OAQPS = Office of Air Quality Planning and Standards

ORD = Office of Research and Development

PM = Particulate matter

RT = Residence time

APCD:

DS = Dry scrubber

DSI = Dry sorbent injection

ESP = Electrostatic precipitator

FF = Fabric filter

PBS = Packed-bed scrubber

WS = Wet scrubber

**Table 3-28. Congener-specific profile for Camellia Memorial Lawn Crematorium**

Congener/congener group	Mean facility emission factor	
	Assuming nondetect set to zero (ng/body)	Assuming nondetect set to ½ detection limit (ng/body)
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 <sub>DF</sub>	501	508
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	543	550
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 (1990c).



**Table 3-29. 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 <sub>DF</sub>	319	329	780	780
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	325	341	961	961

Source: U.S. EPA (1999f).

**Table 3-30. Operational data for the Woodlawn Cemetery crematorium,  
scrubber inlet**

Parameter	Mean value		
	675 °C	870 °C	980 °C
Particulate matter (gr/dscf @ 7% O <sub>2</sub> )	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 (1999f).

**Table 3-31. 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
1,2,3,7,8-PeCDD	67	60
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	1,721	1,721
2,3,7,8-TCDF	156	156
1,2,3,7,8-PeCDF	112	117
2,3,4,7,8-PeCDF	312	317
1,2,3,4,7,8-HxCDF	319	319
1,2,3,6,7,8-HxCDF	308	308
1,2,3,7,8,9-HxCDF	401	401
2,3,4,6,7,8-HxCDF	300	300
1,2,3,4,6,7,8-HpCDF	1,326	1,387
1,2,3,4,7,8,9-HpCDF	135	138
OCDF	530	530
Total I-TEQ <sub>DF</sub>	410	329
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	434	341
Total TCDD	467	467
Total PeCDD	838	838
Total HxCDD	1,923	1,923
Total HpCDD	2,384	2,384
Total OCDD	1,721	1,721
Total TCDF	3,586	3,586
Total PeCDF	2,441	2,441
Total HxCDF	3,575	3,575
Total HpCDF	1,897	1,958
Total OCDF	530	530
Total CDD/CDF	19,362	19,424

Source: CARB (1990c); U.S. EPA (1999f).

**Table 3-32. 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 <sub>DF</sub>	0.11	0.11
Total TEQ <sub>DF</sub> -WHO98	0.12	0.12

Source: U.S. EPA (2000e).

**Table 3-33. 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 (1990f) (2 facilities) U.S. EPA (1999) (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 <sub>DF</sub>	NR	NR	6.65	6.87
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	NR	NR	6.74	7.01
Total CDD/CDF	1,266	1,268	256	262

NR = Not reported

**Table 3-34. CDD/CDF air emission factors for tire combustion**

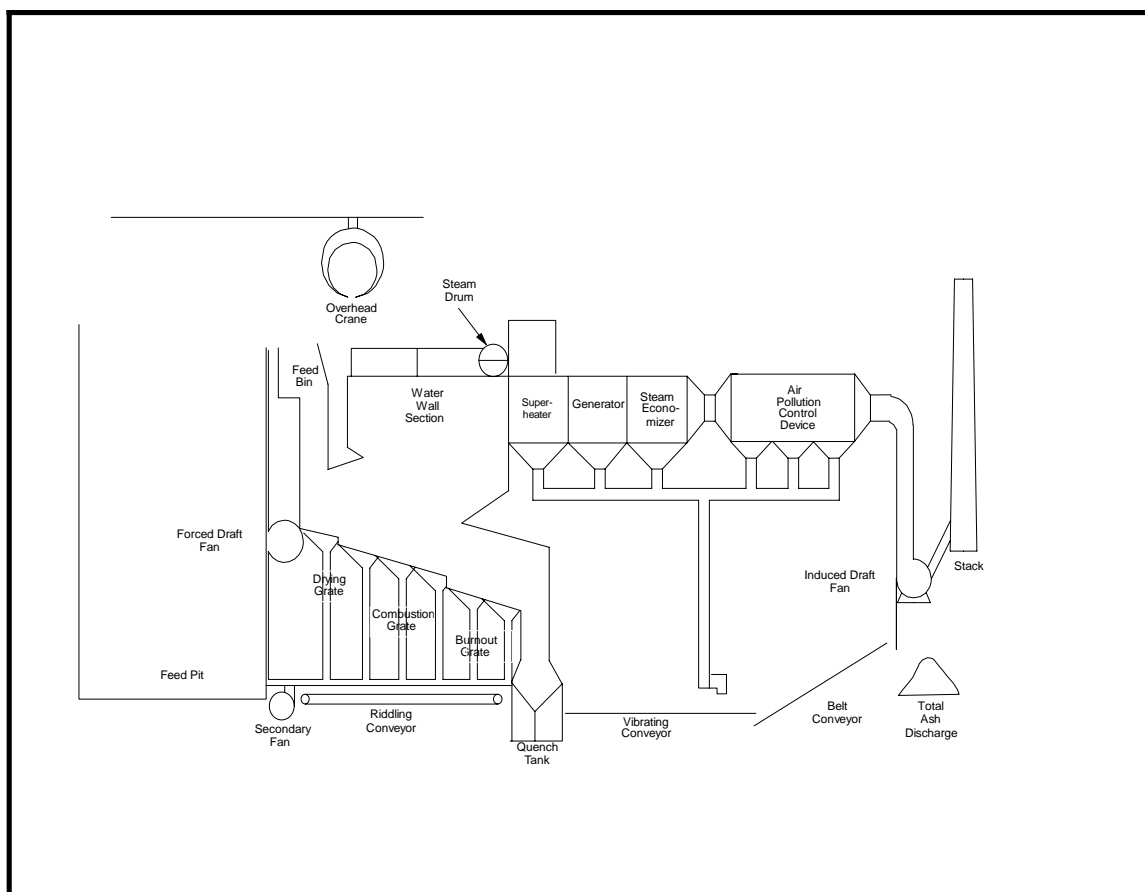
Congener/congener group	Mean facility emission factor (ng/kg)	
	Assuming nondetect set to zero	Assuming nondetect set to $\frac{1}{2}$ detection limit
2,3,7,8-TCDD	0.149	0.149
1,2,3,7,8-PeCDD	0.006	0.026
1,2,3,4,7,8-HxCDD	0.018	0.023
1,2,3,6,7,8-HxCDD	0.055	0.062
1,2,3,7,8,9-HxCDD	0.036	0.048
1,2,3,4,6,7,8-HpCDD	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	0.166
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 <sub>DF</sub>	0.282	0.311
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	0.281	0.318
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 (1991a).

**Table 3-35. 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 <sub>DF</sub>	0.061	0.082
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	0.062	0.087
Total CDD/CDF	5.941	6.037

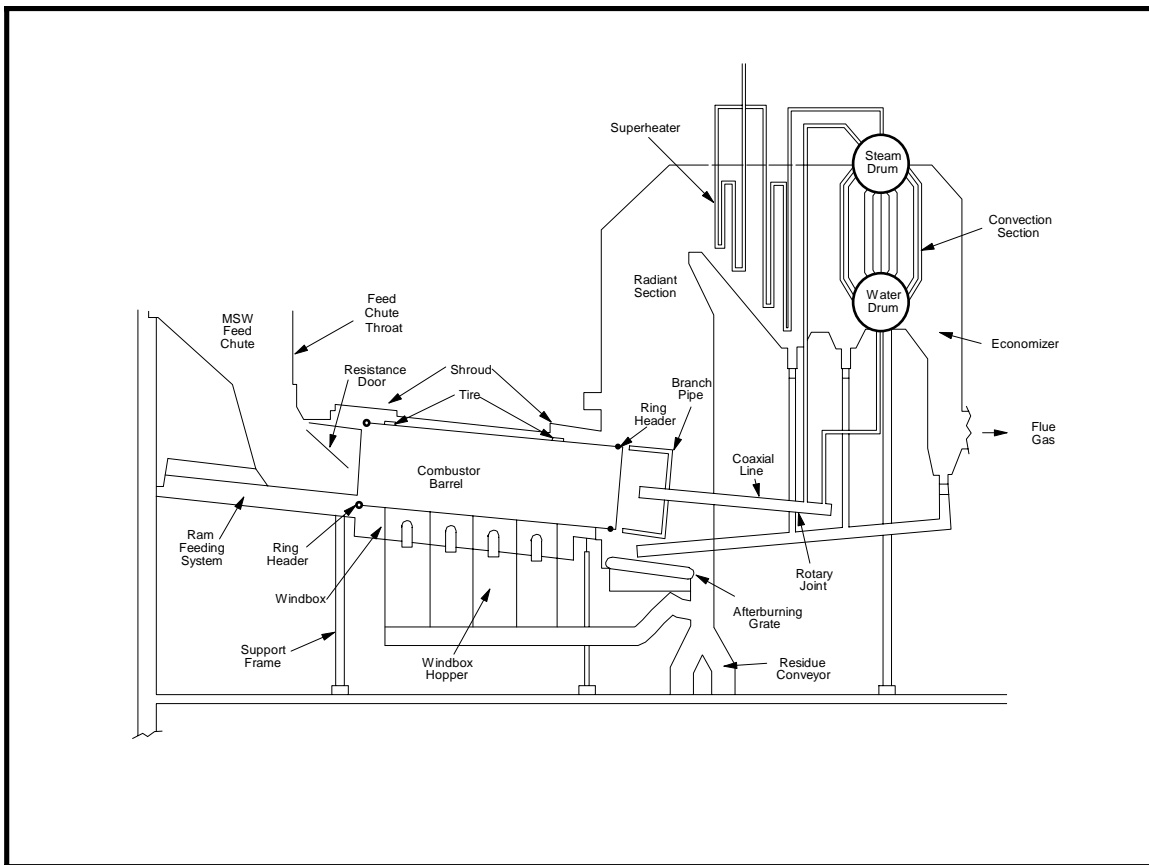
Source: NCASI (1995).



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

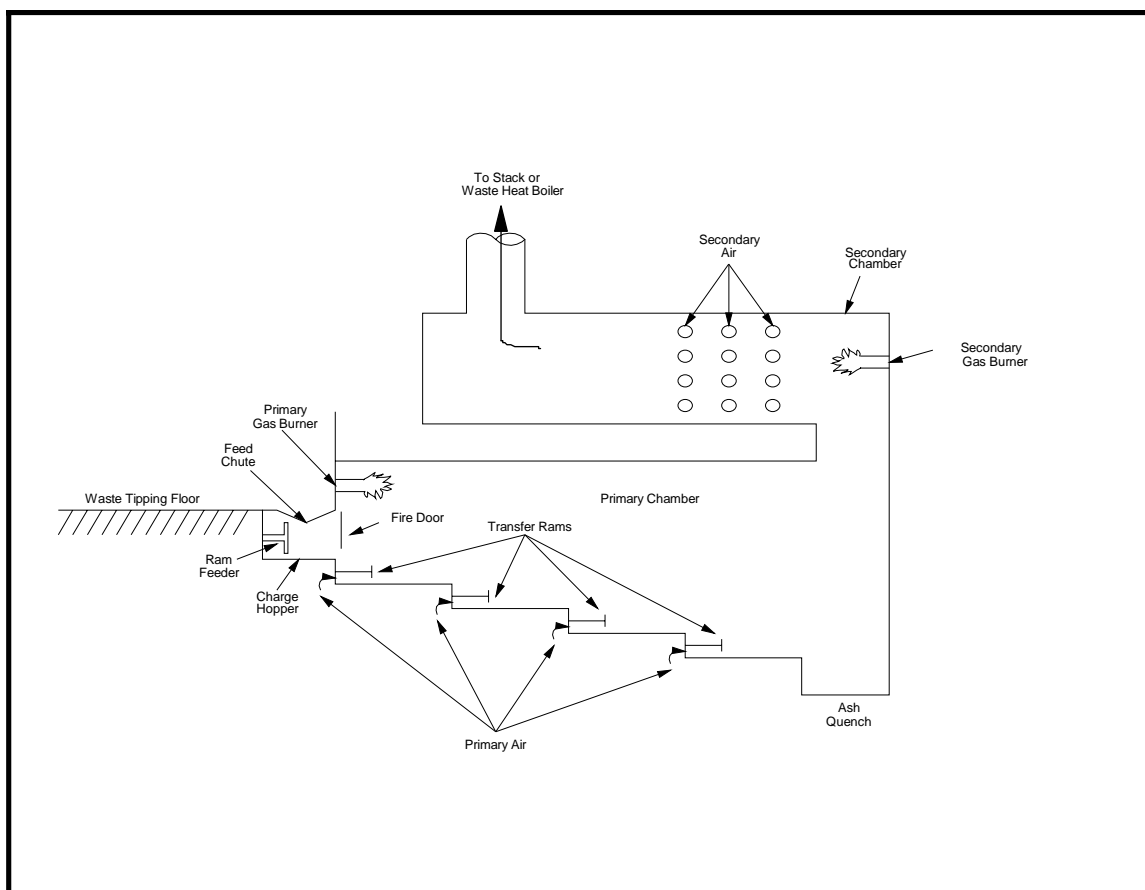
Source: U.S. EPA (1997b).





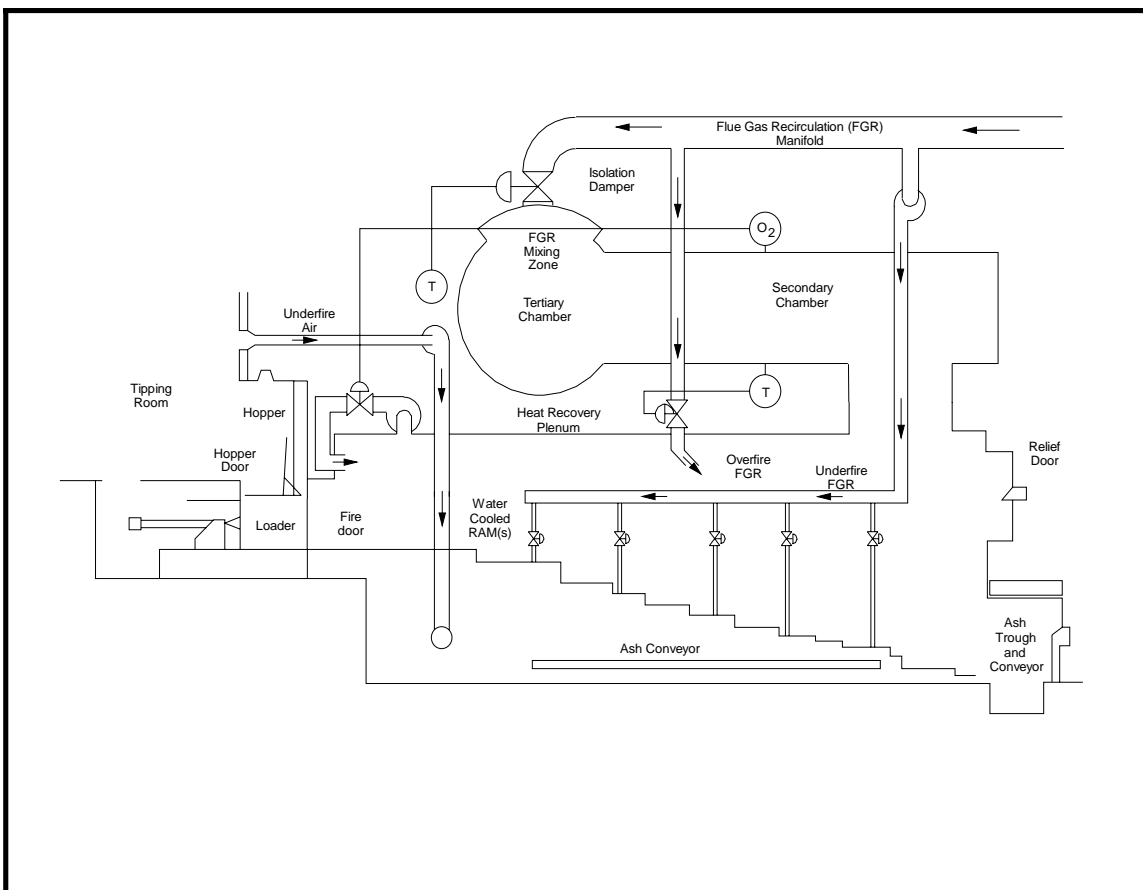
**Figure 3-2. Typical mass burn rotary kiln combustor.**

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



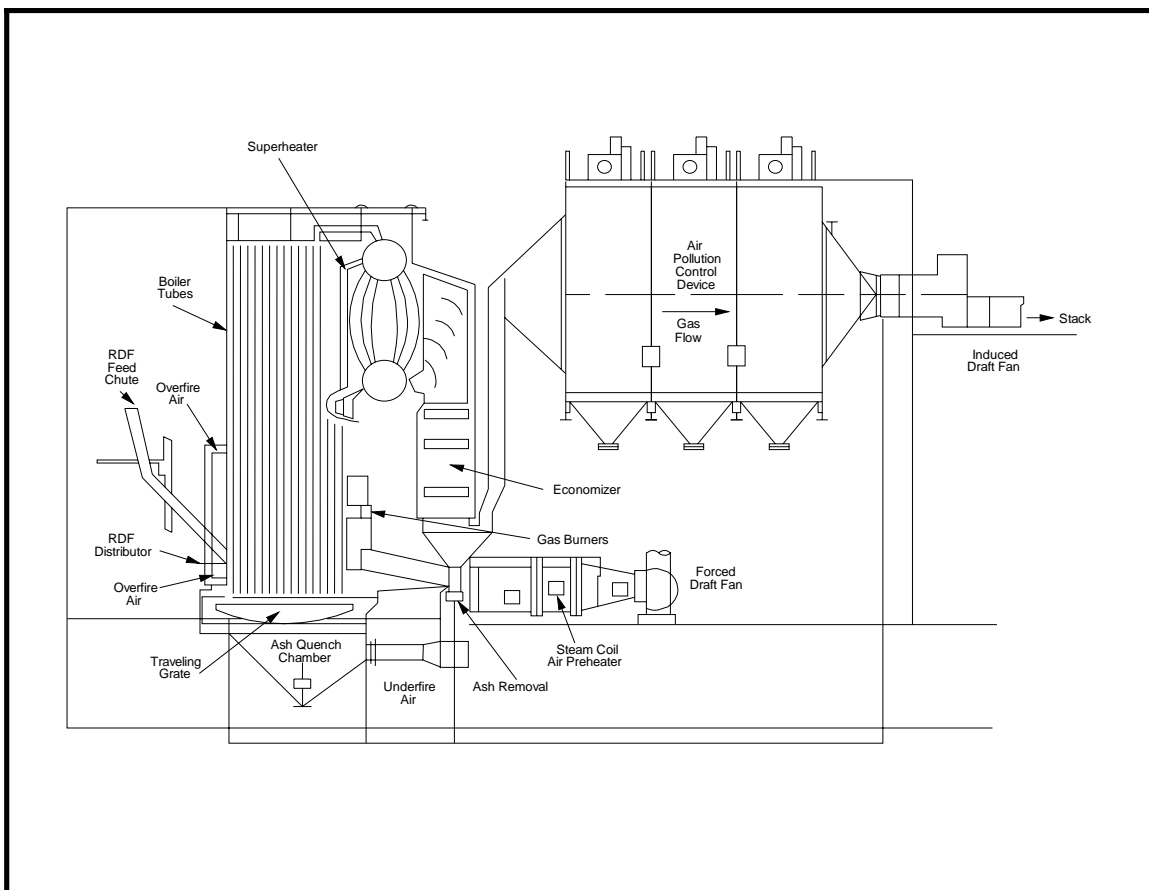
**Figure 3-3. Typical modular starved-air combustor with transfer rams.**

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



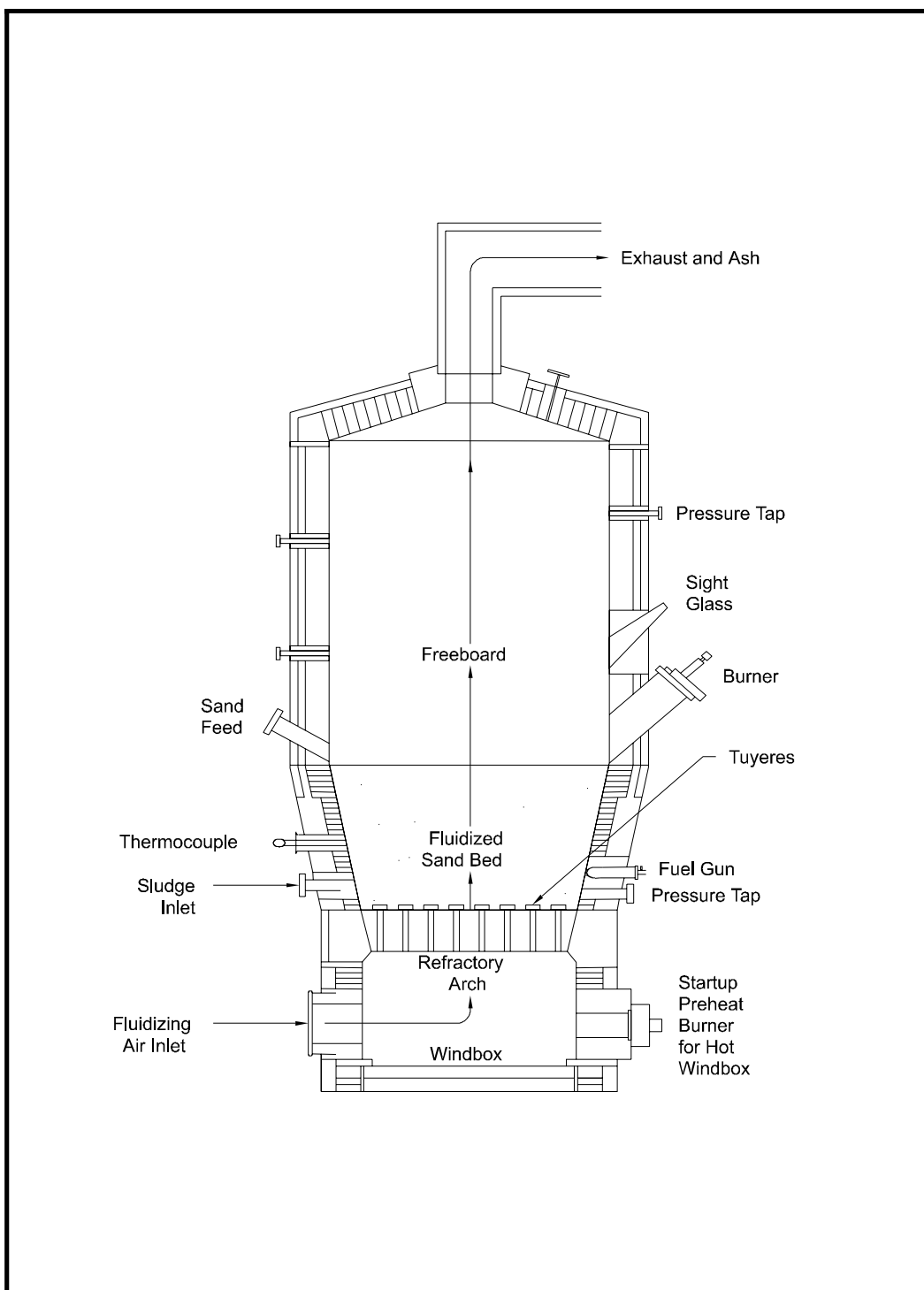
**Figure 3-4. Typical modular excess-air combustor.**

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



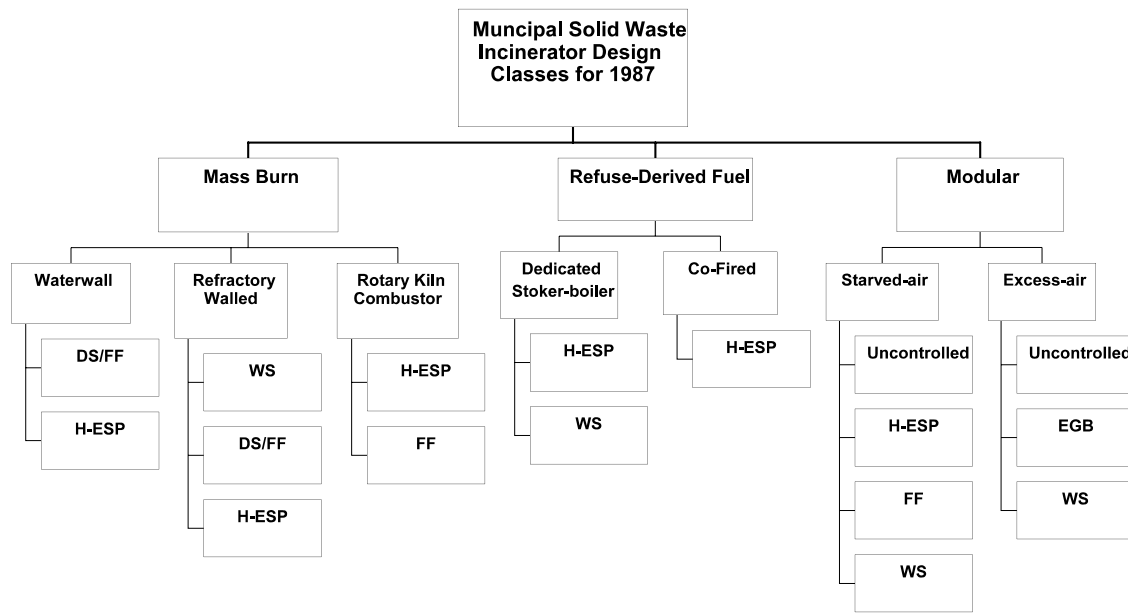
**Figure 3-5. Typical dedicated refuse-derived fuel-fired spreader stoker boiler.**

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



**Figure 3-6. Fluidized-bed refuse-derived fuel incinerator.**

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



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

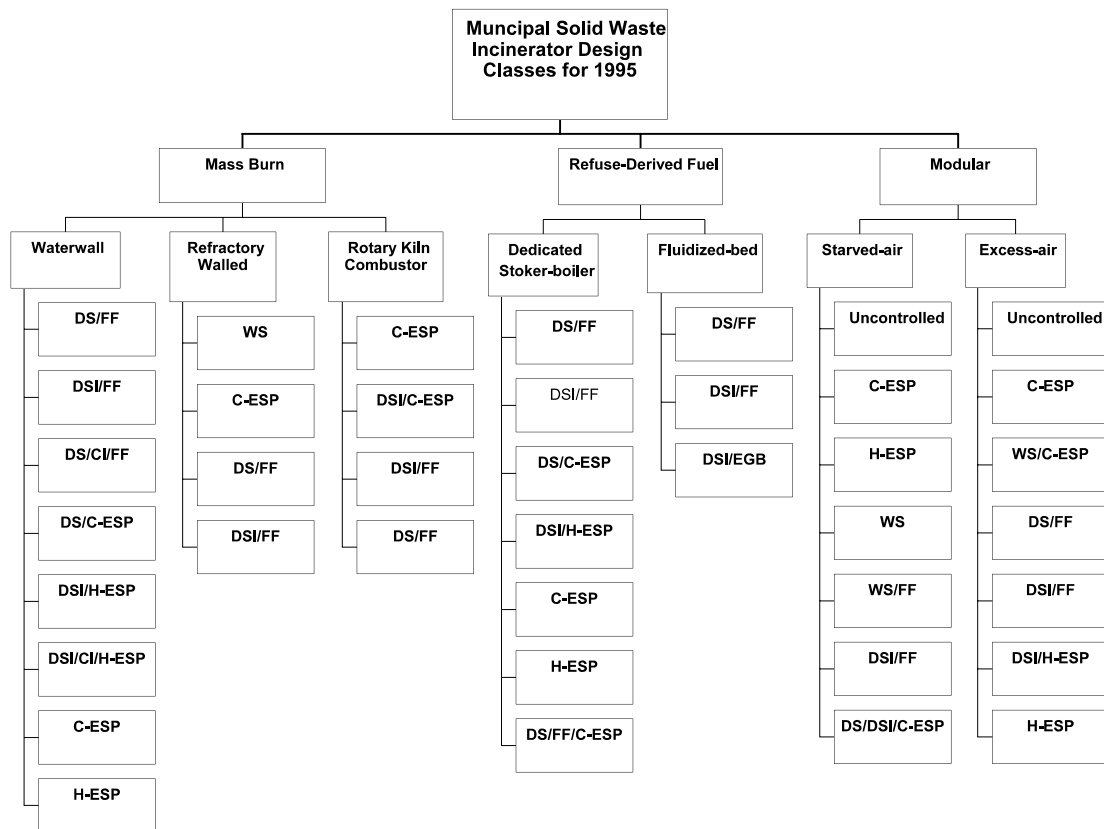
DS/FF = Dry scrubber combined with a fabric filter

EGB = Electrogranular activated carbon bed

FF = Fabric filter

H-ESP = Hot-sided electrostatic precipitator (temperature at control device is greater than 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 below less than 230 °C)

DS/CI/FF = Dry scrubber with carbon injection and fabric filter

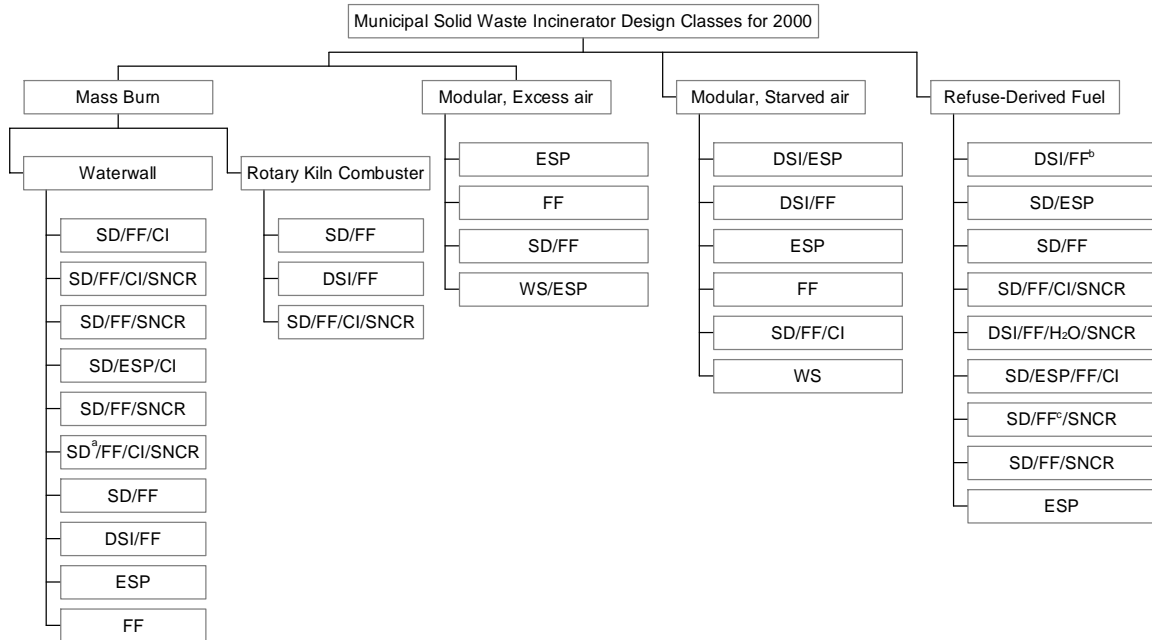
DS/FF = Dry scrubber combined with a fabric filter

DSI/FF = Dry sorbent injection coupled with a fabric filter

EGB = Electrogranular activated carbon bed

H-ESP = Hot-sided electrostatic precipitator (temperature at control device is greater than 230 °C)

WS = Wet scrubber



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

<sup>a</sup>Also equipped with furnace dry sorbent injection system

<sup>b</sup>Also equipped with flue gas cooling (280–290 °F)

<sup>c</sup>Also equipped with compact hybrid particulate collector system

CI = Carbon injection

DSI = Dry sorbent injection

ESP = Electrostatic precipitator

FF = Fabric filter

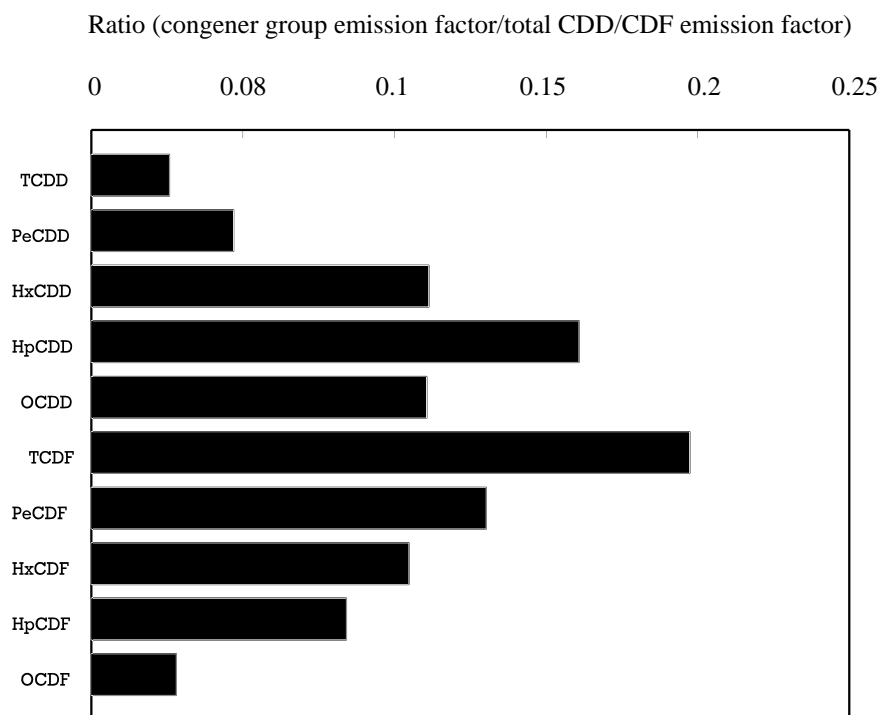
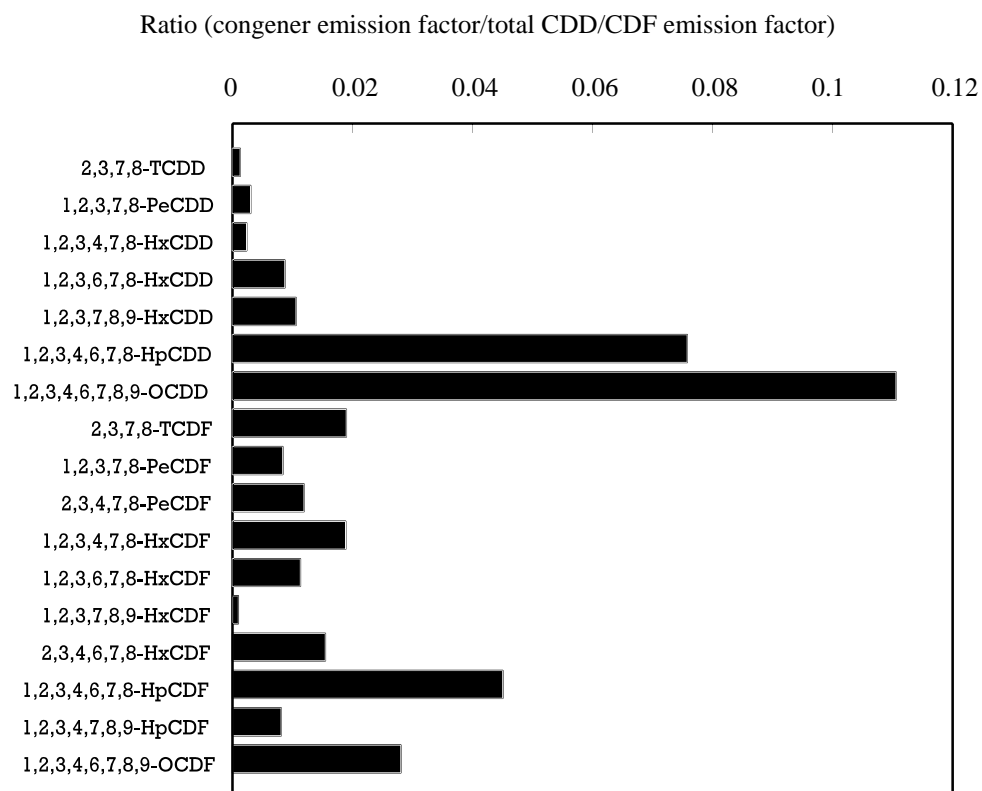
H<sub>2</sub>O = Water scrubber

SD = Spray dryer

SNCR = Selective noncatalytic reduction

WS = Wet scrubber





**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.**

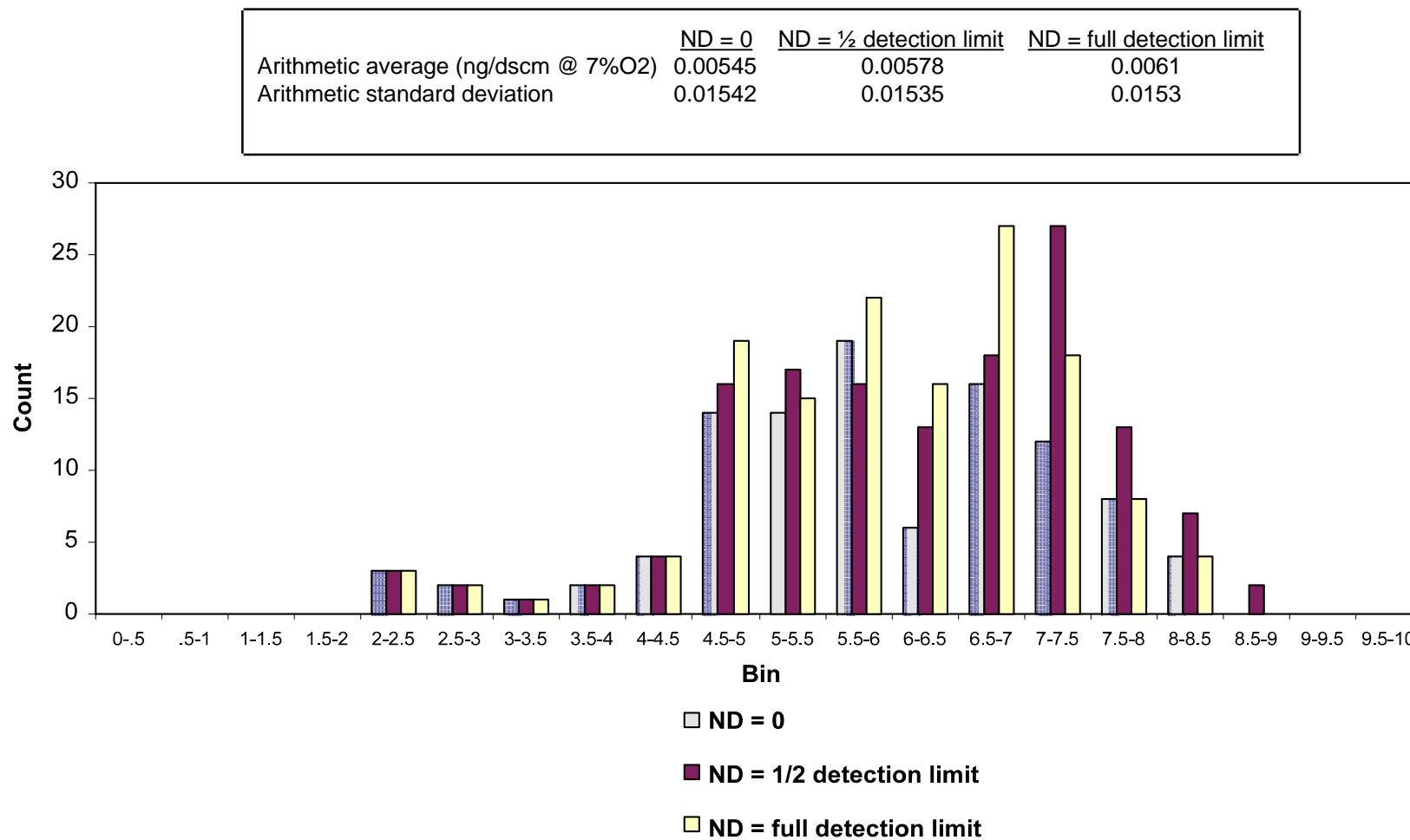


Figure 3-11. 2,3,7,8-TCDD frequency distribution (negative natural log concentration).

	<u>ND = 0</u>	<u>ND = 1/2 detection limit</u>	<u>ND = full detection limit</u>
Arithmetic average (ng/dscm @ 7%O <sub>2</sub> )	0.01589	0.0163	0.01669
Arithmetic standard deviation	0.03375	0.03364	0.0336

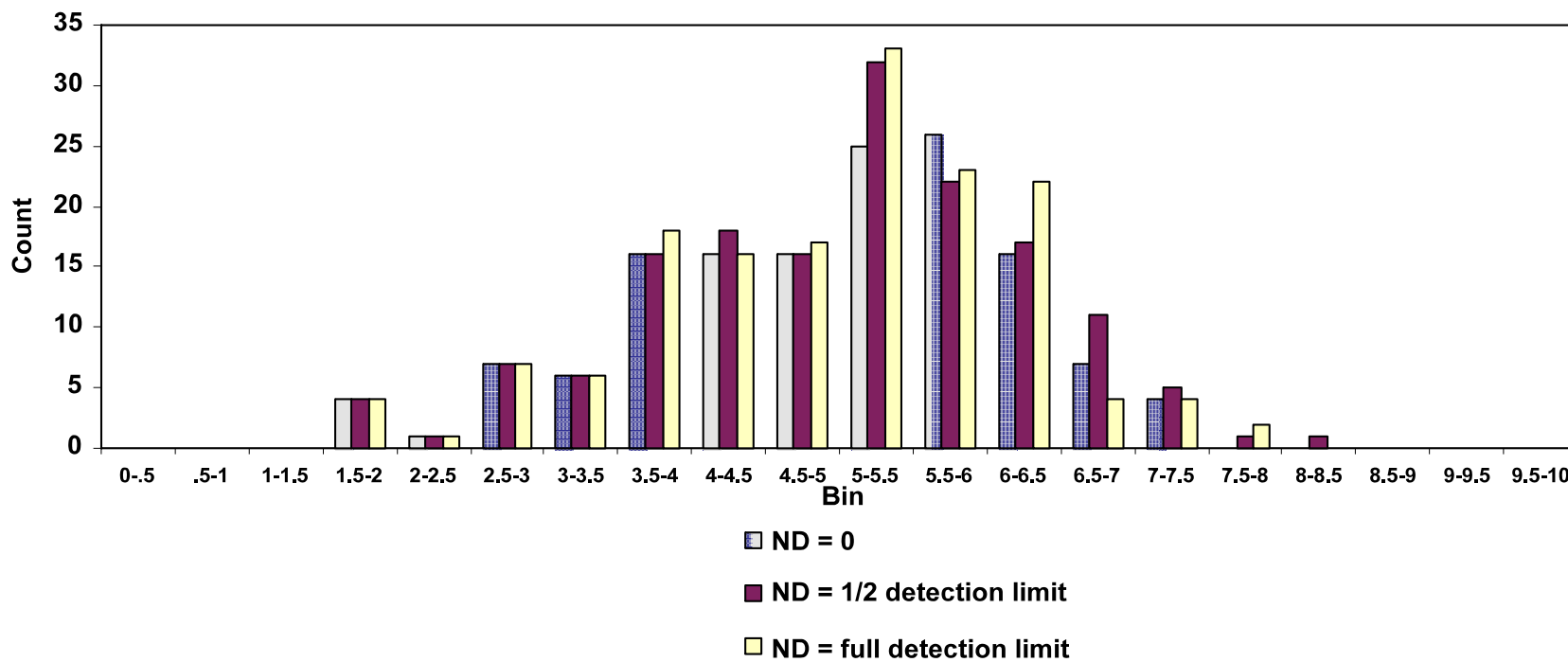
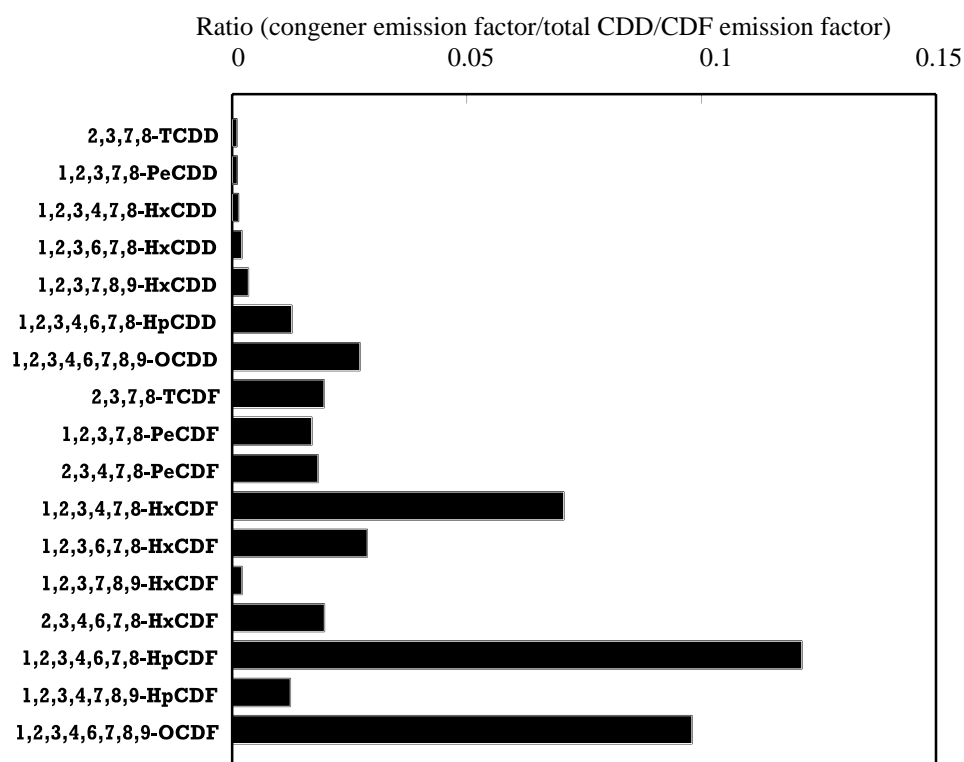
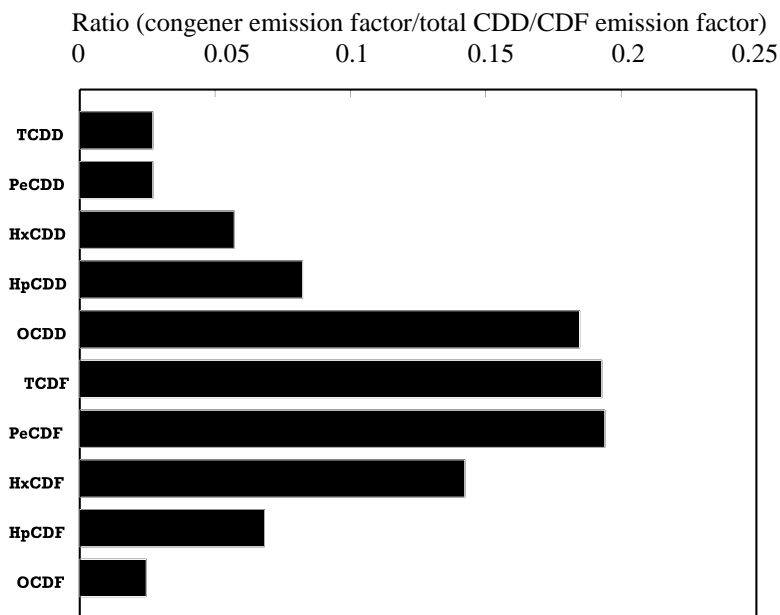
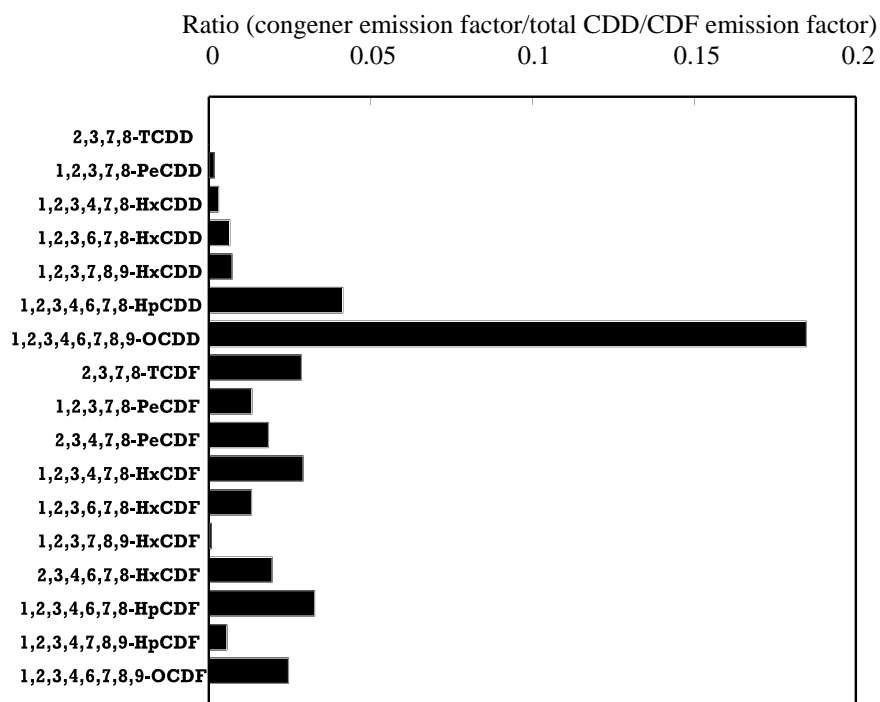


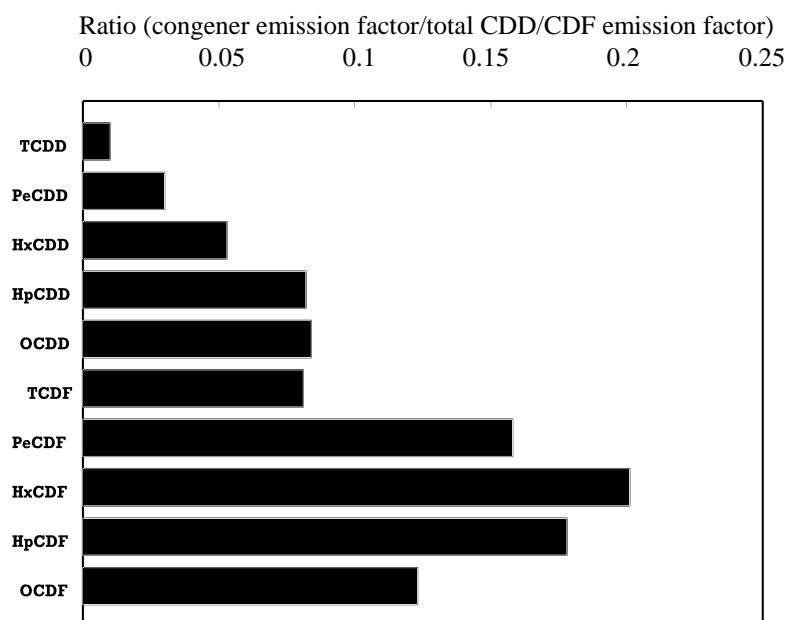
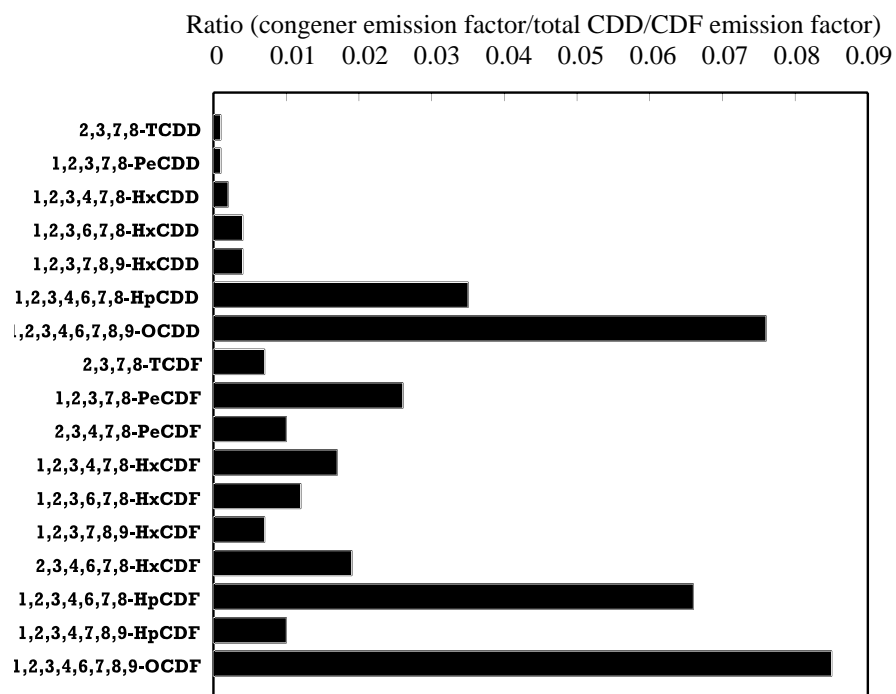
Figure 3-12. 1,2,3,7,8-PeCDD frequency distribution (negative natural log concentration).



**Figure 3-13. Congener profile for air emissions from hazardous waste incinerators.**

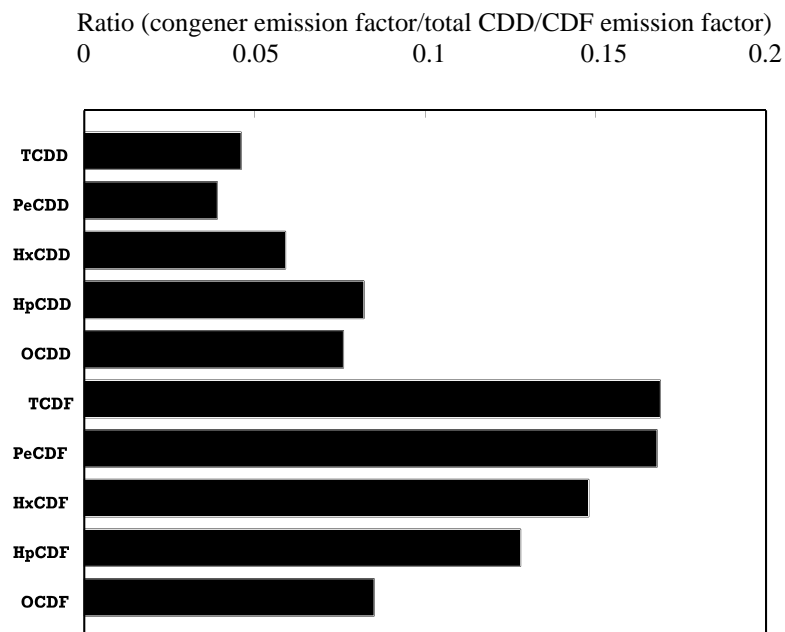
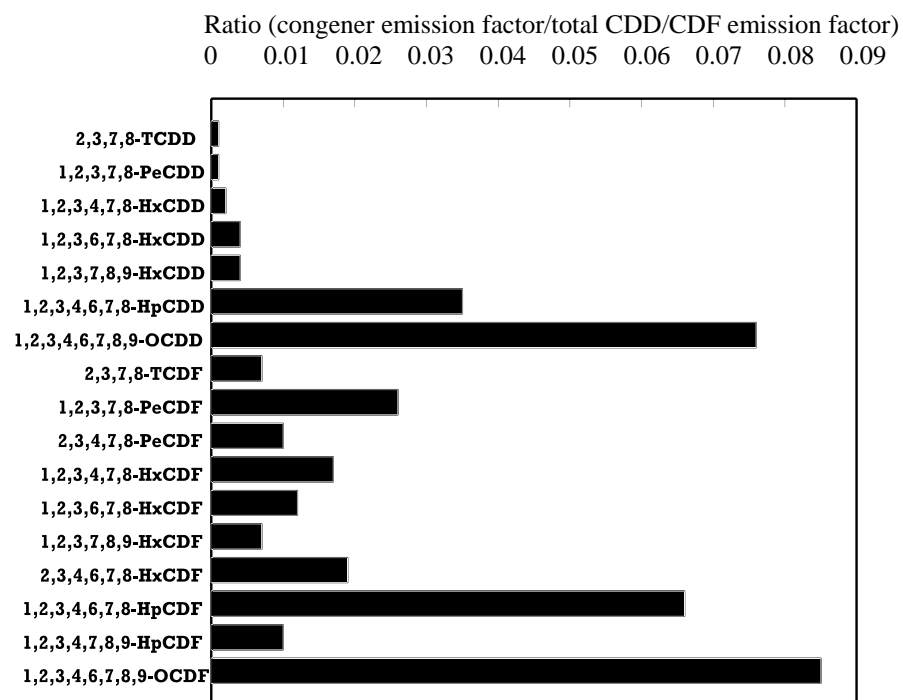


**Figure 3-14. Congener and congener group profiles for air emissions from boilers and industrial furnaces burning hazardous waste.**

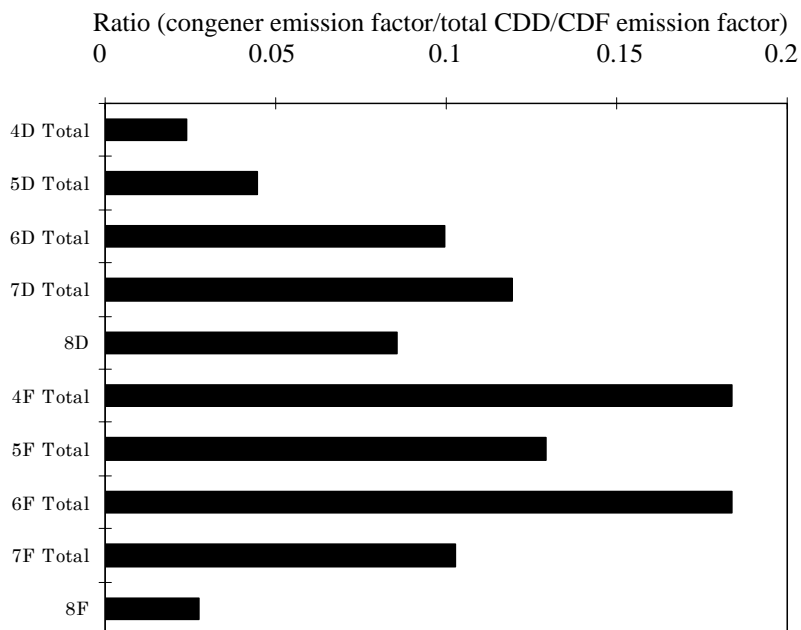
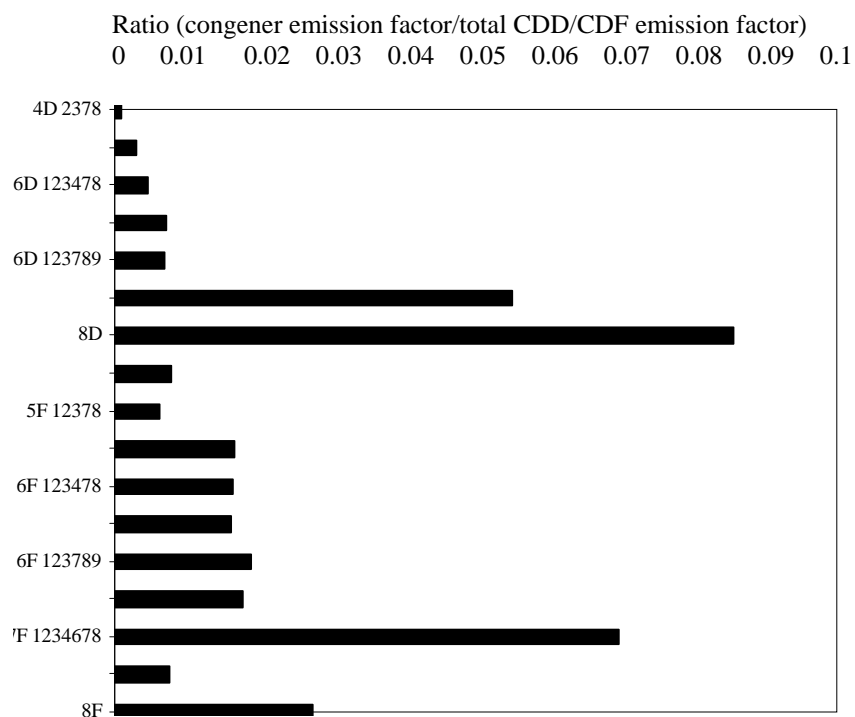


Nondetects set equal to zero.

**Figure 3-15. Congener and congener group profiles for air emissions from medical waste incinerators without air pollution control devices.**



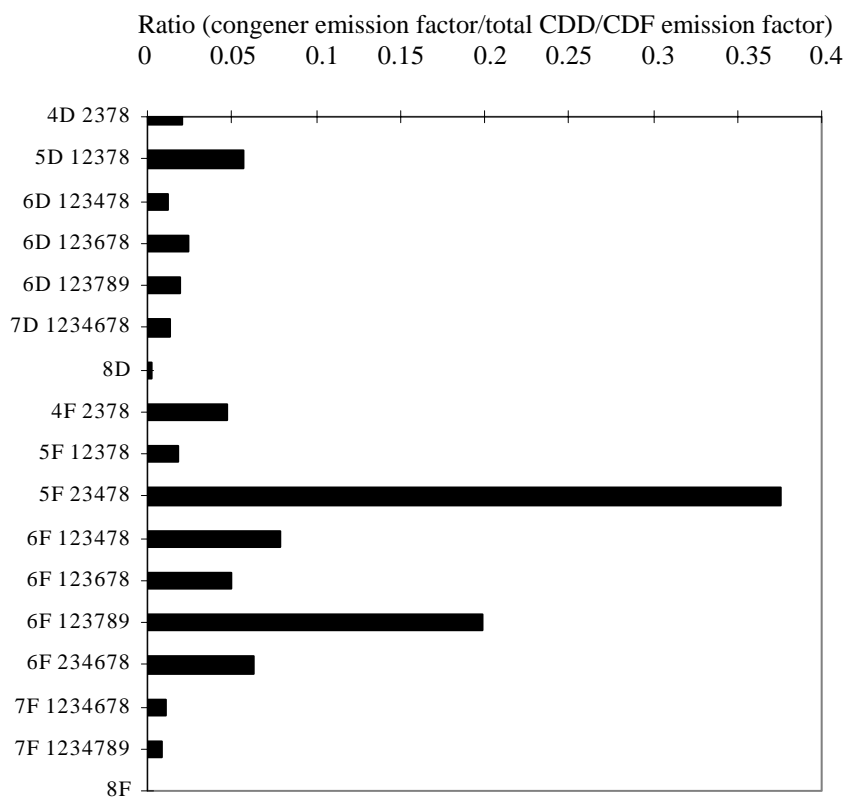
**Figure 3-16. Congener and congener group profiles for air emissions from medical waste incinerators equipped with a wet scrubber and fabric filter.**



**Figure 3-17. Congener and congener group profiles for air emissions from the crematoria at Camellia Memorial Lawn Crematorium and Woodlawn Cemetery.**

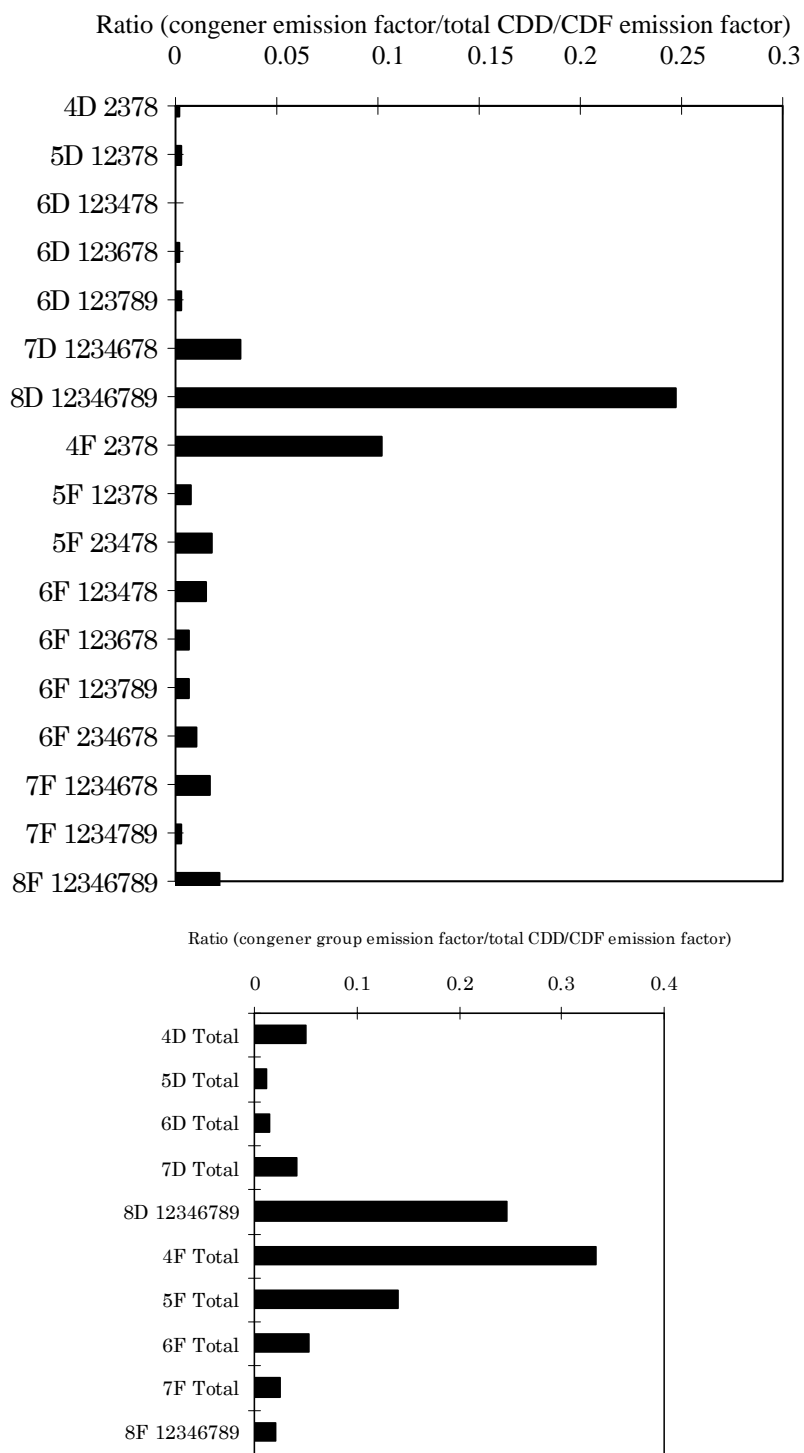
Source: CARB (1990c); U.S. EPA (1999f).



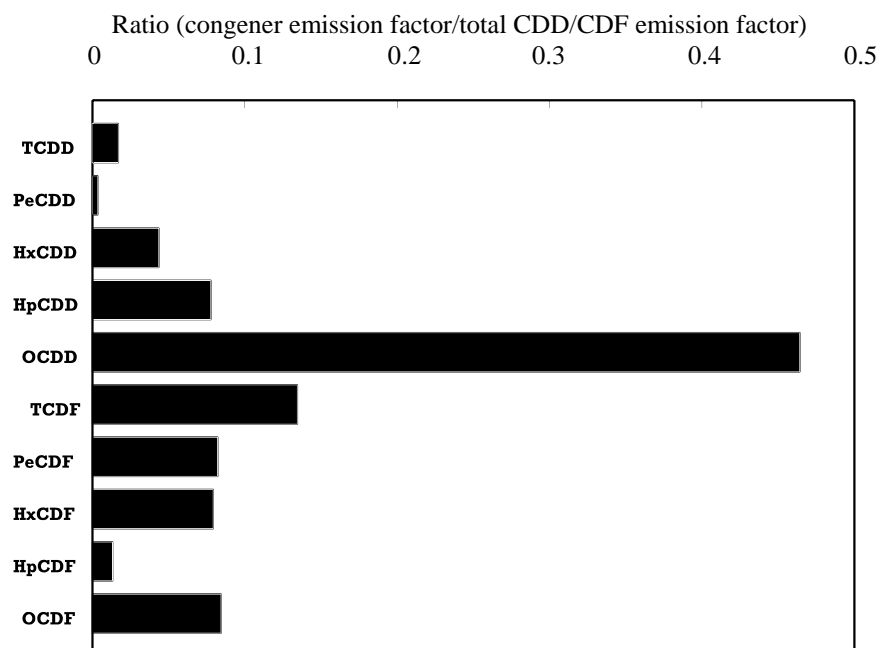
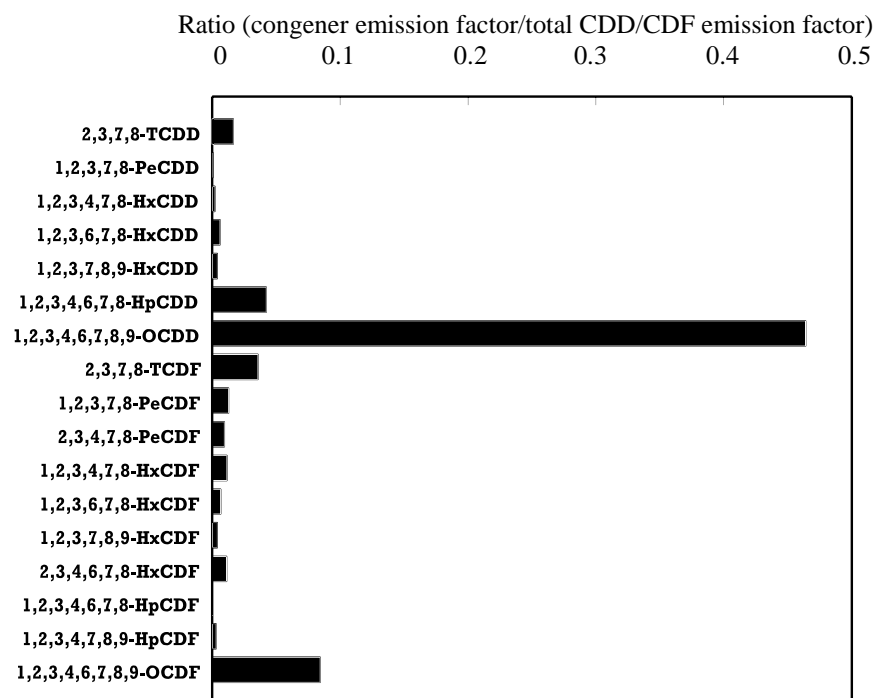


**Figure 3-18. Congener profile for air emissions from the University of Georgia animal crematorium.**

Source: U.S. EPA (2000e).



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



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

Source: CARB (1991a); nondetects set equal to zero.

## **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 measurement 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 emissions from tailpipe measurements on Swedish cars. Approximately 20 to 220 pg I-TEQ<sub>DF</sub> from tetra- and penta-CDDs/CDFs were reported per kilometer driven for four cars running on leaded gasoline. For this study, an unleaded gasoline was used, with tetramethyl lead (0.15 g/L, or 0.57 g/gal) and 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

1 mixture of chlorinated and brominated scavengers (Marklund et al., 1990). Also, the lead  
2 content of the fuel used (0.15 g lead/L), although the normal lead content for Swedish fuels at the  
3 time, was higher than the lead content of leaded gasoline in the United States during the late  
4 1980s (lowered to 0.1 g lead/gal, or 0.026 g lead/L effective January 1, 1986). Marklund et al.  
5 (1987) reported a striking similarity between the TCDF and PeCDF congener profiles in the car  
6 exhausts and those found in emissions from municipal waste incinerators. For two cars running  
7 on unleaded gasoline, CDD/CDF emissions were below the detection limit (DL), which  
8 corresponded to approximately 13 pg I-TEQ<sub>DF</sub>/km driven.

9 Table 4-1 presents a summary of the results of Marklund et al. (1987) and subsequent  
10 studies, which are discussed below. Tables 4-2 and 4-3 present the results of tailpipe emission  
11 studies reported for diesel-fueled trucks and cars, respectively. The results of studies of leaded  
12 gasoline-fueled cars are shown in Table 4-4 and those for unleaded gasoline-fueled cars in Tables  
13 4-5 and 4-6. Figures 4-1, 4-2, and 4-3 present congener and congener group profiles for  
14 emissions from diesel-fueled vehicles, leaded gasoline-fueled vehicles, and unleaded gasoline-  
15 fueled vehicles, respectively.

16 Virtually no testing of vehicle emissions for CDDs/CDFs in the United States has been  
17 reported. In 1987, the California Air Resources Board (CARB) produced a draft report on the  
18 testing of the exhausts of four gasoline-fueled cars and three diesel-fueled vehicles (one truck,  
19 one bus, and one car) (CARB, 1987a). However, CARB indicated to EPA that the draft report  
20 should not be cited or quoted to support general conclusions about CDDs/CDFs in motor vehicle  
21 exhausts because of the small sample size of the study and because the use of low-resolution  
22 rather than high-resolution mass spectrometry in the study resulted in high DLs and inadequate  
23 selectivity in the presence of interferences (Lew, 1993).

24 CARB stated that the results of a single sample from the heavy-duty diesel truck could be  
25 reported, because congeners from most of the homologue groups were present in the sample at  
26 levels that could be detected by the analytical method and there were no identified interferences  
27 in this sample. This test was conducted under steady-state conditions (50 km/hr) for 6 hr with an  
28 engine with a fuel economy of 5.5 km/L. The TEQ emission factor of this one sample was  
29 equivalent to 7,190 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (7,290 pg I-TEQ<sub>DF</sub>/L) of fuel burned. Assuming a fuel  
30 economy of 5.5 km/L yields an emission factor of 1,307 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/km (1,325 pg I-  
31 TEQ<sub>DF</sub>/km). Assuming that nondetect values are zero yields TEQ emission factors of 3,280 pg

1 TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (3,720 pg I-TEQ<sub>DF</sub>/L) of fuel burned and 596 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/km (676 pg I-  
2 TEQ<sub>DF</sub>/km) driven (Lew, 1996).

3 Haglund et al. (1988) sampled exhaust gases from three different vehicles (one car fueled  
4 with leaded gasoline and one with unleaded gasoline and a heavy-duty diesel truck) for the  
5 presence of brominated dibenzo-*p*-dioxins (BDDs) and brominated dibenzofurans (BDFs). The  
6 authors concluded that the dibromoethane scavenger added to the tested gasoline probably acted  
7 as a halogen source. TBDF emissions were measured as 23,000 pg/km in the car with leaded  
8 gasoline and 240 pg/km in the car with unleaded gasoline. TBDD and PeBDF emissions were  
9 measured as 3,200 and 980 pg/km, respectively, in the car with leaded gasoline. All BDDs/BDFs  
10 were below DLs in the diesel truck emissions.

11 Bingham et al. (1989) analyzed the exhausts of four cars using leaded gasoline (uniformly  
12 having the following lead and organics content: 0.45 g/L tetramethyl lead, 0.22 g/L  
13 dichloroethane, and 0.2 g/L dibromoethane) and the exhaust of one car using unleaded gasoline.  
14 Analytical results and DLs were reported for only 5 of the 17 toxic CDD/CDF congeners. TEQ  
15 emission rates for the cars using leaded fuel, based on detected congeners only, ranged from 1 to  
16 39 pg I-TEQ<sub>DF</sub>/km. CDDs/CDFs were not detected in the exhaust from the vehicle using  
17 unleaded fuel; the total TEQ emission rate for this car, based on one-half the DLs for the five  
18 reported congeners, was 20 pg I-TEQ<sub>DF</sub>/km.

19 Marklund et al. (1990) tested Swedish cars fueled with commercial fuels, measuring  
20 CDD/CDF emissions before and after the muffler. Both new and old vehicles were tested. The  
21 tests were done on three cars using unleaded gasoline and two cars using leaded gasoline (0.15 g  
22 Pb/L with dichloroethane and dibromoethane scavengers). CDDs/CDFs were not detected in the  
23 fuels at a DL of 2 pg I-TEQ<sub>DF</sub>/L but were detected at a level of 1,200 pg I-TEQ<sub>DF</sub>/L in the new  
24 semisynthetic engine lube oil used in the engines. The test driving cycle used (31.7 km/hr as a  
25 mean speed, 91.2 km/hr as a maximum speed, and 17.9% of time spent idling) yielded fuel  
26 economies ranging from approximately 9 to 10 km/L (22 to 24 miles/gal) in the various cars.  
27 The reported ranges of emission factors were

- 28
- 29 • Leaded gas, before muffler: 2.4 to 6.3 pg I-TEQ<sub>DF</sub>/km (21 to 60 pg I-TEQ<sub>DF</sub>/L of fuel  
30 consumed)
- 31
- 32 • Leaded gas, in tailpipe: 1.1 to 2.6 pg I-TEQ<sub>DF</sub>/km (10 to 23 pg I-TEQ<sub>DF</sub>/L)

- Unleaded gas, catalyst-equipped, measured in tailpipe: 0.36 pg I-TEQ<sub>DF</sub>/km (3.5 pg I-TEQ<sub>DF</sub>/L)
- Unleaded gas, before muffler: 0.36 to 0.39 pg I-TEQ<sub>DF</sub>/km (3.5 pg I-TEQ<sub>DF</sub>/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<sub>DF</sub>/L) was realized in this diesel fuel test than in the gasoline tests conducted (5 pg I-TEQ<sub>DF</sub>/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<sub>DF</sub>-WHO<sub>98</sub>/L (1,080 pg I-TEQ<sub>DF</sub>/L)
- Unleaded fuel (catalyst-equipped): 7.9 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (7.2 pg I-TEQ<sub>DF</sub>/L)
- Unleaded fuel (not catalyst-equipped): 60.2 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (50.9 pg I-TEQ<sub>DF</sub>/L)
- Diesel fuel: 24.8 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (20.8 pg I-TEQ<sub>DF</sub>/L)

In 1991, 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. Tables 4-2 through 4-6 show the results from tests that were not conducted under normal operating conditions with commercial fuels and for which congener-specific emission results were presented in Hutzinger et al. (1992).

- Leaded fuel: 72 to 1,417 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (52 to 1,184 pg I-TEQ<sub>DF</sub>/L)
- Unleaded fuel (not catalyst-equipped): 102 to 181 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (96 to 177 pg I-TEQ<sub>DF</sub>/L)
- Unleaded fuel (catalyst-equipped): 9.6 to 28 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (10 to 26 pg I-TEQ<sub>DF</sub>/L)
- Diesel fuel (cars): 12 to 140 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (10 to 130 pg I-TEQ<sub>DF</sub>/L)
- Diesel fuel (trucks): 79 to 82 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (70 to 81 pg I-TEQ<sub>DF</sub>/L)

Although no specific details on the methodology used were provided, Hagenmaier (1994) reported that analyses of emissions of a diesel-fueled bus run either on steady-state or on 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<sub>DF</sub>/km; range, 11.7 to 18.7 pg I-TEQ<sub>DF</sub>/km; standard deviation, 3.5 pg I-TEQ<sub>DF</sub>/km) was a factor of 3 below the average of the two city driving tests (49.9 pg I-TEQ<sub>DF</sub>/kg; range, 3 to 96.8 pg I-TEQ<sub>DF</sub>/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<sub>DF</sub>/km with a standard deviation of 38.3 pg I-TEQ<sub>DF</sub>/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 depicts the results of the analysis. I-TEQ values ranged from 2 to 18 pg I-TEQ/m<sup>3</sup>, 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 3.46 to 5.33 pg I-TEQ/g of exhaust particles. Suspended PM was also collected from an electrostatic precipitator (ESP) connected to a highway tunnel. The I-TEQ for the suspended PM was 242 pg I-TEQ/g, two orders of magnitude higher than the I-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 7.13 to 14 pg I-TEQ/g of 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 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 the tunnel monitors are detecting 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.

Rappe et al. (1988) reported the CDD/CDF content of two air samples (60 m<sup>3</sup> per sample) collected from a tunnel in Hamburg, Germany, in January 1986 to be 0.44 and 0.59 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/m<sup>3</sup> (0.42 and 0.58 pg I-TEQ<sub>DF</sub>/m<sup>3</sup>). 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-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 downhill lanes. Emission rates for light-duty and heavy-duty vehicle classes in the uphill and downhill lanes 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 weekend measurements).

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
- 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 miles per hour (mph) and vehicles 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<sub>DF</sub> 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<sub>DF</sub>), 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. During the same period, background concentrations were determined outside the tunnel. 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<sub>DF</sub> concentration in the air sampled with the filter with PUF device

was 74 to 78% of the value obtained with the 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<sub>DF</sub>/m<sup>3</sup> for tunnel air vs. 35 fg I-TEQ<sub>DF</sub>/m<sup>3</sup> for outside air; filter only: 100 fg I-TEQ<sub>DF</sub>/m<sup>3</sup> for tunnel air vs. 58 fg I-TEQ<sub>DF</sub>/m<sup>3</sup> 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-November 1995, Gertler et al. (1996, 1998) conducted a study at the Fort McHenry Tunnel in Baltimore, Maryland. 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 vehicles. The air volume entering and leaving the tunnel bore that is used by most of the heavy-duty vehicles (i.e., approximately 25% of the vehicles using the bore are heavy-duty) 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 vehicles 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 vehicles, are presented in Table 4-11. The average TEQ emission factor was reported to be 182 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/mile (172 pg I-TEQ<sub>DF</sub>/km). The major uncertainties identified by the study authors were tunnel air volume measurement, sampler flow volume control, and analytical measurement of CDDs/CDFs.

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 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 dominates 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 or diesel fuel. For reference year 2000, the 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 traveled (VMT). The estimates include calculations by month, road type, and vehicle type. To develop the VMT, OAQPS relied on the data supplied by the Federal Highway Administration (FHWA).

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:

<u>Vehicle Type</u>	<u>Billion km</u>
• 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:

<u>Vehicle Type</u>	<u>Billion km</u>
• 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 VMT), and buses accounted for 10 billion km (6.4 billion VMT) (U.S. DOC, 1997). In 1992, diesel-fueled trucks accounted for 14.4% of total truck vehicle km driven; gasoline-fueled trucks accounted for the remaining 85.6% (U.S. DOC, 1995b). 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 vehicle kilometers driven (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, 1995a). In 1987, diesel-fueled trucks accounted for 17.2% of total truck kilometers driven (U.S. DOC, 1995b). 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 liters for 2000. The activity level for each equipment type is:

<u>Vehicle Type</u>	<u>Million Liters</u>
• Recreational equipment, 2-stroke engines:	2,032.77
• Construction and mining equipment, 2-stroke engines:	102.21
• Industrial equipment, 2-stroke engines:	1.14
• Lawn and garden equipment, 2-stroke engines:	1,192.40
• Agricultural equipment, 2-stroke engines:	3.40
• Commercial equipment, 2-stroke engines:	79.49
• Logging equipment, 2-stroke engines:	26.50
• Recreational equipment, 4-stroke engines:	1,782.93
• Construction and mining equipment, 4-stroke engines:	473.18
• Industrial equipment, 4-stroke engines:	579.16
• Lawn and garden equipment, 4-stroke engines:	8,100.78
• Agricultural equipment, 4-stroke engines:	306.62
• Commercial equipment, 4-stroke engines:	3,255.45
• Logging equipment, 4-stroke engines:	37.85
• Airport ground support equipment, 4-stroke engines:	7.57
• Industrial equipment, 4-stroke engines, other oil field equipment:	124.92
• Pleasure craft, 2-stroke:	3,607.50
• Pleasure craft, 4-stroke:	1,374.10
• Railroad, 4-stroke:	3.79

For off-highway diesel-driven vehicles, diesel railroad equipment, and diesel commercial marine vessels, OAQPS calculated national activity levels of 40,125.37, 12,491.86, and 7,684.39 million liters, respectively, for reference year 2000. For diesel commercial marine vessels, the national activity level comprises port emissions (5,905.24 million liters) and underway emissions (1,968.41 million liters). The activity level for each type of diesel railroad equipment is:

<u>Diesel Locomotive Type</u>	<u>Million Liters</u>
• Class I locomotives:	10,561.30
• Class II/III locomotives:	700.30
• Passenger trains:	230.91
• Commuter trains:	215.77
• Yard locomotives:	794.94

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 are provided for informational purposes only, as emission estimates for these years could not be calculated due to the lack of emission factors.

*Farm use* includes sales for use in tractors, irrigation pumps, and other agricultural machinery, as well as fuel used for crop drying, smudge pot fuel, and space heating of buildings. Sales were 11,352.45 million liters in 1987 and 13,158.1 liters in 1995.

*Railroad use* includes sales to railroads for any use, including diesel fuel for locomotives and fuel used for heating buildings operated by railroads. Sales were 10,788.42 liters in 1987 and 12,980.18 liters in 1995.

*Marine vessels* 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 liters in 1987 and 8,854.08 liters in 1995.

*Off-highway use* includes sales for use in (a) construction equipment, including earthmoving equipment, cranes, stationary generators, air compressors, etc., and (b) sales for

nonconstruction off-highway uses such as logging. Sales were 5,905.24 liters in 1987 and 8,225.7 liters 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 are developed below 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<sub>DF</sub>/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 dichloroethane and dibromoethane as scavengers (1.1 to 6.3 pg I-TEQ<sub>DF</sub>/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<sub>DF</sub>/L of fuel (approximately 129 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/km [108 pg I-TEQ<sub>DF</sub>/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<sub>DF</sub>/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<sub>DF</sub>/L (approximately 7.2 to 142 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/km [5.2 to 118 pg I-TEQ<sub>DF</sub>/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) is 532 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (450 pg I-TEQ<sub>DF</sub>/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 is approximately 53 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/km (45 pg I-TEQ<sub>DF</sub>/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 the average emission factor developed above (53 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/km [45 pg I-TEQ<sub>DF</sub>/km], assuming nondetect values are zero) with the estimate for kilometers driven by leaded gasoline-fueled vehicles in 1987 (708 billion km) suggests that 37.5 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (31.9 g I-TEQ<sub>DF</sub>) 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 leaded gasoline-fueled vehicles, in conjunction with the emission factor of 53 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/km (45 pg I-TEQ<sub>DF</sub>/km), yields an annual emission of 1.6 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (1.3 g I-TEQ<sub>DF</sub>) 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<sub>DF</sub>/km. Marklund et al. (1990) reported emission factors of 0.36 and 0.39 pg I-TEQ<sub>DF</sub>/km for two noncatalyst-equipped cars and an emission factor of 0.36 pg I-TEQ<sub>DF</sub>/km for one catalyst-equipped car. Hagenmaier et al. (1990) reported an emission factor of 5.1 pg I-TEQ<sub>DF</sub>/km for one noncatalyst-equipped car and 0.7 pg I-TEQ<sub>DF</sub>/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<sub>DF</sub>/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<sub>DF</sub>/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

1 catalyst-equipped cars (Hagenmaier et al. 1990; Schwind et al., 1991; Hutzinger et al., 1992) is  
2 15.6 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (14.9 pg I-TEQ<sub>DF</sub>/L) (see Table 4-6). A low confidence rating is  
3 assigned to this emission factor because the European fuels and emission control technology used  
4 may have differed from U.S. fuels and technology and also because the emission factor range is  
5 based on tests with only three catalyst-equipped cars.

6 OAQPS calculated emissions for reference year 2000 for dioxins and furans from  
7 gasoline-fueled vehicles using the final version of the MOBILE6 model. On-road emissions  
8 were calculated by converting the emission factor of 15.6 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (14.9 pg I-  
9 TEQ<sub>DF</sub>/L) to a milligram per mile basis using a conversion factor of 3.78e-09 and assuming a  
10 fuel economy of 21.5 miles/gal. The new emission factor was then multiplied by the  
11 corresponding county-level VMT in miles per year. The off-highway gasoline equipment  
12 emission estimates for reference year 2000 were developed by multiplying the mean emission  
13 factor of 15.6 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (14.9 pg I-TEQ<sub>DF</sub>/L) by 2000 activity estimates developed  
14 from NONROAD model runs prepared for the National Emissions Inventory. The activity  
15 estimates represent county-level gasoline consumption in gallons. The emission factor was  
16 converted from pg/L to mg/gallon by multiplying by a conversion factor of 3.78e-09. The use of  
17 these methodologies resulted in national estimates for reference year 2000 of 7 g TEQ<sub>DF</sub>-WHO<sub>98</sub>  
18 (6.7 g I-TEQ<sub>DF</sub>) for on-highway gasoline vehicles and 0.36 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (0.35 g I-TEQ<sub>DF</sub>) for  
19 off-highway gasoline equipment.

20 Applying the same emission factors from Gertler et al. (1996, 1998) and assuming an  
21 average fuel economy of 10 km/L yields an emission factor of 1.6 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/km (1.5 pg  
22 I-TEQ<sub>DF</sub>/km). Applying this emission factor to the estimate derived for VKD in 1995 by all  
23 gasoline-fueled vehicles (2,947 billion km) suggests that 4.7 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (4.4 g I-TEQ<sub>DF</sub>)  
24 were emitted from vehicles using unleaded fuels in 1995. Applying the same emission factors to  
25 the estimate derived above for VKD in 1987 by unleaded gasoline-fueled vehicles (2,231 billion  
26 km) suggests that 3.6 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (3.3 g I-TEQ<sub>DF</sub>) may have been emitted in 1987. The  
27 emission estimates for all reference years were assigned a low confidence rating on the basis of  
28 the low rating given to the emission factor.

29 *Diesel fuel.* Limited data are available upon which to base an evaluation of the extent of  
30 CDD/CDF emissions resulting from diesel fuel combustion, and these data address only  
31 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 (1987a) and Gullett and Ryan (1997). CARB reported a relatively high emission factor of 676 pg I-TEQ<sub>DF</sub>/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<sub>DF</sub>/km (mean of 29 pg I-TEQ<sub>DF</sub>/km).

The results of several tailpipe studies conducted in Europe have also been published. Marklund et al. (1990) reported no emissions at a detection limit of 100 pg I-TEQ<sub>DF</sub>/L (or 18 pg I-TEQ<sub>DF</sub>/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<sub>DF</sub>/L (or 6 to 15 pg I-TEQ<sub>DF</sub>/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 detection limit of 1 pg/L of fuel consumed for individual congeners. For diesel-fueled cars, Hagenmaier et al. (1990) reported an emission factor of 24 pg I-TEQ<sub>DF</sub>/L (or approximately 2.4 pg I-TEQ<sub>DF</sub>/km) for one tested car. Schwind et al. and Hutzinger et al. reported emission factors of 5 to 13 pg I-TEQ<sub>DF</sub>/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<sub>DF</sub> or TEQ<sub>DF</sub>-WHO<sub>98</sub>. 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<sub>DF</sub>/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 (1987a) 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;

1 and (c) technology differences likely existed between the 1988 Norwegian and the 1987 and  
2 1995 U.S. vehicle fleets.

3 The tunnel study conducted in Baltimore, Maryland, by Gertler et al. (1996, 1998) shares  
4 the disadvantages of all tunnel studies relative to studies that directly measured CDDs and CDFs  
5 in tailpipe emissions. Specifically, tunnel studies rely on indirect measurements (rather than  
6 tailpipe measurements), which may introduce bias, and the emission factors calculated from  
7 these studies reflect driving conditions of only the vehicle fleet using the tunnel and not  
8 necessarily of the overall vehicle fleet under other driving conditions.

9 However, the Gertler et al. study does have strengths that are lacking in the Oehme et al.  
10 (1991) tunnel study, and it has advantages over the two U.S. diesel truck tailpipe studies,  
11 including: (a) the study was conducted in the United States (fairly recently) and thus reflects  
12 current U.S. fuels and technology, (b) virtually no vehicle using the tunnel used leaded gasoline,  
13 (c) the tunnel walls and streets were cleaned 1 week prior to the start of sampling and, in  
14 addition, the study analyzed road dust and determined that resuspended road dust contributed  
15 only about 4% of the estimated emission factors, (d) heavy-duty vehicles comprised, on average,  
16 a relatively large percentage (25.7%) of vehicles using the tunnel, and (e) a large number of  
17 heavy-duty vehicles—approximately 33,000—passed through the tunnel during the sampling  
18 period, which generates confidence that the emission factor is representative of interstate trucks.

19 Considering the strengths and weaknesses of the available emission factor data from the  
20 tailpipe and tunnel studies, the mean TEQ emission factor reported by Gertler et al. (1996,  
21 1998)—182 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/km (172 pg I-TEQ<sub>DF</sub>/km)—is assumed to represent the best  
22 current estimate of the average emission factor for on-road diesel-fueled trucks. This emission  
23 factor is assigned a low confidence rating because it may not be representative of emission rates  
24 for the entire fleet of diesel-fueled trucks under the wide array of driving conditions encountered  
25 on the road.

26 For reference year 2000, OAQPS developed national CDD/CDF TEQ emission estimates  
27 for on-highway diesel vehicles, off-highway diesel equipment, diesel railroad equipment, and  
28 diesel commercial marine vessels. For on-highway diesel vehicles, OAQPS combined the  
29 calculated mean emission factors from Gertler et al. (1996, 1998) with the OAQPS estimate for  
30 vehicle miles driven. The pg/km emission factors were first converted to a mg/mile basis using a  
31 conversion factor of 1.61e-09. OAQPS estimated national emissions of 65.4 g TEQ<sub>DF</sub>-WHO<sub>98</sub>

(61.7 g I-TEQ<sub>DF</sub>) 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 2000 emissions, 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<sub>DF</sub>-WHO<sub>98</sub> (21 g of I-TEQ<sub>DF</sub>), 4.3 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (4 g of I-TEQ<sub>DF</sub>), and 6.8 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (6.4 g of I-TEQ<sub>DF</sub>) 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<sub>DF</sub>-WHO<sub>98</sub>/km (1.5 pg I-TEQ<sub>DF</sub>/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<sub>DF</sub>-WHO<sub>98</sub> (31.5 g of I-TEQ<sub>DF</sub>) 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<sub>DF</sub>-WHO<sub>98</sub> (26.3 g of I-TEQ<sub>DF</sub>) 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, 2003d) and a conversion factor of 1.61E-09 g-km/pg-mile to obtain emission factors of 0.51 ng I-TEQ<sub>DF</sub>/L and 0.54 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/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 liters), marine vessels (7,068.35 million liters), and railroad use (10,801.5 million liters), EPA estimates the

following emissions for 1987: 8.8 g of I-TEQ<sub>DF</sub> (9.4 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) for off-highway equipment; 3.6 g of I-TEQ<sub>DF</sub> (3.8 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) for marine vessels; and 5.5 g of I-TEQ<sub>DF</sub> (5.8 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) for railroad use. Similarly, using the 1995 activity factors for off-highway equipment (21,409.71 million liters), marine vessels (8,864.81 million liters), and railroad use (12,995.91 million liters), EPA estimates the following emissions for 1995: 11 g of I-TEQ<sub>DF</sub> (12 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) for off-highway equipment; 4.5 g of I-TEQ<sub>DF</sub> (4.8 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) for marine vessels; and 6.6 g of I-TEQ<sub>DF</sub> (7 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) 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 the reference year 1987, wood energy consumption is estimated to have been 2,437 trillion British thermal units (Btu), or 3.2% of 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 wood fuel consumption in 1987, 72% in 1995, and 80% in 2000. The residential sector accounted for 35% of total wood fuel consumption in 1987, 25% in 1995, and 18% in 2000. The commercial sector accounted for approximately 2% of total wood fuel 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; Gillespie, 2002). 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 in 1987, 1995, and 2000, respectively. 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). The emissions from combustion of a variety of wood fuels were measured (natural beech wood, natural wood chips, uncoated chipboard chips, waste wood chips from building demolition, and household paper and plastic waste). 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 burn of beech wood sticks: 0.77 ng I-TEQ<sub>DF</sub>/kg  
(0.064 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup>)

- Closed-door burn of beech wood sticks: 1.25 ng I-TEQ<sub>DF</sub>/kg  
(0.104 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup>)
- Closed-door burn of household waste: 3,230 ng I-TEQ<sub>DF</sub>/kg  
(114.4 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup>)

#### Furnaces

- Natural wood chips: 0.79 to 2.57 ng I-TEQ<sub>DF</sub>/kg
- Chipboard chips (uncoated): 0.29 to 0.91 ng I-TEQ<sub>DF</sub>/kg
- Waste wood chips from building demolition: 26 to 173.3 ng I-TEQ<sub>DF</sub>/kg

Vickelsoe 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 emissions as low as possible). Total CDD/CDF emissions varied widely for the 24 different 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 flue gas concentration for wood stoves (considering wood and stove types) were reported to be 1.9 and 0.18 ng Nordic TEQ/Nm<sup>3</sup>, 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<sub>DF</sub>/kg (average of about 2.2 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub>/kg (average of about 20 ng I-TEQ<sub>DF</sub>/kg). The authors noted that the



1 measured emission factors for fireplaces were considerably higher than those reported by others  
2 (see Bröker et al., 1992, below) and assigned “great uncertainty” to the emission factors.

3 Bröker et al. (1992) reported results of a series of three tests with a wood stove and a  
4 fireplace. The average, minimum, and maximum emission factors measured for the wood stove  
5 tests ranged from 0.53 to 0.94 ng I-TEQ<sub>DF</sub>/kg. The geometric mean of the two average values  
6 was 0.71 ng I-TEQ<sub>DF</sub>/kg. The average of the minimum and maximum emission factors measured  
7 for the fireplace tests ranged from 0.2 to 1.06 ng I-TEQ<sub>DF</sub>/kg. The geometric mean of these two  
8 average values is 0.46 ng I-TEQ<sub>DF</sub>/kg.

9 Launhardt and Thoma (2000) conducted an investigation on organic pollutants from a  
10 domestic heating system using various solid biofuels. Tests were conducted using a multifuel  
11 furnace designed for domestic applications. Table 4-12 shows the average dioxin concentration  
12 in the flue gas for the four fuels used: spruce wood, wheat straw, hay, and triticale. The  
13 concentrations in the flue gas range from 52 to 891 pg TEQ/m<sup>3</sup>.

14 Environment Canada (2000) conducted a study on the release of dioxins and furans into  
15 the atmosphere by residential wood combustors. The study analyzed two wood stoves believed  
16 to be representative of stoves used in Canada: a conventional wood stove that was popular in the  
17 early 1980s and an advanced combustion, noncatalytic, EPA-certified wood stove. Each stove  
18 was tested using hard maple and black spruce wood. Results from the study ranged from 0.222  
19 to 0.952 ng I-TEQ/kg wood (see Table 4-13). Because these tests took place in North America  
20 using indigenous wood and they included the analysis of an EPA-certified wood stove, the mean  
21 value of the Environment Canada study (0.5 ng I-TEQ/kg wood) will be used to determine the  
22 national emission estimate for residential burning of clean wood in fireplaces and stoves. This  
23 emission factor is assigned a low confidence rating because it is judged to be nonrepresentative  
24 of all residential wood combustion (e.g., home fireplaces).

25 Several studies have reported that combustion of treated or manufactured wood in stoves  
26 and fireplaces can result in significantly higher CDD/CDF emission factors. A few researchers  
27 (e.g., Vikelsoe et al., 1993) have reported high CDD/CDF emission rates when  
28 pentachlorophenol (PCP)-contaminated wood is combusted in residential wood stoves and  
29 furnaces. The European Inventory (Quab and Fermann, 1997) used the results of these studies to  
30 derive best estimates of CDD/CDF emission factors for combustion of “slightly contaminated  
31 wood (excluding PCP)” and “PCP-contaminated wood” to be 50 and 500 ng I-TEQ<sub>DF</sub>/kg,

1 respectively. Although it is likely that there is some residential combustion of these types of  
2 wood in the United States, there are no corresponding activity level data upon which to base a  
3 national annual estimate of emissions.

#### 4 5 **4.2.1.2. Activity Level Information**

6 In 1987, 22.5 million households in the United States burned wood (EIA, 1991). Wood  
7 was used as the primary heating fuel in 5 million of those households and as a secondary source  
8 for aesthetic purposes (i.e., in fireplaces) in 17.4 million (EIA, 1991, 1997b). Lower numbers  
9 were reported for 1995: wood was reported to be used as the primary fuel in only 3.53 million  
10 households (EIA, 1997b). More rural low-income households consumed wood as a primary  
11 heating fuel than did other sectors of the population. The majority of these households used  
12 wood-burning stoves as the primary heating appliance. Although fireplaces were the most  
13 common type of wood-burning equipment in the residential sector, only 7% of fireplace users  
14 reported using fireplaces for heating an entire home (EIA, 1991, 1994).

15 In 1987, residential wood consumption was 852 trillion Btu (44.8 million metric tons),  
16 or 35% of total U.S. consumption (EIA, 1997b). Residential wood consumption in 1995 was 596  
17 trillion Btu (31.4 million metric tons), or 25% of total U.S. wood energy consumption (EIA,  
18 1997b). The Energy Information Administration (EIA) estimated that 433 trillion Btu (23  
19 million metric tons) of wood were consumed in residences in 2000 (EIA, 2003b). These  
20 production estimates are given high confidence ratings because they are based on recent  
21 government survey data.

22 OAQPS developed emission estimates for residential wood combustion from the results  
23 of a study by EPA's Emission Factor and Inventory Group (U.S. EPA, 2001d). The activity data  
24 for residential wood combustion were based on the type of combustion unit. Activity data for  
25 wood stoves and fireplaces with inserts were estimated on the basis of total amount of wood  
26 consumed in a year. OAQPS used 1997 national activity data to extrapolate an estimate for 1999  
27 by applying a growth rate factor based on wood energy consumption data from EIA. Activity  
28 data for fireplaces were estimated on the basis of number of homes in the U.S. with usable  
29 fireplaces, as reported by the U.S. Census Bureau.

30 OAQPS assumed that the extent of wood consumption in residential combustion units is  
31 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 level estimates in million metric tons per year for each wood combustion category are:

- Fireplaces: 2.79 million metric tons/yr
- Fireplaces with inserts, certified catalytic: 0.92 million metric tons/yr
- Fireplaces with inserts, certified noncatalytic: 0.47 million metric tons/yr
- Fireplaces with inserts, noncertified: 7.64 million metric tons/yr
- Noncatalytic wood stoves: 0.26 million metric tons/yr
- Catalytic wood stoves: 0.64 million metric tons/yr
- Conventional wood stoves: 10.60 million metric tons/yr

### 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 the best estimate of the emission factor (0.5 ng I-TEQ<sub>DF</sub>/kg wood) 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<sub>DF</sub>, 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, e, f, g). 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<sub>DF</sub>/kg of wood burned.

In the second study (CARB, 1990e), 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

1 it burned a mixture of permitted fuel supplemented by urban wood waste at a ratio of 7:3. From  
2 this study, the average TEQ emission factor for total CDDs/CDFs was calculated to be 0.82 ng I-  
3 TEQ<sub>DF</sub>/kg of wood burned.

4 In the third study (CARB, 1990f), CDDs/CDFs in the emissions from twin fluidized-bed  
5 combustors designed to burn wood chips for the generation of electricity were measured. The air  
6 pollution control device (APCD) system consisted of ammonia injection for controlling nitrogen  
7 oxides and a multicyclone and ESP for controlling PM. During testing, the facility burned wood  
8 wastes and agricultural wastes allowed by existing permits. From this study, the average TEQ  
9 emission factor for total CDDs/CDFs was calculated to be 1.32 ng I-TEQ<sub>DF</sub>/kg of wood burned.

10 In the fourth study (CARB, 1990g), CDDs/CDFs in the emissions from a quad-cell wood-  
11 fired boiler were measured. During testing, the fuel consisted of wood chips and bark. The flue  
12 gases passed through a multicyclone and an ESP before entering the stack. From this study, the  
13 average TEQ emission factor for total CDDs/CDFs was calculated to be 0.5 ng I-TEQ<sub>DF</sub>/kg of  
14 wood burned.

15 NCASI (1995) presented stack emission test results for five boilers burning bark or wood  
16 residues. One of these facilities, equipped with a multicyclone, normally burned bark in  
17 combination with sludge and coal. Another facility, equipped with an ESP, normally fired  
18 pulverized coal. The other three facilities were spreader-stokers equipped with multicyclones or  
19 ESPs. Although stack gas flow rates were obtained during these tests, accurate measurements of  
20 the amounts of bark and wood fired were not made and had to be estimated from steam  
21 production rates. The average TEQ emission factor for these facilities was 0.46 ng TEQ<sub>DF</sub>-  
22 WHO<sub>98</sub>/kg (0.4 ng I-TEQ<sub>DF</sub>/kg of feed).

23 The mean of the emission factors derived from the four CARB studies and five NCASI  
24 studies—0.6 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg wood (0.56 ng I-TEQ<sub>DF</sub>/kg wood), assuming nondetect values  
25 are zero—is used in this document as most representative of industrial wood combustion. This  
26 emission factor was assigned a medium confidence rating. However, these mean emission  
27 factors may not be appropriate for the combustion of waste wood containing elevated chlorine  
28 content. NCASI (1995) concluded that CDD/CDF emissions from facilities burning salt-laden  
29 wood residue may be considerably higher than those from facilities burning salt-free wood.

30 Similarly, Umweltbundesamt (1996) reported the results of stack gas testing at  
31 approximately 30 facilities of varying design types burning various types of wood fuel. He noted

1 that CDD/CDF emissions were elevated when the combustion conditions were poor, as  
2 evidenced by elevated carbon monoxide emissions and/or when the fuel contained elevated  
3 chlorine levels. Umweltbundesamt attributed the correlation between elevated CDD/CDF  
4 emissions and elevated chlorine content of the fuel to the fire-retardant effects of chlorine, which  
5 may have inhibited complete combustion. The chlorine content of untreated wood and of bark  
6 were reported as 0.001 to 0.01% by weight and 0.01 to 0.02% by weight, respectively.  
7 Chipboard can contain up to 0.2% chlorine by weight because of binding agents used to  
8 manufacture the chipboard. Preservative-treated wood and PVC-coated wood were reported to  
9 contain chlorine contents as high as 1.2 and 0.3% by weight, respectively.

10 The facility tested by EPA in 1987 (U.S. EPA, 1987a) was located at a lumber products  
11 plant that manufactures overlay panels and other lumber wood products. Nearly all the wood fed  
12 to the lumber plant had been stored in sea water adjacent to the facility and therefore had a  
13 significant concentration of inorganic chloride. The wood-fired boiler tested was a three-cell  
14 dutch oven equipped with a waste heat boiler. The feed wood was a mixture of bark, hogged  
15 wood, and green and dry planer shavings. The exhaust gases from the boiler passed through a  
16 cyclone and fabric filter prior to discharge from the stack. From this study, an average emission  
17 factor for total CDDs/CDFs of 1,020 ng/kg of wood burned (with a range of 552 to 1,410 ng/kg)  
18 was reported for the three collected samples. An average TEQ emission factor of 17.1 ng  
19 I-TEQ<sub>DF</sub>/kg of wood burned (with a range of 7.34 to 22.8 ng/kg) was estimated by EPA using  
20 measured congener group concentrations and concentrations of 2,3,7,8-TCDD and 2,3,7,8-  
21 TCDF. Similar emission factors were reported by Luthe et al. (1998) from testing conducted  
22 during the 1990s at four Canadian coastal, salt-laden wood-fueled boilers—1.4, 2.6, 17.4, and  
23 27.6 ng I-TEQ<sub>DF</sub>/kg of wood combusted.

24 The overall average of the five tested facilities in Canada and the United States is 13.2 ng  
25 I-TEQ<sub>DF</sub>/kg of wood combusted. The confidence rating assigned to this emission factor is low  
26 because it is based on reporting of limited congener data at one U.S. facility and testing at four  
27 non-U.S. sources and because the fraction of salt-laden wood combusted across facilities is likely  
28 to have been highly variable.

29 For the reference year 2000, NCASI provided congener-specific estimates of CDD/CDF  
30 releases from the pulp and paper industry, including emissions from wood residue-fired boilers  
31 (Gillespie, 2002). The emission factors were taken from the “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 0.018  $\mu\text{g TEQ}_{\text{DF-}}^{\text{WHO}_{98}}$ /ton of wood (see Table 4-15).

#### **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 (2003a) 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 an ad hoc telephone survey of mills in the Pacific Northwest (Oregon and Washington) to produce a conservative estimate—254,000 metric tons (0.8% of the estimated 32.6 million metric tons of industrial wood consumed that year)—of the amount of salt-laden wood burned at U.S. pulp and paper mills in 1995. NCASI suspected that a similar fraction of industrial wood combusted in 1987 by pulp and paper mills was salt-laden (Gillespie, 1998).

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

1 responding mills in Washington reported some combustion of salt-laden wood. The estimated  
2 percentage of salt-laden wood to total wood consumption in the Washington mills was 17%.

3 As noted above, the majority of industrial wood combustion (97%) occurs in two  
4 industries: the paper and allied products industry and the lumber and wood products industry.  
5 The relative amounts of wood combusted by each of these two industries were the same in 1990  
6 and 1992, the only years for which these statistics are readily available (EIA, 1991, 1994).  
7 Therefore, it can be assumed that the percentage of total wood combusted nationally by the  
8 lumber and wood products industry that is salt-laden is the same percentage as for the paper and  
9 allied products industry, 0.8%. Therefore, the total percentage of wood combusted by industry  
10 that is salt-laden is 1.6%. For the reference years 1987, 1995, and 2000, this equates to 0.5, 0.5,  
11 and 0.8 million metric tons, respectively. These activity level estimates are assigned a low  
12 confidence rating because they are possibly nonrepresentative of the activity levels for the source  
13 category combusting salt-laden wood.

#### 14 15 **4.2.2.3. Emission Estimates**

16 Applying the average TEQ emission factor from the four CARB and five NCASI studies  
17 (0.6 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg wood [0.56 ng I-TEQ<sub>DF</sub>/kg wood]) to the estimated quantities of  
18 nonsalt-laden wood burned by industrial facilities in 1987 (33.2 million metric tons), 1995 (32.6  
19 million metric tons), and 2000 (51.5 million metric tons) yields estimated TEQ emissions to air  
20 of 19.9 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (18.6 g I-TEQ<sub>DF</sub>) in 1987, 19.6 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (18.3 g I-TEQ<sub>DF</sub>) in  
21 1995, and 30.9 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (28.8 g I-TEQ) in 2000.

22 Applying the average TEQ emission factor from the five studies on boilers combusting  
23 salt-laden wood (13.2 ng I-TEQ<sub>DF</sub>/kg wood) to the estimated quantities of salt-laden wood burned  
24 by industrial facilities in 1987 (0.5 million metric tons), 1995 (0.5 million metric tons), and 2000  
25 (0.8 million metric tons) yields estimated TEQ emissions to air of 6.6 g I-TEQ<sub>DF</sub> in both 1987  
26 and 1995 and 10.6 g I-TEQ<sub>DF</sub> in 2000.

27 Total emissions for 1987, 1995, and 2000 are estimated to have been 26.5, 26.2, and 41.5  
28 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (25.2, 24.9, and 39.4 g I-TEQ<sub>DF</sub>), respectively. Of the 2000 estimate, NCASI  
29 estimates that 0.74 g TEQ<sub>DF</sub>-WHO<sub>98</sub>/yr of dioxins were emitted from pulp and paper wood-fired  
30 boilers (Gillespie, 2002). As noted above, the total emissions are based on tests conducted at  
31 nine facilities in two industries that account for 97% of total industrial wood fuel combustion.



1 The remaining 3% of industrial combustion and the combustion of wood by the commercial  
2 sector (for which no reliable activity level estimates are available) may not be well represented  
3 by the emission factors used above, particularly if poorly controlled combustors or treated wood  
4 (e.g., treated with PCP or plastics) are burned. The emission estimates for 1987, 1995, and 2000  
5 are given a low confidence level because the activity level estimates were assigned a low  
6 confidence rating .

#### 7 8 **4.2.3. Solid Waste from Wood Combustion (Residential and Industrial)**

9 The measurement of CDDs/CDFs in chimney soot and bottom ash from wood-burning  
10 stoves and fireplaces has been reported by several researchers (Bumb et al., 1980; Nestricks and  
11 Lamparski, 1982, 1983; Clement et al., 1985b; Bacher et al., 1992; Van Oostam and Ward, 1995;  
12 and Dumler-Gradl et al., 1995a).

13 Bumb et al. (1980) detected TCDDs (nondetects to 0.4 µg/kg), HxCDDs (0.2 to 3 µg/kg),  
14 HpCDDs (0.7 to 16 µg/kg), and OCDD (0.9 to 25 µg/kg) in residues from the wall of a home  
15 fireplace and from the firebrick of another home fireplace; for lack of a suitable analytical  
16 method, analysis was not performed for PeCDDs. Neither of the fireplaces sampled by Bumb et  
17 al. (1980) had burned preservative-treated wood.

18 Nestricks and Lamparski (1982, 1983) expanded the research of Bumb et al. by conducting  
19 a survey of CDD concentrations in chimney soot from residential wood-burning units in three  
20 rural areas of the United States. Samples were collected from the base of six chimneys in each of  
21 the three study areas. Samples were not collected from units where any type of treated or  
22 manufactured wood had been burned. For lack of a suitable analytical method, analysis was not  
23 performed for PeCDDs. The results of this survey are summarized in Table 4-16. There was  
24 wide variation in the results across soot samples, with standard deviations for congeners and  
25 congener groups often equal to or exceeding the mean value; however, CDDs in each congener  
26 group were detected in the soot from almost all sampled units. The authors concluded that the  
27 results did not appear to present any easily discernible patterns with respect to geographic region,  
28 furnace operational parameters, or wood fuel type. They attributed the wide variability observed  
29 to differences in design of the units, which affected the sampling point or the conditions at the  
30 sampling point, and possible contamination of the fuel wood.

Clement et al. (1985b) 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. Clement et al. (1985b) also presents total CDD/CDF concentration data for bottom ashes from outside open-air burning of wood. No analyses were reported for individual congeners. The results for the congener groups are presented below. The quantities of ashes produced by the outside open-air burning test were not presented; hence it is not possible to readily determine the quantities of CDDs/CDFs disposed of.

<u>Congener group</u>	<u>Concentration (µg/kg)</u>
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<sup>3</sup>/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 dominated the CDDs in each congener group except octa. Also, the less-chlorinated congener groups dominated the more highly chlorinated congener groups for both the CDDs and the CDFs. The TEQ content of the chimney soot was 755 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (720 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub>-WHO<sub>98</sub>/kg (211 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub> content of 7,706 ng I-TEQ<sub>DF</sub>/kg, or 20 to 90 times greater than the concentrations found in the soot from the other two tested stoves.

Dumler-Gradl et al. (1995a) analyzed chimney soot samples collected by chimney sweeps from 188 residences in Bavaria. The summary results of the survey, the largest published survey of its kind to date, are presented in Table 4-18. As in Nestrack and Lamparski (1982, 1983) and Clement et al. (1985b), 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.

Location	Type of residual	I-TEQDF (ng/kg)	I-TEQDF (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 ashes (“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-

1 impregnated woods. These samples had total TEQs (assumed to be I-TEQs) ranging from 0.07  
2 to 89 ppt, the highest being the fly ash samples (52 and 89 ppt). The quantities produced by the  
3 boilers that were tested were not reported; hence it is not possible to readily determine the  
4 quantities of CDDs/CDFs disposed of.

5 Carpenter (2001) reported the results of analyses of two ash samples from wood-burning  
6 facilities in New Hampshire. Both samples were from the burning of clean (i.e., untreated) wood  
7 chips, sawdust, and bark. The first sample was a combination of fly ash and bottom ash. The  
8 second sample was only fly ash, but it was a combination of fly ash from two wood-burning  
9 boilers. For the first sample, none of the 2,3,7,8-substituted congeners were detected at DLs that  
10 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.  
11 (All other congeners had a DL of 4.9 ng/kg.) For the second sample, all but two congeners were  
12 below DLs (which ranged from 0.379 to 0.831 ng/kg). The two congeners that exceeded DLs  
13 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  
14 that the nondetected congeners were not present, I-TEQ<sub>DF</sub> concentration is 0.011 ng/kg. The  
15 quantities of the ash produced were not reported.

16 In a CARB report of emissions from a wood waste-fired incinerator (CARB, 1990b), data  
17 are given for CDDs and CDFs for four ash samples. The concentrations of 2,3,7,8-substituted  
18 CDD/CDF congeners for each of those four tests were all below the method detection limits  
19 (MDLs) except for OCDD, which was detected in three samples at concentrations of 14, 18, and  
20 32 ng/kg, and 2,3,7,8-TCDF, which was detected in one sample at a concentration of 2.2 ng/kg.  
21 The MDLs for each CDD and CDF congener ranged from 0.63 ppt (for 2,3,7,8-TCDD) to 9.5 ppt  
22 (for HpCDF congeners). Total CDD and CDF values are given for each of the four samples.  
23 However, those values assume that nondetected congeners are at the MDL level. Consequently,  
24 the total CDD and total CDF values are biased high. The average of the four total CDD values is  
25 28.8 ng/kg (with a range of 20.3 to 44 ng/kg). The average of the four total CDF values is 21.9  
26 ng/kg (with a range of 16 to 26.9 ng/kg).

27 In CARB (1990e), data are presented for CDDs/CDFs for several samples of ESP waste  
28 ash from a wood-fired boiler. The report provides sample results for 2 weeks of sampling  
29 conducted at the facility. During the first week, the boiler burned fuels that were allowed by the  
30 facility permit; during the second week, the boiler burned a mixture containing 70% permitted  
31 fuel and 30% urban wood wastes. For the six samples collected over the 3 days of the first week,

1 many of the concentrations of CDD/CDF congeners in the ESP ash were below the DLs. The  
2 reported CDD concentrations in ESP waste ash ranged from 24 to 264 ng/kg, and the CDF  
3 concentrations ranged from 12 to 151 ng/kg. However, those values assume that nondetected  
4 congeners were present at the detection level. One sample did not have any nondetect values for  
5 CDDs. The total CDD concentration for this sample was 264 ng/kg, or about 11.4 ng/kg TEQ<sub>DF</sub>-  
6 WHO<sub>98</sub> (8.3 ng/kg I-TEQ<sub>DF</sub>). The TEQ<sub>DF</sub>-WHO<sub>98</sub> and I-TEQ<sub>DF</sub> CDF concentrations for this  
7 sample are both less than 1.5 ng/kg. These values are less than 1 ng/kg for the other five  
8 samples. All of the samples had some nondetects for the CDF analysis.

9 Six samples were also collected over 3 days during the second week of sampling, when  
10 the 70/30 permitted/urban wood waste mix was burned. For the samples from the second week,  
11 the CDD concentrations in ESP waste ash ranged from 1,365 to 3,190 ng/kg, and the CDF  
12 concentrations ranged from 2,866 to 11,282 ng/kg. CARB (1990e) assumed that nondetected  
13 congeners were present at the detection level; however, this is a reasonable estimate for this data  
14 set because there was only one nondetect value. Table 4-20 presents the average congener  
15 concentrations for these samples. The report did not present quantities of ESP ashes produced by  
16 the boiler; therefore, it is not possible to readily determine the quantities of CDDs/CDFs  
17 disposed.

18 Appendix II of Luthe et al. (1998) shows TEQ concentrations (assumed to be I-TEQ<sub>DF</sub>) in  
19 ashes collected from APCDs from “salt-laden” wood steam boilers. The I-TEQ<sub>DF</sub> content of  
20 ashes from three of the primary multiclone hoppers varied significantly, 0.0978, 0.186, and 9.375  
21 µg/kg. Two samples of ash were taken from the secondary multiclone hoppers. The secondary  
22 multiclone removes dust from the primary multiclone emissions; therefore, the ash is finer than  
23 primary dust. The I-TEQ<sub>DF</sub> values for the ash were 1.073 and 20.879 µg/kg. The I-TEQ<sub>DF</sub> values  
24 for two samples taken from the ESP that collects dust from the secondary multiclone emissions,  
25 which therefore is finer than multiclone dust, are 3.926 and 8.044 µg/kg. No data are given for  
26 individual congeners. In fact, because the reference discusses only “dioxins,” it is unclear  
27 whether the TEQ data are for CDDs or for CDDs plus CDFs. Quantities of collected ash were  
28 not given.

29 Table II of a report by Luthe et al. (1996) presents data for the “TEQs [assumed to be I-  
30 TEQs] on particulates from a secondary collection device for boilers at four paper mills burning  
31 salt-laden wood. Eight data points are given (two for each mill), the average of which is 3.6

1     μg/kg. The range of values is 1.3 to 8 μg/kg. As in Luthe et al. (1998), no data are given for  
2     individual congeners. It is also unclear whether the TEQ data are for CDDs or for CDDs plus  
3     CDFs. Quantities of collected ash are not given.

4             Table 5-16 of the National Dioxin Survey (U.S. EPA, 1987a) contains data indicating that  
5     the bottom ash from wood combustion from one source (it is not indicated whether it was a  
6     boiler) contained 140 ng/kg of 2,3,7,8-TCDD, 138,200 ng/kg of CDDs, and 7,400 ng/kg of  
7     CDFs. For a second wood combustion source, the ash contained no detectable 2,3,7,8-TCDD,  
8     but it did contain about 125 ng/kg of CDDs and nondetectable levels of CDFs. The fabric filter  
9     dust from the second source contained 100 ng/kg of 2,3,7,8-TCDD, 1,143,600 ng/kg of CDDs,  
10    and 315,600 ng/kg of CDFs. Specific data for congeners and for ash/dust quantities are not  
11    given.

12            NCASI also provided information on emissions from wood residue boiler ash for  
13    reference year 2000 (Gillespie, 2002). As with the boiler emissions, emission factors for the  
14    boiler ash were taken from the “NCASI Handbook of Chemical Specific Information for SARA  
15    Section 313 Form R Reporting.” Total TEQ concentrations were estimated to be 13.2 ng/kg.  
16    Because 72% of the total ash produced is landfilled, emission estimates were 2.21 g TEQ<sub>DF</sub>-  
17    WHO<sub>98</sub>/yr for ash landfilled and 0.62 g/yr for ash not landfilled (see Table 4-15). It is not known  
18    at this time whether the amount of dioxin in nonlandfilled ash results in an environmental  
19    release. Therefore, this value was not included in the inventory.

#### 21    **4.3. OIL COMBUSTION**

22            The two major categories of fuel oils that are burned by combustion sources are distillate  
23    oils and residual oils. These oils are further distinguished by grade: numbers 1 and 2 are  
24    distillate oils, 5 and 6 are residual oils, and 4 is either distillate oil or a mixture of distillate and  
25    residual oils. Number 6 fuel oil is sometimes referred to as Bunker C. Distillate oils are more  
26    volatile and less viscous than residual oils. They have negligible nitrogen and ash content and  
27    usually contain less than 0.3% sulfur (by weight). Distillate oils are used mainly in domestic and  
28    small commercial applications. The heavier residual oils (5 and 6), being more viscous and less  
29    volatile than distillate oils, must be heated for ease of handling and to facilitate proper  
30    atomization. Because residual oils are produced from the residue after the lighter fractions  
31    (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, 1995b).

#### **4.3.1. Residential/Commercial Oil Combustion**

No testing data could be located for the CDD/CDF content of air emissions from residential/commercial oil-fired combustion units in the United States. However, EPA (U.S. EPA, 1997b) 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 of oil) obtained from AP-42 (U.S. EPA, 1995b). The TEQ emission factor estimate 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 assigned a low confidence rating because they were developed from soot samples and may not be representative of the source category. These emission factors are presented in Table 4-21, and the congener group profile is presented in Figure 4-6.

Because the representativeness of the emission factor of 1987 emissions is uncertain, no national emission estimate is proposed at this time. For reference year 1995, a preliminary estimate of potential national TEQ emissions from this source category was made using the emission factor presented in Table 4-21 (190 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L [150 pg I-TEQ<sub>DF</sub>/L] of oil combusted). Distillate fuel oil sales to the residential/commercial sector totaled 39.7 billion L in 1995 (EIA, 1997a). Applying the emission factors from U.S. EPA (1997b) to this fuel oil sales estimate results in estimated emissions of 7.5 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (6 g I-TEQ<sub>DF</sub>) in 1995.

For reference year 1987, assuming a barrel of oil contains 158.99 liters, distillate fuel oil sales to the residential and commercial sector totaled 28.1 billion liters (177 million barrels) and 16.2 billion liters (102 million barrels), respectively (EIA, 1999). Likewise, residual oil sales to the commercial sector in 1987 totaled 6.7 billion liters (42 million barrels) (EIA, 1999). Using the emission factor presented in Table 4-21 (150 pg I-TEQ<sub>DF</sub>/L of oil combusted and 190 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L of oil combusted), EPA estimates that 4.22 g I-TEQ<sub>DF</sub> or 5.35 g TEQ<sub>DF</sub>-WHO<sub>98</sub> were emitted in 1987 for the residential sector for home heating with distillate oil. For the institutional/commercial sector, EPA estimates TEQ emissions of 1.34 g I-TEQ<sub>DF</sub> (1.54 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) for residual oil and 3.24 g I-TEQ<sub>DF</sub> (3.73 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) for distillate oil for the year

1 1987, using an emission factor of 200 pg I-TEQ<sub>DF</sub>/L of oil combusted (230 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L  
2 of oil combusted) (see Section 4.3.2). Because the representativeness of the emission factor for  
3 1987 emissions is uncertain, EPA has given this estimate a low confidence rating.

4 For reference year 1995, a low confidence estimate of potential national TEQ emissions  
5 from this source category was made using the same emission factors used for the 1987 estimates.  
6 Distillate fuel oil sales to the residential and commercial sector totaled 26.2 and 13.5 billion  
7 liters, respectively, in 1996 (EIA, 1997a). Applying the respective emission factors to these fuel  
8 oil sales estimates results in estimated emissions of 3.93 g I-TEQ<sub>DF</sub> (4.98 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) for  
9 the residential sector and 2.7 g I-TEQ<sub>DF</sub> (3.11 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) for the institutional/commercial  
10 sector in 1995. Residual oil sales to the commercial sector in 1995 totaled 3.7 billion liters (23  
11 million barrels) (EIA, 1999). Applying the emission factor of 200 pg I-TEQ<sub>DF</sub>/L of oil  
12 combusted (230 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L of oil combusted) (see Section 4.3.2) yields TEQ emissions  
13 of 0.73 g I-TEQ<sub>DF</sub> (0.84 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) for residual oil in 1995.

14 For reference year 2000, OAQPS developed national emission estimates for residual oil  
15 and distillate oil consumed in institutional/commercial heating and distillate oil consumed in  
16 residential heating. OAQPS used state-level 2000 activity data (EIA, 2003b), which were  
17 allocated to counties by the 1999 county-to-state proportion of employment for numerous SIC  
18 codes, as identified by the U.S. Census Bureau for 2000. OAQPS estimated that 2.82 billion L of  
19 residual oil and 12.7 billion L of distillate oil were consumed in institutional/commercial heating  
20 in 2000. Applying the emission factor of 230 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (200 pg I-TEQ<sub>DF</sub>/L) of oil  
21 combusted (see Section 4.3.2) yields TEQ emissions of 0.65 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (0.56 g I-TEQ<sub>DF</sub>)  
22 for residual oil and 2.92 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (2.53 g I-TEQ<sub>DF</sub>) for distillate oil for 2000. OAQPS  
23 estimated that 23.9 billion L of distillate oil were consumed for residential heating in 2000.  
24 Using the emission factors discussed above (U.S. EPA, 1997b), OAQPS estimated emissions of  
25 4.54 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (3.59 g I-TEQ<sub>DF</sub>) from distillate oil used for residential heating in 2000.  
26 These emission estimates for all years are given a low confidence rating because the emission  
27 factor was given a low confidence rating.  
28



#### 4.3.2. Utility Sector and Industrial Oil Combustion

Preliminary CDD/CDF emission factors were reported (U.S. EPA, 1997b) for oil-fired utility boilers using the results of boiler tests conducted over several years. The data are 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<sub>DF</sub> emission factor was reported to be 366 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (314 pg I-TEQ<sub>DF</sub>/L) of 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 is 93.6 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (83.1 pg I-TEQ<sub>DF</sub>/L) of oil burned when nondetect values are treated as zero.

The TEQ emission factors reported by EPRI (1994) are less than the median TEQ emission factor reported by EPA by a factor of 3 to 4 (U.S. EPA, 1997b). For purposes of this assessment, the EPA median and EPRI mean emission factors were averaged for an emission factor of 230 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (200 pg I-TEQ<sub>DF</sub>/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<sub>DF</sub>-WHO<sub>98</sub>/L (200 pg I-TEQ<sub>DF</sub>/L) to these residual fuel oil sales results in estimated TEQ emissions of 17.8 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (15.5 g I-TEQ<sub>DF</sub>) for 1987 and 10.7 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (9.3 g I-TEQ<sub>DF</sub>) 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, 2003b), which were allocated to counties by the 1999 county-to-state proportion of employment for numerous SIC codes, as identified by the U.S. Census Bureau for 2000. 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<sub>DF</sub>-WHO<sub>98</sub>/L (200 pg I-TEQ<sub>DF</sub>/L) to estimate 2000 TEQ emissions of 1.69 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (1.47 g I-TEQ<sub>DF</sub>) from residual oil consumption and 7.25 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (6.3 g I-TEQ<sub>DF</sub>) from distillate oil combustion. Emission estimates for all reference years were 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, 1997b) 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<sup>-</sup>/kg) were reported to contain 0.1 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup> (2,000 pg I-TEQ<sub>DF</sub>/kg) of 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<sup>-</sup>/kg) contained 0.2 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup> (4,800 pg I-TEQ<sub>DF</sub>/kg) of oil burned. The flue gases from a steam boiler consisting of a rotary cup burner fueled by processed spent oil (240 mg Cl<sup>-</sup>/kg) contained 0.3 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup> (6,000 pg I-TEQ<sub>DF</sub>/kg) of 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<sub>DF</sub>/kg of oil burned.

From these data, Bremmer et al. (1994) derived an average emission factor for combustion of used oil of 4,000 pg I-TEQ<sub>DF</sub>/kg of oil burned. Bremmer et al. also reported measuring CDD/CDF emissions from a river barge and a container ship fueled with gas oil (less than 2 ng/kg of organic chlorine). The exhaust gases contained from 0.002 to 0.2 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup>. From these data, Bremmer et al. derived an average emission factor for inland oil-fueled vessels of 1,000 pg I-TEQ<sub>DF</sub>/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, 2003). Of the 980 million metric tons of

1 coal consumed in 2000, 891 million metric tons (90.9%) were consumed by electric utilities,  
2 including independent power producers; 85.4 million metric tons (8.7%) were consumed by the  
3 industrial sector, including 26.2 million metric tons consumed by coke plants; and 3.7 million  
4 metric tons (0.4%) were consumed by residential and commercial sources (EIA, 2003). In 1995,  
5 coal consumption (872 million metric tons of coal) accounted for approximately 22% of the  
6 energy consumed from all sources in the United States (U.S. DOC, 1997). Of this total, 88.4%  
7 (771 million metric tons) were consumed by electric utilities; 11% (96 million metric tons) were  
8 consumed by the industrial sector, including consumption of 30 million metric tons by coke  
9 plants; and 0.6% (5.3 million metric tons) were consumed by residential and commercial sources  
10 (EIA, 1997b). Comparable figures for 1987 for total coal consumption of 759 million metric  
11 tons are as follows: consumption by electric utilities, 651 million metric tons; consumption by  
12 coke plants, 33.5 million metric tons; consumption by other industries, 68.2 million metric tons;  
13 and consumption by the residential and commercial sectors, 6.3 million metric tons (EIA, 1995c).  
14 These production estimates are assigned a high confidence rating because they are based on  
15 detailed studies specific to the United States.

16 The following two subsections discuss the results of relevant emission studies for the  
17 utility/industrial and residential sectors, respectively, and present annual TEQ emission estimates  
18 for reference years 1987, 1995, and 2000.

#### 20 **4.4.1. Utilities and Industrial Boilers**

21 Few studies have been performed to measure CDD/CDF concentrations in emissions  
22 from coal-fired plants. Those studies did not have the congener specificity or DLs necessary to  
23 fully characterize this potential source (U.S. EPA, 1987a; NATO, 1988; Wienecke et al., 1992).  
24 The results of more recent testing of coal-fired utility and industrial boilers in the Netherlands  
25 (Bremmer et al., 1994), the United Kingdom (Cains and Dyke, 1994; CRE, 1994), Germany  
26 (Umweltbundesamt, 1996), and the United States (Riggs et al., 1995; EPRI, 1994) have achieved  
27 lower DLs.

28 Bremmer et al. (1994) reported the results of emission measurements at two coal-fired  
29 facilities in the Netherlands. The emission factor reported for a pulverized coal electric power  
30 plant equipped with an ESP and a wet scrubber for sulfur removal was 0.35 ng I-TEQ<sub>DF</sub>/kg of  
31 coal combusted (0.02 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup> at 11% oxygen). The emission factor reported for a grass-

1 drying chain grate stoker equipped with a cyclone APCD was 1.6 ng I-TEQ<sub>DF</sub>/kg of coal fired  
2 (0.16 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup> at 11% oxygen).

3 Cains and Dyke (1994) reported an emission factor of 102 to 109 ng I-TEQ<sub>DF</sub>/kg of coal  
4 at a small-scale facility in the United Kingdom that was equipped with an APCD consisting of  
5 only a grit arrester. CRE (1994) reported results of testing at 13 commercial and industrial coal-  
6 fired boilers in the United Kingdom, with TEQ emission factors ranging from 0.04 to 4.8 ng I-  
7 TEQ<sub>DF</sub>/kg coal combusted (mean value of 0.6 ng I-TEQ<sub>DF</sub>/kg). CRE also reported testing results  
8 for one coal-fired power plant, 0.06 ng I-TEQ<sub>DF</sub>/kg of coal combusted. Umweltbundesamt  
9 (1996) reported that the I-TEQ<sub>DF</sub> content of stack gases from 16 coal-burning facilities in  
10 Germany ranged from 0.0001 to 0.04 ng I-TEQ<sub>DF</sub>/m<sup>3</sup>; however, the data provided in that report  
11 did not enable emission factors to be calculated.

12 In 1993, the U.S. Department of Energy (DOE) sponsored a project to assess emissions of  
13 hazardous air pollutants at coal-fired power plants. As part of the project, CDD/CDF stack  
14 emissions were measured at seven U.S. coal-fired power plants. The preliminary results of the  
15 project, concentrations in stack emissions, were reported by Riggs et al. (1995) and are  
16 summarized in Table 4-23. The levels reported for individual 2,3,7,8-substituted congeners were  
17 typically very low (less than or equal to 0.033 ng/Nm<sup>3</sup>) or not detected. In general, CDF levels  
18 were higher than CDD levels. OCDF and 2,3,7,8-TCDF were the most frequently detected  
19 congeners (at four of the seven plants). Table 4-24 presents characteristics of the fuel used and  
20 the APCD employed at each plant. Riggs et al. (1995) could not attribute variations in emissions  
21 between plants to any specific fuel or operational characteristic.

22 As mentioned in Section 4.3.2, EPRI sponsored the FCEM project to gather information  
23 of consistent quality on power plant emissions. Testing for CDD/CDF emissions was performed  
24 on four coal-fired power plants equipped with cold-sided ESPs. Two plants burned bituminous  
25 coal and two burned sub-bituminous coal. The results of the testing were integrated into the final  
26 results of the DOE project discussed above (Riggs et al., 1995) and published in 1994 (EPRI,  
27 1994). The average congener and congener group emission factors derived from this 11-facility  
28 data set, as reported in EPRI (1994), are presented in Table 4-25. Congener and congener group  
29 profiles for the data set are presented in Figure 4-8. The average emission factor, assuming  
30 nondetect values are zero, is 0.078 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (0.079 ng I-TEQ<sub>DF</sub>/kg) of 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.

Applying the TEQ emission factor of 0.078 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (0.079 ng I-TEQ<sub>DF</sub>/kg) of 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<sub>DF</sub>-WHO<sub>98</sub> (51.4 g I-TEQ<sub>DF</sub>) in 1987, 60.1 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (60.9 g I-TEQ<sub>DF</sub>) in 1995, and 69.5 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (70.4 g I-TEQ<sub>DF</sub>) in 2000. These emission estimates are assigned a medium confidence rating because the emission factor 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<sub>DF</sub>/kg coal combusted. 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<sub>DF</sub>/kg for 1987, 39.6 g I-TEQ<sub>DF</sub>/kg for 1995, and 35.4 g I-TEQ<sub>DF</sub>/kg of 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.

#### 4.4.2. Residential Coal Combustion

In the residential sector, coal is usually combusted in underfeed 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 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<sub>DF</sub>/m<sup>3</sup>, or 2.74 ng I-TEQ<sub>DF</sub>/kg) than for the “normal” coal (0.015 ng I-TEQ<sub>DF</sub>/m<sup>3</sup>, or 0.34 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub>/kg for anthracite coal and 5.7 to 9.3 ng I-TEQ<sub>DF</sub>/kg (midpoint of 7.5 ng I-TEQ<sub>DF</sub>/kg) for bituminous coal.

CDD/CDF emission factors were estimated (U.S. EPA, 1997b) 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, 1995b). The TEQ emission factors estimated (60 and 98.5 ng I-TEQ<sub>DF</sub>/kg of 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, 1997b). EPA stated that the estimated factors should be considered

1 representative of maximum emission factors because soot may not be representative of the PM  
2 actually emitted to the atmosphere. These emission factors are presented in Table 4-26; congener  
3 group profiles are presented in Figure 4-9.

4 Although the congener group profiles of the measurements by Thub et al. (1995) and the  
5 estimates by EPA (U.S. EPA, 1997b) are similar, the TEQ emission factors of the two studies  
6 differ by factors of 175 to 289. The emission factors used by Eduljee and Dyke (1996) to  
7 estimate national annual TEQ emissions from residential coal combustion in the United  
8 Kingdom fall in between the other two sets of estimates but are still about one to two orders of  
9 magnitude greater than the estimated emission factor for industrial and utility coal combustors  
10 (see Section 4.4.1).

11 For 1987 and 1995, preliminary estimates of potential national TEQs were derived using  
12 the emission factors of Eduljee and Dyke (1996). U.S. EPA (1997b) reported that 72.5% of the  
13 coal consumed by the residential sector in 1990 was bituminous and 27.5% was anthracite.  
14 Assuming that these relative proportions reflect the actual usage in 1987 and 1995, then  
15 application of the emission factors from Eduljee and Dyke (2.1 ng I-TEQ<sub>DF</sub>/kg of anthracite coal  
16 and 7.5 ng I-TEQ<sub>DF</sub> of bituminous coal) to the consumption values of 6.3 and 5.3 million metric  
17 tons in 1987 and 1995, respectively, (U.S. DOC, 1997) results in an estimated TEQ emission of  
18 37.9 and 32.0 g I-TEQ<sub>DF</sub> in 1987 and 1995, respectively. These estimates should be regarded as  
19 preliminary indications of possible emissions from this source category because the emission  
20 factor is judged to be clearly nonrepresentative of the sources. Further testing is needed to  
21 confirm the true magnitude of these emissions.

22 For 2000, OAQPS developed national emission estimates for coal combustion for  
23 residential heating. The activity level for residential coal combustion was taken from state-level  
24 2000 activity data (EIA, 2003b). Because EIA no longer disaggregates coal consumption into  
25 anthracite versus bituminous/lignite, OAQPS estimated each state's coal consumption using the  
26 state's 1999 proportion of anthracite versus bituminous/lignite to total coal consumption.  
27 Emissions were allocated to the county level as a proportion of state population in states that  
28 consume anthracite coal and bituminous and lignite coal for residential heating. OAQPS  
29 estimated that in 2000, 67,400 metric tons of anthracite coal and 343,000 metric tons of  
30 bituminous and lignite coal were consumed for residential heating. Applying the TEQ emission  
31 factors of 2.1 ng I-TEQ<sub>DF</sub>/kg of anthracite coal combusted and 7.5 ng I-TEQ<sub>DF</sub>/kg of bituminous

coal combusted (Eduljee and Dyke, 1996) to these production factors yields preliminary estimates of annual emissions of 0.14 g I-TEQ<sub>DF</sub> of anthracite coal and 2.6 g I-TEQ<sub>DF</sub> of bituminous/sub-bituminous coal in 2000.

#### **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, 1999b), 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 limits of detection. Consequently, the values overestimate actual concentrations.

EPA (U.S. EPA, 1999c, Section 3.3) 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<sub>DF</sub> and TEQ<sub>DF</sub>-WHO<sub>98</sub> values in columns 5 and 6. Because this does not constitute an environmental release, the values are not included in the inventory.



**Table 4-1. Descriptions and results of vehicle emission testing studies for CDDs and CDFs**

Study	Country	Fuel type	Scavenger <sup>a</sup>	Catalyst equipped	Number of test vehicles	TEQ emission factor <sup>b</sup> (pg/km driven)	Driving cycle; sampling location
CARB (1987a); Lew (1996)	United States	Diesel (truck)	No	NR	1	676–1325 <sup>c</sup> [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	No Yes	No No	2 2	0.36–0.39 2.4–6.3	FTP-73 test cycle; before muffler FTP-73 test cycle; before muffler
		Unleaded Leaded	No Yes	Yes No	1 2	0.36 1.1–2.6 <sup>d</sup>	FTP-73 test cycle; in tailpipe FTP-73 test cycle; in tailpipe
		Diesel (truck)	No	NR	1	Not detected (<18) <sup>c</sup>	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 <sup>c</sup> [6.0] 0.7 <sup>c</sup> [0.8] 108 <sup>c</sup> [129] 2.1 <sup>c</sup> [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	–	–	–	<sup>e</sup>	520 <sup>f</sup>  38 <sup>f</sup>  Avg = 280 9500 <sup>f</sup>  720 <sup>f</sup>  Avg = 5100	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
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 <sup>c</sup> [7.2–142] 9.6–17.7 <sup>c</sup> [10.2–18.1] 1–2.6 <sup>c</sup> [1–2.8] 1–13 <sup>c</sup> [1.2–14] 13–15 <sup>c</sup> [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)

**Table 4-1. Descriptions and results of vehicle emission testing studies for CDDs and CDFs (continued)**

Study	Country	Fuel type	Scavenger <sup>a</sup>	Catalyst equipped	Number of test vehicles	TEQ emission factor <sup>b</sup> (pg/km driven)	Driving cycle; sampling location
Gertler et al. (1996, 1998) (tunnel study)	United States	Diesel (truck)	—	—	8	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

<sup>a</sup>Except in Marklund et al. (1987), dichloroethane and dibromoethane were used as scavengers.

<sup>b</sup>Values listed are in units of I-TEQ<sub>DF</sub>. Values in brackets are in units of TEQ<sub>DF</sub>-WHO<sub>98</sub>.

<sup>c</sup>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 (1987a) for a 1984 heavy-duty diesel truck, 5.5 km/L (13.2 miles/gal), was used.

<sup>d</sup>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<sub>DF</sub>/km.

<sup>e</sup>Tests were conducted over portions of 4 days, with traffic rates of 8000–14,000 vehicles/day. Heavy-duty vehicles (defined as vehicles over 7 m in length) ranged from 4 to 15% of total.

<sup>f</sup>Emission factors are reported in units of pg Nordic TEQ/km driven; the values in units of I-TEQ<sub>DF</sub>/km are expected to be about 3 to 6% higher.

<sup>g</sup>Tests were conducted over 5 days, with heavy-duty vehicle rates of 1800–8700 vehicles per 12-hr sampling event. Heavy-duty vehicles accounted for 21 to 28% of all vehicles.

NR = Not reported

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

Congener/congener group	Automobile tailpipe emission study results				Mean emission factors	
	63 km/hr <sup>a</sup>	Idling (test no. 25) <sup>b</sup>	57 km/hr (test no. 24) <sup>b</sup>	57 km/hr (full load) (test no. 28) <sup>b</sup>	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	604.7	606.7
Total I-TEQ <sub>DF</sub> (nondetect set to 0)	20.8	100.7	10.4	129.6	65.4	
Total I-TEQ <sub>DF</sub> (nondetect set to ½ DL)	22.2 <sup>c</sup>	100.7	10.4	129.6		65.7
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect set to 0)	24.8	103.1	11.9	140.4	70	
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect set to ½ DL)	26.2	103.1	1.9	140.4		70.4

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

Congener/congener group	Automobile tailpipe emission study results				Mean emission factors	
	63 km/hr <sup>a</sup>	Idling (test no. 25) <sup>b</sup>	57 km/hr (test no. 24) <sup>b</sup>	57 km/hr (full load) (test no. 28) <sup>b</sup>	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	3,217	
Total CDD/CDF (nondetect set to ½ DL)	926.3	3,957	968	7,018		3,217

<sup>a</sup>Source: Hagenmaier et al. (1990).<sup>b</sup>Source: Schwind et al. (1991); Hutzinger et al. (1992).<sup>c</sup>An I-TEQ<sub>DF</sub> emission factor of 23.6 pg/L is reported in Hagenmaier et al. (1990); however, an I-TEQ<sub>DF</sub> 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 for diesel-fueled trucks (pg/L)**

Congener/congener group	Truck tailpipe study results			Mean emission factors	
	50 km/hr (test no. 40) <sup>a</sup>	90 km/hr (full load) (test no. 42) <sup>a</sup>	50 km/hr <sup>b</sup>	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	1,170	406.5	227,300	76,292	83,739
Total I-TEQ <sub>DF</sub> (nondetect set to 0)	81	70	3,720	1,290	
Total I-TEQ <sub>DF</sub> (nondetect set to ½ DL)	81	70	7,290		2,480
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect set to 0)	82	79	3,280	1,150	
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect set to ½ DL)	82	79	7,190		2,450

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

Congener/congener group	Truck tailpipe study results			Mean emission factors	
	50 km/hr (test no. 40) <sup>a</sup>	90 km/hr (full load) (test no. 42) <sup>a</sup>	50 km/hr <sup>b</sup>	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	1,080,500	362,538	
Total CDD/CDF (nondetect set to ½ DL)	4,340	2,778	1,104,700		370,596

<sup>a</sup>Source: Schwind et al. (1991); Hutzinger et al. (1992).<sup>b</sup>Source: Lew (1993, 1996).

ND = Not detected; value in parenthesis is the detection limit

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

Congener/congener group	Automotive tailpipe emission study results							Mean emission factors	
	FTP cycle <sup>a</sup>	63 km/hr <sup>b</sup>	Idling (test no. 12) <sup>c</sup>	Full load (test no. 13) <sup>c</sup>	64 km/hr (test no. 14) <sup>c</sup>	Rated power (test no. 15) <sup>c</sup>	FTP cycle (test no. 22) <sup>c</sup>	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	4,900
Total I-TEQ <sub>DF</sub> (nondetect set to 0)	65.9	1,075	≥52	≥300	≥1,184	≥56	419	≥450	
Total I-TEQ <sub>DF</sub> (nondetect set to ½ DL)	102	1,080	≥52	≥300	≥1,184	≥56	419		≥456
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect set to 0)	65.9	1,287	≥72	≥352	≥1,417	≥75	454	≥532	
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect set to ½ DL)	111	1,291	≥72	≥352	≥1,417	≥75	454		≥539

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

Congener/congener group	Automotive tailpipe emission study results							Mean emission factors	
	FTP cycle <sup>a</sup>	63 km/hr <sup>b</sup>	Idling (test no. 12) <sup>c</sup>	Full load (test no. 13) <sup>c</sup>	64 km/hr (test no. 14) <sup>c</sup>	Rated power (test no. 15) <sup>c</sup>	FTP cycle (test no. 22) <sup>c</sup>	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	≥49,066	
Total CDD/CDF (nondetect set to ½ DL)	23,940	85,937	6,199	≥36,326	94,597	74,160	19,480		≥49,212

<sup>a</sup>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).

<sup>b</sup>Source: Hagenmaier et al. (1990).

<sup>c</sup>Source: Schwind et al. (1991); Hutzinger et al. (1992).

NR = Not reported

ND = Not detected; value in parenthesis is the reported detection limit



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

Congener/congener group	Automotive tailpipe emission study results						Mean emission factors	
	FTP cycle <sup>a</sup>	63 km/hr <sup>b</sup>	FTP cycle (test no. 21) <sup>c</sup>	64 km/hr (test no. 17) <sup>c</sup>	64 km/hr (test no. 20) <sup>c</sup>	64 km/hr (test no. 31/2) <sup>c</sup>	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	979	998
Total 2,3,7,8-CDF	64	427.9	1,024	694	829	2,417	910.4	936
Total I-TEQ <sub>DF</sub> (nondetect set to 0)	6.4	50.9	96.4	122	144	177	99.5	
Total I-TEQ <sub>DF</sub> (nondetect set to ½ DL)	26.2	50.9	96.4	122	144	177		103
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect set to 0)	6.4	60.2	102	138	148	181	106	
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect set to ½ DL)	26.9	60.2	102	138	148	181		109

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

Congener/congener group	Automotive tailpipe emission study results						Mean emission factors	
	FTP cycle <sup>a</sup>	63 km/hr <sup>b</sup>	FTP cycle (test no. 21) <sup>c</sup>	64 km/hr (test no. 17) <sup>c</sup>	64 km/hr (test no. 20) <sup>c</sup>	64 km/hr (test no. 31/2) <sup>c</sup>	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	5,875	
Total CDD/CDF (nondetect set to ½ DL)	249	3,963	5,076	6,431	4,421	15,176		5,886

<sup>a</sup>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.

<sup>b</sup>Source: Hagenmaier et al. (1990).

<sup>c</sup>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 for unleaded gasoline-fueled automobiles (with catalytic converters) (pg/L)**

Congener/congener group	Automotive tailpipe emission study test results				Mean emission factors	
	63 km/hr <sup>a</sup>	64 km/hr (test no. 29) <sup>b</sup>	64 km/hr (test no. 30) <sup>b</sup>	64 km/hr (test no. 18) <sup>b</sup>	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	321
Total 2,3,7,8-CDF	70.1	156.6	310.8	263	200	201
Total I-TEQ <sub>DF</sub> (nondetect set to 0)	7.2	16	10.1	26.3	14.9	
Total I-TEQ <sub>DF</sub> (nondetect set to ½ DL)	7.2	16.2	16.8	26.4		16.6
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect set to 0)	7.8	17.1	9.6	28	15.6	
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect set to ½ DL)	7.8	17.3	18.3	28.1		17.9

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

Congener/congener group	Automotive tailpipe emission study test results				Mean emission factors	
	63 km/hr <sup>a</sup>	64 km/hr (test no. 29) <sup>b</sup>	64 km/hr (test no. 30) <sup>b</sup>	64 km/hr (test no. 18) <sup>b</sup>	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	1,095	1,133	910	
Total CDD/CDF (nondetect set to ½ DL)	483.4	928	1,087	1,133		945

<sup>a</sup>Source: Hagenmaier et al. (1990).<sup>b</sup>Source: Schwind et al. (1991); Hutzinger et al. (1992).

ND = Not detected; value in parenthesis is the reported detection limit

**Table 4-7. Total dioxin emission concentrations from heavy-duty diesel engines**

<b>Sample</b>	<b>Concentration in exhaust<sup>a</sup> (pg I-TEQ/m<sup>3</sup>)</b>	<b>Sample volume (m<sup>3</sup>)</b>
Stationary engine 1 (S1)	6.1	32.89
Stationary engine 2 (S2)	61 <sup>b</sup>	10.35
Stationary engine 3 (S3)	18 <sup>c</sup>	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

<sup>a</sup>Detection limit for sampling: 4.1 pg/m<sup>3</sup> for stationary samples, 4.5 pg/m<sup>3</sup> for truck samples.

<sup>b</sup>Analysis could not be confirmed.

<sup>c</sup>High analytical detection limit (11 pg/m<sup>3</sup>).

Source: Geueke et al. (1999).

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

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	161	294	187	26,000
I-TEQ	3.73	5.33	3.46	242

Source: Miyabara et al. (1999).

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

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	642	1030	925
I-TEQ	10.6	7.13	14

Source: Miyabara et al. (1999).

**Table 4-10. European tunnel study test results (pg/m<sup>3</sup>)**

Congener/congener group	Tunnel air Germany <sup>a</sup>	Tunnel air Germany <sup>a</sup>	Tunnel air Belgium <sup>b</sup>	Tunnel air Norway (workdays) <sup>c,d</sup>	Tunnel air Norway (weekend) <sup>c,d</sup>
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	2.782	2.31	0.84
Total 2,3,7,8-CDF	2.5	2.34	1.33	7.98	5.82
Total I-TEQ <sub>DF</sub> (nondetect set to 0)	0.58	0.42	0.096	0.91	0.48
Total I-TEQ <sub>DF</sub> (nondetect set to ½ DL)	0.59	0.44	0.096	0.91	0.48
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect set to 0)	0.73	0.55	0.106	1	0.49
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (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

<sup>a</sup>Source: Rappe et al. (1988).

<sup>b</sup>Source: Wevers et al. (1992).

<sup>c</sup>Source: Oehme et al. (1991).

<sup>d</sup>Listed values are the differences between the concentrations at the inlet and outlet of the northbound tunnel lanes.

DL = Detection limit

ND = Not detected; value in parenthesis is the detection limit

NR = Not reported



**Table 4-11. Baltimore Harbor tunnel study: estimated emission factors for heavy-duty diesel vehicles (pg/km)<sup>a</sup>**

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	147
1,2,3,4,6,7,8-HpCDD	0	401	729	111	2,438	963	2,080	960
OCDD	0	3,361	3,382	1,120	9,730	5,829	7,620	4,435
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
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	267
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	4,328	1,335	7,028	10,515	5,725
Total 2,3,7,8-CDF	95.7	1,108	1,684	1,684	784	1,371	1,362	1,107
Total I-TEQ <sub>DF</sub>	73.8	175	170	170	96	153	303	172
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	93.8	182	175	175	97	147	337	182
Total TCDD	245	0	140	165	311	109	97.3	152
Total PeCDD	110	21.9	83.3	35.6	174	0	165	84.2
Total HxCDD	677	0	753	54.5	2,009	1,666	2,971	1,162
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	4,435
Total TCDF	0	901	1,314	656	2,416	1,007	687	997
Total PeCDF	124	119	1,152	78.4	1,055	282	626	491
Total HxCDF	136	319	852	67.6	444	719	619	451
Total HpCDF	0	223	814	144	513	354	637	384
Total OCDF	0	239	401	175	416	534	370	305
Total CDD/CDF	1,291	5,987	10,390	2,638	22,766	12,434	18,168	10,525

**Table 4-11. Baltimore Harbor tunnel study: estimated emission factors for heavy-duty diesel vehicles (pg/km)<sup>a</sup>**  
**(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	
Heavy-duty vehicles as % of total vehicles	21.2	22	22.6	34	28.8	24.2	27.4	25.7

<sup>a</sup>Listed 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).

**Table 4-12. Average CDD/CDF concentration in flue gas**

<b>Fuel</b>	<b>Concentration (pg TEQ/m<sup>3</sup>)</b>	<b>Number of trials</b>
Spruce wood	52	7
Wheat straw	656	5
Hay (set-aside land)	891	4
Triticale (whole crop)	52	5

Source: Launhardt and Thoma (2000).

**Table 4-13. Results from Environment Canada residential wood stove analysis (pg TEQ/kg wood)**

Congener	U.S. EPA-certified						Conventional					
	Maple			Spruce			Maple			Spruce		
	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	846	1,012	998	486	496	628	298	331	269	228	198	240
Average (ng/kg wood)	0.952			0.537			0.299			0.222		

Source: Environment Canada (2000).

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

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 <sub>DF</sub>	0.82	0.85	0.4	0.41	0.56	0.58
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	0.84	0.87	0.46	0.46	0.6	0.62
Total CDD/CDF	38.69	38.93	14.593	14.674	24.155	24.294

CARB = California Air Resources Board

NCASI = National Council for Air and Stream Improvement

Sources: CARB (1990b, e, f, g); NCASI (1995).

**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 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	1.77e-02	7.43e+08	1.32e+01	6.19e+08 (ash not landfilled)
				2.21e+09 (ash landfilled)

NCASI = National Council for Air and Stream Improvement

Source: Gillespie (2002).

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

Congener/ congener group	U.S. east region <sup>a</sup>	U.S. west region <sup>a</sup>	U.S. central region <sup>a</sup>	German farmhouse <sup>b</sup>	Canadian wood stove <sup>c</sup>	Canadian fireplace <sup>c</sup>	Canadian wood stove <sup>d</sup>
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 <sup>e</sup>	522 <sup>e</sup>	1,831 <sup>e</sup>	35	NR	NR	ND (10)
1,2,3,6,7,8-HxCDD	250 <sup>e</sup>	522 <sup>e</sup>	1,831 <sup>e</sup>	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	3,450	4,175	21,437	525	NR	NR	2,454
Total 2,3,7,8-CDF	NR	NR	NR	3,680	NR	NR	659
Total I-TEQ <sub>Df</sub>	≥ 125	≥ 112	≥ 479	720	NR	NR	211
Total TEQ <sub>Df</sub> -WHO <sub>98</sub>	≥ 123	≥ 110	≥ 467	755	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

<sup>a</sup>Source: Nestrick and Lamparski (1982, 1983); mean values listed, six samples collected in each region.

<sup>b</sup>Source: Bacher et al. (1992).

<sup>c</sup>Source: Clement et al. (1985b).

<sup>d</sup>Source: Van Oostdam and Ward (1995); mean of two samples, nondetect values assumed to be zero.

<sup>e</sup>Analytical method could not distinguish between congeners; listed value is the sum of both congeners.

NR = Not reported

ND = Not detected; value in parenthesis is the reported detection limit

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

<b>Congener/congener group</b>	<b>Canadian wood stove ash</b>	<b>Canadian wood stove ash</b>	<b>Canadian wood stove ash</b>	<b>Canadian fireplace ash</b>
2,3,7,8-TCDD	NR	NR	NR	NR
1,2,3,7,8-PeCDD	NR	NR	NR	NR
1,2,3,4,7,8-HxCDD	NR	NR	NR	NR
1,2,3,6,7,8-HxCDD	NR	NR	NR	NR
1,2,3,7,8,9-HxCDD	NR	NR	NR	NR
1,2,3,4,6,7,8-HpCDD	NR	NR	NR	NR
OCDD	NR	NR	NR	NR
2,3,7,8-TCDF	NR	NR	NR	NR
1,2,3,7,8-PeCDF	NR	NR	NR	NR
2,3,4,7,8-PeCDF	NR	NR	NR	NR
1,2,3,4,7,8-HxCDF	NR	NR	NR	NR
1,2,3,6,7,8-HxCDF	NR	NR	NR	NR
1,2,3,7,8,9-HxCDF	NR	NR	NR	NR
2,3,4,6,7,8-HxCDF	NR	NR	NR	NR
1,2,3,4,6,7,8-HpCDF	NR	NR	NR	NR
1,2,3,4,7,8,9-HpCDF	NR	NR	NR	NR
OCDF	NR	NR	NR	NR
Total 2,3,7,8-CDD	NR	NR	NR	NR
Total 2,3,7,8-CDF	NR	NR	NR	NR
Total TEQ	NR	NR	NR	NR
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

NR = Not reported.

ND = Not detected; value in parenthesis is the reported detection limit

Source: Clement et al. (1985b).



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

Unit type	Fuel type	Number of samples	CDD/CDF concentrations in soot (ng I-TEQ <sub>DF</sub> /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. (1995a).

**Table 4-19. Fly ash from wood-working industry (ng/kg)**

<b>Congener/congener group</b>	<b>Average concentration</b>	<b>I-TEQ<sub>DF</sub></b>	<b>TEQ<sub>DF</sub>-WHO<sub>98</sub></b>
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
TOTAL TCDD TEQ		95–110	145–160
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
TOTAL CDF TEQ		89–90	89–90

Source: Pohlandt and Marutzky (1994).

**Table 4-20. Electrostatic precipitator waste ash from wood-fired industrial boiler (ng/kg)**

<b>Congener/congener group</b>	<b>Average concentration</b>	<b>I-TEQ<sub>DF</sub></b>	<b>TEQ<sub>DF</sub>-WHO<sub>98</sub></b>
2,3,7,8-TCDD Total TCDD	17.85 239	17.85 —	17.85 —
1,2,3,7,8-PeCDD Total PeCDD	30.67 226.83	15.33 —	30.67 —
1,2,3,4,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD Total HxCDD	20.33 26.33 23.33 300	2.03 2.63 2.33 —	2.03 2.63 2.33 —
1,2,3,4,6,7,8-HpCDD Total HpCDD	325 706.67	3.25 —	3.25 —
Total OCDD	786.67	0.79	0.08
TOTAL CDD	2,439.17	44.22	58.85
2,3,7,8-TCDF Total TCDF	285 2,713.33	28.5 —	28.5 —
1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF Total PeCDF	154.5 641.67 2,666.67	7.73 320.83 —	7.73 320.83 —
1,2,3,4,7,8-HxCDF 1,2,3,6,7,8-HxCDF 2,3,4,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF Total HxCDF	244.83 179.67 296.67 7.28 1,520	24.48 17.97 29.67 0.73 —	24.48 17.97 29.67 0.73 —
1,2,3,4,6,7,8-HpCDF 1,2,3,4,7,8,9-HpCDF Total HpCDF Total OCDF	147.67 21.33 248.33 48.33	1.48 0.21 — 0.05	1.48 0.21 — 0
TOTAL CDF	7,196.67	431.64	431.6
TOTAL DIOXINS/FURANS		475.64	490.44

Source: CARB (1990e, Table 30).

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

<b>Congener/ congener group</b>	<b>Mean facility emission factor (pg/L oil)</b>	<b>WHO- TEF</b>	<b>Emission factor (pg TEQ<sub>DF</sub>- WHO<sub>98</sub>/L oil)</b>	<b>I-TEF</b>	<b>Emission factor (pg I-TEQ<sub>DF</sub>/L oil)</b>
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
<b>TOTAL</b>			<b>190</b>		<b>149</b>

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

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

Congener/congener group	U.S. EPA (1997b) median emission factor <sup>a,b</sup>	EPRI (1994) mean emission factor <sup>a,c</sup>	
		Nondetect set to zero	Nondetect set to 1/2 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	1,453	2,766	3,047
Total 2,3,7,8-CDF	1,141	414	883
Total I-TEQ <sub>DF</sub>	314	83.1	147
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	366	93.6	167
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	3,179	3,931

<sup>a</sup>Assumes a density for residual fuel oil of 0.87 kg/L.

<sup>b</sup>Number of facilities not reported.

<sup>c</sup>Based on two cold-side power plants equipped with electrostatic precipitators.

NR = Not reported

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

Congener/congener group	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6	Plant 7
2,3,7,8-TCDD	ND (3.5)	ND (3.5)	1	ND (2)	ND (3.3)	ND (2.6)	ND (1.7)
1,2,3,7,8-PeCDD	ND (0.56)	ND (4.8)	ND (1.8)	ND (10)	ND (4.7)	ND (3.2)	ND (1.8)
1,2,3,4,7,8-HxCDD	ND (0.56)	ND (5.7)	ND (3.6)	ND (10)	ND (15.4)	ND (2.7)	ND (2)
1,2,3,6,7,8-HxCDD	ND (0.44)	5	ND (1.8)	ND (10)	ND (9.9)	ND (4.2)	ND (1.4)
1,2,3,7,8,9-HxCDD	ND (0.56)	4.9	ND (1.8)	ND (10)	ND (12.1)	ND (4.3)	ND (1.2)
1,2,3,4,6,7,8-HpCDD	ND (1.7)	29	ND (1.8)	ND (10)	ND (26.4)	4.3	2.4
OCDD	ND (12)	32	ND (14)	ND (20)	ND (131)	20	21.6
2,3,7,8-TCDF	ND (1.7)	8.1	7.8	ND (2)	ND (3.3)	13	0.7
1,2,3,7,8-PeCDF	ND (1)	ND (5.7)	7.2	ND (10)	ND (3.2)	ND (5.7)	ND (1.1)
2,3,4,7,8-PeCDF	2.4	ND (19)	6.6	ND (10)	ND (3.2)	ND (4.8)	ND (1.4)
1,2,3,4,7,8-HxCDF	3.3	16	8.4	ND (10)	ND (16.4)	ND (5.1)	ND (1.8)
1,2,3,6,7,8-HxCDF	1.1	ND (5)	2.9	ND (10)	ND (5.8)	ND (4)	ND (1.3)
1,2,3,7,8,9-HxCDF	ND (0.44)	11	ND (1.8)	ND (10)	ND (8.8)	ND (6.9)	ND (1.5)
2,3,4,6,7,8-HxCDF	ND (2)	ND (4.2)	3	ND (10)	ND (16.4)	ND (2.5)	ND (2)
1,2,3,4,6,7,8-HpCDF	2	29	6	ND (10)	ND (23)	ND (30)	ND (2.2)
1,2,3,4,7,8,9-HpCDF	ND (0.63)	ND (6.1)	ND (3.6)	ND (10)	ND (15.4)	ND (5)	ND (2.1)
OCDF	5.6	33	2.4	ND (20)	ND (131)	ND (19)	11.4
Total 2,3,7,8-CDD	0	71	1	0	0	24.3	24
Total 2,3,7,8-CDF	14	97	44.3	0	0	13	12.1
Total TCDD	1.8	12	12	NR	6.7	ND (2.6)	ND (55)
Total PeCDD	ND (1)	4.4	6	ND (10)	ND (4.7)	ND (3.2)	ND (32)
Total HxCDD	1.3	18	2.7	ND (10)	ND (26.3)	ND (4)	ND (24)
Total HpCDD	3.4	45	ND (2.4)	ND (10)	ND (26.4)	ND (14)	ND (8.1)
Total OCDD	ND (12)	32	ND (14)	ND (20)	ND (131)	20	21.6
Total TCDF	ND (5.2)	29	78	ND (2)	ND (3.3)	88	ND (37)
Total PeCDF	5.4	33	61	ND (10)	ND (6.6)	14	3
Total HxCDF	7.6	39	29	ND (10)	ND (16.4)	ND (5)	ND (27)
Total HpCDF	4.3	34	9	ND (10)	ND (29.5)	ND (20)	2.9
Total OCDF	5.6	33	2.4	ND (20)	ND (131)	ND (19)	11.4
Total CDD/CDF	29	279	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) <sup>a</sup>			
			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

<sup>a</sup>Temperature at pollution control device and stack.

ESP = Electrostatic precipitator

FF = Fabric filter

FGD = Flue gas desulfurization system

Source: Riggs et al. (1995).

**Table 4-25. CDD/CDF emission factors for coal-fired utility/industrial power plants (ng/kg coal)<sup>a</sup>**

Congener/congener group	Mean emission factor	
	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 <sub>DF</sub>	0.079	0.124
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	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

<sup>a</sup>Eleven-facility data set.

Source: EPRI (1994).



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

<b>Congener</b>	<b>“Salt” lignite<sup>a</sup></b>	<b>“Normal” lignite<sup>a</sup></b>	<b>Anthracite<sup>b</sup></b>	<b>Bituminous<sup>b</sup></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 <sup>c</sup>	22.37	3.38	NR	NR
Total 2,3,7,8-CDF <sup>c</sup>	13.6	3.2	NR	NR
Total I-TEQ <sub>DF</sub> <sup>c</sup>	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

<sup>a</sup>Source: Thub et al. (1995); listed results represent means of three flue gas samples.

<sup>b</sup>Source: U.S. EPA (1997b); 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.

<sup>c</sup>Values as reported in sources.

NR = Not reported

**Table 4-27. Coal-fired utility solid wastes**

<b>Congener</b>	<b>Mean concentration<sup>a</sup> (ng/kg)</b>	<b>Grams per year disposed of in solid waste<sup>b</sup> 1987</b>	<b>Grams per year disposed of in solid waste<sup>c</sup> 1995</b>	<b>I-TEQ<sub>DF</sub> /yr (g) 1995</b>	<b>TEQ<sub>DF</sub> WHO<sub>98</sub>/yr (g) 1995</b>
2,3,7,8-TCDD <sup>d</sup>	0.17	10	10	9.72	9.72
1,2,3,7,8-PeCDD <sup>d</sup>	0.25	14	14	7.15	14.3
1,2,3,4,7,8-HxCDD <sup>d</sup>	0.35	20	20	2	2
1,2,3,6,7,8-HxCDD <sup>d</sup>	0.28	16	16	1.6	1.6
1,2,3,7,8,9-HxCDD <sup>e</sup>	0.3	17	17	1.72	1.72
1,2,3,4,6,7,8-HpCDD <sup>f</sup>	0.59	33	34	0.34	0.34
OCDD <sup>g</sup>	10.54	593	603	0.6	0.6
2,3,7,8-TCDF <sup>h</sup>	0.19	11	11	1.09	1.09
1,2,3,7,8-PeCDF <sup>d</sup>	0.17	10	10	0.49	0.49
2,3,4,7,8-PeCDF <sup>d</sup>	0.17	10	10	4.86	4.86
1,2,3,4,7,8-HxCDF <sup>e</sup>	0.25	14	14	1.43	1.43
1,2,3,6,7,8-HxCDF <sup>d</sup>	0.18	10	10	1.03	1.03
2,3,4,6,7,8-HxCDF <sup>d</sup>	0.28	16	16	1.6	1.6
1,2,3,7,8,9-HxCDF <sup>d</sup>	0.24	14	14	1.37	1.37
1,2,3,4,6,7,8-HpCDF <sup>e</sup>	0.29	16	17	0.17	0.17
1,2,3,4,7,8,9-HpCDF <sup>d</sup>	0.35	20	20	0.2	0.2
OCDF <sup>i</sup>	0.59	33	34	0.03	<0.01
<b>TOTAL</b>				<b>35.41</b>	<b>41.98</b>

<sup>a</sup>Source: U.S. EPA (1999b, Table 2-9).

<sup>b</sup>Assumes that solid waste quantity for 1987 is 98.4% of 1995 quantity, based on total utility coal use in those years (see Section 4.4).

<sup>c</sup>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 (1999c). Assumes all waste characteristics are same as for comanaged wastes.

<sup>d</sup>All 17 analyses were nondetects.

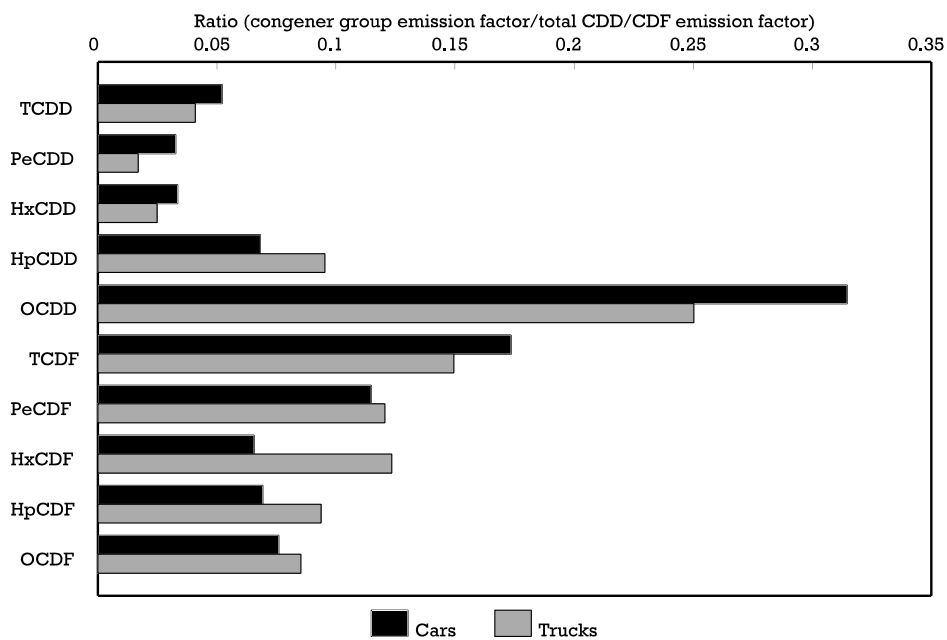
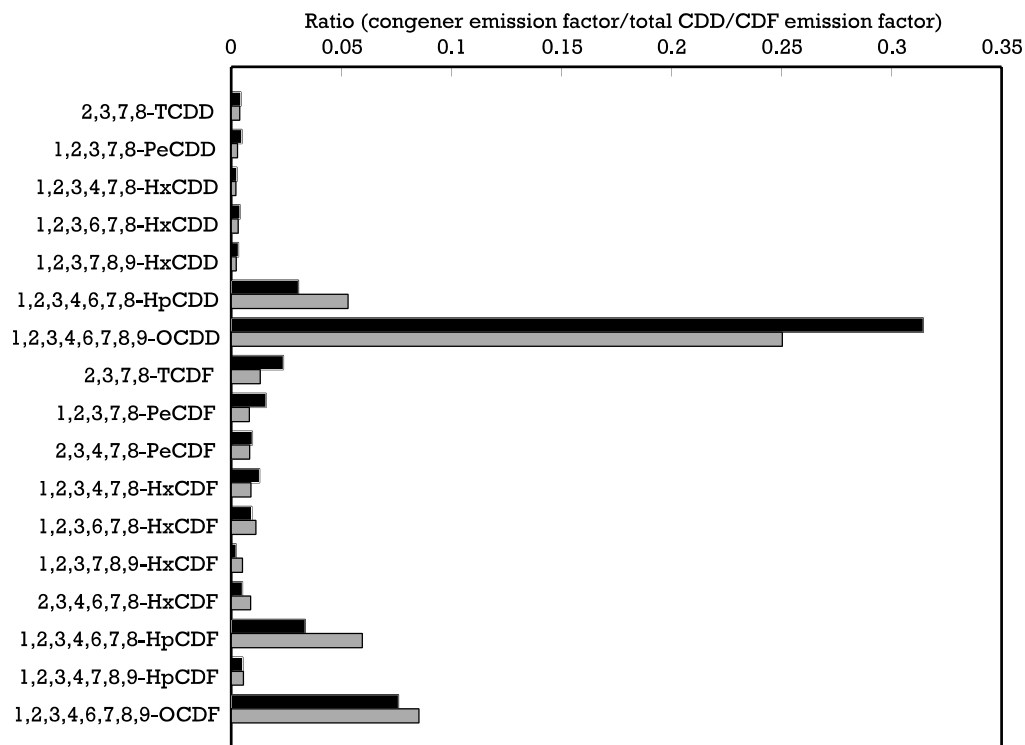
<sup>e</sup>Sixteen of the 17 analyses were nondetects.

<sup>f</sup>Eleven of the 17 analyses were nondetects.

<sup>g</sup>Five of the 17 analyses were nondetects.

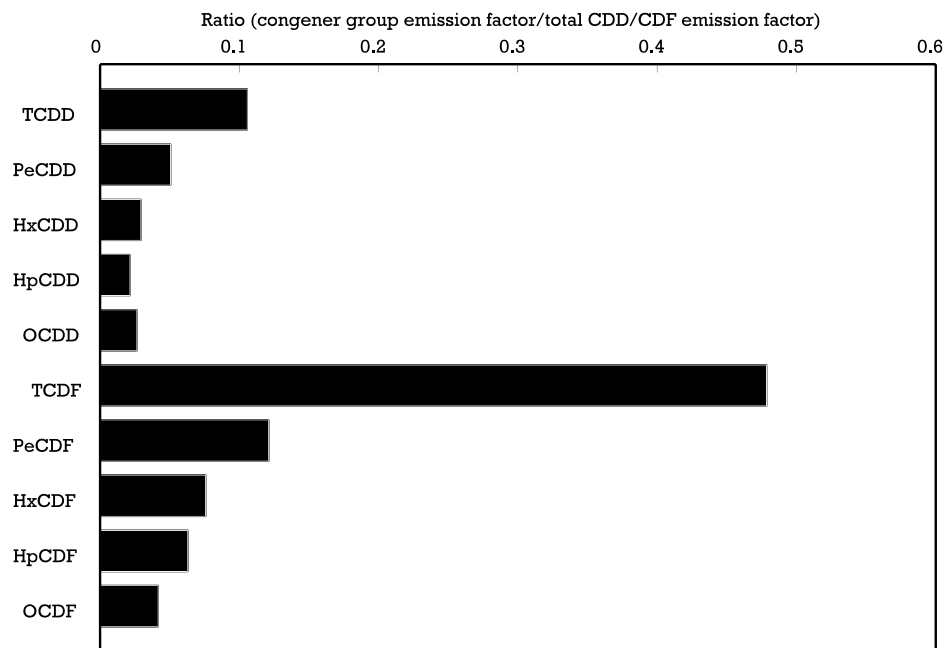
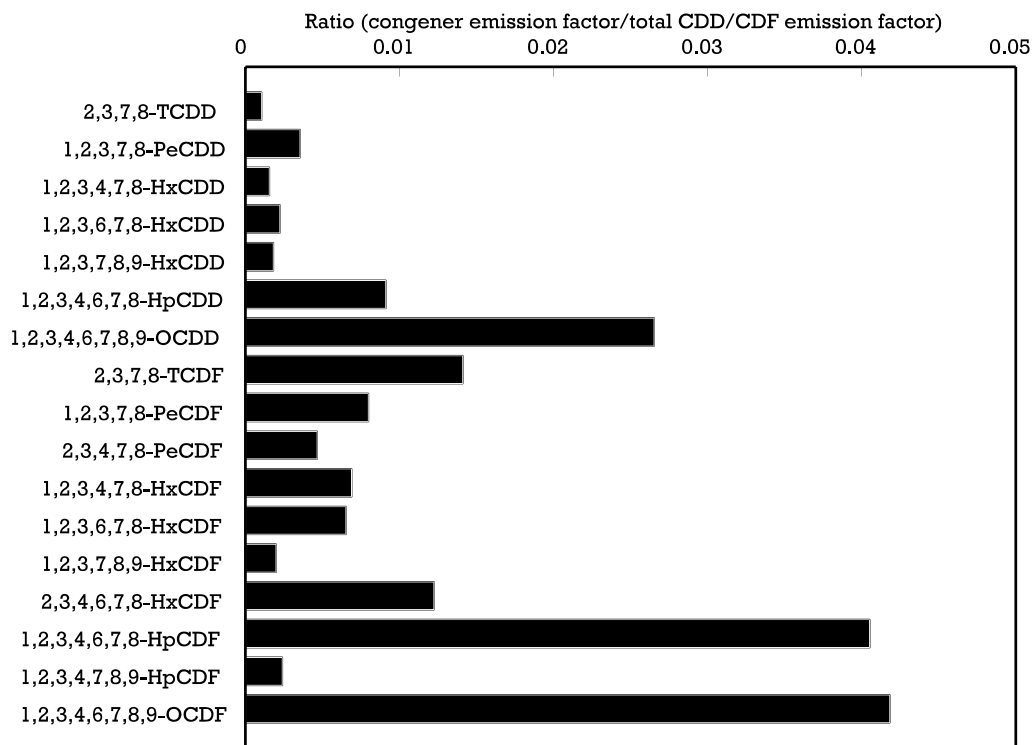
<sup>h</sup>Fourteen of the 17 analyses were nondetects.

<sup>i</sup>Fifteen of the 17 analyses were nondetects.



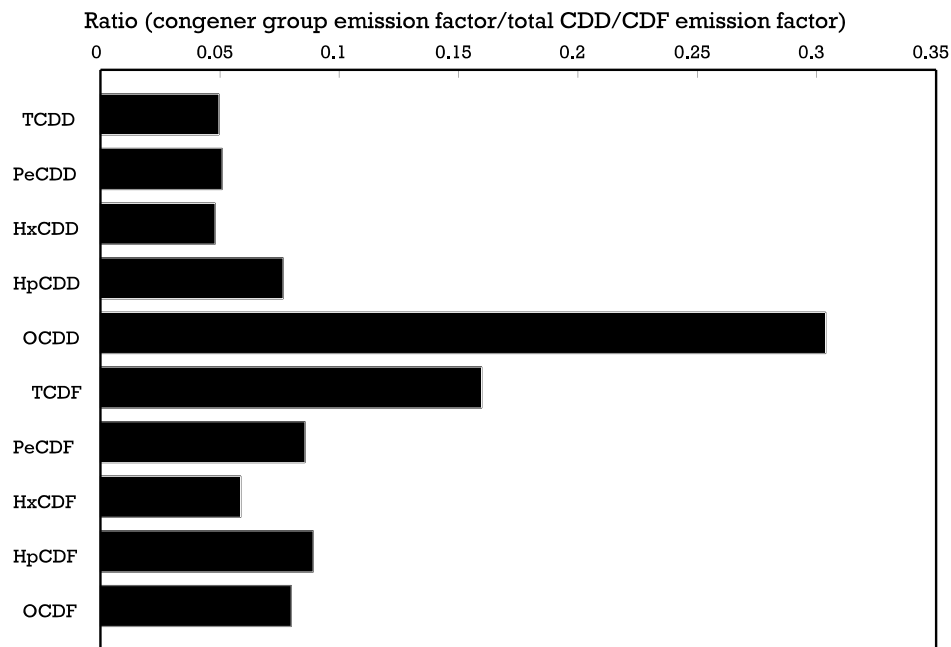
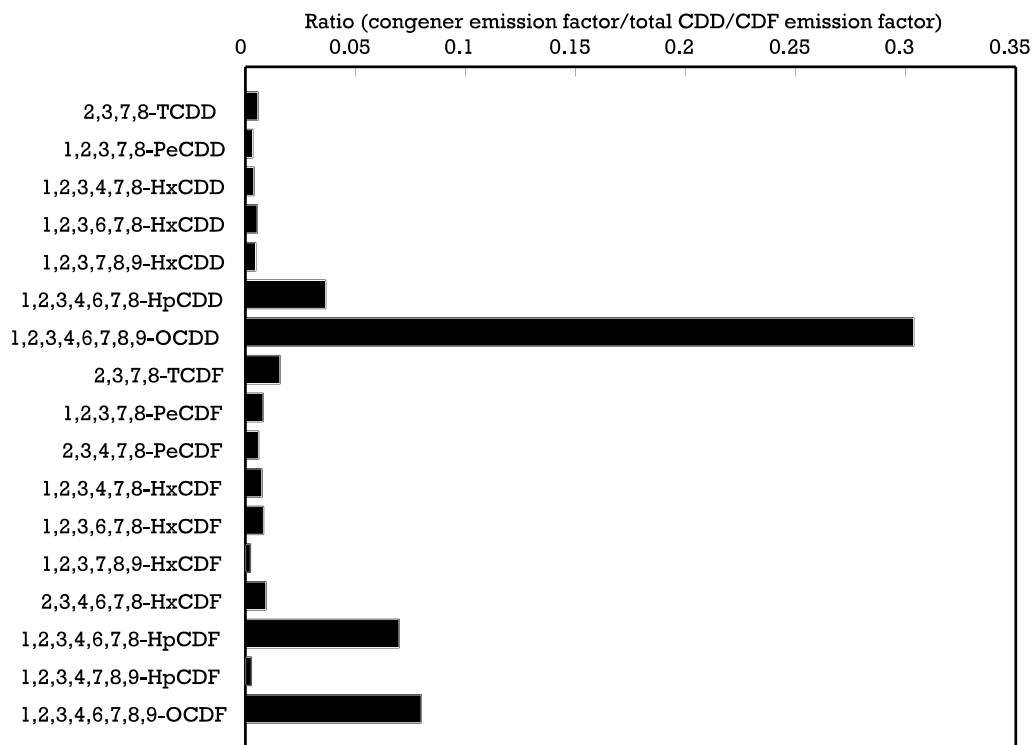
Note: Based on profiles calculated from emission factors (ND = ½ DL) from Tables 4-2 and 4-3.

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



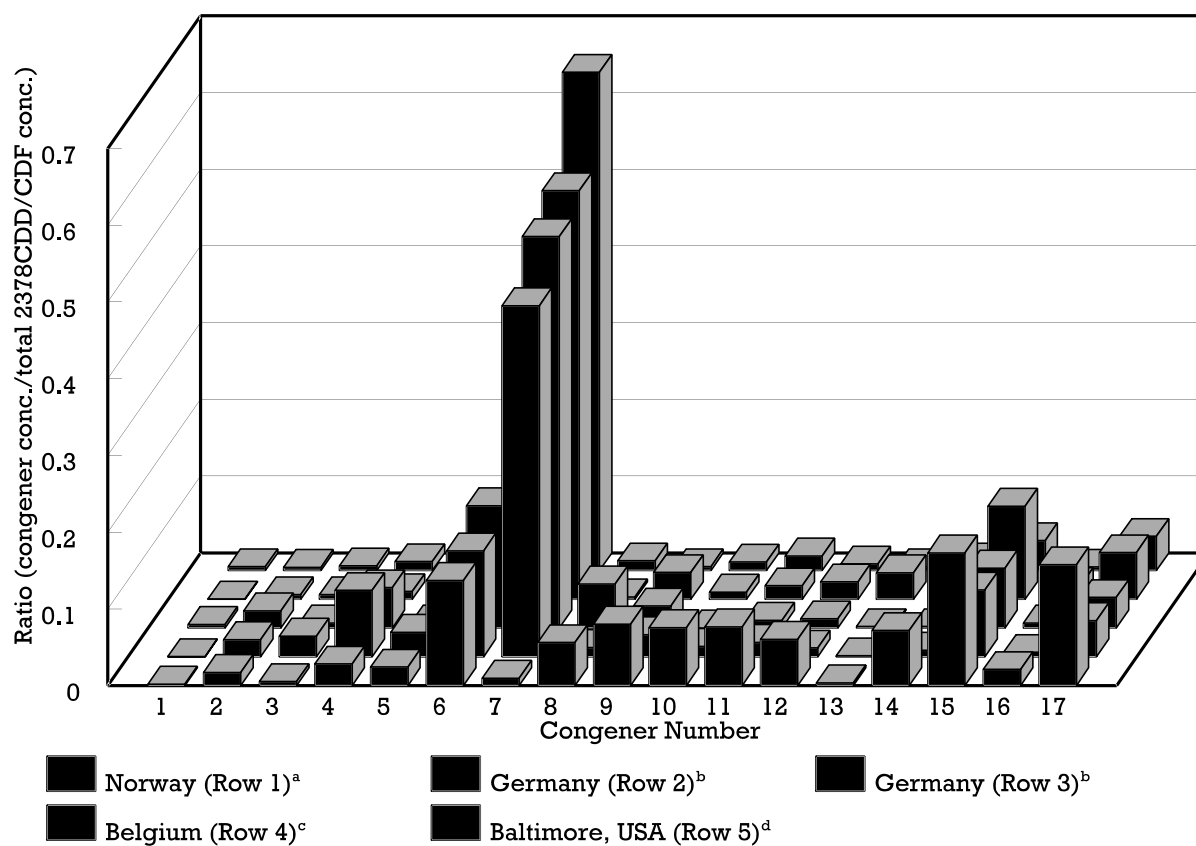
Note: Based on profiles calculated from emission factors (ND = ½ DL) from Table 4-4.

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



Note: Profiles are for catalytic converter equipped vehicles; based on data from Table 4-6.

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



Note: Congener numbers refer to the congeners in order as listed in Table 4-7.

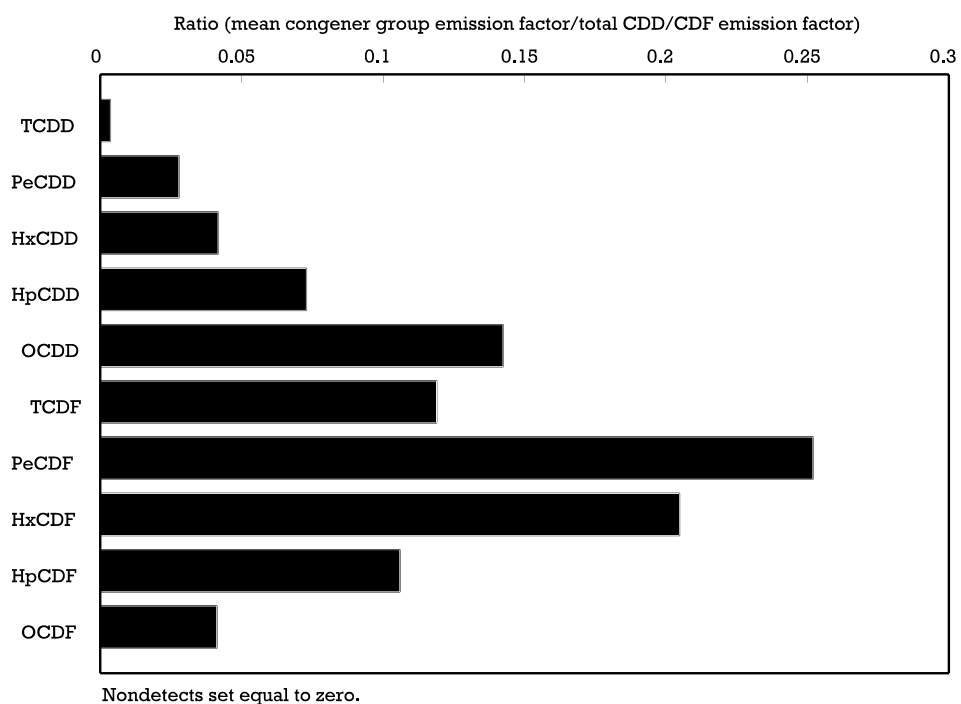
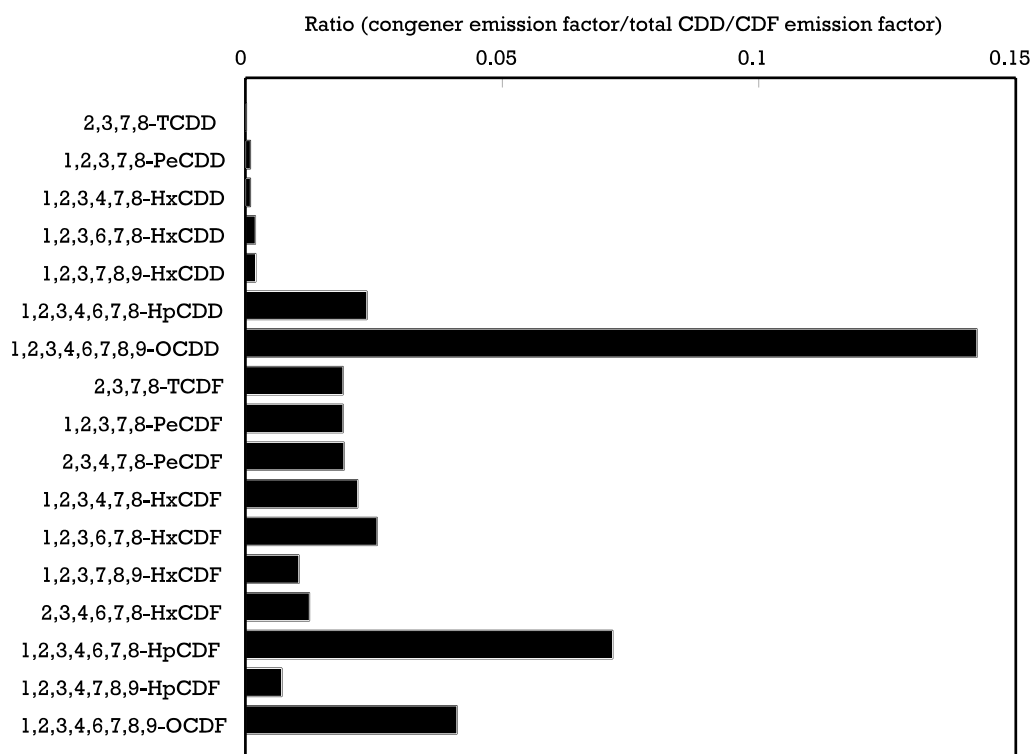
**Figure 4-4. Tunnel air concentrations.**

<sup>a</sup>Source: Oehme (1991).

<sup>b</sup>Source: Rappe et al. (1988).

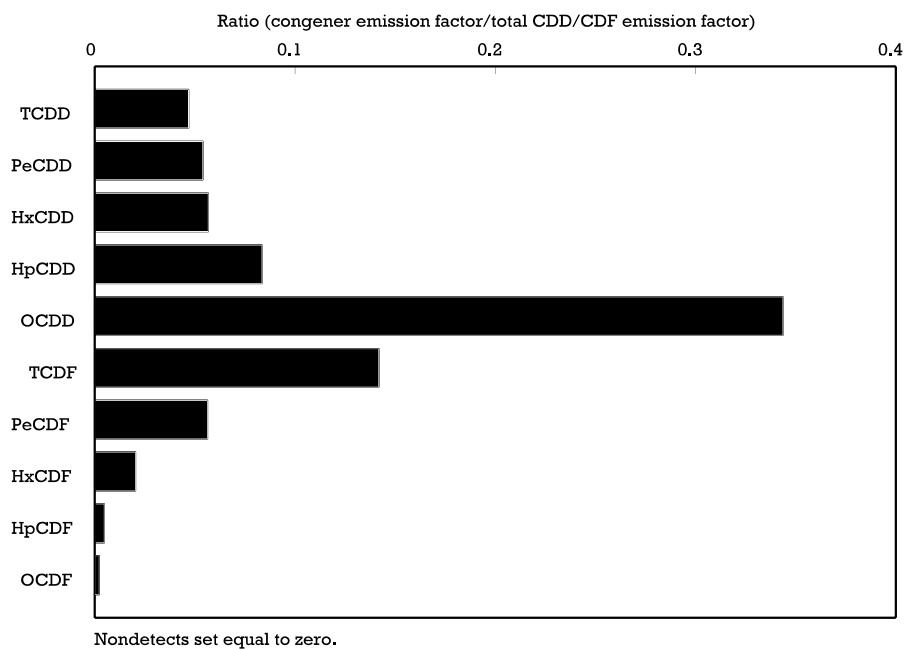
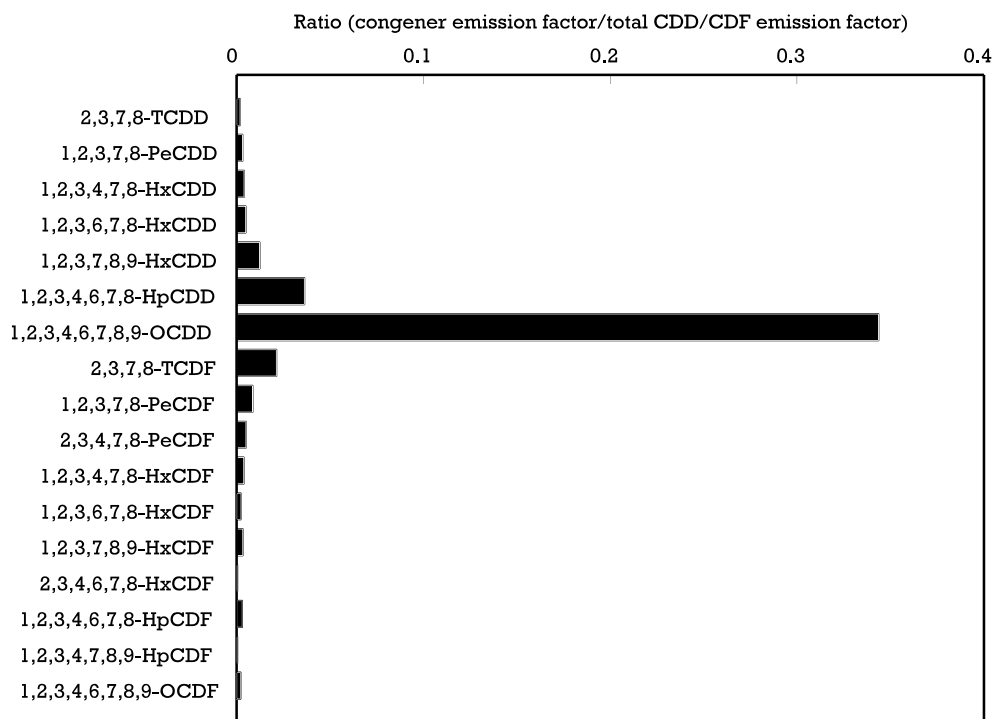
<sup>c</sup>Source: Wevers et al. (1992).

<sup>d</sup>Source: Gertler et al. (1996, 1998).



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

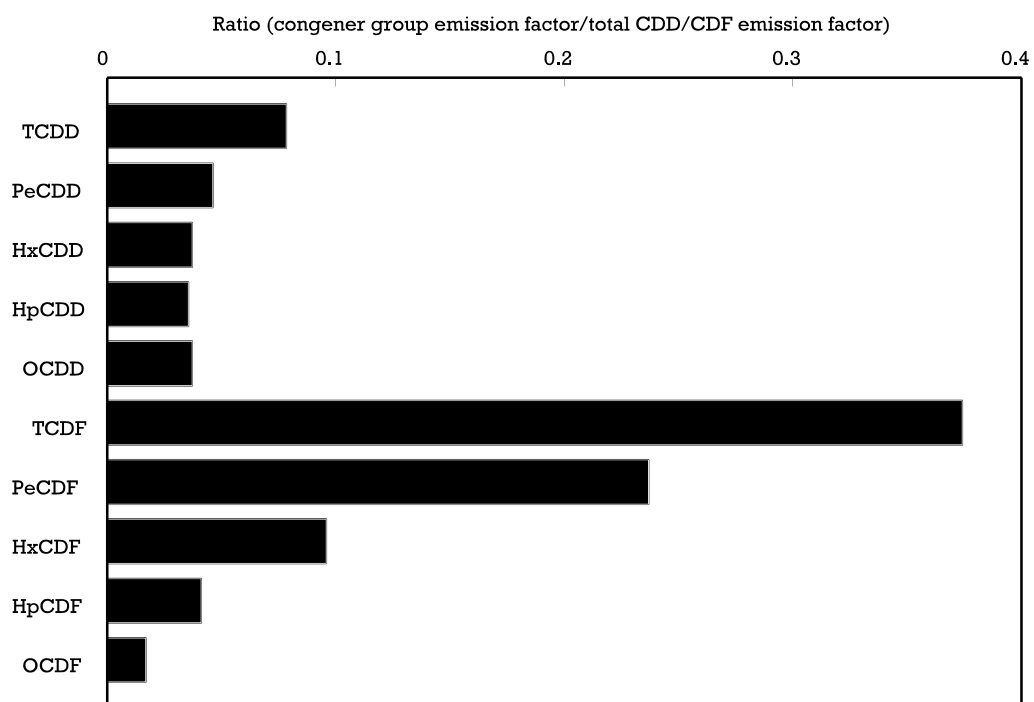
Sources: CARB (1990b, e, f, g).



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

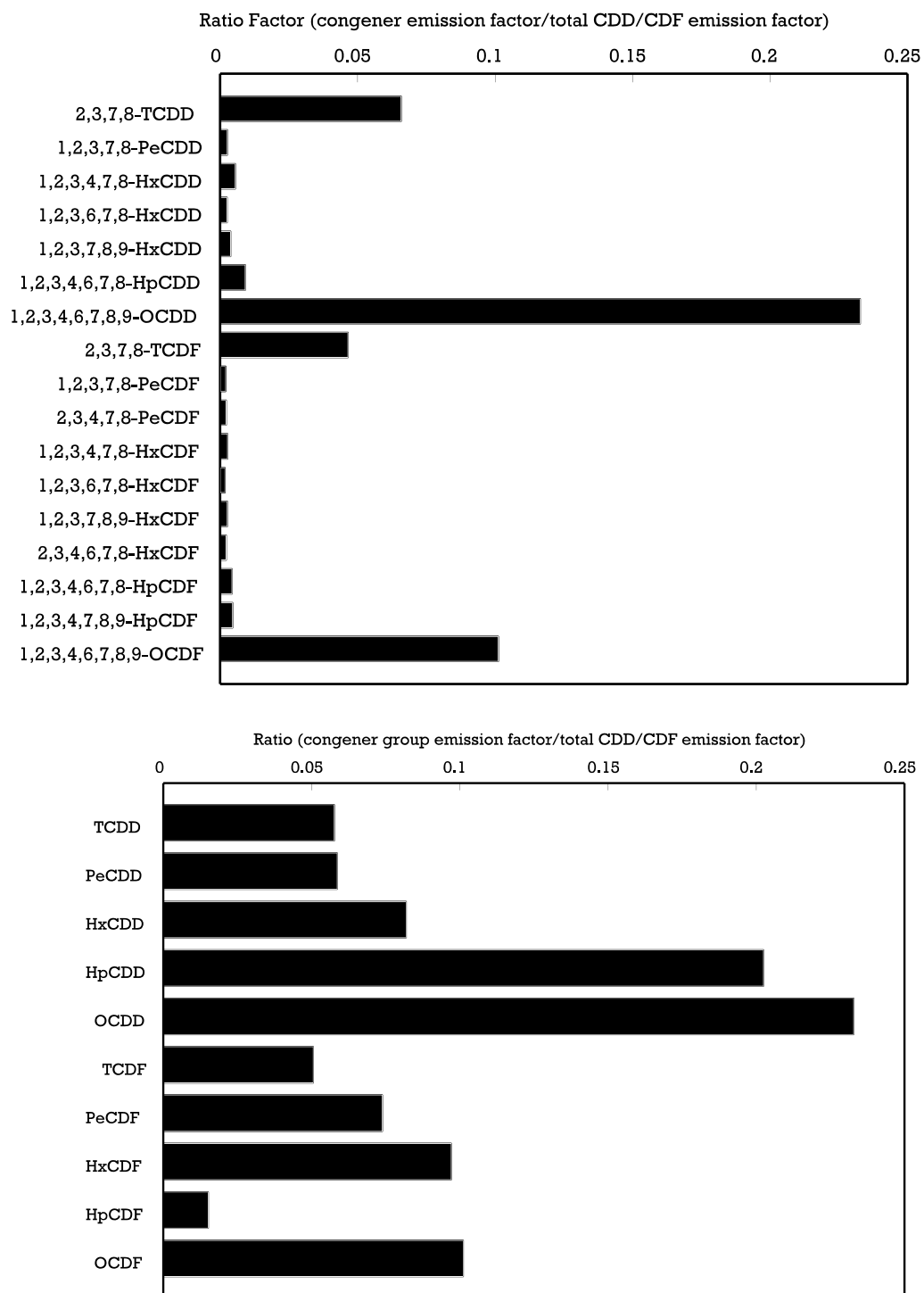
Source: NCASI (1995).





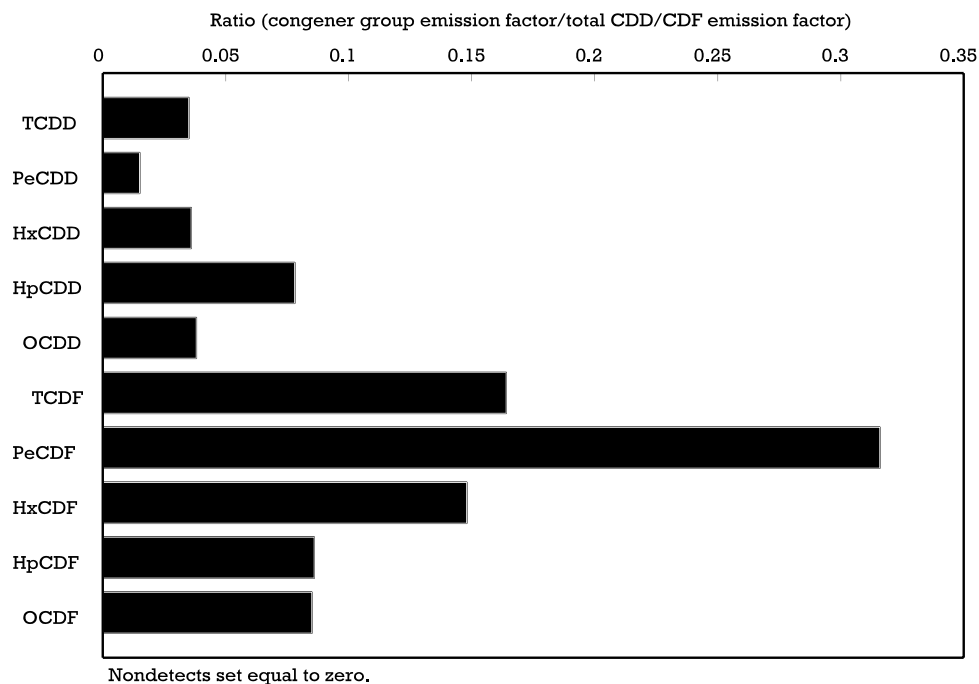
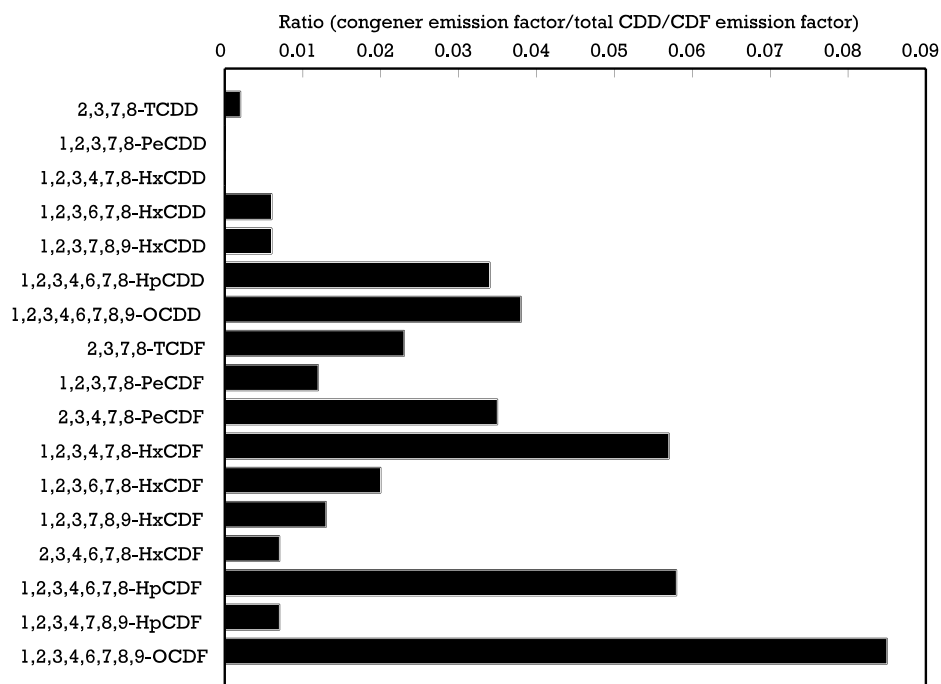
**Figure 4-6. Congener group profile for air emissions from residential oil-fueled furnaces.**

Source: U.S. EPA (1995c).



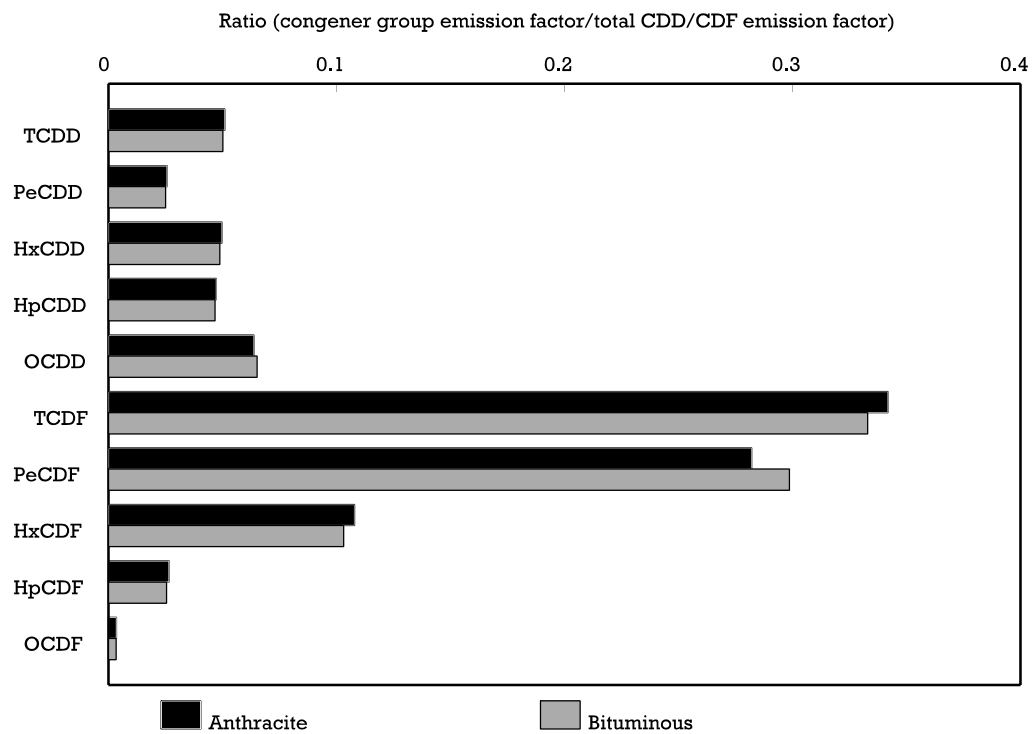
**Figure 4-7. Congener and congener group profiles for air emissions from industrial oil-fueled boilers.**

Source: U.S. EPA (1995c; 1997b).



**Figure 4-8. Congener and congener group profiles for air emissions from industrial/utility coal-fueled combustors.**

Source: EPRI (1994).



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

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

## 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 subdivided into two categories: those that burn hazardous waste and those that do not. Additionally, 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 below 232 °C. The following subsections describe 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.

#### 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.

1 As the meal moves through the cement kiln and is heated by hot combustion gases, water is  
2 vaporized and pyroprocessing of materials occurs.

3 The cement kiln consists of three thermal zones to produce cement clinker. Zone 1 is at  
4 the upper end of the kiln where the raw meal is added. Temperatures in this zone typically range  
5 from ambient up to 600 °C. In this area of the kiln, moisture is evaporated from the raw meal.  
6 Zone 2 is known as the calcining zone. Calcining occurs when the hot gases from the  
7 combustion of primary fuels dissociate calcium dioxide from the limestone and form calcium  
8 oxide. In this zone, temperatures range from 600 to 900 °C. Zone 3, the burning or sintering  
9 zone, is the lowest and hottest region of the kiln. Here, temperatures in excess of 1,500 °C  
10 induce the calcium oxide to react with silicates, iron, and aluminum in the raw materials to form  
11 the cement clinker. The formation of clinker actually occurs close to the combustion of primary  
12 fuel. The chemical reactions that occur in zone 3 are referred to as pyroprocessing.

13 The cement clinker, which leaves the kiln at the hot end, is a gray, glass-hard material  
14 consisting of dicalcium silicate, tricalcium silicate, calcium aluminate, and tetracalcium  
15 aluminoferrite. At this point, the temperature of the clinker is about 1,100 °C. The hot clinker is  
16 then dumped onto a moving grate, where it cools as it passes under a series of cool-air blowers.  
17 After it is cooled to ambient temperature, the clinker is ground into a fine powder and mixed with  
18 gypsum to produce the Portland cement product.

19 Cement kilns can be either wet process or dry process. In the wet process, the raw  
20 materials are ground and mixed with water to form a slurry, which is fed into the kiln through a  
21 pump. This is an older process. A greater amount of heat energy is needed in the wet process  
22 kiln than in other types of kilns. These kilns consume about 5 to 7 trillion Btu per ton of clinker  
23 product to evaporate the additional water. In the dry process, a preheater is used to dry the raw  
24 meal before it enters the kiln. A typical preheater consists of a vertical tower containing a series  
25 of cyclone-type vessels. Raw meal is added at the top of the tower and hot exhaust gases from  
26 the kiln operation preheat the meal, thus lowering the fuel consumption of the kiln. Dry kilns are  
27 now the most popular type of cement kiln.

28 Portland cement clinker production in the United States is estimated to have been 52  
29 billion kg in 1987 (U.S. DOC, 1996), 67.6 billion kg in 1995 (U.S. DOC, 1996), and 75.2 billion  
30 kg in 2000 (PCA, 2001, 2003a). The 2000 estimate is based on the assumption that of the annual

1 maximum clinker capacity reported for that reference year (PCA, 2001), only 90% was actually  
2 produced (PCA, 2003a).

### 3 4 **5.1.2. Cement Kilns That Burn Hazardous Waste**

5 The high temperatures achieved in cement kilns make the kilns an attractive technology  
6 for combusting hazardous waste as supplemental fuel. Sustaining the relatively high combustion  
7 temperatures that are needed to form cement clinker (1,100 to 1,500 °C) requires the burning of a  
8 fuel with a high energy output. Therefore, coal or petroleum coke is typically used as the primary  
9 fuel source. Because much of the cost of operating the cement kiln at high temperatures is  
10 associated with the consumption of fossil fuels, some cement kiln operators burn hazardous  
11 liquid and solid waste as supplemental fuel. In 2000, approximately 60% of all facilities burned  
12 hazardous waste as the primary fuel to offset the amount of coal/coke purchased and burned by  
13 the kiln (PCA, 2001). Organic hazardous waste may have a heating value similar to that of coal  
14 (9,000 to 12,000 Btu/lb for coal). The kiln operator may charge the waste generator a disposal  
15 fee to combust the hazardous waste; this fee also offsets the cost of kiln operation. The high-  
16 energy and ignitable wastes include diverse substances, such as waste oils, spent organic  
17 solvents, sludges from the paint and coatings industry, waste paints and coatings from auto and  
18 truck assembly plants, and sludges from the petroleum refining industry (Greer et al., 1992).

19 The conditions in the cement kiln mimic conditions of hazardous waste incineration. For  
20 example, the gas residence time in the burning zone is typically 3 sec at temperatures in excess of  
21 1,500 °C (Greer et al., 1992). The method of introducing liquid and solid hazardous waste into  
22 the kiln is a key factor in the complete consumption of the waste during the combustion of the  
23 primary fuel. Liquid hazardous waste is either injected separately or blended with the primary  
24 fuel (coal). Solid waste is mixed and burned along with the primary fuel.

25 Trial burns have consistently shown that destruction and removal efficiencies of 99.99 to  
26 99.9999% can be achieved for very stable organic wastes using cement kilns (Greer et al., 1992).  
27 Hazardous waste was combusted at 34 of the 212 kilns operating in 1995 (Federal Register,  
28 1996b) and at 33 of the 201 kilns operating in 2000 (e-mail correspondence between M. Benoit,  
29 Cement Kiln Recycling Coalition, and K. Riley, Versar, Inc., dated February 24, 2003; PCA,  
30 2001). Other types of supplemental fuel used by these facilities include natural gas, fuel oil,  
31 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 SO<sub>2</sub> can be formed during pyroprocessing of the sulfur-laden minerals and fuels, but the minerals have high alkalinity, which partially neutralizes SO<sub>2</sub> 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, 1997d). 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, 1997d). 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 in this document for deriving emission factors is 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, 1996c). More recent CDD/CDF emissions data were also obtained from tests



conducted in 2000 at 3 cement kilns burning hazardous waste (U.S. EPA, 2002b) 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, 1996c)

The average TEQ emission factors based on the data reported by EPA in 1996 (U.S. EPA, 1996c) are 0.000941 to 232 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (average of 22.48 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg [20.91 ng I-TEQ<sub>DF</sub>/kg]) clinker produced for cement kilns burning hazardous waste and 0.000012 to 2.76 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (average of 0.29 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg [0.27 ng I-TEQ<sub>DF</sub>/kg]) clinker produced for cement kilns burning nonhazardous waste.

These data show that the average emission factor for kilns burning hazardous waste is 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)—are likely affecting CDD/CDF emissions.

Previous attempts to understand these differences using parametric testing of cement kilns yielded mixed results. EPA conducted a limited comparison (U.S. EPA, 1997d) 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<sub>DF</sub> 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<sub>DF</sub> stack gas concentrations were substantially greater (3- to 29-fold greater) than those for the baseline operating conditions.

Subsequently, 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 exist, 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.

$$EF_{CK} = \frac{C \times F_v}{I_{cl}} \quad (5-1)$$

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.

$$EF_{avgCK} = \frac{EF_{CK_1} + EF_{CK_2} + EF_{CK_3} + \dots + EF_{CK_N}}{N} \quad (5-2)$$

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 are 30.7 and 1.11 ng  $TEQ_{DF-WHO_{98}}$ /kg clinker produced, respectively.

#### **5.1.4.2. Emissions Data for 1999 and 2000** (U.S. EPA, 2002b; Bell, 1999)

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, 1996c).

1 The results of three tests conducted in 2000 for cement kilns burning hazardous waste  
2 showed average TEQ emission factors ranging from 0.08 to 6.1 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (0.07 to 5.4  
3 I-TEQ/kg) clinker produced. The average TEQ emission factor for these three facilities is 2.2 ng  
4 TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (2 I-TEQ/kg) clinker produced. The results obtained from these three  
5 facilities fall within the range of results obtained from the 1989 to 1996 data (U.S. EPA, 1996c);  
6 however, two of the facilities (Holnam plant in Holly Hill, South Carolina, and Giant plant in  
7 Bath, Pennsylvania) had results that fell toward the low end of the data range.

8 Because of the limited availability of new emissions data, EPA investigated whether  
9 cement kilns burning hazardous waste had changed their operating practices, in particular,  
10 whether APCDs were still operating above 232 °C. The emissions data from the three facilities  
11 tested in 2000 indicated APCD temperatures between 246 and 260 °C. However, according to  
12 representatives from a number of hazardous waste-burning cement kilns, at least 85% of the kilns  
13 operating in 2000 operated with inlet APCD temperatures below 232 °C. For the 1987 and 1995  
14 national emission estimates, it was assumed that 20% of the facilities operated with APCD inlet  
15 temperatures below 232 °C and 80% operated above 232 °C. Of the test runs conducted between  
16 1989 and 1996 at temperatures above 232 °C, the majority of the inlet APCD temperatures were  
17 below 316 °C. The individual emission factors for the kilns with APCD inlet temperatures  
18 below 316 °C were all less than 7 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg clinker produced. The kiln with the  
19 highest inlet APCD temperature (385 °C) had the highest TEQ emission factor (150 ng TEQ<sub>DF</sub>-  
20 WHO<sub>98</sub>/kg clinker produced). This kiln, however, stopped burning hazardous waste before 2000.

#### 21 22 **5.1.4.3. Emission Factor Estimates for Cement Kilns Burning Hazardous Waste**

23 For reference years 1987 and 1995, EPA estimated the TEQ emission factor by  
24 subdividing the emissions data reported in 1996 (U.S. EPA, 1996c; i.e., 1989 through 1996 data)  
25 by inlet APCD temperature above and below 232 °C. For cement kilns operating at temperatures  
26 above 232 °C, the TEQ emission factor is 30.7 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg clinker produced, and for  
27 cement kilns operating at temperatures below 232 °C, the TEQ emission factor is 1.11 ng TEQ<sub>DF</sub>-  
28 WHO<sub>98</sub>/kg clinker produced. These emission factors are presented in Table 5-1 and the average  
29 congener profile is presented in Figure 5-1.

30 Because a vast majority of the facilities had reduced their APCD inlet temperature to  
31 below 232 °C in 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 (U.S. EPA, 1996c; i.e., 1989 through 1996 data) for facilities that were still operating in 2000 with the newer data reported (U.S. EPA, 2002b). Therefore, emission tests from five facilities (U.S. EPA, 1996c) 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 5.95 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/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, 1996c; i.e. 1989 through 1996 data), EPA combined the results from the two data sets to obtain a TEQ emission factor estimate of 0.27 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/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.

#### **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 was 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 United States (U.S. DOC, 1996), and of this amount, Health (1995) reported that 61.3 billion kg were produced by cement kilns burning nonhazardous waste; therefore, approximately 6.3 billion kg were produced by cement kilns burning hazardous waste. Based on the fact that 9.3% of the clinker 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 (PCA, 2003a). 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 burning nonhazardous 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, 1996c).

### 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. If the percentages of hazardous waste-burning kilns with input temperatures less than and greater than 232 °C represent the actual distribution of activity level in the industry, then these percentages, coupled with the TEQ emission factors presented in Table 5-1 and Table 5-3 (hazardous waste cement

1 kilns and nonhazardous waste cement kilns, respectively) and the activity levels established in  
2 Section 5.1.5 can be used to calculate the annual national TEQ emission estimates shown in  
3 Table 5-4.

4 Overall, 131 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (122 g I-TEQ<sub>DF</sub>) were produced by cement kilns in 1987.  
5 Of this amount, 116.7 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (108.6 g I-TEQ<sub>DF</sub>) were produced by hazardous waste-  
6 burning cement kilns with inlet APCD temperatures greater than 232 °C, 1.1 g TEQ<sub>DF</sub>-WHO<sub>98</sub>  
7 (1 g I-TEQ<sub>DF</sub>) were produced by cement kilns burning hazardous waste with inlet APCD  
8 temperatures less than 232 °C, and 12.7 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (12.3 g I-TEQ<sub>DF</sub>) were produced by  
9 cement kilns burning nonhazardous waste. In 1995, a total of 173 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (161 g I-  
10 TEQ<sub>DF</sub>) were produced by cement kilns. Of this amount, 154.7 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (144 g I-TEQ<sub>DF</sub>)  
11 were produced by hazardous waste-burning cement kilns with inlet APCD temperatures greater  
12 than 232 °C, 1.4 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (1.3 g I-TEQ<sub>DF</sub>) were produced by cement kilns burning  
13 hazardous waste with inlet APCD temperatures less than 232 °C, and 16.6 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (15.9  
14 g I-TEQ<sub>DF</sub>) were produced by cement kilns burning nonhazardous waste.

15 The overall rating for these emission estimates is low because the emission factors had a  
16 low confidence rating.

#### 18 **5.1.6.2. Estimates for Reference Year 2000**

19 National estimates of CDD/CDF air emissions (g TEQ/yr) from all Portland cement kilns  
20 for reference year 2000 were made by multiplying the average TEQ emission factors by an  
21 estimate of the annual activity level (cement clinker produced) for each the two categories  
22 (hazardous waste and nonhazardous waste). The TEQ emission factors presented in Table 5-2  
23 and Table 5-3 (hazardous waste-burning and nonhazardous waste-burning cement kilns,  
24 respectively) and the activity levels established in Section 5.1.5 were used to calculate the annual  
25 national TEQ emission estimates shown in Table 5-5. Overall, 85.6 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (79.9 g I-  
26 TEQ<sub>DF</sub>) were produced by cement kilns in 2000. Of this amount, 68.4 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (63.3 g I-  
27 TEQ<sub>DF</sub>) were produced by hazardous waste-burning cement kilns and 17.2 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (16.6  
28 g I-TEQ<sub>DF</sub>) were produced by cement kilns burning nonhazardous waste. This estimated amount  
29 produced by cement kilns not burning hazardous waste is on the same order of magnitude as the  
30 44 g TEQ<sub>DF</sub>-WHO<sub>98</sub> predicted in the National Emission Standards for Hazardous Air Pollutants

1 for the Portland Cement Manufacturing Industry, promulgated on June 14, 1999 (Federal  
2 Register, 1999a).

3 All of these emission estimates have an overall confidence rating of low because the  
4 emission factors had a low confidence rating.

#### 5 6 **5.1.7. EPA Regulatory Activities**

7 Under the authority of the Clean Air Act, EPA promulgated national emission standards  
8 for new and existing cement kilns burning nonhazardous waste in May 1999 (Federal Register,  
9 1999a, 2004). The regulations are specific to the I-TEQ concentration in the combustion gases  
10 leaving the stack. Existing and new cement kilns either combusting or not combusting hazardous  
11 waste as auxiliary fuel cannot emit more than 0.2 ng I-TEQ/dscm. In addition, the temperature of  
12 the combustion gases measured at the inlet to the air pollution control device cannot exceed 232  
13 °C. The rule requires owners or operators of facilities to test for CDDs/CDFs every 2½ years.  
14 The Office of Air Quality Planning and Standards (OAQPS) expects this rule to reduce I-TEQ<sub>DF</sub>  
15 emissions from existing and new facilities by 36% over the next few years (Federal Register,  
16 1999a, 2004).

17 In July 1999, under the joint authority of the Clean Air Act and the Resource  
18 Conservation and Recovery Act (RCRA), EPA promulgated national emission standards for  
19 combustion facilities (including cement kilns) burning hazardous waste (Federal Register,  
20 1999b).

#### 21 22 **5.1.8. Solid Waste from Cement Manufacturing: Cement Kiln Dust**

23 EPA characterized CKD (the solid residual material generated during the manufacturing  
24 of cement) in a report to Congress (U.S. EPA, 1993g) that was based in part on a 1991 survey of  
25 cement manufacturers conducted by the Portland Cement Association (PCA). Survey responses  
26 were received from 64% of the active cement kilns in the United States. On the basis of the  
27 survey responses, EPA estimated that in 1990 the U.S. cement industry generated about 12.9  
28 million metric tons of gross CKD and 4.6 million metric tons of net CKD, of which 4.2 million  
29 metric tons were land-disposed. The material collected by the APCD system is called gross CKD  
30 (or as-generated CKD); it is either recycled back into the kiln system or removed from the system  
31 for disposal (becoming net CKD or as-managed CKD). As discussed below, low levels of dioxin



1 have been measured in CKD. This material is disposed of in permitted landfills and therefore is  
2 not considered to be an environmental release. On this basis, it is not included in the inventory  
3 of dioxin releases presented in this report. However, for informational purposes only, this  
4 section develops estimates of the amount of dioxin in CKD for the reference years 1987, 1995,  
5 and 2000.

6 The PCA recently provided current estimates of the amount of CKD removed from the  
7 manufacturing process for beneficial reuse and long-term management units (i.e., landfill  
8 disposal) in 1990, 1995, and 2000. Possible beneficial reuses include municipal waste daily  
9 cover material, municipal waste landfill final cover material, soil stabilization for roadways or  
10 other structures, waste neutralization/stabilization/solidification (food wastes, hazardous wastes,  
11 etc.), and agricultural soil amendment. The PCA estimated that the amount of CKD beneficially  
12 reused on or off site was 752 million kg in 1990, 652 million kg in 1995, and 575 million kg in  
13 2000. The amount of CKD disposed of annually in landfills was estimated to be 2.7 billion kg in  
14 1990, 3.1 billion kg in 1995, and 2.2 billion kg in 2000.

15 In its report to Congress, EPA also included the results of sampling and analysis of CKD  
16 and clinker conducted in 1992 and 1993 (U.S. EPA, 1993g). The purposes of the sampling and  
17 analysis efforts were to (a) characterize the CDD/CDF content of clinker and CKD, (b) determine  
18 the relationship, if any, between the CDD/CDF content of CKD and the use of hazardous waste  
19 as fuel, and (c) determine the relationship, if any, between the CDD/CDF content of CKD and  
20 the use of wet-process and dry-process cement kilns.

21 Clinker samples were collected from five cement kilns burning nonhazardous waste and  
22 six kilns burning hazardous waste. CDDs/CDFs were not detected in any of the samples. Tetra-  
23 through octa-chlorinated CDDs/CDFs were detected in the gross CKD samples obtained from 10  
24 of the 11 kilns and in the net CKD samples obtained from 8 of the 11 kilns. The CDD/CDF  
25 content for gross CKD ranged from 0.008 to 247 ng I-TEQ<sub>DF</sub>/kg and from 0.045 to 195 ng I-  
26 TEQ<sub>DF</sub>/kg for net CKD. Analyses for seven PCB congeners were also conducted, but no  
27 congeners were detected in any clinker or CKD sample.

28 Mean CDD/CDF concentrations in net CKD generated by the kilns burning hazardous  
29 waste were higher (35 ng I-TEQ<sub>DF</sub>/kg) than in net CKD generated by the facilities burning  
30 nonhazardous waste (0.003 ng I-TEQ<sub>DF</sub>/kg). These calculations of mean values treated nondetect  
31 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 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, 1993g) 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<sub>DF</sub>/kg.

CDD/CDF congener data for CKD from Holnam, Inc., Seattle, Washington, 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 were as follows, assuming that nondetect values were zero:

<u>Date</u>	<u>Location</u>	<u>I-TEQ (ng/kg)</u>	<u>I-TEQ (mg/day)</u>
05/15/96	Not stated	0.038	0.0038
10/21/97	HLMN bin	0.67	0.0674
10/21/97	HLMN final	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, 1999d). 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 (2003b). 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<sub>DF</sub>/kg for cement kilns

burning hazardous waste (which includes the high value discussed above) and 0.003 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub> in 1987, 3.6 g I-TEQ<sub>DF</sub> in 1995, and 3.3 g I-TEQ<sub>DF</sub> in 2000 were produced from CKD that was beneficially reused, and approximately 14.9 g I-TEQ<sub>DF</sub> in 1987, 17.7 g I-TEQ<sub>DF</sub> in 1995, and 12.8 g I-TEQ<sub>DF</sub> 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<sub>DF</sub> in 1987, 0.0016 g I-TEQ<sub>DF</sub> in 1995, and 0.0014 g I-TEQ<sub>DF</sub> in 2000 were produced from CKD that was beneficially reused and approximately 0.0067 g I-TEQ<sub>DF</sub> in 1987, 0.0079 g I-TEQ<sub>DF</sub> in 1995, and 0.0056 g I-TEQ<sub>DF</sub> 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, 1999b). 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, 1999d).

## **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<sub>DF</sub> to air in 1990 (Federal Register, 1998b) and 2.4 g I-TEQ<sub>DF</sub> in 1997 (Federal Register, 1999b); 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, 2002b). 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<sub>DF</sub>-WHO<sub>98</sub>/kg (2.063 ng I-TEQ<sub>DF</sub>/kg) of waste feed, assuming nondetect values of zero. These were 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, yields 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, 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 are estimated as 1.86 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (1.79 g I-TEQ<sub>DF</sub>) 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, 1996i). “Hot mix” asphalt paving materials can be manufactured by (a) batch mix plants, (b) continuous mix plants, (c) parallel-flow drum mix plants, and (d) counterflow drum mix plants (U.S. EPA, 1998c).

1           Bremmer et al. (1994) reported the CDD/CDF emissions factor for an asphalt mixing  
2 plant in the Netherlands as 47 ng I-TEQ<sub>DF</sub> per metric ton of produced asphalt. No congener-  
3 specific emission factors were reported. The mixing plant heated old asphalt to about 150 °C in  
4 an individual recycling drum with kiln exhaust gases that were mixed with ambient air and  
5 heated to a temperature of 300 to 400 °C. Parallel to this recycling drum was the main drum,  
6 which dried and heated the aggregate (sand and gravel/granite chippings) to a temperature of  
7 about 220 °C. The kiln exhaust gases leaving the recycling drum were led along the main burner  
8 of the main drum for incineration. The old asphalt, the minerals from the main drum, and new  
9 bitumen from a hot storage tank (about 180 °C) were mixed in a mixer to form new asphalt.  
10 Natural gas fueled the plant during the sample collection period, and 46% of the feed was old  
11 asphalt. The plant's APCD system consisted of cyclones and an FF.

12           Umweltbundesamt (1996) reported lower emission factors for three tested facilities in  
13 Germany that were also equipped with FFs. These three facilities were fueled by oil or butane  
14 gas and used old asphalt at rates ranging from 30 to 60% of the feed. The emission factors  
15 calculated from the stack gas concentrations, gas flow rates, and hourly throughputs for these  
16 three facilities were 0.2, 3.5, and 3.8 ng I-TEQ<sub>DF</sub>/metric ton of asphalt produced.

17           OAQPS directed Midwest Research Institute to conduct emissions testing at asphalt  
18 concrete production plants in 1997 (U.S. EPA, 2001b). The institute performed emissions tests  
19 on the inlet and outlet of FFs that control emissions from the counterflow rotary dryer process  
20 used at the asphalt plant in Clayton, North Carolina, and from the parallel-flow rotary dryer  
21 process used at the asphalt plant in Cary, North Carolina. In both processes, virgin aggregate of  
22 various sizes was fed to the drum by cold-feed controls in proportions dictated by the final mix  
23 specifications. Aggregate was delivered at the opposite end of the burner in the counter-flow  
24 continuous drum mix process and at the same end as the burner in the parallel-flow continuous  
25 drum mix process.

26           The Clayton facility used an FF for particulate matter (PM) control, and the Cary facility  
27 used a knockout box as the primary control and an FF as a secondary control. The average  
28 asphalt production rates at the Clayton facility were 171, 276, 240, and 185 tons/hr for the four  
29 test runs and 201, 199, and 163 tons/hr for the three test runs at the Cary facility. Mix  
30 temperatures for both facilities ranged from 148 to 155 °C. Emission profiles from both facilities  
31 indicated low releases of dioxin into the air. The average emission factor developed for the

seven test runs was 0.0011 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg processed (see Table 5-8 for congener-specific TEQs).

Approximately 25 million metric tons of asphalt bitumen were produced in the United States in 1992. An identical quantity was produced in 1990 (U.S. DOC, 1995a). Bitumen constitutes approximately 5% by weight of finished paving asphalt (Bremmer et al., 1994). Thus, an estimated 500 million metric tons of paving asphalt are produced in the United States annually. Approximately 500 million tons of hot mix asphalt paving materials were produced at the estimated 3,600 active asphalt plants in the United States in 1996 (U.S. EPA, 1998c). This activity level was adopted for 1987, 1995, and 2000 with a high confidence level. The activity level is given a high rating because it is based on a comprehensive survey.

For reference years 1987 and 1995, a preliminary estimate of the potential magnitude of annual TEQ emissions for U.S. production of asphalt can be obtained by averaging the emission factors for the four facilities reported by Bremmer et al. (1994) and Umweltbundesamt (1996). Applying this average emission factor (14 ng I-TEQ<sub>DF</sub>/metric ton of asphalt produced) to the activity level of 500 million metric tons of paving asphalt produced annually yields an annual emission of 7 g I-TEQ<sub>DF</sub>/yr (congener-specific results were not reported in either report; therefore, TEQ<sub>DF</sub>-WHO<sub>98</sub> estimates could not be calculated). The preliminary estimates for 1987 and 1995 have been revised in this report to use the emission factor developed from two U.S. facilities (i.e., 1.1 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/metric ton of asphalt produced). This changes the emission estimates for these years to 0.55 g TEQ<sub>DF</sub>-WHO<sub>98</sub>/yr. Since activity levels have remained constant, this emission estimate also applies to the year 2000. These emission estimates are still considered to be preliminary, since the emission factor is based on testing at only 2 of 3,600 total facilities.

#### **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 or 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, the Canadian Ministry of the Environment detected concentrations of CDDs in an internal waste stream of spent caustic at a petroleum refinery that ranged from 1.8 to 22.2 µg/L and CDFs ranging from 4.4 to 27.6 µg/L (Maniff and Lewis, 1988). 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<sub>DF</sub>/L) and wastewater sludges (0.26 to 2.4 ng I-TEQ<sub>DF</sub>/kg) at a refinery in Ohio. The levels of detected total CDDs/CDFs in the wastewater

1 and sludge were much lower ( $<3$  ng/L and  $<1$   $\mu\text{g/kg}$ , respectively) than the levels reported by  
2 Maniff and Lewis (1988). No CDDs/CDFs were detected in the final treated effluent (less than  
3  $0.2$  ng I-TEQ<sub>DF</sub>/L). The data collected in the study were acknowledged to be too limited to  
4 enable identifying the source(s) of the CDDs/CDFs within the refinery. The study authors also  
5 presented in an appendix to their report the results of analyses of wastewater from the catalyst  
6 regeneration processes at two other U.S. refineries. In both cases, untreated wastewaters  
7 contained CDDs/CDFs at levels ranging from high pg/L to low ng/L (results were reported for  
8 congener group totals, not specific congeners). However, CDDs/CDFs were not detected in the  
9 only treated effluent sample collected at one refinery.

10 Thompson et al. (1990) reported total CDD and CDF concentrations of  $8.9$  ng/m<sup>3</sup> and  $210$   
11 ng/m<sup>3</sup>, respectively, in stack gas samples from a Canadian petroleum refinery's reforming  
12 operation. They also observed CDDs/CDFs in the pg/L to ng/L range in the internal washwater  
13 from a scrubber of a periodic/cyclic regenerator.

14 Beard et al. (1993) conducted a series of benchtop experiments to investigate the  
15 mechanism(s) of CDD/CDF formation in the catalytic reforming process. A possible pathway  
16 for the formation of CDFs was found, but the results could not explain the formation of CDDs.  
17 Analyses of the kiln exhaust gas from burning coked catalysts revealed the presence of  
18 unchlorinated dibenzofuran in quantities up to  $220$   $\mu\text{g/kg}$  of catalyst. Chlorination experiments  
19 indicated that dibenzofuran and possibly biphenyl and similar hydrocarbons act as CDF  
20 precursors and can become chlorinated in the catalyst regeneration process. Corrosion products  
21 on the steel piping of the process plant seem to be the most likely chlorinating agent.

22 In May 1994, EPA's Office of Water conducted a sampling and analytical study of  
23 catalyst regeneration wastewater for CDDs/CDFs at three petroleum refining plants (Kirby,  
24 1994). The study objectives were to determine the analytical method best suited for determining  
25 CDDs/CDFs in refinery wastewater and to screen and characterize wastewater discharges from  
26 several types of reforming operations for CDDs/CDFs. The report for this study (Kirby, 1994)  
27 also presented results submitted voluntarily to EPA by two other facilities. The sampled internal  
28 untreated wastewaters and spent caustics were found to contain a wide range of CDD/CDF  
29 concentrations,  $0.1$  pg I-TEQ<sub>DF</sub>/L to  $57.2$  ng I-TEQ<sub>DF</sub>/L. The study results also showed that 90%  
30 of the TEQ was contained in the wastewater treatment sludges generated during the treatment of  
31 wastewater and caustic from the regeneration process.



1 In 1995, EPA issued a notice of its proposed intent to not designate spent reformer  
2 catalysts as a listed hazardous waste under RCRA (Federal Register, 1995b). The final rule was  
3 issued in August 1998 (Federal Register, 1998a). The Agency's assessment of current  
4 management practices associated with recycling of reforming catalyst found no significant risks  
5 to human health or the environment. The Agency estimated that 94% of the approximately 3,600  
6 metric tons of spent reformer catalyst sent off site by refineries are currently recycled for their  
7 precious metal content. However, EPA made no determination of the "listability" of spent  
8 caustic residuals formed during regeneration of spent reforming catalyst. The Agency did  
9 identify the potential air releases from the combustion of the reforming catalyst prior to  
10 reclamation as being possibly of concern. The Agency requested comments on (a) opportunities  
11 for removing dioxin prior to discharge of scrubber water into the wastewater treatment system,  
12 (b) opportunities to segregate this wastestream, and (c) potential health risks associated with  
13 insertion of dioxin-contaminated media back into the refinery process (such as the coker). In this  
14 proposed rulemaking, EPA also noted the possibility of dioxin releases to air during regeneration  
15 operations.

16 As part of its regulatory investigation under RCRA, EPA's Office of Solid Waste  
17 commissioned a study to analyze and discuss existing data and information concerning  
18 CDD/CDF formation in the treatment of catalytic reformer wastes. This report (SAIC, 1994)  
19 also identified potential process modifications that may prevent the formation of CDDs/CDFs.  
20 The report's authors concluded that, although the available data indicate that CDDs/CDFs can be  
21 generated during the catalyst regeneration process, the available data indicate that CDD/CDF  
22 concentrations in treated wastewater and in solid waste are minimal. Releases to air could result  
23 from vented kiln exhaust gases at some facilities. In addition, the CDDs/CDFs formed could  
24 possibly be reintroduced into other refining operations (e.g., the coker) and resulting products.

25 In 1998, emissions from the caustic scrubber used to treat gases from the external  
26 regeneration unit of a refinery in California were tested (CARB, 1999). This facility uses a  
27 continuous regeneration process. The reactor is not taken off line during regeneration; rather,  
28 small amounts of catalyst are continuously withdrawn from the reactor and are regenerated. The  
29 emissions from the regeneration unit are neutralized by a caustic scrubber before being vented to  
30 the atmosphere. The catalyst recirculation rate during the three tests ranged from 733 to 1,000  
31 lb/hr.

1 All 2,3,7,8-substituted CDDs/CDFs were detected in each of the three samples collected.  
2 The average emission factors in units of ng/barrel of reformer feed are presented in Table 5-9.  
3 The congener profile is presented in Figure 5-4. The samples showed a wide range in  
4 concentrations of the CDD/CDF congeners (up to fivefold difference); however, the congener  
5 profile was consistent in all samples. The concentrations of the individual furan congener groups  
6 were always higher than the concentrations of the corresponding dioxin congener group. The  
7 average TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factor for these three tests is 3.18 ng TEQ/barrel and the  
8 average I-TEQ<sub>DF</sub> is 3.04 ng TEQ/barrel.

9 In 1991, stack testing was performed on the exhaust from one of the three semi-  
10 regenerative catalytic reforming units of a refinery in California (Radian Corporation, 1991). A  
11 caustic solution is introduced to the exhaust to neutralize HCl emissions from the catalyst beds  
12 prior to release to the atmosphere. The tested unit was considered to be representative of the  
13 other units. Each unit is periodically (approximately once per year) taken off line so the catalyst  
14 beds can be regenerated. The tested unit has a feed capacity of 7,000 barrels per day.  
15 Approximately 59,500 pounds of catalyst were regenerated during the tested regeneration cycle,  
16 which lasted for 62 hr.

17 The average emission factors for this facility (in units of ng/barrel of reformer feed) are  
18 presented in Table 5-9 and the congener profile is presented in Figure 5-4. The majority of the  
19 2,3,7,8-substituted CDD congeners were not detected during testing. In contrast, the majority of  
20 the 2,3,7,8-substituted CDF congeners were detected. The average TEQ<sub>DF</sub>-WHO<sub>98</sub> emission  
21 factor (assuming nondetect values are zero) is 1.04e-03 ng TEQ/barrel and the average I-TEQ<sub>DF</sub>  
22 emission factor is 1.01e-03 ng TEQ/barrel. These values are three orders of magnitude less than  
23 the emission factor reported in CARB (1999). The calculation of these emission factors involved  
24 several assumptions: the unit is regenerated once per year, the unit operates at capacity (7,000  
25 barrels/day), and the facility operates 362 days per year.

26 The average of the two facility emission factors, 1.59 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/barrel (1.52 ng I-  
27 TEQ<sub>DF</sub>/barrel) of reformer feed, is assumed to apply to all reference years (1987, 1995, and 2000)  
28 and is assigned a low confidence rating. Only one continuous and only one semiregenerative unit  
29 in the United States have been tested. Combined, these two facilities represent less than 1% of  
30 the catalytic reforming capacity in U.S. petroleum refineries in 1987 (3.805 million barrels per  
31 day), 1995 (3.867 million barrels per day), and 2000 (3.770 million barrels per 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, 2002a). 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 1987, 1995, and 2000, then applying the average emission factors of TEQ/barrel yields annual emissions of 2.21 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (2.11 g I-TEQ<sub>DF</sub>) in 1987, 2.24 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (2.14 g I-TEQ<sub>DF</sub>) in 1995, and 2.19 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (2.09 g I-TEQ<sub>DF</sub>) 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 the CDD/CDF content of the 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.

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, 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.

1           Formation of CDDs/CDFs has been reported in combustion studies with other media in  
2           this temperature range of 200 to 900 °C. However, it is known that a process likened by Guerin  
3           et al. (1992) to steam distillation takes place in the region behind the char line because of high,  
4           localized concentrations of water and temperatures of 200 to 400 °C. At least 1,200 tobacco  
5           constituents (e.g., nicotine, n-paraffin, some terpenes) are transferred intact from the tobacco into  
6           the smoke stream by distillation in this region, and it is plausible that CDDs/CDFs present in the  
7           unburned tobacco would be subject to similar distillation.

8           Bumb et al. (1980), using low-resolution mass spectrometry, analyzed the CDD content  
9           of mainstream smoke from the burning of a U.S. brand of unfiltered cigarette. A package of 20  
10          cigarettes was combusted in each of two experiments. Approximately 20 to 30 puffs of 2 to 3 sec  
11          duration were collected from each cigarette on a silica column. Hexa-, hepta-, and octa-CDDs  
12          were detected at levels of 0.004 to 0.008, 0.009, and 0.02 to 0.05 ng/g, respectively.

13          Muto and Takizawa (1989) employed a continuous smoking apparatus to measure CDD  
14          congener concentrations in the mainstream smoke generated from the combustion of one kind of  
15          filtered cigarette (brand not reported). The apparatus pulled air at a constant continuous rate  
16          (rather than a pulsed rate) through a burning cigarette and collected the smoke on a series of traps  
17          (glass fiber filter, polyurethane foam, and XAD-II resin). The CDD content of the smoke, as well  
18          as the CDD content of the unburned cigarette and the ash from the burned cigarettes, were also  
19          analyzed using low-resolution mass spectrometry. The results are presented in Table 5-10, and  
20          the congener group profiles are presented in Figure 5-5. Table 5-11 and Figure 5-6 present the  
21          mainstream smoke results on a mass-per-cigarette basis to enable comparison with the results of  
22          other studies.

23          The major CDD congener group found was HpCDD, which accounted for 84% of total  
24          CDDs found in the cigarette, 94% of total CDDs found in smoke, and 99% of total CDDs found  
25          in the ash. The 2,3,7,8-HpCDDs also accounted for the majority of the measured TEQ in the  
26          cigarettes and smoke; however, none were measured in the ash. Although no PeCDDs were  
27          detected in the cigarette, PeCDDs were detected at low levels in the smoke, indicating probable  
28          formation during combustion. On the basis of the similarities in the congener group profiles for  
29          the three media, the study authors concluded that most of the CDDs found in the cigarette smoke  
30          result from volatilization of CDDs/CDFs present in the unburned cigarette rather than being  
31          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<sub>DF</sub> and a TEQ<sub>DF</sub>-WHO<sub>98</sub> 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 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<sub>DF</sub>-WHO<sub>98</sub>/cigarette (0.9 pg I-TEQ<sub>DF</sub>/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<sub>DF</sub>-WHO<sub>98</sub>/cigarette (1.96 pg I-TEQ<sub>DF</sub>/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<sub>DF</sub>-WHO<sub>98</sub> content ranged from 1.9 to 14 pg/pack (1.4 to 12.6 pg/pack on an I-TEQ<sub>DF</sub> basis). The Chinese cigarette brand contained significantly lower CDDs/CDFs and TEQs than 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 in the CDF congener group profiles of the tested cigarette brands. The Japanese and Taiwanese cigarettes show CDD congener group profiles different from the other countries' cigarettes.

1 Brown et al. (2002) estimated that 440 billion cigarettes were consumed in the United  
2 States in 2000. In 1995, approximately 487 billion cigarettes were consumed in the United States  
3 and by U.S. overseas armed forces personnel. In 1987, approximately 575 billion cigarettes were  
4 consumed. According to the Tobacco Institute (1995), per capita U.S. cigarette consumption,  
5 based on total U.S. population aged 16 and over, was a record high of 4,345 in 1963, declining to  
6 2,415 in 1995 and 1,563 in 2000 (USDA, 1997; U.S. Census Bureau, 2000). The activity level  
7 estimates by Brown et al. (2002) were adopted and a high confidence rating is assigned because  
8 they are based on known consumption rates.

9 The available emission factor data presented above provide the basis for two methods of  
10 estimating the amount of TEQs that may have been released to the air in the United States in  
11 2000, 1995, and in 1987 from the combustion of cigarettes. The confidence rating assigned to  
12 the emission factor is low because of the very limited amount of testing performed to date. First,  
13 an annual emission estimate for 2000 of 0.19 g TEQ (on a TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub> basis) is  
14 obtained if it is assumed that (a) the average TEQ content of seven brands of U.S. cigarettes  
15 reported by Matsueda et al. (1994)—8.8 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/pack (8.6 pg I-TEQ<sub>DF</sub>/pack)—is  
16 representative of cigarettes smoked in the United States, (b) CDDs/CDFs are not formed and the  
17 congener profile reported by Matsueda et al. (1994) is not altered during combustion of  
18 cigarettes, and (c) all CDDs/CDFs contributing to the TEQ are released from the tobacco during  
19 smoking.

20 The second method of estimating is based on the assumption that the TEQ emission rates  
21 for a common Swedish brand of cigarette reported by Löfroth and Zebühr (1992) for mainstream  
22 smoke (0.96 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/cigarette [0.9 pg I-TEQ<sub>DF</sub>/cigarette]) and sidestream smoke (2.08  
23 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/cigarette [1.96 pg I-TEQ<sub>DF</sub>/cigarette]) are representative of the emission rates  
24 for U.S. cigarettes. For 2000, the two methods yield estimates of 0.13 g TEQ<sub>DF</sub>-WHO<sub>98</sub> and 0.67  
25 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (0.63 g I-TEQ<sub>DF</sub>). For 1995, the two methods yield estimates of 0.21 g (on a  
26 TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub> basis) and 1.48 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (1.41 g I-TEQ<sub>DF</sub>). For 1987, the two  
27 methods yield estimates of 0.25 g TEQ (on a TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub> basis) and 1.75 g  
28 TEQ<sub>DF</sub>-WHO<sub>98</sub> (1.67 g I-TEQ<sub>DF</sub>).

29 For purposes of this report, the best estimates of annual emissions are assumed to be the  
30 average of the annual emissions estimated by the two methods for 2000, 1995, and 1987 (0.4 g,  
31 0.8 g, and 1 g TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub>, respectively). These emissions were assigned a low

confidence rating because the emission factor had a low confidence rating. Although these emission quantities are relatively small when compared to 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. HpBDF and OBDF 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<sup>2</sup>/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 replaced and discarded, 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, 1997b).

The used GAC can contain compounds that are precursors to the formation of CDDs/CDFs during the thermal treatment process. EPA measured precursor compounds in spent GAC that was used as a feed material to a carbon reactivation furnace tested during the National Dioxin Study (U.S. EPA, 1987a). 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, 1997b) 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<sub>DF</sub> emission factor (treating nondetect values as zero) was 0.76 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (0.64 ng I-TEQ<sub>DF</sub>/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 section 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 and combustion section 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, 1997b) reported a TEQ emission factor of 1.73 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub>-WHO<sub>98</sub> 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.

1 The industrial GAC reaction furnace test data indicate that an average of 0.64 ng  
2 I-TEQ<sub>DF</sub>/kg of GAC may be released. The I-TEQ<sub>DF</sub> emission rate for the reactivation unit at the  
3 county water treatment facility was 1.73 ng I-TEQ<sub>DF</sub>/kg carbon. Low confidence ratings are  
4 given to these emission factors because only two GAC reactivation furnaces were stack-tested  
5 and not all congeners were analyzed at the industrial GAC facility.

6 The mass of GAC that is reactivated annually in carbon reactivation furnaces is not  
7 known. However, a rough estimate, to which a low confidence rating is assigned, is the mass of  
8 virgin GAC shipped each year by GAC manufacturers. According to the U.S. Department of  
9 Commerce (1990c), 48,000 metric tons of GAC were shipped in 1987. EPA reported that in  
10 1990, water and wastewater treatment operations consumed 65,000 metric tons of GAC (U.S.  
11 EPA, 1995c, 1997b). The 1990 activity level is used in this document as a surrogate for the 1995  
12 and 2000 activity levels.

13 Applying the average TEQ emission factor of 1.2 ng (TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub>) per kg  
14 of reactivated carbon for the two tested facilities to the estimates of potential GAC reactivation  
15 volumes, yields annual release estimates of 0.06 g (TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub>) in 1987 and  
16 0.08 g (TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub>) in 1995 and 2000 (assuming that the activity level for 1990 is  
17 representative of the 1995 and 2000 activity levels). These emission estimates are assigned a low  
18 confidence rating because both the activity and emission factor estimates had low confidence  
19 ratings.

## 20 21 **5.8. KRAFT BLACK LIQUOR RECOVERY BOILERS**

22 Kraft black liquor recovery boilers are associated with the production of pulp in the  
23 making of paper using the Kraft process. In this process, wood chips are cooked in large vertical  
24 vessels called digesters at elevated temperatures and pressures in an aqueous solution of sodium  
25 hydroxide and sodium sulfide. Wood is broken down into two phases: a soluble phase  
26 containing primarily lignin and an insoluble phase containing the pulp. The spent liquor (called  
27 black liquor) from the digester contains sodium sulfate and sodium sulfide, which the industry  
28 recovers for reuse in the Kraft process.

29 In the recovery of black liquor chemicals, weak black liquor is first concentrated in  
30 multiple-effect evaporators to about 65% solids. The concentrated black liquor also contains 0.5  
31 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 and one was judged to have high potential for CDD/CDF emissions, 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 include congener group concentrations but lack 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, is 0.028 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (0.029 ng I-TEQ<sub>DF</sub>/kg) of black liquor solids, assuming nondetect values are zero, and 0.078 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (0.068 ng I-TEQ<sub>DF</sub>/kg), assuming nondetect values are 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.

1 A 1995 survey of the industry indicated that 215 black liquor recovery boilers were in  
2 operation at U.S. pulp and paper mills. All but one of these boilers used ESPs for control of  
3 particulate emissions; the one unique facility used dual scrubbers. In addition, ESPs were  
4 reported to have been the predominant means of particulate control at recovery boilers for the  
5 past 20 years (Gillespie, 1998).

6 The amounts of black liquor solids burned in Kraft black liquor recovery boilers in the  
7 United States during 1987 and 1995 were 69.8 million metric tons and 80.8 million metric tons,  
8 respectively (American Paper Institute, 1992; American Forest and Paper Association, 1997).  
9 These activity level estimates are assigned a high confidence rating because they are based on  
10 comprehensive industry survey data. Combining the emission factors derived above with the  
11 activity level estimates for 1987 and 1995 yields estimated annual emissions from this source of  
12 approximately 2 g (TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub>) in 1987 and 2.3 g (TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub>) in  
13 1995. These emission estimates were assigned a medium confidence rating because the emission  
14 factor had a medium confidence rating.

15 For 2000, NCASI provided estimates of activity levels for Kraft recovery furnaces and  
16 Kraft lime kilns and CDD/CDF releases, including emissions from 11 Kraft recovery furnaces  
17 and four Kraft lime kilns (Gillespie, 2002). The activity levels were reported to be 90.7 million  
18 metric tons for Kraft recovery furnaces and 13 million metric tons for Kraft lime kilns. These  
19 activity level estimates are assigned a high confidence rating because they are based on  
20 comprehensive industry survey data. Emission factors were taken from the NCASI Handbook of  
21 Chemical Specific Information for SARA Section 313 Form R Reporting. The factors provided  
22 in this handbook were compiled from valid test data supplied to NCASI by a variety of sources,  
23 including NCASI member companies who had performed the tests in response to a regulatory  
24 program. They were assigned a high confidence rating because they are based on a  
25 comprehensive survey of stack emissions. Congener-specific CDD/CDF TEQ emission factors  
26 were provided for both source categories (Table 5-14). Using the congener-specific emission  
27 factors and the activity levels provided above, NCASI estimated CDD/CDF TEQ<sub>DF</sub>-WHO<sub>98</sub>  
28 emissions for each congener (Table 5-14) and reported total emissions as 0.75 g TEQ<sub>DF</sub>-  
29 WHO<sub>98</sub>/yr and 6.9e-5 g TEQ<sub>DF</sub>-WHO<sub>98</sub>/yr for Kraft recovery furnaces and Kraft lime kilns,  
30 respectively. This 2000 emission estimate was rated as high confidence because both the  
31 emission factor and activity level were 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<sub>DF</sub>/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. (1994) and Douben et al. (1995) were not reported. Umweltbundesamt (1996) reported relatively low emission factors (approximately 0.002 and 0.007 ng I-TEQ<sub>DF</sub>/kg) for two glass manufacturing facilities in Germany.

**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

1 (1996) reported low emissions (0.016 to 0.028 ng I-TEQ<sub>DF</sub>/kg) during tests at two lime kilns in  
2 Germany.

3 **Ceramics and rubber manufacturers.** Douben et al. (1995) estimated annual emissions  
4 from ceramic manufacturers and rubber manufacturers in the United Kingdom. Lexen et al.  
5 (1993) had previously detected high concentrations of CDDs/CDFs in emissions from a ceramic  
6 manufacturer in Sweden that occasionally glazed ceramics by volatilization of sodium chloride in  
7 a coal-fired oven. Lexen et al. (1993) also detected high pg/L levels of I-TEQ<sub>DF</sub> in the scrubber  
8 water from the vulcanization process at a Swedish rubber manufacturer.

**Table 5-1. CDD/CDF emission factors for cement kilns burning hazardous waste for reference years 1987 and 1995**

Congener/ congener group	Kilns burning hazardous waste mean emission factor (nondetect values set equal to zero) (ng/kg clinker produced)	
	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 <sub>DF</sub>	28.58	1.04
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	30.7	1.11
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	22.92

APCD = Air pollution control device

Source: U.S. EPA (1996c).

**Table 5-2. CDD/CDF emission factors for cement kilns burning hazardous waste for reference year 2000**

Congener/congener group	Mean emission factor (ng/kg clinker produced)	
	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	0.1	0.11
1,2,3,7,8-PeCDD	1.05	0.55
1,2,3,4,7,8-HxCDD	1.35	0.69
1,2,3,6,7,8-HxCDD	3.14	1.18
1,2,3,7,8,9-HxCDD	3.41	1.3
1,2,3,4,6,7,8-HpCDD	15.8	6.14
OCDD	4.86	2.57
2,3,7,8-TCDF	12.12	3.03
1,2,3,7,8-PeCDF	2.03	1.06
2,3,4,7,8-PeCDF	4.08	2.29
1,2,3,4,7,8-HxCDF	3.22	1.35
1,2,3,6,7,8-HxCDF	1.38	0.69
1,2,3,7,8,9-HxCDF	0.28	0.23
2,3,4,6,7,8-HxCDF	2.61	1.23
1,2,3,4,6,7,8-HpCDF	1.22	0.54
1,2,3,4,7,8,9-HpCDF	0.37	0.22
OCDF	0.36	0.23
Total I-TEQ <sub>DF</sub>	5.49	2.87
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	5.95	3.13
Total TCDD	161.5	40.75
Total PeCDD	217.62	37.68
Total HxCDD	330.66	83.76
Total HpCDD	62.87	7.26
Total OCDD	4.86	2.57
Total TCDF	103.57	18.34
Total PeCDF	43.22	6.15
Total HxCDF	18.72	4.13
Total HpCDF	1.29	1.03
Total OCDF	0.36	0.23
Total CDD/CDF	864.55	347.91

Source: U.S. EPA (1996c); U.S. EPA (2002b).



**Table 5-3. CDD/CDF emission factors for cement kilns burning nonhazardous waste for reference years 1987, 1995, and 2000<sup>a</sup>**

Congener/congener group	Mean emission factor (ng/kg clinker produced)	
	Nondetect set to zero	Nondetect set to 1/2 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 <sub>DF</sub>	0.26	0.27
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	0.27	0.3
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

<sup>a</sup>The same CDD/CDF emission factor was assumed for all three years.

Source: U.S. EPA (1996c); Bell (1999).

**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 <sub>DF</sub>	TEQ <sub>DF</sub> - WHO <sub>98</sub>		I-TEQ <sub>DF</sub>	TEQ <sub>DF</sub> - WHO <sub>98</sub>
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

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

Category	TEQ CCD/CDF concentrations (ng/kg clinker)		Activity level (billion kg clinker/yr)	Annual TEQ emission (g/yr)	
	I-TEQ <sub>DF</sub>	TEQ <sub>DF</sub> - WHO <sub>98</sub>		I-TEQ <sub>DF</sub>	TEQ <sub>DF</sub> - WHO <sub>98</sub>
Hazardous waste	5.49	5.95	11.5	63.3	68.4
Nonhazardous waste	0.26	0.27	63.7	16.6	17.2
<b>TOTAL</b>			<b>75.2</b>	<b>79.9</b>	<b>85.6</b>

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

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	2.48	33.4
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	2.4	274	274

**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 <sub>DF</sub> /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

**Table 5-8. Congener-specific profile for hot-mix asphalt plants**

Congener	Mean emission factor (2 facilities) (ng/kg combusted)	
	Nondetect set to zero	Nondetect set to ½ detection limit
2,3,7,8-TCDD	1.62e-05	6.27e-04
1,2,3,7,8-PeCD	2.70e-05	4.12e-04
1,2,3,4,7,8-HxCDD	4.30e-06	8.61e-05
1,2,3,6,7,8-HxCDD	2.95e-05	1.06e-04
1,2,3,7,8,9-HxCDD	2.09e-05	9.99e-05
1,2,3,4,6,7,8-HpCDD	1.23e-05	2.71e-05
OCDD	5.81e-07	4.76e-06
2,3,7,8-TCDF	4.32e-04	4.88e-04
1,2,3,7,8-PeCDF	9.07e-05	1.08e-04
2,3,4,7,8-PeCDF	1.21e-04	4.10e-04
1,2,3,4,7,8-HxCDF	9.64e-05	1.62e-04
1,2,3,6,7,8-HxCDF	2.95e-05	8.12e-05
1,2,3,7,8,9-HxCDF	1.73e-04	2.14e-04
2,3,4,6,7,8-HxCDF	4.83e-05	1.10e-04
1,2,3,4,6,7,8-HpCDF	1.58e-05	2.71e-05
1,2,3,4,7,8,9-HpCDF	6.91e-06	2.17e-05
OCDF	1.19e-07	3.13e-06
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	1.12e-03	2.99e-03

Source: U.S. EPA (2001b).

**Table 5-9. CDD/CDF emission factors for petroleum catalytic reforming units**

Congener/congener group	Semiregenerative unit (ng/barrel) <sup>a</sup>		Continuous regeneration unit (ng/barrel) <sup>a</sup>	
	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	6.77e+00	6.77e+00
Total 2,3,7,8-CDF	9.94e-03	1.00e-02	3.76e+01	3.76e+01
Total I-TEQ <sub>DF</sub>	1.01e-03	1.08e-03	3.04e+00	3.04e+00
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	1.04e-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

<sup>a</sup>One barrel assumed to be equivalent to 139 kg.

ND = Not detected

Sources: Radian Corporation (1991); CARB (1999).

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

Congener/congener group	Cigarette (pg/g)	Concentrations	
		Mainstream smoke (ng/m <sup>3</sup> )	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 <sup>a</sup>	2.15 <sup>a</sup>	0.56 <sup>a</sup>
1,2,3,6,7,8-HxCDD	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
1,2,3,7,8,9-HxCDD	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
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 <sub>DF</sub>	13.9	8.5	0.06
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	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

<sup>a</sup>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).

**Table 5-11. CDD/CDF emissions in cigarette smoke**

Congener/congener group	Concentrations normalized to a per cigarette basis (pg/cig)			
	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	<sup>b</sup>	0.05	0.34	0.6
1,2,3,7,8,9-HxCDD	<sup>b</sup>	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 <sup>c</sup>	2.1 <sup>c</sup>
1,2,3,7,8-PeCDF	NR	0.13	0.34 <sup>c</sup>	0.8 <sup>c</sup>
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 <sup>c</sup>	3.8 <sup>c</sup>
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 <sub>DF</sub>	1.49	0.09	0.9	1.96
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	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

<sup>a</sup>Emissions calculated assuming 0.0035 m<sup>3</sup> of smoke are inhaled per 20 cigarettes smoked (Muto and Takizawa, 1992).

<sup>b</sup>Muto and Takizawa (1989) reported a value only for total 2,3,7,8-HxCDDs (0.38 pg/cig).

<sup>c</sup>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



**Table 5-12. CDD/CDF concentrations in cigarette tobacco**

Congener/congener group	Concentrations in brands from various countries (pg/pack)						
	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 <sub>DF</sub>	8.6	4.6	12.6	9.3	1.4	3.8	9.1
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	8.8	5.1	14	10.7	1.9	3.9	10.5
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

<sup>a</sup>Value reported only for total 2,3,7,8-substituted HxCDDs.

<sup>b</sup>Value reported only for total 2,3,7,8-substituted PeCDFs.

<sup>c</sup>Value reported only for total 2,3,7,8-substituted HxCDFs.

<sup>d</sup>Value reported only for total 2,3,7,8-substituted HpCDFs.

Source: Matsueda et al. (1994).

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

Congener	U.S. EPA (1987) (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 <sub>DF</sub>	0.10 <sup>a</sup>	0.15 <sup>a</sup>	0.029	0.065
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	0.10 <sup>a</sup>	0.16 <sup>a</sup>	0.028	0.072
Total CDD/CDF	11.71	12.17	3.386	3.566

<sup>a</sup>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

**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 <sub>DF</sub> -WHO <sub>98</sub> (ng/lb BLS)	Emissions (ng/yr)	TEQ <sub>DF</sub> -WHO <sub>98</sub> (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

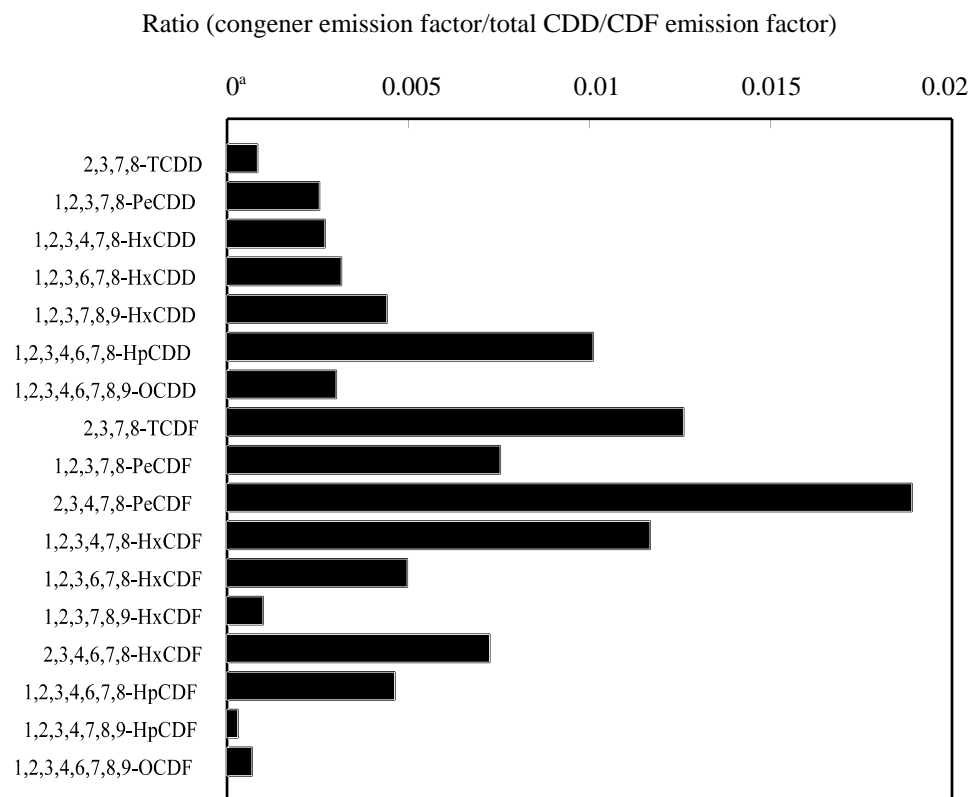
BLS = Black liquor solids

CaO = Calcium oxide

**Table 5-15. Concentrations of CDD/CDF in candle materials and emissions**

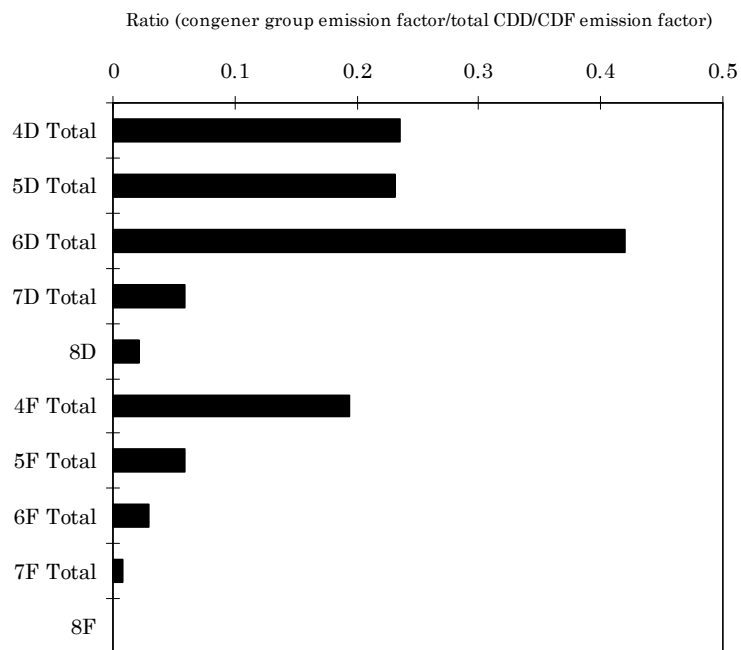
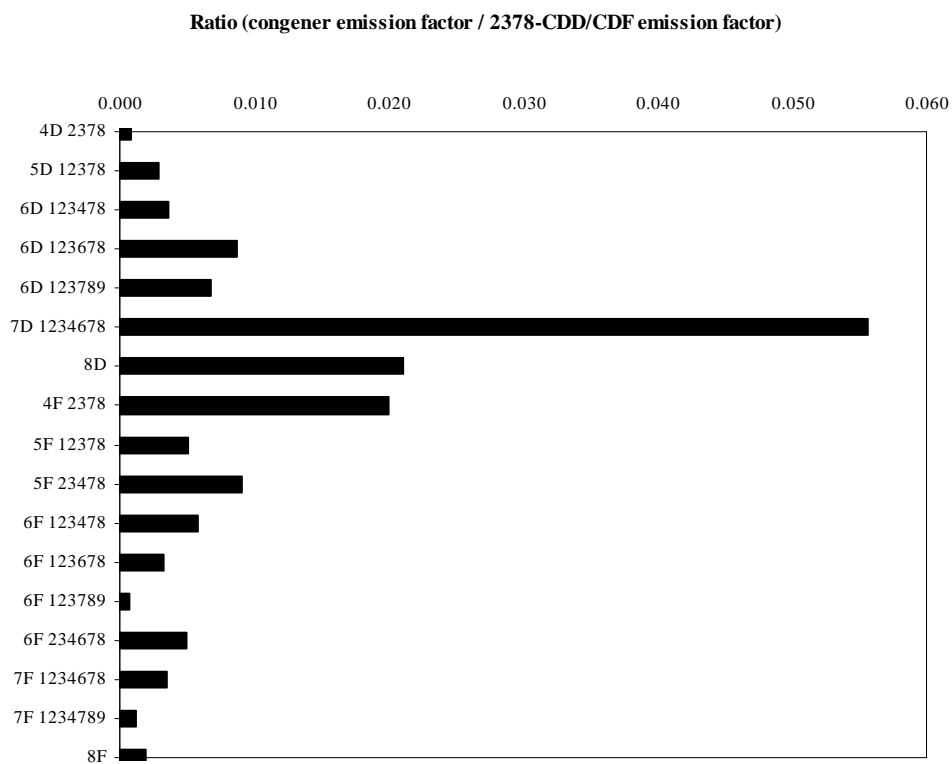
Wax material	Candle component	Concentration			Emission factor
		CDD/CDF (ng I-TEQ <sub>DF</sub> /kg)	Total chlorophenols (µg/kg)	Total chlorobenzenes (µg/kg)	CDD/CDF (ng I-TEQ <sub>DF</sub> /kg burnt wax)
Paraffin	Wax	0.59	14.8	130	0.015
Stearin	Wax	1.62	32.3	330	0.027
Beeswax	Wax	10.99	256	120	0.004
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).

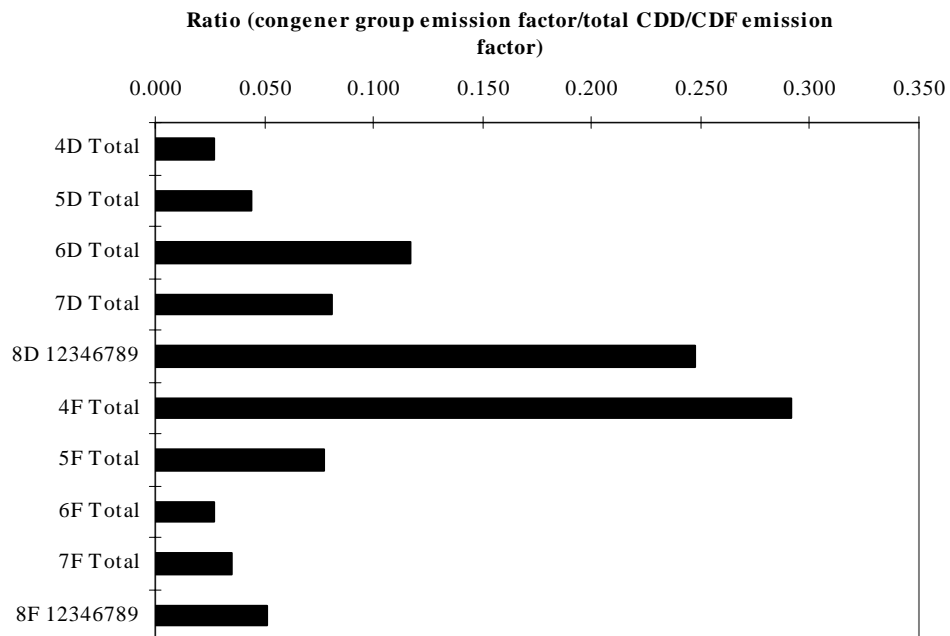
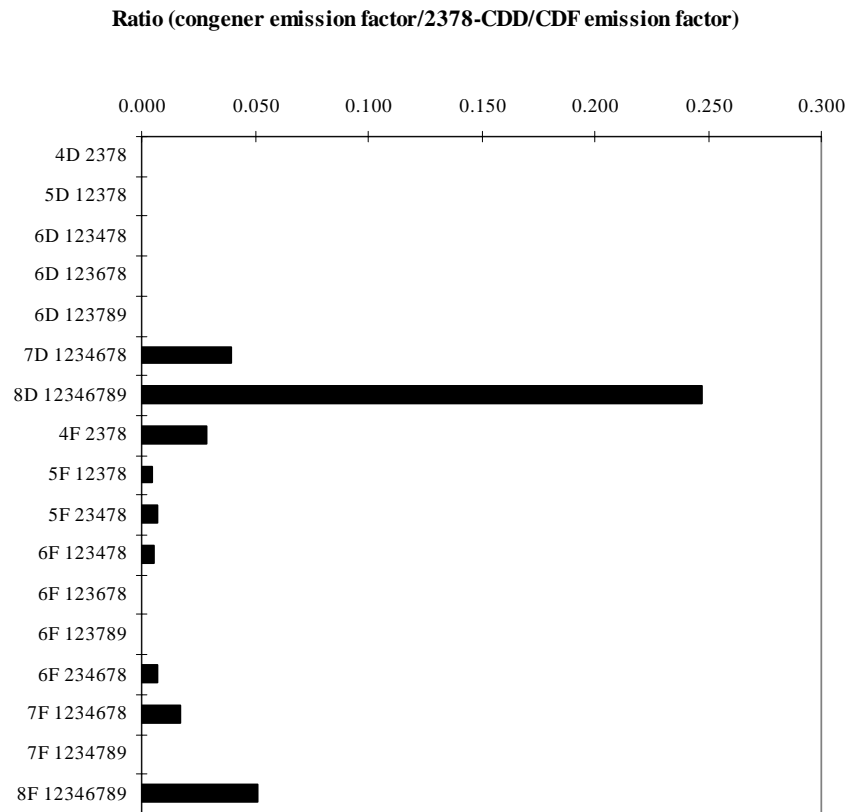


<sup>a</sup>Nondetect set equal to zero.

**Figure 5-1. Congener profile for air emissions from cement kilns burning hazardous waste for reference years 1987 and 1995.**

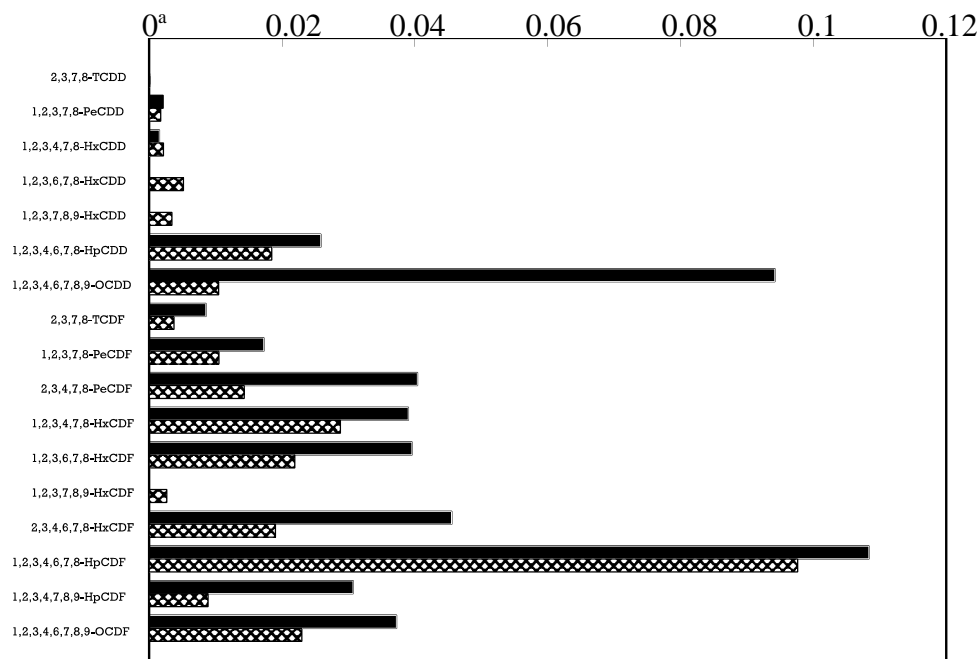


**Figure 5-2. Congener profile for air emissions from cement kilns burning hazardous waste for reference year 2000.**



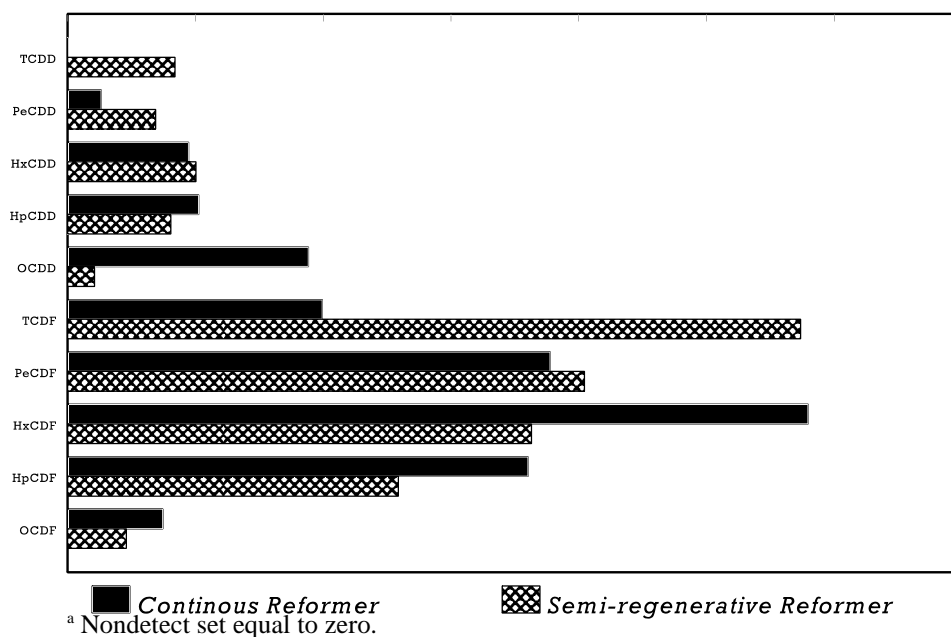
**Figure 5-3. Congener profile for air emissions from cement kilns burning nonhazardous waste for reference years 1987, 1995, and 2000.**

Ratio (mean congener emission factor/total CDD/CDF emission factor)



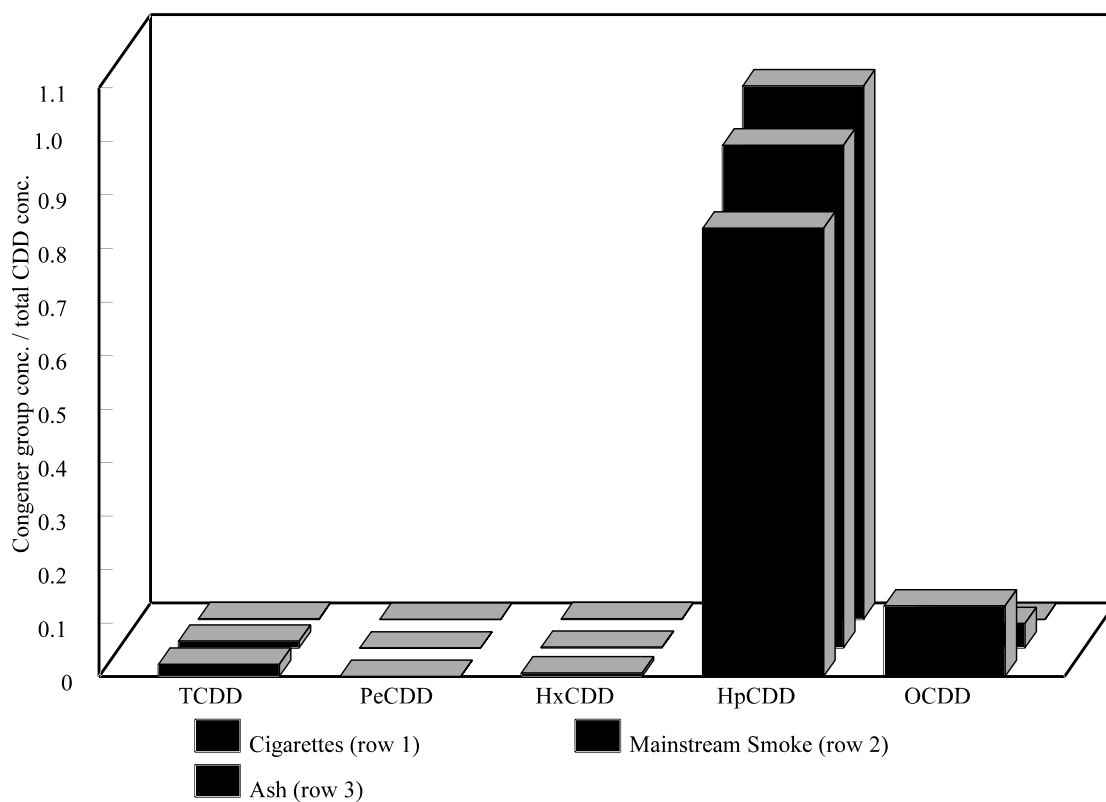
Ratio (mean congener emission factor/total CDD/CDF emission factor)

0<sup>a</sup> 0.05 0.1 0.15 0.2 0.25 0.3 0.35



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

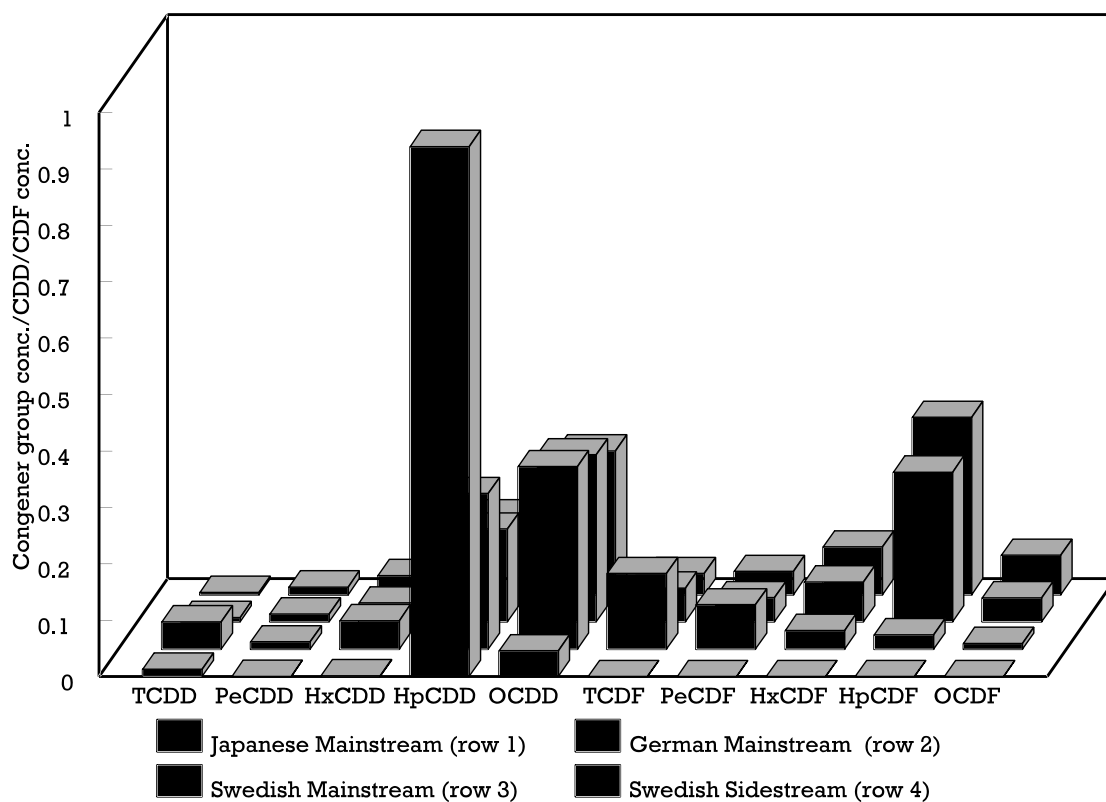
Source: CARB (1999); Radian (1991).



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

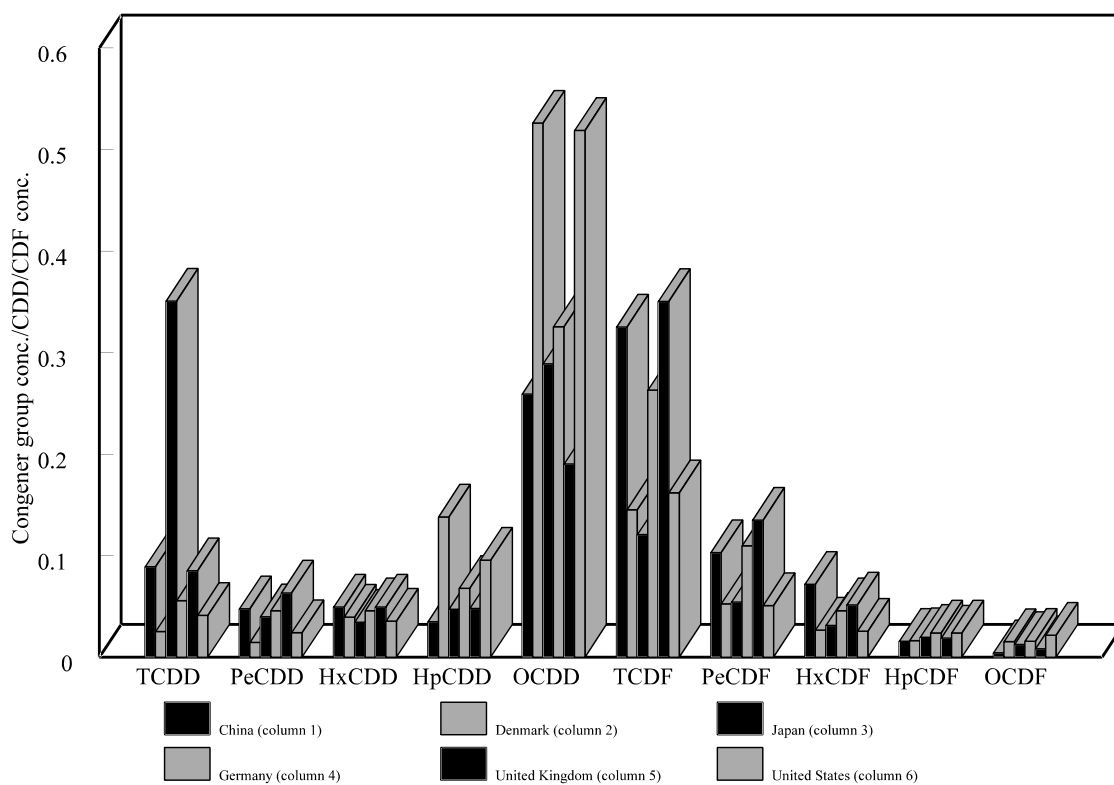
Source: Matsueda et al. (1994).





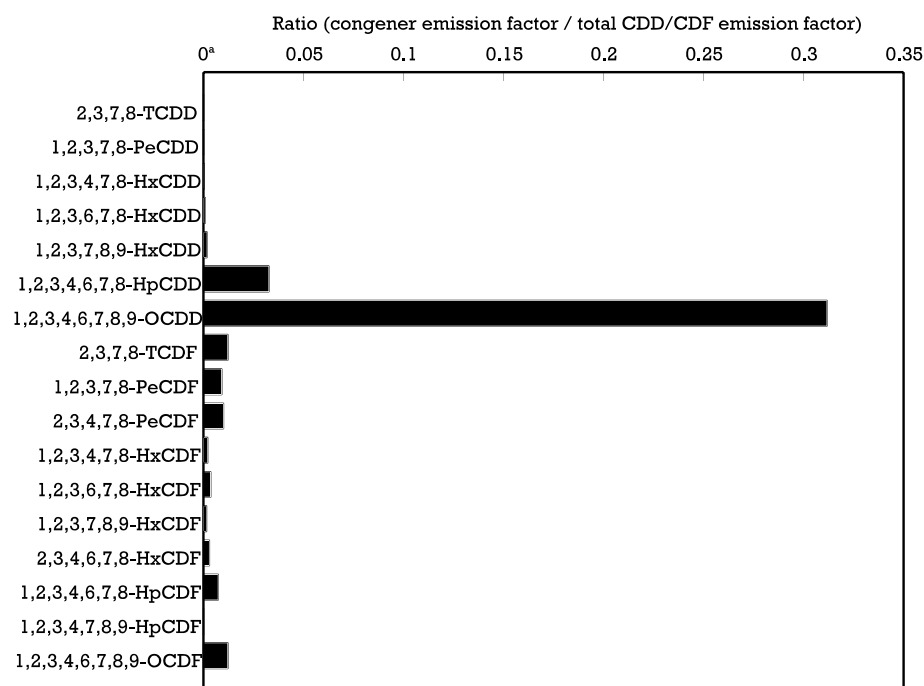
**Figure 5-6. Congener group profiles for mainstream and sidestream cigarette smoke.**

Source: Matsueda et al. (1994).

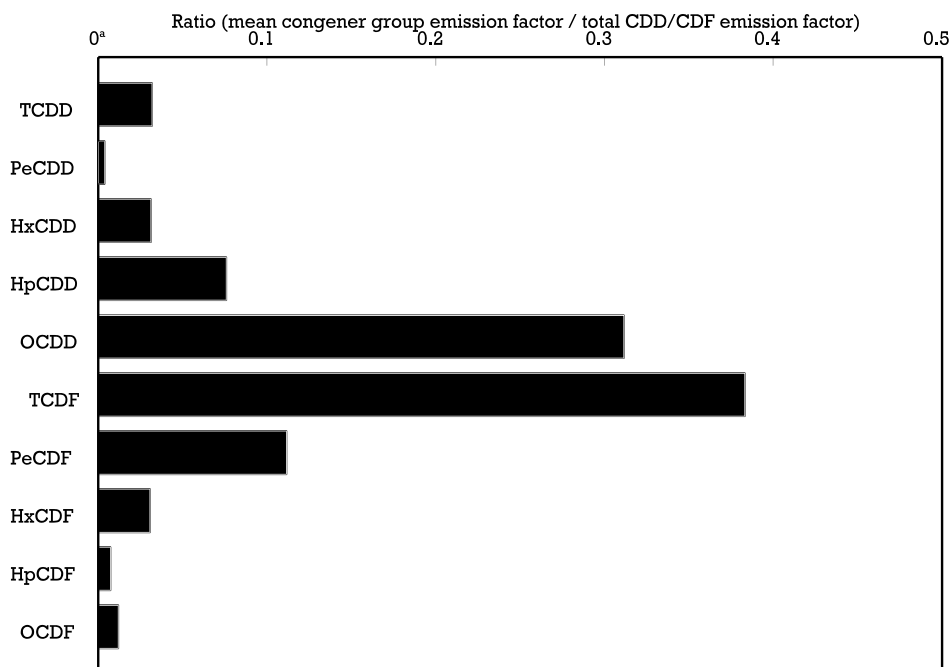


**Figure 5-7. Congener group profiles for cigarette tobacco from various countries.**

Source: Matsueda et al. (1994).



<sup>a</sup>Nondetect set equal to zero.



**Figure 5-8. Congener and congener group profiles for air emissions from Kraft black liquor recovery boilers.**

Source: NCASI (1995).

## 6. COMBUSTION SOURCES OF CDDs/CDFs: MINIMALLY CONTROLLED AND UNCONTROLLED COMBUSTION SOURCES<sup>1</sup>

### 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, 1990d). The TEQ<sub>DF</sub>-WHO<sub>98</sub> and I-TEQ<sub>DF</sub> emission factor calculated from the results of this study is approximately 2.4 ng TEQ/m<sup>3</sup> of 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<sub>DF</sub>/m<sup>3</sup>, 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 (1990d) and Bremmer et al. (1994) studies is 1.4 ng I-TEQ<sub>DF</sub>/m<sup>3</sup> of 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<sub>DF</sub>/m<sup>3</sup>, with most values below 0.1 ng I-TEQ<sub>DF</sub>/m<sup>3</sup>. However, Bremmer et al. (1994) also reported an emission factor of 0.5 ng I-TEQ<sub>DF</sub>/m<sup>3</sup> 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, 1996a). 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

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<sup>1</sup>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.

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 use of a control device.

#### **6.1.2.1. 1987 and 1995 Activity Levels**

EPA estimated that when the 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 use of flares, the corresponding volume of landfill gas burned would be approximately 14 billion m<sup>3</sup>/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<sup>3</sup> of NMOC per 1 ppmv of NMOC (Federal Register, 1993d). 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, 1991b). Thus, a rough approximation of the volume of landfill gas combusted was 4.7 billion m<sup>3</sup>/yr (or 33% of the future expected 14 billion m<sup>3</sup>/yr reduction). This estimate is similar to the 2 to 4 billion m<sup>3</sup> of 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<sup>3</sup> of landfill gas was collected and burned in 1990 for energy recovery purposes. As there were no specific data available for the year 1987, EPA assumed that the mean of this range, 1.35 billion m<sup>3</sup>, would serve as an approximate estimate of the volume of landfill gas combusted in 1987.

#### **6.1.2.2. 2000 Activity Level**

According to the EPA 2001 Inventory of Greenhouse Gas Emissions, approximately 7.7 billion m<sup>3</sup> of landfill gas were combusted in 2000 through 477 landfill flares (average of 16.5 million m<sup>3</sup> landfill gas per flare). In the United States, there are currently more than 1,000 landfill flares (U.S. EPA, 2003b). Assuming that the landfill gas combustion through the 477 landfill flares inventoried is representative of the landfill gas combustion through the more than 1,000 flares in the United States, approximately 16 billion m<sup>3</sup> of landfill gas was 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 is combusted (1.35 billion m<sup>3</sup> in 1987, 4.7 billion m<sup>3</sup> in 1995, and 16 billion m<sup>3</sup> in 2000) with the emission factor of 1.4 ng I-TEQ<sub>DF</sub>/m<sup>3</sup> of flare-combusted gas yields annual emission estimates of 1.9, 6.6, and 22 g I-TEQ<sub>DF</sub>/m<sup>3</sup> 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. (1989b) 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

1 a nitrogen atmosphere. The combustion experiments yielded CDD/CDF concentrations in soot  
2 of 110  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  for a low-molecular-weight PVC, 450  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  for a high-  
3 molecular-weight PVC, and 270  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  for PVC cable. The pyrolysis experiments in the  
4 air atmosphere yielded lower CDD/CDF concentrations in soot: 24.4  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  for a low-  
5 molecular-weight PVC, 18.7  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  for a high-molecular-weight PVC, and up to 41  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  for PVC cable.

7 In general, more CDFs than CDDs were formed. The less-chlorinated CDF congeners  
8 were dominant in the combustion experiments; however, the HpCDF and OCDF congeners were  
9 dominant in the pyrolysis experiments. No CDDs/CDFs were detected in pyrolysis experiments  
10 under a nitrogen atmosphere. Also, no CDDs/CDFs were detected when chlorine-free  
11 polyethylene samples were subjected to the same combustion and pyrolysis conditions.

12 Deutsch and Goldfarb (1988) reported finding CDD/CDF concentrations ranging from  
13 0.04 to 6.6  $\mu\text{g/kg}$  in soot samples collected after a 1986 fire in a State University of New York  
14 lecture hall. The fire consumed or melted plastic furnishings, cleaning products containing  
15 chlorine, wood, and paper.

16 Funcke et al. (1988; as reported in Bremmer et al., 1994, and Rotard, 1993) analyzed 200  
17 ash and soot samples from sites of accidental fires in which PVC was involved. CDDs/CDFs  
18 were detected in more than 90% of the samples at concentrations in the ng I- $\text{TEQ}_{\text{DF}}/\text{kg}$  to  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  range. Fires involving the combustion of materials containing relatively large amounts  
19 of PVC and other chlorinated organic substances resulted in the highest levels of CDDs/CDFs,  
20 with concentrations ranging from 0.2 to 110  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  of residue.

22 Thiesen et al. (1989) analyzed residues from surfaces of PVC-containing materials that  
23 were partially burned during accidental fires at sites in Germany that manufactured or stored  
24 plastics. CDD/CDF concentrations in residues were reported as 0.5  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  for soft PVC,  
25 4.6  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  for PVC fibers, and 28.3  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  for a hard PVC. The ratio of total  
26 CDFs to total CDDs in the three samples ranged from 4:1 to 7:1. The dominant 2,3,7,8-  
27 substituted CDF and CDD congeners in all three samples were 1,2,3,4,6,7,8-HpCDF and  
28 1,2,3,4,6,7,8-HpCDD.

29 In an accidental fire at a Swedish carpet factory in 1987, 200 metric tons of PVC and 500  
30 metric tons of PVC-containing carpet were burned. Marklund et al. (1989) analyzed snow  
31 samples up to 1,500 m downwind from the fire site and found CDD/CDF concentrations in the

1 top 2 cm ranging from 0.32  $\mu\text{g I-TEQ}_{\text{DF}}/\text{m}^2$  at 10 m of the site to 0.01  $\mu\text{g I-TEQ}_{\text{DF}}/\text{m}^2$  at 1,500 m.  
2 Because of an atmospheric inversion and very light wind at the time of the fire, the smoke from  
3 the fire remained close to the ground. The soot deposited onto the snow was thus assumed to be  
4 representative of the soot generated and released from the fire. Wipe samples of soot from  
5 interior posts of the plant that were 5 and 20 m from the fire contained EADON TEQ  
6 concentrations of 0.18 and 0.05  $\mu\text{g}/\text{m}^2$ , respectively. On the basis of these deposition  
7 measurements, the investigators estimated total CDD/CDF emissions from the fire to be less than  
8 3 mg I-TEQ<sub>DF</sub>.

9 Carroll (1996) estimated a soot-associated CDD/CDF emission factor (i.e., not including  
10 volatile emissions) of 28 to 138 ng I-TEQ<sub>DF</sub>/kg of PVC burned for the Swedish carpet factory fire  
11 using the following assumptions: (a) the PVC carpet backing was one-half the weight of the  
12 carpet, (b) the carpet backing contained 30% by weight PVC resin, and (c) 20 to 100% of the  
13 PVC and PVC carpet backing present in the warehouse actually burned. Using the results of  
14 wipe samples collected at downwind distances of up to 6,300 m, Carroll (1996) also estimated a  
15 similar soot-associated emission factor (48 to 240 ng I-TEQ<sub>DF</sub>/kg of PVC burned) for a fire at a  
16 plastics recycling facility in Lengerich, Germany.

17 Fiedler et al. (1993) presented a case study of CDD/CDF contamination and associated  
18 remedial actions taken at a kindergarten in Germany following a fire that destroyed parts of the  
19 roof, windows, and furnishings. Soot collected from the building contained CDDs/CDFs at a  
20 concentration of 45  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  (15  $\mu\text{g I-TEQ}_{\text{DF}}/\text{m}^2$ ). The study authors attributed the  
21 CDDs/CDFs detected to the combustion of plastic and wooden toys, floors, and furnishings;  
22 however, no information was provided on the quantities of those materials.

23 Fiedler and Lindert (1998) presented results of soot sampling following a serious fire at  
24 the airport in Düsseldorf, Germany. Polystyrene sheets and PVC-coated cables were involved in  
25 the fire, together with PCB-containing condensers (bulbs). Surface wipe samples contained up to  
26 0.33  $\mu\text{g I-TEQ}_{\text{DF}}/\text{m}^2$ . Concentrations in soot ranged from 7 to 130  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$ .  
27 Concentrations of polybrominated dibenzo-*p*-dioxins and dibenzofurans were detected in soot at  
28 concentrations as high as 0.9 mg/kg soot.

29 Wichmann et al. (1993, 1995) measured the CDD/CDF content of ash and debris and  
30 deposited surface residues that resulted from experimental test burns of two cars (a 1974 Ford  
31 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 sampled ash and debris and from soot collectors placed at regular intervals up to 420 m downwind of the burn site, the total amounts of CDDs/CDFs in the ash/debris and tunnel surface residues from each vehicle burn experiment were estimated as follows: 1974 model car—0.044 mg I-TEQ<sub>DF</sub>; 1988 model car—0.052 mg I-TEQ<sub>DF</sub>; subway car—2.6 mg I-TEQ<sub>DF</sub>; and railway coach—10.3 mg I-TEQ<sub>DF</sub>. 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 as follows: new car—0.14 µg I-TEQ<sub>DF</sub>/kg; old car—0.3 µg I-TEQ<sub>DF</sub>/kg; subway car—3.1 µg I-TEQ<sub>DF</sub>/kg; and railway coach—5.1 µg I-TEQ<sub>DF</sub>/kg.

### 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<sup>3</sup> 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 and gas phase showed the same congener pattern: decreasing concentration with increasing degree of chlorination, thus indicating no preferential sorption of more highly chlorinated congeners to smoke particulates. However, the CDDs/CDFs found in the gas phase (about 5 ng I-TEQ<sub>DF</sub>/m<sup>3</sup>) 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<sup>2</sup> aluminum sheet resulted in surface contamination of 0.05 µg I-TEQ<sub>DF</sub>/m<sup>2</sup>.

Although it was stated in Merk et al. (1995) that the building was “closed,” subsequent communication with one of the coauthors (Schramm, 1998) 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” in Oxford, England. Bonfire night (November 5) is an annual event during which it is customary to set off fireworks and have bonfires to commemorate

a failed plot to overthrow the king in 1605. Air concentrations before and after bonfire night ranged from 0.15 to 0.17 pg I-TEQ<sub>DF</sub>/m<sup>3</sup>. The air concentration during bonfire night was 0.65 pg I-TEQ<sub>DF</sub>/m<sup>3</sup>. 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, durations of burn, and so forth that were likely to 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 reported in the United States for 1993 (U.S. DOC, 1995a). Detailed estimates were developed of the PVC content of typical homes, including plumbing, wiring, siding and windows, wallpaper, blinds and shades, and upholstery. Statistical data on fire loss (i.e., dollar value) was used to provide the typical loss per recorded fire (9.5% of value), which was assumed to also represent the typical percentage of PVC burned. Extrapolating to all 358,000 one- to two-family unit fires yielded an annual mass of 2,470 metric tons of 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<sub>DF</sub>, with 0.07 to 8.6 g I-TEQ<sub>DF</sub> in soot and 0.4 to 14.2 g I-TEQ<sub>DF</sub> 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. (1989a) and the soot deposition rate on that funnel. These I-TEQ<sub>DF</sub> 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<sub>DF</sub>/yr). The average emission per fire is thus 1.3 to 64 µg I-TEQ<sub>DF</sub>.

Thomas and Spiro (1995) estimated that 20 g I-TEQ<sub>DF</sub> may be released annually to air from structural fires. This estimate assumes an emission factor of 4 ng I-TEQ<sub>DF</sub>/kg of 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<sub>DF</sub>.

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<sub>DF</sub> 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 United States, of which approximately 745,600 (32%) were structural fires (FEMA, 1999). In 1995, approximately 574,000 structural fires were reported in the United States. Of these, 426,000 were reported for 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).

1 **6.2.3.1.3. Emission estimates.** The limited data available on structural fires were judged  
2 inadequate for developing national emission estimates. This conclusion was also reached for  
3 national emission inventories developed for the Netherlands (Bremmer et al., 1994) and the  
4 United Kingdom (U.K. Environment Agency, 1995). However, preliminary estimates can be  
5 calculated by combining the average emission factor of 32  $\mu\text{g}$  I-TEQ<sub>DF</sub>/fire and the number of  
6 structural fires in the United States (745,600 in 1987; 426,000 in 1995; and 512,400 in 2000).  
7 This yields an annual release of 24 g I-TEQ<sub>DF</sub> in 1987, 14 g I-TEQ<sub>DF</sub> in 1995, and 16 g I-TEQ<sub>DF</sub>  
8 in 2000. Confidence in these estimated emissions is very low because of the numerous  
9 assumptions employed in their derivation. If the conclusion of Merk et al. (1995) is assumed to  
10 be correct, that 90% of the CDDs/CDFs formed in fires are in the gaseous phase rather than  
11 particulate phase (particles greater than 0.5  $\mu\text{m}$  diameter), and it is also assumed that the  
12 estimates of Carroll (1996) and Thomas and Spiro (1995) do not totally account for volatile  
13 emissions, then the total CDD/CDF emissions estimated by Carroll and Thomas and Spiro may  
14 be underestimates. Further testing is needed to confirm the true magnitude of these releases.

#### 16 **6.2.3.2. Vehicle Fires**

17 As with structural fires, the limited data available on vehicle fires were judged inadequate  
18 for developing national emission estimates that could be included in the national inventory.  
19 However, a preliminary estimate of the range of potential CDD/CDF emissions that may result  
20 from vehicle fires can be calculated using the results reported by Wichmann et al. (1993, 1995)  
21 for controlled vehicle fires in a tunnel (0.044 mg I-TEQ<sub>DF</sub> for an old car to 2.6 mg I-TEQ<sub>DF</sub> for a  
22 subway car). Although Wichmann et al. did not measure volatile CDDs/CDFs (which were  
23 reported by Merk et al., 1995, to account for the majority of CDDs/CDFs formed during a fire),  
24 the study was conducted in a tunnel, and it is likely that a significant fraction of the volatile  
25 CDDs/CDFs sorbed to tunnel and collector surfaces and were thus measured as surface residues.

26 The number of vehicle fires reported in the United States was approximately 561,530 in  
27 1987 (FEMA, 1997), 406,000 in 1995 (U.S. DOC, 1997), and 341,600 in 2000 (FEMA, 2001).  
28 If it is assumed that 99% of those fires involved cars and trucks (i.e., the approximate percentage  
29 of all U.S. motor vehicles that are in-service cars and trucks; U.S. DOC, 1995a) and that the  
30 applicable emission rate is 0.044 mg I-TEQ<sub>DF</sub> per incident, then the annual TEQ formation is  
31 24.4 g I-TEQ<sub>DF</sub> for 1987, 17.7 g I-TEQ<sub>DF</sub> for 1995, and 14.9 g I-TEQ<sub>DF</sub> for 2000. The emission

factor of 2.6 mg I-TEQ<sub>DF</sub>/fire is assumed to be applicable to the remaining 1% of vehicle fires, thus yielding an emission of 14.6 g I-TEQ<sub>DF</sub>/yr for 1987, 10.6 g I-TEQ<sub>DF</sub>/yr for 1995, and 8.9 g I-TEQ<sub>DF</sub>/yr for 2000. The total TEQ annual emissions for 1987, 1995, and 2000 are roughly estimated to be 39, 28.3, and 23.8 g I-TEQ<sub>DF</sub>/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 MWCs. 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 gas produced by the simulated surface and deep fires. The average CDD/CDF emission rate was reported to be 1 µg Nordic TEQ/kg of 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<sup>3</sup>, an assumed waste burn of 150 m<sup>3</sup> for each surface landfill fire (167 fires in Sweden per year), and an assumed waste burn of 500 m<sup>3</sup> 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 contributions to the measured TEQ were made by 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 by 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 in the United States, because the contents of the 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, 1996b). The population of Sweden was 8,825,417 in 1995 (U.S. DOC, 1995a) 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 is 4 µg TEQ per person per year for both 1995 and 2000. Because congener-specific results were not provided in Persson and Bergström (1991) and Bergström and Björner (1992), it was not possible to derive emission factors in units of TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub>. Applying this factor to the U.S. population of 263,814,000 in 1995 (U.S.

DOC, 1995a) and 281,421,906 in 2000 (U.S. DOC, 2003a) 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; Nestruck 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 the emissions from forest fires. This study reported detection of total CDDs/CDFs in air at levels ranging from about 15 to 400 pg/m<sup>3</sup>. The samples were collected 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<sup>3</sup>. 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 the CDD/CDF levels in soil. The I-TEQ<sub>DF</sub> contents in soil sample composites of the three unburnt areas were 3, 8.7, and 10 ng/kg. The I-TEQ<sub>DF</sub> contents in the soil sample composites of three

1 burnt areas were 2.2, 3.1, and 36.8 ng/kg. Total CDD/CDF contents ranged from 1,050 to 7,700  
2 ng/kg in the unburnt area soil samples and from 1,310 to 27,800 ng/kg in the burnt area soil  
3 samples. OCDD accounted for 94 to 97% of the total CDD/CDF content in all samples.

4 Similarly, a survey of controlled straw-field burning in the United Kingdom (Walsh et al.,  
5 1994) indicated that the straw burning did not increase the CDD/CDF burden in the soil;  
6 however, a change in congener distribution was observed. Soils from three fields were sampled  
7 immediately before and after burning, along with ash from the fire. The mean I-TEQ<sub>DF</sub>  
8 concentrations in the preburn soil, postburn soil, and ash were 1.79, 1.72, and 1.81 ng/kg,  
9 respectively. Concentrations of 2,3,7,8-TCDF were lower in the postburn soils than in the  
10 preburn soils. Conversely, the concentrations of OCDD were higher in the postburn soils,  
11 indicating possible formation of OCDD during the combustion process.

12 Van Oostdam and Ward (1995) reported finding no detectable levels of 2,3,7,8-  
13 substituted CDDs/CDFs in three soil samples and four ash samples following a forest fire in  
14 British Columbia. The DLs on a congener-specific basis (unweighted for TEQ) ranged from 1 to  
15 2 ng/kg. Nondetect values were also reported for ashes at a slash and burn site; the soil contained  
16 about 0.05 ng I-TEQ<sub>DF</sub>/kg, whereas background soil contained about 0.02 ng I-TEQ<sub>DF</sub>/kg.

17 The concentrations presented by Clement and Tashiro (1991) cannot accurately be  
18 converted to an emission factor because the corresponding rates of combustion gas production  
19 and wood consumption are not known. As a result, four alternative approaches were considered  
20 to develop an emission factor.

21 **Soot-based approach.** This approach assumes that the levels of CDDs/CDFs in chimney  
22 soot are representative of the CDDs/CDFs in emissions. The CDD/CDF emission factor is  
23 calculated as the product of the CDD/CDF concentration in soot and the total particulate  
24 emission factor. This calculation involves first assuming that the CDD/CDF levels measured in  
25 chimney soot (720 ng I-TEQ<sub>DF</sub>/kg) by Bacher et al. (1992) are representative of the CDD/CDF  
26 concentrations of particles emitted during forest fires. Second, the total particulate generation  
27 factor must be estimated. Using primarily data for head fires, Ward et al. (1976) estimated the  
28 national average particulate emission factor for wildfires as 150 lb/ton biomass dry weight.  
29 Ward et al. (1993) estimated the national average particulate emission factor for prescribed  
30 burning as 50 lb/ton biomass dry weight. Combining the total particulate generation rates with  
31 the I-TEQ<sub>DF</sub> level in soot results in emission factor estimates of 54 ng of I-TEQ<sub>DF</sub> and 18 ng of I-



1 TEQ<sub>DF</sub>/kg of biomass burned in wildfires and prescribed burns, respectively. These estimated  
2 factors are likely to be overestimates because the levels of CDDs/CDFs measured in chimney  
3 soot by Bacher et al. (1992) may represent the accumulation and enrichment of CDDs/CDFs  
4 measured in chimney soot over time, leading to much higher assumed levels than what is actually  
5 on emitted particles.

6 **Carbon monoxide (CO) approach.** CO is a general indicator of the efficiency of  
7 combustion, and the emission factors of many emission products can be correlated with the CO  
8 emission factor. Data from Schatowitz et al. (1993) for emissions during natural wood burning  
9 in open stoves suggest an emission factor of 10 µg I-TEQ<sub>DF</sub>/kg of CO. Combining this factor  
10 with the CO emission factor during forest fires (roughly 0.1 kg CO/kg of biomass, Ward et al.,  
11 1993) yields an emission factor of 1,000 ng I-TEQ<sub>DF</sub>/kg biomass. This factor is higher than the  
12 soot-based factor discussed above, which is itself considered to be an overestimate. In addition,  
13 although the formation kinetics of CDDs/CDFs during combustion are not well understood,  
14 CDD/CDF emissions have not been shown to correlate well with CO emissions from other  
15 combustion sources.

16 **Wood stove approach.** This approach assumes that the emission factor for residential  
17 wood burning (using natural wood and open door, i.e., uncontrolled draft) applies to forest fires.  
18 As discussed in Section 4.2.1, this approach suggests an emission factor of about 0.5 ng I-  
19 TEQ/kg wood combusted. This value appears more reasonable than the factors suggested by the  
20 soot and CO approaches because it is based on direct measurement of CDDs/CDFs from  
21 combustion of wood rather than on indirect techniques. However, forest fire conditions differ  
22 significantly from combustion conditions in wood stoves. For example, forest fire combustion  
23 does not occur in an enclosed chamber, and the biomass consumed in forest fires is usually green  
24 and includes underbrush, leaves, and grass.

25 **Forest fire simulation approach.** This approach quantifies CDD/CDF emissions  
26 through the combustion of forest biomass in a controlled-burn facility. Using this approach,  
27 Gullet and Touati (2003) estimated CDD/CDF emissions through the testing of three biomass  
28 samples collected from the Oregon coast near Seal Rock and from four biomass samples  
29 collected from the North Carolina Piedmont region, approximately 200 km from the Atlantic  
30 coast. The samples generally consisted of equal portions of live shoots (needles cut from tree  
31 branches) and needle litter gathered from the forest floor. The Oregon samples were composed

1 of pine needles (*Pinus contorta* and *Pinus monticola*) and hemlock needles (*Tyuga heterophylla*);  
2 the North Carolina samples were composed entirely of loblolly pine (*Pinus taeda*). The  
3 combustion of these seven samples, piled approximately 10 cm high, took place on top of an  
4 open, flat combustion platform. CDD/CDF emissions were measured using a Graseby PS-1  
5 sampler and EPA's ambient TO-9 method.

6 As shown in Table 6-2, the overall average total TEQ emission factor for the seven  
7 samples was 20 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (18.6 ng I-TEQ<sub>DF</sub>), assuming nondetects were zero.  
8 Separately, the average total TEQ emission factors for the three Oregon samples and the four  
9 North Carolina samples were 15 ng and 25 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg, respectively. Even though the  
10 average TEQ emission factors for the Oregon and North Carolina runs were similar, CDF  
11 congeners were dominant in the Oregon samples, whereas CDD congeners were dominant in the  
12 North Carolina samples. Figure 6-2 shows the congener profile for the Oregon and North  
13 Carolina samples combined.

14 To test an alternative CDD/CDF sampling method, CDD/CDF emissions from one of the  
15 Oregon samples were also measured using a "Nomad" (a prototype portable sampler designed for  
16 mobile, in-field sampling). The results from both sampling methods showed very similar  
17 CDD/CDF TEQ values, total values, and ratio values. An additional Oregon sample was also  
18 combusted to test influences of fuel configuration on emissions. In this experiment, the biomass  
19 was placed in a metal barrel with air holes cut into the bottom. The results of this test run  
20 showed the highest total TEQ emission value calculated in this study (47 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg).  
21 However, this value is similar to the next highest total TEQ value (46 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg).

22 Because the waxy cuticle layer on pine needles has been demonstrated to absorb  
23 lipophilic compounds from the atmosphere, Gullet and Touati (2003) also extracted a raw, as-  
24 received Oregon biomass sample to determine whether the observed emissions were due to  
25 simple vaporization of existing CDDs/CDFs or the formation of new CDDs/CDFs in the  
26 combustion process. The CDD/CDF concentration in the extracted Oregon biomass sample  
27 measured 1.3 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg, which is approximately 20 times lower than the Oregon  
28 CDD/CDF emission concentrations (average of 25 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg and range of 14 to 46 ng  
29 TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg). The CDD/CDF isomer patterns were similar between the extracted biomass  
30 samples and the emission samples. Therefore, this preliminary evidence suggests CDD/CDF  
31 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.

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 variation of emissions. Therefore, these variables yield uncertainties in the calculation of a representative emission factor through forest fire simulations. However, the emission factor of 20 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (18.6 ng I-TEQ<sub>DF</sub>) calculated through this approach appears to be more reasonable than the factors suggested by the soot, CO, and wood stove approaches, as 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 to the state level, 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 landcover 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 landcover 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 reference years 1995 and 1997. An estimated 5.1 million acres of biomass were burned in 1989 during prescribed burns (Ward et al., 1993). This value of 5.1 million acres is assumed to be an appropriate value to 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 per acre in areas consumed by wildfires (Ward et al., 1976) and 7.44 metric tons per acre in areas consumed in prescribed burns. For reference years 1987 and 1995, approximately 38 million tons were consumed by prescribed burns. For wildfires, approximately 47 million metric tons of biomass were consumed 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 (20 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg biomass [18.6 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub>-WHO<sub>98</sub> (1,581 g I-TEQ<sub>DF</sub>) for 1987; 2,080 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (1,934 g I-TEQ<sub>DF</sub>) for 1995; and 4,880 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (4,538 g I-TEQ<sub>DF</sub>) for 2000. For wildfires specifically, annual reference year emission estimates are 940 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (874.2 g I-TEQ<sub>DF</sub>) for 1987; 1,320 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (1,228 g I-TEQ<sub>DF</sub>) for 1995; and 4,560 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (4,241 g I-TEQ<sub>DF</sub>) for 2000. For prescribed fires specifically, annual emission estimates are 760 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (706.8 g I-TEQ<sub>DF</sub>) for reference years 1987 and 1995 and 320 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (297 g I-TEQ<sub>DF</sub>) 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 the practice of open backyard burning. This practice usually consists of combustion of the refuse in a 208-L capacity steel drum. Holes are punched near the bottom of the drum to allow combustion air to enter. Ignition is achieved with the use of a petroleum fuel, e.g., kerosene. The low combustion temperatures and oxygen-starved conditions associated with the burning of household refuse in “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 the open burning of refuse 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 Department of Health and Department of Environmental

1 Conservation, conducted an initial study that examined, characterized, and quantified emissions  
2 from simulated open burnings of household waste materials in barrels (Lemieux, 1997). The  
3 representative waste was prepared on the basis of the typical percentages of various waste  
4 materials disposed of by New York State residents; hazardous wastes (chemicals, paints, oils,  
5 etc.) were not included in the test waste. A variety of compounds, including CDDs/CDFs, were  
6 measured in the emissions from two simulated open burnings of this “baseline” waste.

7 Combustion studies were subsequently performed by EPA to provide additional baseline  
8 waste tests and to provide an initial indication of the impact of limited variation in waste  
9 composition and combustion conditions on CDD/CDF emissions from a simulated domestic  
10 backyard barrel burn of 6.8 kg of unshredded household waste (Gullet et al., 1999, 2000a, b;  
11 Lemieux et al., 2000; Lemieux, 2000). The results of seven baseline open burning waste tests  
12 were reported in these EPA studies. These tests exhibited variation in the emissions of  
13 CDDs/CDFs, with a one- to two-order of magnitude spread between the lowest and highest  
14 values for individual congeners, congener groups, total CDDs/CDFs, and TEQ values. The  
15 average TEQ emission factor for the seven baseline tests was 72.8 ng I-TEQ<sub>DF</sub>/kg of waste  
16 burned (setting nondetect values equal to zero) and 73.7 ng I-TEQ<sub>DF</sub>/kg of waste burned (setting  
17 nondetect values equal to one-half the DL). The corresponding TEQ<sub>DF</sub>-WHO<sub>98</sub> values were 76.8  
18 and 77.7 ng/kg. Table 6-4 presents the average congener and congener group results for these  
19 tests.

20 In addition to the baseline tests, the combustion experiments included testing at three  
21 different PVC levels: 0, 1, and 7.5% by weight PVC. The average emissions were 14, 201, and  
22 4,916 ng I-TEQ<sub>DF</sub>/kg of waste burned, respectively. Two tests using waste impregnated with  
23 inorganic chloride (CaCl<sub>2</sub>) at a concentration of 7.5% by weight (and no PVC) averaged 734 ng I-  
24 TEQ<sub>DF</sub>/kg. Qualitative comparisons suggest that the tests conducted with higher chlorine, via  
25 PVC or CaCl<sub>2</sub>, resulted in substantial increases in TEQ emissions.

26 Other variations in baseline waste composition included conducting one test with  
27 compressed waste, one test with a double load of waste, and one test in which some of the waste  
28 paper was wetted to simulate high-moisture burns. These tests resulted in a higher mean TEQ  
29 emission factor (534 ng I-TEQ<sub>DF</sub>/kg) than that of the baseline runs.

30 Several waste combustion variables were evaluated, such as average temperatures at  
31 prescribed barrel heights; length of time temperatures (favorable temperature ranges) for

CDD/CDF formation; and measurement of CO, CO<sub>2</sub>, O<sub>2</sub>, 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<sub>DF</sub>/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<sub>DF</sub>-WHO/kg, and 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 enumerating the rural and nonurban population of the United States, is used in this report 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.

### **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%. The mean of all surveys combined was 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 in five central Illinois counties. They found that about 40% of the residents in a typical rural Illinois county burn household

1 waste. The survey also indicated that, on average, those households that burn waste dispose of  
2 approximately 63% of their household waste by burning it in barrels (TRRCPO, 1994).

3 Similar results were obtained in a survey conducted by Zenith Research Group, Inc.,  
4 (2000) for the Western Lake Superior Sanitary District of Minnesota. This survey of 760  
5 residents of selected portions of northwestern Wisconsin and northeastern Minnesota addressed,  
6 in part, the use of burn barrels or other devices to burn household garbage or other materials.  
7 Among all survey respondents, 27.5% admitted they currently use burn barrels or other devices to  
8 burn household garbage or other materials.

9 Environics Research Group conducted a household garbage disposal and burning survey  
10 of 1,516 residents of Ontario, Canada. All respondents resided in detached single-family homes  
11 (Environics Research Group, 2001). Approximately 24% of all respondents reported burning  
12 their household refuse in burn barrels.

13 E.H. Pechan and Associates conducted a residential municipal solid waste survey for the  
14 Mid-Atlantic/Northeast Visibility Union (MANE-VU) states and tribes (Pechan, 2002). The  
15 MANE-VU entities include: Connecticut, Delaware, the District of Columbia, Maine, Maryland,  
16 Massachusetts, New Hampshire, New Jersey, New York, Pennsylvania, the Penobscot Indian  
17 Nation, Rhode Island, the St. Regis Mohawk Tribe, and Vermont. Household waste burning  
18 surveys were conducted by telephone for 72 residents in rural, suburban, and urban jurisdictions,  
19 as classified by the 1990 census. The residents were asked to estimate the number of households  
20 in their jurisdiction that burned household waste or trash. In general, the survey estimated that  
21 11.9% of the rural population burned refuse in backyard burn barrels.

22 The State of California Air Resources Board (CARB) undertook a study of the prevalence  
23 of backyard refuse burning in rural areas of 21 air management districts in California (CARB,  
24 2002). From this study, CARB estimated that approximately 18% of the rural population in  
25 California combusted their household refuse in backyard burn barrels.

26 In 1993, the St. Lawrence County Planning Office in Canton, New York, conducted a  
27 survey of open burning of domestic refuse (St. Lawrence County, 1993). From the survey, it was  
28 concluded that 48.2% of 9,926 households in rural areas of the County burned household refuse  
29 in burn barrels.

30 In 1997, the State of Maine Department of Conservation Forestry Bureau surveyed rural  
31 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 domestic refuse was being combusted state-wide in approximately 8,510 burn barrels. In relation to the total population, it was noted that 1 burn barrel existed for every 144 people.

#### **6.5.2.2. *Estimates of Activity Level***

The following chart summarizes the steps taken in estimating total quantity of household refuse combusted in backyard burn barrels in the years 1987, 1995, and 2000.

#### **Steps taken in estimating total quantity of household refuse (kg/yr) combusted in burn barrels**

		Reference year	Reference year	Reference year
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 of the U.S.	59,000,000	52,700,000	50,700,000
3.	Percent nonurban population burning	28%	40%	40%
4.	Adjusted population burning MSW in barrels	16,726,500	21,080,000	20,280,000
5.	Per capita MSW generation rate, kg/yr	616	616	616
6.	Percent of MSW generated is burned at homes	63%	63%	63%

7.	Adjusted per capita	388	388	388
	MSW burned, kg/yr			
8.	Total refuse generated	6,491,220,120	8,180,726,400	7,870,262,400
	by rural, nonurban			
	population burning			
	MSW, kg/yr			

Steps 1 and 2: The U.S. Census Bureau Statistical Abstract of the United States was used to determine population size.

Step 3: The assumption of the percent of rural population combusting refuse in burn barrels was derived from surveys as follows:

a. Reference year 2000 used the overall mean prevalence rate from 6 surveys (CARB, 2002; Zenith Research Group, 2003; Environics, 2001; Pechan and Associates, 2004; St Lawrence County, 1993; and TRRCPO, 1994). This produced a mean prevalence of 28%. This overall mean percentage should reflect the impact of state bans and/or restrictions on the practice of open burning of refuse.

b. Reference years 1995 and 1987 used the survey of TRRCPO (1994). This produced a prevalence of 40%. This mean percentage should reflect the fact that the practice of open burning of refuse was not banned or restricted by the majority of the states.

Step 4: The above mean prevalence rates were used 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).

Step 5: The annual per capita household refuse generation rate is from the Municipal Solid Waste Fact Book (2000). The figure of 616 kg/person/year is the result of subtracting out weight of yard waste from the per capita generation rate.

Step 6: The assumption that 63% of municipal solid waste (MSW) generated in rural areas is burned in backyard burn barrels and is derived from a survey conducted in rural counties of Illinois (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*

Actual amounts of refuse combusted in burn barrels in the United States is unknown and must be estimated. The EPA Office of Air Quality Planning and Standards (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, 2002d). 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 the year 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, Estimates of activity level) by the dioxin emission factor. The emission factor was 76.8 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (72.8 ng I-TEQ<sub>DF</sub>/kg) of waste burned.

Annual nationwide TEQ emissions for 1987, 1995, and 2000 were calculated using eq 6-1.

$$E_{TEQ} = EF_{TEQ} \times AL \quad (6-1)$$

Where:

$E_{TEQ}$  = Annual  $TEQ_{DF}$  emissions, g/yr

$EF_{TEQ}$  =  $TEQ_{DF}$  emission factor, 76.8 ng  $TEQ_{DF}$ -WHO<sub>98</sub>/kg of 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, the estimated nationwide  $TEQ_{DF}$  emissions were

Reference year 1987: 604 g  $TEQ_{DF}$ -WHO<sub>98</sub> (573 g I- $TEQ_{DF}$ )

Reference year 1995: 628 g  $TEQ_{DF}$ -WHO<sub>98</sub> (595 g I- $TEQ_{DF}$ )

Reference year 2000: 498.53 g  $TEQ_{DF}$ -WHO<sub>98</sub> (472.56 g I- $TEQ_{DF}$ )

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 and Touati (2003) measured an average CDD/CDF emission factor of 20 ng  $TEQ_{DF}$ -WHO<sub>98</sub>/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<sub>98</sub>/kg developed by Gullet (2003) will be used for residential yard waste burning.

## 6.6.2. Activity Level Information

Pechan (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 its household yard waste burning survey. The 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 burn household yard waste and that households typically conduct two to three burns per year. Additionally, as indicated by information provided by three respondents, 1 to 3 cubic yards of yard waste is 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, 2002d). 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, 2001a). 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 is 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 takes place in counties where the urban population exceeded 80% of the total population (i.e., urban plus rural). Using this method,

1 OAQPS estimated that 255,000 metric tons of leaf and 255,000 metric tons of brush (total of  
2 510,000 metric tons of yard waste) were burned in 2000.

### 3 4 **6.6.3. Emission Estimate**

5 Using the emission factor of 20 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (18.6 ng I-TEQ<sub>DF</sub>/kg) and the  
6 activity level of 510,000 metric tons yard waste burned in 2000, CDD/CDF emissions from open  
7 burning of yard waste were 10.2 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (9.5 g I-TEQ<sub>DF</sub>) in 2000. Assuming 772 and  
8 754 million kg of yard waste were burned in 1987 and 1995, respectively, then 15.4 g TEQ<sub>DF</sub>-  
9 WHO<sub>98</sub> (14.4 g I-TEQ<sub>DF</sub>) and 15.19 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (14 g I-TEQ<sub>DF</sub>) were emitted in 1987 and  
10 1995, respectively. These should be regarded as preliminary estimates of possible emissions  
11 from this source; further testing is needed to confirm the true magnitude of emissions. This is  
12 because both the emission factor and activity levels are judged to be clearly nonrepresentative of  
13 the source category.

## 14 15 **6.7. LAND-CLEARING DEBRIS BURNING**

### 16 **6.7.1. Emissions Data**

17 Land clearing is the clearing of land for the construction of new buildings (residential and  
18 nonresidential) and highways. During the clearing process trees, shrubs, and brush are often torn  
19 out, collected in piles, and burned. As with residential yard waste burning, it is assumed that the  
20 burning of land-clearing debris may generate CDDs/CDFs because emissions have been detected  
21 from forest and brush fires. No direct measurements of CDD/CDF emissions from the burning  
22 of land-clearing debris have been performed, so the average emission factor of 20 ng TEQ<sub>DF</sub>-  
23 WHO<sub>98</sub>/kg, which was used for both forest fires and residential yard waste burning, is also used  
24 for burning of land clearing debris (see Sections 6.4 and 6.6).

### 25 26 **6.7.2. Activity Level Information**

27 Activity levels associated with land clearing debris were calculated by OAQPS on a  
28 county-level basis using the number of acres disturbed through residential, nonresidential, and  
29 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 Census Bureau for single-family units, two-family units, and apartments. 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:

<u>Unit type</u>	<u>Acres per building</u>
Single-family unit	1/4
Two-family unit	1/3
Apartment	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 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:

<u>Road type</u>	<u>Acres per mile</u>
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 the 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 is as follows:



1	<u>Fuel</u>	<u>Fuel loading factor (tons/acre)</u>
2	Hardwood	99
3	Softwood	57
4	Grass	4.5

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 estimates that approximately 27.7 and 26.4 million metric tons of biomass were burned by land clearing in 1987 and 1995, respectively.

### 12 6.7.3. Emission Estimate

Using the emission factor of 20 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (18.6 ng I-TEQ<sub>DF</sub>/kg) and the activity level estimates in Section 6.7.2.4, CDD/CDF emissions from land clearing burning were 568 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (528 g I-TEQ<sub>DF</sub>) in 2000, 528 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (491 g I-TEQ<sub>DF</sub>) in 1995, and 553 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (515 g I-TEQ<sub>DF</sub>) 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.

20 **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, 1991b; O'Keefe and Smith, 1989; Williams et al., 1985). For example, analyses of soot samples from a Binghamton, New York, office building fire detected 20 µg/g of total CDDs (0.6 to 2.8 µg/g of 2,3,7,8-TCDD) and 765 to 2,160 µg/g of total CDFs (12 to 270 µg/g of 2,3,7,8-TCDF). At that site, the fire involved the combustion of 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 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 for 0.8 sec 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<sub>DF</sub> 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

1 monoaromatic compounds as well as three PeCB congeners were reported as having been  
2 detected in the ash from the 1980 eruption of Mount St. Helens. Gribble hypothesized that the  
3 formation of these PCB compounds was the result of rapid, incomplete, high-temperature  
4 combustion of chloride-containing plant material in the eruption zone. However, he presented no  
5 information indicating formation of CDDs/CDFs by volcanoes.

6 Lamparski et al. (1990) analyzed groundfall ash samples collected at various distances  
7 and locations from Mount St. Helens following the eruption in 1980. The findings of this study  
8 indicate that volcanic particulate emissions were free of detectable PCBs and nearly free of  
9 detectable CDDs (0.8 ng/kg HpCDD detected) upon exiting the volcano and remained so  
10 throughout their period of deposition in the blast zone. However, upon transport through the  
11 atmosphere, measurable and increasing levels of CDDs and PCBs were detected in deposited ash  
12 as it passed from rural to urban environments. The authors hypothesized that CDDs and PCBs in  
13 the atmosphere became associated with the volcanic ash particulates through gas-phase sorption  
14 or particulate agglomeration.

15 Takizawa et al. (1994) investigated the CDD/CDF content of volcanic dust fall from two  
16 active volcanoes in Japan (Mt. Fugendake and Sakurajima). The study was not designed to  
17 determine whether the CDDs/CDFs observed were formed by the volcanoes or were scavenged  
18 from the atmosphere by the falling dust and ash. The dust fall was collected for 1-month periods  
19 during July and October 1992; two samples of the volcanic ash were collected in 1992. The  
20 results of the sample analyses for 2,3,7,8-substituted CDDs and CDFs, presented in Table 6-7,  
21 show that no 2,3,7,8-substituted congeners with less than seven chlorines were detected;  
22 however, the authors reported that non-2,3,7,8-substituted congeners in the less-chlorinated  
23 congener groups were detected.

## 24 25 **6.10. FIREWORKS**

26 In order to produce various effects and illuminations, modern fireworks contain not only  
27 black powder but also substances such as chlorine-based oxidizers, flame-coloring copper salts,  
28 and pulverized polyvinylchloride, which are known to be involved in dioxin-forming processes.  
29 During deflagration of pyrotechnics, core temperatures reach as high as 2,500 °C, which would  
30 most likely inhibit the formation of organic pollutants. However, CDDs/CDFs may be generated

1 in the areas adjacent to the combustion zone, where temperatures are lower and dwell times are  
2 longer. Therefore, CDDs/CDFs may be generated during the cooling period of the deflagration  
3 products because the temperatures of the smoke and ash are within the possible temperature  
4 range of dioxin formation (Fleischer et al., 1999).

5 During a celebration in Oxford, England, that was accompanied by fireworks and  
6 bonfires, Dyke and Coleman (1995) reported a fourfold increase in CDD/CDF TEQ  
7 concentrations in the ambient air (see Section 6.2.2). Air concentrations before and after the  
8 celebration ranged from 0.15 to 0.17 pg I-TEQ<sub>DF</sub>/m<sup>3</sup>. The air concentration during the  
9 celebration was 0.65 pg I-TEQ<sub>DF</sub>/m<sup>3</sup>. Fleischer et al. (1999) conducted an experiment to measure  
10 the air emissions resulting specifically from the following seven types of fireworks: firecracker,  
11 cone fountain, jumping jack, whistler, sparkling rocket, roman candle, and four-color fountain.  
12 The paper cartridges and charges were separated from each firework and deflagrated separately in  
13 a steel chamber. CDD/CDF concentrations were measured both in air samples and in paper and  
14 ash samples. The results indicated that dioxins were not present in significant quantities in the  
15 air samples collected. Therefore, Fleisher et al. suspected that the increased background  
16 concentration of CDDs/CDFs detected by Dyke and Coleman (1995) was due mainly to the  
17 bonfires and not the fireworks. However, concentrations of HpCDD and OCDD/F were present  
18 in the paper and ash collected after the fireworks were detonated at concentrations ranging from  
19 less than the DL (10 ng/kg) to 1,200 ng/kg. Table 6-8 depicts the results of Fleischer's tests.  
20 Given the lack of information on the potential for CDD/CDF emissions from fireworks, the  
21 emissions cannot be quantified.

## 22 23 **6.11. OPEN BURNING AND OPEN DETONATION OF ENERGETIC MATERIALS**

24 Open burning and open detonation (OB/OD) practices are routinely used to destroy  
25 surplus or unserviceable energetic materials. Mitchell and Suggs (1998) conducted a study to  
26 determine emission factors from OB/OD in which air samples were collected for CDD/CDF  
27 analysis during four burns and after three detonations. The results of the study indicated that  
28 emission levels of CDDs/CDFs as a result of disposal of energetic materials by OB/OD were  
29 nondetectable.

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

<b>Congener/congener group</b>	<b>Mean facility emission factor<sup>a</sup> (ng/m<sup>3</sup> gas combusted)</b>
2,3,7,8-TCDD	0.018
1,2,3,7,8-PeCDD	0.092
1,2,3,4,7,8-HxCDD	0.074
1,2,3,6,7,8-HxCDD	0.074
1,2,3,7,8,9-HxCDD	0.259
1,2,3,4,6,7,8-HpCDD	0.755
OCDD	4.414
2,3,7,8-TCDF	14.074
1,2,3,7,8-PeCDF	0.385
2,3,4,7,8-PeCDF	1.136
1,2,3,4,7,8-HxCDF	1.455
1,2,3,6,7,8-HxCDF	0.422
1,2,3,7,8,9-HxCDF	0.11
2,3,4,6,7,8-HxCDF	0.681
1,2,3,4,6,7,8-HpCDF	1.215
1,2,3,4,7,8,9-HpCDF	0.073
OCDF	0.639
Total 2,3,7,8-CDD	5.686
Total 2,3,7,8-CDF	20.192
Total I-TEQ <sub>DF</sub>	2.392
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	2.433
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

<sup>a</sup>Assumes heat content of 1.86e+07 J/m<sup>3</sup> for landfill gas (Federal Register, 1996a).

NR = Not reported

Source: CARB (1990d).

**Table 6-2. CDD/CDF emission factors for forest fires**

Congener	Mean emission factor (ng/kg)	
	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	965.54	965.95
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	19.90	20.07
Total I-TEQ <sub>DF</sub>	18.59	18.77

Source: Gullet (2003).

**Table 6-3. Forest fire fuel loading factors**

<b>Region</b>	<b>Fuel loading factors (tons per acre)</b>	
	<b>Wildfires</b>	<b>Prescribed burning</b>
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 (2002e).

**Table 6-4. CDD/CDF air emission factors from barrel burning of household waste**

Congener/congener group	Average air emission factors <sup>a</sup> (ng/kg waste burned)	
	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	136.6	135.4
Total 2,3,7,8-CDF	545.8	540.4
Total I-TEQ <sub>DF</sub>	73.7	72.8
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	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

<sup>a</sup>Listed values are the arithmetic averages of seven tests for the congeners and the averages of five tests for the congener groups.

Sources: Lemieux (2000), Gullett et al. (1999, 2000a, 2000b).



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

Congener/congener group	Average concentration in composite ash sample		I-TEQ <sub>DF</sub>		TEQ <sub>DF</sub> -WHO <sub>98</sub>	
	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	14,851	1,556	-	-	-	-
Total CDF	34,040	5,800	-	-	-	-
Total CDD/CDF	48,891	7,356	-	-	-	-

Source: Lemieux (1997).

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

<b>Compound</b>	<b>Avid recycler</b>	<b>Nonrecycler</b>
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).

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

2,3,7,8-substituted congener group	Dust fall (mg/km <sup>2</sup> /month) <sup>a</sup>		Volcanic ash (ng/kg) <sup>b</sup>	
	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

<sup>a</sup>Dust fall measured from the active volcano Fugendake.

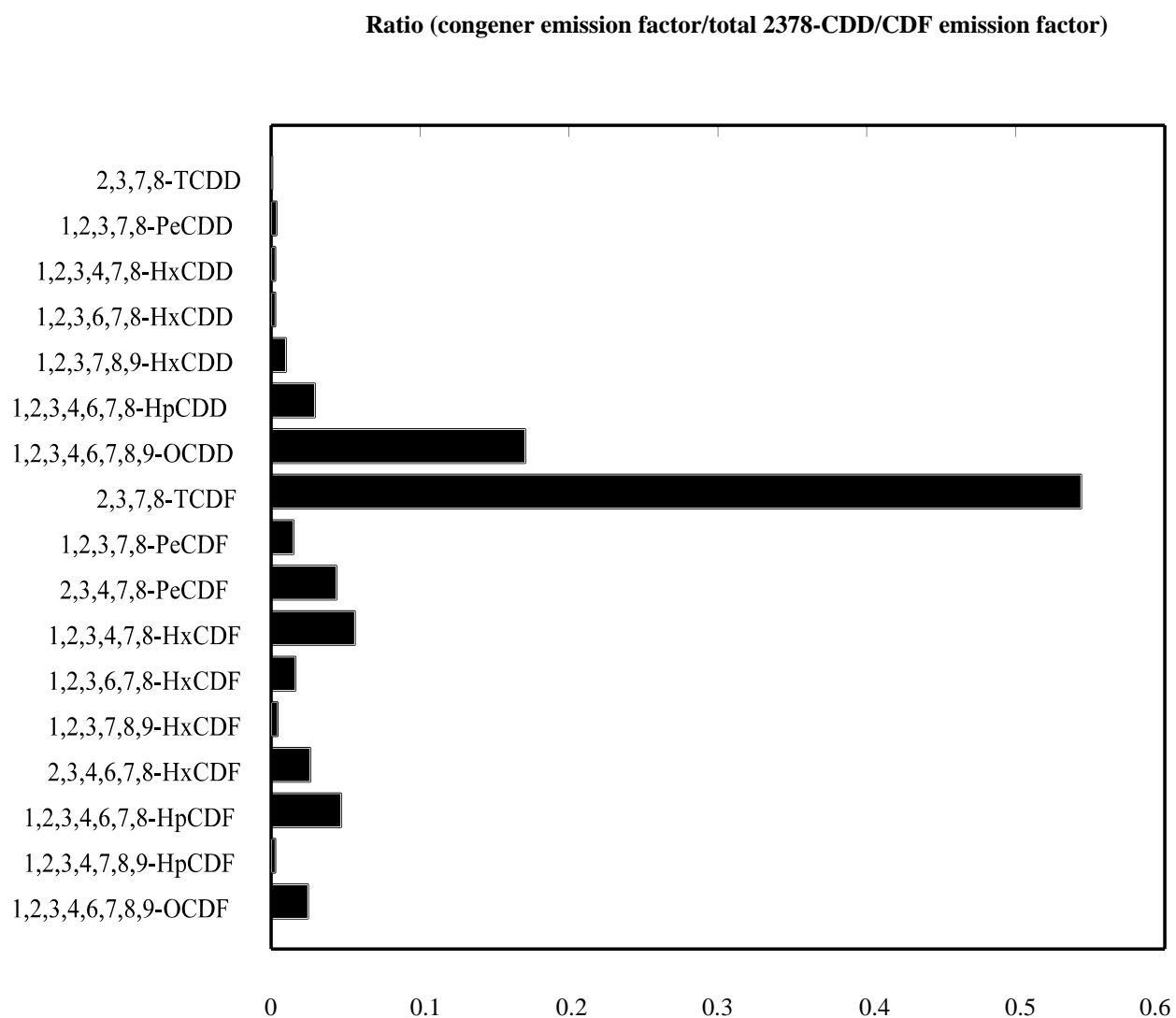
<sup>b</sup>Volcanic ash measured from the active volcano Sakurajima.

Source: Takizawa et al. (1994).

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

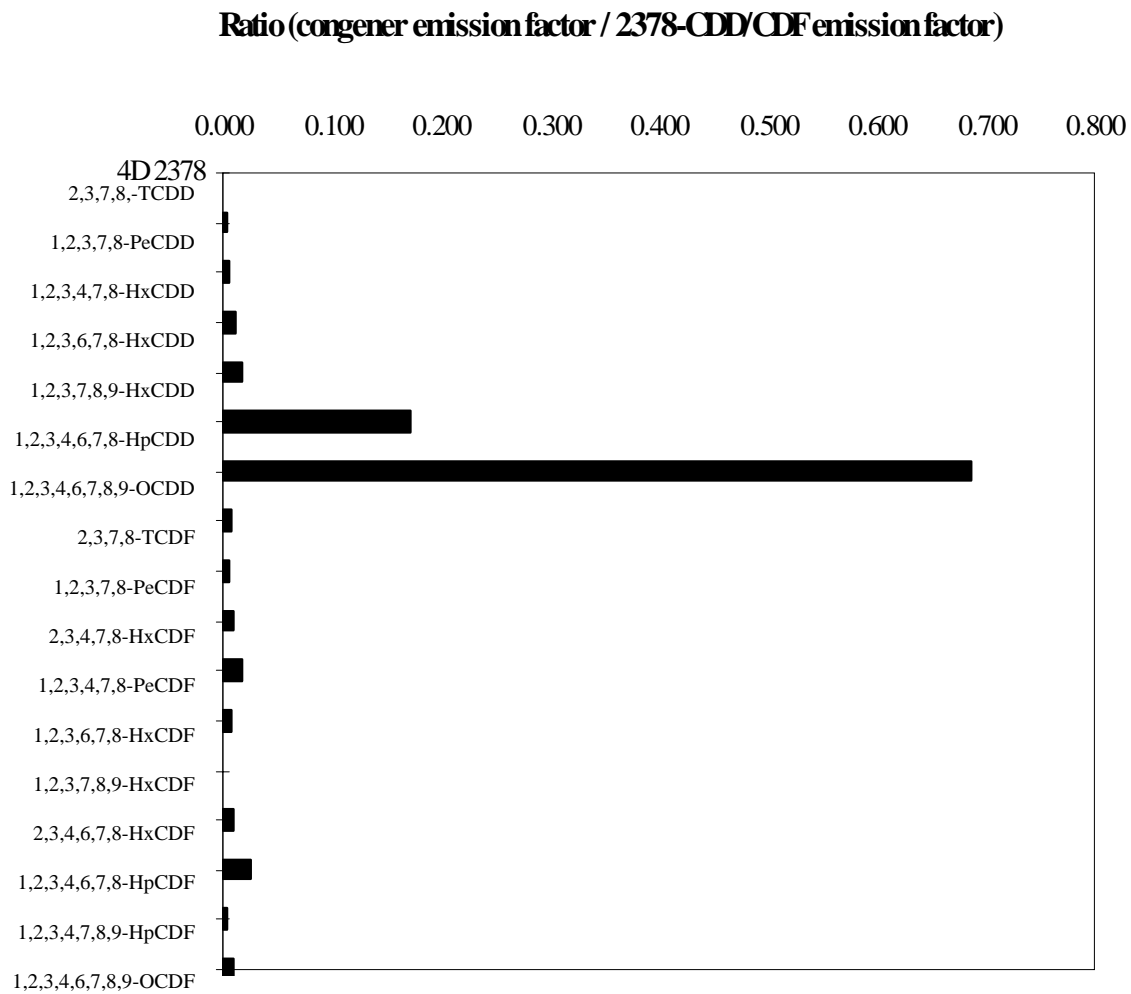
Product	Paper Cartridges			Charge		
	HpCDD	OCDD	OCDF	HpCDD	OCDD	OCDF
Firecracker	16	322	79	<10	535	26
Cone fountain	111	384	22	<10	<10	<10
Jumping Jack	<10	33	24	<10	28	<10
Whistler	22	353	121	<10	35	1200
Sparkling rocket	30	129	12	<10	13	<10
Roman candle	<10	426	39	<10	<10	22
Four-color fountain	<10	18	<10	<10	<10	<10

Source: Fleischer et al. (1999).



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

Source: CARB (1990d).



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

Source: Gullet and Touati (2003).

## **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 manufacturing facilities. Oehme et al. (1989) reported the presence of CDDs/CDFs in the wastewater of a magnesium refining facility and in the receiving water sediments downstream of a nickel refining facility in Norway. The information from this study is insufficient for evaluating CDD/CDF emissions, if any, from the smelting/refining of magnesium and nickel in the United States. The potential for formation and release of CDDs/CDFs by primary copper smelters in the United States has been reported by Environmental Risk Sciences (1995) to be negligible. Lexen et al. (1993) reported finding few or no CDDs/CDFs in solid wastes from a primary aluminum smelter. Bramley (1998) indicated that the smelting/refining of titanium may be a source of CDDs/CDFs. The findings of these studies are discussed in the following subsections.

#### **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 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: main stack, plant tail gas stack, and vent fume exhaust (Secor International Inc., 1995a, b). The two facilities that were tested (Phelps Dodge Mining Co. in Playas, New Mexico, and Cyprus Miami Mining Co. in Claypool, Arizona) were selected as representative of the other facilities in the industry because of their similarity to the 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 assessment of the process chemistry and technology, the operating conditions, and process stream compositions indicate that although there is some potential for

CDD/CDF formation in this industry, 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 ( $\text{CuFeS}_2$ ) rather than carbon (fossil fuels), (b) low concentrations of organic carbon and chloride are present in raw materials and reagents, (c) high concentrations of  $\text{SO}_2$  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.

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, 2001a). 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 each run were 3.8, 1.7, and 0.7 pg TEQ/ $\text{m}^3$ , respectively. 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.

In 1995, eight primary smelters were in operation in the United States, one of which closed at the end of the 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, 1997c). In 2000, four primary smelters of copper were in operation in the United States, producing 1.61 million metric tons of copper (USGS, 2002).

The results of this assessment 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 (1995) calculated the annual TEQ emission to air to be less than 0.5 g I-TEQ<sub>DF</sub> 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<sub>DF</sub> as well. Because the number of facilities was reduced in 2000, the national emission estimate is 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<sub>DF</sub> were released to the environment in wastewater and 6 g I-TEQ<sub>DF</sub> 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<sub>2</sub>) was produced by heating MgO/coke pellets in a shaft furnace in a pure chlorine atmosphere to about 700 to 800 °C. The MgCl<sub>2</sub> was then electrolyzed to form metallic magnesium and chloride. The chloride excess from the MgCl<sub>2</sub> 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 PM. 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<sub>2</sub> 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<sub>2</sub> produced. The APCD controls consisted of three water scrubbers, a wet electrostatic precipitator (ESP), and an incinerator.



1 From 1950 to 2000, the United States was the world's largest producer of metallic  
2 magnesium (Kramer, 1995). In 1995, three magnesium production facilities were operating in  
3 the United States. As in the Norwegian plant, an electrolytic process (electrolysis of  $\text{MgCl}_2$ ) was  
4 used at the plants in Texas (capacity of 65,000 metric tons/yr) and Utah (capacity of 40,000  
5 metric tons/yr) to recover metallic magnesium from  $\text{MgCl}_2$ . However, these two facilities  
6 reportedly used seawater and lake brines as the source of magnesium, and the procedures to  
7 obtain and purify  $\text{MgCl}_2$  did not involve chlorinating furnaces and carbonized pellets (Lockwood  
8 et al., 1981). A thermic process was used to recover magnesium from dolomite at the facility in  
9 Washington (capacity of 40,000 metric tons/yr) (Kramer, 1995). In thermic processes,  $\text{MgO}$ , a  
10 component of calcinated dolomite, is reacted with a metal such as silicon (usually alloyed with  
11 iron) to produce metallic magnesium. In 2000, the Magnesium Corporation of America facility  
12 near Rowley, Utah, was the only operational magnesium smelting facility in the United States.

13 Monitoring of wastewater discharges from U.S. magnesium production facilities for  
14 CDD/CDF content has not been reported. Wastewater discharges of CDDs/CDFs reported for  
15 the Norwegian facility (Oehme et al., 1989), discussed in the previous paragraphs, are not  
16 adequate to support development of wastewater emission factors for U.S. facilities because of  
17 possible differences in the processes used to manufacture  $\text{MgCl}_2$  and pollution control  
18 equipment.

19 Monitoring of air emissions for CDD/CDF content has been reported for the Magnesium  
20 Corporation of America facility near Rowley, Utah (Western Environmental Services and  
21 Testing, Inc., 2000). The average emission rates (for three tests) reported for the melt reactor  
22 stack and the cathode stack were 0.31 mg I-TEQ<sub>DF</sub>/hr and 0.16 mg I-TEQ<sub>DF</sub>/hr, respectively.

23 Emissions data were judged inadequate for developing national emission estimates for  
24 1987 that could be included in the national inventory. The confidence in the degree to which the  
25 one tested facility represents the emissions from the other two U.S. facilities is low. However, an  
26 estimate of the potential TEQ annual emissions for 1995 from U.S. primary magnesium  
27 production facilities can be made by assuming that the average total emission factor for the Utah  
28 facility measured in May 2000 (0.47 mg I-TEQ<sub>DF</sub>/hr ) is representative of the other two facilities  
29 for magnesium production. Specifically, if it is assumed that this facility operated for 24 hr/day  
30 for 365 days in 1995, then the annual release in 1995 would have been 4.1 g I-TEQ<sub>DF</sub>. If it is  
31 further assumed that this facility operated at 98% of its rated capacity of 40,000 metric tons/yr,

1 then the production-based emission factor would be 105 ng I-TEQ<sub>DF</sub>/kg of magnesium produced.  
2 Applying this emission factor to 98% of the industry's production capacity in 1995 (142,000  
3 metric tons) yields a preliminary annual emission estimate of 14.6 g I-TEQ<sub>DF</sub> in 1995.

4 In 2000, the Magnesium Corporation of America facility near Rowley, Utah, was the only  
5 operational magnesium smelting facility. Production of primary magnesium at this facility was  
6 400,000 metric tons in 2000. Using the emission factor of 105 ng I-TEQ<sub>DF</sub>/kg of magnesium  
7 produced, the national estimate for dioxin releases in 2000 due to primary magnesium smelting is  
8 42 g I-TEQ/yr. The emission factor has a high confidence rating because it was developed using  
9 data from this facility; therefore, the emission estimate is assigned a high confidence level.

### 11 **7.1.3. Primary Nickel Smelting and Refining**

12 Oehme et al. (1989) reported that certain primary nickel refining processes generate  
13 CDDs and CDFs, primarily CDFs. Although the current low-temperature process used at the  
14 Norwegian facility is estimated to result in releases to water of only 1 g I-TEQ<sub>DF</sub>/yr, a high-  
15 temperature (800 °C) process to convert nickel chloride to nickel oxide that had been used for  
16 17 yr at the facility is believed to have resulted in significant releases in earlier years, based on  
17 the ppb levels of CDFs detected in aquatic sediments downstream of the facility.

18 According to Kuck (1995), the only nickel mining and smelting complex in the United  
19 States (located in Oregon) had a capacity of 16,000 metric tons/yr. The facility had been on  
20 standby since August 1993 and had no production in 1994. The facility restarted operations in  
21 April 1995 and produced 8,290 metric tons of nickel that year. In 1998, the smelter closed  
22 because of low nickel prices (USGS, 2002).

23 Monitoring of discharges for CDD/CDF content at this one U.S. facility has not been  
24 reported. Emissions of CDDs/CDFs were reported for a Norwegian facility in the late 1980s, as  
25 discussed above. The emissions information contained in the Norwegian study (Oehme et al.,  
26 1989) is not adequate to support development of emission factors for the U.S. facility for 1987  
27 and 1995. Because the facility closed in 1998, emission estimates for 2000 for primary nickel  
28 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 ( $\text{Al}_2\text{O}_3$ ), 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 ( $\text{Na}_3\text{AlF}_6$ ) 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, 1997d, e). 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<sub>4</sub>). The TiCl<sub>4</sub> is separated from other chlorides by double distillation. The TiCl<sub>4</sub> 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, Oregon, and the other in Henderson, Nevada. 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, 1997f). 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. EA, 2001f). 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, 2001f). Therefore, they are not considered to cause environmental releases per 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, 1997b).

### **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, 1997b).

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, 1997b).

CDD/CDF emissions to air have been measured at six U.S. secondary aluminum operations. Four facilities were tested in 1995 and two facilities were tested in 1992. Three of

1 the four 1995 tests were conducted by EPA in conjunction with the Aluminum Association to  
2 identify emission rates from facilities with potentially maximum-achievable-control-technology-  
3 grade operations and APCD equipment. The fourth test was performed by EPA (U.S. EPA,  
4 1995h). Results from two facilities tested by the California Air Resources Board (CARB) in  
5 1992 were presented in two confidential reports.

6 The first facility tested in 1995 was a top-charge melt furnace (Advanced Technology  
7 Systems, Inc., 1995). During testing, the charge material to the furnace was specially formulated  
8 to contain no oil, paint, coatings, rubber, or plastics (other than incidental amounts). The  
9 CDD/CDF emissions from such a clean charge, 0.27 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (0.26 ng I-TEQ<sub>DF</sub>/kg)  
10 charge material, would be expected to represent the low end of the normal industry range.

11 The second facility operated a sweat furnace to preclean the scrap and a reverberatory  
12 furnace to smelt the precleaned aluminum (U.S. EPA, 1995h). Stack emissions were controlled  
13 by an afterburner operated at 788 °C. The TEQ emission factor for this facility was 3.37 ng  
14 TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (3.22 ng I-TEQ<sub>DF</sub>/kg) aluminum produced.

15 The third facility employed a crusher/roasting dryer as a precleaning step followed by a  
16 reverberatory furnace (Galson Corporation, 1995). The emissions from the two units were  
17 vented separately. The exhaust from the crusher/dryer was treated with an afterburner and a  
18 fabric filter (FF). The exhaust from the furnace passed through an FF with lime injection. Both  
19 stack exhausts were tested, and the combined TEQ emission factor was 13.55 ng TEQ<sub>DF</sub>-  
20 WHO<sub>98</sub>/kg (12.95 ng I-TEQ<sub>DF</sub>/kg) aluminum produced. Because the activity level of the facility  
21 at the time of sampling was treated as confidential business information, the calculated emission  
22 factor was based on the reported typical production rates of the two operations: 26,000 lb/hr for  
23 the crusher/dryer and 6,700 lb/hr for the furnace.

24 The fourth facility operated a scrap roasting dryer followed by a sidewall reverberatory  
25 furnace (Envisage Environmental Inc., 1995). The emissions from the two units were vented  
26 separately. Exhaust from the dryer passed through an afterburner and a lime-coated FF. The  
27 exhaust from the furnace passed through a lime-coated FF. Both stack exhausts were tested, and  
28 the combined TEQ emission factor was 37.94 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (36.03 ng I-TEQ<sub>DF</sub>/kg) of  
29 charge material. Problems with the scrap dryer were discovered after the testing was completed.  
30 Also, operating conditions during testing were reported to represent more worst-case than typical  
31 operations.

1 The two facilities tested by CARB in 1992, which were reported in two confidential  
2 reports (CARB, 1992a, b, as reported in U.S. EPA, 1997b) had TEQ emission factors of  
3 consumed 55.68 and 23.44 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (52.21 and 21.67 ng I-TEQ<sub>DF</sub>/kg) of scrap  
4 aluminum. One facility was equipped with a venturi scrubber; the other was assumed to be  
5 uncontrolled (U.S. EPA, 1997b).

6 The congener and congener group emission factors derived from these stack tests are  
7 presented in Table 7-3. The average congener and congener group profiles are presented in  
8 Figure 7-1. The average of the TEQ emission factors measured at the six tested facilities  
9 (including the facility at which a specially formatted clean charge was used) is 22.4 ng TEQ<sub>DF</sub>-  
10 WHO<sub>98</sub>/kg (21.1 ng I-TEQ<sub>DF</sub>/kg) of scrap feed. (Although the emission factors at two of the  
11 facilities tested in 1995 are based on the output rather than the input rate, the two rates are  
12 assumed, for purposes of this report, to be roughly equivalent.) Although the 1992 and 1995  
13 testing was conducted at U.S. facilities, a low confidence rating is assigned to the average  
14 emission factor because it is based on the results of testing at only six facilities, several of which  
15 may have more effective APCDs than the other facilities in the industry.

16 For comparison purposes, the European Commission uses 22 ng I-TEQ<sub>DF</sub>/kg scrap  
17 aluminum as the typical emission factor for the European Dioxin Inventory (Quab and Fermann,  
18 1997). Umweltbundesamt (1996) reported stack testing results for 25 aluminum smelters and  
19 foundries in Germany. This study provided sufficient data to enable calculation of TEQ emission  
20 factors for 11 of the tested facilities. The calculated emission factors ranged from 0.01 to 167 ng  
21 I-TEQ<sub>DF</sub>/kg of scrap feed. Three facilities had emission factors exceeding 100 ng I-TEQ<sub>DF</sub>/kg,  
22 and two facilities had emission factors of less than 1 ng I-TEQ<sub>DF</sub>/kg. The mean emission factor  
23 for the 11 facilities was 42 ng I-TEQ<sub>DF</sub>/kg.

24 Approximately 727,000 metric tons of scrap aluminum were consumed by 67 secondary  
25 aluminum smelters in 1987 (U.S. DOC, 1995c). In 1995, consumption of scrap aluminum by the  
26 76 facilities that compose the secondary aluminum smelting industry had nearly doubled to 1.3  
27 million metric tons (USGS, 1997a; The Aluminum Association, 1997). In 2000, secondary  
28 aluminum smelters consumed 1.6 million metric tons of scrap aluminum (USGS, 2002). A high  
29 confidence rating is assigned to these production estimates because they are based on government  
30 survey data. Applying the I-TEQ<sub>DF</sub> emission factor of 21.1 ng TEQ/kg of scrap feed to these  
31 consumption values yields estimated annual emissions of 15.3 g I-TEQ<sub>DF</sub> in 1987, 27.4 g I-TEQ<sub>DF</sub>

1 in 1995, and 33.8 g I-TEQ<sub>DF</sub> in 2000. Applying the TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factor of 22.4 ng  
2 TEQ/kg to the consumption values yields estimated annual emissions of 16.3 g TEQ<sub>DF</sub>-WHO<sub>98</sub> in  
3 1987, 29.1 g TEQ<sub>DF</sub>-WHO<sub>98</sub> in 1995, and 35.9 g TEQ<sub>DF</sub>-WHO<sub>98</sub> in 2000. These emission  
4 estimates are assigned a low confidence rating because the rating given to the emission factor  
5 was low.

6 It should be noted that a significant amount of scrap aluminum is also consumed by other  
7 segments of the aluminum industry. However, this scrap is generally from metal manufacturing  
8 processes, including metal and alloy production (e.g., borings, turnings, and dross), rather than  
9 old scrap that results from recycling of consumer products (e.g., cans, radiators, auto shredders).  
10 In 1995, integrated aluminum companies consumed 1.4 million metric tons of scrap aluminum  
11 and independent mill fabricators consumed 0.68 million metric tons (USGS, 1997a).

### 13 **7.2.2. Secondary Copper Smelters**

14 Secondary copper smelting is part of the scrap copper, brass, and bronze reprocessing  
15 industry. Brass is an alloy of copper and zinc; bronze is an alloy of copper and tin. Facilities in  
16 this industry fall into three general classifications: secondary smelting, ingot making, and  
17 remelting. Similar processing equipment may be used at all three types of facilities, so the  
18 distinguishing features are not immediately apparent (U.S. EPA, 1994g).

19 The feature that distinguishes secondary smelters from ingot makers and remelters is the  
20 extent to which pyrometallurgical purification is performed. A typical charge at a secondary  
21 smelter may contain from 30 to 98% copper. The secondary smelter upgrades the material by  
22 reducing the quantity of impurities and alloying materials, thereby increasing the relative  
23 concentration of copper. This degree of purification and separation of the alloy constituents does  
24 not occur at ingot makers and remelters. Feed material to a secondary copper smelter is a  
25 mixture of copper-bearing scrap such as tubing, valves, motors, windings, wire, radiators,  
26 turnings, mill scrap, printed circuit boards, telephone switching gear, and ammunition casings.  
27 Nonscrap items like blast furnace slags and drosses from ingot makers or remelters may represent  
28 a portion of the charge. The secondary smelter operator uses a variety of processes to separate  
29 the alloy constituents. Some purify the scrap in the reductive atmosphere of a blast furnace and  
30 then purify the charge in the oxidizing atmosphere of a converter. Other secondary smelters



perform all purification by oxidation in top-blown rotary converters or in reverberatory furnaces (U.S. EPA, 1994g).

The ingot makers blend and melt scrap copper, brass, and bronze of various compositions to produce a specification brass or bronze ingot. When necessary, the ingot makers 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, 1994g).

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, 1994g).

#### **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 air pollution control equipment in place were considered typical for the source category. 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. Fabric filters (FFs) controlled particulate emissions, and the flue gas was then discharged into a common stack. The estimated emission factors derived for this site are presented in Table 7-4. 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<sub>DF</sub>/kg (810 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/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, Pennsylvania (Franklin Smelting and Refining Co.), was conducted by Applied Geotechnical & Environmental Services Corporation (AGES, 1992). Similar to the facility tested by EPA in 1984–1985, this facility processed low-purity copper-bearing scrap, telephone switch gear, and slags, as well as higher copper content materials (U.S. EPA, 1994g). 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, 1994g). The APCD equipment installed on the blast furnace included an afterburner, cooling tower, and baghouse. 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 baghouse compartments were inoperable (AGES, 1992). The estimated emission factors derived for this site from the AGES results are presented in Table 7-4. The emission factors are based on the total weight of scrap fed to the blast furnace. The TEQ emission factor was 16,618 ng I-TEQ<sub>DF</sub>/kg (16,917 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/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, Illinois, 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, 1994g). 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 7-4. The emission factors are based on the total weight of scrap feed going to the furnace. The TEQ emission factor was 3.60 ng I-TEQ<sub>DF</sub>/kg (3.66 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg) of scrap.

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<sub>DF</sub>/kg and from 0.005 to 1.56 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub>/kg. A smelter in Austria is reported to have a TEQ emission factor of 4 ng I-TEQ<sub>DF</sub>/kg. The minimum, typical, and maximum default emission factors selected in LUA are 5, 50, and 400 ng I-TEQ<sub>DF</sub>/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.

#### **7.2.2.2. Activity-Level Information**

In 1987, four secondary copper smelters were in operation: Franklin Smelting and Refining Co. (Philadelphia, Pennsylvania), Chemetco, Inc. (Alton, Illinois), Southwire Co. (Carrollton, Georgia), and a facility located in Gaston, South Carolina, 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 (Edelstein, 1999). In 1995, only three of these four facilities were in

operation. The Southwire facility in Gaston (previously owned by AT&T) was closed in January 1995. The Franklin facility subsequently 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 facility (Edelstein, 1999). In May 2000, the Southwire Co. closed its 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 in 2001, and that Chemetco operated for 10 of 12 months in 2001, Chemetco's 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 would have been 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). The presence of chlorinated plastics in copper scraps used as feed for smelters is believed to increase the 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 (i.e., U.S. EPA, 1987a; AGES, 1992) had the following characteristics: both processed low-purity scrap containing significant quantities of plastics 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, 1994g). The other tested U.S. facility used oxidizing rather than reducing conditions and processed relatively high-purity scrap (Sverdrup, 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

1 emission factor in 1987 and 1995. Combining this emission factor (16,618 ng I-TEQ<sub>DF</sub>/kg  
2 [16,917 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg] of scrap feed) with the estimated smelter capacities (data are not  
3 available on the amount of scrap processed) for this facility in 1987 (13,600,000 kg) and 1995  
4 (16,000,000 kg) yields TEQ emission estimates of 226 g I-TEQ<sub>DF</sub> (230 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) in 1987  
5 and 266 g I-TEQ<sub>DF</sub> (271 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) in 1995. This facility ceased operations in 1997.

6 The Chemetco facility operated in 1987, 1995, and 2000. Similarly, for purposes of this  
7 report, the TEQ emission factor for the Chemetco facility is considered to be representative of the  
8 TEQ emission factor for this facility for 1987, 1995, and 2000. Combining this emission factor  
9 (3.60 ng I-TEQ<sub>DF</sub>/kg [3.66 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg] of scrap feed) with the estimated smelter  
10 capacities of 120,000,000 kg in 1987 and 135,000,000 kg in 1995 yields TEQ estimates of 0.43 g  
11 I-TEQ<sub>DF</sub> (0.44 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) in 1987 and 0.49 g I-TEQ<sub>DF</sub> (0.49 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) in 1995.  
12 Combining the same emission factor with the scrap consumption for this facility in 2000  
13 (235,000,000 kg) yields a TEQ estimate of 0.85 g I-TEQ<sub>DF</sub> (0.86 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) for 2000.

14 The facility in Gaston, South Carolina, was in operation during 1987 but ceased  
15 operations in 1995. Prior to 1990, when this facility was owned by AT&T, the plant processed a  
16 great deal of high-plastics-content scrap (such as whole telephones). This scrap was fed to a  
17 pyrolysis unit prior to entering the blast furnace. In addition to a blast furnace, the facility also  
18 had an oxidizing reverberatory furnace for processing higher purity scrap. The facility had  
19 separate FFs for the blast furnace, the converters, and the reverberatory furnace (U.S. EPA,  
20 1994g). Because this facility processed low-purity, high-plastics-content scrap in 1987, and  
21 presumably processed much of this in the reducing atmosphere of a pyrolysis unit and blast  
22 furnace, the average of the TEQ emission factors for the Tier 4 (U.S. EPA, 1987a) and Franklin  
23 facilities (8,700 ng I-TEQ<sub>DF</sub>/kg [8,860 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg]) was used to estimate potential  
24 emissions in 1987 of 740 g I-TEQ<sub>DF</sub> (753 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) (assuming an activity level of  
25 85,000,000 kg). This activity level is the estimated capacity of the facility; data were not  
26 available on the amount of scrap processed.

27 The Southwire facility had both a blast furnace and a reverberatory furnace. In 1992,  
28 approximately 50% of incoming scrap was processed in each furnace (U.S. EPA, 1994g). Unlike  
29 the two tested facilities and the Gaston facility, the Southwire facility stopped processing plastic-  
30 coated scrap in the 1970s. In addition, this facility had a more complex APCD system, which  
31 may have reduced the formation and release of CDDs/CDFs. The blast furnace processed gases

1 passed through an afterburner (871°C), U-tube coolers, and an evaporative spray system before  
2 entering the FF at a temperature of 107 to 191°C. For these reasons, EPA has determined that  
3 the existing emissions data for secondary smelters cannot reliably be used to generate a  
4 quantitative estimate of potential emissions during 1987, 1995, or 2000 for this facility.

5 Total secondary copper smelter emissions for 1987 are the sum of the Franklin smelting  
6 facility emissions (271 g TEQ<sub>DF</sub>-WHO<sub>98</sub> or 266 g I-TEQ<sub>DF</sub>), the Chemetco smelter facility (0.44 g  
7 TEQ<sub>DF</sub>-WHO<sub>98</sub> or 0.43 g I-TEQ<sub>DF</sub>) and the Gaston, South Carolina, facility (753 g TEQ<sub>DF</sub>-  
8 WHO<sub>98</sub> or 740 g I-TEQ<sub>DF</sub>). Total secondary copper smelter emissions for 1987 are 983.44 g  
9 TEQ<sub>DF</sub>-WHO<sub>98</sub> (966.43 g I-TEQ<sub>DF</sub>).

10 Total secondary copper smelter emissions for 1995 are the sum of the Franklin smelting  
11 facility emissions (271 g TEQ<sub>DF</sub>-WHO<sub>98</sub> 266 g I-TEQ<sub>DF</sub>) and the Chemetco smelter facility (0.49  
12 g TEQ<sub>DF</sub>-WHO<sub>98</sub> or 0.49 g TEQ<sub>DF</sub>-WHO<sub>98</sub> ). Total secondary copper smelter emissions for 1995  
13 are 271.49 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (266.49 I-TEQ<sub>DF</sub>).

14 The Chemetco smelter provides the TEQ emissions estimate for the year 2000. Total  
15 secondary copper smelter emissions for 2000 are 0.86 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (0.85 g I-TEQ<sub>DF</sub>).  
16 A high confidence rating is assigned to the production and consumption estimates because they  
17 are based on government survey data. A low confidence rating is assigned to the TEQ emission  
18 estimates because they are based on limited measurements made at three smelters, one of which  
19 was not in operation in 1987 or 1995.

20 It should be noted that a significant amount of scrap copper is consumed by other  
21 segments of the copper industry. In 1995 and 2000, brass mills and wire-rod mills consumed  
22 886,000 and 1,070,000 metric tons of copper-based scrap, respectively; foundries and  
23 miscellaneous manufacturers consumed 71,500 and 96,200 metric tons, respectively (USGS,  
24 1997a; Edelstein, 2001). As noted above, however, these facilities generally do not conduct any  
25 significant purification of the scrap. Rather, the scrap consumed is already of alloy quality, and  
26 processes employed typically involve only melting, casting, and extruding. Thus, the potential  
27 for formation of CDDs/CDFs is expected to be much less than the potential during secondary  
28 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, 1994h).

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, 1994h).

In 1987, the lead smelting industry consisted of 24 facilities producing 0.72 million metric tons of lead (U.S. EPA, 1994h). In 1995, there were 23 companies producing 0.97 million metric tons (USGS, 1997a), 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 (or 0.28 million metric tons). Reverberatory furnaces and blast and electric furnaces co-located with reverberatory furnaces accounted for 74% of capacity (or 1.01 million metric tons). Rotary furnaces accounted for the remaining 5% of capacity (or 0.07 million metric tons) (U.S. EPA, 1994h).

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 (see Table 7-5). 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 lead smelters using the results of emission tests performed by EPA at three smelters (a blast furnace [U.S. EPA, 1995e], a co-located blast/reverberatory furnace [U.S. EPA, 1992e], and a rotary kiln furnace [U.S. EPA, 1995d]). 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<sub>DF</sub>-WHO<sub>98</sub>/kg (0.63 to 8.31 ng I-TEQ<sub>DF</sub>/kg)
- Reverberatory/co-located furnace: 0.05 to 0.42 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (0.05 to 0.41 ng I-TEQ<sub>DF</sub>/kg)
- Rotary furnace: 0.24 to 0.66 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (0.24 to 0.66 ng I-TEQ<sub>DF</sub>/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 following estimated air emissions in g I-TEQ<sub>DF</sub> for 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.

Configuration	Estimated annual TEQ emissions (g TEQ) <sup>a</sup>					
	Ref. year 1987		Ref. year 1995		Ref. year 2000	
	TEQ <sub>DF</sub> -WHO <sub>98</sub>	I-TEQ <sub>DF</sub>	TEQ <sub>DF</sub> -WHO <sub>98</sub>	I-TEQ <sub>DF</sub>	TEQ <sub>DF</sub> -WHO <sub>98</sub>	I-TEQ <sub>DF</sub>
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
<b>TOTAL</b>	<b>1.288</b>	<b>1.223</b>	<b>1.721</b>	<b>1.632</b>	<b>2.484</b>	<b>2.354</b>

<sup>a</sup>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 sinter plant (Knepper, 1981; Capes, 1983; U.S. EPA, 1995b).

Several European investigators have reported that iron ore sinter plants are major sources of airborne emissions of CDDs/CDFs (Rappe, 1992b; 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 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. sinter plants ranges from 0.1 to 0.75% (Calcagni et al., 1998).

Sinter plants in Sweden have been reported to emit up to 3 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup> stack gas, or 2 to 4 g I-TEQ<sub>DF</sub>/yr (Rappe, 1992b; 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<sub>DF</sub>/dscm (at 11% oxygen). The other two facilities, both equipped with cyclones, had emission factors of 6.3 and 9.6 ng I-TEQ<sub>DF</sub>/dscm (at 7% oxygen). Lahl (1993, 1994) reported stack emissions for sintering plants in Germany (after passage through mechanical filters and electrostatic precipitators) ranging from 3 to 10 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup>. 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<sub>DF</sub>/m<sup>3</sup> (at 7% oxygen); the majority of emissions in 1996 were around 3 ng I-TEQ<sub>DF</sub>/m<sup>3</sup> (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 sinter 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. sinter 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 sinter 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<sub>DF</sub>/Nm<sup>3</sup> and 0.81 ng I-TEQ<sub>DF</sub>/Nm<sup>3</sup> for the WS and the FF, respectively. The corresponding TEQ emission factors are 0.62 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (0.55 ng I-TEQ<sub>DF</sub>/kg) sinter and 4.61 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (4.14 ng I-TEQ<sub>DF</sub>/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 7-7. Figure 7-4 presents the congener profiles for these facilities. Although concentrations were higher from the FF than from the scrubber, both concentrations were low relative to what had been reported from testing at German, Dutch, Swedish, and Canadian sinter plants. These differences may be due to differences between the operation or APCDs of U.S. sinter plants and the tested European plants.

1 Most of the U.S. integrated iron and steel plants, including those with sinter plants, have  
2 eliminated the purchase and use of chlorinated organics in their facilities. Their rolling mill oils  
3 (lubricants and hydraulic fluids) do not contain chlorinated compounds. In addition, routine  
4 analysis of waste materials going to the sinter plant have not detected any chlorinated solvents.  
5 Finally, none of the U.S. plants use an ESP to control emissions from the sinter windbox  
6 (Calcagni et al., 1998).

7 In 1996 (data were not readily available for 1995), 11 sintering plants were operating in  
8 the United States, with a total annual production capacity of about 17.6 million metric tons  
9 (Metal Producing, 1996). Since the 1980s, the size of this industry has decreased dramatically.  
10 In 1982, 33 facilities were in operation, with a combined total capacity of 48.3 million metric  
11 tons (U.S. EPA, 1982b). The nine U.S. sinter plants operating in 1995 had a combined capacity  
12 of 15.6 million metric tons (Calcagni et al., 1998). In 1987, sinter consumption by iron and steel  
13 plants was 14.5 million metric tons (AISI, 1990); in 1995, consumption was 12.4 million metric  
14 tons (Fenton, 1996), or approximately 70% of production capacity, assuming that production  
15 capacity in 1995 was the same as in 1996. These activity level estimates are assigned a  
16 confidence rating of medium.

17 As shown in Table 7-8, 59% of 1998 sinter production capacity was at facilities with WSs  
18 and 41% was at facilities with FFs. If it is assumed that these proportions of APCD-to-  
19 production capacity existed in 1995 and that actual production in 1995 was equal to sinter  
20 consumption at iron and steel plants (12.4 million metric tons), then estimated TEQ emissions  
21 from WS-equipped facilities were 4.5 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (4 g I-TEQ<sub>DF</sub>) and emissions from FF-  
22 equipped facilities were 23.4 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (21 g I-TEQ<sub>DF</sub>), for a total of 27.9 g TEQ<sub>DF</sub>-  
23 WHO<sub>98</sub> (25.1 g I-TEQ<sub>DF</sub>). These emission estimates are assigned an overall medium confidence  
24 rating on the basis of the medium rating for the activity level estimates.

25 If these same assumptions are applied to the 1987 sinter consumption rate of 14.5 million  
26 metric tons, then estimated TEQ emissions from WS-equipped facilities were 5.3 g TEQ<sub>DF</sub>-  
27 WHO<sub>98</sub> (4.7 g I-TEQ<sub>DF</sub>) and emissions from FF-equipped facilities were 27.4 g TEQ<sub>DF</sub>-WHO<sub>98</sub>  
28 (24.6 g I-TEQ<sub>DF</sub>), for a total of 32.7 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (29.3 g I-TEQ<sub>DF</sub>). These emission  
29 estimates are less certain than the estimates for 1995 because of uncertainties concerning actual  
30 APCDs in place in 1987 and the content of waste feed (i.e., oil content and presence of

chlorinated organics in the oil) at that time. Consequently, a low confidence rating is assigned to the emission factor and the emission 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 wet scrubbers and facilities with fabric filters as was done for 1995 and 1987, then estimated TEQ emissions from wet scrubber-equipped facilities were 3.9 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (3.4 g I-TEQ<sub>DF</sub>) and emissions from fabric filter-equipped facilities were 23.7 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (21.3 g I-TEQ<sub>DF</sub>), for a total of 27.6 TEQ<sub>DF</sub>-WHO<sub>98</sub> (24.4 g I-TEQ<sub>DF</sub>) for the year 2000. This emission estimate is assigned a high confidence rating based on 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<sub>DF</sub>/kg of coal consumed. Bremmer et al. estimated minimal CDD/CDF air emissions (0.002 ng I-TEQ<sub>DF</sub>/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. For coke making and coke ovens, emissions were estimated on the basis of plant capacity and estimated production and were reported as 0.3 ng I-TEQ/kg coke produced (see Table 7-5).

Although no testing of CDD/CDF emissions from U.S. coke plants has been reported upon which to base an estimate of national emissions, 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<sub>DF</sub>/kg of coal consumed). These calculations yield annual

emissions of 7.7, 6.9, and 6.03 g I-TEQ<sub>DF</sub> 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 TEQ/dry Nm<sup>3</sup> (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<sup>3</sup> or 1.7 ng Nordic TEQ/kg of feedstock). Much lower emissions (0.1 ng Nordic TEQ/dry Nm<sup>3</sup> or 0.6 ng Nordic TEQ/kg of 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<sup>3</sup>) were detected in flue gases prior to the FF.

1 The congener profiles of raw flue gas samples (prior to the APCD) showed that CDFs  
2 rather than CDDs were predominant in all three feedstock types. The congener profile from the  
3 test burn with PVC-containing feedstock showed a higher chlorinated congener content than was  
4 observed with the other feedstocks.

5 Eduljee and Dyke (1996) used a range of 0.7 to 10 ng I-TEQ<sub>DF</sub>/kg of scrap feed to  
6 estimate national emissions for the United Kingdom. This range was assumed to be  
7 representative of no-chlorine and high-chlorine operations. However, the study authors provided  
8 little information on the supporting emission test studies (i.e., tested facility operational  
9 materials, feed rates, congener-specific emission rates).

10 Umweltbundesamt (1996) reported stack testing results for a variety of electric arc  
11 furnaces in Germany. Sufficient data were provided in the report to enable calculation of TEQ  
12 emission factors for six of the tested facilities. Two facilities had emission factors exceeding 1  
13 ng I-TEQ<sub>DF</sub>/kg of scrap processed, and two facilities had emission factors less than 0.1 ng I-  
14 TEQ<sub>DF</sub>/kg of scrap. The mean emission factor was 1.15 ng I-TEQ<sub>DF</sub>/kg of scrap. The TEQ  
15 concentrations in the stack gases at these facilities (corrected to 7% oxygen) ranged from less  
16 than 0.1 to 1.3 ng I-TEQ<sub>DF</sub>/m<sup>3</sup>.

17 The report commissioned by Environment Canada in 2000 to review steel production  
18 processes at Canadian plants (Charles E. Napier Company, Ltd., 2000) included information on  
19 emissions from iron sintering and provided information on emissions from electric arc furnaces,  
20 which were estimated on the basis of plant capacity and estimated production. An average  
21 emission factor of 2.1 ng I-TEQ<sub>DF</sub>/kg steel produced was developed (see Table 7-5).

22 In March 2000, Environment Canada reported on source testing for the determination of  
23 CDD/CDF emissions from a facility in Ontario (Cianciarelli, 2000). Sampling was conducted on  
24 the exhaust stack of the electric arc furnace of Dofasco Inc., and both concentrations and  
25 emission rates were provided (see Table 7-9). Total CDD/CDF concentrations were reported to  
26 be 51.15 pg TEQ/m<sup>3</sup>, and the total emission rate was reported to be 0.47 ng TEQ/kg steel  
27 produced. In August 2000, the Emissions Research and Measurement Division of Environment  
28 Canada conducted source testing to determine CDDs/CDFs from the electric arc furnace of  
29 another facility, Gerdau Courtice Steel Inc. (Cianciarelli, 2001a). These results (presented in  
30 Table 7-9) 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<sup>3</sup>, 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<sub>DF</sub>/kg steel derived from the data reported in Umweltbundesamt (1996) and the three Environment Canada reports (Charles E. Napier Company, Ltd., 2000; Cianciarelli, 2000, 2001a). This calculation yields an annual emission estimate of 37.3 g I-TEQ<sub>DF</sub> in 1987, 46.5 g I-TEQ<sub>DF</sub> in 1995, and 59.3 g I-TEQ<sub>DF</sub> 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, 1997b).

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 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, 1997b).

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% (or 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, 1997b). 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, 1993a, as reported in U.S. EPA, 1997b). 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 7-10. The calculated TEQ emission factor for this set of tests is 0.42 ng TEQ<sub>DF</sub>-WHO<sub>98</sub> (0.37 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub>/kg of metal charge, and four facilities had emission factors less than 0.1 ng I-TEQ<sub>DF</sub>/kg of metal charge. The emission factors span more than four orders of magnitude. The mean emission factor was 1.26 ng I-TEQ<sub>DF</sub>/kg of metal feed.

In 1997, EPA conducted testing for emissions of dioxins at two ferrous foundries (U.S. EPA, 1999a, b). 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 7-11. 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 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<sub>DF</sub>/kg of metal feed) derived from the data reported in Umweltbundesamt (1996), CARB (1993), and U.S. EPA (1997) with an estimated activity level for U.S. foundries.

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 yield annual emission estimates of 11.3 g I-TEQ<sub>DF</sub>, 17.1 g I-TEQ<sub>DF</sub>, and 13.9 g I-TEQ<sub>DF</sub> 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,

1 scrap electric wire is mechanically chopped into fine particles. The insulating material is then  
2 removed by mixing, followed by settling of the heavier metal (telephone conversations between  
3 T. Leighton, Versar, Inc., and R. Garino, Institute of Scrap Recycling Industries, March 2, 1993,  
4 and T. Leighton and J. Sullivan, Triple F. Dynamics, March 8, 1993).

5 EPA measured dioxin-like compounds emitted to the air from a scrap wire reclamation  
6 incinerator during its 1986 National Dioxin Study of combustion sources (U.S. EPA, 1987a).  
7 EPA determined that the tested facility was typical of this industrial source category at that time.  
8 Insulated wire and other metal-bearing scrap material were fed to the incinerator on a steel pallet.  
9 The incinerator operated in a batch mode, with the combustion cycles for each batch of scrap  
10 feed lasting between 1 and 3 hr. Natural gas was used to incinerate the material. Although most  
11 of the wire had a tar-based insulation, PVC-coated wire was also fed to the incinerator.  
12 Temperatures during combustion in the primary chamber furnace were about 570 °C. The tested  
13 facility was equipped with a high-temperature, natural gas-fired afterburner (980 to 1090 °C).  
14 Emission factors estimated for this facility are presented in Table 7-12. The estimated TEQ  
15 emission factor (based only on 2,3,7,8-TCDD, 2,3,7,8-TCDF, OCDD, and OCDF) is 15.8 ng  
16 TEQ<sub>DF</sub>-WHO<sub>98</sub> (16.9 ng I-TEQ<sub>DF</sub>/kg) of scrap feed. Figure 7-5 presents a congener group profile  
17 based on these emission factors.

18 Bremmer et al. (1994) reported emission factors for three facilities in the Netherlands that  
19 subsequently ceased operations. Emission rates at a facility burning underground cables and  
20 cables containing PVC ranged from 3.7 ng I-TEQ<sub>DF</sub>/kg to 14 ng I-TEQ<sub>DF</sub>/kg. The emission rates  
21 at a second facility ranged from 21 ng I-TEQ<sub>DF</sub>/kg of scrap (when burning copper core coated  
22 with greasy paper) to 2,280 ng I-TEQ<sub>DF</sub>/kg of scrap (when burning lead cable). The third facility,  
23 which burned motors, was reported to have an emission rate of 3,300 ng I-TEQ<sub>DF</sub>/kg of scrap.  
24 On the basis of these measurements, Bremmer et al. used emission rates of 40 ng I-TEQ<sub>DF</sub>/kg of  
25 scrap and 3,300 ng I-TEQ<sub>DF</sub>/kg of scrap for estimating national emissions in the Netherlands for  
26 facilities burning wires and cables and those burning motors.

27 Although limited emission testing has been conducted at one U.S. facility, the activity  
28 level for this industry sector in reference years 1987, 1995, and 2000 is unknown; therefore, an  
29 estimate of national emissions cannot be made. It is uncertain how many facilities in the United  
30 States still combust scrap wire. Trade association and industry representatives state that U.S.  
31 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 small-scale, unregulated burning of scrap wire 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<sub>DF</sub>/kg, respectively. A significantly higher geometric mean concentration (19,000 ng I-TEQ<sub>DF</sub>/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 7-13. 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.

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<sub>DF</sub>/kg of scrap for illegal, unregulated burning of cables in the Netherlands.

## **7.7. DRUM AND BARREL RECLAMATION FURNACES**

Hutzinger and Fiedler (1991b) reported detecting CDDs/CDFs in stack gas emissions from drum and barrel reclamation facilities at levels ranging from 5 to 27 ng/m<sup>3</sup>. 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).

1 Drum and barrel reclamation facilities operate a burning furnace to thermally clean used  
2 55-gallon steel drums of residues and coatings. The drums processed at these facilities come  
3 from a variety of sources in the petroleum and chemical industries. The thermally cleaned drums  
4 are then repaired, repainted, relined, and sold for reuse. The drum-burning process subjects the  
5 used drums to an elevated temperature in a tunnel furnace fired by auxiliary fuel for a sufficient  
6 time so that the paint, interior linings, and previous contents are burned or disintegrated. Used  
7 drums are loaded onto a conveyor that moves at a fixed speed. As the drums pass through the  
8 preheat and ignition zone of the furnace, residual contents of the drums drain into the furnace ash  
9 trough. A drag conveyor moves these sludges and ashes to a collection pit. The drums are air-  
10 cooled as they exit the furnace. Exhaust gases from the burning furnace are typically drawn  
11 through a breeching fan to a high-temperature afterburner.

12 The afterburner at the facility tested by EPA operated at an average of 827 °C during  
13 testing and achieved a 95% reduction in CDD/CDF emissions (U.S. EPA, 1987a). Emission  
14 factors estimated for this facility are presented in Table 7-14. On the basis of the measured  
15 congener and congener group emissions, the average TEQ emission factor is estimated to be 17.5  
16 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/drum (16.5 ng I-TEQ<sub>DF</sub>/drum). The congener group profile is presented in  
17 Figure 7-6.

18 Approximately 2.8 to 6.4 million 55-gallon drums are reclaimed by incineration annually  
19 in the United States (telephone conversation between C. D. Ruiz, Versar, Inc., and P. Rankin,  
20 Association of Container Reconditioners, December 21, 1992). This estimate is based on the  
21 assumption that 23 to 26 incinerators are in operation; each incinerator, on average, handles 500  
22 to 1,000 drums/day; and, on average, each incinerator operates 5 days/wk, with 14 days  
23 downtime/yr for maintenance activities. The weights of 55-gallon drums vary considerably;  
24 however, on average, a drum weighs 38 lb (or 17 kg); therefore, an estimated 48 to 109 million  
25 kg of drums are incinerated annually. For 1987 and 1995, EPA assumed that 4.6 million drums  
26 were burned each year (i.e., the midpoint of the range); applying the emission factors developed  
27 above, the estimated annual emission of TEQ is 0.08 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (0.08 g I-TEQ<sub>DF</sub>).

28 In 1997, the Reusable Industrial Packaging Association estimated that approximately 35  
29 million 55-gallon barrels were reclaimed in 1997 (RIPA, 1997). Assuming the number of drums  
30 treated in 1997 has remained constant through 2000, the estimate for 2000 would be 0.61 g  
31 TEQ<sub>DF</sub>-WHO<sub>98</sub> (0.58 g I-TEQ<sub>DF</sub>).

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

**Table 7-1. CDD/CDF emission concentrations for primary copper smelters**

Congener/congener group	Emission concentrations (pg TEQ/m <sup>3</sup> @ 11% oxygen)		
	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
<b>TOTAL</b>	<b>3.8</b>	<b>1.7</b>	<b>0.7</b>

Source: Cianciarelli (2001a).

**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	
Falconbridge, Sudbury, Ontario (nickel and copper)	Roasting	Cyclone/ESP	559
	Electric smelting		
	Peirce-Smith converters		
Noranda, Horne smelter, Noranda, Quebec	Noranda reactor	ESP	<1
	Noranda continuous converter		
Noranda, Gaspé smelter, Murdockville, Quebec	Reverberatory furnace	ESP	
	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	FF	<100
	Reverberatory anode furnace	Waste heat boiler, FF	
	Hearth furnace (for tin/lead)	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

Source: Charles E. Napier Company, Ltd. (2002).



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

<b>Congener/ congener group</b>	<b>Mean facility emission factor<sup>a</sup></b>	<b>Mean facility emission factor<sup>b</sup></b>	<b>Mean facility emission factor<sup>c</sup></b>	<b>Mean facility emission factor<sup>d</sup></b>	<b>Mean facility emission factor<sup>e</sup></b>	<b>Mean facility emission factor<sup>e</sup></b>
2,3,7,8-TCDD	ND (0.01)	0.13	0.51	2.17	1.97	0.845
1,2,3,7,8-PeCDD	0.02	0.39	1.19	3.84	7.1	3.64
1,2,3,4,7,8-HxCDD	0.05	0.24	1.35	2.88	4.26	2.82
1,2,3,6,7,8-HxCDD	0.13	0.86	1.52	5.39	5.3	4.12
1,2,3,7,8,9-HxCDD	0.15	1.26	2.51	7.22	5.3	2.02
1,2,3,4,6,7,8-HpCDD	0.51	7.67	2.6	18.01	28.9	19.3
OCDD	0.42	14.97	1.01	NR	33.2	24.3
2,3,7,8-TCDF	0.44	0.74	14.2	47.12	23.2	4.84
1,2,3,7,8-PeCDF	0.06	1.51	10.47	20.01	33.8	1.18
2,3,4,7,8-PeCDF	0.17	2.44	11.06	29.6	48	23.3
1,2,3,4,7,8-HxCDF	0.32	2.44	21.84	52.32	46.1	17.6
1,2,3,6,7,8-HxCDF	0.11	2.69	7.1	16.31	46.1	16.9
1,2,3,7,8,9-HxCDF	0.02	1.02	0.47	1.2	22	1.35
2,3,4,6,7,8-HxCDF	0.3	3.82	7.09	22.96	39	16
1,2,3,4,6,7,8-HpCDF	0.07	11.39	14.61	35.29	122	42.6
1,2,3,4,7,8,9-HpCDF	0.03	5.5	1.21	5.17	27.1	6.2
OCDF	0.3	30.4	3.15	18.77	60.5	29.5
Total I-TEQ <sub>DF</sub> <sup>f</sup>	0.26	3.22	12.95	36.03	52.21	21.67
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> <sup>f</sup>	0.27	3.37	13.55	37.94	55.68	23.44
Total TCDD	NR	3.30	46.03	NR	47.8	0.845
Total PeCDD	NR	4.91	28.07	NR	64	3.64
Total HxCDD	NR	11.45	35.51	NR	78	8.95
Total HpCDD	NR	14.71	6.01	NR	58.5	19.3
Total OCDD	0.42	14.97	1.01	NR	33.2	24.3
Total TCDF	NR	29.67	161.8	NR	620	4.84
Total PeCDF	NR	28.73	222.75	NR	585	35.1
Total HxCDF	NR	32.23	115.32	NR	515	52
Total HpCDF	NR	39.44	39.94	NR	247	48.8
Total OCDF	0.3	30.4	3.15	18.77	60.5	29.5
Total CDD/CDF	NR	209.81	659.6	NR	2309	227

<sup>a</sup>Source: Advanced Technology Systems, Inc. (1995).<sup>b</sup>Source: U.S. EPA (1995h).

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

<sup>c</sup>Source: Galson Corporation (1995).

<sup>d</sup>Source: Envisage Environmental, Inc. (1995).

<sup>e</sup>Source: CARB (1992a, 1992b), as reported in U.S. EPA (1997b).

<sup>f</sup>TEQ calculations assume nondetect values are zero.

NR = Not reported

ND = Not detected (value in parenthesis is the detection limit)

**Table 7-4. CDD/CDF emission factors for secondary copper smelters (ng/kg scrap feed)**

<b>Congener/ congener group</b>	<b>Mean EPA Tier 4 emission factor<sup>a,b</sup></b>	<b>Franklin smelting facility mean emission factor<sup>c</sup></b>	<b>Chemetco smelting facility mean emission factor<sup>d</sup></b>
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 <sub>DF</sub> <sup>e</sup>	779 <sup>f</sup>	16,618	3.6
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> <sup>e</sup>	810 <sup>f</sup>	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	38,890	688,139	204.33

<sup>a</sup>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.

<sup>b</sup>Source: U.S. EPA (1987a).

<sup>c</sup>Source: AGES (1992).

<sup>d</sup>Source: Sverdrup Corp. (1991).

<sup>e</sup>TEQ calculations assume nondetect values are zero.

<sup>f</sup>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)

**Table 7-5. CDD/CDF emission estimates for Canadian coke oven facilities, blast furnace facilities, and electric arc furnaces**

Company/facility	Location	Plant capacity (net tonnes/yr)	Estimated production (net tonnes)	Estimated CDD/CDF emissions (g I-TEQ)	Estimated CDD/CDF emission factor (ng I-TEQ/kg)
<b>Coke oven facilities</b>					
Algoma Steel Inc.	Sault Ste. Marie, Ontario	1,021,000	979,000	0.29	0.296
Dofasco Inc.	Hamilton, Ontario	1,656,000	1,588,000	0.48	0.302
Stelco Inc. Lake Erie Steel	Nanticoke, Ontario	563,000	540,000	0.16	0.296
Stelco Inc., Hilton Works	Hamilton, Ontario	1,035,000	993,000	0.3	0.302
TOTAL		4,275,000	4,100,000	1.23	
<b>Blast furnace facilities</b>					
Algoma Steel Inc	Sault Ste. Marie, Ontario	2,270,000	2,177,000	<0.01	NA
Dofasco Inc.	Hamilton, Ontario	2,725,000	2,613,000	<0.01	NA
Stelco Inc. Lake Erie Steel	Nanticoke, Ontario	1,680,000	1,611,000	<0.01	NA
Stelco Inc., Hilton Works	Hamilton, Ontario	2,720,000	2,608,000	<0.01	NA
TOTAL		9,395,000	9,009,000	<0.1	
<b>Electric arc furnaces</b>					
AltaSteel Ltd.	Edmonton, Alberta	295,000	256,000	0.67	2.62
Atlas Specialty Steels	Welland, Ontario	218,000	189,000	0.49	2.59
Atlas Stainless Steels	Tracy, Quebec	118,000	103,000	0.27	2.62
Co-Steel Lasco	Whitby, Ontario	907,000	788,000	0.79	1
Dofasco Inc.	Hamilton, Ontario	1,225,000	1,065,000	0.5	0.469
Gerdau MRM Steel Inc.	Cambridge, Ontario	290,000	252,000	0.66	2.62
Gerdan MRM Steel Inc.	Selkirk, Manitoba	281,000	244,000	0.63	2.58
IPSCO Inc.	Regina, Saskatchewan	907,000	788,000	1.13	1.43
Ispat Sidbec Inc.	Contrecoeur, Quebec	1,633,000	1,419,000	3.69	2.6
Ivanco Rolling Mills Inc.	L'Original, Ontario	408,000	355,000	0.92	2.59
Slater Steels, Hamilton Specialty Bar Div.	Hamilton, Ontario	363,000	315,000	0.82	2.6
Stelco-McMaster Ltée	Contrecoeur, Quebec	499,000	434,000	1.13	2.6

**Table 7-5. CDD/CDF emission estimates for Canadian coke oven facilities, blast furnace facilities, and electric arc furnaces (continued)**

<b>Company/facility</b>	<b>Location</b>	<b>Plant capacity (net tonnes/yr)</b>	<b>Estimated production (net tonnes)</b>	<b>Estimated CDD/CDF emissions (g I-TEQ)</b>	<b>Estimated CDD/CDF emission factor (ng I-TEQ/kg)</b>
Sydney Corp.	Sydney, Nova Scotia	454,000	395,000	0.4	1.01
<b>TOTAL</b>		7,598,000	6,603,000	12.1	

Source: Charles E. Napier Company, Ltd. (2000).

**Table 7-6. CDD/CDF emission factors for secondary lead smelters<sup>a</sup>**

Congener/congener group	Blast furnace <sup>b</sup> (ng/kg lead produced)		Blast/reverb <sup>c</sup> (ng/kg lead produced)		Rotary kiln <sup>d</sup> (ng/kg lead produced)	
	Before scrubber	After scrubber	Before scrubber	After scrubber	Before scrubber	After scrubber
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	0.4	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	9.52	0.82	0.68	0.61	0.35	2.87
Total 2,3,7,8-CDF	33.28	2.74	3.75	0.51	0.88	2.68
Total I-TEQ <sub>DF</sub> (nondetect set to zero)	8.31	0.63	0.41	0.05	0.24	0.66
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (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 0)	380.43	41.92	15.36	7.66	16.76	45.57
Total CDD/CDF (nondetect set to ½ detection limit)	380.44	42.27	15.36	7.74	16.8	45.62

<sup>a</sup>Except where noted, emission factors were calculated assuming nondetect values are zero.

<sup>b</sup>Source: U.S. EPA (1995e).

<sup>c</sup>Source: U.S. EPA (1992e).

<sup>d</sup>Source: U.S. EPA (1995d).

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

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	19.535	19.82
Total I-TEQ <sub>DF</sub>	0.55	0.55	4.14	4.14
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	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	0.05	0.192
Total CDD/CDF <sup>a</sup>	4.73	4.73	24.48	24.77

<sup>a</sup>The listed values for total CDD/CDF include only the 17 toxic congeners.

Source: Calcagni et al. (1998).

**Table 7-8. Operating parameters for U.S. iron ore sinter plants**

<b>Company</b>	<b>Location</b>	<b>1998 capacity (1000 metric ton/yr)</b>	<b>Current air pollution control device</b>
AK Steel	Middletown, OH	907	Wet scrubber
AK Steel <sup>a</sup>	Ashland, KY	816 <sup>a</sup>	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 <sup>a</sup>	Weirton, WV	1,179 <sup>a</sup>	NA
Wheeling-Pittsburgh Steel	East Steubenville, WV	519	Wet scrubber
WCI Steel	Warren, OH	477	Fabric filter
TOTAL		17,597 <sup>b</sup>	

<sup>a</sup>Not in operation during 1998 (Calcagni et al., 1998).

<sup>b</sup>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).



**Table 7-9. CDD/CDF emission concentrations and rates for Canadian electric arc furnaces**

Congener	Mean facility concentration (pg TEQ/m <sup>3</sup> )				Mean facility emission rate (ng TEQ/tonne steel)			
	Run 1	Run 2	Run 3	Avg.	Run 1	Run 2	Run 3	Avg.
<b>Dofasco Inc.</b>								
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	1.6	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	63.26	69.76	51.15	213.8	547.1	654.9	471.9
<b>Gerdau Courtice Steel Inc.</b>								
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	61.3	125.5	1896	832	524	1084

Source: Cianciarelli (2000).

**Table 7-10. CDD/CDF emission factors for a U.S. ferrous foundry**

<b>Congener/congener group</b>	<b>Mean facility emission factor (ng/kg scrap feed)</b>
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	0.262
Total 2,3,7,8-CDF	1.888
Total I-TEQ <sub>DF</sub> (for reported congeners)	0.372
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	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 (1993a), as reported in U.S. EPA (1997b).

**Table 7-11. 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 (1999a, 1999b).

**Table 7-12. CDD/CDF emission factors for a scrap wire incinerator**

Congener/congener group	Mean facility emission factor <sup>a</sup> (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 <sub>DF</sub>	16.9 <sup>b</sup>
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	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	3,273

<sup>a</sup>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.

<sup>b</sup>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).

**Table 7-13. 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	<sup>a</sup>		<sup>a</sup>		<sup>a</sup>	
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	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
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 <sub>DF</sub>	19,000		2.9		1.3	
Total CDD/CDF	510,000		85		48.5	

<sup>a</sup>Analytical method used had low sensitivity for TCDDs; results were not reported.

Source: Harnly et al. (1995).

**Table 7-14. CDD/CDF emission factors for a drum and barrel reclamation facility**

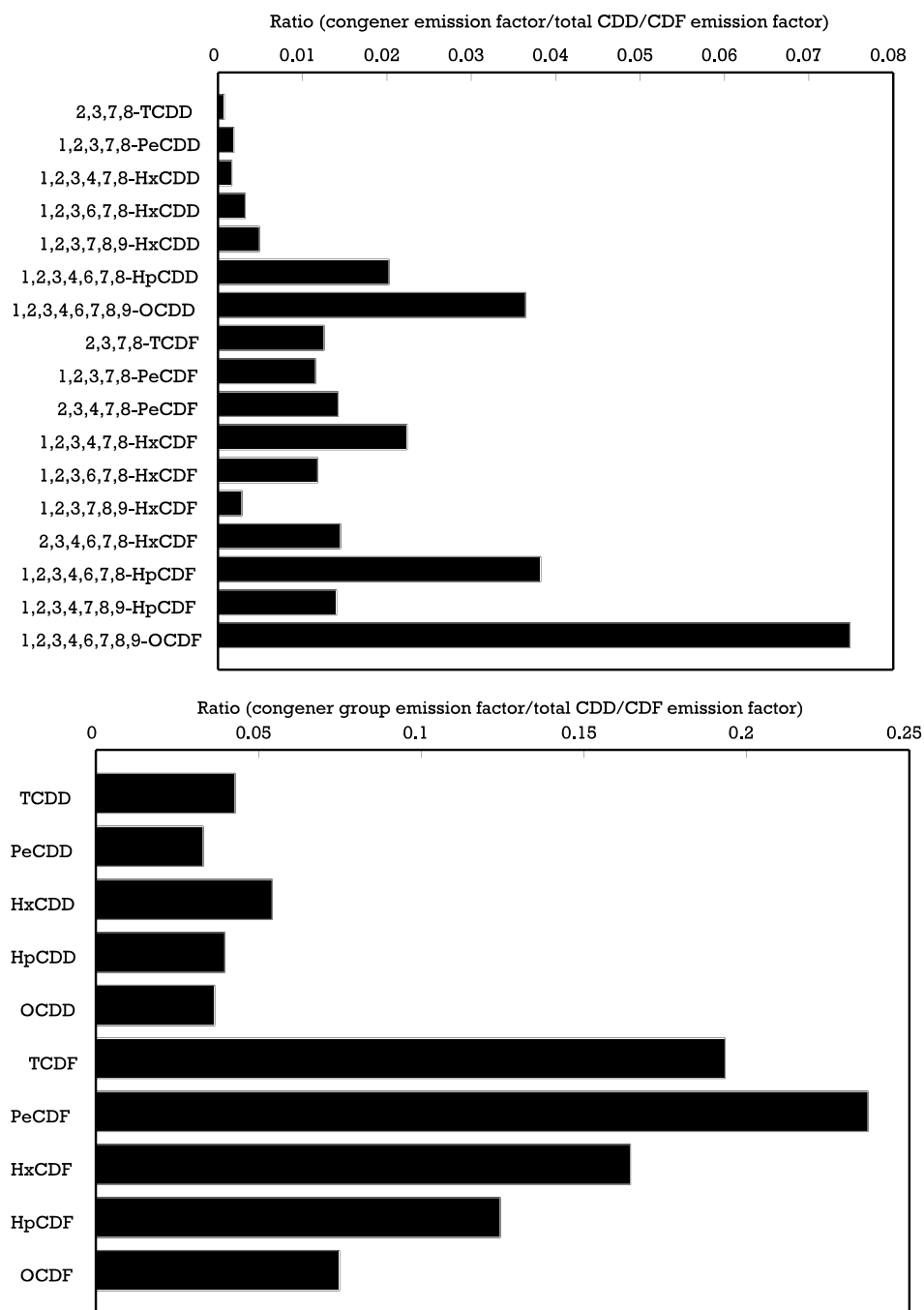
Congener/congener group	Mean facility emission factor <sup>a</sup> (ng/drum)
2,3,7,8-TCDD	2.09
1,2,3,7,8-PeCDD	NR
1,2,3,4,7,8-HxCDD	NR
1,2,3,6,7,8-HxCDD	NR
1,2,3,7,8,9-HxCDD	NR
1,2,3,4,6,7,8-HpCDD	NR
OCDD	37.5
2,3,7,8-TCDF	36.5
1,2,3,7,8-PeCDF	NR
2,3,4,7,8-PeCDF	NR
1,2,3,4,7,8-HxCDF	NR
1,2,3,6,7,8-HxCDF	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 <sub>DF</sub>	16.5 <sup>b</sup>
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	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	1,303

<sup>a</sup>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.

<sup>b</sup>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).

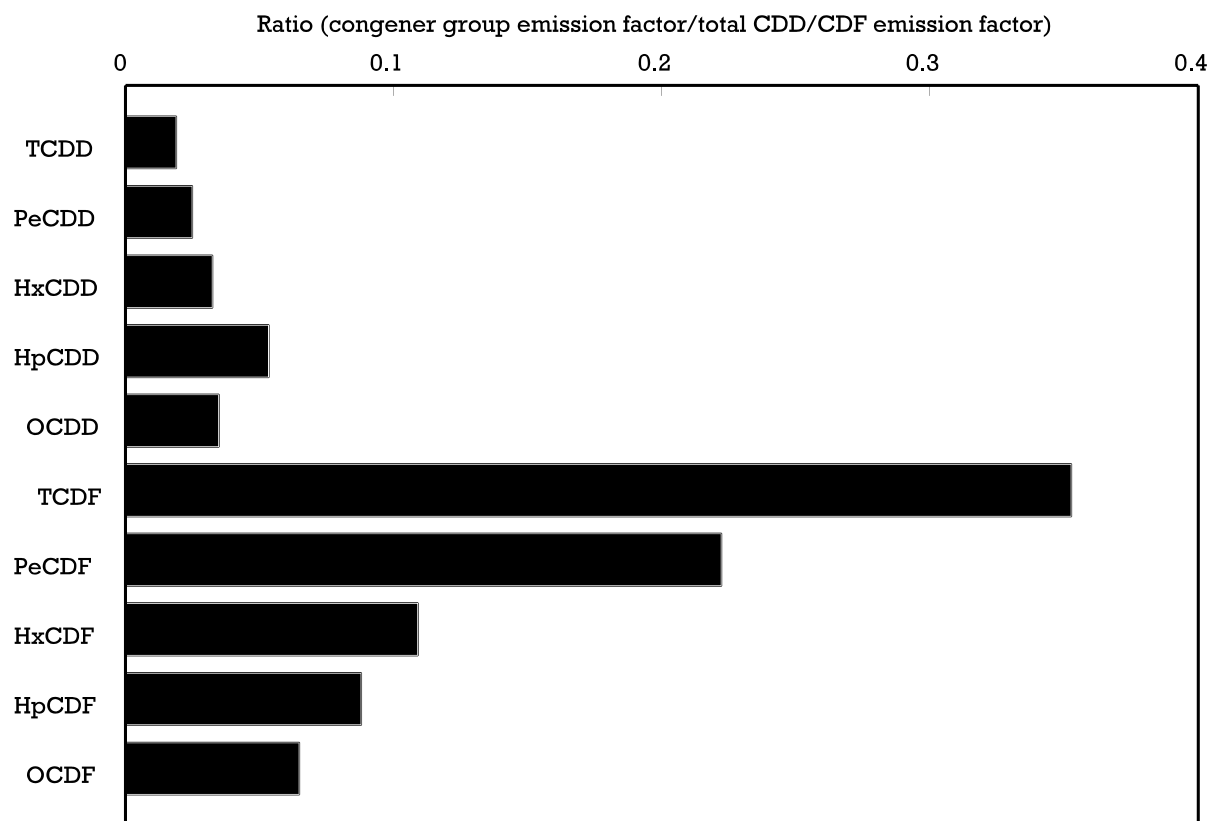
NR = Not reported

Source: U.S. EPA (1987a).



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

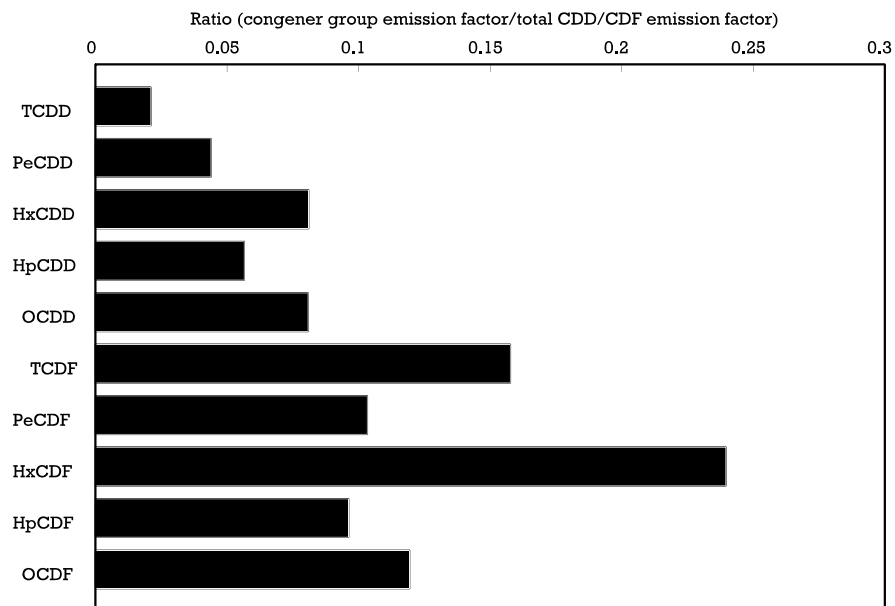
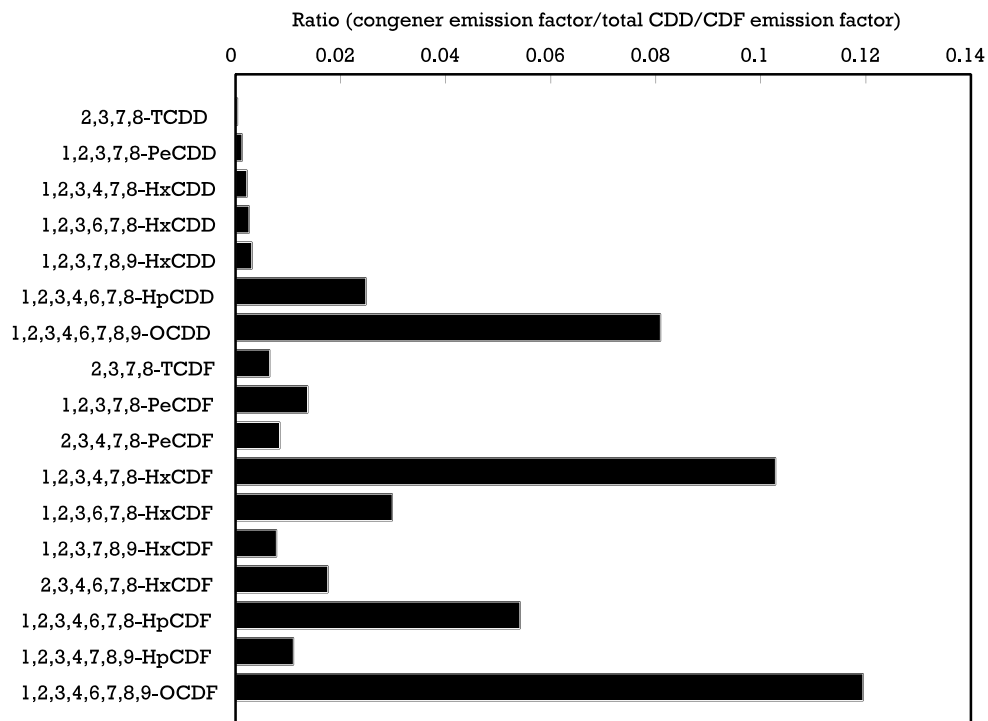
Sources: U.S. EPA (1995h); Galson Corporation (1995).



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

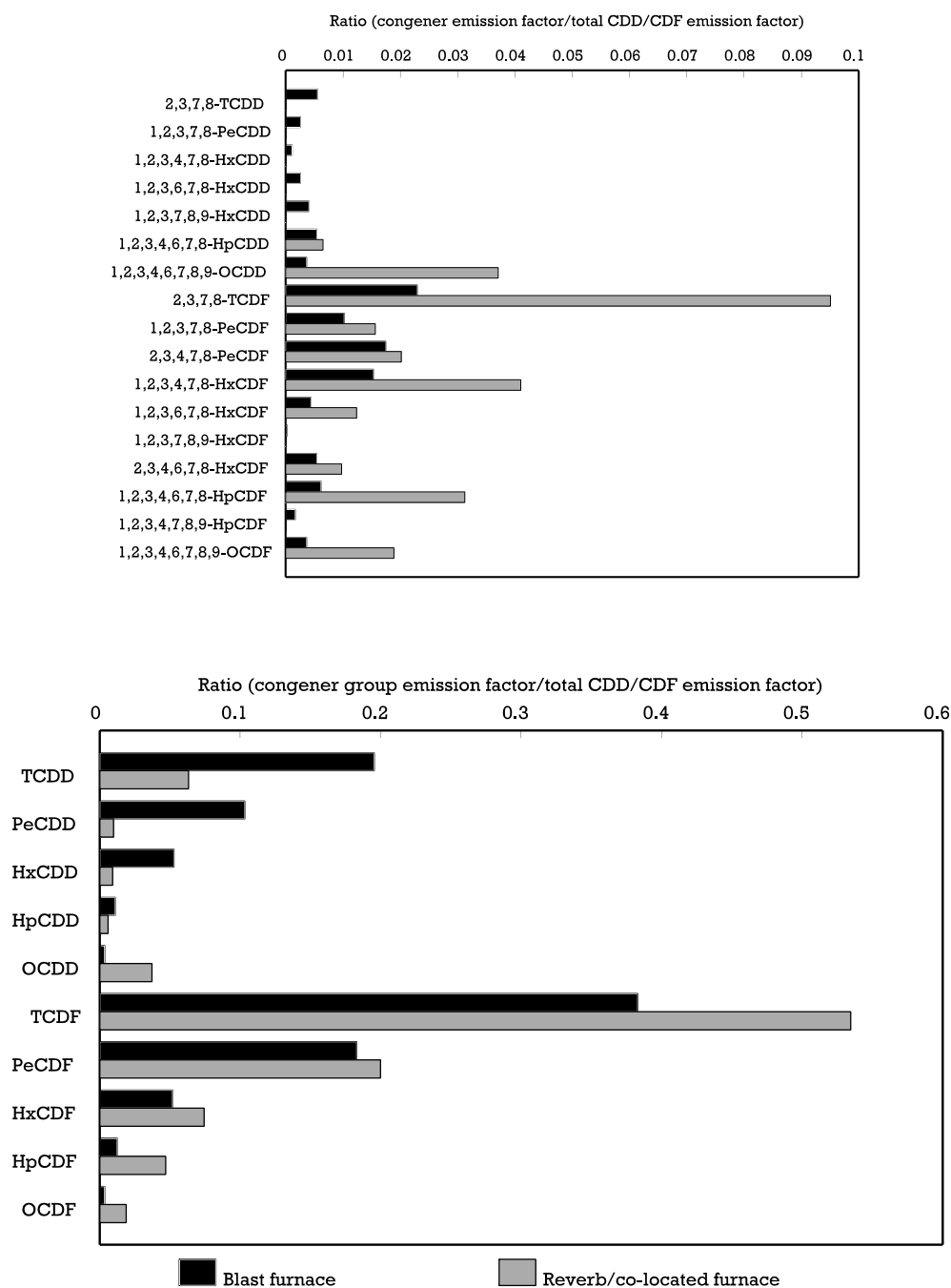
Source: U.S. EPA (1987c).





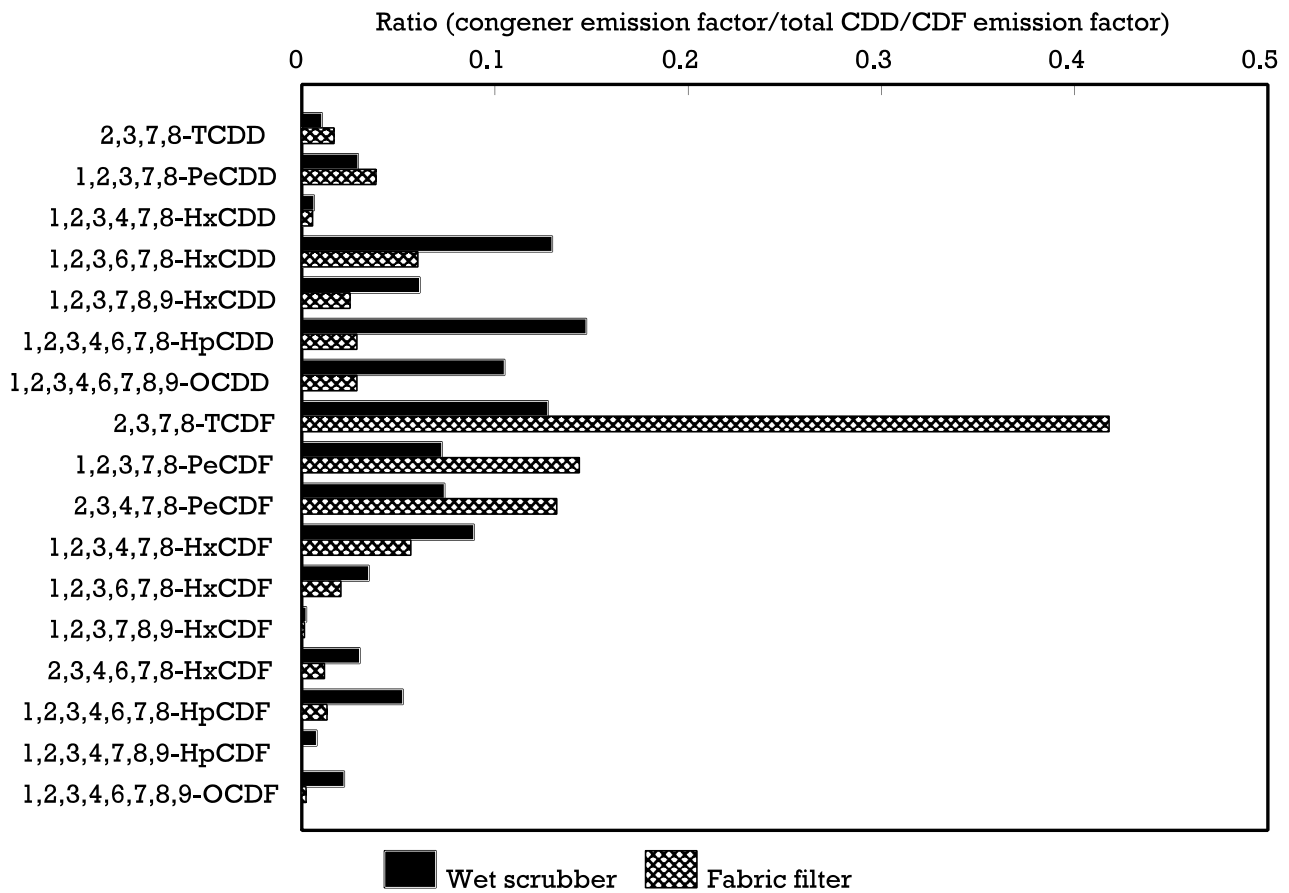
**Figure 7-2b. Congener and congener group profiles for a closed secondary copper smelter.**

Source: AGES (1992).



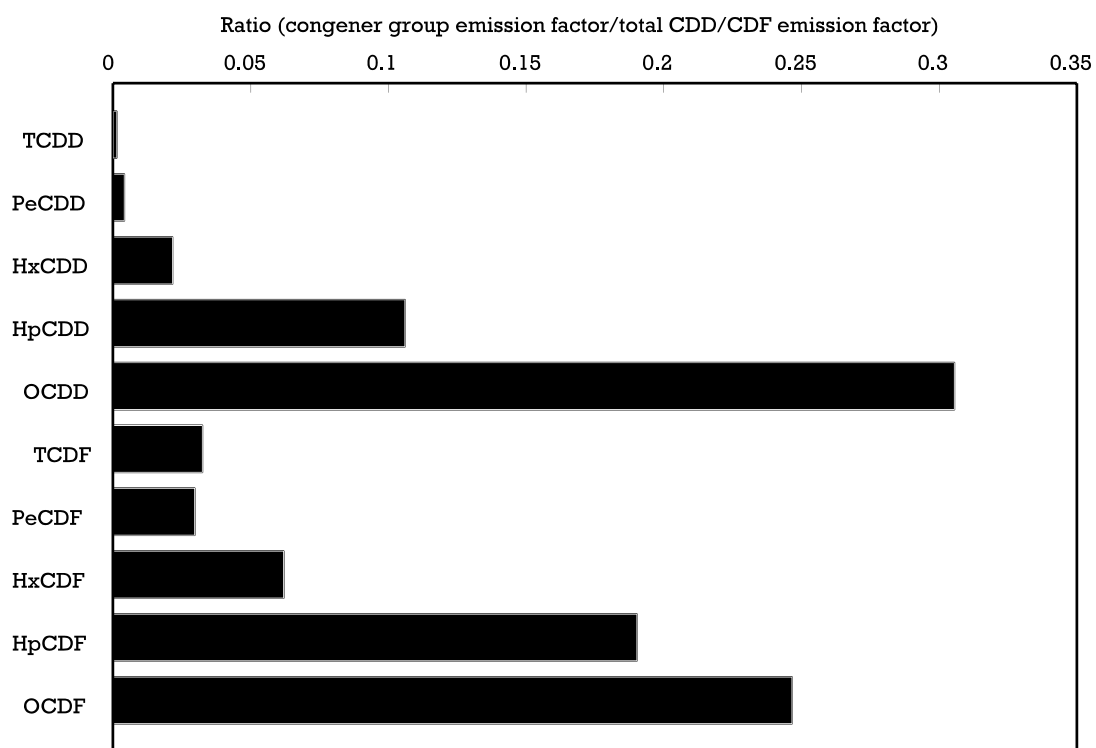
**Figure 7-3. Congener and congener group profiles for air emissions from secondary lead smelters.** Profiles are for emissions from fabric filters; nondetect values set equal to zero.

Sources: U.S. EPA (1992e, 1995d, e).



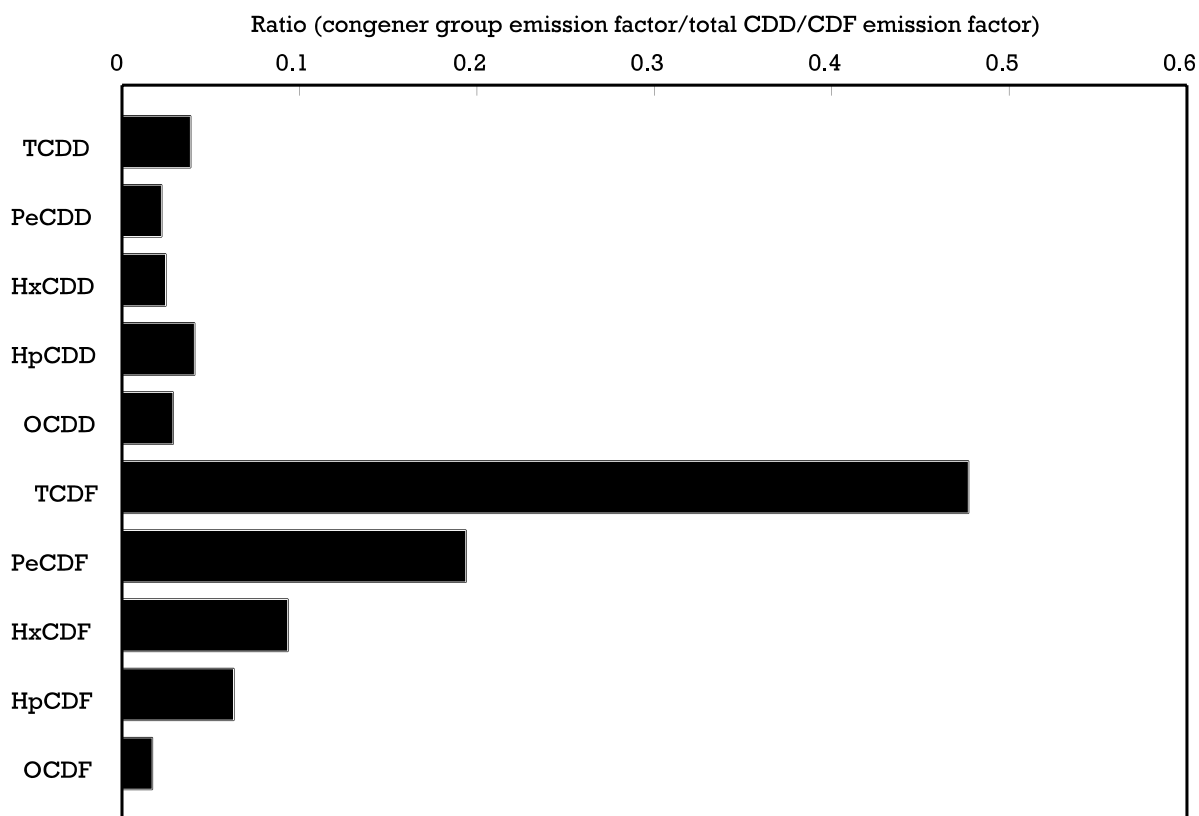
**Figure 7-4. Congener profiles for air emissions from U.S. iron ore sinter plants.**

Source: Calcagni et al. (1998).



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

Source: U.S. EPA (1987a).



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

Source: U.S. EPA (1987a).

## 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 by the U.S. industry, EPA and the U.S. 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. That 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, 1990a) 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 through 8-3 present congener profiles for each matrix (normalized to total CDD/CDF and total I-TEQ<sub>DF</sub>) using the median reported concentrations.

1 After examination of the raw, mill-specific data, EPA (U.S. EPA, 1990a) concluded that  
2 the congener profiles were fairly consistent across matrices within mills and that 2,3,7,8-TCDD  
3 and 2,3,7,8-TCDF accounted for the majority of TEQ in the samples. Using the median  
4 concentrations and treating nondetect values as either zero or one-half the detection limit (DL),  
5 EPA concluded that 2,3,7,8-TCDF accounted for 95.4 to 99.5% of the total  $TEQ_{DF-WHO_{98}}$  (95.8  
6 to 99% of the total I- $TEQ_{DF}$ ) in pulp, 94.1 to 96.5% of the  $TEQ_{DF-WHO_{98}}$  (94.1 to 95.8% of the  
7 I- $TEQ_{DF}$ ) in sludge, and 81.7 to 96.4% of the  $TEQ_{DF-WHO_{98}}$  (81.1 to 91.7% of the I- $TEQ_{DF}$ ) in  
8 effluent.

9 NCASI reported on a similar full-congener analysis study for samples collected from  
10 eight mills during the mid-1990s (Gillespie, 1997). The results of these analyses are presented in  
11 Table 8-2. The frequency of detection of 2,3,7,8-TCDD and 2,3,7,8-TCDF was significantly  
12 lower than in the 1988 study; therefore, deriving meaningful summary statistics concerning the  
13 relative importance of 2,3,7,8-TCDD and 2,3,7,8-TCDF to the total TEQ is difficult. With all  
14 nondetect values assumed to be zero, 2,3,7,8-TCDD and 2,3,7,8-TCDF accounted for 97% of the  
15 total effluent  $TEQ_{DF-WHO_{98}}$  (91% of the I- $TEQ_{DF}$ ), 53% of the total sludge  $TEQ_{DF-WHO_{98}}$   
16 (46% of the I- $TEQ_{DF}$ ), and 87% of the total pulp  $TEQ_{DF-WHO_{98}}$  (87% of the I- $TEQ_{DF}$ ). Because  
17 of the high frequency of nondetects when all nondetect values are one-half the DL, 2,3,7,8-  
18 TCDD and 2,3,7,8-TCDF accounted for only 13% of the total effluent I- $TEQ_{DF}$ , 13% of the total  
19 sludge I- $TEQ_{DF}$ , and 28% of the total pulp I- $TEQ_{DF}$ .

20 In 1992, the pulp and paper industry conducted its own NCASI-coordinated survey of  
21 2,3,7,8-TCDD and 2,3,7,8-TCDF emissions (NCASI, 1993). Ninety-four mills participated in  
22 the study, and NCASI assumed that the remaining 10 (of 104) operated at the same levels as  
23 measured in the 1988 104 Mill Study. All nondetect values were counted as one-half the DL. If  
24 a DL was not reported, it was assumed to be 10 pg/L for effluent and 1 ng/kg for sludge or  
25 bleached pulp. The data used in the report were provided by individual pulp and paper  
26 companies that had been requested by NCASI to generate the data using the same protocols used  
27 in the 104 Mill Study.

28 In 1993, as part of its efforts to develop revised effluent guidelines and standards for the  
29 pulp, paper, and paperboard industry, EPA published the development document for the  
30 guidelines and standards being proposed for this industry (U.S. EPA, 1993d). The development  
31 document presented estimates of the 2,3,7,8-TCDD and 2,3,7,8-TCDF annual discharges in  
32 wastewater from the mills in this industry as of January 1, 1993. To estimate these discharges,

1 EPA used the most recent information about each mill from four databases (104 Mill Study, EPA  
2 short-term monitoring studies at 13 mills, EPA long-term monitoring studies at eight mills, and  
3 industry self-monitoring data submitted to EPA). The 104 Mill Study data were used for only  
4 those mills that did not report making any process changes subsequent to the 104 Mill Study and  
5 did not submit any more recent effluent monitoring data.

6 Gillespie (1994) and Gillespie (1995) reported the results of 1993 and 1994 updates,  
7 respectively, to the 1992 NCASI survey. As in the 1992 survey, companies were requested to  
8 follow the same protocols for generating data used in the 104 Mill Study. Gillespie (1994, 1995)  
9 reported that fewer than 10% of mills had 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in  
10 effluent above the nominal DLs of 10 pg/L and 100 pg/L, respectively. EPA obtained similar  
11 results in its short- and long-term sampling for 18 mills; 2,3,7,8-TCDD was detected at four  
12 mills, and 2,3,7,8-TCDF was detected at nine mills (U.S. EPA, 1993d).

13 Gillespie (1994) reported that wastewater sludges at most mills (90%) contained less than  
14 31 ng/kg of 2,3,7,8-TCDD and less than 100 ng/kg of 2,3,7,8-TCDF. Gillespie (1995) reported  
15 that 90% of the mills had 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in sludge of less than  
16 17 ng/kg and 76 ng/kg, respectively, in 1994. U.S. EPA (1993d) reported similar results but  
17 found detectable levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF in sludges from 64% and 85%,  
18 respectively, of the facilities sampled.

19 In Gillespie (1994), nearly 90% of the bleached pulps contained less than 2 ng/kg of  
20 2,3,7,8-TCDD and less than 160 ng/kg of 2,3,7,8-TCDF. Gillespie (1995) reported that 90% of  
21 the bleached pulps contained 1.5 ng/kg or less of 2,3,7,8-TCDD and 5.9 ng/kg or less of 2,3,7,8-  
22 TCDF. The final levels in white paper products would correspond to levels in bleached pulp, so  
23 bleached paper products would also be expected to contain less than 2 ng/kg of 2,3,7,8-TCDD.

24 On April 15, 1998, EPA promulgated effluent limitations guidelines and standards for  
25 certain segments of the pulp, paper, and paperboard industry (Federal Register, 1998c). The  
26 industry segments covered by this rulemaking (i.e., the bleached paper-grade kraft and soda  
27 subcategory and the paper-grade sulfite subcategory) are those segments responsible for more  
28 than 90% of the bleached chemical pulp production in the United States. For this rule, EPA  
29 updated the estimates of baseline loadings made in 1993 for the proposed rule by using more  
30 recent data collected by EPA, NCASI (including the 1994 NCASI survey), and individual  
31 facilities (U.S. EPA, 1997f). 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.

#### **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, 1990a) and for 1995 (U.S. EPA, 1997f) 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, 1993d), 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 (1993d) 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, indicating 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 if 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 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 the “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 (1509 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, 1.72 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 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 chloralkali 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 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., 1990b, 1991; Rappe, 1993; Strandell et al., 1994). During the 1980s, titanium metal anodes were developed to replace graphite electrodes (U.S. EPA, 1982a; 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).

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. (1994) suggested that chlorination of polycyclic aromatic hydrocarbons present in the rubber linings of the electrolytic cell may have formed the CDFs found in the one sample analyzed.

Although EPA does not regulate CDDs/CDFs specifically, it issued restrictions under the Resource Conservation and Recovery Act (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).

### 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. (1990c) 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<sub>DF</sub>/L. Hutzinger and Fiedler (1991a) reported finding no CDDs/CDFs at a detection limit 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 detection limit of 1 µg/kg.

Hutzinger and Fiedler (1991a) reported the results of analyses of samples of ferric chloride (FeCl<sub>3</sub>), aluminum trichloride (AlCl<sub>3</sub>), CuCl<sub>2</sub>, CuCl, silicon tetrachloride (SiCl<sub>4</sub>), and titanium tetrachloride (TiCl<sub>4</sub>) for their content of HpCDF, OCDF, HpCDD, and OCDD. The sample of FeCl<sub>3</sub> contained HpCDF and OCDF in the low µg/kg range, but no HpCDD or OCDD was detected at a DL of 0.02 µg/kg. One of the two samples of AlCl<sub>3</sub> analyzed also contained a low (µg/kg) concentration of OCDF. The samples of CuCl<sub>2</sub> and CuCl contained concentrations of HpCDF, OCDF, and OCDD of less than 1 µg/kg. The results are presented in Table 8-6.

## 8.3. MANUFACTURE OF HALOGENATED ORGANIC CHEMICALS

Several chemical production processes generate CDDs/CDFs (Versar, 1985; Hutzinger and Fiedler, 1991a). 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 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, 1992a).

### 8.3.1. Chlorophenols

Chlorophenols have been widely used for a variety of pesticidal applications. The more-highly chlorinated phenols (tetra- and pentachlorophenol [PCP]) and their sodium salts have been used primarily for wood preservation. The less-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, 1991a). (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, 1991a).

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 chlorophenolate condensation (Ree et al., 1988; Gilman et al., 1988; Hutzinger and Fiedler, 1991a).

The limited information on CDD/CDF concentrations in chlorophenols published in the 1970s and early 1980s was compiled by Versar (1985) and Hutzinger and Fiedler (1991a). The results of several major studies cited by these reviewers (Firestone et al., 1972; Rappe et al., 1978a, 1978b) are presented in Table 8-7. Typically, CDDs/CDFs were not detected in monochlorophenols and dichlorophenols (DCP) but were reported in trichlorophenols (TrCP) and tetrachlorophenols (TeCP). More recent results of testing of 2,4-dichlorophenol (2,4-DCP), 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) that 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 tetra-chlorophenols. Tables 8-8 and 8-9 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 8-10 lists all wastes in which CDDs/CDFs are specifically regulated by EPA as hazardous 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 in the waste extract listed in Table 8-10 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

1 limitations do not specifically regulate CDDs or CDFs. The effluent limitations for the  
2 individually regulated chlorinated phenols are less than or equal to 39 µg/L for facilities that use  
3 biological end-of-pipe treatment.

4 DCPs and TrCPs are subject to reporting under the dioxin/furan test rule, which is  
5 discussed in Section 8.3.7 of this report. Since the effective date of that rule (June 5, 1987), only  
6 the 2,4-DCP isomer has been commercially produced in (or imported to) the United States, and  
7 as noted in Table 8-7, no CDDs/CDFs were detected in the product. Testing is required for the  
8 other DCPs and TrCPs, if manufacture or importation resumes. Similarly, TeCPs were subject to  
9 reporting under the Dioxin/Furan Pesticide Data Call-In (DCI) (discussed in Section 8.3.8 of this  
10 report). Since issuance of the DCI, the registrants of TeCP-containing pesticide products have  
11 elected to no longer support the registration of their products in the United States.

12 In January 1987, EPA entered into a settlement agreement with PCP manufacturers that  
13 set limits, effective in February 1989, on the allowed uses of PCP and its salts and the maximum  
14 allowable concentrations of 2,3,7,8-TCDD and HxCDDs. Section 8.3.8 discusses the 1987 PCP  
15 settlement agreement and includes estimates of current releases of CDDs/CDFs associated with  
16 use of PCP in the United States. Section 12.3.1 provides an estimate of the amount of  
17 CDDs/CDFs that may have entered the environment or that are contained within treated wood  
18 products as a result of prior use of PCP and PCP-Na.

19 Since the late 1980s, U.S. commercial production of chlorophenols has been limited to  
20 2,4-dichlorophenol (2,4-DCP) and PCP. As noted above, disposal of wastes generated during  
21 the manufacture of chlorophenols is strictly regulated, and thus releases to the environment are  
22 expected to be negligible. With regard to releases associated with the use of 2,4-DCP, no  
23 CDDs/CDFs have been detected in 2,4-DCP. Releases associated with the use of PCP are  
24 presented in Sections 8.3.8 and 12.3.1.

### 25 26 **8.3.2. Chlorobenzenes**

27 Chlorobenzenes have been produced in the United States since 1909. U.S. production  
28 operations were developed primarily to provide chemical raw materials for the production of  
29 phenol, aniline, and various pesticides based on the higher chlorinated benzenes. Because of  
30 (incremental) changes in the processes used to manufacture phenol and aniline and the phaseout  
31 of highly chlorinated pesticides such as DDT and hexachlorobenzene, U.S. production of  
32 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 more-highly chlorinated benzenes (Ree et al., 1988; Hutzinger and Fiedler, 1991a; 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). Ferric chloride 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 (MCBz) and dichlorobenzene (DCBz). 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 (1) oxygen as a nuclear substituent (i.e., presence of chlorophenols) and (2) 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, 1991a). 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 8-11 summarizes the very limited published information on CDD/CDF contamination of chlorobenzene products. The presence of CDDs/CDFs has been reported in TCBz, PeCBz, and HCBz. No CDDs/CDFs have been reported in MCBz or DCBz. Conflicting data exist concerning the presence of CDDs/CDFs in TCBz. 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 (1991a) reported unpublished results of Dr. Hans Hagenmaier showing CDD/CDF congener group concentrations ranging from 0.02 to 0.074 µg/kg in a sample of mixed TCBz. Because the TCBz examined by Hagenmaier contained about 2% hexachlorocyclohexane, it is



reasonable to assume that the TCBz 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-DCBz manufacturing processes used in the United States are not likely to form CDDs/CDFs. MCBz, DCBz, and TCBz 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 PeCBz and 1,2,4,5-TeCBz (Federal Register, 1993c). This rule requires persons to submit a notice to EPA at least 90 days before manufacturing, importing, or processing 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 HCBz 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 8-10 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 8-10 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 MCBz, 1,2-dichlorobenzene (1,2-DCBz), 1,4-dichlorobenzene (1,4-DCBz), and, to a much lesser extent, 1,2,4-trichlorobenzene (1,2,4-TCBz). As noted above, CDD/CDF formation is not

1 expected under the normal operating conditions of the processes currently used in the United  
2 States to produce these four chemicals. No tetra-, penta-, or hexachlorinated benzenes are now  
3 intentionally produced or used in the United States (Bryant, 1993). Thus, releases of  
4 CDDs/CDFs from the manufacture of chlorobenzenes in 1995 were estimated to be negligible.  
5 Because the information available on CDD/CDF content of MCBz to PeCBz is very limited and  
6 is based primarily on unpublished European data, and because information on the chlorobenzene  
7 manufacturing processes in place during 1987 is not readily available, no emission estimates can  
8 be made for 1987.

### 9 10 **8.3.3. Chlorobiphenyls**

11 PCBs are manufactured by the direct batch chlorination of molten biphenyl in the  
12 presence of a catalyst, followed by separation and purification of the desired chlorinated  
13 biphenyl fractions. During the manufacture of PCBs, the inadvertent production of CDFs also  
14 occurs. This section addresses potential releases of CDDs/CDFs associated with leaks and spills  
15 of PCBs. CDFs have been shown to form when PCB-containing transformers and capacitors  
16 undergo malfunctions or are subjected to fires that result in accidental combustion of the  
17 dielectric fluid. This combustion source of PCB-associated CDFs is discussed in Section 6.6.  
18 Section 11.2 addresses releases of dioxin-like PCBs.

19 PCB production is believed to have occurred in 10 countries. The total amount of PCBs  
20 produced worldwide since 1929 (i.e., the first year of known production) is estimated to total 1.5  
21 billion kg. Initially, PCBs were primarily used as dielectric fluids in transformers. After World  
22 War II, PCBs found steadily increasing use as dielectric fluids in capacitors, as heat-conducting  
23 fluids in heat exchangers, and as heat-resistant hydraulic fluids in mining equipment and vacuum  
24 pumps. PCBs also were used in a variety of "open" applications (i.e., uses from which PCBs  
25 cannot be recollected) including plasticizers, carbonless copy paper, lubricants, inks, laminating  
26 agents, impregnating agents, paints, adhesives, waxes, additives in cement and plaster, casting  
27 agents, dedusting agents, sealing liquids, fire retardants, immersion oils, and pesticides (DeVoogt  
28 and Brinkman, 1989).

29 PCBs were manufactured in the United States from 1929 until 1977. U.S. production  
30 peaked in 1970, with a volume of 38.56 million kg. Monsanto Corporation, the major U.S.  
31 producer, voluntarily restricted the use of PCBs in 1971, and annual production fell to 18.14  
32 million kg in 1974. Monsanto Corporation ceased PCB manufacture in mid-1977 and shipped

the last inventory in October 1977. Regulations issued by EPA beginning in 1977, principally under TSCA (40 CFR 761), strictly limited the production, import, use, and disposal of PCBs. (See Section 4.1 for details on TSCA regulations.) 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; DeVogt and Brinkman, 1989).

Monsanto Corporation marketed technical-grade mixtures of PCBs primarily under the trade name Aroclor. The Aroclors 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%. The following list shows the percentages of total Aroclor production, by (Aroclor mixture) during 1957 to 1977, as reported by Brown (1994).

<u>Aroclor</u>	<u>1957–1977 U.S. Production (%)</u>
1221	0.96
1016	12.88
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 technical-grade mixtures of PCBs manufactured in other countries included *Clophen* (Germany), *Fenclor* and *Apirolino* (Italy), *Kanechlor* (Japan), *Phenoclor* and *Pyrallene* (France), *Sovtel* (USSR), *Delor* and *Delorene* (Czechoslovakia), and *Orophene* (German Democratic Republic) (DeVogt and Brinkman, 1989). Some of the mixtures marketed under these trade names were similar in terms of chlorine content (by weight percent and average number of chlorines per molecule) to various Aroclors,

as shown below. Mixtures that are comparable in terms of chlorine content were marketed under several trade names, as shown below.

<u>Aroclor</u>	<u>Clophen</u>	<u>Pyralene</u>	<u>Phenoclor</u>	<u>Fenclor</u>	<u>Kanechlor</u>
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

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 (i.e., TCDF through HxCDF) concentrations ranging from 0.8 to 2 mg/kg. Bowes et al. (1975b) employed 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 8-12 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 reported concentrations of specific CDD/CDF congeners in commercial PCB mixtures (Bowes et al., 1975b; Brown et al., 1988; Hagenmaier, 1987; Malisch, 1994). Table 8-13 presents the results of these four studies. Only the Hagenmaier (1987) and Malisch (1994) 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 (1987) and Malisch (1994) and the corresponding levels in the Aroclor mixtures reported by Bowes et al. (1975b) and Brown et al. (1988).

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 (i.e., samples from previously used capacitors and transformers) and unused samples of Aroclors 1016, 1242, 1254, and 1260. The concentration

1 ranges reported for the used and unused Aroclors were similar, leading Brown et al. (1988) to  
2 conclude that CDFs are not formed during the normal use of PCBs in electrical equipment.

3 Amounts of CDD/CDF TEQ emissions that may have been released to the environment  
4 during 1987, 1995, and 2000 from spills and leaks of in-service PCBs cannot be accurately  
5 estimated because reliable data regarding leaked and spilled PCBs are not available.  
6

#### 7 **8.3.4. Polyvinyl Chloride**

8 PVC resins are produced when free radical initiators are used to induce the  
9 polymerization of vinyl chloride monomer (VCM). With the exception of one plant that uses a  
10 process involving the catalytic reaction of acetylene and HCl to manufacture VCM directly,  
11 VCM is typically produced by the thermal dehydrochlorination (commonly known as cracking)  
12 of ethylene dichloride (EDC). The cracking of EDC requires elevated pressure (20 to 30  
13 atmospheres) and temperature (450 to 650 °C) and yields VCM and HCl at about a 1:1 molar  
14 ratio. EDC is produced by two different methods: (1) direct chlorination of ethylene with  
15 chlorine in the presence of a catalyst at a temperature of 50 to 60 °C and pressure of 4 to 5  
16 atmospheres, and (2) oxychlorination, which involves reaction of ethylene with HCl and oxygen  
17 in the presence of a catalyst at temperatures generally less than 325 °C. The primary source of  
18 HCl for the oxychlorination process is the HCl produced from the cracking of EDC to form  
19 VCM. All VCM plants, with the exception of the one facility noted above, are integrated with  
20 EDC production facilities (Vinyl Institute, 1998).

21 Although it has generally been recognized that CDDs/CDFs are formed during the  
22 manufacture of EDC, VCM, and PVC, manufacturers and environmental public interest groups  
23 have disagreed as to the quantity of CDDs/CDFs that are formed and released to the environment  
24 in wastes and possibly in PVC products. Although EPA regulates emissions from EDC/VCM  
25 production facilities under the Clean Water Act (40 CFR 61), the Clean Air Act (40 CFR 414),  
26 and RCRA (40 CFR 268, waste codes F024, K019, and K020), CDDs/CDFs are not specifically  
27 regulated pollutants; as a consequence, monitoring data for CDDs/CDFs in emissions are  
28 generally lacking.

29 In 1993, Greenpeace International issued a report on CDD/CDF emissions associated  
30 with the production of EDC/VCM (Greenpeace, 1993). Greenpeace estimated that 5 to 10 g I-  
31 TEQ<sub>DF</sub> are released to the environment (air, water, and ground combined) annually for every  
32 100,000 metric tons of VCM produced. This emission factor was based on data gathered by

1 Greenpeace on four European plants. The Vinyl Institute responded with a critique of the  
2 Greenpeace report (ChemRisk, 1993). Miller (1993) summarized the differing views of the two  
3 parties. According to Miller, European PVC manufacturers claimed the emission factor was 0.01  
4 to 0.5 g I-TEQ<sub>DF</sub>/100,000 metric tons of VCM, but although Greenpeace and ChemRisk used  
5 basically the same monitoring information to develop their emission factors, Greenpeace  
6 adjusted the emission factor to account for unquantified fugitive emissions and waste products  
7 that contain unspecified amounts of CDDs/CDFs.

8 In 1995, Greenpeace issued another report (Stringer et al., 1995) reiterating the  
9 organization's concern that the generation and emission of CDDs/CDFs may be significant and  
10 urging that further work be initiated to quantify and prevent emissions. Stringer et al. (1995)  
11 presented the results of analyses of three samples of chlorinated wastes obtained from U.S.  
12 EDC/VCM manufacturing facilities. The three wastes were characterized according to EPA  
13 hazardous waste classification numbers as an F024 waste (waste from the production of short-  
14 chain aliphatics by free radical catalyzed processes), a K019 waste (heavy ends from the  
15 distillation of ethylene from EDC production), and a probable K020 waste (heavy ends from  
16 distillation of VC in VCM manufacture). Table 8-14 presents the analytical results reported by  
17 Stringer et al. (1995). This study acknowledged that because EDC/VCM production  
18 technologies and waste treatment and disposal practices are very site-specific, the limited  
19 information available on CDD/CDF generation and emissions made it difficult to quantify  
20 amounts of CDDs/CDFs generated and emitted.

21 In response to the lack of definitive studies, and at the recommendation of EPA, U.S.  
22 PVC manufacturers initiated an extensive monitoring program, the Dioxin Characterization  
23 Program, to evaluate the extent of any CDD/CDF releases to air, water, and land, as well as any  
24 product contamination. Manufacturers performed emission and product testing at various  
25 facilities that were representative of various manufacturing and process control technologies. In  
26 1998, the Vinyl Institute completed studies of CDD/CDF releases in wastewater, wastewater  
27 treatment plant solids, and stack gases, as well as studies of CDD/CDF content of products (i.e.,  
28 PVC resins and EDC sold as products) (Vinyl Institute, 1998).

29 After the completion of the studies, the Vinyl Institute created an external advisory group  
30 to advise the institute on the conduct of the Dioxin Characterization Program and to provide an  
31 independent review of the program results. In its final evaluation report, the advisory group  
32 judged the industry's coverage to be fairly comprehensive in terms of the number of facilities

1 and waste streams sampled. The number of samples of PVC product, stack emissions,  
2 wastewaters, and wastewater sludges obtained from the different types of manufacturing  
3 facilities was deemed by the advisory group to provide a sufficient database to evaluate annual  
4 industry releases. The advisory group concluded that the process established by the Vinyl  
5 Institute to ensure that data collected as part of its Dioxin Characterization Program were  
6 representative of normal process operations was a good one. After auditing the Vinyl Institute's  
7 estimates of annual releases, the advisory group concluded that the data were properly validated  
8 and that the results were extrapolated to annual industry release estimates in a creditable  
9 scientific manner.

10 EPA reviewed the Vinyl Institute (1998) studies and concurred with the conclusions of  
11 the external advisory group. EPA assigned a high confidence rating to the activity level  
12 estimates and a medium confidence rating to the emission factor estimates developed by the  
13 Vinyl Institute.

14 In September 2002, the Chlorine Chemistry Council (CCC) met to review dioxin release  
15 estimates for 2000 for various EDC/VCM manufacturing facilities. Several companies provided  
16 stack gas emissions and wastewater emissions data, as well as a discussion of how they  
17 generated the release and transfer estimates reported in the TRI for 2000. In March 2004, the  
18 CCC met again to discuss the results, to date, of the Chlorine Chemistry Council CDD/CDF Data  
19 Validation Study for PVC/EDC/VCM and chlor-alkali facilities. The study's goal was to  
20 provide facility-specific water, air, and land release estimates for the years 2000 and 2002. As of  
21 the date of this report, data validation studies were provided for 16 of 20 facilities in the CCC  
22 that were considered chlor-alkali production facilities and PVC/EDC/VCM manufacturing  
23 plants.

#### 24 25 **8.3.4.1. Wastewater**

26 The Vinyl Institute (1998) presented results for treated wastewater samples collected  
27 during April and May of 1995 at six sites that manufactured only PVC, at three sites that  
28 manufactured EDC and VCM, and at one site that manufactured EDC, VCM, and PVC. In terms  
29 of production, the six PVC-only sites represent approximately 15% of the total estimated 1995  
30 U.S. and Canadian PVC production. Together, the three EDC/VCM sites and the one  
31 EDC/VCM/PVC site represent 27% of the total estimated 1995 U.S. EDC production. Samples  
32 taken from PVC-only sites were taken from sites that manufactured suspension PVC resin as

well as those that manufactured dispersion PVC resin. Samples for the other four sites were taken from sites that used direct and oxychlorination processes, fixed and fluidized beds, and low- and high-temperature direct chlorination. The wastewater samples from one of the EDC/VCM sites, one of the PVC-only sites, and the EDC/VCM/PVC site were taken from effluents derived from process areas not limited to EDC/VCM, EDC/VCM/PVC, or PVC manufacturing.

The results of the sampling are presented in Table 8-15. In all samples, the method detection limit (MDL) for all congeners except OCDD and OCDF was 10 pg/L or less. The MDL for OCDD and OCDF was 50 pg/L or less. CDDs/CDFs were detected in two of the six samples from PVC-only sites (0.52 and 2 pg I-TEQ<sub>DF</sub>/L, assuming nondetect values are equal to zero [ND = 0]). The overall mean TEQ concentrations were 0.88 pg I-TEQ<sub>DF</sub>/L (assuming ND = 0) and 4.7 pg I-TEQ<sub>DF</sub>/L (assuming ND = 1/2 MDL). CDDs/CDFs were detected in all four of the samples from EDC/VCM/PVC sites. The overall mean TEQ concentrations were 0.42 pg I-TEQ<sub>DF</sub>/L (assuming ND = 0) and 4.4 pg I-TEQ<sub>DF</sub>/L (assuming ND = 1/2 MDL).

Using these sample results, the Vinyl Institute developed I-TEQ<sub>DF</sub> emission factors for the two site categories: PVC-only and EDC/VCM/PVC manufacturing facilities. First, individual site release rates were estimated using the treated wastewater effluent flow rate recorded by the site during sampling, assuming that the site continuously released CDDs/CDFs at its calculated total I-TEQ<sub>DF</sub>, 24 hr/day, 360 day/yr, at the recorded water effluent rate. The total releases from each site category (PVC-only or EDC/VCM/PVC facilities) were then estimated by averaging the individual release rates per 1000 metric ton of PVC or EDC using the estimated 1995 PVC and EDC production statistics for the sampled sites. These values were then scaled up to estimate total U.S. releases in treated wastewater from the site categories. It is not possible using the data presented in the Vinyl Institute study to calculate emission factors for TEQ<sub>DF</sub>-WHO<sub>98</sub>. However, because 1,2,3,7,8-PeCDD was not detected in any wastewater sample, the TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factors would be lower than the I-TEQ<sub>DF</sub> emission factors.

The mean emission factors derived from the sample results for the PVC-only facilities are 2.3 µg I-TEQ<sub>DF</sub>/1,000 metric tons of PVC (ND = 0) and 29 µg I-TEQ<sub>DF</sub>/1,000 metric tons of PVC (ND = 1/2 MDL). The mean emission factors for the EDC/VCM/PVC facilities are 2.9 µg I-TEQ<sub>DF</sub>/1,000 metric tons (ND = 0) and 15 µg I-TEQ<sub>DF</sub>/1,000 metric tons of EDC (ND = 1/2 MDL).



1 The Vinyl Institute (1998) combined these emission factors with 1995 industry  
2 production statistics (5,212 metric tons of PVC and 11,115 metric tons of EDC) to yield release  
3 estimates of 0.011 g I-TEQ<sub>DF</sub> (ND = 0) and 0.15 g I-TEQ<sub>DF</sub> (ND = 1/2 DL) from PVC-only  
4 manufacturing sites and 0.032 g I-TEQ<sub>DF</sub> (ND = 0) and 0.17 g I-TEQ<sub>DF</sub> (ND = 1/2 DL) from  
5 EDC/VCM and EDC/VCM/PVC facilities for a total I-TEQ<sub>DF</sub> release to water in 1995 of 0.043 g  
6 (ND = 0) and 0.32 g (ND = 1/2 DL).

7 Data validation studies of the CCC provided water release estimates for 16 facilities that  
8 were considered chlor-alkali production facilities and PVC/EDC/VCM manufacturing plants  
9 (CCC, 2004). Half of these facilities were not involved with the production of PVC/EDC/VCM.  
10 Tables 8-16 and 8-17 depict the congener-specific data associated with the water releases from  
11 the PVC/EDC/VCM manufacturing plants and the chlor-alkali production facilities, respectively.  
12 For the reference year 2000, water releases for PVC/EDC/VCM manufacturing facilities were  
13 23.8 g I-TEQ<sub>DF</sub> (22.6 g TEQ<sub>DF</sub>-WHO<sub>98</sub>), while water releases for chlor-alkali plants were 1.85 g  
14 I-TEQ<sub>DF</sub> (1.82 g TEQ<sub>DF</sub>-WHO<sub>98</sub>). More than 99% of the water releases from PVC/EDC/VCM  
15 plants occurred at three facilities. More than 98% of the water releases from chlor-alkali plants  
16 occurred at three facilities, with one facility accounting for over 58% of the water releases.  
17 These emission estimates are assigned a medium confidence rating on the basis of the medium  
18 rating given to the emission factor estimates.

#### 19 20 **8.3.4.2. Wastewater Treatment Plant Solids**

21 The Vinyl Institute (1998) presented results for 14 samples collected in 1996 from nine  
22 EDC/VCM/PVC manufacturing sites. Samples were collected from 4 of the 5 U.S. sites that  
23 manufactured EDC, VCM, and PVC; 3 of the 7 U.S. sites that manufactured EDC and VCM but  
24 not PVC; and 2 of the 21 sites that manufactured PVC but not EDC or VCM. On the basis of  
25 1995 production data, the two PVC-only sites manufactured approximately 4.7% of the total  
26 estimated U.S. and Canadian PVC resin produced. The sampled EDC/VCM and  
27 EDC/VCM/PVC sites manufactured 56% of the total estimated 1995 U.S. EDC produced.  
28 Samples from the PVC-only sites were taken from sites that manufactured suspension PVC resin  
29 as well as sites that manufactured dispersion PVC resin. Samples taken from the EDC/VCM and  
30 EDC/VCM/PVC sites were taken from sites that used direct and oxychlorination processes, fixed  
31 and fluidized EDC reactor beds, low- and high-temperature direct chlorination, and air, oxygen,  
32 and mixed air-oxygen feeds.

On the basis of the sample results, the Vinyl Institute determined that the results for facilities using different EDC reactor bed technologies (fluidized bed vs. fixed bed) appeared to differ significantly; therefore, they developed annual I-TEQ<sub>DF</sub> emission estimates for three categories: PVC-only, EDC/VCM/PVC fixed-bed, and EDC/VCM/PVC fluidized-bed facilities. Nine U.S. sites use fixed-bed technology and six use fluidized-bed technology. Four of each type of facility were sampled by the Vinyl Institute. It is not possible, using the data presented in the Vinyl Institute (1998), to calculate emission factors for TEQ<sub>DF</sub>-WHO<sub>98</sub>. Because 1,2,3,7,8-PeCDD was detected in only 3 of 10 samples but OCDD and OCDF were detected in all samples, it is likely that the TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factors would not be significantly different from the I-TEQ<sub>DF</sub> emission factors.

Results of the sampling are presented in Table 8-15. The MDLs for all congeners were less than 150 ng/kg and usually less than 10 ng/kg. CDDs/CDFs were detected in all samples. The ranges of TEQ concentrations (dry-weight basis) for the two PVC-only facilities were 1.1 to 2.6 ng I-TEQ<sub>DF</sub>/kg (ND = 0) and 2.8 to 4.4 ng I-TEQ<sub>DF</sub>/kg (ND = 1/2 MDL). On an emission-factor basis, the ranges were 1.7 to 46 µg I-TEQ<sub>DF</sub>/1,000 metric tons of PVC produced (ND = 0) and 4.3 to 78 µg I-TEQ<sub>DF</sub>/1,000 metric ton of PVC produced (ND = 1/2 DL). The range of TEQ concentrations for the samples from the EDC/VCM or EDC/VCM/PVC sites were 88 to 6,850 ng I-TEQ<sub>DF</sub>/kg (ND = 0) and 93 to 6,850 ng I-TEQ<sub>DF</sub>/kg (ND = 1/2 DL). On an emission-factor basis, the ranges were 28 to 4,000 µg I-TEQ<sub>DF</sub>/1,000 metric tons of EDC (ND = 0) and 29 to 4,000 µg I-TEQ<sub>DF</sub>/1,000 metric tons of EDC (ND = 1/2 DL).

The annual amounts of I-TEQ<sub>DF</sub> generated in 1995 in each of the three facility categories were estimated by the Vinyl Institute as follows. First, total annual contributions at each sampled site were estimated by multiplying the I-TEQ<sub>DF</sub> from the sample by the annual production of wastewater solids at that site. These annual site contributions of I-TEQ<sub>DF</sub> were then summed for each of the three facility types and multiplied by the ratio of each category's total annual production of PVC or EDC to the sum of the annual production of the sampled sites in that category.

The Vinyl Institute (1998) combined these emission factors with 1995 industry production statistics to yield estimated amounts of I-TEQ<sub>DF</sub> in wastewater treatment plant solids. For PVC-only facilities, estimated amounts are 0.069 g I-TEQ<sub>DF</sub>/yr (ND = 0) and 0.12 g I-TEQ<sub>DF</sub>/yr (ND = 1/2 DL), assuming an annual PVC production of 5,212,000 metric tons. For EDC/VCM/PVC fixed-bed facilities, the estimated amounts of TEQ are 1 g I-TEQ<sub>DF</sub>/yr (ND = 0)

or ND = 1/2 DL), assuming an EDC annual production volume of 5,400,000 metric tons. For EDC/VCM/PVC fluidized-bed facilities, the estimated amount of TEQ is 11 g I-TEQ<sub>DF</sub>/yr (ND = 0 or ND = 1/2 DL), assuming EDC annual production volume of 5,600,000 metric tons. Thus, total amounts of TEQ in wastewater treatment plant solids are estimated to have been 12.1 g I-TEQ<sub>DF</sub> in 1995 (ND = 0 or ND = 1/2 DL).

According to the Vinyl Institute survey data, member companies dispose of wastewater solids by three methods: (1) RCRA hazardous waste landfilling (approximately 1% of industry total solids), (2) landfarming (approximately 6%), and (3) secure on-site landfilling (93%). Solids disposed of by methods 1 and 3 are assumed to be well controlled to prevent release into the general environment, whereas solids disposed of by landfarming are not as well controlled and could be released to the environment. Therefore, an estimated 0.73 g I-TEQ<sub>DF</sub> (6% of 12.1 g I-TEQ<sub>DF</sub>) can be considered as potentially released to the environment in 1995.

From the data validation studies presented in March 2004, only one facility (the Georgia Gulf facility in Plaquemine, LA) reported releases resulting from land farming activities in 2000 (CCC, 2004). The congener-specific profile is presented in Table 8-18. Releases to land from PVC/EDC/VCM facilities in 2000 were 1.36 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (1.45 g I-TEQ<sub>DF</sub>).

These emission estimates are assigned a medium confidence rating on the basis of the medium rating given to the emission factor estimates.

#### **8.3.4.3. Stack Gas Emissions**

By grouping similarities of design and service, the Vinyl Institute (1998) subcategorized thermal destruction units at EDC/VCM and/or PVC manufacturing units into three categories: 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 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. The Vinyl Institute gathered test data 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 represent 70% of total U.S. and Canadian EDC/VCM/PVC production in 1995.

Annual I-TEQ<sub>DF</sub> emission estimates were generated by the Vinyl Institute by combining estimated emissions from tested units (i.e., 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 by multiplying 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 using the data presented in the Vinyl Institute report to calculate emission factors for TEQ<sub>DF</sub>-WHO<sub>98</sub>.

The Vinyl Institute estimates of most likely and upper-bound emissions during 1995 for these three categories are as follows:

Category	Most likely emission estimate (g I-TEQ <sub>DF</sub> /yr)	Upper-bound emission estimate (g I-TEQ <sub>DF</sub> /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 Vinyl Institute (1998) also estimated emissions that may result 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, the institute estimated that potential emissions to air from this source category would be 0.65 g I-TEQ<sub>DF</sub>/yr (most-likely estimate) and 2.3 g I-TEQ<sub>DF</sub>/yr (upper-bound estimate). Combining these third-party release estimates with those developed above yields a 1995 estimate of 11.2 g I-TEQ<sub>DF</sub>/yr.

Data validation studies of the CCC indicate that eight PVC/EDC/VCM manufacturing facilities released 5.51 g I-TEQ<sub>DF</sub> (5.46 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) to air, while two chlor-alkali production plants reported releases to air of 0.08 g TEQ<sub>DF</sub>-WHO<sub>98</sub> in 2000 (CCC, 2004). More than 85% of the air releases from PVC/EDC/VCM manufacturing facilities occurred at two facilities. Congener-specific profiles of the release estimates are provided in Tables 8-19 and 8-20. These emission estimates for 1995 and 2000 are assigned a medium confidence rating on the basis of the medium rating given to the emission factor estimates.

#### **8.3.4.4. 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 are summarized in Table 8-19. The 14 sampled sites

1 represent approximately 74% of estimated 1995 U.S. and Canadian suspension and mass PVC  
2 resin production. CDDs/CDFs were detected in only one sample (0.043 ng I-TEQ<sub>DF</sub>/kg,  
3 assuming ND = 0). The overall mean TEQ concentrations were 0.002 ng I-TEQ<sub>DF</sub>/kg (ND = 0)  
4 and 0.7 ng I-TEQ<sub>DF</sub>/kg (ND = 1/2 MDL). The MDLs were 2 ng/kg or less for all congeners in  
5 all samples except for OCDD and OCDF, which had MDLs of 6 ng/kg or less.

6 The same study also presented results for six samples from four of the seven U.S.  
7 facilities manufacturing dispersion PVC resins. CDDs/CDFs were detected in five of the  
8 samples. The results are summarized in Table 8-21. In terms of production, the four sampled  
9 sites represent approximately 61% of estimated 1995 U.S. dispersion PVC resin production. The  
10 results ranged from not detected to 0.008 ng I-TEQ<sub>DF</sub>/kg (overall mean = 0.001 ng I-TEQ<sub>DF</sub>/kg,  
11 assuming ND = 0, and 0.4 ng I-TEQ<sub>DF</sub>/kg, assuming ND = 1/2 MDL). The MDLs were 2 ng/kg  
12 or less for all congeners in all samples except OCDD and OCDF, which had MDLs of 4 ng/kg or  
13 less.

14 Results were also presented for five samples from 5 of the 15 U.S. facilities  
15 manufacturing EDC. The results are summarized in Table 8-21. In terms of production, the five  
16 sampled sites represent approximately 71% of total U.S. estimated 1995 EDC produced.  
17 CDDs/CDFs were detected in only one sample (0.03 ng I-TEQ<sub>DF</sub>/kg). The overall mean TEQ  
18 concentrations were 0.006 ng I-TEQ<sub>DF</sub>/kg (ND = 0) and 0.21 ng I-TEQ<sub>DF</sub>/kg (ND = 1/2 MDL).  
19 The MDLs for all congeners were 1 ng/kg or less.

20 Using 1995 U.S. production data, 4.846 million metric tons of suspension and mass PVC,  
21 0.367 million metric tons of dispersion PVC resins, and 1.362 million metric tons of EDC were  
22 produced. Based on the average TEQ concentration observed, the Vinyl Institute estimated that  
23 the total I-TEQ<sub>DF</sub> contents of suspension/mass PVC resins, dispersion PVC resins, and EDC was  
24 0.01 g, 0.004 g, and 0.008 g, respectively (ND = 0), and 3.39 g, 0.15 g, and 0.29 g, respectively  
25 (ND = 1/2 MDL). Therefore, total I-TEQ<sub>DF</sub> present in PVC in 1995 was estimated to be between  
26 0.02 g (ND = 0) and 3.83 g (ND = 1/2 MDL). It is not possible using the data presented in the  
27 Vinyl Institute report to calculate emission factors for TEQ<sub>DF</sub>-WHO<sub>98</sub>. However, because  
28 neither 1,2,3,7,8-PeCDD nor OCDD was detected in any sample, the TEQ<sub>DF</sub>-WHO<sub>98</sub> emission  
29 factors would be very similar to the I-TEQ<sub>DF</sub> emission factors.

30 In 2000, approximately 6.55 million metric tons of PVC and 9.91 million metric tons of  
31 EDC were produced in North America (C&EN, 2002). In 1995, approximately 5.58 million  
32 metric tons of PVC and 7.83 million metric tons of EDC were produced in North America

(C&EN, 2002). Of this total, approximately 94% of PVC production and approximately 17% of EDC production occurred in the United States and were sold as products. The breakdown of PVC manufacturing was as follows: 87 % of PVC produced was for suspension and mass PVC products and 7 % was for dispersion PVC resins. Assuming these percentages remained the same for 2000, it is estimated that approximately 5.69 million metric tons of suspension and mass PVC and 0.43 million metric tons of dispersion PVC resins were produced, and 1.72 million metric tons of EDC were produced. Applying the same average TEQ observed in the Vinyl Institute samples from 1998, EPA estimated the total I-TEQ<sub>DF</sub> 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 (ND = 0) and 3.99 g, 0.17 g, and 0.36 g, respectively (ND = 1/2 MDL). Therefore, total I-TEQ<sub>DF</sub> present in PVC in 2000 was estimated to be between 0.02 g (ND = 0) and 4.52 g (ND = 1/2 MDL).

### 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, 1991a). These compounds are produced in large quantities. In 1992, 14.6 million metric tons of halogenated hydrocarbons were produced (U.S. International Trade Commission, 1946–1994). The production of 1,2-dichloroethane and vinyl chloride accounted for 82% of this total production. Highly chlorinated CDDs/CDFs (hexa- to octachlorinated 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 the company Promochem (Hutzinger and Fiedler, 1991a; 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 are 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).

1 These effluent limitations do not specifically address CDDs or CDFs. The following chlorinated  
2 aliphatic compounds are regulated: 68 µg/L for 1,2-dichloroethane and 22 µg/L for  
3 tetrachloroethylene. Similarly, OSW promulgated restrictions on land disposal of wastes  
4 generated during the manufacture of many chlorinated aliphatics (40 CFR 268); however, these  
5 restrictions do not specifically regulate CDDs/CDFs.

### 6 7 **8.3.6. Dyes, Pigments, and Printing Inks**

8 Several researchers analyzed various dyes, pigments, and printing inks obtained in  
9 Canada and Germany for the presence of CDDs/CDFs (Williams et al., 1992; Hutzinger and  
10 Fiedler, 1991a; Santl et al., 1994). The following subsections discuss the findings of those  
11 studies.

#### 12 13 **8.3.6.1. Dioxazine Dyes and Pigments**

14 Williams et al. (1992) analyzed the CDD/CDF content in dioxazine dyes and pigments  
15 available in Canada. As shown in Table 8-20, OCDD and OCDF concentrations in the ng/kg  
16 range and HpCDD, HxCDD, and PeCDD concentrations in the µg/kg range were found in Direct  
17 Blue 106 dye (three samples), Direct Blue 108 dye (one sample), and Violet 23 pigments (six  
18 samples) (Williams et al., 1992). These dioxazine pigments are derived from chloranil, which  
19 has been found to contain high levels of CDDs/CDFs and has been suggested as the source of  
20 contamination among these dyes (Christmann et al., 1989a; Williams et al., 1992; U.S. EPA,  
21 1992b). In May 1990, EPA received test results showing that chloranil was heavily  
22 contaminated with dioxins; levels as high as 2,903 µg TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (3,065 µg I-TEQ<sub>DF</sub>/kg)  
23 were measured in samples from four importers (mean value of 1,388 µg TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg  
24 [1,754 µg I-TEQ<sub>DF</sub>/kg]) (U.S. EPA, 1992b; Remmers et al., 1992). (See Section 8.3.7 for  
25 analytical results.)

26 In the early 1990s, EPA learned that I-TEQ<sub>DF</sub> levels in chloranil could be reduced by  
27 more than two orders of magnitude (to less than 20 µg/kg) through manufacturing feedstock and  
28 process changes. EPA's Office of Pollution Prevention and Toxics subsequently began efforts to  
29 complete an industry-wide switch from the use of contaminated chloranil to low-dioxin  
30 chloranil. Although chloranil is not manufactured in the United States, significant quantities are  
31 imported. As of May 1992, EPA had negotiated agreements with all chloranil importers and  
32 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  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  (Federal Register, 1993a; U.S. EPA, 1993c).

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  $\mu\text{g TEQ}_{\text{DF-WHO}_{98}}/\text{kg}$  (1,754  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$ ), then the maximum release into the environment via processing wastes and finished products was 50.6 g  $\text{TEQ}_{\text{DF-WHO}_{98}}$  (64 g  $\text{I-TEQ}_{\text{DF}}$ ). If it is assumed that the import volume in 1995 was also 36,500 kg but that the imported chloranil contained 10  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$  on average, then the total potential annual TEQ release associated with chloranil in 1995 was 50.6 g  $\text{TEQ}_{\text{DF-WHO}_{98}}$  (64 g  $\text{I-TEQ}_{\text{DF}}$ ).

In 1986, EPA promulgated the Inventory Update Rule (IUR) that requires the partial updating of the Toxic Substances Control Act (TSCA) Chemical Inventory database. Every four years, chemical manufacturers and importers of chemicals listed on the TSCA inventory that produce at one plant site or import at production volume levels of 10,000 or more pounds must report the range of chemical production or import. According to information entered in the TSCA database, 10,000 to 500,000 pounds (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 above (10  $\mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$ ), the total potential annual TEQ release associated with chloranil in 2000 was 0.05 to 2.27 g  $\text{I-TEQ}_{\text{DF-WHO}_{98}}$  (mean of 1.16 g  $\text{I-TEQ}_{\text{DF}}$ ).

#### **8.3.6.2. Phthalocyanine Dyes and Printing Inks**

Hutzinger and Fiedler (1991a) found CDDs/CDFs (tetra-, penta-, and hexachlorinated congeners) in the  $\mu\text{g}/\text{kg}$  range in a sample of a Ni-phthalocyanine dye. No CDDs/CDFs were detected (DL of 0.1 to 0.5  $\mu\text{g}/\text{kg}$ ) in two samples of Cu-phthalocyanine dyes and in one Co-phthalocyanine dye (Hutzinger and Fiedler, 1991a).

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 8-21. The TEQ<sub>DF</sub>-WHO<sub>98</sub> content of the inks ranged from 17.7 to 87.2 ng/kg (15 to 88.6 ng/kg on an I-TEQ<sub>DF</sub> 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 release 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 if the dioxin contamination in the product actually results in a release to the open and circulating environment.

### **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, 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 BDDs/BDFs in certain commercial organic chemicals (Federal Register, 1987c). 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, 2003f). 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. Thoma and Hutzinger (1989) also analyzed analytical-grade samples of two other brominated flame retardants, pentabromophenol and tetrabromophthalic anhydride; no BDDs or BDFs were detected (DLs not reported).

### **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.

**Actions to regulate 2,4,5-T and Silvex.** In 1983, EPA cancelled the sale of Silvex and 2,4,5-T for all uses (Federal Register, 1987e). 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.

**Actions to regulate PCP.** 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

1 EPA's determinations. After carefully considering the comments and alternatives suggested  
2 during the prehearing stage of the administrative proceedings, EPA concluded that certain  
3 changes to the 1984 notice were appropriate. These changes, finalized in 1986 (Federal Register,  
4 1986), included the following: (a) all wood preservative uses of PCP and its salts were classified  
5 as "restricted use" only by certified applicators, (b) specific worker protection measures were  
6 required, (c) limits were placed on the HxCDD content of PCP, and (d) label restrictions for  
7 home and farm uses of PCP prohibited its application indoors and to wood intended for interior  
8 use (with a few exceptions) as well as its application in a manner that might result in direct  
9 exposure of domestic animals or livestock or in the contamination of food, feed, or drinking and  
10 irrigation water.

11 EPA subsequently amended its Notice on the wood preservative uses to establish reliable  
12 and enforceable methods for implementing certified limits for HxCDD and 2,3,7,8-TCDD in  
13 registered wood preservative pesticide products (Federal Register, 1987a). Levels of 2,3,7,8-  
14 TCDD were not allowed to exceed 1 ppb in any product, and after February 2, 1989, any  
15 manufacturing-use PCP released for shipment could not contain HxCDD levels that exceeded an  
16 average of 2 ppm over a monthly release or a batch level of 4 ppm (a gradually phased-in  
17 requirement). On January 21, 1987, EPA prohibited the registration of PCP and its salts for most  
18 nonwood uses (Federal Register, 1987b). EPA deferred action on several uses (uses in  
19 pulp/paper mills, oil wells, and cooling towers) pending receipt of additional exposure, use, and  
20 ecological effects data. On January 8, 1993, EPA issued a press advisory stating that its special  
21 review of these deferred nonwood uses was being terminated because all of these uses had been  
22 either voluntarily cancelled by the registrants or cancelled by EPA for failure of the registrants to  
23 pay the required annual maintenance fees (U.S. EPA, 1993f).

24 PCP was one of the most widely used biocides in the United States prior to the regulatory  
25 actions to cancel and restrict certain of its wood and nonwood preservative uses. PCP was  
26 registered for use as a herbicide, defoliant, mossicide, and mushroom house biocide. It also  
27 found use as a biocide in pulp-paper mills, oil wells, and cooling towers. These latter three uses  
28 were terminated on or before 1993 (U.S. EPA, 1993f). However, the major use (greater than  
29 80% of consumption) of PCP was and continues to be wood preservation.

30 The production of PCP for wood preserving began on an experimental basis in the 1930s.  
31 In 1947, nearly 3,200 metric tons of PCP were reported to have been used in the United States by  
32 the commercial wood preserving industry. Use in this industry steadily increased through the

1 mid-1970s (American Wood Preservers Institute, 1977). Although domestic consumption  
2 volumes are not available for all years, it is estimated, on the basis of historical  
3 production/export data for PCP reported in Mannsville (1983), that 90 to 95% of production  
4 volume has typically been consumed domestically rather than exported. A reasonable estimate  
5 of average annual domestic PCP consumption during the period 1970 to 1995 is about 400,000  
6 metric tons. This estimate assumes an average annual consumption rate of 20,000 metric tons/yr  
7 during the 1970s, 15,000 metric tons/yr during the 1980s, and 10,000 metric tons/yr during the  
8 1990s.

9 Table 8-8 presents a compilation of published data on the CDD/CDF content of  
10 technical-grade PCP. The only samples that have been analyzed for all dioxin-like CDDs/CDFs  
11 were manufactured in the mid to late 1980s. Figure 8-4 presents these data in graphical form. It  
12 is evident from the figures that the predominant congener groups are OCDD, OCDF, HpCDF,  
13 and HpCDD, and the dominant 2,3,7,8-substituted congeners are OCDD, 1,2,3,4,6,7,8-HpCDD,  
14 and OCDF. Waddell et al. (1995) tested analytical-grade PCP (from Aldrich Chemical Co.) for  
15 CDD/CDF content and found the same congener profile; however, the CDD/CDF levels were  
16 three to four orders of magnitude lower. Table 8-9 presents a similar compilation of published  
17 data on the CDD/CDF content of PCP-Na. The table shows the same patterns of dominant  
18 congeners and congener groups reported for PCP.

19 Samples of technical PCP manufactured during the mid to late 1980s contained about 1.7  
20 mg TEQ<sub>DF-WHO98</sub>/kg (3 mg I-TEQ/kg), based on the data presented in Table 8-8. No published  
21 reports could be located that present the results of any congener-specific analyses of PCP  
22 manufactured since the late 1980s. However, monthly measurements of CDD/CDF congener  
23 group concentrations in technical PCP manufactured for use in the United States have been  
24 reported to EPA from 1987 to the present (KMG-Bernuth, 1997; Pentachlorophenol Task Force,  
25 1997; U.S. EPA, 1999a). The average congener group concentrations reported to EPA for the  
26 years 1988 (i.e., one year after EPA regulations were imposed limiting HxCDD and 2,3,7,8-  
27 TCDD concentrations in PCP) to 1999 are presented in Table 8-8. In general, the average  
28 congener group concentrations during the period 1988 to 1999 are lower by factors of 2 to 4 than  
29 those observed in the mid to late 1980s' full congener analysis samples. If it is assumed that the  
30 toxic CDD/CDF congeners have also been reduced by similar factors, then the TEQ content of  
31 PCP manufactured since 1988 is about 0.6 mg TEQ<sub>DF-WHO98</sub>/kg (1 mg I-TEQ/kg).

1 An estimated 12,000 metric tons of PCP were used for wood preservation in the United  
2 States in 1987 (WHO, 1991). An estimated 8,400 metric tons were used in 1994 (American  
3 Wood Preservers Institute, 1995); for purposes of this report, it is assumed that an identical  
4 amount was used in 1995. In 1999, approximately 7,710 metric tons of PCP were produced  
5 annually in the United States (Council of Great Lakes Industries, 1999); for purposes of this  
6 report, it is assumed that an identical amount was produced in 2000. Assuming that 95% of the  
7 production volume was consumed domestically (Mannsville, 1983), and that all of the PCP  
8 produced in 2000 was used for wood preservation, approximately 7,325 metric tons of PCP was  
9 used in the United States for wood preservation. Combining these activity level estimates with  
10 the TEQ concentration estimates presented above indicates that 20,000 ug TEQ<sub>DF</sub>-WHO<sub>98</sub>  
11 (36,000 ug I-TEQ<sub>DF</sub> ), 4,800 ug TEQ<sub>DF</sub>-WHO<sub>98</sub> (8,400 ug I-TEQ<sub>DF</sub> ), and 4,175 ug TEQ<sub>DF</sub>-  
12 WHO<sub>98</sub> (7,325 ug I-TEQ<sub>DF</sub> ) were incorporated into PCP-treated wood products in 1987, 1995,  
13 and 2000, respectively. These amounts in PCP products are not considered an environmental  
14 release and therefore are not included in the inventory. As discussed below, there is some  
15 evidence that releases could occur, but no consistent estimation approach could be found.

16 Although the estimates of the mass of TEQ in treated wood are fairly certain, no studies  
17 are available that provide measured CDD/CDF release rate data from which a reliable estimate  
18 can be made of the amount of CDDs/CDFs that have or will volatilize or leach from treated  
19 wood. Several recent field studies, discussed in the following paragraphs, demonstrate that  
20 CDDs/CDFs do apparently leach into soil from PCP-treated wood, but the studies do not provide  
21 release rate data. No studies were located that provide any measured CDD/CDF volatilization  
22 rates from PCP-treated wood. Although CDDs/CDFs have very low vapor pressures, they are  
23 not bound to, nor do they react with, the wood in any way that would preclude volatilization.  
24 Several studies, discussed below, have attempted to estimate potential CDD/CDF volatilization  
25 releases using conservative assumptions or modeling approaches, but these estimates span many  
26 orders of magnitude.

27 Gurprasad et al. (1995) analyzed three PCP-treated utility poles and their surrounding  
28 surface soils for penta- through octa-CDD content. All three poles showed significant levels of  
29 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),  
30 but no PeCDD. Surface soils collected 2 cm from the poles also had detectable levels of  
31 HxCDD, HpCDD, and OCDD; however, no consistent pattern was found between the CDD  
32 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 similar patterns of PCP distribution in soils surrounding poles as 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. EPRI (1995) 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 EPRI (1995), 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 6 to 8 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 were 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; while 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 of 200 and 400 times, respectively, lower 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, respectively, higher in concentration.

Bremmer et al. (1994) estimated an annual release of 15 to 125 g of I-TEQ<sub>DF</sub> 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 3000 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 CDD/CDF and PCP across the range of CDD/CDF concentrations observed in the 20-plus samples (2.6 to 427 pg CDD/CDF/m<sup>3</sup>), there did appear to be a positive correlation at the sites with more elevated CDD/CDF concentrations. Bremmer et al. (1994) reported that the average ratio of PCP to I-TEQ<sub>DF</sub> air concentrations at these elevated sites to be  $1:5 \times 10^{-6}$  (or about the same ratio as the concentration of I-TEQ<sub>DF</sub> 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 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 of I-TEQ<sub>DF</sub> could volatilize from PCP-treated wood in the United States annually. Eitzer and Hites (1987) derived a dramatically different estimate of CDD/CDF volatilization from PCP-treated wood in the United States: 3 kg/yr of total CDD/CDF (or 66 g of I-TEQ<sub>DF</sub> per year, assuming an I-TEQ<sub>DF</sub> 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 EPA, which was cited as the source of the 0.1% emission factor (U.S. EPA, 1980), 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.

1           Eduljee and Dyke (1996) and Douben et al. (1995) estimated that 0.8 g of I-TEQ<sub>DF</sub> is  
2 released to the air annually from PCP-treated wood in the United Kingdom. This estimate was  
3 based on the assumed emission of 0.1% of the CDD/CDF present in PCP-treated wood during  
4 the first year of the service life of the wood that was assumed by Eitzer and Hites (1987). No  
5 emission was assumed for subsequent years of use of the treated wood.

6           The California Air Resources Board (Chinkin et al., 1987) generated estimates of  
7 CDD/CDF volatilization releases at wood treatment facilities from bundles of treated wood that  
8 remain on site for 1 month prior to shipment. An “adapted” version of a model developed by  
9 McCord (1981) was used for estimating volatile releases from a constantly filling lagoon. The  
10 model is primarily driven by chemical-specific vapor pressures and air diffusivity coefficients.  
11 Chinkin et al. did not provide all model input parameter values used to generate the emission  
12 estimates. However, running the model with typical dimensions for treated poles yields an I-  
13 TEQ<sub>DF</sub> emission rate on the order of 6E-12 g/yr-pole, an extremely low number (170 billion  
14 poles would together emit 1 g TEQ/yr).

15           **Actions to identify other pesticides containing CDDs/CDFs.** In addition to cancelling  
16 some pesticide registrations and establishing product standards, EPA’s Office of Pesticide  
17 Programs (OPP) issued two DCIs in 1987. Pesticide manufacturers are required to register their  
18 products with EPA in order to market them commercially in the United States. Through the  
19 registration process, mandated by FIFRA, EPA can require that the manufacturer of each active  
20 ingredient generate a wide variety of scientific data through several mechanisms. The most  
21 common process is the five-phase reregistration process, with which the manufacturers (i.e.,  
22 registrants) of older pesticide products must comply. In most registration activities, registrants  
23 must generate data under a series of strict testing guidelines, 40 CFR 158—Pesticide Assessment  
24 Guidelines (U.S. EPA, 1988b). EPA can also require additional data from registrants, when  
25 necessary, through various mechanisms, including the DCI process.

26           The purpose of the first DCI, dated June and October 1987, “Data Call-In Notice for  
27 Product Chemistry Relating to Potential Formation of Halogenated Dibenzo-*p*-dioxin or  
28 Dibenzofuran Contaminants in Certain Active Ingredients,” was to identify, using an analysis of  
29 raw materials and process chemistry, those pesticides that might contain halogenated dibenzo-*p*-  
30 dioxin (HDD) and halogenated dibenzofuran (HDF) contaminants. The 93 pesticides (76  
31 pesticide active ingredients) to which the DCI applied, along with their corresponding  
32 Shaughnessey and Chemical Abstract code numbers, are presented in Table 8-29. (The



1 Shaughnessey code is an internal EPA tracking system. It is of interest because chemicals with  
2 similar code numbers are similar in chemical nature [e.g., salts, esters, and acid forms of 2,4-D].)

3 All registrants supporting registrations for these chemicals were subject to the  
4 requirements of the DCI unless their product qualified for a Generic Data Exemption (i.e., a  
5 registrant exclusively used a FIFRA-registered pesticide product[s] as the source[s] of the active  
6 ingredient[s] identified in Table 8-29 in formulating their product[s]). Registrants whose  
7 products did not meet the Generic Data Exemption were required to submit the types of data  
8 listed below to enable EPA to assess the potential for formation of tetra- through hepta-HDD or  
9 HDF contaminants during manufacture. Registrants, however, had the option to voluntarily  
10 cancel their product or “reformulate to remove an active ingredient” to avoid having to comply  
11 with the DCI.

- 12  
13 • Product identity and disclosure of ingredients. EPA required submittal of a  
14 Confidential Statement of Formula (CSF), based on the requirements specified in 40  
15 CFR 158.108 and 40 CFR 158.120, Subdivision D: Product Chemistry. Registrants  
16 who had previously submitted still-current CSFs were not required to resubmit this  
17 information.
- 18  
19 • Description of beginning materials and manufacturing process. Under the  
20 requirements mandated by 40 CFR 158.120, Subdivision D, EPA required submittal  
21 of a manufacturing process description for each step of the manufacturing process,  
22 including specification of the range of acceptable conditions of temperature, pressure,  
23 or pH at each step.
- 24  
25 • Discussion of the formation of impurities. Under the requirements mandated by 40  
26 CFR 158.120, Subdivision D, EPA required submittal of a detailed discussion and  
27 assessment of the possible formation of HDDs and HDFs.

28  
29 The second DCI, dated June and October 1987, “Data Call-In for Analytical Chemistry  
30 Data on Polyhalogenated Dibenzo-*p*-Dioxins/Dibenzofurans (HDDs and HDFs),” was issued for  
31 68 pesticides (16 pesticide active ingredients) suspected to be contaminated by CDDs/CDFs (see  
32 Table 8-28). All registrants supporting registrations for these pesticides were subject to the  
33 requirements of this DCI unless the product qualified for various exemptions or waivers.  
34 Pesticides covered by the second DCI were strongly suspected by EPA to contain detectable  
35 levels of CDDs/CDFs.

1 Under the second DCI, registrants whose products did not qualify for an exemption or  
2 waiver were required to generate and submit the following types of data in addition to the data  
3 requirements of the first DCI:  
4

- 5 • Quantitative method for measuring CDDs or CDFs. Registrants were required to  
6 develop an analytical method for measuring the HDD/HDF content of their products.  
7 The DCI established a regimen for defining the precision of the analytical method.  
8 Target LOQs were established in the DCI for specific CDD/CDF congeners (see  
9 Table 8-23).  
10
- 11 • Certification of limits of CDDs or CDFs. Registrants were required to submit a  
12 “Certification of Limits” in accordance with 40 CFR 158.110 and 40 CFR 158.120,  
13 Subdivision D. Analytical results were required that met the guidelines described  
14 above.  
15

16 Registrants could select one of two options to comply with the second DCI. The first  
17 option was to submit relevant existing data, develop new data, or share the cost to develop new  
18 data with other registrants. The second option was to alleviate the DCI requirements through  
19 several exemption processes, including a Generic Data Exemption, voluntary cancellation,  
20 reformulation to remove the active ingredient of concern, an assertion that the data requirements  
21 did not apply, or the application or award of a low-volume, minor-use waiver.

22 The data contained in CSFs, as well as any other data generated under 40 CFR 158.120,  
23 Subdivision D, are typically considered confidential business information (CBI) under the  
24 guidelines prescribed in FIFRA because they usually contain information regarding proprietary  
25 manufacturing processes. In general, all analytical results submitted to EPA in response to both  
26 DCIs are considered CBI and cannot be released by EPA into the public domain. Summaries  
27 based on the trends identified in that data, as well as data made public by EPA, are summarized  
28 below.

29 The two DCIs included 161 pesticides. Of these, 92 are no longer supported by  
30 registrants. Following evaluation of the process chemistry submissions required under the DCIs,  
31 OPP determined that formation of CDDs/CDFs was not likely during the manufacture of 43 of  
32 the remaining 69 pesticides; thus, analysis of samples of these 43 pesticides was not required by  
33 OPP. Evaluation of process chemistry data is ongoing at OPP for an additional 7 pesticides.  
34 Tables 8-29 and 8-30 indicate which pesticides are no longer supported, those for which OPP

determined that CDD/CDF formation is unlikely, and those for which process chemistry data or analytical testing results are under review (U.S. EPA, 1995f).

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 (Funk, 1996). Figure 8-5 presents a congener profile for 2,4-D based on the average congener concentrations reported in Table 8-33.

Schechter 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 Schechter 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 8-31). The total TEQ concentration measured in one of the samples was similar to what Schechter et al. (1997) reported for the U.S. samples; no TEQ was detected in the other sample.

As discussed in Section 12.2.1, 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 the year 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 in 2,4-D in the year 2000. An estimated 26,300 and 30,400 metric tons were used during 1995 and 1987, respectively (U.S. EPA, 1997e, 1988c). 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<sub>DF</sub>-WHO<sub>98</sub> concentration is 1.1 µg/kg (0.7 µg I-TEQ<sub>DF</sub>/kg). Combining this TEQ concentration with the activity level estimates for 1995 and 1987 indicates that 28.9 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (18.4 g I-TEQ<sub>DF</sub>) were released in 1995 and 33.4 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (21.3 g I-TEQ<sub>DF</sub>) 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.

## **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 sewers from lands or urban surfaces contaminated by product uses or deposition of previous emissions to air (discussed in Section 12.2.1), household wastewater, industrial wastewater, chlorination operations within the wastewater treatment facility, or a combination of all the above (Rappe, 1992a; 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, in a series of recent studies, 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

1 concentrations of total CDDs/CDFs in the four samples ranged from 3,900 to 7,100 pg/L and  
2 were very similar in congener profile, with OCDD being the dominant congener, followed by the  
3 hepta- and hexa-CDDs. Because of the similar concentrations and congener profiles found, the  
4 authors concluded that the presence of CDDs/CDFs in washing machine wastewater is  
5 widespread. A simple mass balance performed using the results (Horstmann and McLachlan,  
6 1994a) showed that the CDDs/CDFs found in the four washing machine wastewater samples  
7 could account for 27 to 94% of the total CDDs/CDFs measured in the sludge of the local  
8 wastewater treatment plant.

9 Horstmann et al. (1993a) performed additional experiments that showed that detergents,  
10 commonly used bleaching agents, and the washing cycle process itself were not responsible for  
11 the observed CDDs/CDFs. To determine whether the textile fabric or fabric finishing processes  
12 could account for the observed CDDs/CDFs, Horstmann et al. (1993b), Horstmann and  
13 McLachlan (1994a, b), and Klasmeier and McLachlan (1995) analyzed the CDDs/CDFs content  
14 of raw cotton cloth, white synthetic materials, and more than 100 new textile finished products.  
15 Low concentrations were found in most products (less than 50 ng/kg of total CDDs/CDFs), but a  
16 small percentage contained high concentrations, up to 290 µg/kg of total CDDs/CDFs. On the  
17 basis of the concentrations and patterns found, the authors concluded that neither unfinished new  
18 fabrics nor common cotton finishing processes could explain the CDD/CDF levels found in  
19 wastewater; rather, the use of CDD-/CDF-containing textile dyes and pigments and the use in  
20 some developing countries of PCP to treat unfinished cotton appeared to be the sources of the  
21 detected CDDs/CDFs.

22 Horstmann and McLachlan (1994a, b, 1995) reported the results of additional  
23 experiments showing that the small percentage of clothing items with high CDD/CDF levels  
24 could be responsible for the quantity of CDDs/CDFs observed in household wastewater and  
25 sewage sludge. They demonstrated that the CDDs/CDFs can be gradually removed from the  
26 fabric during washing; they can be transferred to the skin, subsequently transferred back to other  
27 textiles, and then washed out, or they can be transferred to other textiles during washing and then  
28 removed during subsequent washing.

#### 29 30 **8.4.1.2. Releases to Water**

1 **8.4.1.2.1. Emissions data.** The presence of CDDs/CDFs in sewage sludge suggests that  
2 CDDs/CDFs may also be present in the wastewater effluent discharges of POTWs; however, few  
3 studies reporting the results of effluent analyses for CDDs/CDFs have been published.

4 Rappe et al. (1989a) tested the effluent from two Swedish POTWs for all 2,3,7,8-  
5 substituted CDD/CDF congeners. OCDD was detected in the effluents from both facilities at  
6 concentrations ranging from 14 to 39 pg/L. Rappe et al. detected 1,2,3,4,6,7,8-HpCDD and  
7 1,2,3,4,6,7,8-HpCDF in the effluent of one facility at concentrations of 2.8 and 2 pg/L,  
8 respectively. No 2,3,7,8-substituted tetra-, penta-, and hexa-CDDs or CDFs were detected (DLs  
9 of 0.2 to 20 pg/L).

10 Ho and Clement (1990) reported the results of sampling during the late 1980s of 37  
11 POTWs in Ontario, Canada, for each of the five CDD/CDF congener groups with four to eight  
12 chlorines. The sampled facilities included 27 secondary treatment facilities, seven primary  
13 treatment facilities, one tertiary plant, and two lagoons. The facilities accounted for about 73%  
14 of the sewage discharged by POTWs in Ontario. No CDDs/CDFs were detected (DL in low  
15 ng/L range) in the effluents from the lagoons and the tertiary treatment facility. Only OCDD and  
16 TCDF were detected in the effluents from the primary treatment facilities (two and one effluent  
17 samples, respectively). HpCDD, OCDD, TCDF, and OCDF were detected in the effluents from  
18 the secondary treatment facilities (detected in four or fewer samples at levels ranging from 0.1 to  
19 11 ng/L).

20 Gobran et al. (1995) analyzed the raw sewage and final effluent of an Ontario, Canada,  
21 wastewater treatment plant for CDD/CDF congeners over a 5-day period. Although HpCDD,  
22 OCDD, HpCDF, and OCDF were detected in the raw sewage (12 to 2,300 pg/L), no  
23 CDDs/CDFs were detected in the final effluent at congener-specific DLs ranging from 3 to 20  
24 pg/L.

25 The California Regional Water Quality Control Board (CRWQCB, 1996) reported the  
26 results of effluent testing at nine POTWs in the San Francisco area. A total of 30 samples were  
27 collected between 1992 and 1995 and 1 to 6 samples were analyzed for each POTW. As  
28 summarized in Table 8-32, the overall mean TEQ concentration is 0.27 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L  
29 (0.29 pg I-TEQ<sub>DF</sub>/L). With the exception of OCDD, most 2,3,7,8-substituted CDD/CDF  
30 congeners were seldom detected.

31 Rappe et al. (1998) analyzed effluent samples from 17 POTWs in Mississippi, 10 of  
32 which receive input from industrial facilities. Treatment processes at the facilities include the

1 use of one or more of the following: lagoons, activated sludge, aerated digestion, wetlands,  
2 oxidative ditch, and trickling filter. Additionally, 12 of the facilities use chlorine gas in the  
3 treatment process. The wastewater flows at the facilities range from 0.11 to 39.75 million liters  
4 per day; however, wastewater flow rates were not known for two facilities. Table 8-33 presents  
5 the concentrations of dioxins measured in the effluent samples for each facility and total TEQ  
6 emission factors. Concentrations were only congener-specific for 2,3,7,8-TCDD; 2,3,7,8-TCDF;  
7 1,2,3,7,8-PeCDD; 2,3,4,7,8-PeCDF; OCDD; and OCDF. Also provided were concentrations for  
8 total HxCDD and total HpCDD. The total TEQ concentrations reported by Rappe et al.  
9 (assuming ND = 1/2 DL) ranged from 0.274 to 3.84 pg I-TEQ<sub>DF</sub>/L (average of 0.86 pg/I-  
10 TEQ<sub>DF</sub>/L). Because concentrations for all congeners were not provided, emission factors could  
11 not be calculated in TEQ<sub>DF</sub>-WHO<sub>98</sub>.

12 The CRWQCB (1996) data were collected to provide representative effluent  
13 concentrations for the San Francisco area. These data cannot be considered to be representative  
14 of CDD/CDF effluent concentrations at the 16,000-plus POTWs nationwide. Therefore, the data  
15 can be used only to generate a preliminary estimate of the potential mass of CDD/CDF TEQ that  
16 may be released annually by U.S. POTWs.

17  
18 **8.4.1.2.2. Activity level information.** Based on the results of the 1996 and 2000 Clean Water  
19 Needs Surveys, estimates show that approximately 122 billion liters and 148 billion liters of  
20 wastewater were treated daily by POTWs in the United States in 1996 and 2000, respectively  
21 (U.S. EPA, 1997c, 2004).

22 Wastewater treatment data were not available for the year 1987, however, an estimate  
23 was developed using the population of the United States as a surrogate. In 2000, the population  
24 of the United States was approximately 281 million people. Using the estimate of water treated  
25 daily by POTWs in 2000, approximately 527 L/person of wastewater were treated daily by  
26 POTWs. In 1990, the population of the United States was approximately 249 million people.  
27 Assuming the population did not change drastically between 1987 and 1990, and assuming that  
28 the daily domestic wastewater treatment per person remained constant between 1987 and 2000,  
29 EPA estimates that approximately 131 billion liters of wastewater were treated daily at POTWs  
30 in 1987.

1 **8.4.1.2.3. Emission Estimates.** By multiplying the amount of wastewater treated by 365 days/yr  
2 and by the “overall mean” TEQ concentrations reported by CRWQCB (i.e., 0.27 pg TEQ<sub>DF</sub>-  
3 WHO<sub>98</sub>/L and 0.29 pg I-TEQ<sub>DF</sub>/L), yields annual TEQ release estimates of 12.9 g TEQ<sub>DF</sub>-  
4 WHO<sub>98</sub> (13.9 g of I-TEQ<sub>DF</sub>), 12 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (13 g of I-TEQ<sub>DF</sub>), and 14.6 g TEQ<sub>DF</sub>-WHO<sub>98</sub>  
5 (15.7 g I-TEQ<sub>DF</sub>) for 1987, 1995, and 2000, respectively. These estimates should be regarded as  
6 preliminary indications of possible emissions from this source.

#### 8 **8.4.1.3. Sewage Sludge Land Disposal**

9 Sewage sludge is the solid, semi-solid, or liquid residue generated during the treatment of  
10 wastewater. During wastewater treatment, nutrients, pathogens, inorganic compounds (metals  
11 and trace elements), and organic compounds (CDDs/CDFs, PCBs, and surfactants) from the  
12 incoming wastewater are partitioned to the resulting sewage sludge (National Research Council,  
13 2002). The sludge is either disposed of through methods such as incineration or landfill/surface  
14 disposal or beneficially used through methods such as land application.

15 Sewage sludge that is applied to land is referred to as biosolids. In order to be applied to  
16 the land, the biosolids must be treated to meet land application regulatory requirements (Federal  
17 Register, 1993b). With respect to land application, biosolids are often used for crop production,  
18 gardening, forestry, turf growth, and landscaping. Some other uses include strip mine and gravel  
19 pit reclamation and wetland restoration. Land application of biosolids is beneficial because it  
20 improves the physical and chemical properties of the soil needed for plant growth, it reduces the  
21 need for other disposal methods, and it reduces or eliminates the need for commercial fertilizers.  
22 Commercial fertilizers often have higher nutrient contents than do biosolids; therefore, the  
23 application of biosolids to land in lieu of commercial fertilizers may reduce the impacts of high  
24 levels of excess nutrients entering the environment (U.S. EPA, 1999e).

26 **8.4.1.3.1. Emissions data.** EPA conducted the National Sewage Sludge Survey in 1988 and  
27 1989 to obtain national data on sewage sludge quality and management. As part of this survey,  
28 EPA analyzed sludges from 174 POTWs that employed at least secondary wastewater treatment  
29 for more than 400 analytes, including CDDs/CDFs. Although sludges from only 16% of the  
30 POTWs had detectable levels of 2,3,7,8-TCDD, all sludges had detectable levels of at least one  
31 CDD/CDF congener (U.S. EPA, 1996a). I-TEQ<sub>DF</sub> concentrations as high as 1,820 ng/kg dry  
32 weight were measured. The congener-specific results of the survey are presented in Table 8-36.



1 If all nondetect values found in the study are assumed to be zero, then the mean and median I-  
2 TEQ<sub>DF</sub> concentrations of the sludges from the 174 POTWs are 50 and 11.2 ng/kg (dry-weight  
3 basis), respectively. If the nondetect values are set equal to the DL, then the mean and median I-  
4 TEQ<sub>DF</sub> concentrations are 86 and 50.4 ng/kg, respectively (U.S. EPA, 1996a; Rubin and White,  
5 1992).

6 Green et al. (1995) and Cramer et al. (1995) reported the results of analyses of 99  
7 samples of sewage sludge collected from wastewater treatment plants across the United States  
8 during the summer of 1994 as part of the 1994/1995 Association of Metropolitan Sewerage  
9 Agencies (AMSA) survey. These data are summarized in Table 8-37. To calculate average  
10 results in units of TEQ, Green et al. averaged the results from all samples collected from the  
11 same facility to ensure that the results were not biased toward the concentrations found at  
12 facilities from which more than one sample was collected. Also, eight samples were excluded  
13 from the calculation of the overall TEQ averages because it was unclear as to whether they were  
14 duplicate samples from other POTWs. POTW average TEQ concentrations were calculated for  
15 74 POTWs. If all nondetect values are assumed to be zero, then the overall study mean and  
16 median I-TEQ<sub>DF</sub> concentrations are 47.7 and 33.4 ng I-TEQ<sub>DF</sub>/kg (dry weight basis), respectively  
17 (standard deviation of 44.7 ng I-TEQ<sub>DF</sub>/kg). The corresponding mean and median TEQ<sub>DF</sub>-  
18 WHO<sub>98</sub> concentrations are 36.3 and 25.5 ng/kg, respectively (standard deviation, 38.6).

19 The mean and median results reported by Green et al. (1995) and Cramer et al. (1995) are  
20 very similar in terms of total TEQ to those reported by EPA for samples collected five years  
21 earlier (U.S. EPA, 1996a; Rubin and White, 1992). The predominant congeners in both data sets  
22 are the octa- and hepta-CDDs and CDFs. Although not present at high concentrations, 2,3,7,8-  
23 TCDF was commonly detected.

24 In addition to effluents, Rappe et al. (1998) also analyzed the levels of CDDs and CDFs  
25 in municipal sewage sludge from the 17 POTWs in Mississippi. Table 8-38 presents the  
26 concentrations of dioxins measured in the sewage sludge samples and total TEQ emission factors  
27 reported by Rappe et al. Concentrations were only congener specific for 2,3,7,8-TCDD; 2,3,7,8-  
28 TCDF; 1,2,3,7,8-PeCDD; 2,3,4,7,8-PeCDF; OCDD; and OCDF. Also provided were  
29 concentrations for total HxCDD and total HpCDD. The TEQ emission factors (assuming ND =  
30 1/2 DL) reported by Rappe et al. ranged from 2.26 to 1,270 ng I-TEQ<sub>DF</sub>/kg. The predominant  
31 congeners in all samples were the octa- and hepta-CDDs. The sludge with the highest  
32 concentrations of octa- and hepta-CDDs was from the Picayune POTW, which receives

1 industrial inputs, including effluents from wood treatment facilities that likely contain PCP. In  
2 general, the sludge with the lowest TEQ values were from the facilities that do not receive  
3 effluent from industrial facilities. Additionally, the samples with the two lowest TEQ values  
4 were from facilities that do not use free chlorine as a disinfectant.

5 In 1999, sewage sludge samples from a POTW in Ohio were collected and analyzed for  
6 CDDs/CDFs (U.S. EPA, 2000f). The facility, which accepts both domestic and industrial  
7 wastewater, employs secondary wastewater technology. Assuming nondetects are zero, the  
8 mean TEQ emission factor is 21.9 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (dry-weight basis). These results are  
9 presented in Table 8-39.

10 In 2000 and 2001, AMSA conducted another survey of dioxin-like compounds in sewage  
11 sludge (Alvarado et al., 2001). A total of 200 sewage sludge samples were collected from 171  
12 POTWs located in 31 states. Assuming nondetects are zero, TEQ emission factors range from  
13 0.08 to 3,578.61 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg. The mean and median TEQ emission factors are 34.5  
14 and 11.79 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg, respectively.

15 EPA conducted another National Sewage Sludge Survey to characterize the dioxin and  
16 dioxin-like equivalence levels in biosolids produced by 6857 POTWs operating in the United  
17 States in 2001 (U.S. EPA, 2002a). Samples were collected from 94 POTWs using secondary or  
18 higher treatment practices. All facilities had been sampled previously as part of the 1988/1989  
19 National Sewage Sludge Survey. The overall mean and median TEQ<sub>DF</sub>-WHO<sub>98</sub> concentrations  
20 were 75 and 15 ng/kg, respectively. However, when the data were weighted using the daily  
21 influent wastewater flow rates (i.e., the number of facilities with wastewater flow rate  
22 >100 Mg/day, >10 but ≤100 Mg/day, >1 but ≤10 Mg/day, and ≤1 Mg/day), the overall mean and  
23 median TEQ<sub>DF</sub>-WHO<sub>98</sub> concentrations were 21.7 and 15.5 ng/kg, respectively. These data are  
24 summarized in Table 8-40.

25 The CDD/CDF concentrations and congener group patterns observed in the U.S. surveys  
26 are similar to those reported for sewage sludges in several other Western countries. Stuart et al.  
27 (1993) reported mean CDD/CDF concentrations of 23.3 ng I-TEQ<sub>DF</sub>/kg (dry weight) for three  
28 sludges from rural areas, 42.3 ng I-TEQ<sub>DF</sub>/kg for six sludges from light industry/domestic areas,  
29 and 52.8 ng I-TEQ<sub>DF</sub>/kg for six sludges from industrial/domestic areas collected during 1991–  
30 1992 in England and Wales. Näf et al. (1990) reported concentrations ranging from 31 to 40 ng  
31 I-TEQ<sub>DF</sub>/kg (dry weight) in primary and digested sludges collected from the POTW in  
32 Stockholm, Sweden, during 1989. Gobran et al. (1995) reported an average concentration of

15.7 ng I-TEQ<sub>DF</sub>/kg in anaerobically digested sludges from an industrial/domestic POTW in Ontario, Canada. In all three studies, the congener group concentrations increased with 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<sub>DF</sub> concentration values reported in the 1988/1989 sewage sludge survey (U.S. EPA, 1996a) 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<sub>DF</sub>/kg) of the mean I-TEQ<sub>DF</sub> concentration values (ND = DLs) reported by U.S. EPA (1996a) (50 ng I-TEQ<sub>DF</sub>/kg) and by Green et al. (1995) and Cramer et al. (1995) (36.3 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg [47.7 ng I-TEQ<sub>DF</sub>/kg]). Therefore, the overall average mean emission factor for the reference years 1987 and 1995 is 36.3 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (48.9 ng I-TEQ<sub>DF</sub>/kg). The emission factor of 21.7 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/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, 1993b). 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 are 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.

U.S. EPA (1999) 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) (NRC, 2002) analyzed the amount of biosolids being applied to land in 2002. Citing 2001 data (unpublished) from the Wisconsin Department of Natural Resources, 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, an estimated 5,900 of these sewage

1 sludge generators either land applied or publicly distributed more than 3.4 million dry tons of  
2 biosolids annually. The volume of biosolids, by use and disposal practices, is presented in Table  
3 8-44. The volume of biosolids and their distribution among the various categories estimated by  
4 the NRC are very close to those estimated by the EPA.

5  
6 **8.4.1.3.3. Emission estimates.** The annual potential releases of CDDs/CDFs are determined by  
7 multiplying the mean total TEQ concentrations by the sludge volumes generated. The results for  
8 reference years 1987, 1995, and 2000 are reported in Table 8-41, 8-42, and 8-43, respectively.  
9 For reference year 1987, the total annual potential release from nonincinerated sludges was 151 g  
10  $\text{TEQ}_{\text{DF-WHO}_{98}}$ . Of this amount, 2.6 g  $\text{TEQ}_{\text{DF-WHO}_{98}}$  (3.5 g I- $\text{TEQ}_{\text{DF}}$ ) entered commerce as a  
11 product for distribution and marketing and 76.6 g  $\text{TEQ}_{\text{DF-WHO}_{98}}$  (103 g I- $\text{TEQ}_{\text{DF}}$ ) was applied  
12 to land. The remaining 71.8 g  $\text{TEQ}_{\text{DF-WHO}_{98}}$  did not result in an environmental release because  
13 it was sent to RCRA Subtitle D landfills or disposal sites. For reference year 1995, the total  
14 annual potential release from nonincinerated sludges was 178 g  $\text{TEQ}_{\text{DF-WHO}_{98}}$ . Of this amount,  
15 3 g  $\text{TEQ}_{\text{DF-WHO}_{98}}$  (4 g I- $\text{TEQ}_{\text{DF}}$ ) entered commerce as a product for distribution and  
16 marketing, and 116.1 g  $\text{TEQ}_{\text{DF-WHO}_{98}}$  (156.5 g I- $\text{TEQ}_{\text{DF}}$ ) was applied to land. The remaining  
17 58.9 g  $\text{TEQ}_{\text{DF-WHO}_{98}}$  did not result in an environmental release because it was sent to RCRA  
18 Subtitle D landfills or disposal sites. For the year 2000, the total annual release of  
19 nonincinerated sludges was 111 g  $\text{TEQ}_{\text{DF-WHO}_{98}}$ . Of this amount, 1.9 g  $\text{TEQ}_{\text{DF-WHO}_{98}}$  (1.9 g  
20 I- $\text{TEQ}_{\text{DF}}$ ) entered commerce as a product for distribution and marketing, and 78.2 g  $\text{TEQ}_{\text{DF-}}$   
21  $\text{WHO}_{98}$  (78.2 g I- $\text{TEQ}_{\text{DF}}$ ) was applied to land. The remaining 30.9 g  $\text{TEQ}_{\text{DF-WHO}_{98}}$  did not  
22 result in an environmental release because it was sent to RCRA Subtitle D landfills or disposal  
23 sites.

24 These release estimates are assigned a high confidence rating for both the production and  
25 emission factor estimates. The high rating was based on the judgment that the 174 facilities  
26 tested as part of the 1988/1989 National Sewage Sludge Survey by EPA (U.S. EPA, 1996a), the  
27 74 facilities tested as part of the 1994/1995 AMSA Survey (Green et al., 1995 and Cramer et al.,  
28 1995), and the 94 facilities tested as part of the 2001 National Sewage Sludge Survey (EPA  
29 2002) were reasonably representative of the variability in POTW technologies and sewage  
30 characteristics nationwide.

## 31 32 **8.4.2. Drinking Water Treatment Plants**

1           There is no strong evidence that chlorination of water for drinking purposes results in the  
2 formation of CDDs/CDFs. Few surveys of CDD/CDF content in finished drinking water have  
3 been conducted. Those that have been published have only rarely reported the presence of any  
4 CDDs/CDFs, even at low pg/L DLs, and in those cases, CDDs/CDFs were also present in the  
5 untreated water.

6           Rappe et al. (1989b) reported the formation of tetra- through octa-CDFs when tap water  
7 and double-distilled water were chlorinated using chlorine gas. The CDF levels found in the  
8 single samples of tap water and double-distilled water were 35 and 7 pg I-TEQ<sub>DF</sub>/L, respectively.  
9 No CDDs were detected at DLs ranging from 1 to 5 pg/L. However, the water samples were  
10 chlorinated at a dosage rate of 300 mg/L, which is considerably higher (by one to two orders of  
11 magnitude) than the range of dosage rates typically used to disinfect drinking water. The authors  
12 hypothesized that the CDFs or their precursors were present in chlorine gas.

13           Rappe et al. (1990a) analyzed a 1,500 L sample of drinking water from a municipal  
14 drinking water treatment plant in Sweden. Although the untreated water was not analyzed, a  
15 sludge sample from the same facility was analyzed. The large sample volume enabled DLs on  
16 the order of 0.001 pg/L. The TEQ content of the water and sludge was 0.0029 pg I-TEQ<sub>DF</sub>/L and  
17 1.4 ng/kg, respectively. The congener patterns of the drinking water and sludge sample were  
18 very similar, suggesting that the CDDs/CDFs detected in the finished water were present in the  
19 untreated water.

#### 20 21 **8.4.3. Soaps and Detergents**

22           As discussed in Section 8.4.1, CDDs/CDFs were detected in nearly all sewage sludges  
23 tested, whether the sludges were obtained from industrialized areas or from rural areas. Because  
24 of the ubiquitous presence of CDDs/CDFs in sewage sludge, several studies have been  
25 conducted to determine their source(s). A logical category of products to test, because of their  
26 widespread use, is detergents, particularly those that contain or release chlorine during use (i.e.,  
27 hypochlorite-containing and dichloroisocyanuric acid-containing detergents). The results of  
28 studies conducted to date, summarized below, indicate that CDDs/CDFs are not formed during  
29 use of chlorine-free detergents, chlorine-containing or chlorine-releasing detergents, or chlorine  
30 bleach during household bleaching operations.

31           Sweden's Office of Nature Conservancy (1991) reported that the results of a preliminary  
32 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<sub>DF</sub>/L (the water-only control sample contained <2.8 pg I-TEQ<sub>DF</sub>/L). The CDD/CDF content of the laundry drainwater samples ranged from <1.1 to <4.6 pg I-TEQ<sub>DF</sub>/L (the water-only control sample contained <4.4 pg I-TEQ<sub>DF</sub>/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. (1990c) 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<sub>DF</sub>-WHO<sub>98</sub>/L (0.447 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub>-WHO<sub>98</sub>/kg [9.4 ng I-TEQ<sub>DF</sub>/kg]) and tall resin (196 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg [200 ng I-TEF<sub>DF</sub>/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 more-highly chlorinated congeners were very similar. Table 8-44 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., 1990c), 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; 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

1 nor common cotton finishing processes could explain the CDD/CDF levels found in laundry  
2 wastewater.

3 Fuchs et al. (1990) reported that the dry-cleaning solvent redistillation residues collected  
4 from 12 commercial and industrial dry-cleaning operations contained considerable amounts of  
5 CDDs/CDFs. The reported I-TEQ<sub>DF</sub> content ranged from 131 to 2,834 ng/kg, with the dominant  
6 congeners being OCDD and HpCDD. Towara et al. (1992) demonstrated that neither the use of  
7 chlorine-free solvents nor variation of the dry-cleaning process parameters lowered the  
8 CDD/CDF content of the residues.

9 Umlauf et al. (1993) conducted a study to characterize the mass balance of CDDs/CDFs  
10 in the dry-cleaning process. The soiled clothes (containing 16 pg total CDDs/CDFs per kg)  
11 accounted for 99.996% of the CDD/CDF input. Input of CDDs/CDFs from indoor air containing  
12 0.194 pg/m<sup>3</sup> accounted for the remainder (0.004%). The dry-cleaning process removed 82.435%  
13 of the CDDs/CDFs in the soiled clothing. Most of the input CDDs/CDFs (82.264%) were found  
14 in the solvent distillation residues. Air emissions (at 0.041 pg/m<sup>3</sup>) accounted for 0.0008% of the  
15 total input, which was less than the input from indoor air. The fluff (at a concentration of  
16 36 ng/kg) accounted for 0.1697%, and water effluent (at a concentration of 0.07 pg/L) accounted  
17 for 0.0000054%.

18 Horstmann and McLachlan (1994a, b, 1995) analyzed 35 new textile samples (primarily  
19 cotton products) obtained in Germany for CDDs/CDFs. Low levels were found in most cases  
20 (total CDD/CDF less than 50 ng/kg). The dominant congeners were OCDD and HpCDD.  
21 However, several colored T-shirts from a number of clothing producers had extremely high  
22 levels, with concentrations up to 290,000 ng/kg. Because the concentrations in identical T-shirts  
23 purchased at the same store varied by up to a factor of 20, the authors concluded that the source  
24 of CDDs/CDFs was not a textile finishing process, because a process source would have resulted  
25 in a more consistent level of contamination. Klasmeier and McLachlan (1995) subsequently  
26 analyzed 68 new textile products obtained in Germany for OCDD and OCDF. Most samples had  
27 nondetectable levels (42 samples <60 ng/kg). Only four samples had levels exceeding 500  
28 ng/kg.

29 Horstmann and McLachlan (1994a, b) reported finding two different congener group  
30 patterns in the more contaminated of the 35 textile products. One pattern agreed with the  
31 congener pattern for PCP reported by Hagenmaier and Brunner (1987), whereas the other pattern  
32 was similar to that reported by Remmers et al. (1992) for chloranil-based dyes. The authors



1 hypothesized that the use of PCP to preserve cotton, particularly when it is randomly strewn on  
2 bales of cotton as a preservative during sea transport, was the likely source of the high levels  
3 occasionally observed. Although the use of PCP for nonwood uses was prohibited in the United  
4 States in 1987 (see Section 8.3.8), PCP is still used in developing countries, especially to  
5 preserve cotton during sea transport (Horstmann and McLachlan, 1994a).

6 Horstmann and McLachlan (1994a, b) conducted additional experiments that  
7 demonstrated that the small percentage of clothing items with high CDD/CDF levels could be  
8 responsible for the quantity of CDDs/CDFs observed in household wastewater (see Section  
9 8.4.1.1).

**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 <sup>a,b</sup>	55.7			798			3,212		
Total 2,3,7,8-CDF <sup>a,b</sup>	18			272.5			310		
Total I-TEQ <sub>DF</sub> (nondetect = 0) <sup>b</sup>	8.28			90.12			58.89		
Total I-TEQ <sub>DF</sub> (nondetect = 1/2 DL) <sup>b</sup>	8.56			91.72			66.57		
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect = 0) <sup>b</sup>	8.24		89.47				56.02		
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect = 1/2 DL) <sup>b</sup>	8.59		91.7				66.09		
Total CDD/CDF <sup>b</sup>	120			1,695			4,013		

<sup>a</sup>Calculated assuming nondetect values were zero.<sup>b</sup>Sum of median values.

DL = Detection limit

ND = Not detected (value in parenthesis is the detection limit)

Source: U.S. EPA (1990a).

**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 <sup>a</sup>	2.7				492				103			
Total 2,3,7,8-CDF <sup>a</sup>	10.7				8.4				2.3			
Total I-TEQ <sub>DF</sub> (nondetect = 0) <sup>a</sup>	1.53				3				1.5			
Total I-TEQ <sub>DF</sub> (nondetect = ½ DL) <sup>a</sup>	6.4				12.9				53.6			
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect = 0) <sup>a</sup>	1.5				2.6				1.4			
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect = ½ DL) <sup>a</sup>	7.6				15.2				66.5			

<sup>a</sup> Sum of mean values.

DL = Detection limit

ND = Not detected (value in parenthesis is the detection limit)

Source: Gillespie (1997).

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

<b>Matrix</b>	<b>Congener</b>	<b>U.S. EPA 1988<sup>a</sup></b>	<b>NCASI 1992<sup>b</sup></b>	<b>U.S. EPA 1993<sup>c</sup></b>	<b>NCASI 1993<sup>b</sup></b>	<b>NCASI 1994<sup>b</sup></b>	<b>U.S. EPA 1995<sup>d</sup></b>
Effluent	2,3,7,8-TCDD	201	22	71	19	14.6	16
	2,3,7,8-TCDF	1,550	99	341	76	49	120
	TEQ	356	32	105	27	19.5	28
Sludge <sup>e</sup>	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

<sup>a</sup>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. Data from 104 Mill Study (U.S. EPA, 1990a).

<sup>b</sup>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. 1992 NCASI survey (NCASI, 1993), 1993 update (Gillespie, 1994), and 1994 update (Gillespie, 1995).

<sup>c</sup>The discharges in effluent and sludge were estimated in U.S. EPA (1993d, 1997f) for January 1, 1993. The TEQ discharge in pulp was estimated by multiplying the 1988 discharge estimate by the ratio of the 1988 and 1993 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).

<sup>d</sup>The discharges in effluent and sludge were estimated in U.S. EPA (1997f) for mid-1995. The TEQ discharge in pulp was estimated by multiplying the 1988 discharge estimate by the ratio of the 1988 and 1995 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).

<sup>e</sup>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).

-- = No information given

**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. <sup>a</sup> (pg/L)	TEQ emissions (ng/yr)	TEQ conc. <sup>a</sup> (ng/kg)	TEQ emissions (ng/yr)	TEQ conc. <sup>a</sup> (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
TOTAL	4.90e-01	1.02e+09	1.72		2.01e-02	5.82e+08
Residuals total				1.93e+09		
Residuals not landfilled				9.44e+08		

<sup>a</sup>TEQ concentrations are in TEQ<sub>DF</sub>-WHO<sub>98</sub>.

Source: Gillespie (2002).

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

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 <sup>a</sup>	1.02	2.21	2.45	0.7
Total 2,3,7,8-CDF <sup>a</sup>	152.37	341.7	339.6	303
Total I-TEQ <sub>DF</sub> <sup>a</sup>	14.2	30.5	30.2	27.7
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> <sup>a</sup>	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 <sup>a</sup>	263.14	661.48	647.76	--

<sup>a</sup>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).

**Table 8-6. CDD/CDF concentrations in metal chlorides (µg/kg)**

<b>Congener group</b>	<b>FeCl<sub>3</sub></b>	<b>AlCl<sub>3</sub><sup>a</sup></b>	<b>AlCl<sub>3</sub><sup>a</sup></b>	<b>CuCl<sub>2</sub></b>	<b>CuCl</b>	<b>TiCl<sub>4</sub></b>	<b>SiCl<sub>4</sub></b>
Total TCDD	--	--	--	--	--	--	--
Total PeCDD	--	--	--	--	--	--	--
Total HxCDD	--	--	--	--	--	--	--
Total HpCDD	ND	ND	ND	0.03	ND	ND	ND
Total OCDD	ND	ND	0.1	0.6	0.03	ND	ND
Total TCDF	--	--	--	--	--	--	--
Total PeCDF	--	--	--	--	--	--	--
Total HxCDF	--	--	--	--	--	--	--
Total HpCDF	12	ND	ND	0.1	0.08	ND	ND
Total OCDF	42	ND	34	0.5	0.2	ND	ND

<sup>a</sup>AlCl<sub>3</sub> was tested twice.

ND = Not detected; detection limit of 0.02 µg/kg

-- = No information given

Source: Hutzinger and Fiedler (1991a).

**Table 8-7. CDD/CDF concentrations in mono- through tetrachlorophenols (mg/kg)**

<b>Congener/ congener group</b>	<b>2-CP<sup>a</sup></b>	<b>2,4-DCP<sup>a</sup></b>	<b>2,6-DCP<sup>a</sup></b>	<b>2,4,5-TrCP (Na salt)<sup>a</sup></b>	<b>2,4,5-TrCP<sup>a</sup></b>	<b>2,4,6-TrCP<sup>a</sup></b>	<b>2,4,6-TrCP (Na salt)<sup>b, c</sup></b>	<b>2,3,4,6-TeCP<sup>a</sup></b>	<b>2,3,4,6-TeCP (Na salt)<sup>b, c</sup></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
<b>TOTAL</b>	--	--	--	--	--	--	--	--	--

<sup>a</sup>Source: Firestone et al. (1972); because of poor recoveries, authors stated that actual CDD/CDF levels may have been considerably higher than those reported.

<sup>b</sup>Source: Rappe et al. (1978a); common Scandinavian commercial chlorophenols.

<sup>c</sup>Source: Rappe et al. (1978b); common Scandinavian commercial chlorophenols.

ND = Not detected (value in parenthesis is the detection limit, if reported)

+ = Detected but not quantified

-- = No information given



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

Congener/ congener group	1973 <sup>a</sup>	1978 <sup>b</sup>	1979 <sup>c</sup>	1984 <sup>d</sup>	1985	1986	1987 <sup>f</sup>	1987 <sup>g</sup>	1985–88 <sup>e</sup>	1991 <sup>h</sup>	1988–99 <sup>i</sup>	1988–99 <sup>i</sup>	Un- known <sup>k</sup>
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 <sup>l</sup>	--	--	--	712,300	1.688e+20	1.038e+20	811,860	891,435	2.813e+20	--	--	--	334,090
Total 2,3,7,8-CDF <sup>l</sup>	--	--	--	--	--	--	130,076	158,230	--	--	--	--	22,280
Total I-TEQ <sub>DF</sub> <sup>l</sup>	--	--	--	1,970	--	--	1,853	2,321	--	≥1,270	--	--	810
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> <sup>l</sup>	--	--	--	1,304	--	--	1,088	1,488	--	>127	--	--	525
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 <sup>l</sup>	655,800	1,280,000	1,834,400	941,500	2,111,692	1,447,335	1,085,000	1,270,000	3,178,598	1,459,000	--	468,240	--

<sup>a</sup>Source: Buser and Bosshardt (1976); mean of 10 samples of “high” CDD/CDF-content PCP received from Swiss commercial sources in 1973.

<sup>b</sup>Source: Rappe et al. (1978b); sample of U.S. origin, “presumably prepared by alkaline hydrolysis of hexachlorobenzene.”

<sup>c</sup>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).

<sup>d</sup>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).

<sup>e</sup>Source: Pentachlorophenol Task Force (1997); samples of “penta” manufactured in 1985, 1986, and 1988.

<sup>f</sup>Source: Hagenmaier and Brunner (1987); sample of Witophen P (Dynamit Nobel - Lot no. 7777) (obtained in Germany).

<sup>g</sup>Source: Hagenmaier and Brunner (1987); sample of PCP produced by Rhone Poulenc (obtained in Germany).

<sup>h</sup>Source: Harrad et al. (1991); PCP-based herbicide formulation from NY State Dept. Environmental Conservation.

<sup>i</sup>Source: Pentachlorophenol Task Force (1997); average of monthly batch samples for the period January 1987 to August 1996.

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

<sup>j</sup>Source: KMG-Bermuth, Inc. (1997); 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).

<sup>k</sup>Source: Schecter et al. (1997); sample found stored in a barn in Vermont.

<sup>l</sup>Calculated assuming nondetects were zero.

<sup>k</sup>Source: Schecter et al. (1997); sample found stored in a barn in Vermont.

<sup>l</sup>Calculated assuming nondetects were zero.

ND = Not detected (value in parenthesis is the detection limit)

-- = No information given

**Table 8-9. Historical CDD/CDF concentrations in pentachlorophenol-Na (PCP-Na) (µg/kg)**

Congener/congener group	1969 <sup>a</sup>	1973 <sup>b</sup>	1973 <sup>c</sup>	1987 <sup>d</sup>	1987	1992 <sup>f</sup>	1980s <sup>g</sup>
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 <sup>h</sup>	--	--	--	53,063	35,289	1,059,253	118,878
Total 2,3,7,8-CDF <sup>h</sup>	--	--	--	38,795	4,499	126,492	43,841
Total I-TEQ <sub>DF</sub> <sup>h</sup>	--	--	--	452	79.5	3,374	1,201
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> <sup>h</sup>	--	--	--	406	58.5	2,566	1,096
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 <sup>h</sup>	--	15,980	235,990	117,859	43,752	1,348,751	378,742

<sup>a</sup>Source: Firestone et al. (1972); mean of two samples of PCP-Na obtained in the United States between 1967 and 1969.

<sup>b</sup>Source: Buser and Bosshardt (1976); mean of five samples of “low” CDD/CDF-content PCP-Na received from Swiss commercial sources.

<sup>c</sup>Source: Buser and Bosshardt (1976); sample of “high” CDD/CDF-content PCP-Na received from a Swiss commercial source.

<sup>d</sup>Source: Hagenmaier and Brunner (1987); sample of Dowicide-G purchased from Fluka; sample obtained in Germany.

<sup>e</sup>Source: Hagenmaier and Brunner (1987); sample of Preventol PN (Bayer AG); sample obtained in Germany.

<sup>f</sup>Source: Santl et al. (1994); 1992 sample of PCP-Na from Prolabo, France.

<sup>g</sup>Source: Palmer et al. (1988); sample of a PCP-Na formulation collected from a closed sawmill in California in the late 1980s.

<sup>h</sup>Calculated assuming nondetect values were zero.

ND = Not detected (value in parenthesis is the detection limit).

-- = No information given.

**Table 8-10. Summary of specific dioxin-containing wastes that must comply with land disposal restrictions<sup>a</sup>**

<b>EPA hazardous waste number</b>	<b>Waste description</b>	<b>Land disposal restriction effective date</b>	<b>Regulated waste constituent</b>
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 8-10. Summary of specific dioxin-containing wastes that must comply with land disposal restrictions<sup>a</sup> (continued)**

<b>EPA hazardous waste number</b>	<b>Waste description</b>	<b>Land disposal restriction effective date</b>	<b>Regulated waste constituent</b>
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

<sup>a</sup>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.

**Table 8-11. CDD/CDF concentrations in chlorobenzenes (µg/kg)**

<b>Congener/congener group</b>	<b>MCBz<sup>a</sup></b>	<b>1,2-DCBz (for synthesis)<sup>a</sup></b>	<b>1,2,4-TrCBz (“pure”)<sup>b</sup></b>	<b>Mixed TrCBz (47%)<sup>a</sup></b>	<b>1,2,4,5-TeC Bz (99%)<sup>a</sup></b>	<b>PeCBz (98%)<sup>a</sup></b>	<b>HCBz (97%)<sup>a</sup></b>	<b>HCBz<sup>b</sup></b>
Total TCDD	ND (0.02)	0.3	ND (0.1)	0.027	ND (0.02)	ND (0.02)	ND (20)	--
Total PeCDD	ND (0.02)	ND (0.02)	ND (0.1)	0.14	0.2	ND (0.02)	ND (20)	--
Total HxCDD	ND (0.02)	ND (0.02)	ND (0.1)	0.259	0.5	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)	0.5	ND (0.1)	0.272	0.2	ND (0.02)	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)	ND (0.1)	0.03	1.5	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	--	--	--	1.904	--	--	--	--

<sup>a</sup>Source: Hutzinger and Fiedler (1991a); unpublished results of tests performed at the University of Bayreuth, Germany, and by Dr. H. Hagenmaier.

<sup>b</sup>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

**Table 8-12. Concentrations of CDD/CDF congener groups in unused commercial polychlorinated biphenyl (PCB) mixtures (mg/kg)**

PCB mixture	Year of manufacture	CDF congener group concentrations						CDD congener group concentrations						Source
		TCDF	PeCDF	HxCDF	HpCDF	OCDF	Total CDF	TCDD	PeCDD	HxCDD	HpCDD	OCDD	Total CDD	
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	--	6.377	2.402	0.805	0.108	0.016	9.708	0.0007	ND	0.001	0.006	0.031	0.039	e
Clophen A-30	--	0.713	0.137	0.005	0.001	ND	0.855	ND	ND	ND	0.005	0.025	0.03	d
Aroclor 1248	1969	0.5	1.2	0.3	--	--	22.2352	--	--	--	--	--	--	b
Clophen A-40	--	1.289	0.771	0.144	0.02	0.011		ND	ND	ND	0.012	0.03	0.042	d
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	--	5.402	2.154	2.214	0.479	0.069	10.318	ND	ND	ND	0.011	0.027	0.038	d
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	--	15.786	11.655	4.456	1.517	0.639	34.052	0.0004	0.002	0.002	0.003	0.015	0.022	e
Clophen A-60	--	16.34	21.164	7.63	2.522	1.024	48.681	ND	ND	ND	0.014	0.032	0.046	d
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

<sup>a</sup>Source: Bowes et al. (1975a).<sup>b</sup>Source: Erickson (1986).<sup>c</sup>Source: ATSDR (1993).<sup>d</sup>Source: Hagenmaier (1987).<sup>e</sup>Source: Malisch (1994).

ND = Not detected

-- = No information given

**Table 8-13. 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 <sup>a</sup>	A-30 <sup>b</sup>	A-40 <sup>b</sup>	A-50 <sup>b</sup>	A-60 <sup>a</sup>	A-60 <sup>b</sup>	1016 <sup>c</sup>	1242 <sup>c</sup>	1248 <sup>d</sup>	1254 <sup>c</sup>	1254 <sup>c</sup>	1254 <sup>c</sup>	1254 <sup>d</sup>	1260 <sup>c</sup>	1260 <sup>c</sup>	1260 <sup>c</sup>
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 <sup>c</sup>	9,746.4	885.5	2,276.61	10,355.7	34,074.4	48,726.5	--	--	--	--	--	--	--	--	--	--
Total I-TEQ <sub>DF</sub> <sup>c</sup>	407.2	11.3		409.6	1,439.2	2,179	--	--	--	--	--	--	--	--	--	--
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> <sup>c</sup>	407.2	11.3		409.5	1,439	2,178	--	--	--	--	--	--	--	--	--	--

<sup>a</sup>Source: Malisch (1994).<sup>b</sup>Source: Hagenmaier (1987).<sup>c</sup>Source: Brown et al. (1988).<sup>d</sup>Source: Bowes (1975b).<sup>e</sup>Calculated assuming nondetect values were zero.

ND = Not detected

-- = No information given



**Table 8-14. Reported CDD/CDF concentrations in wastes from polyvinyl chloride (PVC) manufacture (µg/kg)**

<b>Congener/congener group</b>	<b>F024 waste</b>	<b>K019 waste</b>	<b>K020 waste</b>
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 <sub>DF</sub>	20	5,928	3.2
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	19.7	6,333	2.6
Total TCDD	3.1	1,230	1.9
Total PeCDD	3.6	3,540	1.7
Total HxCDD	1.3	3,950	<sup>a</sup>
Total HpCDD	5	1,270	1.7
Total OCDD	15	1,060	3
Total TCDF	15	20,600	6
Total PeCDF	65	45,300	11
Total HxCDF	300	63,700	27
Total HpCDF	450	16,600	58
Total OCDF	390	43,500	650
Total CDD/CDF	1,248	200,750	760.3

<sup>a</sup>Congener group concentration reported in source is not consistent with reported congener concentrations.

Source: Stringer et al. (1995).

**Table 8-15. CDD/CDF measurements in treated wastewater and wastewater solids from U.S. EDC/VCM/PVC manufacturers**

Congener/congener groups	Treated wastewater						Wastewater solids					
	PVC-only facilities			EDC/VCM/PVC facilities			EDC/VCM/PVC facilities			PVC-only facilities		
	No. detects/ samples	Concentration range <sup>a</sup> (ng/L)		No. detects/ samples	Concentration range <sup>a</sup> (ng/L)		No. detects/ samples	Concentration range <sup>b,c</sup> (ng/kg)		No. detects/ samples	Concentration range <sup>b,c</sup> (ng/kg)	
		Min.	Max.		Min.	Max.		Min.	Max.		Min.	Max.
2,3,7,8-TCDD	0/6	ND	ND	0/4	ND	ND	4/8	ND	109	1/2	ND	2
1,2,3,7,8-PeCDD	0/6	ND	ND	0/4	ND	ND	3/8	ND	320	0/2	ND	ND
1,2,3,4,7,8-HxCDD	0/6	ND	ND	0/4	ND	ND	4/8	ND	455	1/2	ND	3.2
1,2,3,6,7,8-HxCDD	0/6	ND	ND	0/4	ND	ND	7/8	ND	520	1/2	ND	2.3
1,2,3,7,8,9-HxCDD	0/6	ND	ND	0/4	ND	ND	6/8	ND	645	1/2	ND	2.4
1,2,3,4,6,7,8-HpCDD	2/6	ND	26	1/4	ND	14	8/8	74	3,230	2/2	28	35
OCDD	1/6	ND	260	1/4	ND	130	8/8	390	9,700	2/2	200	640
2,3,7,8-TCDF	0/6	ND	ND	0/4	ND	ND	8/8	18	460	0/2	ND	ND
1,2,3,7,8-PeCDF	0/6	ND	ND	0/4	ND	ND	8/8	36	1,500	0/2	ND	ND
2,3,4,7,8-PeCDF	0/6	ND	ND	0/4	ND	ND	8/8	50	1,750	0/2	ND	ND
1,2,3,4,7,8-HxCDF	1/6	ND	5.8	0/4	ND	ND	8/8	180	7,550	1/2	ND	3.6
1,2,3,6,7,8-HxCDF	1/6	ND	3.8	0/4	ND	ND	8/8	74	3,650	1/2	ND	2.4
1,2,3,7,8,9-HxCDF	0/6	ND	ND	0/4	ND	ND	8/8	78	2,800	1/2	ND	3.8
2,3,4,6,7,8-HxCDF	1/6	ND	6.1	1/4	ND	6.5	7/8	ND	425	0/2	ND	ND
1,2,3,4,6,7,8-HpCDF	1/6	ND	26	3/4	ND	78	8/8	570	20,600	1/2	9.7	12
1,2,3,4,7,8,9-HpCDF	1/6	ND	6.2	2/4	ND	20	7/8	ND	12,000	1/2	ND	2
OCDF	2/6	ND	33	4/4	ND	900	8/8	1,800	4,200,000	2/2	39	43
Mean I-TEQ <sub>DF</sub> (nondetect = 0)		0.42			0.88			1,680			1.9	
Mean I-TEQ <sub>DF</sub> (nondetect = ½ DL)			4.4			4.7			1,680			3.6
Total TCDD	0/6	ND	ND	0/4	ND	ND	6/8	ND	730	1/2	ND	6.3
Total PeCDD	0/6	ND	ND	0/4	ND	ND	5/8	ND	1,630	1/2	ND	3.3
Total HxCDD	0/6	ND	ND	0/4	ND	ND	7/8	ND	3,915	1/2	ND	14
Total HpCDD	2/6	ND	48	1/4	ND	22	8/8	74	5,300	2/2	58	64
Total OCDD	1/6	ND	260	1/4	ND	130	8/8	390	9,700	2/2	200	640
Total TCDF	0/6	ND	ND	0/4	ND	ND	8/8	210	9,800	1/2	ND	4.8
Total PeCDF	0/6	ND	ND	0/4	ND	ND	8/8	380	18,000	1/2	ND	4
Total HxCDF	1/6	ND	30	1/4	ND	14	8/8	750	31,000	2/2	1.5	11
Total HpCDF	1/6	ND	49	3/4	ND	140	8/8	880	39,400	2/2	11	18
Total OCDF	2/6	ND	33	4/4	ND	900	8/8	1,800	4,200,000	2/2	39	43

<sup>a</sup>Method detection limits for individual samples were less than 10 pg/L for all congeners and congener groups except OCDD and OCDF, which had MDLs less than 50 pg/L.

<sup>b</sup>Dry-weight basis.

<sup>c</sup>Methods detection limits for all congeners were less than 150 ng/kg and usually were less than 10 ng/kg.

**Table 8-15. CDD/CDF measurements in treated wastewater and wastewater solids from U.S. EDC/VCM/PVC manufacturers (continued)**

Source: Vinyl Institute (1998).

EDC = Ethylene dichloride  
VCM = Vinyl chloride monomer  
PVC = Polyvinyl chloride  
DL = Detection limit  
ND = Not detected

**Table 8-16. Emissions data for wastewater from PVC/EDC/VCM manufacturing facilities**

Congener	Annual Release to Water (g/yr)							
	Dow Chemical Freeport, TX	Dow Chemical Plaquemine, LA	Georgia Gulf Plaquemine, LA	Occidental Convent, AL	Occidental Deer Park, TX	Occidental Ingleside, TX	Occidental LaPorte, TX	PPG Industries Lake Charles, LA
2,3,7,8-TCDD	0.00E+00	6.45E-02	6.90E-04	0.00E+00	0.00E+00	1.79E-02	0.00E+00	0.00E+00
1,2,3,7,8-PeCDD	0.00E+00	1.19E-01	3.55E-03	0.00E+00	0.00E+00	9.25E-02	0.00E+00	2.37E-03
1,2,3,4,7,8-HxCDD	5.64E-01	8.70E-01	3.98E-03	0.00E+00	2.20E-03	8.38E-02	0.00E+00	5.28E-03
1,2,3,6,7,8-HxCDD	0.00E+00	0.00E+00	4.46E-03	0.00E+00	2.64E-03	8.55E-02	0.00E+00	6.27E-03
1,2,3,7,8,9-HxCDD	3.52E-01	5.34E-01	5.00E-03	0.00E+00	2.45E-03	7.70E-02	0.00E+00	4.60E-03
1,2,3,4,6,7,8-HpCDD	1.98E+01	2.90E+01	3.43E-02	3.26E-04	7.67E-02	9.50E-02	0.00E+00	4.03E-01
OCDD	1.23E+02	6.29E+02	1.18E-01	1.49E-01	1.19E+00	1.84E-01	5.18E-02	2.97E+00
2,3,7,8-TCDF	2.77E+00	4.78E+00	7.61E-03	2.85E-04	5.08E-05	1.60E-02	0.00E+00	6.47E+00
1,2,3,7,8-PeCDF	3.71E+00	3.77E+00	6.57E-03	6.00E-04	2.35E-03	8.91E-02	0.00E+00	1.43E+01
2,3,4,7,8-PeCDF	1.67E+00	2.01E+00	2.11E-02	1.03E-04	3.68E-03	8.89E-02	0.00E+00	1.08E+01
1,2,3,4,7,8-HxCDF	2.76E+01	2.22E+01	2.00E-02	1.72E-02	3.71E-02	8.83E-02	4.21E-02	1.23E+01
1,2,3,6,7,8-HxCDF	0.00E+00	0.00E+00	1.41E-02	1.89E-04	2.77E-02	1.03E-01	0.00E+00	3.96E+00
1,2,3,7,8,9-HxCDF	0.00E+00	1.08E+00	9.34E-03	0.00E+00	2.89E-02	9.80E-02	0.00E+00	3.23E+00
2,3,4,6,7,8-HxCDF	6.08E+00	3.82E+00	7.89E-03	0.00E+00	1.44E-02	9.68E-02	0.00E+00	1.57E+00
1,2,3,4,6,7,8-HpCDF	1.31E+02	1.64E+02	1.11E-01	2.51E-04	6.90E-01	1.00E-01	1.18E-01	4.41E+00
1,2,3,4,7,8,9-HpCDF	1.93E+01	1.18E+01	2.41E-02	0.00E+00	2.61E-01	9.70E-02	3.18E-02	2.64E+00
OCDF	3.31E+02	3.81E+02	4.05E-01	3.55E-02	5.85E+00	1.85E-01	6.72E-01	1.21E+01
Total I-TEQ <sub>DF</sub>	6.91E+00	7.71E+00	2.28E-02	2.04E-03	3.08E-02	1.81E-01	6.43E-03	8.98E+00
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	6.50E+00	6.86E+00	2.41E-02	1.87E-03	2.45E-02	2.27E-01	5.78E-03	8.97E+00

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**Table 8-17. Emissions data for wastewater from chlor-alkali production facilities**

Congener	Annual Release to Water (g/yr)							
	Dow Chemical Midland, TX	Occidental Battleground, TX	Occidental Deer Park, TX	Occidental Delaware City, DE	Occidental Hahnville, LA	Occidental Mobile, AL	Occidental Muscle Shoals, AL	PPG Industries Natrium, WV
2,3,7,8-TCDD	0.00E+00	0.00E+00	2.40E-02	0.00E+00	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	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1,2,3,4,7,8-HxCDD	1.72E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1,2,3,6,7,8-HxCDD	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1,2,3,7,8,9-HxCDD	0.00E+00	0.00E+00	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-HpCDD	5.44E-01	0.00E+00	7.79E-01	0.00E+00	1.33E-02	0.00E+00	0.00E+00	2.21E-01
OCDD	3.63E+00	4.83E-01	2.15E+01	4.09E-03	9.74E-02	1.15E-03	1.13E-09	3.13E+00
2,3,7,8-TCDF	1.55E-02	0.00E+00	6.31E-01	1.02E-03	1.93E-01	2.88E-04	3.94E-08	6.38E-02
1,2,3,7,8-PeCDF	0.00E+00	0.00E+00	1.20E+00	0.00E+00	8.97E-01	0.00E+00	1.33E-07	6.23E-02
2,3,4,7,8-PeCDF	8.64E-03	0.00E+00	2.07E-01	0.00E+00	8.51E-01	0.00E+00	7.99E-08	3.29E-01
1,2,3,4,7,8-HxCDF	5.90E-02	0.00E+00	2.11E+00	0.00E+00	2.96E+00	0.00E+00	1.85E-07	1.11E-01
1,2,3,6,7,8-HxCDF	0.00E+00	0.00E+00	3.80E-01	0.00E+00	1.18E+00	0.00E+00	9.76E-08	0.00E+00
1,2,3,7,8,9-HxCDF	0.00E+00	0.00E+00	2.03E-03	0.00E+00	6.31E-01	0.00E+00	2.29E-08	0.00E+00
2,3,4,6,7,8-HxCDF	3.96E-02	0.00E+00	0.00E+00	0.00E+00	6.00E-01	0.00E+00	3.28E-08	0.00E+00
1,2,3,4,6,7,8-HpCDD	8.81E-01	0.00E+00	5.91E-01	2.31E-03	4.47E+00	6.49E-04	1.32E-07	1.54E-01
1,2,3,4,7,8,9-HpCDD	1.45E-02	0.00E+00	5.66E-03	0.00E+00	6.89E-01	0.00E+00	6.30E-08	0.00E+00
OCDF	1.25E+00	0.00E+00	4.88E+00	0.00E+00	1.75E+00	0.00E+00	1.34E-07	6.60E-01
Total I-TEQ <sub>DF</sub>	3.67E-02	4.83E-04	5.40E-01	1.30E-04	1.08E+00	3.64E-05	8.65E-08	1.93E-01
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	3.23E-02	4.83E-05	5.16E-01	1.26E-04	1.08E+00	3.54E-05	8.64E-08	1.89E-01

Source: Chlorine Chemistry Council CDD/CDF Data Validation Project (2004).

**Table 8-18. Congener-Specific land releases for PVC/EDC/VCM manufacturing facilities**

Congener	Annual Release to Land (g/yr)
	Georgia Gulf Plaquemine, LA
2,3,7,8-TCDD	4.19E-03
1,2,3,7,8-PeCDD	3.91E-02
1,2,3,4,7,8-HxCDD	1.23E-01
1,2,3,6,7,8-HxCDD	1.22E-01
1,2,3,7,8,9-HxCDD	7.77E-02
1,2,3,4,6,7,8-HpCDD	1.71E+00
OCDD	8.64E+00
2,3,7,8-TCDF	7.65E-02
1,2,3,7,8-PeCDF	3.54E-01
2,3,4,7,8-PeCDF	3.70E-01
1,2,3,4,7,8-HxCDF	2.69E+00
1,2,3,6,7,8-HxCDF	2.11E+00
1,2,3,7,8,9-HxCDF	1.54E+00
2,3,4,6,7,8-HxCDF	5.95E-01
1,2,3,4,6,7,8-HpCDD	2.81E+01
1,2,3,4,7,8,9-HpCDD	6.54E+00
OCDF	1.18E+02
Total I-TEQ <sub>DF</sub>	1.45E+00
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	1.36E+00

Source: Chlorine Chemistry Council CDD/CDF Data Validation Project (2004).

**Table 8-19. Congener-specific air emissions for PVC/EDC/VCM manufacturing facilities**

Congener	Annual Release to Air (g/yr)							
	Dow Chemical Freeport, TX	Dow Chemical Plaquemine, LA	Georgia Gulf Plaquemine, LA	Occidental Convent, AL	Occidental Deer Park, TX	Occidental Ingleside, TX	Occidental LaPorte, TX	PPG Industries Lake Charles, LA
2,3,7,8-TCDD	1.42E-02	6.11E-05	1.64E-03	4.53E-03	0.00E+00	5.96E-03	0.00E+00	2.28E-04
1,2,3,7,8-PeCDD	1.98E-01	4.98E-03	2.68E-03	1.03E-02	9.76E-03	3.38E-02	6.81E-03	2.20E-04
1,2,3,4,7,8-HxCDD	1.01E+00	2.80E-02	2.83E-03	3.79E-03	4.72E-02	1.07E-01	9.37E-03	1.89E-03
1,2,3,6,7,8-HxCDD	0.00E+00	0.00E+00	2.34E-03	9.96E-03	3.27E-02	1.22E-01	1.65E-02	7.61E-04
1,2,3,7,8,9-HxCDD	3.86E-01	1.18E-02	1.26E-03	4.84E-03	5.64E-02	8.99E-02	9.83E-03	4.50E-04
1,2,3,4,6,7,8-HpCDD	3.73E+00	1.02E-01	1.64E-02	5.68E-03	1.37E+00	1.58E+00	1.51E-01	6.09E-03
OCDD	9.46E+00	2.65E-01	1.24E-01	4.74E-03	1.35E+01	9.51E+00	4.75E-01	3.95E-02
2,3,7,8-TCDF	1.26E+00	2.63E-02	9.20E-02	1.52E-02	5.71E-02	4.38E-02	7.78E-03	1.29E-02
1,2,3,7,8-PeCDF	1.80E+00	3.84E-02	7.21E-02	1.74E-02	1.21E-01	3.54E-01	2.42E-02	1.28E-02
2,3,4,7,8-PeCDF	1.28E+00	3.15E-02	3.46E-02	9.22E-03	1.42E-01	3.71E-01	2.53E-02	8.71E-03
1,2,3,4,7,8-HxCDF	1.20E+01	3.96E-01	1.71E-01	1.44E-02	1.38E+00	3.58E+00	4.13E-02	4.81E-02
1,2,3,6,7,8-HxCDF	0.00E+00	0.00E+00	7.09E-02	8.52E-03	5.82E-01	3.38E+00	3.62E-02	2.50E-02
1,2,3,7,8,9-HxCDF	3.43E-01	4.77E-03	4.17E-02	3.15E-03	5.55E-01	7.73E-01	8.02E-03	9.68E-03
2,3,4,6,7,8-HxCDF	2.50E+00	4.80E-02	1.33E-02	1.33E-03	5.56E-02	1.94E+00	4.09E-02	8.79E-03
1,2,3,4,6,7,8-HpCDD	3.23E+01	1.47E+00	3.17E-01	1.96E-02	1.19E+01	2.57E+01	2.49E-01	2.77E-01
1,2,3,4,7,8,9-HpCDD	5.34E+00	9.81E-02	3.43E-02	2.36E-03	2.32E+00	5.13E+00	2.31E-02	4.12E-02
OCDF	6.69E+01	3.21E+00	1.01E+00	1.53E-02	5.28E+01	4.69E+01	2.31E-01	7.50E-01
Total I-TEQ <sub>DF</sub>	3.08E+00	9.19E-02	6.82E-02	2.16E-02	5.81E-01	1.61E+00	3.92E-02	2.01E-02
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	3.11E+00	9.12E-02	6.85E-02	2.67E-02	5.26E-01	1.58E+00	4.19E-02	1.95E-02

Source: Chlorine Chemistry Council CDD/CDF Data Validation Project (2004).

**Table 8-20. Congener-specific air emissions for chlor-alkali production facilities**

Congener	Annual Release to Air (g/yr)	
	Dow Chemical Midland, TX	PPG Industries Natrium, WV
2,3,7,8-TCDD	2.65E-02	2.81E-03
1,2,3,7,8-PeCDD	3.86E-03	0.00E+00
1,2,3,4,7,8-HxCDD	8.05E-03	0.00E+00
1,2,3,6,7,8-HxCDD	0.00E+00	2.01E-03
1,2,3,7,8,9-HxCDD	3.32E-03	2.01E-03
1,2,3,4,6,7,8-HpCDD	2.03E-02	8.67E-02
OCDD	8.63E-02	2.08E-01
2,3,7,8-TCDF	2.28E-02	4.38E-02
1,2,3,7,8-PeCDF	9.10E-03	3.21E-03
2,3,4,7,8-PeCDF	7.63E-03	3.01E-02
1,2,3,4,7,8-HxCDF	6.61E-02	4.42E-02
1,2,3,6,7,8-HxCDF	0.00E+00	6.42E-03
1,2,3,7,8,9-HxCDF	1.82E-03	6.02E-03
2,3,4,6,7,8-HxCDF	9.03E-03	2.17E-02
1,2,3,4,6,7,8-HpCDD	1.48E-01	1.42E-01
1,2,3,4,7,8,9-HpCDD	2.78E-02	3.89E-02
OCDF	2.25E-01	6.38E-02
Total I-TEQ <sub>DF</sub>	4.61E-02	3.36E-02
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	4.77E-02	3.33E-02

Source: Chlorine Chemistry Council CDD/CDF Data Validation Project (2004).



**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 <sup>d</sup>		
	No. detects/ samples <sup>a</sup>	Range <sup>b</sup> (ng/kg)		No. of detects/ samples	Range <sup>c</sup> (ng/kg)		No. detects/ samples	Range <sup>c</sup> (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 <sub>DF</sub> (nondetect = 0)		0.002			0.001			0.001	
Mean I-TEQ <sub>DF</sub> (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

<sup>a</sup>Two of these 22 samples were duplicate samples from two sites. The results were averaged and treated as one sample for each site.

<sup>b</sup>Method detection limits (MDLs) for individual samples were less than 2 ng/kg for all congeners and congener groups except OCDD and OCDF, which had MDLs less than 6 ng/kg.

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<sup>c</sup>MDLs for individual samples were less than 2 ng/kg for all congeners and congener groups except OCDD and OCDF, which had MDLs less than 4 ng/kg.

<sup>d</sup>“Sales” EDC is defined as EDC sold commercially for non-VCM uses or exported from the United States.

<sup>e</sup>MDLs were less than 1 ng/kg for all congeners in all samples.

DL = Detection limit

ND = Not detected

Source: Vinyl Institute (1998).

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**Table 8-22. CDD/CDF concentrations in samples of dioxazine dyes and pigments (µg/kg) (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 <sup>a</sup>										
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	1,031	139	3,799	1,591	157	444
Total I-TEQ <sub>DF</sub> <sup>b</sup>	56.4	30.3	19.5	0.1	16.0	1.4	18.9	12.7	2.7	2.7
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> <sup>b</sup>	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 <sup>b</sup>	54,533	30,012	19,112	47	8,275	957	14,882	9,540	1,787	1,880

<sup>a</sup>Results listed for 1,2,3,4,7,8-HxCDF include concentrations for 1,2,3,6,7,8-HxCDF.<sup>b</sup>Calculations assume nondetected values are equal to zero.

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

ND = Not detected (value in parenthesis is the detection limit)

-- = Not reported

Source: Williams et al. (1992).

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

<b>Congener/congener group</b>	<b>Rotogravure (2-color)</b>	<b>Rotogravure (4-color)</b>	<b>Offset (4-color)</b>	<b>Offset (4-color)</b>
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 <sub>DF</sub> <sup>a</sup>	88.6	62.4	35.4	15
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	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
<b>Total CDD/CDF</b>	<b>14,422</b>	<b>8,527</b>	<b>4,813</b>	<b>1,451</b>

<sup>a</sup>Calculations assume nondetect values were zero.

ND = Not detected (value in parenthesis is the detection limit)

-- = Not reported

Source: Santl et al. (1994).

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

<b>Currently manufactured or imported as of June 5, 1987</b>	
<b>CAS No.</b>	<b>Chemical name</b>
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 <sup>a</sup>
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 <sup>a</sup>
<b>Not currently manufactured or imported as of June 5, 1987<sup>b</sup></b>	
<b>CAS No.</b>	<b>Chemical name</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

<sup>a</sup>No longer manufactured in or imported into the United States (Cash, 1993).

<sup>b</sup>As of August 5, 1995, neither manufacture nor importation of any of these chemicals had resumed in the United States (Holderman, 1995).

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

<b>Chlorinated dioxins and furans</b>	<b>Brominated dioxins and furans</b>	<b>LOQ (µg/kg)</b>
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

**Table 8-26. Precursor chemicals subject to reporting requirements under Toxic Substances Control Act Section 8(a)<sup>a</sup>**

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-toloxo 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

<sup>a</sup>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.



**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**

<b>CAS number</b>	<b>Chemical name</b>	<b>No. of chemical companies that submitted data</b>	<b>No. of positive studies</b>	<b>Congeners detected (detection range in µg/kg)</b>
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 8-26
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(tribromophenoxy)-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

<sup>a</sup>No 2,3,7,8-substituted dioxins and furans detected above the test rule target limits of quantitation (see Table 8-18).

Source: Holderman and Cramer (1995).

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

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 <sub>DF</sub> <sup>a</sup>	263	2,874	814	3,065	211
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> <sup>a</sup>	31	2,532	85	2,903	156

<sup>a</sup>Calculated assuming nondetect values are zero.

ND = Not detected (value in parenthesis is the minimum detection limit)

Source: Remmers et al. (1992).

**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 number	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-triodobenzoate	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	--

**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 number	Support withdrawn	Testing required
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	--
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	Not available	Yes	--
62209	4-Chloro-2-phenylphenol, potassium salt	53404-21-0	Yes	--
62210	6-Chloro-2-phenylphenol	85-97-2	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 number	Support withdrawn	Testing required
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	--
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)]	Not available	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	Not available	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	--

**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 number	Support withdrawn	Testing required
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-xylene]	88-04-0	No	No
97003	Piperalin [3-(2-Methylpiperidino)propyl 3,4-dichlorobenzoate]	3478-94-2	No	No
100601	Fenamiphos	Not available	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	--
108201	Diflubenuron [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-trifluoromethylphenyl-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

**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 number	Support withdrawn	Testing required
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-(trifluoromethyl)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

-- = No information given

**Table 8-30. Status of second pesticide data call-in: pesticides suspected of being contaminated with dioxins**

Shaughnessey code	Pesticide [active ingredient]	CAS number	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 isopropanol series)	Not available	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)	Not available	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-Dimethylethylamine 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	--



**Table 8-30. Status of second pesticide data call-in: pesticides suspected of being contaminated with dioxins (continued)**

Shaughnessey code	Pesticide [active ingredient]	CAS number	Support withdrawn	Testing required
30034	Triethylamine 2,4-dichlorophenoxyacetate	2646-78-8	No	No
30035	Triisopropanolamine 2,4-dichlorophenoxyacetate	32341-80-3	No	No
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	MCPD acid [2-(2-Methyl-4-chlorophenoxy)propionic acid]	7085-19-0	No	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 number	Support withdrawn	Testing required
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	--
44902	Hexachlorophene, Na salt [Monosodium 2,2'-methylenebis(3,4,6-trichlorophenolate)]	5736-15-2	Yes	--
44904	Hexachlorophene, K salt [Potassium 2,2'-methylenebis(3,4,6-trichlorophenolate)]	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)	Not available	Yes	--
63007	Tetrachlorophenols, potassium salt	53535-27-6	Yes	--
64203	Bithionolate sodium [Disodium 2,2'-thiobis(4,6-dichlorophenolate)]	6385-58-6	Yes	--
64212	Phenachlor [2,4,6-Trichlorophenol]	88-06-2	Yes	--
64219	Potassium 2,4,6-trichlorophenolate	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) methanesulfonamide]	69462-14-2	Yes	--

-- = No information given

**Table 8-31. Summary of analytical data submitted to EPA in response to pesticide data call-in(s)**

Shaughnessey code	Pesticide		Number of positive submissions <sup>a</sup> 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 (MCP)	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

<sup>a</sup>“Positive” is defined as the detection of any congener at a concentration equal to or exceeding the limits of quantitation listed in Table 8-23.

Sources: U.S. EPA (1995a); personal communication from S. Funk, U.S. EPA, to D. Cleverly, U.S. EPA, March 27, 1996.

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

<b>Congener</b>	<b>EPA LOQ<sup>a</sup> (µg/kg)</b>	<b>Total no. of technicals</b>	<b>Number of technicals greater than LOQ</b>	<b>Observed maximum conc. (µg/kg)</b>	<b>Average conc.<sup>b</sup> (µg/kg)</b>
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	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 <sup>c</sup>					5.6
I-TEQ <sub>DF</sub>					0.7
TEQ <sub>DF</sub> -WHO <sub>98</sub>					1.1

<sup>a</sup>LOQ required by EPA in the data call-in.

<sup>b</sup>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.

<sup>c</sup>Total equals the sum of the individual congener averages.

LOQ = Limit of quantitation

-- = Analyses not performed

Source: U.S. EPA Office of Pesticide Program file.

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

Congener/Congener group	Acbar Super (Gaza City <sup>a</sup> )	Amco Super (Gaza City <sup>a</sup> )	(Bethlehem)	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	--	--
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	--	--
Total I-TEQ <sub>DF</sub> (nondetect = 0) <sup>b</sup>	0.082	0.066	0.85	0.142	0.0023	0.0009	0.0012	0.0014	0.0013	0.0019	0.0078	ND
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (nondetect = 0) <sup>b</sup>	0.134	0.061	1.449	0.156	0.003						0.013	ND
Total TCDD	--	--	--	--	--	--	--	--	--	--	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

<sup>a</sup>2,4-D manufactured in Europe and packaged in Palestine.<sup>b</sup>Calculated assuming nondetect values are zero.

ND = not detected (value in parenthesis is the detection limit)

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

-- = No information given

Sources: Schecter et al. (1997); Maunaga et al. (2001).

**Table 8-34. Mean CDD/CDF measurements in effluents from nine U.S. publicly owned treatment works (POTWs)**

Congener/congener group	No. of detections/samples	Range of DLs (pg/L)	Range of detected concentrations (POTW mean basis) (pg/L)		Overall mean concentrations <sup>a</sup>	
			Minimum	Maximum	Nondetect set to 0 (pg/L)	Nondetect set to ½ DL (pg/L)
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	99.75	30.57	47.98
Total 2,3,7,8-CDF			ND	16.6	2.37	15.49
Total I-TEQ <sub>DF</sub>			ND	2.42	0.29	3.66
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>			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	99.75	42	71.96

<sup>a</sup>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: CRWQCB (1996).

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

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 <sup>a</sup>	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	2500	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 S	ND (0.16)	ND (0.24)	ND (0.24)	ND (0.11)	1.2	4.5	59	0.77	0.32
Hattiesburg N	ND (0.19)	0.18	ND (0.26)	ND (0.13)	0.96	9.1	73	2.9	0.457
Average (nondetect = 0)	0.17	1.42	0.36	0.2	4.43	16.3	221.76	8.99	0.81

<sup>a</sup>Blind double.

ND = Not detected (value in parenthesis is the detection limit)

Source: Rappe et al. (1998).



**Table 8-36. CDD/CDF concentrations measured in EPA's 1998/1999 National Sewage Sludge Survey**

Congener	Percent detected	Maximum concentration detected (ng/kg)	Median concentration (ng/kg)		Mean concentration (ng/kg)	
			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 <sub>DF</sub>		1,820	50.4	11.2	86 <sup>a</sup>	50 <sup>a</sup>
Total 2,3,7,8-CDD/CDF		--	--	--	--	--

<sup>a</sup>Values presented by Rubin and White (1992) for 175 rather than 174 publicly owned treatment works.

-- = No information given

Source: U.S. EPA (1996a); for publicly owned treatment works with multiple samples, the pollutant concentrations were averaged before the summary statistics presented in the table were calculated.

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

Congener	Percent detected	Maximum concentration detected (ng/kg)	Median concentration (ng/kg)		Mean concentration (ng/kg)	
			Nondetect set to detection limit	Nondetect set to zero	Nondetect set to detection limit <sup>a</sup>	Nondetect set to zero <sup>a</sup>
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 <sub>DF</sub> (facility basis) <sup>b</sup>		246	49.6	33.4	64.5 (50.1)	47.7 (44.7)
Total 2,3,7,8-CDD/CDF		73,520	7,916	7,881	14,110 (14,390)	13,880 (14,200)
Average TEQ <sub>DF</sub> -WHO <sub>98</sub> (facility basis) <sup>b</sup>			44.6	25.5	57.2 (44.4)	36.3 (38.6)

<sup>a</sup>Value in parenthesis is the standard deviation.

<sup>b</sup>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.

Source: Green et al. (1995); Cramer et al. (1995).

**Table 8-38. Sewage sludge concentrations from publicly owned treatment works in Mississippi (ng/kg dry matter)**

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 <sup>a</sup>	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	1,300	4,400	180	33
Hattiesburg N	ND (0.035)	1.7	4	2	310	3,600	27,000	980	70.4
Average (nondetect = 0)	1.2	9.7	11	3.4	1,900	26,000	55,000	2,000	116 ± 323

<sup>a</sup>Blind double.

ND = Not detected (value in parenthesis is the detection limit)

Source: Rappe et al. (1998).

**Table 8-39. CDD/CDF concentrations measured in 1999 from a publicly owned treatment works facility in Ohio**

Congener	Median Concentration (ng/kg)	
	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 <sub>DF</sub> -WHO <sub>98</sub>	21.87	21.88

Source: U.S. EPA (2000).

**Table 8-40. CDD/CDF concentrations measured in the EPA 2001 National Sewage Sludge Survey**

Congener	Mean concentration (ng/kg)	
	Nondetect set to zero	Nondetect set to $\frac{1}{2}$ 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 <sub>DF</sub> -WHO <sub>98</sub>	21.7	15.5

Source: U.S. EPA (2002a).

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

Use/disposal practice	Volume disposed of (thousands of dry metric tons/yr)	Percent of total volume	Potential dioxin release <sup>a</sup> (g of TEQ/yr)	
			I-TEQ <sub>DF</sub>	TEQ <sub>DF</sub> -WHO <sub>98</sub>
Land application	1,714	32 <sup>b</sup>	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 <sup>c</sup>	1,819	33.9	89.1	66
Sludge incinerators and co-incinerators <sup>d</sup>	865	16.1	e	e
Ocean disposal	(336) <sup>f</sup>	(6.3) <sup>f</sup>	f	f
<b>TOTAL</b>	<b>5,357</b>	<b>100</b>	<b>204</b>	<b>151</b>

<sup>a</sup>Potential dioxin TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (column 2) by the average of the mean I-TEQ<sub>DF</sub> 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<sub>DF</sub>-WHO<sub>98</sub> used the mean concentration of 36.3 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg for the results reported by Green et al. (1995) and Cramer et al. (1995).

<sup>b</sup>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.

<sup>c</sup>Landfills used for disposal of sewage sludge and solid waste residuals.

<sup>d</sup>Co-incinerators treat sewage sludge in combination with other combustible waste materials.

<sup>e</sup>See Section 3.5 for estimates of CDD/CDF releases to air from sewage sludge incinerators.

<sup>f</sup>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, 1993b). 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.

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

Use/disposal practice	Volume disposed of (thousands of dry metric tons/yr)	Percent of total volume	Potential dioxin release <sup>a</sup> (g TEQ/yr)	
			I-TEQ <sub>DF</sub>	TEQ <sub>DF</sub> -WHO <sub>98</sub>
Land application <sup>b</sup>	2,500	41	122.3	90.7
Advanced treatment <sup>c</sup>	700	12	34.2	25.4
Other beneficial use <sup>d</sup>	500	7	24.5	18.2
Surface disposal/landfill	1,100	17	53.8	39.9
Incineration	1,400	22	e	e
Other disposal method	100	1	4.9	3.6
<b>TOTAL</b>	<b>6,300</b>	<b>100</b>	<b>240</b>	<b>178</b>

<sup>a</sup>Potential dioxin TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (column 2) by the average of the mean I-TEQ<sub>DF</sub> 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<sub>DF</sub>-WHO<sub>98</sub> used the mean concentration of 36.3 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg for the results reported by Green et al. (1995) and Cramer et al. (1995).

<sup>b</sup>Without further processing or stabilization, such as composting.

<sup>c</sup>Such as composting.

<sup>d</sup>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, 1993b). Therefore, it is estimated that 3 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (4 g I-TEQ<sub>DF</sub>) were released through distribution and marketing in 1995.

<sup>e</sup>See Section 3.5 for estimates of CDD/CDF releases to air from sewage sludge incinerators.

Sources: Federal Register (1990, 1993b).

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

Use/disposal practice	Volume disposed of (thousands of dry metric tons/yr)	Percent of total volume	Potential dioxin release <sup>a</sup> (g TEQ/yr)
			TEQ <sub>DF</sub> -WHO <sub>98</sub>
Land application <sup>b</sup>	2,800	43	60.8
Advanced treatment <sup>c</sup>	800	12.5	17.4
Other beneficial use <sup>d</sup>	500	7.5	10.9
Surface disposal/landfill	900	14	19.5
Incineration	1,500	22	e
Other disposal method	100	1	2.17
<b>TOTAL</b>	<b>6,600</b>	<b>100</b>	<b>111</b>

<sup>a</sup> Potential dioxin TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (i.e., column 2) by the average of the mean TEQ<sub>DF</sub>-WHO<sub>98</sub> concentrations in sludge reported by U.S. EPA (2002).

<sup>b</sup> Without further processing or stabilization, such as composting.

<sup>c</sup> Such as composting.

<sup>d</sup> 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, 1993b). Therefore, it is estimated that 1.9 g TEQ<sub>DF</sub>-WHO<sub>98</sub> were released through distribution and marketing in 2000.

<sup>e</sup> 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**

<b>Use/disposal practice</b>	<b>Volume disposed of (thousands of dry metric tons/yr)</b>	<b>Percent of total volume</b>
Land application	3,100	61
Surface disposal/landfill	940	18
Incineration	1,000	20
Other	64	1
<b>TOTAL</b>	<b>5,100</b>	<b>100</b>

Source: NRC (2002).

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

<b>Congener/congener group</b>	<b>Liquid soap (ng/L)</b>	<b>Tall oil (ng/kg)</b>	<b>Tall resin (ng/kg)</b>
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 <sup>a</sup>	3.8	14.2	13,213.1
Total 2,3,7,8-CDF <sup>a</sup>	1.123	25.2	43
Total I-TEQ <sub>DF</sub> <sup>a</sup>	0.447	9.4	200
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> <sup>a</sup>	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
<b>Total CDD/CDF<sup>a</sup></b>	<b>25.57</b>	<b>491.5</b>	<b>23,900</b>

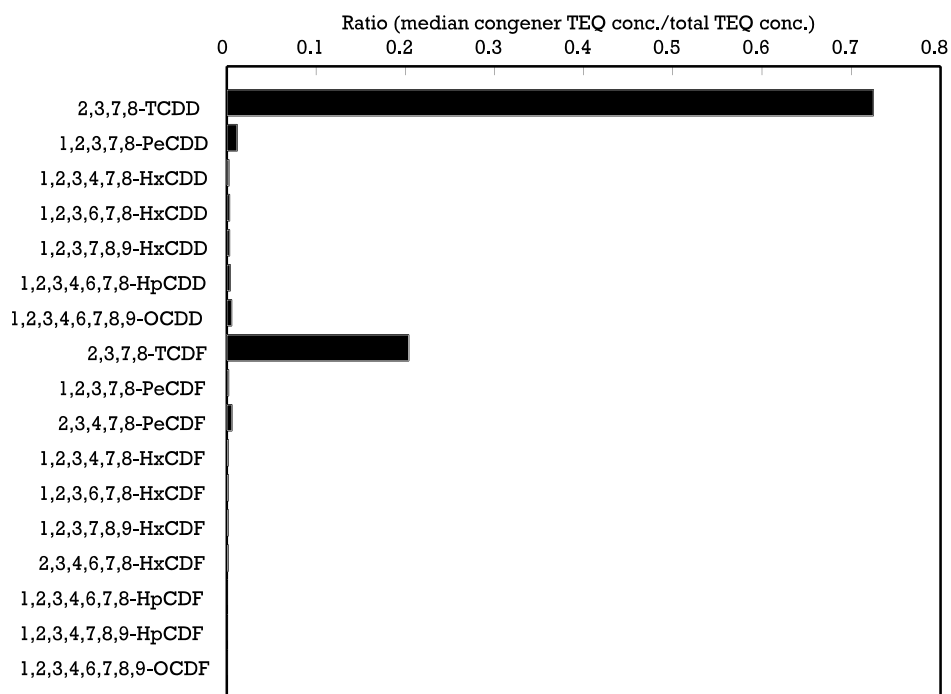
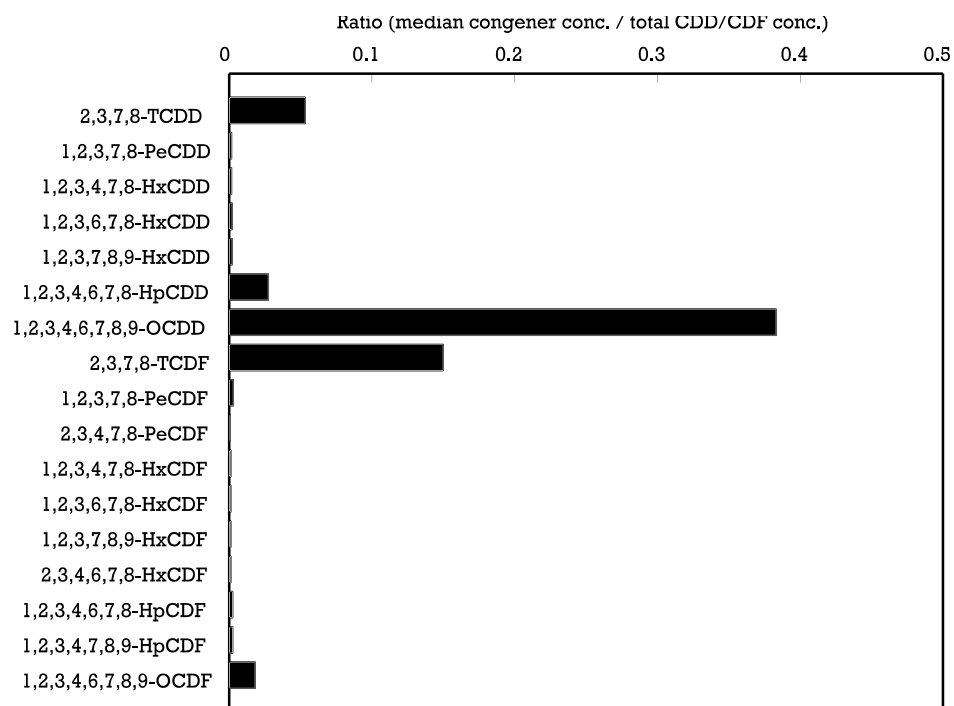
<sup>a</sup>Calculations assume nondetect values are zero.

ND = Not detected (value in parenthesis is the detection limit)

NA = Not analyzed

-- = No information given

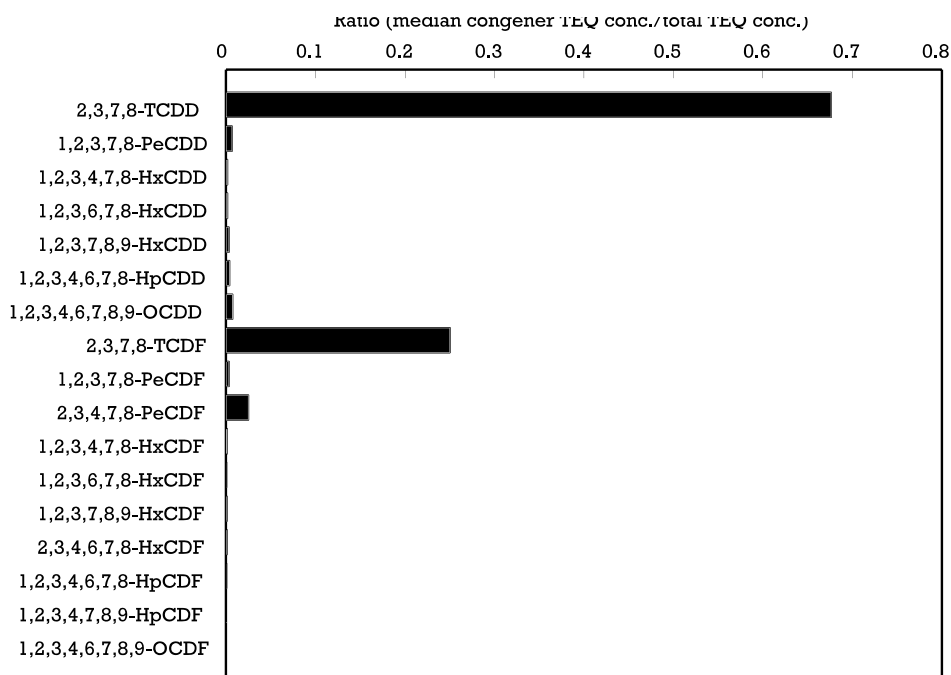
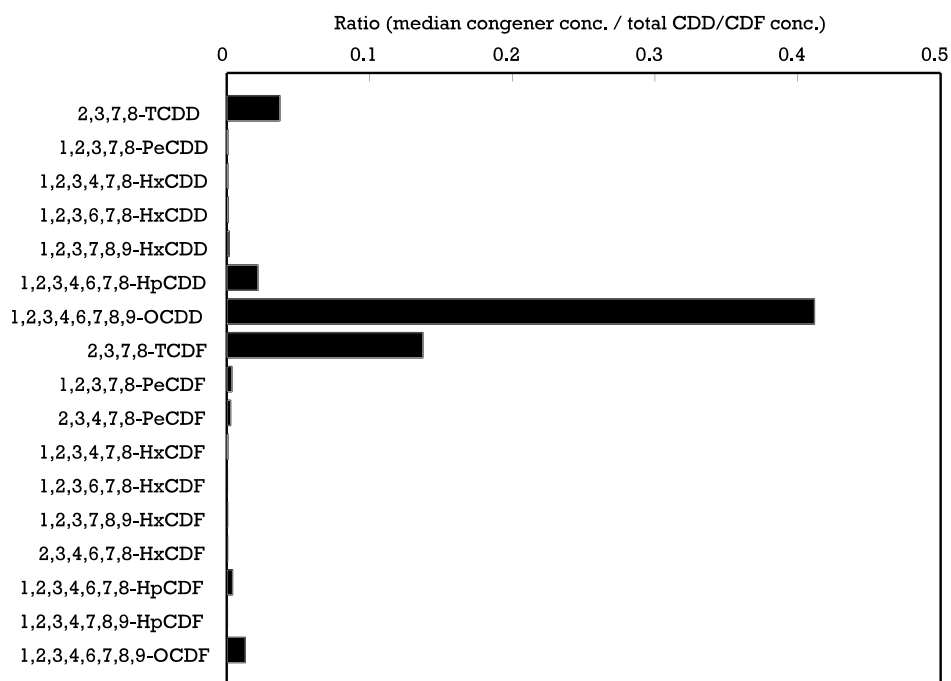
Source: Rappe et al. (1990c).



Nondetects set equal to 1/2 detection limit.

**Figure 8-1. 104 Mill Study full congener analysis results for pulp.**

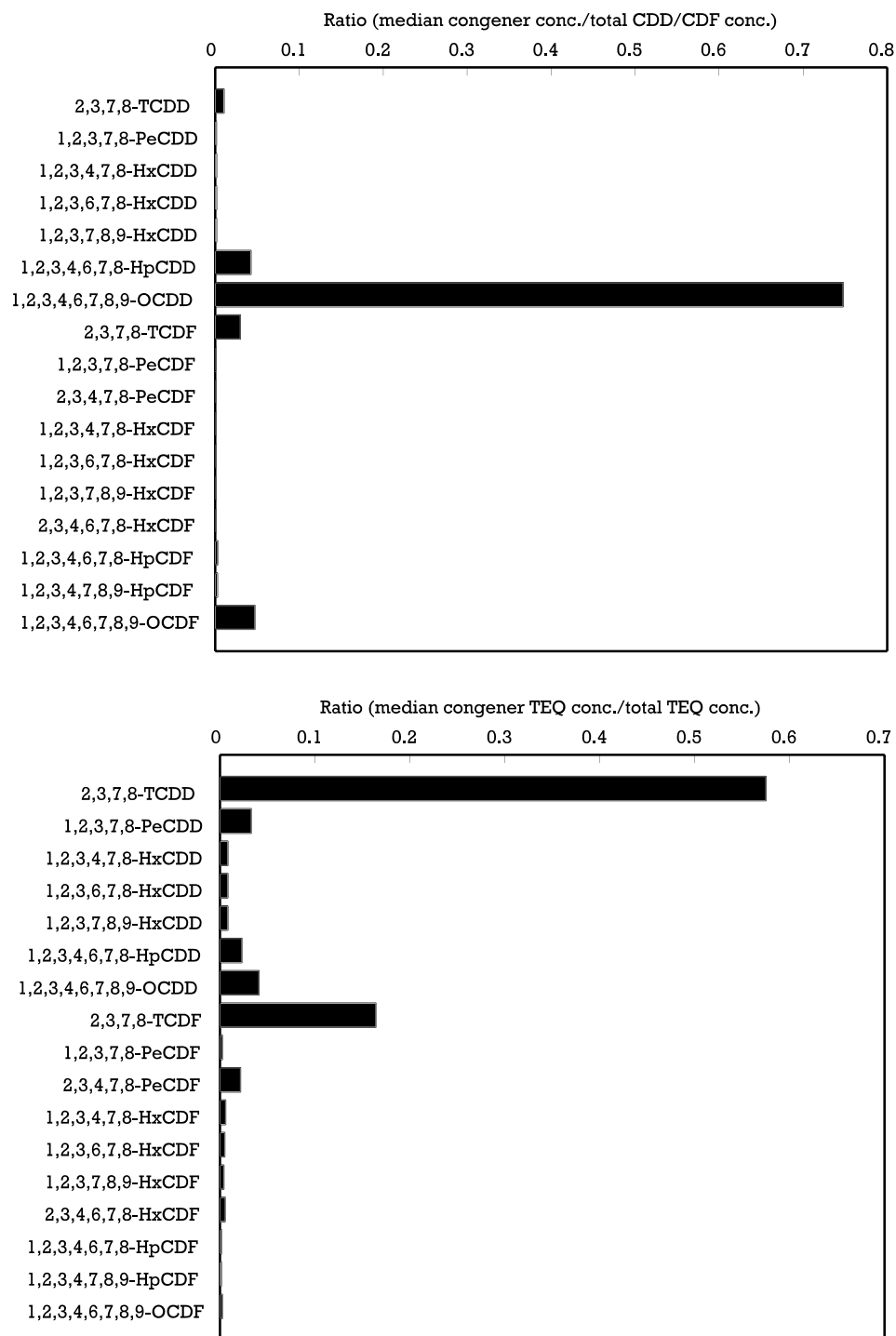
Source: Median concentrations from U.S. EPA (1990a).



Nondetects set equal to 1/2 detection limit.

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

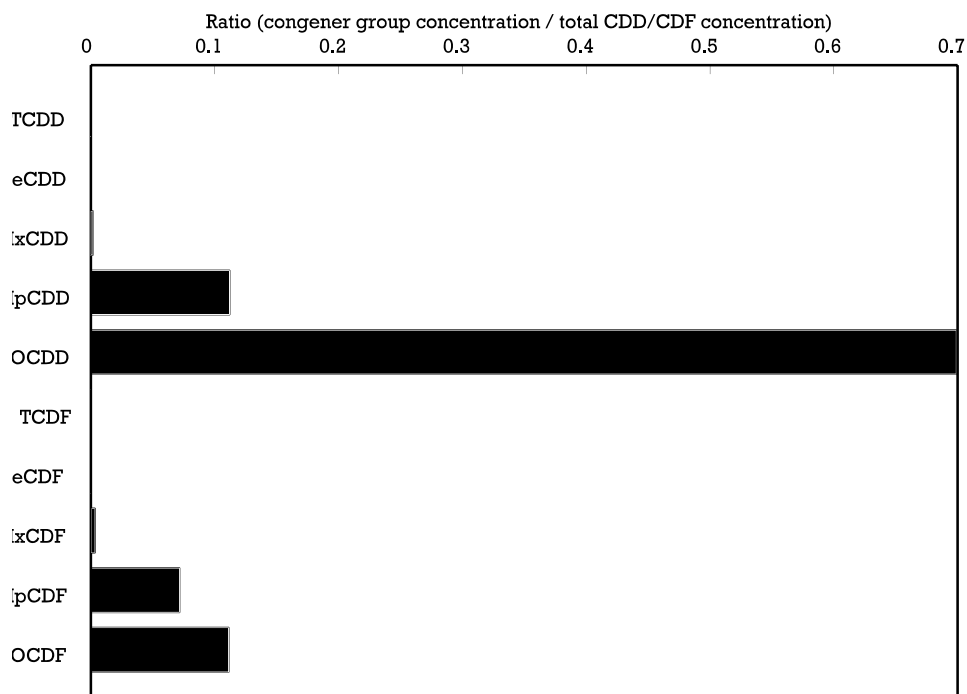
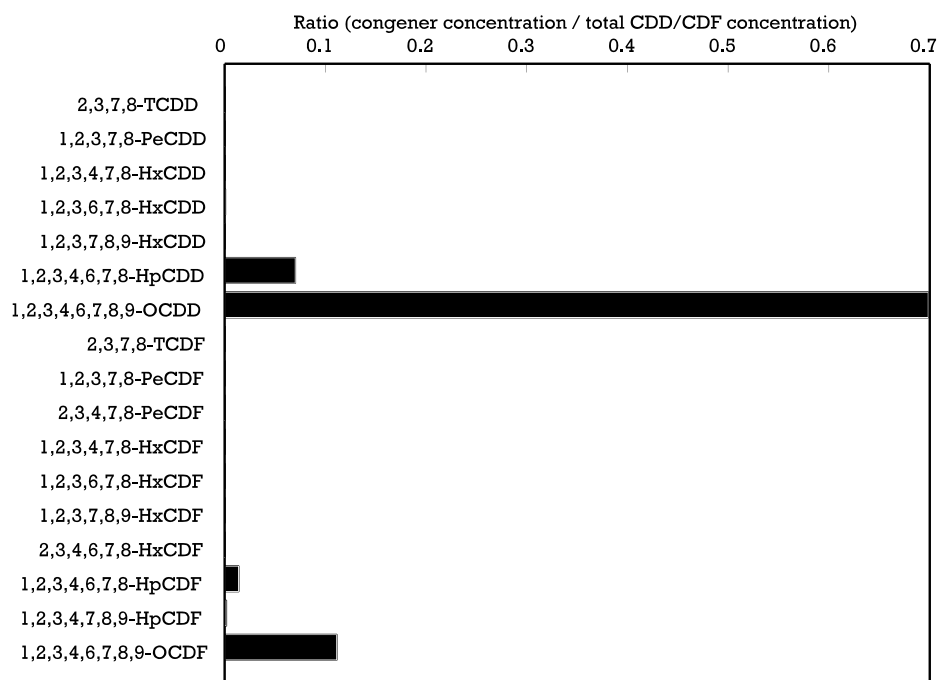
Source: Median concentrations from U.S. EPA (1990a).



Nondetects set equal to ½ detection limit.

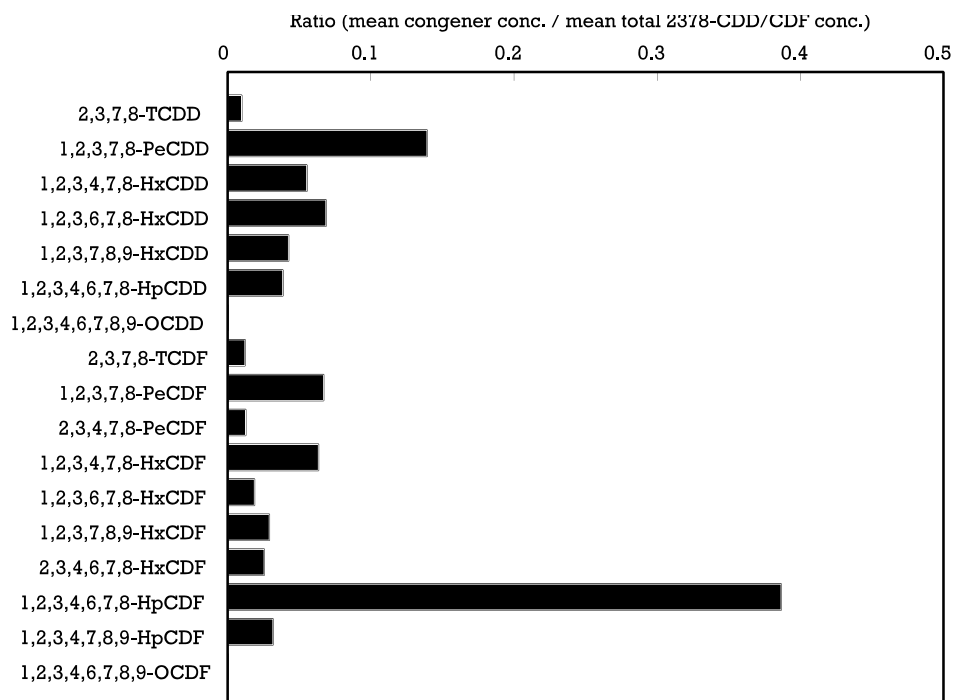
**Figure 8-3. 104 Mill Study full congener analysis results for effluent**

Source: Median concentrations from U.S. EPA (1990a).



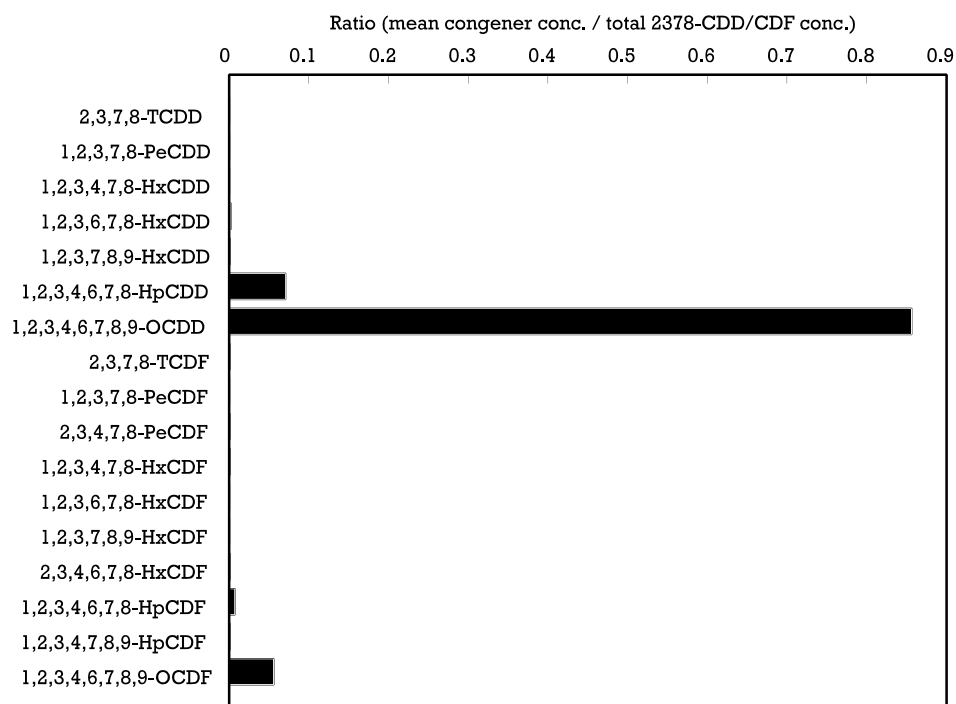
Nondetects set equal to zero.

**Figure 8-4. Congener and congener group profiles for technical-grade PCP**  
(based on data reported in Table 8-7).

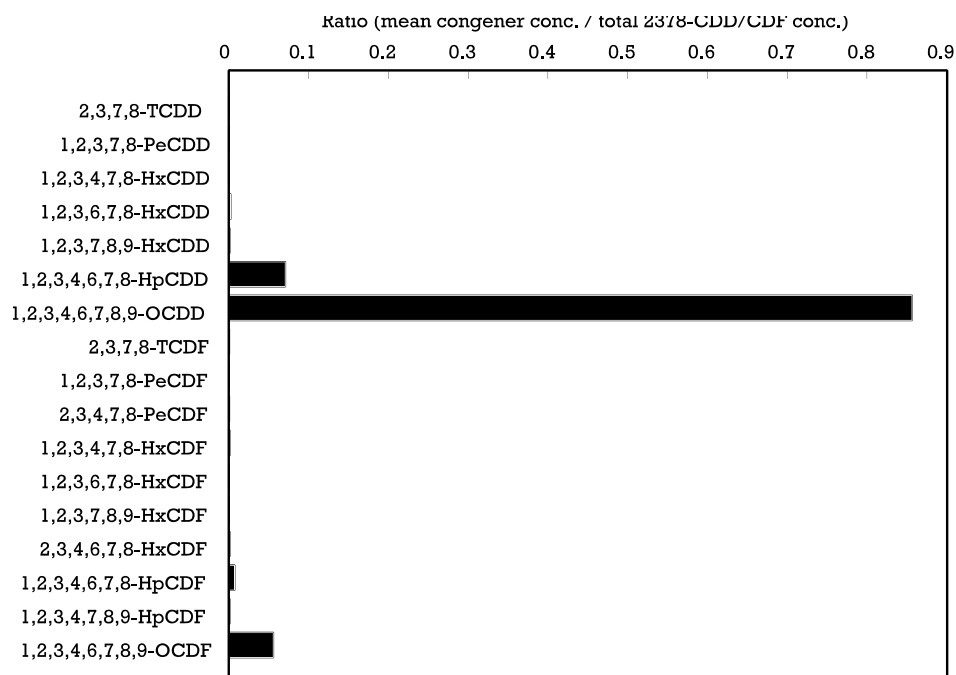


Nondetect set equal to zero.

**Figure 8-5. Congener profile for 2,4-D (salts and esters)** (based on mean concentrations reported in Table 8-26).



Nondetects set equal to 1/2 detection limit.



**Figure 8-6. Congener profiles for sewage sludge**

Source: Green et al. (1995).



## 9. BIOLOGICAL SOURCES OF CDDs/CDFs

Numerous laboratory and field research studies have demonstrated that biochemical 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 origin of the CDDs/CDFs that were recently discovered in ball clay deposits is not yet determined, and natural occurrence is still considered a possibility. Chapter 13 discusses this topic in detail.

### 9.1. BIOTRANSFORMATION OF CHLOROPHENOLS

Biochemical formation of CDDs/CDFs, particularly the more-highly chlorinated congeners, from chlorophenol precursors is possible, as indicated in laboratory studies with solutions of trichlorophenols and 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 and CDFs were typically the dominant congener groups found. The I-TEQ<sub>DF</sub> content of the composts ranged from 0.8 to 35.7 ng I-TEQ<sub>DF</sub>/kg. The CDDs/CDFs found in compost may be primarily the result of 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) reported a conversion efficiency of PCP to OCDD of about 0.01%, Morimoto and Kenji (1995) reported a conversion efficiency of PCP to OCDD of 0.8%, 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, New York. Concentrations measured in 12 finished composts ranged from 14 to 41 ng I-TEQ<sub>DF</sub>/kg (mean of 3 ng I-TEQ<sub>DF</sub>/kg). The concentrations in the five active compost samples (1 to 30 days in age) ranged from 7.7 to 54 ng I-TEQ<sub>DF</sub>/kg (mean of 21 ng I-TEQ<sub>DF</sub>/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<sub>DF</sub>/kg) than the levels found in the composts, suggesting that the source(s) of CDDs/CDFs in the composts was different than the source(s) affecting local soils.

The authors 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 indicated to them 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 of 33 µg/kg), and the PCP levels in the active compost samples ranged from 17 to 210 µg/kg (mean of 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 of composts at three municipal yard waste composting facilities (5 to 91 ng I-TEQ<sub>DF</sub>/kg, mean of 30 ng I-

TEQ<sub>DF</sub>/kg), two municipal solid waste composting facilities (19 to 96 ng I-TEQ<sub>DF</sub>/kg, mean of 48 ng I-TEQ<sub>DF</sub>/kg), and one municipal facility composting solid waste and dewatered sewage sludge (37 to 87 ng I-TEQ<sub>DF</sub>/kg, mean of 56 ng I-TEQ<sub>DF</sub>/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 higher 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<sub>DF</sub>/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<sub>DF</sub>/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 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 neutrophil 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  $\mu\text{mol}$  of CDD/CDF per mol of chlorophenol substrate.

## **9.2. 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 less-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. The following paragraphs discuss studies that examined the products of biodegradation in sediments, compost, and sewage sludge.

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, Florida. 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<sup>-1</sup> to 0.0175 wk<sup>-1</sup> (i.e., half-lives of approximately 1 to 4 yr). However, Adriaens et al. (1995) 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 two HxCDDs (1,2,3,4,7,8- and 1,2,3,6,7,8-). Thus, removal of the peri-substituted (1,4,6,9) chlorines was favored, with enrichment of 2,3,7,8-substituted congeners. No less-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 Passaic River sediments. The initial concentration of 2,3,7,8-TCDD ( $20 \pm 4$  µg/L) decreased by 30% to  $14 \pm 2$  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

1 results of studies that specify likely involvement of chlorophenols are described in Section 9.1.  
2 Another possible formation mechanism was suggested by Vikelsoe et al. (1994), who reported  
3 that more-highly chlorinated CDD/CDF congeners are formed when humic acid is reacted with a  
4 peroxidase enzyme, hydrogen peroxide, and sodium chloride. It is expected that some organic  
5 material in compost and sewage sludge has a humic-like structure. Several additional studies are  
6 described below in which the potential involvement of chlorophenols could not be assessed  
7 because chlorophenol concentrations in the composts were not reported.

8 Schäfer et al. (1993) monitored the seasonal changes in the CDD/CDF content, as well as  
9 the extent of CDD/CDF formation, in composts from a vegetable and garden waste composting  
10 operation in Germany. Finished compost samples were collected and analyzed every 2 months  
11 for 1 yr. An annual cycle was observed in TEQ concentrations, with peak concentrations in the  
12 summer (approximately 8.5 ng I-TEQ<sub>DF</sub>/kg) being 2.5 times higher than the lowest concentrations  
13 observed in the winter (approximately 3.5 ng I-TEQ<sub>DF</sub>/kg). No seasonal source was apparent that  
14 could explain the observed differences in seasonal levels.

15 The CDD/CDF contents of the starting waste materials for two compost cycles (March  
16 and September) were measured to monitor the extent of CDD/CDF formation during  
17 composting. For the March cycle sample, most 2,3,7,8-substituted CDD/CDF congeners  
18 decreased in concentration during composting. Four CDF congeners showed a slight increase in  
19 concentration (less than 10%). For the September cycle sample, OCDD and HpCDD  
20 concentrations increased 300% during composting. Less than 10% increases were observed for  
21 HxCDDs and OCDF; all other 2,3,7,8-substituted CDD/CDF congeners showed decreases in  
22 concentrations during composting.

23 Krauss et al. (1994) measured the extent of CDD/CDF formation during the composting  
24 of household waste using a laboratory compost reactor. After 11 wk, the TEQ content of the  
25 compost increased from 3 to 4.5 ng. The largest increases in mass content were observed for  
26 HpCDD (primarily 1,2,3,4,6,7,8-HpCDD) and OCDD. TCDD, PeCDD, and HxCDD showed no  
27 change in mass content. All CDF congener groups showed decreases in mass content; however,  
28 the concentrations in both the starting and finished compost were close to the analytical detection  
29 limits.

30 Oberg et al. (1994) reported the results of monitoring of two household waste composts  
31 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 with 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 less-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<sub>DF</sub> concentrations in the raw sludges were 20 and 200 ng I-TEQ<sub>DF</sub>/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 on 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<sub>DF</sub>/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.

These data do not provide a basis for making a release estimate via biotransformation, therefore biotransformation releases are classified as Category E (not quantifiable).

### **9.3. 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, 2001b). 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.

1           Stevens and Jones (1993) published results of CDD and CDF detection in animal manure  
2 applied to farmland in the United Kingdom. Manure from six milking dairy cows was sampled  
3 at six farms in the northern United Kingdom. In addition, single samples of sheep, chicken, and  
4 pig manure were collected from other farms in the region. The samples were shipped to a  
5 laboratory for trace chemical analysis. Samples were analyzed using high-resolution gas  
6 chromatography coupled with high-resolution mass spectrometry and a capillary column for the  
7 identification of CDD/CDF congeners. Recoveries of the internal standard ranged from 51 to  
8 94%, with a mean of 74% for CDD/CDF congeners. Table 9-2 summarizes the results of the  
9 study. The pig and chicken manure contained approximately 0.2 ng WHO-TEQ/kg, and the cow  
10 manure averaged 3.6 ng WHO-TEQ/kg in concentration.

11           This study provides extremely limited data on the possible levels and occurrences of  
12 dioxin-like compounds in farm animal manure, and, therefore, these data are clearly not  
13 representative of national releases of dioxin-like compounds from the land application of all farm  
14 animal manure in the United States. Accordingly, EPA currently considers this source to be  
15 unquantifiable (Category E) in terms of dioxin emissions.



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

Species	Numbers of individuals on farms in 2000 <sup>a</sup>	Average weight of animal (lbs) <sup>b</sup>	Total live weight on farms (lbs)	Manure generation rate factor (dry weight lb per lb live unit weight per day) <sup>c</sup>	Manure generated (lb/yr dry weight)	Manure produced (kg 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	1400	1.29e+10	1e-02	4.71e+10	2.13e+10
Total					4.25e+11	1.93e+11

<sup>a</sup>Source: U.S. Census Bureau (2001b).

<sup>b</sup>Source: U.S. EPA (2001e).

<sup>c</sup>Source: Stevens and Jones (2003).

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

<b>Congener</b>	<b>Cows (n = 6) (mean)</b>	<b>Sheep (n = 1)</b>	<b>Pig (n = 1)</b>	<b>Chicken (n = 1)</b>
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
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 CDD/CDF	920	700	26	33
WHO-TEQ	3.6	2.1	0.19	0.2

Source: Stevens and Jones (1993).

## 10. PHOTOCHEMICAL SOURCES OF CDDs/CDFs

### 10.1. PHOTOTRANSFORMATION OF CHLOROPHENOLS

Several researchers have demonstrated that CDDs/CDFs can be formed via photolysis of PCP under laboratory conditions. These studies are described below. 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 that was pressure-treated in the laboratory with PCP. In the first set of experiments, wood veneers (southern pine) treated with purified PCP or with 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 (i.e., 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

1 ultraviolet (UV) radiation (5-hr exposure to 254 nm radiation from low-pressure mercury lamps).  
2 Before irradiation, the three solutions tested contained approximately 1 mg/L of PCP or PCP-Na,  
3 but the CDD/CDF content of one solution varied dramatically from those of the other two (1.5  
4 vs. 2,066 and 2,071 pg I-TEQ<sub>DF</sub>/L). Irradiation resulted in nearly total destruction of PCP  
5 (greater than 99% loss) in all three experiments. An overall net increase in I-TEQ<sub>DF</sub>-content was  
6 observed in the initially low I-TEQ<sub>DF</sub>-content water, but a net decrease was observed for the two  
7 initially high I-TEQ<sub>DF</sub>-content waters.

8 Irradiation of laboratory water containing purified PCP showed an increase in I-TEQ<sub>DF</sub>  
9 concentration from 1.5 pg/L to 214.5 pg/L. The increase was due entirely to the formation of  
10 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  
11 HpCDDs and HpCDFs was also observed. The ratios of the concentrations of these non-2,3,7,8-  
12 congeners to the concentrations of the 2,3,7,8-congeners were 0.6 for HpCDDs and 5 for  
13 HpCDFs. The HpCDD and HpCDF congeners formed indicated that the operative mechanism  
14 was photoinduced dechlorination of OCDD at a peri position and dechlorination of OCDF at  
15 only the 1- and 9-peri positions.

16 Irradiation of water containing technical PCP-Na (Dowicide-G) resulted in a net loss in I-  
17 TEQ<sub>DF</sub> content, from 2,065.5 pg/L to 112.7 pg/L. The only 2,3,7,8-substituted congener showing  
18 an increased concentration was 1,2,3,6,7,8-HxCDD. The other congeners originally present in  
19 the technical PCP-Na showed reductions of 80.6 to 100%.

20 The I-TEQ<sub>DF</sub> content of seepage water from a landfill (2,071 pg I-TEQ<sub>DF</sub>/L) was reduced  
21 by a factor of 2 to 1,088 pg I-TEQ<sub>DF</sub>/L. However, several 2,3,7,8-substituted congeners did  
22 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  
23 OCDF).

24 Waddell et al. (1995) also studied the effect of irradiating distilled laboratory water  
25 containing PCP under conditions simulating those used to purify water with UV radiation. The  
26 results obtained were similar to those of Vollmuth et al. (1994). Analytical-grade PCP at a  
27 concentration of 10 mg/L was exposed for 12 min to 200 to 300 nm radiation from a medium-  
28 pressure mercury lamp. All CDD/CDF congener groups increased in concentration over the  
29 12-min exposure period, with the greatest increases observed for OCDD (75-fold increase) and  
30 HpCDDs (34-fold increase). The I-TEQ<sub>DF</sub> content of the solution increased from 4.2 pg I-  
31 TEQ<sub>DF</sub>/L to 137 pg I-TEQ<sub>DF</sub>/L over the 12-min period. The dominant congeners formed, in terms

of both concentration and contribution to I-TEQ<sub>DF</sub>, were 1,2,3,4,6,7,8-HpCDD, OCDD, and 1,2,3,7,8,9-HxCDD.

## **10.2. 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, in most studies, good mass balances were not obtained and the photolytic pathways for CDDs/CDFs were not fully identified, a major photolysis pathway appears to be photodechlorination, resulting in formation of less-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. Sections 10.2.1 through 10.2.4 summarize the key findings of recent environmentally significant studies for the water, soil, and air media.

### **10.2.1. 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 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.

### **10.2.2. 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 <sup>13</sup>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 less-chlorinated congeners were produced from the immediate more-highly 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 <sup>13</sup>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. (1989), 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.

### **10.2.3. 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.) undergoes 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 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.

#### 10.2.4. 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 (1991) 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.

## 11. SOURCES OF DIOXIN-LIKE PCBs

The purpose of this chapter is twofold: (1) to identify sources that release dioxin-like polychlorinated biphenyl (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 produced in relatively large quantities for use in commercial products such as dielectrics, hydraulic fluids, plastics, and paints. They are no longer commercially produced in the United States, but 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.

### 11.1. GENERAL FINDINGS OF THE EMISSIONS INVENTORY

Table 11-1 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 11-1 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 11-2 (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 1.4.2 for details on confidence ratings). Table 11-2 also lists, in the far right column, preliminary estimates of the potential magnitude of emissions from “unquantified” sources (i.e., sources assigned a confidence rating of D) in reference year 1995. Because of large uncertainties for these Category “D” estimates, they are not included in the quantitative inventory.

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

1 regulations enacted beginning in the late 1970s that limited the manufacture/use/disposal of  
2 PCBs, significant quantities were released to the environment in association with (a) the  
3 manufacture of PCBs, (b) the manufacture of products containing PCBs, and (c) the use and  
4 disposal of products containing PCBs as well as materials that may have been contaminated with  
5 trace levels of PCBs from prior PCB use or disposal. Following the ban on PCB production,  
6 releases from these first two categories ceased. The third type of releases, those associated with  
7 product use and disposal, will continue in at least four ways:

- 8  
9 1. Disposal of products containing greater than 2 pounds of PCBs (e.g., dielectric fluids  
10 in transformers and large capacitors), which is controlled by disposal regulations that  
11 have minimized environmental releases;  
12
- 13 2. Disposal of products containing small quantities of PCBs (e.g., small capacitors,  
14 fluorescent lighting fixtures) or trace quantities of PCBs (e.g., wastepapers), which is  
15 subject to disposal as municipal solid waste but which may result in some release to  
16 the general environment;  
17
- 18 3. Leaks and spills of still-in-service PCBs; and  
19
- 20 4. Illegal disposal of PCBs.  
21

22 No significant release of newly formed dioxin-like PCBs is occurring in the United  
23 States. Unlike CDDs/CDFs, PCBs were intentionally manufactured in the United States in large  
24 quantities from 1929 until production was banned in 1977. Although it has been demonstrated  
25 that small quantities of dioxin-like PCBs can be produced during waste combustion, no strong  
26 evidence exists that they are produced in significant quantities as by-products during combustion  
27 or chemical processes. The widespread occurrence of dioxin-like PCBs in the U.S. environment  
28 most likely reflects past releases associated with PCB production, use, and disposal. Further  
29 support for this finding is based on observations of reductions since the 1980s in PCB  
30 concentrations in Great Lakes sediment and in other areas.  
31

## 32 **11.2. RELEASES OF COMMERCIAL PCBs**

33 PCBs were commercially manufactured by the direct batch chlorination of molten  
34 biphenyl with anhydrous chlorine in the presence of a catalyst, followed by separation and

1 purification of the desired chlorinated biphenyl fractions. The degree of chlorination was  
2 controlled by the chlorine contact time in the reactor. Commercial PCB production is believed to  
3 have been confined to 10 countries. Total PCBs produced worldwide since 1929 (the first year  
4 of known production) has been estimated at 1.5 million metric tons.

5 Initially, PCBs were used primarily as dielectric fluids in transformers. After World War  
6 II, PCBs found steadily increasing use as dielectric fluids in capacitors, as heat-conducting fluids  
7 in heat exchangers, and as heat-resistant hydraulic fluids in mining equipment and vacuum  
8 pumps. PCBs also were used in a variety of “open” applications (i.e, uses from which PCBs  
9 cannot be recollected), including plasticizers, carbonless copy paper, lubricants, inks, laminating  
10 agents, impregnating agents, paints, adhesives, waxes, additives in cement and plaster, casting  
11 agents, dedusting agents, sealing liquids, fire retardants, immersion oils, and pesticides (DeVoogt  
12 and Brinkman, 1989).

13 U.S. production peaked in 1970, with a volume of 39,000 metric tons. In 1971,  
14 Monsanto Corporation, the major U.S. producer, voluntarily restricted the sale of PCBs for all  
15 applications, with the exception of “closed electrical systems.” Annual production fell to 18,000  
16 metric tons in 1974. Monsanto ceased PCB manufacture in mid-1977 and shipped the last  
17 inventory in October of that year. Regulations issued by EPA beginning in 1977, principally  
18 under Toxic Substances Control Act (40 CFR 761), have strictly limited the production, import,  
19 use, and disposal of PCBs. The estimated cumulative production and consumption volumes of  
20 PCBs in the United States from 1930 to 1975 are 635,000 metric tons produced, 1,400 metric  
21 tons imported (primarily from Japan, Italy, and France), 568,000 metric tons sold in the United  
22 States, and 68,000 metric tons exported (Versar, Inc., 1976). The reliability of these values is  
23 +5% and –20% (Versar, Inc., 1976).

24 Monsanto Corporation marketed technical-grade mixtures of PCBs primarily under the  
25 trade name Aroclor. The Aroclor mixtures are identified by a four-digit numbering code in  
26 which the last two digits indicate the chlorine content by weight percent. The exception to this  
27 coding scheme is Aroclor 1016, which contains only mono- through hexachlorinated congeners  
28 with an average chlorine content of 41%. From 1957 until 1972, Monsanto also manufactured  
29 several blends of PCBs and polychlorinated terphenyls (PCTs) under the trade names Aroclor  
30 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).

<u>Aroclor</u>	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.

<u>Aroclor</u>	<u>Clophen</u>	<u>Pyralene</u>	<u>Phenoclor</u>	<u>Fenclor</u>	<u>Kanechlor</u>
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; and 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 11-3 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 11-3 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.

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 either to potential limitations in the GC columns used by various researchers to separate similar eluting congeners or to 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 11-3.

Because of the wide variability in the reported results, the uncertainty associated with the mean concentrations reported in Table 11-3 is very large.

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 composition of PCB mixtures changes over time through partitioning, chemical transformation,

1 and preferential bioaccumulation (U.S. EPA, 1996g). Dioxin-like PCB congeners differ by up to  
2 one to two orders of magnitude in their water solubility, vapor pressure,  $K_{ow}$  value, and Henry's  
3 Law constant. Thus, although all the dioxin-like PCB congeners are poorly soluble in water and  
4 have very low vapor pressures, they will volatilize and leach at different rates. Similarly, because  
5 the congeners differ somewhat in their rates of biodegradation, bioaccumulation, and  
6 photodegradation, the congener patterns found in environmental media and biota will vary from  
7 those found in commercial mixtures.

8 Although environmental mixtures are often characterized in terms of Aroclors, this  
9 characterization can be both imprecise and inappropriate. Qualitative and quantitative errors can  
10 arise from judgements in comparing GC/MS peaks for a sample with the characteristic peak  
11 patterns for different Aroclors, particularly for environmentally altered patterns (U.S. EPA,  
12 1996g). For the same reason, it can be both imprecise and inappropriate to infer concentrations  
13 of dioxin-like PCB congeners in an environmental sample on the basis of characterization of the  
14 sample's Aroclor content and knowledge of the dioxin-like congener content in the commercial  
15 Aroclor. Safe (1994) wrote, "Regulatory agencies and environmental scientists have recognized  
16 that the composition of PCBs in most environmental extracts does not resemble the compositions  
17 of the commercial product." Similarly, ATSDR (1993) stated, "It is important to recognize that  
18 the PCBs to which people may be exposed are likely to be different from the original PCB source  
19 because of changes in congener and impurity composition resulting from differential partitioning  
20 and transformation in the environment and differential metabolism and retention."  
21

#### 22 **11.2.1. Approved PCB Disposal/Destruction Methods**

23 In 1978, EPA began regulating the disposal of PCBs and PCB-contaminated waste under  
24 TSCA, PL 94-469. The disposal regulations, published in the Code of Federal Regulations, 40  
25 CFR, Part 761, state that the preferred disposal method is incineration at 1,200 °C or higher. If  
26 the waste contains material that cannot be destroyed by incineration, EPA clearance must be  
27 obtained to dispose of the waste in a chemical waste landfill or by another approved manner.

28 The PCB disposal regulations describe disposal of three distinct types of PCB waste:  
29 PCBs, PCB articles (items containing PCBs), and PCB containers. Within these categories,  
30 further distinctions are made on the basis of the PCB concentration in the waste. The acceptable  
31 disposal methods are based on the PCB concentrations in the specific waste to be destroyed. The

1 acceptable disposal methods are Annex I incinerators, high-efficiency boilers, Annex II chemical  
2 waste landfills, and other approved methods. The following paragraphs and Table 11-4 provide  
3 brief descriptions of these disposal methods. More complete descriptions of the specific  
4 methodologies are provided in 40 CFR, Part 761.

#### 6 **11.2.1.1. *Approved Incinerators/High-Efficiency Boilers***

7 PCB Annex I incinerators must meet the specific technical standards and criteria listed in  
8 Annex I of EPA's PCB regulations. The minimum operating requirements for disposal of liquid  
9 wastes are 2 sec at 1,200 °C with 3% excess oxygen (measured in the stack gas) or 1.5 sec at  
10 1,600 °C with 2% excess oxygen (measured in the stack gas). Monitoring requirements,  
11 approval conditions, and trial burn requirements are prescribed in Annex I. Commercial or  
12 industrial incinerators intending to destroy liquid PCB wastes must demonstrate compliance with  
13 the Annex I requirements through a comprehensive trial burn program. Annex I incinerators  
14 operating at optimum performance level should destroy 99.997% of liquid PCB waste, with a  
15 resulting maximum emission factor of 0.03 g/kg.

16 Criteria for Annex I incinerators were established for the destruction of liquid PCB  
17 wastes; however, these incinerators also may be used for disposal of nonliquid PCB items (such  
18 as capacitors), provided that a destruction and removal efficiency of 99.9999% and a maximum  
19 emission factor of 0.001 g/kg are met.

20 High-efficiency boilers may be used to destroy PCBs and PCB-contaminated waste with  
21 PCB concentrations not exceeding 500 ppm. Conventional industrial and utility boilers may be  
22 designated as high-efficiency boilers if they are operated under the prescribed combustion  
23 conditions defined in the PCB disposal regulations. The PCB regulations do not specify a  
24 minimum PCB destruction efficiency for high-efficiency boilers; however, EPA-approved boilers  
25 operated according to the regulations have reported destruction efficiencies in excess of 99.99%,  
26 with a corresponding maximum emission factor of 0.1 g/kg (U.S. EPA, 1987c).

#### 28 **11.2.1.2. *Approved Chemical Waste Landfills***

29 Approved chemical waste landfills can be used for the disposal of some, but not all, PCB  
30 wastes. PCB-contaminated materials acceptable for land disposal in an approved landfill include  
31 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.

#### **11.2.1.3. *Other Approved Disposal Methods***

Other thermal and nonthermal destruction techniques may be approved by EPA Regional Administrators if these processes can effect 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.

#### **11.2.2. Emission Estimates**

Table 11-5 lists the amounts of PCBs reported in EPA's TRI as transferred off-site for treatment, energy recovery, or disposal between 1988 and 2000. 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 the dioxin-like congeners.

### 11.2.3. Accidental Releases of 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 and/or destruction) have been limited to accidental release of in-service PCBs (U.S. EPA, 1987c). 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 subsections.

#### 11.2.3.1. *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 of 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).

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

1 potentially spill onto the surrounding ground. PCB capacitors typically fail by rupturing,  
2 exposing the contained PCBs to the environment. Failure is caused by environmental and  
3 weathering effects (e.g., lightning) or material failures (e.g., metal fatigue).

4 As of mid-1988, the total population of in-service PCB transformers and large PCB  
5 capacitors was estimated to have decreased from 140,000 to 110,000 and from 3.3 million to 1.9  
6 million, respectively (Versar, Inc., 1988). PCB transformers have normal operating lifetimes of  
7 30 years and 40 years, respectively. The accelerated retirement rate over this 7-yr period was  
8 attributed to EPA's PCB Electrical Use Rule (Federal Register, 1982b), which required the  
9 removal of 950 food/feed industry transformers by 1985 and removal of 1.1 million unrestricted-  
10 access large PCB capacitors by October 1988. In addition, EPA's PCB Transformer Fires Rule  
11 (Federal Register, 1985b) required the removal by 1990 of 7,600 480-volt network transformers.

12 More recent inventories of PCB-containing electrical equipment are not available.  
13 However, an Information Collection Request submitted by EPA to the Office of Management  
14 and Budget for information on uses, locations, and conditions of PCB electrical equipment  
15 estimated that there may be 150,000 owners of PCB-containing transformers used in industry,  
16 utilities, government buildings, and private buildings (Federal Register, 1997a). It is expected,  
17 and is demonstrated by the reported PCB transfers in the EPA's TRI (see Table 11-5), that many  
18 owners of PCB electrical equipment have removed PCB-containing equipment to eliminate  
19 potential liability.

#### 21 **11.2.3.2. Accidental Fires**

22 The available information is not adequate to support an estimate of potential annual  
23 releases of dioxin-like PCBs from accidental electrical equipment fires. For fires involving PCB  
24 transformers or capacitors, the amount of PCBs released is dependent on the extensiveness of the  
25 fire and the speed at which it is extinguished. A number of these fires are documented. A New  
26 York fire involving 200 gallons of transformer fluid containing some 65% by weight PCBs  
27 resulted in a release of up to 1,300 pounds of PCBs. A capacitor fire that burned uncontrolled for  
28 2 hr in Sweden resulted in the destruction of 12 large utility capacitors containing an estimated  
29 25 pounds each of PCBs, for a total potential release of 300 pounds. However, data are  
30 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 may be claimed by the submitter to be confidential information. The annual number of PCB transformer fires is estimated at approximately 20 per year; the number of PCB capacitor fires is unknown (U.S. EPA, 1987c). 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.

#### **11.2.4. 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 analyzed sludges from 175 publicly owned treatment works (POTWs) that employed at least secondary wastewater treatment for more than 400 analytes, including seven of the Aroclors. 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 (detection limit was typically about 200 µg/kg dry weight) (U.S. EPA, 1996a). Analyses were not performed for dioxin-like PCB congeners. The Aroclor-specific results of the survey are presented in Table 11-7.

Gutenmann et al. (1994) reported similar results in a survey of sludges from 16 large U.S. cities for Aroclor 1260 content. At a detection limit of 250 µg/kg (dry weight), the investigators detected Aroclor 1260 at only one facility (4,600 µg/kg). 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 PCB.

Although PCBs, measured as Aroclors, were not commonly detected in sewage sludge at µg/kg levels by U.S. EPA (1996a) 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 of 1994. These data are summarized in Table 11-8. Results from all samples collected from the same facility were averaged by Green et al. (1995) and Cramer et al. (1995) to ensure that results were not biased towards the concentrations

found at facilities from which more than one sample was collected. If all nondetect values are assumed to be zero, then the POTW mean TEQ<sub>P</sub>-WHO<sub>94</sub> and TEQ<sub>P</sub>-WHO<sub>98</sub> concentrations were 25.1 and 24.2 ng TEQ/kg (dry-weight basis), respectively. If the nondetect values are set equal to the detection limits, then the POTW mean TEQ<sub>P</sub>-WHO<sub>94</sub> and TEQ<sub>P</sub>-WHO<sub>98</sub> 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, 2000f). The facility, which accepts both domestic and industrial wastewater, employs secondary wastewater technology. Assuming nondetects are zero, the mean TEQ emission factor is 141 ng TEQ<sub>P</sub>-WHO<sub>98</sub>/kg. These results are presented in Table 11-9.

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 are zero, the mean and median TEQ emission factors were reported as 8.3 and 3.37 ng TEQ<sub>P</sub>-WHO<sub>98</sub>/kg, respectively.

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, 2002a). 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<sub>P</sub>-WHO<sub>98</sub> 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, 1993b). 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, 1999). 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 11-10, 11-11, and 11-12 list the volume, by use and disposal practices, of sludge disposed of annually for reference years 1989, 1995, and 2000.

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<sub>P</sub>-WHO<sub>98</sub> 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<sub>P</sub>-WHO<sub>98</sub> concentration reported by EPA (U.S. EPA, 2002a) 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<sub>P</sub>-WHO<sub>98</sub> (104.2 g TEQ<sub>P</sub>-WHO<sub>94</sub>) in 1987, 118.5 g TEQ<sub>P</sub>-WHO<sub>98</sub> (123.1 g TEQ<sub>P</sub>-WHO<sub>94</sub>) in 1995, and 26.6 g TEQ<sub>P</sub>-WHO<sub>98</sub> in 2000 for nonincinerated sludges.

Of the 101 g TEQ<sub>P</sub>-WHO<sub>98</sub> 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<sub>P</sub>-WHO<sub>98</sub> 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<sub>P</sub>-WHO<sub>98</sub> 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 per 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 11-2.

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 the emission factors were weighted on the basis of wastewater flow rates of all POTWs in the United States.

### **11.3. 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 mg/kg 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.

### **11.4. COMBUSTION SOURCES**

#### **11.4.1. 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, 1987c); the average test results yielded an emission factor of 18 µg PCBs/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, 1987c). The results indicated that paper products such as magazine covers and paper towels contained up to 139 µg/kg of 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. RDF 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, 1987c).

Shane et al. (1990) analyzed fly ash from five MWCs for PCB congener group content. Total PCB levels ranged from 99 to 322  $\mu\text{g/kg}$  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 detection limit for this Aroclor analysis was 5  $\mu\text{g/kg}$ . Aroclor 1254 was detected in two of the seven bottom ash samples (26 and 8  $\mu\text{g/kg}$ ) and in five of the eight fly ash/bottom ash mixtures (range of 6 to 33  $\mu\text{g/kg}$ ).

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.

#### **11.4.2. Industrial Wood Combustion**

Emissions of PCB congener groups (but not individual congeners) were measured during stack testing at two industrial wood-burning facilities (CARB, 1990e, f). Table 11-13 presents the average of the congener group (mono- through decachlorobiphenyl) emission factors for these two facilities. No tetra- or more-highly chlorinated congeners (the congener groups containing the dioxin-like PCBs) were detected at either facility at detection limits corresponding to emission factors in the low range of ng/kg of wood combusted.



1 In CARB (1990e), PCBs were measured in the emissions from two spreader stoker wood-  
2 fired boilers operated in parallel by an electric utility for generating electricity. The exhaust gas  
3 stream from each boiler was passed through a dedicated electrostatic precipitator (ESP), after  
4 which the gas streams were combined and emitted to the atmosphere through a common stack.  
5 Stack tests were conducted both when the facility burned fuels allowed by existing permits and  
6 when the facility burned a mixture of permitted fuel supplemented by urban wood waste at a ratio  
7 of 70:30.

8 In CARB (1990f), PCBs were measured in the emissions from twin fluidized-bed  
9 combustors designed to burn wood chips to generate electricity. The air pollution control device  
10 (APCD) system consisted of ammonia injection for controlling nitrogen oxides and a multiclone  
11 and an ESP for controlling PM. During testing, the facility burned wood wastes and agricultural  
12 wastes allowed by existing permits.

#### 14 **11.4.3. Medical Waste Incineration**

15 As discussed in Section 3.3, EPA has issued nationally applicable emission standards and  
16 guidelines that address CDD/CDF emissions from medical waste incinerators (MWIs). Although  
17 PCBs are not addressed in these regulations, the database of stack test results at MWIs compiled  
18 for this rulemaking does contain limited data on PCB congener group emission factors. Data are  
19 available for two MWIs lacking add-on APCD equipment and for two MWIs with add-on APCD  
20 equipment in place. The average congener group emission factors derived from these test data  
21 are presented in Table 11-14. Because data are available for only 4 of the estimated 1,065  
22 facilities that make up this industry, and because these data do not provide congener-specific  
23 emission factors, no national estimates of total PCB or dioxin-like PCB emissions are being  
24 made at this time.

#### 26 **11.4.4. Tire Combustion**

27 As discussed in Section 3.6, tires are burned in a variety of facilities including dedicated  
28 tire burners, cement kilns, industrial boilers, and pulp and paper combustion facilities. Emissions  
29 of PCB congener groups (but not individual congeners) were measured during stack testing of a  
30 tire incinerator (CARB, 1991a). The facility consisted of two excess air furnaces equipped with  
31 steam boilers to recover the energy from the heat of combustion. Discarded whole tires were fed

1 to the incineration units at rates ranging from 2,800 to 5,700 kg/hr during the 3 testing days. The  
2 furnaces were equipped to burn natural gas as auxiliary fuel. The steam produced from the  
3 boilers drove electrical turbine generators that produced 14.4 megawatts of electricity. The  
4 facility was equipped with a dry acid gas scrubber and a fabric filter for the control of emissions  
5 prior to exiting the stack. Table 11-15 presents the congener group (mono- through  
6 decachlorobiphenyl) emission factors for this facility. The emission factor for the total of the  
7 tetra- through heptachlorinated congener groups was about 1.2 µg/kg of tire processed. Because  
8 these data do not provide PCB congener-specific emission factors, no estimates of emissions of  
9 dioxin-like PCBs can be made.

#### 11 **11.4.5. Cigarette Smoking**

12 Using high-resolution mass spectrometry, Matsueda et al. (1994) analyzed tobacco from  
13 20 brands of commercially available cigarettes collected in 1992 from Japan, the United States,  
14 Taiwan, China, the United Kingdom, Germany, and Denmark for the PCB congeners 77, 126,  
15 and 169. Table 11-16 presents the results of the study. However, no studies that examined the  
16 tobacco smoke for the presence of these congeners have been reported. Thus, it is not known  
17 whether the PCBs present in the tobacco are destroyed or volatilized during combustion or  
18 whether PCBs are formed during combustion.

19 The combustion processes operating during cigarette smoking are complex and could be  
20 used to support either of these potential mechanisms. As reported by Guerin et al. (1992), during  
21 a puff, gas phase temperatures reach 850 °C at the core of the firecone, and solid phase  
22 temperatures reach 800 °C at the core and 900 °C or greater at the char line. Thus, temperatures  
23 are sufficient to cause at least some destruction of CDDs/CDFs initially present in the tobacco.  
24 Both solid and gas phase temperatures rapidly decline to 200 to 400 °C within 2 mm of the char  
25 line. Formation of dioxin-like PCBs has been reported in combustion studies with other media in  
26 this temperature range (Sakai et al., 1994). However, it is known that a process likened by  
27 Guerin et al. (1992) to steam distillation takes place in the region behind the char line because of  
28 high localized concentrations of water and temperatures of 200 to 400 °C. At least 1,200 tobacco  
29 constituents (e.g., nicotine, n-paraffin, some terpenes) are transferred intact from the tobacco into  
30 the smoke stream by distillation in this area, and it is plausible that PCBs present in the unburned  
31 tobacco would be subject to similar distillation.

1 Brown et al. (2002) estimated that 440 billion cigarettes were consumed in the United  
2 States in 2000. In 1995, approximately 487 billion cigarettes were consumed in the United States  
3 and by U.S. Armed Forces personnel stationed overseas. In 1987, approximately 575 billion  
4 cigarettes were consumed. According to the Tobacco Institute (1995), per capita U.S. cigarette  
5 consumption, based on total U.S. population aged 16 years and over, was at a record high of  
6 4,345 in 1963, declining to 2,415 in 1995, and 1,563 in 2000 (USDA, 1997; U.S. Census Bureau,  
7 2000). The activity level estimates by Brown et al. (2002) were adopted here and assigned a high  
8 confidence rating because they were based on well established rates of consumption.

9 A preliminary rough estimate of potential emissions of dioxin-like PCBs can be made  
10 using the following assumptions: (a) the average TEQ<sub>P</sub>-WHO<sub>98</sub> content of seven brands of U.S.  
11 cigarettes reported by Matsueda et al. (1994), 0.64 pg/pack (0.032 pg/cigarette), is representative  
12 of cigarettes smoked in the United States; (b) dioxin-like PCBs are neither formed nor destroyed,  
13 and the congener profile reported by Matsueda et al. (1994) is not altered during combustion of  
14 cigarettes; and (c) all dioxin-like PCBs contributing to the TEQ are released from the tobacco  
15 during smoking. On the basis of these assumptions, the calculated annual emissions would be  
16 0.018 g TEQ<sub>P</sub>-WHO<sub>98</sub>, 0.016 g TEQ<sub>P</sub>-WHO<sub>98</sub>, and 0.014 g TEQ<sub>P</sub>-WHO<sub>98</sub> for reference years  
17 1987, 1995, and 2000, respectively.

#### 18 19 **11.4.6. Sewage Sludge Incineration**

20 EPA derived an emission factor of 5.4 µg of total PCBs per kg of dry sewage sludge  
21 incinerated (U.S. EPA, 1996f). This emission factor was based on measurements conducted at  
22 five multiple-hearth incinerators controlled with wet scrubbers. However, it is not known what  
23 fraction of the emissions was dioxin-like PCBs.

24 In 1999, stack tests were conducted at a multiple-hearth incinerator in Ohio equipped  
25 with a venturi scrubber and a three-tray impingement conditioning tower (U.S. EPA, 2000f).  
26 Four test runs were conducted; however, the first test run was aborted, and the CDD/CDF results  
27 from the fourth test run were determined to be statistical outliers ( $p < 0.05$ ). The back-half  
28 emission concentrations for test run 4 were 50 to 60% lower than back-half emission  
29 concentrations for test runs 2 and 3. Overall, total CDD/CDF emissions measured during test run  
30 4 were 73.3 ng/kg, whereas those measured during test runs 2 and 3 were 215 and 173 ng/kg,  
31 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 0.51 ng TEQ<sub>P</sub>-WHO<sub>98</sub>/kg (see Table 11-17). This emission factor was assigned a low confidence rating because it is based on limited surveys that are judged to be possibly nonrepresentative.

In 1988, approximately 199 sewage sludge incineration facilities combusted about 0.865 million metric tons of dry sewage sludge (Federal Register, 1993b). 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 (Maw, 1998). Using trends in wastewater flow rates from the 1988 National Sewage Sludge Survey and from the 1984 to 1996 Needs Surveys, EPA estimated that in 2000 approximately 6.4 million metric tons of dry sewage sludge would have been generated (U.S. EPA, 1999). Of this amount, EPA projected that 22% (1.42 million metric tons) would have been incinerated. These activity estimates were assigned a confidence rating of medium because they were based on surveys judged to be representative of sludge generation rates.

Using the above estimated amounts of sewage sludge incinerated per year and the average TEQ emission factor of 0.51 ng TEQ<sub>P</sub>-WHO<sub>98</sub>/kg, the estimated annual releases of total PCBs to air were 0.44 g TEQ<sub>P</sub>-WHO<sub>98</sub> in 1987, 1.1 g TEQ<sub>P</sub>-WHO<sub>98</sub> in 1995, and 0.72 g TEQ<sub>P</sub>-WHO<sub>98</sub> in 2000. These emissions were assigned a low confidence rating because the emission factor was given a low rating.

#### **11.4.7. 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  $1.02 \times 10^{-2}$   $\mu\text{g TEQ}_\text{P}$ -WHO<sub>94</sub>/kg and  $5.26 \times 10^{-3}$   $\mu\text{g TEQ}_\text{P}$ -WHO<sub>98</sub>/kg of waste burned (see Table 11-18). These limited emissions data were judged to be inadequate for estimating national emissions. The activity level for backyard barrel burning is discussed in Section 6.5.

#### **11.4.8. Petroleum Refining Catalyst Regeneration**

As discussed in Section 5.3, 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). 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 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 PCB congener groups were detected in each of the three samples collected. The average congener group emission factors in units of ng per barrel of reformer feed are presented in Table 11-19. 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.

### **11.5. NATURAL SOURCES**

This section discusses biotransformation and photochemical transformation of other PCBs. While there is some evidence that these processes occur, the data were considered insufficient for developing release estimates.

### 11.5.1. Biotransformation of Other PCBs

Studies show that under anaerobic conditions, biologically mediated reductive dechlorination to less-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 hexa- and more chlorinated PCBs. The rate of aerobic biodegradation decreases with increasing chlorination. The half-lives for biodegradation of tetra-PCBs in fresh surface water and soil are 7 to 60+ days and 12 to 30 days, respectively. For penta- and more-highly 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

1 River, and Woods Pond (Brown et al., 1987; Rhee et al., 1989; Van Dort and Bedard, 1991;  
2 Abramowicz, 1990; Bedard et al., 1995; Bedard and May, 1996). The altered PCB congener  
3 distribution patterns found in these sediments (i.e., different patterns with increasing depth or  
4 distance from known sources of PCBs) have been interpreted as evidence that bacteria may  
5 dechlorinate PCBs in anaerobic sediment.

6 Reported results of laboratory studies confirm anaerobic degradation of PCBs. Chen et  
7 al. (1988) found that “PCB-degrading” bacteria from the Hudson River could significantly  
8 degrade the mono-, di-, and tri-PCB components of a 20 ppm Aroclor 1221 solution within 105  
9 days. These congener groups make up 95 percent of Aroclor 1221. No degradation of more-  
10 highly chlorinated congeners (present at 30 ppb or less) was observed, and a separate 40-day  
11 experiment with tetra-PCB also showed no degradation.

12 Rhee et al. (1989) reported degradation of mono- to penta-substituted PCBs in  
13 contaminated Hudson River sediments held under anaerobic conditions in the laboratory (N<sub>2</sub>  
14 atmosphere) for 6 months at 25 °C. Amendment of the test samples with biphenyl resulted in  
15 greater loss of PCBs. No significant decreases in the concentrations of the more highly  
16 chlorinated congeners (more than five chlorines) were observed. No evidence of degradation  
17 was observed in samples incubated in CO<sub>2</sub>/H<sub>2</sub> atmospheres. Abramowicz (1990) hypothesized  
18 that this result could be an indication that, in the absence of CO<sub>2</sub>, a selection is imposed favoring  
19 organisms capable of degrading PCBs to obtain CO<sub>2</sub> and/or low-molecular-weight metabolites as  
20 electron receptors.

21 Risatti (1992) examined the degradation of PCBs at varying concentrations (10,000 ppm,  
22 1,500 ppm, and 500 ppm) in the laboratory with “PCB-degrading” bacteria from Waukegan  
23 Harbor. After 9 months of incubation at 22 °C, the 500 ppm and 1,500 ppm samples showed no  
24 change in PCB congener distributions or concentrations, thus indicating a lack of degradation.  
25 Significant degradation was observed in the 10,000 ppm sediment, with at least 20 congeners  
26 ranging from TrCBs to PeCBs showing decreases.

27 Quensen et al. (1988) also demonstrated that microorganisms from PCB-contaminated  
28 sediments (Hudson River) dechlorinated most tri- through hexa-PCBs in Aroclor 1242 under  
29 anaerobic laboratory conditions. The Aroclor 1242 used to spike the sediment contained  
30 predominantly tri- and tetra-PCBs (85 mol percent). Three concentrations of the Aroclor,  
31 corresponding to 14, 140, and 700 ppm on a sediment dry-weight basis, were used.

1 Dechlorination was most extensive at the 700 ppm test concentration: 53% of the total chlorine  
2 was removed in 16 weeks, and the proportion of TeCBs through HxCBs decreased from 42 to  
3 4%. Much less degradation was observed in the 140 ppm sediment, and no observable  
4 degradation was found in the 14 ppm sediment. These results and those of Risatti (1992) suggest  
5 that the organism(s) responsible for this dechlorination may require relatively high levels of  
6 PCBs as a terminal electron acceptor to maintain a growing population.

7 Quensen et al. (1990) reported that dechlorination of 500 ppm spike concentrations of  
8 Aroclor 1242, 1248, 1254, and 1260 by microorganisms from PCB-contaminated sediments in  
9 the Hudson River and Silver Lake occurred primarily at the meta- and para- positions; ortho-  
10 substituted mono- and di-PCBs increased in concentration. Significant decreases over the  
11 incubation period (up to 50 weeks) were reported for dioxin-like PCBs 156, 167, 170, 180, and  
12 189. Of the four dioxin-like TeCBs and PeCBs detected in the Aroclor spikes (IUPAC Nos. 77,  
13 105, 114, and 118), all decreased significantly in concentration, with the possible exception of  
14 PeCB 114 in the Aroclor 1260-spiked sediment.

15 Nies and Vogel (1990) reported similar results with Hudson River sediments incubated  
16 anaerobically and enriched with acetone, methanol, or glucose. Approximately 300 ppm of  
17 Aroclor 1242 (31 mol percent TeCBs, 7 mol percent PeCBs, and 1 mol percent HxCBs) were  
18 added to the sediments prior to incubation for 22 weeks under an N<sub>2</sub> atmosphere. Significant  
19 dechlorination was observed, primarily at the meta- and para-positions on the more highly  
20 chlorinated congeners (TeCBs, PeCBs, and HxCBs), resulting in the accumulation of less-  
21 chlorinated, primarily ortho-substituted mono- through tri-substituted congeners. No significant  
22 dechlorination was observed in the control samples (samples containing no added organic  
23 chemical substrate and samples that were autoclaved).

24 Bedard and May (1996) also reported similar findings in the sediments of Woods Pond,  
25 which was believed to be contaminated with Aroclor 1260. Significant decreases in the sediment  
26 concentrations of PCBs 118, 156, 170, and 180 (relative to their concentrations in Aroclor 1260)  
27 were observed. No increases or decreases were reported for the other dioxin-like PCBs.

28 Bedard et al. (1995) demonstrated that it is possible to stimulate substantial microbial  
29 dechlorination of the highly chlorinated PCB mixture Aroclor 1260 in situ with a single addition  
30 of 2,6-dibromobiphenyl. The investigators added 365 g of 2,6-dibromobiphenyl to 6-foot-  
31 diameter submerged caissons containing 400 kg sediment (dry weight) and monitored the change



1 in PCB congener concentrations for a period of 1 yr. At the end of the observation period, the  
2 hexa- through monochlorinated PCBs decreased 74% in the top of the sediment and 69% in the  
3 bottom. The average number of chlorines per molecule dropped 21%, from 5.83 to 4.61, with  
4 the largest reduction observed in meta-chlorines (54% reduction) followed by para-chlorines  
5 (6%). The dechlorination stimulated by 2,6-dibromobiphenyl selectively removed meta-  
6 chlorines positioned next to other chlorines.

7 The findings of these latter studies are significant, because removal of meta- and para-  
8 chlorines from the dioxin-like PCBs should reduce their toxicity and bioaccumulative potential  
9 and also form less-chlorinated congeners that are more amenable to aerobic biodegradation.

10 Van Dort and Bedard (1991) reported the first experimental demonstration of biologically  
11 mediated ortho-dechlorination of a PCB and stoichiometric conversion of that PCB congener  
12 (2,3,5,6-TeCB) to less-chlorinated forms. In that study, 2,3,5,6-TeCB was incubated under  
13 anaerobic conditions with unacclimated methanogenic pond sediment for 37 weeks, with  
14 reported dechlorination to 2,5-DCB (21%); 2,6-DCB (63%); and 2,3,6-TrCB (16%).

#### 15 16 **11.5.2. Photochemical Transformation of Other PCBs**

17 Photolysis and photo-oxidation may be major pathways for destruction of PCBs in the  
18 environment. Research reported to date and summarized below indicates that ortho-substituted  
19 chlorines are more susceptible to photolysis than are meta- and para-substituted congeners; thus,  
20 photolytic formation of more toxic dioxin-like PCBs may occur. Oxidation by hydroxyl radicals,  
21 however, apparently occurs preferentially at the meta- and para-positions, resulting in a net  
22 decrease rather than a net increase in the environmental load of dioxin-like PCBs.

23 On the basis of the data available in 1983, Leifer et al. (1983) concluded that all PCBs,  
24 especially the more highly chlorinated congeners and those that contain two or more chlorines in  
25 the ortho position, photodechlorinate. In general, as the chlorine content increases, the photolysis  
26 rate increases. More recently, Lepine et al. (1992) exposed dilute solutions (4 ppm) of Aroclor  
27 1254 in cyclohexane to sunlight for 55 days in December and January. Congener-specific  
28 analysis indicated that the amounts of many more-highly chlorinated congeners, particularly  
29 mono-ortho-substituted congeners, decreased, whereas those of some less-chlorinated congeners  
30 increased. The results for the dioxin-like PCBs indicated a 43.5% decrease in the amount of  
31 PeCB 114, a 73.5% decrease in the amount of HxCB 156, and a 24.4% decrease in the amount of

HxCB 157. However, TeCB 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 monochlorobiphenyl, 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-dichlorobiphenyl. These reaction rate constants, when taken together with Atkinson's measurements for biphenyl and monochlorobiphenyl 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 11-20 presents these estimated rate constants and the corresponding tropospheric lifetimes and half-lives.

Sedlak and Andren (1991) demonstrated in laboratory studies that OH radicals generated with Fenton's reagent rapidly oxidized PCBs (2-mono-PCB 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 steric 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 (mono-through octa-PCB) in fresh surface water and in cloud water to be 4 to 11 days and 0.1 to 10 days, respectively.

## **11.6. PAST USE OF COMMERCIAL PCBs**

An estimated 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, 1976). Although the focus of this section is on past uses of PCBs

1 within the United States, it is necessary to note that the use and disposal of PCBs in many  
2 countries, coupled with the persistent nature of PCBs, have resulted in their movement and  
3 presence throughout the global environment. The ultimate sink of most PCBs released to the  
4 environment is aquatic sediments. Currently, however, large quantities of PCBs are estimated to  
5 be circulating between the air and water environments or are present in landfills and dumps,  
6 some of which may offer the potential for re-release of PCBs into the air. Tanabe (1988)  
7 presented a global mass balance for PCBs that indicated that as of 1985, 20% of the total PCBs  
8 produced were present in seawater, whereas only 11% were present in sediments (see Table 11-  
9 21). Nearly two-thirds of total global PCB production was estimated by Tanabe to still be in use  
10 in electrical equipment or to be present in landfills and dumps.

11 As discussed in Section 11.2, an estimated 568,000 metric tons of PCBs were sold in the  
12 United States from 1930 to 1975 (Versar, Inc., 1976). Table 11-22 presents annual estimates of  
13 domestic sales by year for each Aroclor from 1957 to 1974. Estimates of PCB usage in the  
14 United States by usage category from 1930 to 1975 are presented in Table 11-23. Prior to  
15 voluntary restrictions by Monsanto Corporation in 1972 on sales for uses other than “closed  
16 electrical systems,” approximately 13% of the PCBs were used in “semi-closed applications,”  
17 and 26% were used in “open-end applications.” Most of the usage for semi-closed and open-end  
18 applications occurred between 1960 and 1972 (Versar, Inc., 1976).

19 Table 11-24 presents estimates of the amounts of individual Aroclors that were directly  
20 released to the environment (water, air, or soil) between 1930 and 1974. Because detailed usage  
21 data were not available for the period 1930 to 1957, Versar, Inc. (1976) assumed that the usage  
22 pattern for this period followed the average pattern for the period 1957 to 1959. The basic  
23 assumption used by Versar, Inc., in deriving these estimates was that PCBs were released on the  
24 order of 5% of those used in closed electrical systems, 60% of those used in semiclosed  
25 applications, and 25% of those used for plasticizers and that 90% of PCBs used for  
26 miscellaneous industrial uses had escaped. The reliability of these release estimates was  
27 assumed to be  $\pm 30\%$ .

28 Versar, Inc. (1976) also estimated that 132,000 metric tons of PCBs were landfilled. This  
29 total comprised 50,000 metric tons from capacitor and transformer production wastes, 36,000  
30 metric tons from disposal of obsolete electrical equipment, and 46,000 metric tons from disposal  
31 of material from open-end applications. An estimated additional 14,000 metric tons of PCBs,

1 although still “in service” in various semi-closed and open-end applications in 1976, were  
2 ultimately destined for disposal in landfills.

3 An estimated 3,702 kg of TEQ<sub>P</sub>-WHO<sub>98</sub> were released directly to the U.S. environment  
4 during the period 1930 to 1977 (see Table 11-25). These estimates are based on the Aroclor  
5 release estimates presented in Table 11-22 and the mean TEQ<sub>P</sub>-WHO<sub>98</sub> concentrations in  
6 Aroclors presented in Table 11-3.

**Table 11-1. Confidence rating classes for 2000 releases from all known and suspected source categories of dioxin-like PCBs**

<b>Source category</b>	<b>Air</b>	<b>Land</b>	<b>Water</b>
Approved PCB disposal	E		
Accidental PCB releases	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	D		
Petroleum refining catalyst regeneration	E		

- 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**.
- 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 = 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.

Blank means not applicable or no data.

**Table 11-2. Inventory of contemporary releases of dioxin-like PCBs (g TEQ<sub>p</sub>-WHO<sub>98</sub>/yr) in the United States for 1987, 1995, and 2000 and preliminary release estimates of dioxin-like PCBs for 2000 (g TEQ<sub>p</sub>-WHO<sub>98</sub>/yr)**

Emission Source Category	2000 Inventory			2000 Preliminary	1995 Inventory			1987 Inventory		
	A	B	C	D	A	B	C	A	B	C
<i>Releases (g TEQ<sub>p</sub>-WHO<sub>98</sub>/yr) to Air</i>										
Cigarettes				0.01						
Sewage sludge incineration			0.72				1.1			0.44
Backyard barrel burning				44.4						
Petroleum refining catalyst regeneration										
<b>Total Quantified Releases to Air<sup>c</sup></b>			0.72	44.4			1.1			0.44
<i>Releases (g TEQ<sub>p</sub>-WHO<sub>98</sub>/yr) to Land</i>										
<b>Municipal Sludge</b>										
Nonincinerated sludge	18.8					77.4			51.1	
<b>Total Quantified Releases to Land<sup>c</sup></b>	18.8					77.4			51.1	
<i>Releases (g TEQ<sub>p</sub>-WHO<sub>98</sub>/yr) to Products</i>										
<b>Municipal Sludge Disposal</b>										
Nonincinerated sludge	0.5					2.0			1.7	
<b>Total Quantified Releases to Products<sup>c</sup></b>	0.5					2.0			1.7	

Table 11-3. 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 <sub>P</sub> -WHO <sub>98</sub> conc. (nondetect set to zero) (mg/kg)	Mean conc. <sup>a</sup> (nondetect set to ½ detection limit) (g/kg)	TEQ <sub>P</sub> -WHO <sub>98</sub> conc. <sup>a</sup> (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 <sub>P</sub> -WHO <sub>98</sub>				0.005		0.0200	
Total TEQ <sub>P</sub> -WHO <sub>94</sub>				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 <sub>P</sub> -WHO <sub>98</sub>				0.328		0.333	
Total TEQ <sub>P</sub> -WHO <sub>94</sub>				0.749		0.752	

Table 11-3. Weight percent concentrations of dioxin-like PCBs in aroclors, clophen, 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 <sub>P</sub> -WHO <sub>98</sub> conc. (nondetect set to zero) (mg/kg)	Mean conc. <sup>a</sup> (nondetect set to ½ detection limit) (g/kg)	TEQ <sub>P</sub> -WHO <sub>98</sub> conc. <sup>a</sup> (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 <sub>P</sub> -WHO <sub>98</sub>				7.47		12.5	
Total TEQ <sub>P</sub> -WHO <sub>94</sub>				8.70		13.74	
Aroclor 1248, Clophen A-40, and Kanechlor 400							
3,3',4,4'-TCB	77	13	13	4.36	0.44	4.36	0.44
3,4,4',5-TCB	81	6	4	1.76	0.18	1.77	0.18
2,3,3',4,4'-PeCB	105	9	8	10.12	1.01	10.12	1.01
2,3,4,4',5-PeCB	114	7	6	3.39	1.69	3.4	1.7
2,3',4,4',5-PeCB	118	8	8	20.98	2.1	20.98	2.1
2',3,4,4',5-PeCB	123	7	7	1.48	0.15	1.48	0.15
3,3',4,4',5-PeCB	126	11	6	0.11	10.55	0.14	13.51
2,3,3',4,4',5-HxCB	156	8	8	1.13	0.56	1.13	0.56
2,3,3',4,4',5'-HxCB	157	7	3	0.19	0.09	0.2	0.1
2,3',4,4',5,5'-HxCB	167	7	3	0.16	0.0016	0.16	0.0016
3,3',4,4',5,5'-HxCB	169	12	3	0.01	0.1006	0.041	0.41
2,2',3,3',4,4',5-HpCB	170	5	4	0.96	0	0.97	0
2,2',3,4,4',5,5'-HpCB	180	4	4	1.24	0	1.24	0
2,3,3',4,4',5,5'-HpCB	189	6	1	0.0018	0.0001833	0.06	0.006
Total TEQ <sub>P</sub> -WHO <sub>98</sub>				16.87		20.16	
Total TEQ <sub>P</sub> -WHO <sub>94</sub>				18.55		21.83	



Table 11-3. Weight percent concentrations of dioxin-like PCBs in aroclors, clophen, 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 <sub>P</sub> -WHO <sub>98</sub> conc. (nondetect set to zero) (mg/kg)	Mean conc. <sup>a</sup> (nondetect set to ½ detection limit) (g/kg)	TEQ <sub>P</sub> -WHO <sub>98</sub> conc. <sup>a</sup> (nondetect set to ½ detection limit) (mg/kg)
Aroclor 1254, Clophen A-50, and Kanechlor 500							
3,3',4,4'-TCB	77	15	12	0.8	0.0795	0.83	0.08
3,4,4',5-TCB	81	6	1	7.85	0.79	7.86	0.79
2,3,3',4,4'-PeCB	105	12	11	35.83	3.58	35.83	3.58
2,3,4,4',5-PeCB	114	9	6	12.17	6.08	12.23	6.11
2,3',4,4',5-PeCB	118	11	11	81.65	8.17	81.65	8.17
2',3,4,4',5-PeCB	123	8	8	4.59	0.46	4.59	0.46
3,3',4,4',5-PeCB	126	14	12	0.99	99.46	1.02	101.7
2,3,3',4,4',5-HxCB	156	10	10	11.08	5.54	11.08	5.54
2,3,3',4,4',5'-HxCB	157	9	8	1.91	0.95	1.93	0.97
2,3',4,4',5,5'-HxCB	167	10	9	2.74	0.0274	2.74	0.03
3,3',4,4',5,5'-HxCB	169	14	6	0.08	0.8	0.12	1.23
2,2',3,3',4,4',5-HpCB	170	8	8	5.06	0	5.06	0
2,2',3,4,4',5,5'-HpCB	180	7	7	5.79	0	5.79	0
2,3,3',4,4',5,5'-HpCB	189	7	2	0.045	0.0045429	0.13	0.013
Total TEQ <sub>P</sub> -WHO <sub>98</sub>				125.94			128.67
Total TEQ <sub>P</sub> -WHO <sub>94</sub>				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 <sub>P</sub> -WHO <sub>98</sub>					188.45		191.71
Total TEQ <sub>P</sub> -WHO <sub>94</sub>					192.62		195.89

**Table 11-3. Weight percent concentrations of dioxin-like PCBs in aroclors, clophens, and kanechlors (continued)**

<sup>a</sup>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); Frame et al. (1996b); Frame (1997).

**Table 11-4. 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 <sup>a</sup>
	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 <sup>b</sup> Annex II chemical waste landfill <sup>c</sup>
	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 <sup>b</sup> Annex II chemical waste landfill <sup>c</sup>
	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	Annex I incinerator Drained and rinsed transformers may be disposed of in Annex II chemical waste landfill
		PCB contaminated transformers	Disposal of drained transformers is not regulated
	PCB capacitors <sup>d</sup>		Annex I incinerator
	PCB hydraulic machines	Those containing >1,000 ppm PCB	Drained and rinsed machines may be disposed of as municipal solid waste or salvaged
		Those containing <1,000 ppm PCB	Drained machines may be disposed of as municipal solid waste or salvaged
	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

**Table 11-4. Disposal requirements for PCBs and PCB items (continued)**

PCBs/items	Waste characterization		Disposal requirements
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

<sup>a</sup>Annex I incinerator defined in 40 CFR 761.40.

<sup>b</sup>Requirements for other approved incinerators are defined in 40 CFR 761.10(e).

<sup>c</sup>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).

<sup>d</sup>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 (1987c).

**Table 11-5. 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

<sup>a</sup>Facilities left that particular cell blank on the Form R submissions.

NA = Not available

POTWs = Publicly owned treatment works

Sources: U.S. EPA (1993h, 1995g, 1998b, 2003c).

**Table 11-6. 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	650,797
1999	NA	0	0	a	a		0
1998	NA	0	0	0	a	60,854	60,854
1997	NA	0	0	0	a	3,081	3,081
1996	NA	2.3	114	0	0	4,179	4,295
1995	NA	0	0	0	0	0	0
1994	NA	0	0	0	0	0	0
1993	16	0	0	0	0	120	120
1992	20	0	0	0	0	0.5	0.5
1991	26	0	0	0	0	0	0
1990	NA	2.3	0	0	0	32,372	32,374
1989	NA	0	0	120	0	453	573
1988	122	2.7	0	4.5	0	341	348

<sup>a</sup>Facilities left that particular cell blank on the Form R submissions.

NA = Not available

Sources: U.S. EPA (1993h, 1995g, 1998b, 2003c).

**Table 11-7. Aroclor concentrations measured in EPA's National Sewage Sludge Survey<sup>a</sup>**

Aroclor	Percent detected	Maximum concentration (ng/kg)	Median concentration (ng/kg)	
			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

<sup>a</sup>For POTWs 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 (1996a).

**Table 11-8. Dioxin-like PCB concentrations measured in sludges collected from 74 U.S. publicly owned treatment works (POTWs) during 1994<sup>a,b</sup>**

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 <sub>P</sub> -WHO <sub>94</sub>				9.5	9.5	25.2	25.1
Total TEQ <sub>P</sub> -WHO <sub>98</sub>				9.3	9.2	24.3	24.2

<sup>a</sup>For POTWs with multiple samples, the sample concentrations were averaged by Cramer et al. (1994) to POTW averages before calculation of the total TEQ mean and median values presented in the table. The TEQ<sub>P</sub>-WHO<sub>94</sub> and TEQ<sub>P</sub>-WHO<sub>98</sub> values were calculated on a facility-level basis.

<sup>b</sup>Blank cells indicate that no measurements of these congeners were made.

Source: Green et al. (1995); Cramer et al. (1995).



**Table 11-9. Dioxin-like PCB concentrations in sewage sludge collected from a U.S. publicly owned treatment works during 1999**

Congener	IUPAC number	Mean emission factor (ng/kg)	
		Nondetect set to $\frac{1}{2}$ 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 <sub>P</sub> -WHO <sub>98</sub>		141	141

Source: U.S. EPA (2000f).

**Table 11-10. 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 (thousands of dry metric tons/yr)	Percent of total volume	Potential TEQ <sub>p</sub> -WHO <sub>98</sub> release <sup>a</sup> (g of TEQ/yr)	Potential TEQ <sub>p</sub> -WHO <sub>94</sub> release <sup>a</sup> (g of TEQ/yr)
Land application	1,714	32 <sup>b</sup>	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 <sup>c</sup>	1,819	33.9	44	45.6
Sludge incinerators and co-incinerators <sup>d</sup>	865	16.1	e	e
Ocean disposal <sup>f</sup>	336	6.3	0	0
<b>TOTAL</b>	<b>5,357</b>	<b>100</b>	<b>101</b>	<b>104.2</b>

<sup>a</sup>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<sub>p</sub>-WHO<sub>98</sub>/kg and 25.1 ng TEQ<sub>p</sub>-WHO<sub>94</sub>/kg).

<sup>b</sup>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.

<sup>c</sup>Landfills used for disposal of sewage sludge and solid waste residuals.

<sup>d</sup>Co-incinerators treat sewage sludge in combination with other combustible waste materials.

<sup>e</sup>See Section 11.4.6 for a discussion of dioxin-like PCB releases to air from sewage sludge incinerators.

<sup>f</sup>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, 1993b). 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, 1993b); Green et al. (1995); Cramer et al. (1995).

**Table 11-11. 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 (thousands of dry metric tons/yr)	Percent of total volume	Potential dioxin release <sup>a</sup> (g TEQ/yr)	
			TEQ <sub>P</sub> -WHO <sub>98</sub>	TEQ <sub>P</sub> -WHO <sub>94</sub>
Land application <sup>b</sup>	2,500	41	60.5	62.8
Advanced treatment <sup>c</sup>	700	12	16.9	17.6
Other beneficial use <sup>d</sup>	500	7	12.1	12.6
Surface disposal/Landfill	1,100	17	26.6	27.6
Incineration	1,400	22	e	e
Other disposal method	100	1	2.4	2.5
<b>TOTAL</b>	<b>6,300</b>	<b>100</b>	<b>118.5</b>	<b>123.1</b>

<sup>a</sup>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<sub>P</sub>-WHO<sub>98</sub>/kg and 25.1 ng TEQ<sub>P</sub>-WHO<sub>94</sub>/kg).

<sup>b</sup>Without further processing or stabilization, such as composting.

<sup>c</sup>Such as composting.

<sup>d</sup>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, 1993b). Therefore, it is estimated that 2 g (TEQ<sub>P</sub>-WHO<sub>98</sub> and TEQ<sub>P</sub>-WHO<sub>94</sub>) were released through distribution and marketing in 1995.

<sup>e</sup>See Section 3.5 for estimates of CDD/CDF releases to air from sewage sludge incinerators.

Sources: U.S. EPA (1999e); Green et al. (1995); Cramer et al. (1995).

**Table 11-12. 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 (thousands of dry metric tons/yr)	Percent of total volume	Potential TEQ <sub>DF</sub> -WHO <sub>98</sub> release <sup>a</sup> (g TEQ/yr)
Land application <sup>b</sup>	2,800	43	14.6
Advanced treatment <sup>c</sup>	800	12.5	4.2
Other beneficial use <sup>d</sup>	500	7.5	2.6
Surface disposal/landfill	900	14	4.7
Incineration	1,500	22	e
Other disposal method	100	1	0.5
<b>TOTAL</b>	<b>6,600</b>	<b>100</b>	<b>26.6</b>

<sup>a</sup>Potential dioxin TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (column 2) by the average of the mean TEQ<sub>DF</sub>-WHO<sub>98</sub> concentrations in sludge reported by U.S. EPA (2002) (i.e., 5.22 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg).

<sup>b</sup>Without further processing or stabilization, such as composting.

<sup>c</sup>Such as composting.

<sup>d</sup>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, 1993b). Therefore, it is estimated that 0.5 g TEQ<sub>DF</sub>-WHO<sub>98</sub> were released through distribution and marketing in 2000.

<sup>e</sup>See Section 3.5 for estimates of CDD/CDF releases to air from sewage sludge incinerators.

Sources: U.S. EPA (1999e, 2002a).

**Table 11-13. PCB congener group emission factors for industrial wood combustors<sup>a</sup>**

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	--

<sup>a</sup>Two sites for each congener group.

-- = No information given

Source: CARB (1990e, 1990f).

**Table 11-14. PCB congener group emission factors for medical waste incinerators (MWIs)<sup>a</sup>**

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

<sup>a</sup>See Section 3.3 for details on tested facilities.

APCD = Air pollution control device

-- = No information given

**Table 11-15. PCB congener group emission factors for a tire combustor<sup>a</sup>**

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	2724	1092	1092
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	--

<sup>a</sup>Three samples for each congener group.

Source: CARB (1991a).

**Table 11-16. Dioxin-like PCB concentrations in cigarette tobacco in brands from various countries (pg/pack)<sup>a</sup>**

<b>Congener</b>	<b>IUPAC number</b>	<b>U.S. (avg of 7 brands)</b>	<b>Japan (avg of 6 brands)</b>	<b>United Kingdom (avg of 3 brands)</b>	<b>Taiwan (1 brand)</b>	<b>China (1 brand)</b>	<b>Denmark (1 brand)</b>	<b>Germany (1 brand)</b>
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 <sub>P</sub> -WHO <sub>94</sub>		0.68	0.82	0.64	1.54	0.25	0.24	0.76
Total TEQ <sub>P</sub> -WHO <sub>98</sub>		0.64	0.8	0.62	1.49	0.24	0.23	0.75

<sup>a</sup>Blank cells indicate that no measurements of these congeners were made.

Source: Matsueda et al. (1994).



**Table 11-17. 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 $\frac{1}{2}$ 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 <sub>P</sub> -WHO <sub>98</sub>		0.51	0.51

Source: U.S. EPA (2000f).

**Table 11-18. Dioxin-like PCB emission factors from backyard barrel burning<sup>a</sup>**

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 <sub>p</sub> -WHO <sub>94</sub>		7.93e-03	1.24e-02	1.02e-02
Total TEQ <sub>p</sub> -WHO <sub>98</sub>		4.21e-03	6.31e-03	5.26e-03

<sup>a</sup>Blank cells indicate that the congener was not detected in either of the two duplicate samples.

Source: Lemieux (1997).

**Table 11-19. PCB congener group emission factors for a petroleum catalytic reforming unit<sup>a</sup>**

<b>Congener group</b>	<b>Mean concentration (ng/dscm) (at 12% O<sub>2</sub>)</b>	<b>Mean emission rate (lb/hr)</b>	<b>Mean emission factor (lb/1000 bbl)</b>	<b>Mean emission factor (ng/barrel)</b>
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
<b>Total PCBs</b>	<b>6,155</b>	<b>2.04e-06</b>	<b>2.61e-07</b>	<b>1.18e+02</b>

<sup>a</sup>Three samples and three detections for each congener group.

Source: CARB (1999).

**Table 11-20. 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 <sup>3</sup> /molecule-sec)	Estimated tropospheric lifetime (days) <sup>a</sup>	Estimated tropospheric half-life (days) <sup>a</sup>
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

<sup>a</sup>Calculated using a 24-hr, seasonal, annual, and global tropospheric average OH radical concentration of  $9.7 \times 10^5$  molecule/cm<sup>3</sup> (Prinn et al., 1995).

Source: Atkinson (1995) (based on Atkinson [1991]; Kwok et al. [1995]).

**Table 11-21. Estimated PCB loads in the global environment as of 1985**

<b>Environment</b>	<b>PCB load (metric tons)</b>	<b>Percentage of PCB load</b>	<b>Percentage of world production</b>
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 <sup>a</sup>	783,000		65
World production	1,200,000 <sup>b</sup>		100

<sup>a</sup>Still in use in electrical equipment and other products, and deposited in landfills and dumps.

<sup>b</sup>This value is from Tanabe (1988). DeVoogt and Brinkman (1989) estimated worldwide production to have been 1,500,000 metric tons.

Source: Tanabe (1988).

**Table 11-22. 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	14,651
1958	0	7	51	4,737	1,161	3,035	2,713	83	33	11,821
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	17,296
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	23,494
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	28,334
1968	0	62	41	20,345	2,220	4,033	2,382	327	127	29,536
1969	0	230	124	20,634	2,563	4,455	2,013	323	136	30,479
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	15,559
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	3,412	924	195,596	26,856	56,120	41,525	3,255	1,307	360,620
% 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 11-23. Estimated U.S. usage of PCBs by use category, 1930–1975**

Use class	Use category	Amount used (1000 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 11-24. Estimated direct releases of aroclors to the U.S. environment, 1930–1974<sup>a</sup> (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	14,817
1957	0	903	319	307	423	1,952
1958	0	649	483	416	355	1,903
1959	0	1,042	724	518	507	2,792
1960	0	1,340	556	449	540	2,885
1961	0	1,852	792	587	611	3,841
1962	0	1,811	659	554	571	3,594
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	4,872
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	6,596
1970	0	4,569	697	1,168	474	6,907
1971	76	1,466	51	325	121	1,963
1972	474	22	0	104	9	135
1973	534	141	0	181	0	322
1974	498	141	0	140	0	281
<b>TOTAL</b>	<b>1,582</b>	<b>43,103</b>	<b>13,205</b>	<b>11,572</b>	<b>9,019</b>	<b>76,898</b>
% of total	2.1	56.1	17.2	15	11.7	100

<sup>a</sup>Does not include an additional 132,000 metric tons estimated to have been landfilled during this period.

Source: Versar, Inc. (1976).



**Table 11-25. Estimated releases of dioxin-like PCB TEQs to the U.S. environment, 1930–1977**

<b>Aroclor</b>	<b>Percent of U.S. sales<sup>a</sup> (1957–1974)</b>	<b>Estimated PCB releases (1930–1974)<sup>b</sup> (metric tons)</b>	<b>Estimated mean TEQ<sub>P</sub>-WHO<sub>98</sub> concentration<sup>c</sup> (mg/kg)</b>	<b>Estimated total TEQ<sub>P</sub>-WHO<sub>98</sub> released (kg)</b>
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	--	--	--
<b>TOTAL</b>				<b>3,702</b>

<sup>a</sup>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.

<sup>b</sup>From Table 11-20.

<sup>c</sup>From Table 11-3 (assumes nondetect values are zero).

<sup>d</sup>Data are available for only a few samples of Aroclor 1016 where only two dioxin-like PCB congeners were detected. The total TEQ<sub>P</sub>-WHO<sub>98</sub> released is less than 0.01 kg.

-- = Indicates that release estimates were not made because of relatively low usage amounts

Source: Versar, Inc. (1976).

## 12. 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, 1992b; 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 be underestimates of actual emissions for several reasons. 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 underestimate releases from known sources or may not identify 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. Annual releases from reservoir sources are not counted in the quantitative inventory of dioxin sources because such releases are considered as recirculation of “old” and previously formed dioxin.

### 12.1. POTENTIAL RESERVOIRS

Chapters 2 through 11 discuss both known and suspected sources of newly formed dioxin-like compound releases 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

1 according to both the nature of the release and the contaminant's chemical and physical  
2 properties.

3 For this analysis, reservoirs are defined as materials or places that contain previously  
4 formed CDDs/CDFs or dioxin-like PCBs and have the potential for redistribution and circulation  
5 of these compounds into the environment. Potential reservoirs include soils, sediments, biota,  
6 water, and some anthropogenic materials. Reservoirs become sources when they release dioxin-  
7 like compounds to the circulating environment over a defined time and space. Like other  
8 sources, they would not include purely intermediate products or materials properly disposed in a  
9 secure landfill. Reservoir sources are not included in the quantitative inventory of contemporary  
10 sources because they do not involve original releases but rather the recirculation of past releases.  
11 They can, however, contribute to human exposure and, therefore, are important to consider.

12 The rate of movement from one environmental medium to another is termed "flux," and  
13 it refers to the direction and magnitude of flow and exchange over a reference time period and  
14 space. Figure 12-1 presents a conceptual diagram of flux and exchange of dioxin-like  
15 compounds to multiple environmental compartments, including the principal environmental  
16 reservoirs—soil, water, air, sediment, and biota. This dynamic system consists of fluxes in and  
17 out of the atmosphere as well as other exchanges between reservoirs and the atmosphere.  
18 Movement between media can be induced by volatilization, wet and dry atmospheric particle  
19 and vapor deposition, adsorption, erosion and runoff, resuspension of soils into air, and  
20 resuspension of sediments into water.

## 21 22 **12.2. CHARACTERIZATION OF RESERVOIR SOURCES**

23 This section is organized according to reservoir type (soil, water, sediment, and biota),  
24 with each subsection providing information in three parts: (1) the potential magnitude (mass) of  
25 dioxin-like compounds in the reservoir, (2) the chemical/physical mechanisms responsible for  
26 releases of these compounds, and (3) estimates of potential annual releases from the reservoir if  
27 such estimates are feasible, given the available state of knowledge. Although, anthropogenic  
28 structures (e.g., PCP-treated fenceposts, telephone poles) are potential reservoir sources, they are  
29 not discussed here because they are covered in Chapter 8 (the most detailed discussion is on  
30 PCP, Section 8.3.8).

## 12.2.1. Soil

### 12.2.1.1. *Potential Mass of Dioxin-Like Compounds Present*

In estimating burdens for the U.K., Harrad and Jones (1992b) 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<sup>3</sup>. Coupling these assumptions with the rural and urban U.S. surface areas and TEQ concentrations yields soil burden estimates of 1,350 kg TEQ<sub>DF</sub>-WHO<sub>98</sub> (1,530 kg I-TEQ<sub>DF</sub>) in rural soils and 220 kg TEQ<sub>DF</sub>-WHO<sub>98</sub> (250 kg I-TEQ<sub>DF</sub>) in urban soils in the United States.

Higher concentrations of CDDs/CDFs than those presented above for background urban and rural soils may be present in soils underlain by municipal and industrial waste and in soils at contaminated industrial sites. 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 for these soils at present. Higher concentrations may also be present in the soils of areas that have been treated with pesticides contaminated with 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 in agricultural and nonagricultural settings in the United States as post-emergence herbicides for control of broadleaf weeds and brush. Commercial production in the United States started in 1944 (Esposito et al., 1980) and 2,4-D 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, 1994b, 1997e). Table 12-1 presents a compilation of domestic production, sales, and usage volumes for 2,4-D and its salts and esters.

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 (LOQ) 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 8-25. The average TEQ in these tests was 1.1 µg TEQ<sub>DF</sub>-

WHO<sub>98</sub>/kg (0.7 µg I-TEQ<sub>DF</sub>/kg). Schechter et al. (1997) reported similar concentrations in 2,4-D samples manufactured in Europe and Russia; lower levels were observed in U.S. products. The results of Schechter et al. (1997) are presented in Table 8-27.

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 1975 to 1995 was 550 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (350 g I-TEQ<sub>DF</sub>).

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 12-2 presents a compilation of domestic production, sales, and usage volumes for 2,4,5-T and its salts and esters. As shown in Table 12-2, 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.

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 (Dow Chemical Co., undated). 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). Schechter 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 12-3, indicate a total TEQ<sub>DF</sub>-WHO<sub>98</sub> concentration of 3.26 µg/kg (2.88 µg I-TEQ<sub>DF</sub>/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) the average annual consumptions during the 1950s, 1960s, and 1970s were 2,000, 4,000, and 1,500 metric tons/yr, respectively; and (2) the average 2,3,7,8-TCDD concentrations in 2,4,5-T used over these three decades were 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 1950 to 1979 is 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<sub>DF</sub>-WHO<sub>98</sub> (103 g I-TEQ<sub>DF</sub>) in 1995 (see Section 8.4.1 for details). If this same amount of TEQ had been applied each year during the period 1975 to 1995, the total amount applied would have been 1,500 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (2,000 g I-TEQ<sub>DF</sub>).

#### **12.2.1.2. Mechanisms Responsible for Releases from Surface Soils**

Atmospheric deposition is believed to be the current primary source of dioxin-like compounds in surface soil. 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

1 soils, physical/chemical and biological mechanisms (photolysis and biodegradation) can slowly  
2 alter the composition and amount of compound present. Studies indicate that the dioxin-like  
3 compounds (particularly the more highly chlorinated CDDs/CDFs) exhibit little downward  
4 mobility after they are deposited in or on soil (Puri et al. 1989; Freeman and Schroy, 1985;  
5 Orazio et al., 1992; Paustenbach et al., 1992). However, remobilization of the compounds to the  
6 atmosphere is possible through volatilization and resuspension of soil particles.

7 Young (1983) conducted field studies on the persistence and movement of 2,3,7,8-TCDD  
8 during 1973 to 1979 on a military test area that had been aerially sprayed with 73,000 kg of  
9 2,4,5-T during 1962 to 1970. TCDD levels of 10 to 1,500 ng/kg were found in the top 15 cm of  
10 soil 14 yr after the last application of herbicide at the site. Although actual data were not  
11 available on the amount of 2,3,7,8-TCDD originally applied as a contaminant of the 2,4,5-T, best  
12 estimates indicated that less than 1% of the applied 2,3,7,8-TCDD remained in the soil after  
13 14 yr. Young suggested that photodegradation at the time of and immediately after aerial  
14 application was responsible for most of the disappearance; however, once incorporated into the  
15 soil, the data indicated a half-life of 10 to 12 yr. Similarly, Paustenbach et al. (1992) concluded  
16 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  
17 below the surface could be 25 to 100 yr.

18 Ayris and Harrad (1997) studied the mechanisms affecting volatilization fluxes of several  
19 PCB congeners (PCB numbers 28, 52, 101, 138, and 180) from soil and found positive  
20 correlations between flux and soil temperature, soil moisture content, and soil PCB  
21 concentration. For PCBs, secondary releases from soils (primarily via volatilization) are  
22 believed to currently exceed primary emissions in the U.K. (Harner et al., 1995; Jones and  
23 Alcock, 1996). Lee et al. (1998) quantified PCBs in air samples taken every 6 hr over a 7-day  
24 period in the summer at a rural site in England and found a strong correlation between air  
25 temperature and PCB congener concentrations. The concentrations followed a clear diurnal  
26 cycle, thus providing some evidence that rapid, temperature-controlled soil-to-air exchange of  
27 PCBs influences air concentrations and enables regional/global scale cycling of these  
28 compounds.

29 CDDs/CDFs and PCBs sorbed to soil and urban dust particles can also be moved from  
30 the terrestrial environment to the aquatic environment via stormwater runoff/erosion. Results of  
31 recent research indicate that, for at least some water bodies, erosion/stormwater runoff is  
32 currently the dominant mechanism for CDD/CDF input. Smith et al. (1995) analyzed CDD/CDF

1 concentrations in sediment cores, air, precipitation, soil, and stormwater runoff in an effort to  
2 determine the contributing sources of these compounds to the lower Hudson River. The mass  
3 balance estimates developed from these data for 1990 to 1993 are stormwater runoff entering  
4 tributaries (76% of total CDD/CDF input), anthropogenic wastes (19%), atmospheric deposition  
5 (4%), and shoreline erosion (less than 1%). The authors projected the percent contribution of  
6 these same sources for 1970 as anthropogenic wastes (70%), stormwater runoff into tributaries  
7 (15%), atmospheric deposition (15%), and shoreline erosion (0.1%).

8 Lebeuf et al. (1996) analyzed sediment cores from different locations in the lower St.  
9 Lawrence River Estuary and the Gulf of St. Lawrence. The congener group profiles found in the  
10 samples indicate that the input of CDDs/CDFs is primarily from the atmosphere. Comparison of  
11 the CDD/CDF concentrations in sediments collected from areas where sediment accumulation is  
12 due primarily to fluvial transport with sediments from areas where sediment accumulation is due  
13 primarily to direct atmospheric deposition onto the water indicates that the contribution of  
14 CDDs/CDFs from direct atmospheric deposition represents less than 35% of the sediment  
15 burden. Thus, the primary source of CDDs/CDFs is emissions to the atmosphere upwind of the  
16 estuary that are deposited within the watershed and subsequently transported downstream by  
17 fluvial waters.

18 Paustenbach et al. (1996) and Mathur et al. (1997) reported that stormwater runoff from  
19 15 sites in the San Francisco area contained CDD/CDF TEQ at levels ranging from 0.01 to 65 pg  
20 I-TEQ<sub>DF</sub>/L; most samples contained less than 15 pg I-TEQ<sub>DF</sub>/L. The sites differed widely in land  
21 use; the highest levels measured were obtained from an urban but nonindustrialized area. A  
22 distinct variability was noted in the results obtained at the same sampling location during  
23 different rain events. The profiles of CDDs/CDFs in the urban stormwater samples were similar,  
24 particularly in samples collected at the onset of rain events. Stowe (1996) reported similar  
25 findings from analyses of sediments from three stormwater basins collecting runoff from a  
26 military base, a city street, and parking lots.

27 Fisher et al. (1998) reported that urban runoff samples from eight sites (15 samples) in  
28 the Santa Monica Bay watershed contained CDD/CDF TEQ at levels ranging from 0.7 to 53 pg  
29 I-TEQ<sub>DF</sub>/L (all but one sample were in the range of 0.7 to 10 pg I-TEQ<sub>DF</sub>/L). The samples were  
30 collected in 1988/1989 from continuously flowing storm drains during both dry and storm  
31 periods. The mean concentration measured during storm events, 18 pg I-TEQ<sub>DF</sub>/L, was higher  
32 than concentration observed during dry periods, 1 pg I-TEQ<sub>DF</sub>/L.



### 12.2.1.3. *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 below 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<sub>DF</sub> in 1995). Similarly, the estimate derived below 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., 1998). 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<sub>DF</sub>/L. The wide variability and limited geographic coverage of these data preclude derivation of a national emission 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  $1.9 \times 10^{14}$  L/yr. If it is assumed that urban runoff in the United States averages 1 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (1 pg I-TEQ<sub>DF</sub>/L) (i.e., approximately the midpoint of the range reported by Mathur et al., 1997, and Fisher et al., 1998), this source could contribute a total of 190 g TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub>/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.

1 Assuming that the amount of land classified as urban did not change significantly from 1987 to  
2 1990, the urban areas for each state in 1990 were assumed to be equal to those in 1987.  
3 Similarly, an approximation for urban area for each state was estimated by summing the urban  
4 area acreage available from the 2000 census. An approximation of the 1995 urban area for each  
5 State was estimated by taking the average of the 1990 and 2000 estimates. Multiplying the 30-  
6 year average rainfall by the urban area for each state and summing the results provides an  
7 estimated amount of urban runoff for the conterminous United States. The urban runoff was  
8  $1.24 \times 10^{14}$ ,  $1.33 \times 10^{14}$ , and  $1.42 \times 10^{14}$  L/year for 1987, 1995, and 2000, respectively.  
9 Applying the emission factors generated above, urban runoff contributed 124, 133, and 142 g I-  
10  $\text{TEQ}_{\text{DF}}$  or  $\text{TEQ}_{\text{DF}}\text{-WHO}_{98}$  to U.S. waterways in 1987, 1995, and 2000, respectively. These  
11 numbers are in agreement with the estimate developed using Lockheed Martin (1998) data.

12 **Rural Soil Erosion.** Using acreage and erosion factors for cropland provided in the  
13 2001 Annual National Resources Inventory (USDA, 2003), 1.36, 1.07, 0.96, and 0.91 billion  
14 metric tons of soil and rill erosion were generated in 1987, 1992, 1997, and 2001, respectively.  
15 Likewise, using acreage data for rangeland from USDA (2003) and a soil and rill erosion factor  
16 of 4.2 tons/acre/year (USDA, 1995), approximately 1.55 billion metric tons of soil and rill  
17 erosion were generated in 1987, 1992, 1997, and 2001. For purposes of estimating values for the  
18 reference years 1995 and 2000, it is assumed that the 1995 erosion estimate will be the average  
19 of soil and rill erosion estimates developed for 1992 and 1997, and that the 2001 numbers will  
20 approximate those generated in 2000. The total amount of eroded soil entering waterways is  
21 greater than this value, because this value does not include soil erosion from construction areas,  
22 forests, and other non-crop and non-rangelands. The data summarized in the U.S. EPA, 2000b  
23 report suggest that typical concentrations of CDDs/CDFs in soils in rural areas is about 2.8 ng  
24  $\text{TEQ}_{\text{DF}}\text{-WHO}_{98}/\text{kg}$ . It is not known how well this estimate represents eroded soil from cropland  
25 and rangeland. If these soils contain an average of 1 ng  $\text{TEQ}_{\text{DF}}/\text{kg}$  (i.e., a lower value than the  
26 background value for all types of rural soil), they would contribute 2,900, 2,600, and 2,500 g  
27  $\text{TEQ}_{\text{DF}}\text{-WHO}_{98}$  to the Nation's waterways in 1987, 1995, and 2000, respectively. Given the  
28 uncertainties in both the amount of eroded soil and dioxin levels, these estimates are considered  
29 preliminary (i.e., category D). As with urban runoff, no data were available to make similar  
30 estimates for PCBs.

#### 12.2.1.4. *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 are developed in 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  $\mu\text{m}$  to 0.3  $\mu\text{m}$ , 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  $\mu\text{m}$ , 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  $\mu\text{g}/\text{m}^3$  for rural areas and 5 to 25  $\mu\text{g}/\text{m}^3$  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

1 from soils to be  $1 \times 10^{-3}$  to  $4 \times 10^{-3}$  pg/m<sup>3</sup> in rural areas and 0.01 to 0.05 pg/m<sup>3</sup> in urban areas.  
2 These particulate dioxin concentrations were compared to average total particulate dioxin levels  
3 of 1.36 pg/m<sup>3</sup> in Eitzer and Hites (1989) to arrive at the conclusion that soil re-entrainment could  
4 account for only 1 to 4% of the particulate dioxins in the atmosphere in urban areas and 0.1 to  
5 0.3% of those in rural regions (Kao and Venkataraman, 1995).

6 This information on the size distribution of ambient aerosols and relative CDD/CDF  
7 concentrations in different particle size fractions was integrated with particle size deposition  
8 velocities to estimate the relative contribution to the total mass deposition flux for small and  
9 large particle sizes. Even though re-entrained soil may constitute only a small fraction of the  
10 atmospheric levels of CDDs/CDFs, the contribution of dioxins in re-entrained surface soil to the  
11 total deposition flux could be significant because coarse particles dominate in dry deposition.  
12 Soil re-entrainment could possibly account for as much as 70 to 90% of the total dry deposition  
13 of CDDs/CDFs in urban areas and 20 to 40% in rural regions (Kao and Venkataraman, 1995).

14 Two approaches were used by Jones and Alcock (1996) to assess the potential  
15 significance of CDD/CDF volatilization from soils: the fugacity quotient concept and a simple  
16 equilibrium partitioning model. The fugacity quotient model compares fugacities of individual  
17 CDD/CDF compounds in different environmental media to determine the tendency for these  
18 compounds to accumulate in particular environmental compartments (McLachlan, 1996).  
19 Fugacities for individual compounds, by media, were estimated by Jones and Alcock (1996) on  
20 the basis of physical/chemical properties of the compounds as well as the concentrations in the  
21 media. In this instance, fugacity quotients were calculated for air and soil by dividing each  
22 compound's fugacity for air by that of soil. Quotients near 1 indicate equilibrium conditions  
23 between media; values greater than 1 represent a tendency for flux (volatilization) from soil to  
24 air, and values less than 1 indicate a net flux to the soil from the air. The equilibrium  
25 partitioning model used by Jones and Alcock predicts the maximum (possible "worst case") flux  
26 of CDDs/CDFs from soil to the atmosphere. Air phase-to-soil partition coefficients were  
27 calculated using the ratios of soil and air fugacity capacities. Equilibrium air concentrations  
28 were then calculated using typical U.K. soil concentrations for both urban and rural settings.

29 From the fugacity quotient model, Jones and Alcock (1996) concluded that the less-  
30 chlorinated CDDs/CDFs may be close to soil-air equilibrium in the U.K., whereas for other  
31 congeners, soil is a sink rather than a source to the atmosphere. The authors reported that the  
32 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 12-4 summarizes the calculated fluxes.

During the 1960s and 1970s, levels of total PCBs in U.K. soils reached average levels of approximately 300  $\mu\text{g/kg}$  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.

## **12.2.2. Water**

### **12.2.2.1. *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  $\text{km}^2$  (U.S. DOC, 1995a). 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  $\text{m}^3$ . No compilation of CDD/CDF measurements in inland surface waters is made for this report; however, if it is assumed that the “typical” value used by Duarte-Davidson et al. (1997) for rivers in the U.K., 38  $\text{pg I-TEQ}_{\text{DF}}/\text{m}^3$ , is representative of U.S. waters, then the burden is calculated to be 137 g I- $\text{TEQ}_{\text{DF}}$ .

#### 12.2.2.2. *Mechanisms Responsible for Supply to and Releases from Water*

As discussed in Section 12.2.1, 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

$$F = K_{ol}(C_w - C^*) \quad (12-1)$$

where  $F$  is the flux ( $\text{mol/m}^2\text{-day}$ ),  $C_w$  ( $\text{mol/m}^3$ ) is the dissolved PCB concentration in the bulk water, and  $C^*$  ( $P/H$ ,  $\text{mol/m}^3$ ) is the air concentration expressed as a water concentration in equilibrium with the air. The variable  $P$  is the vapor-phase air concentration measured ( $\text{mol/m}^3$ ) and converted to units of pressure using the ideal gas law;  $H$  is Henry's Law constant ( $\text{atm-m}^3/\text{mol}$ ). The overall mass-transfer coefficient,  $K_{ol}$ , has units of velocity ( $\text{m/day}$ ). 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:

$$1/K_{ol} = 1/k_w + RT/Hk_a \quad (12-2)$$

where  $k_w$  is the water-side mass transfer coefficient (m/day) and  $k_a$  is the air-side mass transfer coefficient (m/day).  $H$  is Henry's Law constant,  $R$  is the universal gas constant ( $8.2057 \times 10^{-5}$  atm-m<sup>3</sup>/mol K), and  $T$  is the absolute temperature, K.

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 12-1).

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<sup>2</sup> per day at low wind speeds (1 to 3 m/sec) to 50 to 1,300 ng/m<sup>2</sup> per day at higher wind speeds (4 to 6 m/sec). On a congener basis, the less-chlorinated congeners dominated total fluxes. The summary of flux calculations is presented in Table 12-5. 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 (1) atmospheric PCB concentrations were higher over contaminated water than over nearby land, (2) atmospheric PCBs over water tended to increase with increasing dissolved PCB concentrations, and (3) 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; and 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.

<u>Water Body</u>	Total PCB volatilization rate (ng/m <sup>2</sup> -day)	<u>Reference</u>
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)

### 12.2.3. Sediment

#### 12.2.3.1. *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 is 5.3 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg (5.3 ng I-TEQ<sub>DF</sub>/kg) dry weight. For most of the lakes, the uppermost layer represents about 10 yr 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<sub>DF</sub>/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<sup>2</sup> (U.S. DOC, 1995a). 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 are located in the top 5 cm of sediment, and (3) that sediment density is 0.13 g dry weight/cm<sup>3</sup>. 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<sub>DF</sub>-WHO<sub>98</sub> (120 kg I-TEQ<sub>DF</sub>).

#### 12.2.3.2. *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



1 sink for persistent hydrophobic organic compounds, because these compounds are likely to be  
2 strongly bound to organic particles in the sediment.

3 For example, Muir et al. (1985) radiolabeled 2,3,7,8-TCDD and studied its dissipation  
4 from sediments (collected from a farm pond and a lake) to the water column in laboratory  
5 studies under static aerobic conditions at 10EC. After 675 days, more than 80% of the labeled  
6 TCDD were still present in the pond sediment, and 87% were still present in the lake sediment.  
7 Aeration had little effect on the dissipation rates.

8 The concept of fugacity is a useful way to estimate the behavior of dioxin-like  
9 compounds in sediments. Fugacity (the tendency of a chemical to escape from a phase) is  
10 expressed in units of pressure (pascals or Pa) and is the partial pressure exerted by the chemical  
11 in each medium. Fugacity models estimate equilibrium concentrations in specific media at given  
12 chemical concentrations in the environment. Clark et al. (1988) suggested evaluating  
13 contaminant concentrations in multiple environmental media by comparing fugacity of adjoining  
14 media (e.g., comparing sediment fugacity with water column fugacity to determine a chemical's  
15 tendency to move from one to the other). The authors evaluated fugacities of certain  
16 organochlorine compounds, including PCBs, in air, water, sediment, fish, and fish-eating birds  
17 and their eggs. The authors presented PCBs fugacities developed from data collected in a study  
18 of the Lake Ontario region. The fugacities of PCBs in various media can be ranked as  
19 birds>fish>water>bottom sediment, indicating that PCBs and other similar chemicals are likely  
20 to remain in bottom sediment and are less likely to re-enter the water column.

#### 21 22 **12.2.3.3. Releases from Sediment to Water**

23 Given the lack of data, no quantitative estimates of annual releases can be made. Ling et  
24 al. (1993) evaluated the fate of various chemicals, including PCBs, in Hamilton Harbour, located  
25 in Ontario, Canada, using a modified version of the Quantitative Water Air Sediment Interaction  
26 (QWASI) fugacity model. Among the processes evaluated were diffusion between air and water  
27 and sediment and water; sediment deposition, resuspension, and burial; and sediment  
28 transformation. Three primary compartments were studied: air, water, and bottom sediments.  
29 The sediment was treated as a simple, well-mixed surface layer of active sediment and the buried  
30 sediment underneath. Chemicals in the active sediment were assumed to be able to exchange  
31 with the overlying water; chemicals in the buried sediment were assumed to be isolated from the  
32 sediment-water exchange. Sediment was assumed to be homogenous rather than heterogenous.

1 The epi- and hypolimnetic compartments of the water column were defined on the basis of a  
2 thermocline, and the atmosphere was defined as a semi-infinite medium of constant, defined  
3 composition.

4 Ling et al. estimated rates of PCB movement on the basis of 1987 loadings using two  
5 models: one with and one without a thermocline. The results for the water-sediment transfer  
6 using the model with a thermocline were ~32 kg/yr entering the hypolimnion from the  
7 epilimnion, ~27 kg/yr entering the surface sediment from the hypolimnion, and ~18 kg/yr  
8 (>50%) going to burial. For sediment-to-water transfer, ~7 kg/yr transferred to the hypolimnion  
9 and then 12.5 kg/yr transferred to the epilimnion. Similar numbers were found in the single  
10 water column model (the model without a thermocline).

11 Both the model with a thermocline and the model without a thermocline predicted  
12 volatilization from the water to the atmosphere—1.6 kg/yr and 1.8 kg/yr, respectively.  
13 However, the actual contribution of PCBs from sediment to air was not determined. A  
14 comparison of estimated concentrations with observed values are presented in Table 12-6. For  
15 PCBs, 68% were buried in the sediment, 20% were exported to Lake Ontario, 5.4% degraded in  
16 the water and sediment, and 6% volatilized. The authors noted that these percentages are  
17 uncertain. At the sediment-water exchange, more than 90% of each chemical was contained in  
18 the sediment because of particle deposition and the high affinity of the chemical for sediment.  
19 There was no indication that contaminants buried in the bottom sediments are transferred  
20 through diffusion mechanisms back to the surface sediments; however, episodic release of these  
21 chemicals from surface sediments can occur through mechanisms such as resuspension during  
22 flooding or lake inversions and uptake/ingestion by benthic biota.

#### 23 24 **12.2.4. Biota**

##### 25 **12.2.4.1. *Potential Mass of Dioxin-Like Compounds Present***

26 The mass of CDDs/CDFs in biota in the United States was not estimated as part of this  
27 report. However, to place perspective on the potential magnitude of this reservoir, 82 g I-TEQ<sub>DF</sub>  
28 have been estimated to be present in biota in the U.K. (50 g in humans and 32 g in vegetation),  
29 which is about three orders of magnitude less than the mass estimated to be present in U.K.  
30 surface soils (Duarte-Davidson et al., 1997; Eduljee and Dyke, 1996). No data are available to  
31 estimate the biota burden in the United States.

#### 12.2.4.2. *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; Horstman 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). Horstman 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, 1993a, j). 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,

1 animal life has a greater potential than does vegetation for being a long-term reservoir source of  
2 CDDs/CDFs. The majority of the dioxin-like compounds released by animals in the form of  
3 waste materials will be released to water or soil. Similarly, upon death, the dioxin-like  
4 compounds remaining in the body will be deposited onto soil or aquatic sediments or will be  
5 ingested by other animals.

#### 6 7 **12.2.4.3. *Approaches for Measuring and Estimating Releases from Biota***

8 Researchers have investigated the uptake and release of CDDs/CDFs by vegetation  
9 through measurement of actual concentrations during uptake and release by vegetation grown in  
10 closed systems (greenhouses). Bacci et al. (1992) conducted uptake and release studies of  
11 1,2,3,4-TCDD by plant foliage in a closed system (specially constructed greenhouse).  
12 Concentrations of TCDD vapor in the greenhouse air were maintained during the 370-hr uptake  
13 phase at a mean concentration of 0.0062 ng/L (air concentration varied slightly from 0.005 to  
14 0.0075 ng/L). To begin the release phase, the TCDD vapor source (amended sand) as well as the  
15 greenhouse walls were removed, and release of CDDs/CDFs from the leaves was measured for  
16 500 hr. The authors concluded that, during uptake, TCDD concentration in the leaves varied as a  
17 function of time and was dependent on the concentration of vapor-phase TCDD in the  
18 surrounding air. They estimated the release of TCDD from the vegetation to be relatively slow,  
19 with a half-life of TCDD of 3,300 hr.

20 McCrady and Maggard (1993) conducted a mass balance study of uptake and release of  
21 dioxin in grass foliage. The results indicated a half-life of dioxin in grass of 128 hr. These  
22 researchers also noted that photodegradation of dioxins on the foliage appeared to be a  
23 significant removal mechanism, in addition to volatilization. They calculated the  
24 photodegradation half-life to be 44 hr.

25 Interpretation of uptake and release data over variable exposure times and contaminant  
26 concentrations has led to the development of models describing air-to-vegetation equilibrium  
27 and kinetics controlling the behavior of dioxin in vegetation. Some earlier fugacity modeling  
28 attempts described the leaf of a plant as behaving as a single compartment. One-compartment  
29 models were described by Bacci et al. (1990a, b), Trapp et al. (1990), and Schramm et al. (1987)  
30 (as cited in Tolls and McLachlan, 1994). Researchers presenting most of the recently developed  
31 models claim that the available data better support the concept of a leaf behaving as two  
32 compartments (Riederer, 1990; Paterson et al., 1991; Horstman and McLachlan, 1992; McCrady

1 and Maggard, 1993; Tolls and McLachlan, 1994; McLachlan et al., 1995). Input parameters  
2 considered by most models include critical chemical characteristics of the contaminant,  
3 characteristics of the plant, exposure times, and contaminant concentrations measured within the  
4 plant. Riederer (1990) suggested treating a leaf as multiple compartments having different  
5 accessibility to the atmosphere and different diffusion resistances.

6 Input parameters for the two-compartment model are octanol/water coefficients,  
7 cuticle/water partition coefficients, aqueous solubility, and saturation vapor pressure of the  
8 chemical of concern. Outputs of the model are prediction of equilibrium concentration in  
9 different leaf tissues, estimates of air-to-vegetation bioconcentration equilibria, and  
10 identification of leaf compartments in which compounds are likely to accumulate. Riederer  
11 (1990) also presented an approach for using the model to semiquantitatively assess the potential  
12 for revolatilization of dioxins from vegetation.

13 One advantage of the model presented by Riederer (1990) is that it considers critical  
14 plant characteristics in the release of dioxins. A plant is an active organism, responding to  
15 changes in its environment and acting accordingly to ensure its survival. Certain plant  
16 characteristics, such as the action of stomata (specialized cells usually on the lower leaf surface  
17 that open and close to control passage of vapors into and out of the leaf interior) and total leaf  
18 volume, are important factors that effect the release rates of vapor phase contaminants from  
19 vegetation.

20 Paterson et al. (1991) also presented a two-compartment model for release of dioxin-like  
21 compounds from vegetation. This model describes a plant as being made up of compartments in  
22 terms of their volume fractions of air, water, and nonpolar (lipid-soluble, or octanol-equivalent)  
23 organic matter. Paterson et al. attempted to show that leaf-air equilibrium and kinetics can be  
24 correlated with chemical properties of the contaminant and properties of the leaf. The authors  
25 suggested that the clearance rate constant ( $k_2$ ) can be correlated with the bioconcentration factor.  
26 This model does not consider critical plant characteristics, such as action of the stomata, and for  
27 this reason it may be less reliable than models that do consider plant characteristics, such as the  
28 model presented by Riederer (1990).

29 Horstman and McLachlan (1992) developed a fugacity model to describe release of  
30 semivolatile organic compounds from the surface of a solid (spruce needles). Their approach  
31 was slightly different in that their goal was instrument/method development, but their data  
32 supported the behavior of a leaf as a two-compartment system.

1 McCrady and Maggard (1993) also collected data supporting the importance of viewing a  
2 leaf as a two-compartment system. They used a two-compartment model similar to the one  
3 described by Paterson et al. (1991) that also does not consider critical plant characteristics and  
4 thus may be less reliable than models that do (e.g., Reiderer, 1990).

5 Tolls and McLachlan (1994) exposed grass cultures for up to 240 hr to several  
6 semivolatile organic compounds and then measured the release of contaminants from the grass.  
7 They developed a two-compartment partitioning model based on the data they collected. The  
8 model consisted of a small surface compartment (the leaf cuticle) and a large interior reservoir  
9 (air spaces within the leaf). Their model assumes that the flux of a chemical is the product of the  
10 fugacity difference (surface fugacity minus reservoir fugacity) and the conductance between the  
11 leaf compartments.

12 In an attempt to validate this model, McLachlan et al. (1995) compared concentrations of  
13 semivolatile organic compounds measured in grass grown under field conditions with  
14 concentrations predicted by their previous laboratory work with a fugacity meter. The  
15 concentrations measured in the grass cultures agreed with results predicted by the mathematical  
16 model described by Tolls and McLachlan (1994).

### 17 18 **12.3. SUMMARY AND CONCLUSIONS**

19 As depicted in Figure 12-1 a set of complex relationships exists among reservoirs and  
20 between reservoirs and contemporary formation sources. The significance of reservoirs for  
21 human exposure is more dependent on their ability to affect the concentration of dioxin-like  
22 compounds in other media than on their size or net release rate. This section first summarizes  
23 and draws conclusions from the limited information available regarding the character and  
24 magnitude of reservoir sources. This information is then used to discuss the implications of  
25 reservoir sources to human exposure.

#### 26 27 **12.3.1. Reservoir Sources**

28 Summary statements about soil reservoir sources:

- 29
- 30 • Soil is likely to be the reservoir source with the greatest potential for release of  
31 CDDs/CDFs to other environmental media, particularly to water. This is due in part  
32 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, for example, 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.

#### 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.

#### 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.

Summary statements about biota reservoir sources:

- The mass of CDDs/CDFs in vegetation at any given time is likely to be small compared to 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 compared to the mass in soil. Similarly, releases are small and occur primarily by excretion and decomposition of dead biomass.

### 12.3.2. 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 compared to 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<sub>DFF</sub> 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



1 general population CDD/CDF TEQ exposure. This suggests that a significant portion of the  
2 CDD/CDF TEQ exposure could be due to releases from the soil and sediment reservoir.

3 **CDD/CDF releases from soil to air and exposure via the terrestrial pathway.**

4 Potentially, soil reservoirs could have vapor and particulate releases that deposit on plants and  
5 enter the terrestrial food chain. The magnitude of this contribution, however, is unknown. EPA  
6 plans future studies in agricultural areas that will compare modeled air concentrations from  
7 primary sources to measured levels as a way to gain further insight to this issue.

**Table 12-1. Historical production, sales, and usage of 2,4-dichlorophenoxy-acetic acid (2,4-D) (metric tons)<sup>a</sup>**

Year	2,4-D, acid			2,4-D, esters and salts (as reported) <sup>b</sup>	
	Production volume (metric tons)	Sales volume (metric tons)	Domestic usage/ disappearance (metric tons)	Production volume (metric tons)	Sales volume (metric tons)
2000	—	—	23,600–28,100 <sup>c</sup>	—	—
1998/99	—	—	23,600–28,100 <sup>d</sup>	—	—
1996/97	—	—	23,600–27,200 <sup>e</sup>	—	—
1994/95	—	—	21,800–26,300 <sup>f</sup>	—	—
1993	—	—	16,800–20,400 <sup>g</sup>	—	—
1992	—	—	16,800–20,400 <sup>g</sup>	—	—
1991	—	—	18,100–29,500 <sup>h</sup>	—	—
1990	—	—	18,100–29,500 <sup>h</sup>	—	—
1989	—	—	18,100–29,500 <sup>i</sup>	—	—
1988	—	—	23,600–30,400 <sup>j</sup>	—	—
1987	—	—	23,600–30,400 <sup>k</sup>	—	—
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 <sup>l</sup>	10,913	7,813
1975	—	—	--	16,134	13,414
1974	—	—	--	6,558	5,991
1973	—	—	--	13,400	13,698
1972	24,948 <sup>b</sup>	—	21,772 <sup>l</sup>	10,192	10,899
1971	—	5,619	15,700 <sup>l</sup>	—	18,654
1970	19,766	7,159	--	—	19,920
1969	21,354	8,521	--	25,854	20,891

**Table 12-1. Historical production, sales, and usage of 2,4-dichlorophenoxy-acetic acid (2,4-D) (metric tons)<sup>a</sup> (continued)**

Year	2,4-D, acid			2,4-D, esters and salts (as reported) <sup>b</sup>	
	Production volume (metric tons)	Sales volume (metric tons)	Domestic usage/ disappearance (metric tons)	Production volume (metric tons)	Sales volume (metric tons)
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 <sup>m</sup>	32,895	25,075
1965	28,721	11,816	22,906 <sup>m</sup>	28,740	21,454
1964	24,364	11,343	19,958 <sup>m</sup>	24,660	18,263
1963	21,007	9,446	15,059 <sup>m</sup>	20,178	16,333
1962	19,503	7,716	16,284 <sup>m</sup>	16,831	13,075
1961	19,682	7,591	14,107 <sup>m</sup>	16,683	12,533
1960	16,413	—	14,107 <sup>m</sup>	15,436	13,661
1959	13,282	7,240	15,468 <sup>m</sup>	12,438	7,070
1958	14,036	6,234	9,662 <sup>m</sup>	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	--	—	—

<sup>a</sup>All values from the U.S. International Trade Commission's (USITC) annual report series *Synthetic Organic Chemicals - United States Production and Sales* unless footnoted otherwise (USITC, 1946–1994).

<sup>b</sup>No data were reported for domestic usage/disappearance of 2,4-D esters and salts.

<sup>c</sup>Source: U.S. EPA (1991i).

<sup>d</sup>Source: U.S. EPA (2000e).

<sup>e</sup>Source: U.S. EPA proprietary data.

<sup>f</sup>Source: U.S. EPA (1997e).

<sup>g</sup>Source: U.S. EPA (1994b).

<sup>h</sup>Source: U.S. EPA (1992f).

**Table 12-1. Historical production, sales, and usage of 2,4-dichlorophenoxyacetic acid (2,4-D) (metric tons)<sup>a</sup> (continued)**

<sup>i</sup>Source: U.S. EPA (1991h).

<sup>j</sup>Source: U.S. EPA (1990e).

<sup>k</sup>Source: U.S. EPA (1988c).

<sup>l</sup>Source: U.S. EPA (1975).

<sup>m</sup>Source: USDA (1970).

— = Not reported to avoid disclosure of proprietary data

-- = No information given

**Table 12-2. Historical production, sales, and usage of 2,4,5-trichlorophen-oxyacetic acid (2,4,5-T) (metric tons)<sup>a</sup>**

Year	2,4,5-T			2,4,5-T, esters and salts (as reported) <sup>b</sup>	
	Production volume (metric tons)	Sales volume (metric tons)	Domestic usage/ disappearance (metric tons)	Production volume (metric tons)	Sales volume (metric tons)
1993	—	—	--	—	—
1992	—	—	--	—	—
1991	—	—	--	—	—
1990	—	—	--	—	—
1989	—	—	--	—	—
1988	—	—	--	—	—
1987	—	—	--	—	—
1986	—	—	--	—	—
1985	—	—	--	—	—
1984	—	—	--	—	—
1983	—	—	--	—	—
1982	—	—	--	—	—
1981	—	—	--	—	—
1980	—	—	900 <sup>c</sup>	—	—
1979	3,200–4,100 <sup>d</sup>	—	--	—	—
1978	—	—	3,200 <sup>e</sup>	—	—
1977	—	—	4,100 <sup>d</sup>	—	—
1976	—	—	--	—	—
1975	—	—	3,200 <sup>e</sup>	—	—
1974	—	—	900 <sup>f</sup>	—	—
1973	—	—	--	—	—
1972	—	—	--	—	—
1971	—	—	694 <sup>g</sup>	—	1,675
1970	—	—	3,200 <sup>e</sup>	5,595	3,272
1969	2,268	—	--	5,273	2,576
1968	7,951	1,329	~7,000 <sup>h,i</sup>	19,297	15,021
1967	6,601	757	~7,000 <sup>h,i</sup>	12,333	11,657
1966	7,026	2,312	7,756 <sup>h</sup>	8,191	4,553
1965	5,262	—	3,266 <sup>h</sup>	6,131	5,977
1964	5,186	1,691	4,037 <sup>h</sup>	5,880	3,128

**Table 12-2. Historical production, sales, and usage of 2,4,5-trichlorophen-oxyacetic acid (2,4,5-T) (metric tons)<sup>a</sup> (continued)**

Year	2,4,5-T			2,4,5-T, esters and salts (as reported) <sup>b</sup>	
	Production volume (metric tons)	Sales volume (metric tons)	Domestic usage/ disappearance (metric tons)	Production volume (metric tons)	Sales volume (metric tons)
1963	4,123	1,928	3,266 <sup>h</sup>	4,543	2,585
1962	3,796	1,021	3,674 <sup>h</sup>	4,765	2,543
1961	3,134	1,196	2,449 <sup>h</sup>	3,536	2,372
1960	2,874	—	2,676 <sup>h</sup>	3,594	1,891
1959	2,516	1,039	2,495 <sup>h</sup>	3,644	1,843
1958	1,668	692	1,724 <sup>h</sup>	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 <sup>e</sup>	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 <sup>e</sup>	—	—
1950	852	297	--	—	—
1949	—	—	--	—	—
1948	—	—	--	—	—
1947	—	—	--	—	—
1946	—	—	--	—	—
1945	—	—	--	—	—

<sup>a</sup>All values from the U.S. International Trade Commission's (USITC) annual report series *Synthetic Organic Chemicals - United States Production and Sales* unless footnoted otherwise (USITC, 1946–1994).

<sup>b</sup>No data were reported for domestic usage/disappearance of 2,4-D esters and salts.

<sup>c</sup>Source: Esposito et al. (1980).

<sup>d</sup>Source: Federal Register (1979).

<sup>e</sup>Source: Thomas and Spiro (1995).

<sup>f</sup>Source: U.S. EPA (1977).

<sup>g</sup>Source: USDA (1971); reflects farm usage only.

<sup>h</sup>Source: USDA (1970); values include military shipments abroad.

<sup>i</sup>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

**Table 12-3. CDD/CDF concentrations in recent sample of 2,4,5-trichloro-phenoxyacetic acid (2,4,5-T)**

<b>Congener/congener group</b>	<b>2,4,5-T sample (µg/kg)</b>
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 <sup>a</sup>	58.2
Total 2,3,7,8-CDF <sup>a</sup>	8.59
Total I-TEQ <sub>DF</sub> <sup>a</sup>	2.88
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> <sup>a</sup>	3.26
Total TCDD	--
Total PeCDD	--
Total HxCDD	--
Total HpCDD	--
Total OCDD	--
Total TCDF	--
Total PeCDF	--
Total HxCDF	--
Total HpCDF	--
Total OCDF	--
Total CDD/CDF	--

<sup>a</sup> Calculated assuming nondetect values are zero.

ND = Not detected (value in parenthesis is the detection limit)

-- = No information given

Source: Schecter et al. (1997).

**Table 12-4. PCB 138 fluxes predicted by Harner et al. (1995)**

<b>Year</b>	<b>Concentration in air (pg/m<sup>3</sup>)</b>	<b>Fugacity in air (Pascals × 10<sup>-9</sup>)</b>	<b>Fugacity in soil (Pascals × 10<sup>-9</sup>)</b>	<b>Concentration in soil (ng/g)</b>	<b>Net flux/direction</b>
1950	4	0.24	1.1	--	air → soil (444 kg/yr)
1965	280	1.5	12	--	air → soil (1000 kg/yr)
1975	--	--	16	--	
1980	49	--	--	--	soil → air (820 kg/yr)
1994	6	--	8.3	--	soil → air (700 kg/yr)

-- = No information given



**Table 12-5. Summary of flux calculations for total PCBs in Green Bay, 1989**

<b>Date</b>	<b>Site</b>	<b>Flux<sup>a</sup> (ng/m<sup>2</sup>-day)</b>
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

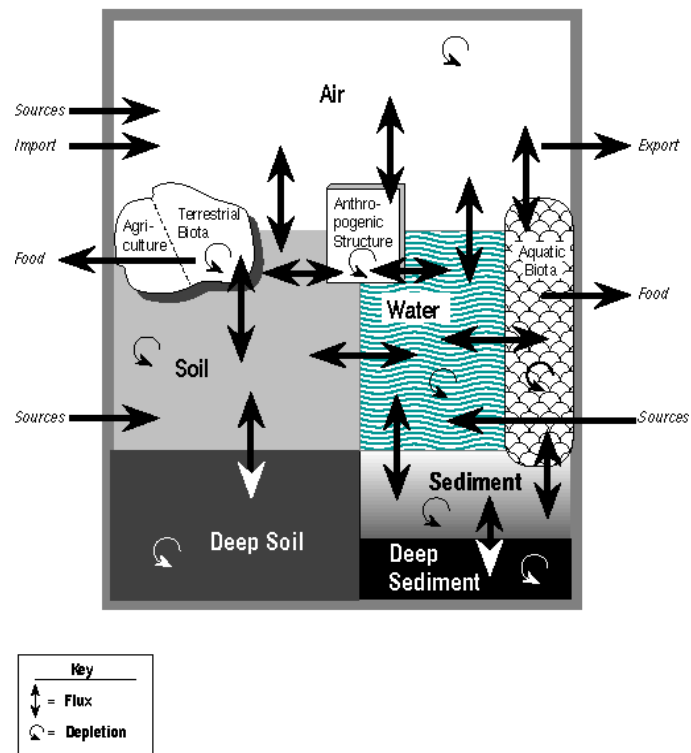
<sup>a</sup>Numbers indicate water-to-air transfer of total PCBs. They represent the sum of individual PCB congener fluxes and are described as “daily” fluxes because they correspond to air samples collected over 5–10 hr and water samples collected over ~1 hr.

Source: Achman et al. (1993).

**Table 12-6. Comparison of estimated PCB concentrations with observed values**

Variable	PCBs
Observed concentration Sediment Water	0.23–1.04 µg/g <20 µg/m <sup>3</sup>
Estimated concentration from model without thermocline Sediment Water Amount in sediment Amount in water Total mass	0.518 µg/g 8.33 µg/m <sup>3</sup> 74.9 kg 2.33 kg 77.2 kg
Estimated concentration from model with thermocline Sediment Hypolimnion Epilimnion Amount in sediment Amount in hypolimnion Amount in epilimnion Total mass	0.527 µg/g 8.48 µg/m <sup>3</sup> 7.93 µg/m <sup>3</sup> 76.3 kg 1.28 kg 1.02 kg 78.6 kg

Source: Ling et al. (1993).



**Figure 12-1. Fluxes among reservoirs.**

## **13. BALL CLAY**

### **13.1. INTRODUCTION**

The purpose of this chapter is to evaluate the potential for environmental releases of dioxin-like compounds during the mining of ball clay and its subsequent uses. 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 the U.S. Department of Agriculture (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 soybean meal 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 soybean meal, chicken feed, and immature chickens.

### **13.2. 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 FDA (Headrick et al., 1999). Total mining of ball clay in 1999 was 1.14 million metric tons (Virta, 2000).

### **13.3. 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 13-1. The limits of detection: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 distribution across all samples (i.e., 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 among the three individual 2,3,7,8-hexa congeners was 5:17:78. This congener pattern was observed in all the raw ball clay samples analyzed.

The mean total TEQ<sub>DF-WHO<sub>98</sub></sub> 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<sub>DF-WHO<sub>98</sub></sub>, 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 range of background  $TEQ_{DF}-WHO_{98}$  concentrations in North American urban and rural surface soils samples are 2 to 21 pg/g and 0.1 to 6 pg/g, respectively (U.S. EPA, 2000b). In soil samples, all 2,3,7,8-CDD/CDF congeners are detected, and 2,3,7,8-TCDD represents less than 1% of total CDD/CDF present. The most prevalent congeners in soils are OCDD followed by OCDF. Table 13-2 compares the mean CDD/CDF congener group concentrations in ball clay with the mean congener group concentrations in rural and urban background soils. This comparison indicates there are few similarities between the ball clay and soils in the congener group distributions.

#### **13.4. 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, Georgia, analyzed the Mississippi mine clays using a broad screen for anthropogenic contaminants and no compounds were found outside of the normal range. 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 are 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. These analyses were used as a basis for comparison to the profile of the 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.

1           The combustion of wood generates a congener profile not unlike that of waste incinerator  
2 (i.e., the ratio of CDD:CDF is <1), and all laterally substituted congeners can be detected in  
3 emissions. The combustion of tree bark produces a congener profile in which the CDD:CDF  
4 ratio is >1, showing only minimal and barely detectable levels of CDFs in the smoke, the  
5 exception being that 2,3,7,8-TCDF is present at approximately 2% of total mass. The dominant  
6 congener in tree bark combustion emissions is OCDD (>30% total CDD/CDF mass), followed by  
7 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8,9-HxCDD.

8           The congener profile of 2,4-D salts and esters seems to mimic a combustion source  
9 profile in the number of congeners represented and in the minimal amount of 2,3,7,8-TCDD  
10 relative to all 2,3,7,8-Cl substituted congeners. Nevertheless, unlike the combustion source  
11 profile, the 1,2,3,7,8-PeCDD and the 1,2,3,4,6,7,8-HpCDF constitute major fractions of total  
12 CDD/CDF contamination present in 2,4-D. The congener profile of technical-grade PCP is  
13 clearly dominated by OCDD and 1,2,3,4,6,7,8-HpCDD; however, only trace amounts of 2,3,7,8-  
14 TCDD are detected in PCP, and 1,2,3,4,6,7,8-HpCDF and OCDF constitute roughly 15% of  
15 typical formulations.

16           Metal smelting and refining processes, such as secondary aluminum, copper, and lead  
17 smelting, also have all the 2,3,7,8-Cl-substituted CDD/CDF congeners in stack emissions. In  
18 secondary aluminum smelting, 2,3,7,8-TCDD is less than 0.1% of total CDDs/CDFs, whereas  
19 PeCDF is nearly 25% of total emissions of dioxin-like compounds, and the CDD/CDF ratio is  
20 <1. Secondary copper operations show a similar pattern of CDD/CDF emissions, but with five  
21 compounds dominating emissions: 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDF; 1,2,3,4,6,7,8-  
22 HpCDF; OCDF; OCDD; and 1,2,3,4,6,7,8-HpCDD. In iron ore sintering, the dominant congener  
23 in emissions of 2,3,7,8-Cl-substituted compounds is 2,3,7,8-TCDF.

24           A number of studies have shown that natural processes can produce chlorinated aromatic  
25 compounds, including dioxin-like compounds. Gribble (1994) reviewed the biological  
26 production of a wide variety of halogenated organic compounds in nature. The Mississippi salt  
27 march grass “needlerush” (*Juncus roemerianus*) contains the aromatic compound 1,2,3,4-  
28 tetrachlorobenzene, and the blue-green alga *Anacystis marina* naturally contains chlorophenol.  
29 The soil fungus *Penicillium sp.* produces 2,4-dichlorophenol, and the common grasshopper is  
30 known to secrete 2,5-dichlorophenol.

1           Urhahn and Ballschmiter (1998) also provide a good review of the chemistry of the  
2   biosynthesis of chlorinated organic compounds under natural conditions. It has been  
3   hypothesized that CDDs, CDFs, and other chlorinated aromatic compounds can be naturally  
4   formed from halogenated humic substances and halomethanes can be formed through  
5   chloroperoxidase-mediated reactions in undisturbed peat bogs (Silk et al., 1997). A similar  
6   chloroperoxidase-mediated biochemical formation of CDDs/CDFs from chlorophenols was  
7   achieved under laboratory conditions by Oberg and Rappe (1992).

8           It has been observed that chlorophenols can be biosynthesized (Gribble, 1994; Silk et al.,  
9   1997), and that chlorophenols are readily adsorbed into peat-bentonite mixtures (Virarghavan and  
10   Slough, 1999). Hoekstra et al. (1999) offered the hypothesis that 2,3,7,8-TCDD, 1,2,3,7,8-  
11   PeCDD, and 1,2,3,7,8,9-HxCDD can be naturally formed in soils of coniferous forests from  
12   chlorinated phenol. These same congeners are also the predominant congeners in the ball clay  
13   from the Mississippi Embayment. Although none of these natural processes can be directly  
14   connected with the presence of dioxin in ball clay, the existence of such mechanisms lends  
15   plausibility to a hypothesis that they are of natural origin.

16           CDDs/CDFs have been found in other clays quite distant from Mississippi Embayment  
17   ball clay deposits. No evidence of anthropogenic sources have been discovered in these areas  
18   either. The presence of CDDs has been discovered in kaolinitic clay mined in Germany (Jobst  
19   and Aldag, 2000). Because no anthropogenic source could be determined to explain the presence  
20   and levels of CDDs in the ball clay, the authors speculated that they were the result of an  
21   unknown geologic process. In addition, the German clay also has a congener profile similar to  
22   that observed in the Mississippi ball clay, with an absence of CDFs at comparable concentrations  
23   and the predominance of the 1,2,3,7,8,9-HxCDD among the toxic hexa-CDDs. The similarity in  
24   the congener profiles in ball clay mined in the United States and Germany suggests a common  
25   origin to the CDDs present in these clays (Ferrario et al., 2000).

26           In summary, no anthropogenic sources have been identified that explain the levels and  
27   profiles of CDDs/CDFs present in the clay. On the other hand, no definitive scientific evidence  
28   has been brought forward that identifies the principal chemical and physical mechanism involved  
29   in the selective chemical synthesis of CDDs under the conditions inherent in the formation of  
30   ball clays some 40 million years ago.



### **13.5. 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.

**Table 13-1. Concentrations of CDDs determined in eight ball clay samples in the United States**

Congener	Concentration (pg/g, dry weight)				
	Mean	Median	Minimum	Maximum	TEQ <sub>DF</sub> -WHO <sub>98</sub>
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).

**Table 13-2. Comparison of the mean CDD/CDF congener group distribution in ball clay with the mean congener group distributions in urban and rural soils in North America**

Congener group	Mean concentration (pg/g, dry weight)		
	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	3,067.1	821.3

Sources: Adapted from U.S. EPA (2000a); Ferrario et al. (2000).

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