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Washington DC 20460

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EPA

The Inventory of Sources of Dioxin in the United States

Review Draft (Do Not Cite or Quote)

Notice

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Exposure Analysis and Risk Characterization Group
National Center for Environmental Assessment
Office of Research and Development
U.S. Environmental Protection Agency
Washington, D.C.

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1. INTRODUCTION

In 1992, the U.S. Environmental Protection Agency's (EPA's) Office of Research and Development (ORD) began an effort to reassess the exposure and health effects associated with dioxin. As originally conceived and drafted, the exposure portion of the Reassessment did not include an emissions inventory component. ORD was concerned that there was inadequate test data to construct an inventory and that the time and resources needed to conduct an extensive testing program was outside the scope of the Reassessment. In 1992, special workshops were held to provide expert review and comment on early drafts of both the exposure and health components of the Reassessment. Reviewers of these early drafts strongly urged EPA to attempt an emissions inventory using the available data. Responding to this suggestion, an inventory was developed and first published in September 1994 as part of the overall draft Reassessment.

The draft Reassessment underwent reviews by both the public and EPA's Science Advisory Board (SAB). The SAB supported the general approach used to produce the draft inventory, but suggested several changes. Most notably, the SAB recommended that the inventory be specific about the time frame it represents. The SAB did not suggest that any of the exposure chapters including the emissions inventory be resubmitted for SAB review.

In addition to SAB comments, EPA received a number of public comments regarding the emission inventory. In response to all of these comments and the availability of additional data, a number of changes have been made to the inventory since the 1994 draft. These changes have resulted in significant revisions to both the inventory structure and actual emission estimates. Consequently, ORD has decided it would be prudent to conduct an additional round of peer review of the revised inventory before incorporating it into the final Reassessment. The purpose of this document is to provide to the peer reviewers and interested members of the public, ORD's most recent estimates of dioxin emissions for the years 1987 and 1995 along with a detailed description of the analytical process and rationale that support these estimates. The peer review of the dioxin emission inventory will be conducted by an expert panel at a meeting to be held June 3-4, 1998, in the Washington, D.C. area. EPA will use the comments of the peer review panel to help guide final revisions to the inventory which will be published as a part of the final Reassessment.

The inventory is supported by an extensive emissions data base. This data base is available in conjunction with this report on a compact disk (CD). The data base includes all emission test data and activity level data used to derive the inventory. Because of the complexity of this data base, ORD elected to have it independently audited for the accuracy of data inputs and calculations.

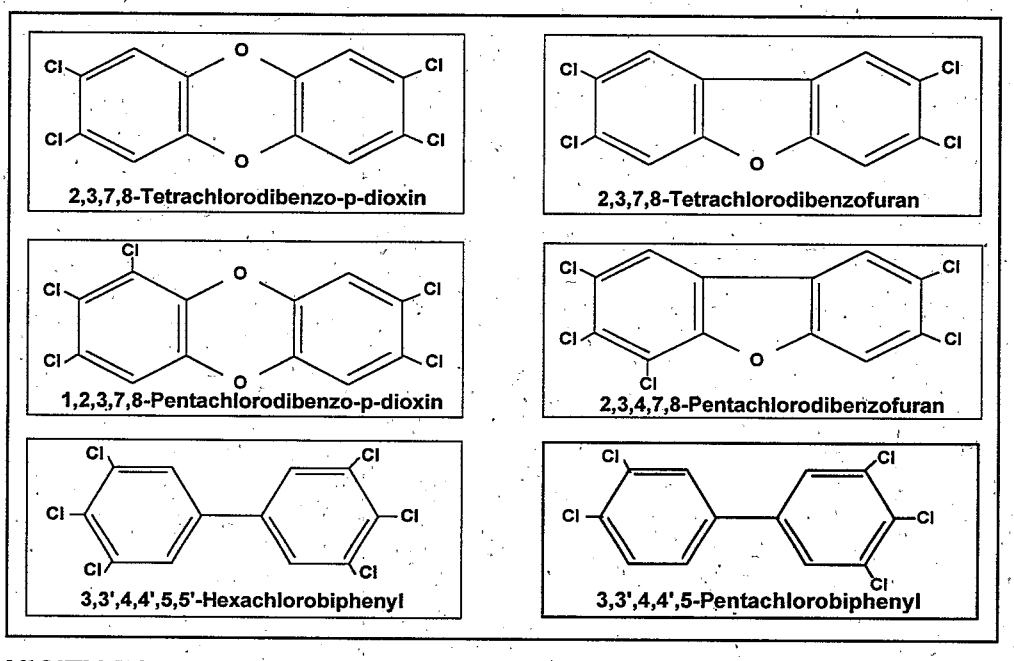
1.1. DESCRIPTION OF DIOXIN-LIKE COMPOUNDS

This document addresses compounds in the following chemical classes: polychlorinated dibenzo-p-dioxins (PCDDs or CDDs), polychlorinated dibenzofurans (PCDFs or CDFs), polybrominated dibenzodioxins (PBDDs or BDDs), polybrominated dibenzofurans (PBDFs or BDFs), and polychlorinated biphenyls (PCBs). The CDDs include 75 individual compounds, and CDFs include 135 different compounds. These individual compounds are technically referred to as congeners. Likewise, the BDDs include 75 different congeners, and the BDFs include an additional 135 congeners. Only 7 of the 75 congeners of CDDs or of BDDs are thought to have dioxin-like toxicity; these are ones with chlorine/bromine substitutions in, at least, the 2, 3, 7, and 8 positions. Only 10 of the 135 possible congeners of CDFs or of BDFs are thought to have dioxin-like toxicity; these also are ones with substitutions in the 2, 3, 7, and 8 positions. While this suggests 34 individual CDDs, CDFs, BDDs, or BDFs with dioxin-like toxicity, inclusion of the mixed chloro/bromo congeners substantially increases the number of possible congeners with dioxin-like activity. There are 209 PCB congeners. Only 13 of the 209 congeners are thought to have dioxin-like toxicity; these are PCBs with four or more chlorines with just 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 in the same plane. Similarly configured polybrominated biphenyls are likely to have similar properties; however, the data base on these compounds, with regard to dioxin-like activity, has been less extensively evaluated. Mixed chlorinated and brominated congeners also exist, increasing the number of compounds considered dioxin-like.

The physical/chemical properties of each congener vary according to the degree and position of chlorine and/or bromine substitution. Very little is known about occurrence and toxicity of the mixed (chlorinated and brominated) dioxin, furan, and biphenyl congeners. The chlorinated and brominated dibenzodioxins and dibenzofurans are tricyclic aromatic

structurally. Certain PCBs (the so-called coplanar or mono-ortho coplanar congeners) are also structurally and conformationally similar. The most widely studied of these compounds is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). This compound, often called simply dioxin, represents the reference compound for this class of compounds. The structure of 2,3,7,8-TCDD and several related compounds is shown in Figure 1-1.

Figure 1-1. Chemical Structure of 2,3,7,8-TCDD and Related Compounds



1.2 TOXICITY EQUIVALENCE FACTORS

The dioxin-like compounds are often found in complex mixtures. For risk assessment purposes, a toxicity equivalency procedure was developed to describe the cumulative toxicity of these mixtures. This procedure involves assigning individual toxicity equivalency factors (TEFs) to the 2,3,7,8 substituted CDD/CDF congeners. These TEF values have been adopted by international convention (U.S. EPA, 1989). Subsequent to the development of the TEFs for CDD/CDFs, TEFs were also developed for PCBs (Ahlborg et al., 1994). TEFs are estimates of the toxicity of dioxin-like compounds relative to the toxicity of 2,3,7,8-TCDD, which is assigned a TEF of 1.0. All other congeners have lower TEF values ranging from 0.5 to 0.00001. Generally accepted TEF values for CDD/CDFs and PCBs are shown in Table 1-1 and Table 1-2, respectively.

TEF values ranging from 0.5 to 0.00001. Generally accepted TEF values for CDD/CDFs and PCBs are shown in Table 1-1 and Table 1-2, respectively.

Calculating the toxic equivalency (TEQ) of a mixture involves multiplying the concentration of individual congeners by their respective TEF. The sum of the TEQ concentrations for the individual congeners is the TEQ concentration for the mixture.

It should be recognized that revisions to the TEFs are periodically considered as new scientific information becomes available. If revisions in the TEFs are adopted, then it would be appropriate to adjust the TEQ release estimates calculated in the inventory.

For purposes of this document, certain naming conventions have been adopted. All quantities representing TEQs are labeled as TEQs. Unless specified otherwise, TEQ values refer to CDD/CDFs and not other dioxin-like compounds. A complete list of abbreviations and naming conventions are presented in Table 1-3. The phrase "dioxin-like compounds" technically would include all the 2,3,7,8 substituted chlorinated and brominated dioxins and furans, the 2,3,7,8 substituted chlorobromo dioxins and furans, and the coplanar PCBs. In this document, however, because of the extremely limited data on the bromo and chlorobromo compounds, this phrase refers only to the 2,3,7,8-substituted CDD/CDFs and coplanar PCBs.

Table 1-1. Toxicity Equivalency Factors (TEF) for CDDs and CDFs

Compound	TEF
Mono-, Di-, and Tri-CDDs	0
2,3,7,8-TCDD	1
Other TCDDs	0
2,3,7,8-PeCDD	0.5
Other PeCDDs	0
2,3,7,8-HxCDD	0.1
Other HxCDDs	0
2,3,7,8-HpCDD	0.01
Other HpCDD	0
OCDD	0.001
Mono-, Di-, and Tri-CDFs	0
2,3,7,8-TCDF	0.1
Other TCDFs	0
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
Other PeCDFs	0
2,3,7,8-HxCDF	0.1
Other HxCDFs	0
2,3,7,8-HpCDF	0.01
Other HpCDFs	0
OCDF	0.001

Source: U.S. EPA (1989)

Table 1-2. Dioxin-Like PCBs

IUPAC No.	Compound	TEF
77	3,3',4,4'-TCB	0.0005
105	2,3,3',4,4'-PeCB	0.0001
114	2,3,4,4',5-PeCB	0.0005
118	2,3',4,4',5-PeCB	0.0001
123	2',3,4,4',5-PeCB	0.0001
126	3,3',4,4',5-PeCB	0.1
156	2,3,3',4,4',5-HxCB	0.0005
157	2,3,3',4,4',5'-HxCB	0.0005
167	2,3',4,4',5,5'-HxCB	0.00001
169	3,3',4,4',5,5'-HxCB	0.01
170	2,2',3,3',4,4',5-HpCB	0.0001
180	2,2',3,4,4',5,5'-HpCB	0.00001
189	2,3,3',4,4',5,5'-HpCB	0.0001

Source: Ahlborg et al. (1994)

Table 1-3. Nomenclature for Dioxin-Like Compounds

Term/Symbol	Definition
Congener	Any one particular member of the same chemical family)e.g., there are 75 congeners of chlorinated dibenzo-p-dioxins).
Congener Group	Group of structurally related chemicals that have the same degree of chlorination (e.g., there are eight congener groups of CDDs, monochlorinated through octochlorinated).
Isomer	Substances that belong to the same congener group (e.g., there are 22 isomers that 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-p-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-p-dioxins, halogens substituted in any position
CDF	Chlorinated dibenzofurans, halogens substituted in any position
PCB	Polychlorinated biphenyls
2378	Halogen substitutions in the 2,3,7,8 positions

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

2. OVERVIEW OF SOURCES

This report summarizes information on the release of CDD/CDFs and dioxin-like PCBs to the environment from known and suspected source categories. Where possible, national estimates have been made of annual releases from source categories in the United States. This collection of emission estimates is referred to as the national inventory. The emission factors and other information used to support development of this inventory are contained in the comprehensive *National Database of Sources of Environmental Releases of Dioxin-Like Compounds in the United States*. This is an electronic database using a spreadsheet format developed by EPA specifically for this effort. The database addresses both combustion and non-combustion source categories. For some source categories, emission factors are developed according to type of technology and type of pollution control systems employed. This electronic database has been published on a compact disk and is available as a companion to this document.

This overview chapter explains the process used by EPA to derive these emission estimates and also summarizes general findings and observations. The remainder of the document discusses CDD/CDF and dioxin-like PCB emissions on a source category basis.

2.1. EMISSIONS INVENTORY METHODOLOGY

In the United States, the major identified sources of environmental release have been grouped into the following classes for the purposes of this report:

- Combustion Sources: CDD/CDFs are formed in most combustion systems. These can include waste incineration (such as municipal solid waste, sewage sludge, medical waste, and hazardous wastes), burning of various fuels (such as coal, wood, and petroleum products), other high temperature sources (such as cement kilns), and poorly controlled combustion sources (such as building fires).

- Metals Smelting and Refining Sources and Processing Sources: CDD/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: CDD/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 have suggested that CDD/CDFs can be formed under certain environmental conditions (e.g., composting) from the action of microorganisms on chlorinated phenolic compounds. Similarly, CDD/CDFs have been reported to be formed during photolysis of highly chlorinated phenols.

- Reservoir Sources: Reservoirs are materials or places which contain previously formed CDD/CDFs or dioxin-like PCBs and have the potential for redistribution and circulation of these compounds into the environment. Potential reservoirs include soils, sediments, vegetation, and PCP-treated wood. Recently, CDD/CDFs have been discovered in ball clay deposits. Although the origin of the CDD/CDFs in these clays has not been confirmed, natural occurrence is a possibility.

For sources in each of the above classes (with the exception of Reservoir Sources), emission estimates have been made in this report for air, land, water and products. Only releases to the "circulating environment" were included in the inventory. The system boundaries are further defined as follows:

- CDD/CDFs and dioxin-like PCBs in final products and waste discharges were included whereas CDD/CDFs and dioxin-like PCBs in intermediate products or waste streams were excluded. For example, the CDD/CDFs in a waste stream going to an incinerator would not be included in the inventory but any CDD/CDFs in the stack emissions would be included.

- CDD/CDFs and dioxin-like PCBs in waste streams applied to land in the form of "land farming" are included whereas those disposed 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.

- Commercial products which contain CDD/CDFs or dioxin-like PCBs and whose subsequent use may result in releases to the environment were included in the inventory. Examples include paper pulp, sewage sludge that is distributed/marketed commercially, and certain pesticides.

The EPA's Science Advisory Board (SAB) reviewed an earlier draft of the national dioxin source emissions inventory and commented that the effort was comprehensive and inclusive of most known sources (U.S. EPA, 1995f). However, the SAB emphasized that source emissions are time-dependant, and recommended that emissions be associated with a specific time reference. In consideration of these comments, EPA has developed in this report emission estimates for two years: 1987 and 1995.

1987 was selected primarily because, prior to this time, little empirical data existed for making source specific emission estimates. 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 that significant advances occurred in emissions measurement techniques and in the development of high resolution mass spectrometry and gas chromatography necessary for analytical laboratories to achieve low level detection of CDD and CDF congeners in environmental samples. Soon after this time, a number of facilities began upgrades specifically intended to reduce CDD/CDF emissions. Consequently, 1987 is also the latest time representative of the emissions occurring before widespread installation of dioxin-specific emission controls.

1995 was selected as the latest time period that could practically be addressed consistent with the time table for producing the rest of the document. The data collected in the companion document to this document on CDD/CDF and dioxin-like PCB levels in environmental media and food were used to characterize conditions in the mid-1990's. So the emissions data and media/food data in these two volumes are presented on a roughly consistent basis.

A key element of the inventory is the method of extrapolation from tested facilities to national estimates. Because only a few U.S. facilities in most source categories have been tested for CDD/CDF emissions, an extrapolation was needed to estimate national emissions for most source categories. Many of the national emission estimates were, therefore, developed using a "top down" approach. The first step in this approach is to derive from the available emission 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 CDD/CDFs or dioxin-like PCBs released into the environment per some measure of activity (e.g., kilograms of material processed per year, vehicle miles traveled per year, etc.). The emission factor was then multiplied by a national value for the activity level basis of the emission factor (e.g., total kg of material processed in the United States annually).

Although no categories had estimates developed from a true "bottom up" approach (i.e., estimates developed using site-specific emissions and activity data for all individual sources in a category and then summed to obtain a national total), existing facility-specific

emissions testing and activity level data for some source categories (e.g., municipal solid waste incinerators) supported a semi- "bottom up" approach. In this approach, facility-specific annual emissions were calculated for those facilities with adequate data. For the untested facilities in the class, a subcategory (or class) emission factor 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 non-tested facilities in the class. Emissions were summed for the tested facilities and non-tested facilities. In summary, this procedure can be represented by the following equations:

$$E_{total} = \sum E_{tested,i} + \sum E_{untested,i}$$
$$E_{total} = \sum E_{tested,i} + \sum (EF_i * A_i)_{untested}$$

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 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 class i (kg/yr)

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

As discussed above, each source emission calculation required estimates of an "emission factor" and the "activity level." For each emission source, the quantity and

quality of the available information for both terms varies considerably. Consequently, it is important that emission estimates be accompanied by some indicator of the uncertainties associated with their development. For this reason, a confidence rating scheme was developed as an 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 used. In a few cases, unpublished references were used (such as personal communication with experts) 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. In some cases, however, draft reports that had undergone more limited review were used. In a few cases, unpublished references were used (such as personal communication with experts) and are clearly noted in the text.

The confidence rating scheme, presented in Table 2-1, provides criteria for assigning a "high," "medium," or "low" confidence rating for both the emission factor and activity terms. The first rating applies to the "activity" term, and the second rating applies to the "emission factor" term. In addition to the confidence rating, the uncertainty in these national release estimates is reflected by presenting, where possible, for each source category, both a central or "best guess" value and a possible range from a lower to upper estimate. These lower and upper estimates are not intended to be absolute bounds, but reasonable estimates of how much higher or lower the true value might be. Insufficient

data were available to statistically derive these ranges; therefore, a judgement-based approach was developed. This approach uses the average or best guess estimate as the central value of a range. The range was determined by treating the central value as a geometric average of the end points of the range and determining those endpoints as follows:

- Low confidence class: Upper end of range is 10 times higher than lower end.
- Medium confidence class: Upper end of range is 5 times higher than lower end.
- High confidence class: Upper end of range is 2 times higher than lower end.

The overall confidence rating assigned to an emission estimate was the lower of the confidence ratings assigned to the corresponding "activity" term and "emission factor" term. It is emphasized that these ranges should be interpreted as judgements which are symbolic of the relative uncertainty among sources, not statistical measures.

In some cases, sufficient information was available to make very preliminary estimates of emissions of CDD/CDFs or dioxin-like PCBs, but the confidence in the activity level estimates or emission factor estimates was so low that it was considered inappropriate to include emission estimates in the inventory. These preliminary estimates are discussed in the text and summarized in Table 2-6.

The emission factors developed for the emissions inventory are intended to be used for estimating the total emissions for a source category rather than for individual facilities. EPA has made uncertainty determinations for each of these emission factors based, in part, on the assumption that by applying them to a group of facilities, the potential for overestimating or underestimating individual facilities will to some extent be self compensating. This means that in using these emission factors one can place significantly greater confidence in an emission estimate for a class than can be placed on an emission estimate of any individual facility. Given the limited amount of data available for deriving emission factors, and the limitations of our understanding about facility-specific conditions that determine formation and control of dioxin-like compounds, the current state of knowledge cannot support the development of emission factors that can be used to accurately estimate emissions on an individual facility-specific basis.

2.2. GENERAL FINDINGS OF THE EMISSIONS INVENTORY

Nationwide emission estimates for the United States inventory are presented in Tables 2-2 and 2-3 (emissions to air, water, land, and product) for the major known or suspeced sources that could have releases of dioxin-like compounds to the environment. The emission factors used to calculate these emission estimates were derived by setting "not detected (ND)" values in test reports as zeros. Because detection limits were not always reported in test reports, it was not possible to consistently develop emission factors on any other basis (e.g., values set at one-half the detection limit) for all source categories. When detection limits were reported for all test reports for a given source category, emission factors were calculated and are presented in this report for both ND equals zero and ND equals one-half the detection limit.

Table 2-2 presents estimated annual releases for the reference time period 1995. Table 2-3 presents estimated annual releases for the reference time period 1987. Table 2-4 lists the emission factors used to derive these emission estimates. For each source listed in these tables, estimated emissions are presented where appropriate and where data are adequate to enable an estimate to be made. Figures 2-1 and 2-2 are charts that visually display the range of emission estimates to air that are reported in Tables 2-2 and 2-3, respectively. Figure 2-3 compares the annual mean TEQ emission estimates for the two reference years. Table 2-5 presents order of magnitude estimates of CDD/CDF emissions from suspected source categories not included in the inventory because uncertainty in the emission factor and/or activity level was deemed too great.

Central estimates of releases of dioxin-like compounds to all environmental media (except products) were approximately 3,000 g TEQ in 1995 and 11,900 g TEQ in 1987. These estimates were generated by summing the emissions across all sources in the inventory. Each of these estimates have an uncertainty range around them which is derived from uncertainties in the estimates for individual sources (for 1987 the range is 5,000 to 29,100 g TEQ and for 1995 the range is 1,200 to 7,900 g TEQ).

The decrease in estimated emissions of dioxin-like compounds between 1987 and 1995 was due primarily to reductions in emissions from municipal and medical waste incinerators. For both categories these emission reductions have occurred from a combination of improved combustion and emission controls and from the closing of a

number of facilities. Regulations recently promulgated or under development should result in some additional reduction in emissions from major combustion sources.

The environmental releases of dioxin-like compounds in the United States occur from a wide variety of sources, but are dominated by releases to the air from combustion sources. The current (i.e., 1995) inventory estimates that emissions from combustion sources are more than an order of magnitude greater than emissions from all other categories combined.

Insufficient data are available to comprehensively estimate point source releases of dioxin-like compounds to water. Sound estimates of releases to water are only available for chlorine bleached pulp and paper mills (356 g TEQ/yr for 1987 and 20 g TEQ/yr for 1995). Other releases to water bodies which cannot be quantified on the basis of existing data include effluents from POTWs and most industrial/commercial sources.

Insufficient data are available to comprehensively estimate releases of dioxin-like compounds to land. Contributions to land can occur in a variety of ways. One way is the intentional disposal of materials containing dioxin-like compounds in properly managed landfills where the potential for releases to the environment (i.e., groundwater or the atmosphere) is assumed to be minimal. Sound estimates of such practices have only been made for the disposal of municipal waste incinerator ash (1,800 g TEQ in 1995), sewage sludge (194 g TEQ in 1995), and pulp and paper mill wastewater sludge (21 g TEQ in 1995). Other materials containing dioxin-like compounds which are typically landfilled include dredge spoils and incinerator ash other than municipal waste incinerator ash. A second way is land application of sewage sludge (207 g TEQ/yr in 1995) and pulp and paper mill wastewater sludges (1.4 g TEQ/yr in 1995). In the past, a third way was the improper land disposal of chemicals and waste products containing dioxin-like compounds.

The change over time in amounts of dioxin-like compounds being land disposed has not been well characterized. Some of the emission controls installed in recent years have reduced dioxin formation and others have removed more CDD/CDFs from air and water emissions and transferred them to solid residues. It is unclear if the net effect of these types of controls would lead to an increase or decrease in amount of CDD/CDFs in solid residues.

Data are available to estimate the amounts of CDD/CDFs and dioxin-like PCBs contained in only a limited number of commercial products. No systematic survey has been

conducted to determine levels of dioxin-like compounds in commercial products. The available data does, however, allow estimates of the amounts of dioxin-like compounds in bleached pulp (24 g TEQ/yr in 1995), POTW sludge used in fertilizers (7.0 g TEQ/yr in 1995), pentachlorophenol-treated wood (25,000 g TEQ/yr in 1995), dioxazine dyes and pigments (<1 g TEQ/yr in 1995) and 2,4-D (18.4 g TEQ/yr in 1995).

The mixture of CDD and CDF congeners in the emission from a source category (i.e., the "congener profile") may serve as a source-specific signature for that category. Although uncertainties exist, these congener profiles may assist researchers in: (1) identification of specific combustion source contributions to near field air measurements of CDD/CDFs; (2) comparing sources in terms of discerning differences in the types and amplitude of CDD/CDF congeners emitted; and (3) providing insights on formation of CDDs and CDFs in various sources and chemicals.

The procedures and results of the U.S. inventory are consistent with the published national inventories for several European countries. Table 2-6 presents CDD/CDF TEQ source-specific air emission estimates reported for West Germany (Fiedler and Hutzinger, 1992); Austria (Riss and Aichinger, 1993); The Netherlands (Koning et al., 1993; Bremmer et al., 1994); Switzerland (Schatowitz et al., 1993); Belgium (Wevers and DeFre, 1995); and the United Kingdom (Douben et al., 1995; UK Department of the Environment, 1995). The emission estimates for West Germany, Switzerland, the United Kingdom, and The Netherlands suggest that municipal waste incinerators and metal smelters/refiners are the largest sources of air emissions. In Austria, domestic combustion of wood is believed to be the largest source followed by emissions from the metallurgical industry. Although an emissions inventory for Sweden has not yet been published, Rappe (1992a) and Lexen et al. (1993) have identified emissions from ferrous and nonferrous metals smelting/refining facilities as potentially the largest current source in Sweden. It should be noted that these emission inventories are expected to change over time due to changing industrial practices, facility closures and upgrades, and regulatory actions.

Some investigators have argued that national inventories such as this one may be underestimating emissions due to the possibility of unknown sources. This claim has been supported with mass balance analyses suggesting that deposition exceeds emissions (Rappe et al., 1991; Harrad et al. 1992b; Brzuzy and Hites, 1995). The uncertainty, however, in both emissions and deposition estimates in the United States prevent the use

of this approach for reliably evaluating this issue. A variety of other factors do indicate, however, that the inventory could underestimate CDD/CDF emissions:

- A number of sources were not included in the inventory even though limited evidence exists (primarily from studies performed in Europe) indicating that these sources can emit CDD/CDFs. These sources include various components of the metals industries such as iron ore sintering and foundries. Table 2-6 presents rough estimates of what U.S. national emissions could be if the emission factors reported in these other studies are representative of emission factors for U.S. facilities.

- The possibility remains that truly unknown sources exist. Many of the sources which are well accepted today were only discovered in the past 10 years. For example, CDD/CDFs were found unexpectedly in the wastewater effluent from bleached pulp and paper mills in the mid 1980s. Ore sintering is now listed as one of the leading sources of CDD/CDF emissions in Germany, but was first reported in the early 1990s.

- Another potentially important source which is not represented in the inventory is reservoirs. In this context, reservoirs are places such as soils, sediments, vegetation or other media which contain dioxin-like compounds originally formed some time in the past and have the potential for current emissions. The dioxin-like compounds in these "reservoirs" can be re-released to the environment by processes such as volatilization and particle resuspension. Such releases may (or may not) add significantly to the mass of dioxin-like compounds circulating in the environment and potentially contributing to human exposure. Two of the largest potential reservoirs are soils and pentachlorophenol (PCP) treated wood. PCP contains low levels of CDD/CDFs and wood which has been treated with this pesticide represents a large reservoir of CDD/CDFs. CDD/CDFs may be released from the PCP-treated wood to the air by volatilization or to surrounding soils by leaching. Although hypothesized to occur, no reliable measurements have been made. Similarly, no empirical evidence exists on the possible magnitude of reservoir emissions from soil to air.

2.3. GENERAL SOURCE OBSERVATIONS

Current emissions of CDD/CDFs to the U.S. environment result principally from anthropogenic activities. Three lines of evidence support this finding:

- Studies of sediment corings in lakes in the United States show a consistent pattern of change in CDD/CDF concentration in the sediments over time. The time period when increases are observed in CDD/CDF levels in sediments coincides with the time period when general industrial activity began increasing rapidly. CDD/CDF concentrations in sediments began to increase around the 1930s, and continued to increase until the 1960s and 1970s. Decreases appear to have occurred only during the most recent time periods (i.e., 1970s and 1980s). These trend observations are consistent among the dated sediment cores collected from over 20 freshwater and marine water bodies in various locations throughout the United States and Europe.

Levels of CDD/CDF in sediments from these lakes are considered to be a reasonable indicator of the rate of environmental deposition. The period of increase generally matches the time when a variety of industrial activities began rising and the period of decline appears to correspond with growth in pollution abatement. Some of these abatements may be linked with dioxin emissions (i.e., elimination of open burning, particulate controls on combustors, phase out of leaded gasoline, and bans or restrictions on PCBs, 2,4,5-T, and PCP.

- No large natural sources of CDD/CDF have been identified. EPA's current estimate of emissions from all sources of CDD/CDFs suggests that forest fires are a minor source of emissions compared to anthropogenic combustion activity. To date, no studies have demonstrated formation of CDD/CDFs by volcanoes. Recently CDD/CDFs have been discovered in ball clay deposits in western MS, KY and TN. Although the origin of the dioxins in these clays may be natural, it has not been confirmed.

- CDD/CDF levels in human tissues from the general population in industrialized countries are higher than levels observed in less-industrialized countries. Human populations in Europe and North America have significantly higher mean tissue levels (e.g., blood, adipose tissues and breast milk) than human populations in developing countries of Asia and South East Asia (Schecter, 1994). In addition, tissues taken from preserved, 140 to 400 year old human remains show almost the complete absence of CDD/CDFs, well below levels found in tissues of modern people (Tong et al., 1990).

No clear evidence exists showing that the emissions of CDD/CDFs from known sources correlate proportionally with general population exposures. Although the emissions inventory shows the relative contribution of various sources to total emissions, it cannot be assumed that these sources make the same relative contributions to human exposure. It is quite possible that the major sources of CDD/CDF in food may not be those sources that represent the largest fractions of total emissions in the United States. The geographic locations of sources relative to the areas from which much of the beef, pork, milk, and fish is produced are important to consider. That is, the agricultural areas which produce much of our food may not necessarily be located near or down wind of the major sources of CDD/CDFs.

Table 2-1. Confidence Rating Scheme for U.S. Emission Estimates

Confidence Rating	Activity Level Estimate	Emission Factor Estimate
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 few facilities believed to be representative of source category
Low	Based on expert judgement or unpublished estimates	Derived from testing at only a few, possibly non-representative facilities or from similar source categories or foreign surveys where differences in industry practices may be likely

Table 2-2. Dioxin-Like Compound Emission Inventory for the United States (Reference Year 1995)

Emission Source	Emissions (g TEQ/yr) to Media															
	Air				Water				Land				Product			
	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]
Waste Incineration																
Municipal waste incineration	492	1,100	2,460	H/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Hazardous waste incineration	2.6	5.7	12.8	H/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Boilers/industrial furnaces	0.12	0.38	1.2	M/L	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Medical waste/pathological incineration	151	477	1,510	L/L	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Crematoria	0.07	0.24	0.75	H/L	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Sewage sludge incineration	2.7	6.0	13.4	H/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Tire combustion	NEG	NEG	NEG	M/L	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Pulp and paper mill sludge incinerators	e	e	e	e	*	*	*	*	*	*	*	*	NA	NA	NA	NA
BioGas combustion	**	**	**	**	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Power/Energy Generation																
Vehicle fuel combustion - leaded[b]	NEG	NEG	NEG	--	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
- unleaded	2.0	6.3	20	H/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
- diesel	10.6	33.5	106	H/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Wood combustion - residential	19.8	62.8	198	H/L	NA	NA	NA	NA	*	*	*	*	NA	NA	NA	NA
- industrial	13.0	29.1	65.0	H/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Coal combustion - residential	**	**	**	**	NA	NA	NA	NA	*	*	*	--	NA	NA	NA	NA
- industrial/utility	32.6	72.8	163	H/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Oil combustion - residential	**	**	**	**	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
- industrial/utility	2.9	9.3	29.0	H/L	*	*	*	*	NA	NA	NA	NA	NA	NA	NA	NA
Other High Temperature Sources																
Cement kilns (haz waste burning)	48.4	153	484	H/M	*	*	*	*	*	*	*	*	*	*	*	*
Cement kilns (non haz waste burning)	5.6	17.8	56.3	H/L	*	*	*	*	*	*	*	*	*	*	*	*
Asphalt mixing plants	**	**	**	**	*	*	*	*	*	*	*	*	*	*	*	*
Petro. refining catalyst regeneration	*	*	*	*	NEG	NEG	NEG	--	*	*	*	*	NA	NA	NA	NA

Table 2-2. Dioxin-Like Compound Emission Inventory for the United States (Reference Year 1995) (continued)

Emission Source	Emissions (g TEQ/yr) to Media															
	Air				Water				Land				Product			
	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]
Cigarette combustion	0.25	0.81	2.5	H/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Carbon reactivation furnaces	NEG	NEG	NEG	--	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Kraft recovery boilers	1.0	2.3	5.0	H/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Minimally Controlled or Uncontrolled Combustion																
Combustion of landfill gas in flares	**	**	**	**	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Landfill fires	**	**	**	**	NA	NA	NA	NA	*	*	*	*	NA	NA	NA	NA
Accidental fires (structural)	*	*	*	*	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Accidental fires (vehicles)	**	**	**	**	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Forest, brush, and straw fires[d]	64.5	208	645	L/L	NA	NA	NA	NA	*	*	*	*	NA	NA	NA	NA
Backyard trash burning	**	**	**	**	NA	NA	NA	NA	*	*	*	*	NA	NA	NA	NA
Uncontrolled combustion of PCBs	*	*	*	*	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Metallurgical Processes																
Ferrous metal smelting/refining																
- Sintering plants	**	**	**	**	*	*	*	*	*	*	*	*	NA	NA	NA	NA
- Coke production	**	**	**	**	*	*	*	*	*	*	*	*	NA	NA	NA	NA
- Electric arc furnaces	**	**	**	**	*	*	*	*	*	*	*	*	NA	NA	NA	NA
- Ferrous foundries	**	**	**	**	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Nonferrous metal smelting/refining													NA	NA	NA	NA
- Secondary aluminum smelting	5.4	17.0	53.8	H/L	*	*	*	*	*	*	*	*	NA	NA	NA	NA
- Secondary copper smelting	171	541	1,710	H/L	*	*	*	*	*	*	*	*	NA	NA	NA	NA
- Secondary lead smelting	0.73	1.63	3.65	M/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Scrap electric wire recovery	*	*	*	*	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Drum and barrel reclamation	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NA	NA	NA	NA

Table 2-2. Dioxin-Like Compound Emission Inventory for the United States (Reference Year 1995) (continued)

Emission Source	Emissions (g TEQ/yr) to Media															
	Air				Water				Land				Product			
	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]
Chemical Manuf./Processing Sources																
Bleached chemical wood pulp and paper mills	*	*	*	*	13.8	19.5	27.6	H/H	1.0	1.4	2.0	H/H	17.0	24.1	34.0	H/H
Mono- to tetrachlorophenols	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--
Pentachlorophenol	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	17,700	25,000	35,400	H/H
Chlorobenzenes	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--
Chlorobiphenyls (leaks/spills)	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NA	NA	NA	NA
Ethylene dichloride/vinyl chloride	*	*	*	*	*	*	*	*	NEG	NEG	NEG	--	*	*	*	*
Dioxazine dyes and pigments	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	0.11	0.36	1.1	L/M
2,4-Dichlorophenoxy acetic acid	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	13.0	18.4	26.0	H/H
Non-incinerated municipal sludge	NA	NA	NA	NA	NA	NA	NA	NA	120	207	375	H/H	4.0	7.0	12.5	H/H
Tall oil-based liquid soaps	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	*	*	*	*
Biological Formation	NA	NA	NA	NA	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Photochemical Formation	*	*	*	*	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Reservoir Sources																
Emissions from chlorophenol-treated wood	*	*	*	*	*	*	*	*	*	*	*	*	NA	NA	NA	NA
TOTAL[c]	1,026	2,745	7,541		14	20	28		121	208	377		17,734	25,050	35,474	

[a] CR = Confidence rating. First letter is rating assigned to "activity level" estimate; second letter is rating assigned to "emission factor." (See Section 2.1 and Table 2-1 for details):
H = High Confidence,
M = Medium Confidence,
L = Low Confidence.

[b] Leaded fuel production in the United States 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.)

[c] TOTAL reflects only the total of the estimates made in this report.

[d] It is not known what fraction, if any, of the estimated emissions from forest fires represents a "reservoir" source. The estimated emissions may be solely the result of combustion.

[e] Included within total for Wood Combustion - Industrial.

[f] Includes releases of dioxin-like PCBs and CDD/CDFs. The confidence ratings for the dioxin-like PCB estimates are H/M. The confidence ratings for the CDD/CDF estimates are H/H.

* Some evidence exists suggesting that this category is a source of CDD/CDF emissions. However, insufficient data are available for making a quantitative or qualitative emission estimate.

** Evidence exists suggesting that this category is a source of CDD/CDF emissions. Preliminary estimates of emissions for reference year 1995 have been made (see Table 2-5), but the confidence in the emission factor estimates and/or activity level estimates are so low that the estimates are too uncertain to include in the inventory.

NA = Not applicable.

NEG = Expected to be negligible (i.e., less than 1 gram per year) or non-existent.

Table 2-3. Dioxin-Like Compound Emission Inventory for the United States (Reference Year 1987)

Emission Source	Emissions (g TEQ/yr) to Media															
	Air				Water				Land				Product			
	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]
Waste Incineration																
Municipal waste incineration	3,540	7,915	17,698	H/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Hazardous waste incineration	2.2	5.0	11.2	M/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Boilers/industrial furnaces	0.24	0.77	2.4	M/L	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Medical waste/pathological incineration	781	2,470	7,810	L/L	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Crematoria	0.05	0.16	0.51	H/L	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Sewage sludge incineration	2.7	6.0	13.4	H/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Tire combustion	NEG	NEG	NEG	M/L	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Pulp and paper mill sludge incinerators	e	e	e	e	*	*	*	*	*	*	*	*	NA	NA	NA	NA
BioGas combustion	**	**	**	**	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Power/Energy Generation																
Vehicle fuel combustion - leaded[b]	10.2	32.4	102	H/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
- unleaded	1.2	3.8	12	H/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
- diesel	8.3	26.3	83.2	H/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Wood combustion - residential	28.3	89.6	283	H/L	NA	NA	NA	NA	*	*	*	*	NA	NA	NA	NA
- industrial	12.3	27.5	61.5	H/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Coal combustion - residential	**	**	**	**	NA	NA	NA	NA	*	*	*	*	NA	NA	NA	NA
- industrial/utility	28	62.6	140	H/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Oil combustion - residential	**	**	**	**	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
- industrial/utility	4.9	15.5	49	H/L	*	*	*	*	NA	NA	NA	NA	NA	NA	NA	NA
Other High Temperature Sources																
Cement kilns (haz waste burning)	37.0	117	370	H/M	*	*	*	*	*	*	*	*	*	*	*	*
Cement kilns (non haz waste burning)	4.3	13.7	43.3	H/L	*	*	*	*	*	*	*	*	*	*	*	*
Asphalt mixing plants	**	**	**	**	*	*	*	*	*	*	*	*	*	*	*	*
Petro. refining catalyst regeneration	*	*	*	**	NEG	NEG	NEG	--	*	*	*	*	NA	NA	NA	NA

Table 2-3. Dioxin-Like Compound Emission Inventory for the United States (Reference Year 1987) (continued)

Emission Source	Emissions (g TEQ/yr) to Media															
	Air				Water				Land				Product			
	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]
Cigarette combustion	0.31	1.0	3.1	H/L	NA	NA	NA	NA	*	*	*	*	NA	NA	NA	NA
Carbon reactivation furnaces	NEG	NEG	NEG	L/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Kraft recovery boilers	0.9	2.0	4.5	H/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Minimally Controlled or Uncontrolled Combustion																
Combustion of landfill gas in flares	**	**	**	**	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Landfill fires	**	**	**	**	NA	NA	NA	NA	*	*	*	*	NA	NA	NA	NA
Accidental fires (structural)	*	*	*	*	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Accidental fires (vehicles)	**	**	**	**	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Forest, brush, and straw fires[d]	53.8	170	538	L/L	NA	NA	NA	NA	*	*	*	*	NA	NA	NA	NA
Backyard trash burning	**	**	**	**	NA	NA	NA	NA	*	*	*	*	NA	NA	NA	NA
Uncontrolled combustion of PCBs	*	*	*	*	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Metallurgical Processes																
Ferrous metal smelting/refining																
- Sintering plants	**	**	**	**	*	*	*	*	*	*	*	*	NA	NA	NA	NA
- Coke production	**	**	**	**	*	*	*	*	*	*	*	*	NA	NA	NA	NA
- Electric arc furnaces	**	**	**	**	*	*	*	*	*	*	*	*	NA	NA	NA	NA
- Ferrous foundries	**	**	**	**	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Nonferrous metal smelting/refining													NA	NA	NA	NA
- Secondary aluminum smelting	3.0	9.5	30.0	H/L	*	*	*	*	*	*	*	*	NA	NA	NA	NA
- Secondary copper smelting	96	304	960	H/L	*	*	*	*	*	*	*	*	NA	NA	NA	NA
- Secondary lead smelters	0.55	1.22	2.73	M/M	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Scrap electric wire recovery	*	*	*	*	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Drum and barrel reclamation	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NA	NA	NA	NA

Table 2-3. Dioxin-Like Compound Emission Inventory for the United States (Reference Year 1987) (continued)

Emission Source	Emissions (g TEQ/yr) to Media															
	Air				Water				Land				Product			
	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]
Chemical Manuf./Processing Sources																
Bleached chemical wood pulp and paper mills	*	*	*	*	252	356	504	H/H	10	14.1	20	H/H	375	505	714	H/H
Mono- to tetrachlorophenols	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG		NEG	NEG	NEG	--
Pentachlorophenol	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG		25,500	36,000	51,000	H/H
Chlorobenzenes	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG		NEG	NEG	NEG	--
Chlorobiphenyls (leaks/spills)	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NA	NA	NA	NA
Ethylene dichloride/vinyl chloride	*	*	*	*	*	*	*	*	NEG	NEG	NEG	--	*	*	*	*
Dioxazine dyes and pigments	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	20	64	200	L/M
2,4-Dichlorophenoxy acetic acid	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	15.1	21.3	30.2	H/H
Non-incinerated sludge	NA	NA	NA	NA	NA	NA	NA	NA	120	207	375	H/H	4.0	7.0	12.5	H/H
Tall oil-based liquid soaps	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	*	*	*	*
Biological Formation	NA	NA	NA	NA	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Photochemical Formation	*	*	*	*	*	*	*	*	*	*	*	*	NA	NA	NA	NA
Reservoir Sources																
Emissions from chlorophenol-treated wood	*	*	*	*	*	*	*	*	*	*	*	*	NA	NA	NA	NA
TOTAL[c]	4,616	11,274	28,220		252	356	504		130	221	395		25,914	36,597	51,957	

[a] CR = Confidence rating. First letter is rating assigned to "activity level" estimate; second letter is rating assigned to "emission factor." (See Section 2.1 and Table 2-1 for details):
H = High Confidence,
M = Medium Confidence,
L = Low Confidence.

[b] Leaded fuel production in the United States 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.)

[c] TOTAL reflects only the total of the estimates made in this report.

[d] It is not known what fraction, if any, of the estimated emissions from forest fires represents a "reservoir" source. The estimated emissions may be solely the result of combustion.

[e] Included within total for Wood Combustion - Industrial.

[f] Includes releases of dioxin-like PCBs and CDD/CDFs. The confidence ratings for the dioxin-like PCB estimates are H/M. The confidence ratings for the CDD/CDF estimates are H/H.

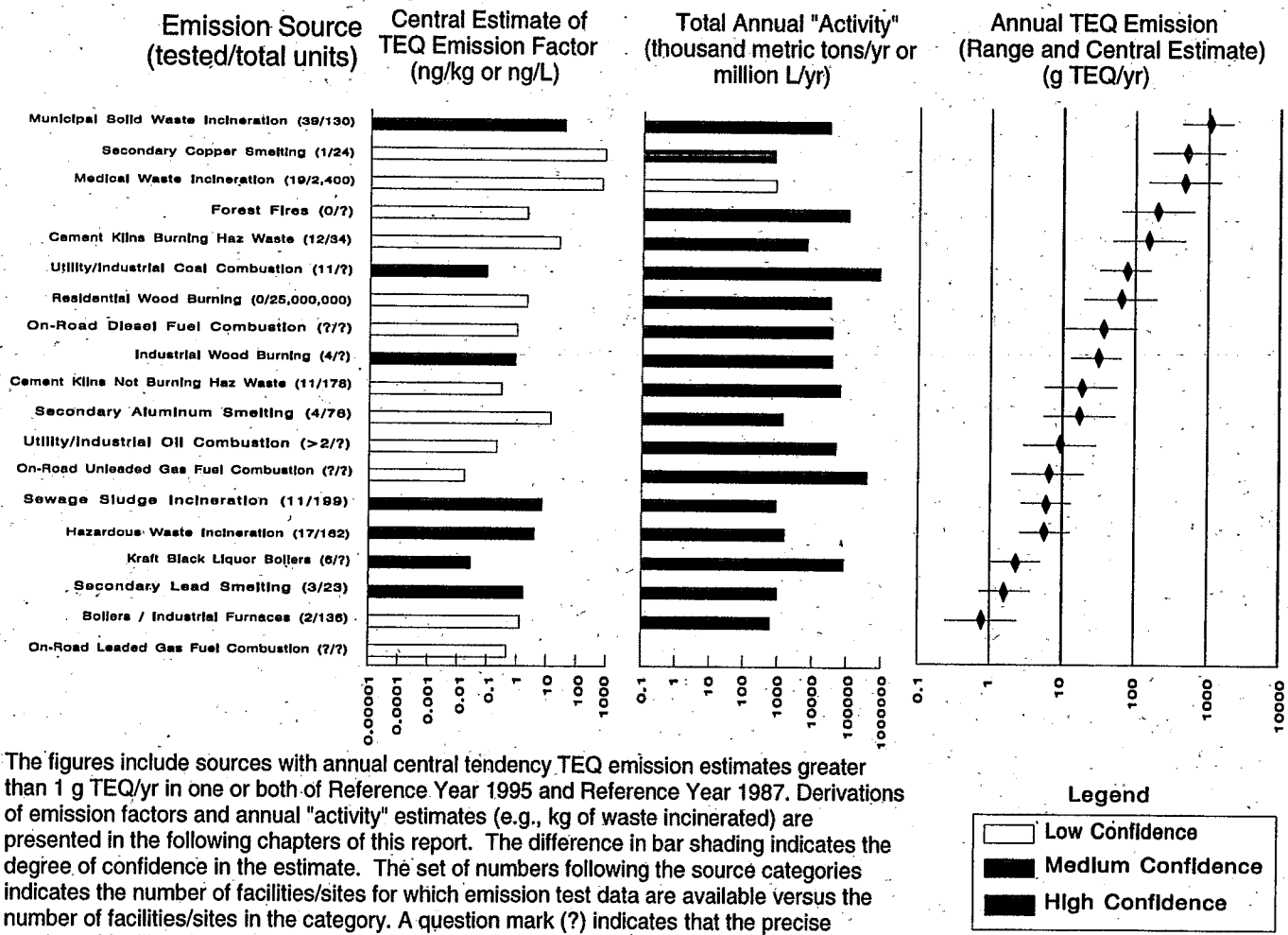
* Some evidence exists suggesting that this category is a source of CDD/CDF emissions. However, insufficient data are available for making a quantitative or qualitative emission estimate.

** Evidence exists suggesting that this category is a source of CDD/CDF emissions. Preliminary estimates of emissions for reference year 1995 have been made (see Table 2-5), but the confidence in the emission factor estimates and/or activity level estimates are so low that the estimates are too uncertain to include in the inventory.

NA = Not applicable.

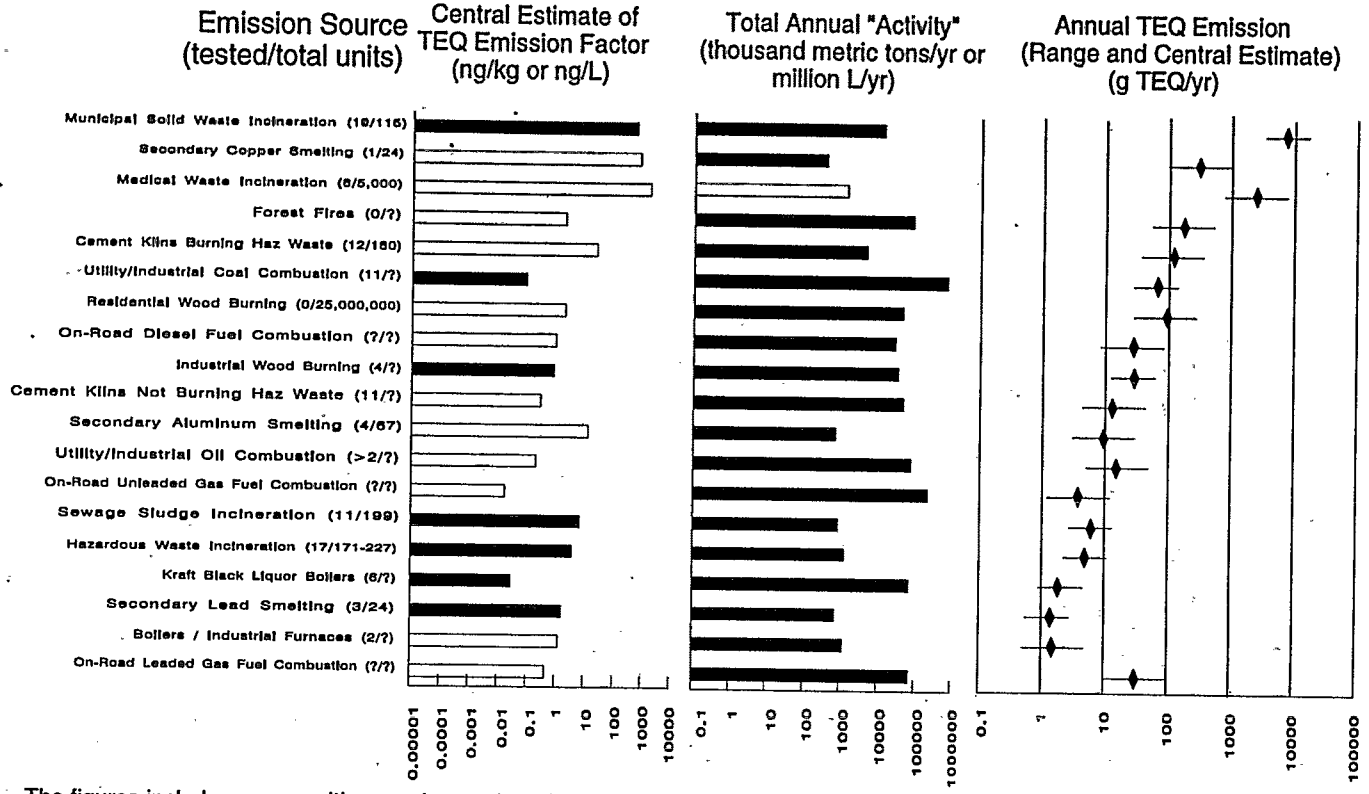
NEG = Expected to be negligible (i.e., less than 1 gram per year) or non-existent.

Figure 2-1. Estimated CDD/CDF TEQ Emissions to Air from Combustion Sources in the United States (Reference Time Period: 1995)



The figures include sources with annual central tendency TEQ emission estimates greater than 1 g TEQ/yr in one or both of Reference Year 1995 and Reference Year 1987. Derivations of 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 2-2. Estimated CDD/CDF TEQ Emissions to Air from Combustion Sources in the United States (Reference Time Period: 1987)



The figures include sources with annual central tendency TEQ emission estimates greater than 1 g TEQ/yr in one or both of Reference Year 1995 and Reference Year 1987. Derivations of 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 2-3. Comparison of Central Tendency Estimates of Annual TEQ Emissions to Air (grams/year) for Reference Years 1987 and 1995

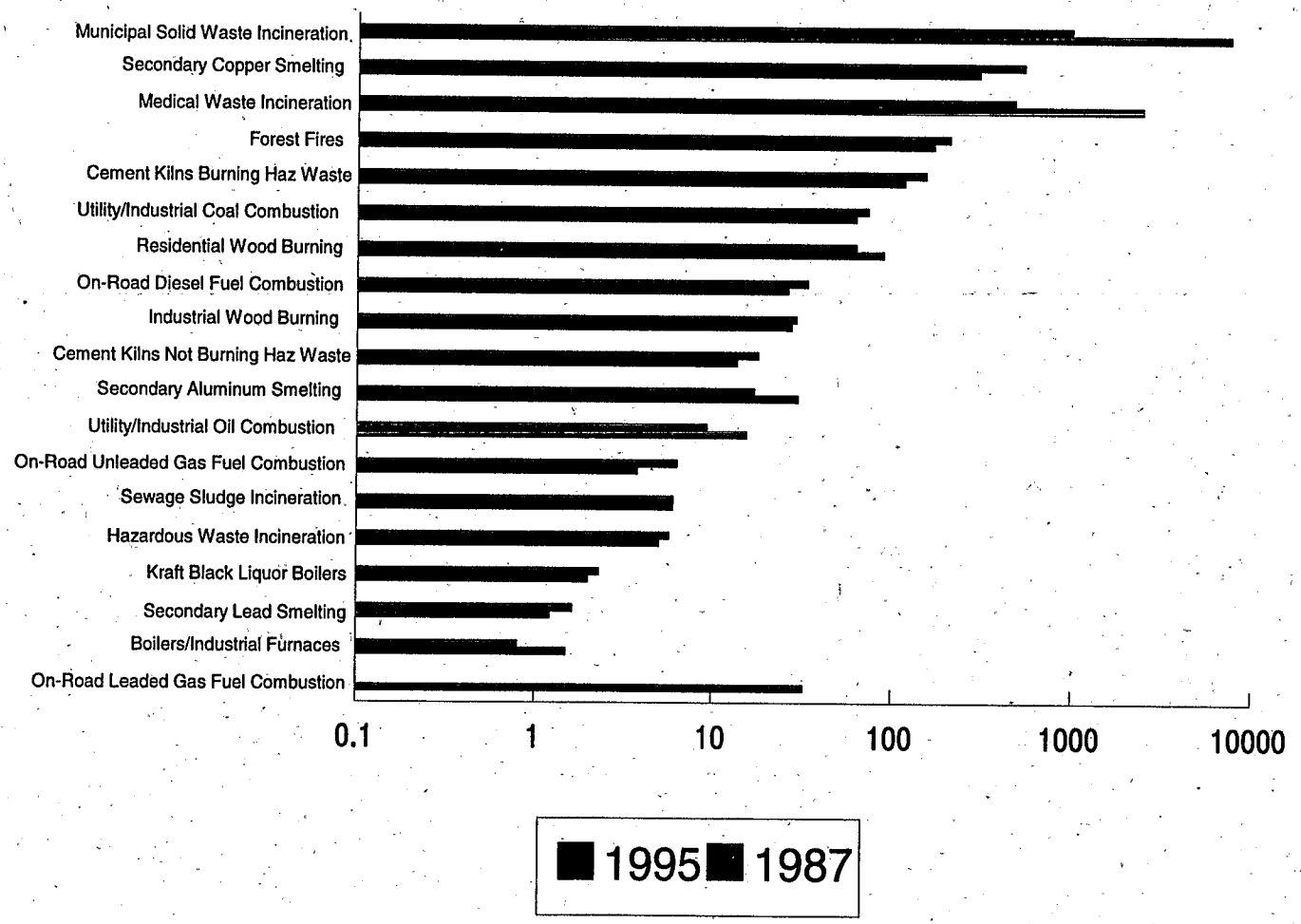


Table 2-4. CDD/CDF TEQ Emission Factors Used to Develop National Emission Inventory Estimates of Releases to Air

Emission Source		TEQ Emission Factor	Emission Factor Units
Waste Incineration			
Municipal waste incineration		a	
Hazardous waste incineration		3.8	ng TEQ/kg waste combusted
Boilers/industrial furnaces		0.64	ng TEQ/kg waste combusted
Medical waste/pathological incineration		a	
Crematoria		500	ng TEQ/body
Sewage sludge incineration		6.94	ng TEQ/kg dry sludge combusted
Tire combustion		0.282	ng TEQ/kg tires combusted
Pulp and paper mill sludge incinerators		b	
BioGas combustion		**	--
Power/Energy Generation			
Vehicle fuel combustion	- leaded[b]	45.7	pg TEQ/km driven
	- unleaded	1.7	pg TEQ/km driven
	- diesel	172	pg TEQ/km driven
Wood combustion	- residential	2	ng TEQ/kg wood combusted
	- industrial	0.82	ng TEQ/kg wood combusted
Coal combustion	- residential	**	--
	- industrial/utility	0.087	ng TEQ/kg coal combusted
Oil combustion	- residential	**	--
	- industrial/utility	0.2	ng TEQ/L combusted
Other High Temperature Sources			
Cement kilns burning hazardous waste		24.34	ng/kg clinker produced
Cement kilns not burning hazardous waste		0.29	ng/kg clinker produced
Asphalt mixing plants		**	--
Petro. refining catalyst regeneration		*	--
Cigarette combustion		0.00043 to 0.0029	pg TEQ/cigarette
Carbon reactivation furnaces		NEG	--
Kraft recovery boilers		0.028	ng TEQ/kg solids combusted
Minimally Controlled or Uncontrolled Combustion			
Combustion of landfill gas in flares		**	--
Landfill fires		**	--
Accidental fires (structural)		*	--
Accidental fires (vehicle)		**	--
Forest, brush, and straw fires		2	ng TEQ/kg biomass combusted
Backyard trash burning		**	--
Uncontrolled combustion of PCBs		*	--

Table 2-4. CDD/CDF TEQ Emission Factors Used to Develop National Emission Inventory Estimates of Releases to Air (continued)

Emission Source	TEQ Emission Factor	Emission Factor Units
Metallurgical Processes		
Ferrous metal smelting/refining		
- Sintering plants	**	--
- Coke production	**	--
- Electric arc furnaces	**	--
- Ferrous foundries	**	--
Nonferrous metal smelting/refining		
- Secondary aluminum smelting	13.1	ng/kg scrap feed
- Secondary copper smelting	779	ng/kg scrap consumed
- Secondary lead smelters	0.051 to 8.31	ng/kg lead produced
Scrap electric wire recovery	*	--
Drum and barrel reclamation	49.4	ng TEQ/drum
Chemical Manuf./Processing Sources		
Bleached chemical wood pulp and paper mills	*	--
Mono- to tetrachlorophenols	NEG	--
Pentachlorophenol	NEG	--
Chlorobenzenes	NEG	--
Chlorobiphenyls (leaks/spills)	NEG	--
Ethylene dichloride/vinyl chloride	*	--
Dioxazine dyes and pigments	NEG	--
2,4-Dichlorophenoxy acetic acid	NEG	--
Non-incinerated sludge	NA	--
Tall oil-based liquid soaps	NEG	--
Biological Formation	NA	--
Photochemical Formation	*	--
Reservoir Sources		
Emissions from chlorophenol-treated wood	*	--

a Different emission factors were derived for various subcategories within this industry.
b Included within total for Wood Combustion - Industrial.
* Some evidence exists suggesting that this category is a source of CDD/CDF emissions. However, insufficient data are available for making a quantitative or qualitative emission estimate.
** Evidence exists suggesting that this category is a source of CDD/CDF emissions. Preliminary estimates of emissions for reference year 1995 have been made (see Table 2-5), but the confidence in the emission factor estimates and/or activity level estimates are so low that the estimates are too uncertain to include in the inventory.

NA = Not applicable.
NEG = Expected to be negligible (i.e., less than 1 gram per year) or non-existent.

Table 2-5. Order of Magnitude Estimates of CDD/CDF Air Emissions from Sources Not Quantified in the National Inventory[a] (Reference Year 1995)

Potential Emission Source	Estimated Emission to Air (g TEQ/yr)
Accidental Vehicle Fires	10
Asphalt Mixing Plants	10
Backyard Trash Burning	1,000
Biogas Combustion	0.1
Coke Production	10
Combustion of Landfill Gas in Flares	10
Electric Arc Furnaces	10
Ferrous Metal Foundries	10
Landfill fires	1,000
Residential/Commercial Coal Combustion	10
Residential/Commercial Oil Combustion	10
Iron Ore Sintering	100

[a] Although some evidence exists that the following categories are sources of CDD/CDF emissions to air, the available data are insufficient for making even order of magnitude emission estimates: petroleum refining catalyst regeneration, uncontrolled combustion of PCBs, scrap electric wire burners, bleached wood pulp and paper mills, manufacturers of ethylene dichloride/vinyl chloride, accidental structural fires, photochemical formation, and chlorophenol-treated wood.

Table 2-6. CDD/CDF Air Emission Inventories for West Germany, Austria, The Netherlands, Switzerland, Belgium, and the United Kingdom

Emission Source	West Germany[a] (1990 basis) (g TEQ/yr)	Austria[b] (1987/88 basis) (g TEQ/yr)	The Netherlands[c] (1991 basis) (g TEQ/yr)	Switzerland[d] (1990 basis) (g TEQ/yr)	Belgium[f] (1995 basis) (g TEQ/yr)	United Kingdom[g] (1995 basis) (g TEQ/yr)	United Kingdom[h] (1994 basis) (g TEQ/yr)
Pulp and Paper Mills							
All sources		4		1 - 5			
Kraft recovery boilers	n	n	n	n	n	n	n
Sludge incinerators	n	n	n	n	n	n	n
Chemical Manuf./Processing Sources							
All manuf./processing sources			0.5				7.1 - 7.3
Chlorine manufacture	n	n	n	n	n	n	n
Manuf. halog. organic chemicals					0.05	0.12 - 0.32	
Manuf. halog. inorganic chemicals	n	n	n	n	n	n	n
Waste Incineration							
Municipal waste incineration	5.4 - 432	2.4 - 7	382	90 - 150	184	460 - 580	400 - 700
Hazardous waste incineration	0.5 - 72	5.3 - 44	16	<1	20.9	1.5 - 8.7	1.2 - 12
Medical waste/pathological incineration	>5.4	2 - 8	2.1	2 - 3	95	18 - 88	22.1 - 106
Crematoria			0.2		0.19	1 - 35	1 - 35
Sewage sludge incineration	0.01 - 1.13	<0.5	0.03		0.75	0.7 - 6	0.7 - 6
Tire combustion						1.7	1.8
Combustion of landfill gas	0.24 - 2.4		0.03		0.012	1.6 - 5.5	1.64 - 5.46
Metallurgical Processes							
Ferrous metal smelting/refining	1.3 - 18.9	1 - 5	28.8	6 - 16	60.7	34 - 97	93 - 2261
- Sintering plants	n	n	n	n	n	n	n
- Coke production	n	n	n	n	n	n	n
- Secondary ferrous smelting	n	n	n	n	n	n	n
Nonferrous metal smelting/refining	38 - 380	7 - 56	1.2		107	5 - 35	9.02 - 51.4
Scrap electric wire recovery			1.5				
Drum and barrel reclamation							<1

Table 2-6. CDD/CDF Air Emission Inventories for West Germany, Austria, The Netherlands, Switzerland, Belgium, and the United Kingdom (continued)

Emission Source	West Germany[a] (1990 basis) (g TEQ/yr)	Austria[b] (1987/88 basis) (g TEQ/yr)	The Netherlands[c] (1991 basis) (g TEQ/yr)	Switzerland[d] (1990 basis) (g TEQ/yr)	Belgium[f] (1995 basis) (g TEQ/yr)	United Kingdom[g] (1995 basis) (g TEQ/yr)	United Kingdom[h] (1994 basis) (g TEQ/yr)
Power/Energy Generation							
Vehicle fuel combustion - all fuel		0.1 - 0.4	7.0	2 - 14	1.71	1 - 45	
- leaded	>7.2						0.2 - 40.5
- unleaded	>0.8						0.06 - 0.86
- diesel	>4.6						23 - 273
Wood combustion - all sources				3 - 22			12.3 - 20.7
- residential		<70	11.2		<122[k]	2 - 18	
- industrial		1 - 5	0.8		<7[l]	1.4 - 2.9	
Coal combustion - all sources							16 - 113
- residential	>1.1				<122[k]	20 - 34	
- industrial/utility		<1	3.7[i]		<9.3[l,m]	5 - 67	
Oil combustion - all sources		<0.5	1.0			0.8 - 2.4[e]	0.5 - 6
- residential	>2.86				<122[k]		
- industrial/utility					<9.3[l,m]		
Other High Temperature Sources							
Cement kilns					20.8	0.2 - 11	0.6 - 40.6
Asphalt mixing plants			0.3			1.6	
Petro. refining catalyst regeneration	n	n	n	n	n	n	n
Cigarette combustion	>0.012						
Accidental fires					2.56		
Uncontrolled combustion of PCBs	n	n	n	n	n	n	n
Carbon reactivation furnaces						0.006	
Landfill fires	n	n	n	n	n	n	n
Lime production					33.4	0.04 - 2.2	0.03 - 0.12
Ceramics and glass manufacture						0.025 - 0.07	

Table 2-6. CDD/CDF Air Emission Inventories for West Germany, Austria, The Netherlands, Switzerland, Belgium, and the United Kingdom (continued)

Emission Source	West Germany[a] (1990 basis) (g TEQ/yr)	Austria[b] (1987/88 basis) (g TEQ/yr)	The Netherlands[c] (1991 basis) (g TEQ/yr)	Switzerland[d] (1990 basis) (g TEQ/yr)	Belgium[f] (1995 basis) (g TEQ/yr)	United Kingdom[g] (1995 basis) (g TEQ/yr)	United Kingdom[h] (1994 basis) (g TEQ/yr)
Natural/Agricultural Sources							
Forest, brush, and straw fires						3.8 - 22	2 - 15
Biological formation	n	n	n	n	n	n	n
Photochemical formation	n	n	n	n	n	n	n
Reservoir Sources							
Emissions from chlorophenol-treated wood			25			0.8	
TOTAL	67 - 926	90 - 210	484	100 - 200	659	560 - 1,100	590 - 3,700

[a] Source: Fiedler and Hutzinger (1992). Single values represent "minimum," and ranges represent "minimum" to "maximum" emission estimates.
[b] Source: Riss and Aichinger (1993).
[c] Source: Koning et al. (1993) and Bremmer et al. (1994).
[d] Source: Schatowitz et al. (1993).
[e] 0.8-2.4 g TEQ/yr from waste oil combustion.
[f] Source: Wevers and DeFre (1995).
[g] Source: Douben et al. (1995). (Her Majesty's Inspectorate of Pollution); Eduljee and Dyke (1996).
[h] Source: UK Department of Environment (1995).
[i] Coal combustion at blast furnaces and coke factories not included.
[j] Total includes sintering processes and coke production.
[k] Total emission from space heating with all fuel types (i.e., wood, coal, and oil) was estimated at 122 g/yr.
[l] Total emission from industrial combustion with all fuel types (i.e., wood, coal, and oil) was estimated at 7 g/yr.
[m] Total emission from production of electricity with all fuel types (i.e., wood, coal, and oil) was estimated at 2.31 g/yr.
[n] This source category was included because it was identified as a known or potential source in the U.S. Inventory (i.e., Table 2-2).

3. COMBUSTION SOURCES OF CDD/CDF: 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, making it more sterile. In keeping with this definition, incinerator systems can be classified by the types of wastes incinerated: municipal solid waste incineration; medical and pathological waste incineration; hazardous waste incineration; sewage sludge incineration; tire incineration; and biogas flaring. Each of these types of incinerators are discussed in this chapter. The purposes of this chapter are 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 these facilities for reference years 1987 and 1995.

Combustion research has developed three theories on the mechanisms involved in the emission of CDDs and CDFs from combustion systems: (1) CDD/CDFs can be introduced into the combustor with the feed and pass through the system unchanged, (2) CDD/CDFs can be formed during combustion, or (3) CDD/CDFs can be formed via chemical reactions in the post-combustion portion of the system. The total CDD/CDF emissions are likely to be the net result of all three mechanisms; however, their relative importance is often uncertain. To the extent practical with the available data, the combustors in each source category were divided into classes judged to have similar 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 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 SOLID WASTE INCINERATION

As discussed previously, CDD/CDF emission theory suggests that CDD/CDF 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. Accordingly, this chapter proposes a classification scheme that divides municipal solid waste incinerators (MSWIs) into a variety of design classes based on those factors. Some APCDs are operated at different temperatures; therefore, operating temperature is used to define some design classes. Because the theory also suggests that feed can influence CDD/CDF emissions, the proposed furnace classification system distinguishes refused-derived fuel from normal municipal solid waste (MSW). This section begins with a description of the MSWI technology and then proposes the design classification scheme. Using this scheme, the MSWI industry is characterized for the reference years 1987 and 1995. Finally, the procedures for estimating emissions are explained, and results summarized.

3.1.1. Description of Municipal Solid Waste Incineration Technologies

For purposes of this report, MSWI furnace types are divided into three major categories: mass burn, modular, and refuse-derived fuel. Each of these furnace types is described below, followed with a description of the APCDs used with these systems.

Furnace Types

Mass Burn: Historically, this furnace type derived its name 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 these others 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 indicates that the combustion capacity of facilities ranges from 90 to 2,700 metric tons of MSW per day. Three subcategories of mass burn (MB) technologies are described below:

- Mass burn refractory-walled (MB-REF) systems represent an older class of MSWIs (generally built in the late 1970s to early 1980s) that were designed only to reduce the volume of waste in need of disposal by 70 to 90 percent. These facilities

usually lacked boilers to recover the combustion heat for energy purposes. In the MB-REF design, the MSW is delivered to the combustion chamber by a traveling grate and/or a ram feeding system. Combustion air in excess of stoichiometric amounts (i.e., more oxygen is supplied than needed for complete combustion) is supplied both below and above the grate.

- Mass burn waterwall (MB-WW) facilities represent enhanced combustion efficiency, as compared with MB-REF incinerators. Although it achieves similar volume reductions, the MB-WW incinerator design provides a more efficient delivery of combustion air, resulting in sustained higher temperatures. Figure 3-1 is a schematic of a typical MB-WW MSWI. The term 'waterwall ' refers to a series of steel tubes, running vertically along the walls of the furnace. The tubes contain water, which when heated by combustion, transfer energy from the heat of combustion to the water. The water reaches boiling temperature, and steam is produced. The steam is then used to drive an electrical turbine generator or for other industrial needs. This transfer of energy is termed 'energy recovery.'

- Mass burn rotary kiln combustors (MB-RC) use a water-cooled rotary combustor, which consists of a rotating combustion barrel configuration mounted at a 15-20° 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 (i.e., 10 to 20 rotations/hour) causes the MSW to tumble, thereby exposing more surface area for complete burnout of the MSW. These systems are also equipped with boilers for energy recovery. Figure 3-2 is a schematic of a typical MB-RC MSWI.

Modular Incinerator: This is the second general type of MSWI furnace used in the United States. As with the mass burn type, modular incinerators burn waste without preprocessing. Modular MSWIs consist of two vertically mounted combustion chambers (i.e., a primary and secondary chamber). In the 1995 inventory, modular combustors' combustion capacity ranged from 4 to 270 metric tons/day. 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 secondary combustion chamber, both of which operate with air levels in excess of stoichiometric requirements (i.e., 100 to 250 percent excess air). Figure 3-3 illustrates a typical modular excess-air MSWI.

- Starved (or controlled) air is a newer type of modular system, which is easier and less expensive to operate than the excess-air systems. In these systems, air is supplied to the primary chamber at sub-stoichiometric levels. The products of incomplete combustion entrain in the combustion gases that are formed in the primary combustion chamber, 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

and uniform temperature of the secondary chamber, combined with the turbulent mixing of the combustion gases, results in low-levels of particulate matter and organic contaminants being formed and emitted. Therefore, many existing modular units lack post-combustion air pollution control devices. Figure 3-4 is a schematic view of a modular starved-air MSWI.

Refuse-Derived Fuel (RDF): The third major type of MSWI furnace technology is designed to combust refuse-derived fuel (RDF). RDF is a general term that describes MSW from which relatively noncombustible items are removed, thereby enhancing the combustibility of the MSW. 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 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 percent excess air. Waterwall tubes, a superheater, and an economizer are used to recover heat for production of steam and/or electricity. The 1995 inventory indicates that dedicated RDF facilities range in total combustion capacity from 227 to 2,720 metric tons/day.

- Cofired RDFs burn both RDF and normal MSW.

- The fluidized-bed RDF (FB-RDF) burns the waste in a turbulent and semi-suspended 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 percent stoichiometric requirements is injected above the sand suspension. Waste-fired FB-RDFs typically operate at 30 to 100 percent excess air levels and at bed temperatures around 815°C (1,500°F). A typical FB-RDF is presented as Figure 3-6. Technology has two basic design concepts: (1) a bubbling-bed incineration unit and (2) a circulating-bed incineration unit. The 1995 inventory indicates that fluidized-bed MSWIs have capacities ranging from 184 to 920 metric tons/day. These systems are usually equipped with boilers to produce steam.

Air Pollution Control Devices (APCDs)

MSWIs are commonly equipped with one or more post-combustion APCDs to remove various pollutants prior to release from the stack (e.g., particulate matter, heavy metals, acid gases, and/or organic contaminants) (U.S. EPA, 1992d). These APCDs include:

- Electrostatic precipitator (ESP),
- Fabric filter (FF),
- Dry scrubber (DS),
- Dry sorbent injection (DSI), and
- Wet scrubber (WS)

Electrostatic Precipitator: The ESP is generally used to collect and control particulate matter 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 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 two for each 30°C increase in temperature (U.S. EPA, 1994f). As temperature increases beyond 300°C, formation rates decline. Although ESPs in this temperature range efficiently remove most particulates and the associated CDD/CDFs, the formation that occurs can result in a net increase in CDD/CDF emissions. This temperature related formation of CDD/CDF within the ESP can be applied to distinguish hot-side ESPs from cold-side ESPs. For purposes of this report, ESPs are classified as follows:

- A cold-side ESP operates at or below 230°C.
- A hot-side ESP operates at an inlet temperature greater than 230°C.

Fabric Filters (FF): FFs are also particulate matter control devices, which remove dioxins associated with particles and any vapors that adsorb to the particles. Six- to 8-inch diameter bags, made from woven fiberglass material, are usually arranged in series. An induction fan forces the combustion gases through the tightly woven fabric. The porosity of the fabric allows the bags to act as filter media and retain a broad range of particles

sizes (i.e., down to less than 1 micrometer in diameter). The FF is sensitive to acid gas; therefore, it is usually operated in combination with spray dryer adsorption of acid gases.

Dry Scrubbers (DS): DSs, also called spray dryer adsorption, involve both the removal of acid gas and particulate matter from the post-combustion gases. By themselves, these units probably have little effect on dioxin emissions. In a typical DS system, hot combustion gases enter a scrubber reactor vessel. An atomized hydrated lime slurry (water plus lime) is injected into the reactor at a controlled velocity (Donnelly, 1992). The hydrated lime slurry rapidly mixes with the combustion gases within the reactor. The water in the hydrated lime slurry quickly evaporates, and the heat of evaporation causes the combustion gas temperature to rapidly decrease. The neutralizing capacity of hydrated lime reduces the combustion gas content of acid gas constituents (e.g., hydrogen chloride gas, and sulfur dioxide gas) by greater than 70 percent. A dry product, consisting of particulate matter and hydrated lime, settles to the bottom of the reactor vessel. DS technology is used in combination with ESPs. The DS reduces ESP inlet temperatures to make a cold-side ESP. DS/FFs have achieved greater than 95 percent reduction and control of CDD/CDFs in MSWI emissions (U.S. EPA, 1992d).

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

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

In addition to the APCDs described above, some less common types are also used in some MSWIs. An example is the Electro Granular Bed (EGB), which consists of a packed bed of activated carbon. An electric field is passed through the packed bed; particles entrained in the flue gases are given a negative charge, and the packed bed is given a positive charge. EGB systems function much like an ESP. Particulate matter is collected within the bed; therefore, they will remove dioxins associated with collected particles and

any vapors that adsorb to the particles. Only one facility in the United States currently employs the EGB system, a fluidized bed-RDF MSWI.

Classification Scheme

Based on the array of MSWI technologies described above, a classification system for deriving CDD/CDF emission estimates was developed. As discussed earlier, it is assumed that facilities with common design and operating characteristics have a similar potential for CDD/CDF emissions. The MSWIs operating in 1987 and 1995 were divided 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. This taxonomy is summarized in Figures 3-7 and 3-8.

3.1.2. Characterization of MSWI Facilities in Reference Years 1995 and 1987

Table 3-1 lists by design/APCD type, the number of facilities and activity level (kg MSW incinerated per year) for MSWIs in the reference year 1995. A similar inventory is provided for reference year 1987 in Table 3-2. This information was derived from four reports: U.S. EPA (1987b), Sytems Applications International (1995), Taylor and Zannes (1996), and Solid Waste Technologies (1994). In general, these studies collected the information via telephone interviews with the plant operators.

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

- The number of facilities stayed about the same (113 in 1987 and 130 in 1995), but the amount of MSW incinerated more than doubled (13.8-billion kg in 1987 and 28.8-billion kg in 1995).
- The dominant furnace technology shifted from modular in 1987 (57 units and 1.4-billion kg) to mass burn waterwall facilities in 1995 (57 units and 17-billion kg).
- The dominant APCD technology shifted from hot-sided ESPs in 1987 (54 units and 11-billion kg) to fabric filters in 1995 (55 units and 16-billion kg).
- 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 facilities in 1995 (0.2-billion kg).

3.1.3. Estimation of CDD/CDF Emissions from MSWIs

Compared to other CDD/CDF source categories, MSWIs have been more extensively evaluated for CDD/CDF emissions. Within the context of this report, adequate emission testing for CDD/CDFs were 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 MSWIs were estimated using a three-step process as described below.

Step 1. Estimation of emissions from all stack tested facilities. The EPA stack testing method (EPA Method 23) produces a measurement of CDD/CDF in units of mass concentration of CDD/CDF (i.e., nanograms per dry standard cubic meter of combustion gas [ng/dscm]) at standard temperature and pressure (20°C and one atmosphere), and adjusted to a measurement of 7 percent 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 below was used to derive annual emission estimates for each tested facility:

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

Where:

E_{TEQ}	=	Annual TEQ emission (g /yr)
C	=	Combustion flue gas TEQ concentration (ng/dscm) (20°C, 1 atm; adjusted to 7% O_2)
V	=	Volumetric flow rate of combustion flue gas (dscm/hour) (20°C, 1 atm; adjusted to 7% O_2)
CF	=	Capacity factor, fraction of time that the MSWI operates (i.e., 0.85)
H	=	Total hours in a year (8,760 hr/yr)

After calculating annual emissions for each tested facility, the emissions were summed across all tested facilities for each reference year. [Note: many of the emission tests do not correspond exactly to these 2 years. In these cases, the equipment conditions present at the time of the test were compared to those during the reference year to determine their applicability.]

Step 2. Estimation of emissions from all non-tested facilities. This step involves multiplying the emission factor and annual activity level for each MSWI design class and

then summing across classes. The activity levels for reference years 1995 and 1987 are summarized in Tables 3-1 and 3-2, 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:

$$EF_{mswi} = \frac{C \ x \ F_v}{I_w} \qquad \text{(Eqn. 3-2)}$$

Where:

EF_{mswi} = 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)

Example: A mass burn waterwall MSWI equipped with cold-sided ESP.

Given:

C = 10 ng TEQ/dscm (20°C, 1 atm; adjusted to 7% O_2)
F_v = 40,000 dscm/hr (20°C, 1 atm; adjusted to 7% O_2)
I_w = 10,000 kg MSW/hr

$$EF_{MBWW} = \frac{10 \ ng}{dscm} \ x \ \frac{40{,}000 \ dscm}{hr} \ x \ \frac{hr}{10{,}000 \ kg}$$

$$EF_{MBWW} = \frac{40 \ ng \ \ TEQ}{kg \ \ MSW \ \ burned}$$

EPA was not able to obtain engineering test reports of CDD/CDF emissions for a number of design classes. In these cases, the above procedure could not be used to derive emission factors. Instead, the emission factors of the tested design class that was judged most similar in terms of dioxin control was assumed to apply to the untested class. The following logic was used to make this decision:

1. The tested APCDs for the furnace type of the untested class were reviewed to see if any operated at a similar temperature.

2. If any operated at similar temperatures, the one with most similar technology was assumed to apply.

3. If none operated at a similar temperature, then the most similar furnace type with same control device was assumed to apply.

Table 3-3 lists all design categories with no tested facilities and shows the class with tested facilities that was judged most similar.

It should be understood that the emission factors for each design class are the same for both reference years. This is 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 simply involves summing emissions from all tested and untested facilities. This process is shown in Tables 3-4 and 3-5 for the reference years 1995 and 1987, respectively. The tables are organized by design class and show separately the emission estimates for the tested and untested facilities. 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 MSWIs for 1995 and 1987

The activity level estimates (i.e., the amount of MSW that is annually combusted by the various MSWI technologies) are given a "high" confidence rating for both 1987 and 1995. For both years, comprehensive surveys of activity levels were conducted by independent sources on virtually all facilities (U.S. EPA, 1987b; Systems Application International, 1995; Taylor and Zannes, 1996; Solid Waste Technologies, 1994).

The emission factor estimates are given a "medium" confidence rating for both 1987 and 1995. A moderate fraction of the facilities were tested in both years: 11 of 113 facilities in 1987 (10 percent), and 27 of 130 facilities (21 percent) in 1995. Moreover, the tested facilities represent 21 and 27 percent of the total activity level of operating MSWIs in 1987 and 1995, 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 times (i.e., upset conditions, start-up and shut-down).

These confidence ratings produce an overall "medium" confidence rating. Using the procedures established for this report for a "medium" confidence rating, the best estimate of the annual emissions is assumed to be the geometric average of a range that varies by a factor of five between the low and high ends. For 1987, the central estimate of the annual emissions is 7,915-g TEQ/yr, and the range is calculated to be 3,540- to 17,698-g TEQ/yr. For 1995, the central estimate of annual emissions is 1,100-g TEQ/yr, and the range is calculated to be 492- to 2,460-g TEQ/yr.

3.1.5 Congener Profiles of MSWI Facilities

The TEQ air emissions from MSWIs are actually a mixture of CDD and CDF congeners. These mixtures can be translated into what are termed 'congener profiles,' which represent the distribution of total CDDs and CDFs present in the mixture. A congener profile may serve as a signature of the types of CDDs and CDFs associated with particular MSWI technology and APCD. Figure 3-9 is a congener profile of a mass-burn waterwall MSWI equipped with a dry scrubber and fabric filter (i.e., the most common type of MSWI and APCD design in use today). In general, the congener profile suggests that OCDD dominates total CDD/CDF emissions. In addition, every toxic CDD/CDF congener is detected in the emissions.

3.1.6 Estimated CDD/CDFs in MSWI Ash

Ash from MSWIs is required to be disposed in permitted landfills. Based on protocols of this report, ash from MSWIs are, therefore, not considered environmental releases of CDD/CDFs and are not included in the inventory. For background purposes, however, some information is presented below about the quantities of CDD/CDFs in ash from MSWIs.

An estimated 7-million metric tons of total ash (bottom ash plus fly ash) were generated by MSWIs in 1992 (telephone conversation between J. Loundsberry, U.S. EPA Office of Solid Waste, and L. Brown, Versar Inc., on February 24, 1993). U.S. EPA

(1991b) indicated that 2- to 5-million metric tons of total ash were produced annually in the late 1980s from MSWIs, with fly ash comprising 5 to 15 percent of the total. U.S. EPA (1990c) reported the results of analyses of MSWI ash samples for CDDs and CDFs. 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 and CDFs. The TEQ levels in the ash (fly ash mixed with bottom ash) ranged from 106 to 466 ng/kg, with a mean value of 258 ng/kg. CDD/CDF levels in fly ash are generally much higher than in bottom ash. For example, Fiedler and Hutzinger (1992) reported levels of 13,000-ng TEQ/kg in fly ash. Multiplying the mean TEQ total ash concentration by the estimated amount of MSWI ash generated annually (approximately 7-million metric tons in 1995 and 5-million metric tons in 1987) yields an estimated annual TEQ in MSWI ash of 1,800-g TEQ/yr in 1995 and 1,300-g TEQ/yr in 1987.

Each of the five facilities sampled in U.S. EPA (1990c) had companion ash disposal facilities equipped with leachate collection systems or some means of collecting leachate samples. Leachate samples were collected and analyzed for each of these systems. Detectable levels were only found in the leachate at one facility (TEQ = 3 ng/L); the only detectable congeners were HpCDDs, OCDD, and HpCDFs.

3.1.7 Current EPA Regulatory and Monitoring Activities

On December 19, 1995, EPA promulgated CDD/CDF emission standards for all existing and new MSWI units with aggregate capacities to combust greater than 35 metric tons per day (Federal Register, 1995e). The specific emission standards (expressed as ng/dscm of total CDD/CDF - based on standard dry gas corrected to 7 percent oxygen) are a function of the size, APCD configuration, and age of the facility as listed below:

1995 Emission standard (ng total CDD/CDF/dscm)	Facility age, size, and APCD
60	• Existing; >225 metric tons/day; ESP-based APCD
30	• Existing; >225 metric tons/day; non-ESP-based APCD
125	• Existing; >35 to ≤225 metric tons/day
13	• New; >35 metric tons/day

States have up to 3 years from promulgation of the Federal standards to submit revised State Implementation Plans to EPA for approval. Once approved, States have the primary responsibility to implement the new standards. This could occur as early as the year 2000. As this date approaches, EPA's Office of air Quality Planning and Standards (OAQPS) estimates that the current estimate of national emissions of CDD/CDFs from existing MSWIs will decline from current levels. OAQPS estimates full compliance by all MSWIs with the 1995 standards will result in an annual emission of about 24-g TEQ/yr (U.S. EPA, 1996d).

3.2. HAZARDOUS WASTE INCINERATION

Hazardous waste incineration (HWI) is the controlled pyrolysis and/or oxidation of potentially dangerous liquid, gaseous and solid waste. HWI is one technology used to manage hazardous waste under RCRA and CERCLA (Superfund) programs. As described below, hazardous wastes are burned in a variety of situations and are covered in a number of different sections in this report.

- Much of the hazardous waste is burned in facilities dedicated to burning waste. Most of these dedicated facilities are located "onsite" at chemical manufacturing facilities and only burn waste associated with their on-site industrial operations. Hazardous waste is also burned at dedicated facilities located "offsite" from manufacturing facilities and accept waste from multiple sources. These fixed location facilities dedicated to burning hazardous waste at both on- and off-site locations 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 dedicated HWIs; therefore, they are discussed in Section 3.2.5.

- A number of cement 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 and operate for a limited duration at any given location. These units are 'mobile' in the sense that they can be transported from one location to another. Due to the transitory nature of these facilities, they are not included in this inventory.

The following subsections review the types of HWI technologies commonly in use in the United States, and present the derivation of emissions estimates of CDD/CDFs from all facilities operating in 1995 and 1987.

3.2.1. Furnace Designs for Dedicated Hazardous Waste Incinerators

The four principal furnace designs employed for the combustion of hazardous waste in the United States are: liquid injection, rotary kiln, fixed hearth, and fluidized-bed incinerators (Dempsey and Oppelt, 1993). The majority of commercial operations are of the rotary kiln incinerator type. On-site (noncommercial) HWI technologies are an equal mix of rotary kiln and liquid injection facilities, with a few additional fixed hearths and fluidized bed operations (U.S. EPA, 1996h). Each of these MWI technologies is discussed below:

Rotary Kiln HWI: Rotary kiln incinerators consist of a rotating kiln, coupled with a high temperature afterburner. Because these are excess air units designed to combust hazardous waste in any physical form (i.e., liquid, semi-solid, or solid), rotary kilns are the most common type of hazardous waste incinerator 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 start-up to reach elevated temperatures. The typical heating value of hazardous waste (i.e., 8,000 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 HWI: Liquid injection incinerators (LIIs) 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 LIIs consist of a refractory-lined steel cylinder mounted either in a horizontal or vertical alignment. The combustion chamber is equipped with one or more waste burners. Because of the rather large surface area of the atomized droplets of liquid hazardous waste, the droplets quickly vaporize. The moisture evaporates, leaving a highly combustible mix of waste fumes and combustion air (U.S. EPA, 1996h). Secondary air is added to the combustion chamber to complete the oxidation of the fume/air mixture.

Fixed Hearth HWI: Fixed hearths, the third principal hazardous waste incineration technology, are starved air or pyrolytic incinerators, which are two-stage combustion units. Waste is ram-fed into the primary chamber and incinerated below stoichiometric requirements (i.e., at about 50 to 80 percent of stoichiometric air requirements). The resulting smoke and pyrolytic combustion products are then passed though a secondary combustion chamber where relatively high temperatures are maintained by the combustion of auxiliary fuel. Oxygen is introduced into the secondary chamber to promote complete thermal oxidation of the organic molecules entrained in the gases.

Fluidized-bed HWI: The fourth hazardous waste incineration technology is the fluidized-bed incinerator, which is similar in design to that used in MSW incineration. (See Section 3.1.) In this configuration, a layer of sand is placed on the bottom of the combustion chamber. The bed is preheated by underfire auxiliary fuel at startup. During combustion of auxiliary fuel at start-up, the hot gases are channeled through the sand at relatively high velocity, and the turbulent mixing of combustion gases and combustion air causes the sand to become suspended (Buonicore, 1992a). This takes on the appearance of a fluid medium, hence the incinerator is termed a 'fluidized bed' combustor The incinerator is operated below the melting point temperature of the bed material. Typical temperatures of the fluid medium are within the range of 650 to 940°C. A constraint on the types of waste burned is that the solid waste particles must be capable of being suspended within the furnace. When the liquid or solid waste is combusted in the fluid medium, the exothermic reaction causes heat to be released into the upper portion of the combustion chamber. The upper portion is typically much larger in volume than the lower portion, and temperatures can reach 1,000°C (Buonicore, 1992a). This high temperature is sufficient to combust volatilized pollutants emanating from the combustion bed.

3.2.2. APCDs for Dedicated Hazardous Waste Incinerators

Most HWIs use APCDs to remove undesirable components from the flue gases that evolved during the combustion of the hazardous waste. These unwanted pollutants include suspended ash particles ("particulate matter" or PM), acid gases, metal, and organic pollutants. The APCD controls or collects these pollutants and reduces their discharge from the incinerator stack to the atmosphere. Levels and kinds of these combustion byproducts are highly site-specific, depending on factors such as waste composition and incinerator system design and operating parameters (e.g., temperature and exhaust gas velocity). The APCD is typically comprised of a series of different devices that work together to clean the exhaust combustion flue gas. Unit operations usually include exhaust gas cooling, followed by particulate matter and acid gas control.

Exhaust gas cooling may be achieved using a waste heat boiler or heat exchanger, mixing with cool ambient air, or injection of a water spray into the exhaust gas. A variety of different types of APCDs are employed for the removal of particulate matter and acid gases. Such devices include: wet scrubbers (such as venturi, packed bed, and ionizing systems), electrostatic precipitators, and fabric filters (sometimes used in combination with dry acid gas scrubbing). In general, the control systems can be grouped into the following three categories: "wet," "dry," and "hybrid wet/dry" systems. The controls for acid gases (either dry or wet systems) cause temperatures to be reduced preceding the control device. This impedes the extent of formation of CDDs and CDFs in the post-combustion area of the typical HWI. It is not unusual for stack concentrations of CDD/CDFs at a particular HWI to be in the range of 1- to 100-ng CDD/CDF/dscm (Helble, 1993), which is low in comparison to other waste incineration systems. The range of total CDD/CDF flue gas concentrations measured in the stack emissions of HWIs during trial burns across the class of HWI facilities, however, has spanned four orders of magnitude (ranging from 0.1 to 1,600 ng/dscm) (Helble, 1993). The APCD systems are described below:

- **Wet Systems:** A wet scrubber is used for both particulate and acid gas control. Typically, a venturi scrubber and packed-bed scrubber are used in a back-to-back arrangement. Ionizing wet scrubbers, wet electrostatic precipitators, and innovative venturi-type scrubbers may be used for more efficient particulate control. Wet scrubbers generate a wet effluent liquid wastestream (scrubber blowdown), are relatively inefficient at fine particulate control compared to dry control techniques,

and have equipment corrosion concerns. However, wet scrubbers do provide efficient control of acid gases and have lower operating temperatures (compared with dry systems), which may help control the emissions of volatile metals and organic pollutants.

- **Dry Systems:** In dry systems, a fabric filter or electrostatic precipitator (ESP) is used for particulate control. A fabric filter or ESP is frequently used in combination with dry scrubbing for acid gas control. Dry scrubbing systems, in comparison with wet scrubbing systems, are inefficient in controlling acid gases.
- **Hybrid Systems:** In hybrid systems, a dry technique (ESP or fabric filter) is used for particulate control, followed by a wet technique (wet scrubber) 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 particulate, efficient capture of acid gases), while avoiding many of the individual disadvantages. In some hybrid systems, known as "zero discharge systems," the wet scrubber liquid is used in the dry scrubbing operation, thus minimizing the amount of liquid byproduct waste.
- **Uncontrolled HWIs:** Facilities that do not use any air pollution control devices fall under a separate and unique category. These are primarily liquid waste injection facilities, which burn low ash and chlorine content wastes; therefore, they are low emitters of PM and acid gases.

3.2.3. Estimation of CDD/CDF Emission Factors for Dedicated Hazardous Waste Incinerators

For purposes of estimating emission factors, this document considers subdividing the combustors in each source category into design classes judged to have similar potential for CDD/CDF emissions. As explained below, it was decided not to subdivide dedicated HWIs.

Combustion research has identified three mechanisms involved in the emission of CDD/CDFs from combustion systems: (1) CDD/CDFs can be introduced into the combustor with the feed and pass through the system not completely burned/destroyed; (2) CDD/CDFs can be formed by chemical reactions inside the combustion chamber; and (3) CDD/CDFs can be formed by chemical reactions outside the combustion chamber. The total CDD/CDF emissions are likely to be the net result of all three mechanisms; however, the relative

importance of the mechanisms can vary among source categories. In the case of HWIs, the third mechanism (i.e., post-combustion formation) is likely to dominate, because HWIs are typically operated at high temperatures and long residence times, and most have sophsiticated real-time monitoring and controls to manage the combustion process. Therefore, any CDD/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 in HWIs can be minimized through 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 PM APCD. If temperature is reduced below 200°C, the low-temperature catalytic formation of CDD/CDFs is substantially retarded.
- **Use of Particulate Matter (Pm) Air Pollution Control Devices**: PM control devices can effectively capture condensed and adsorbed CDD/CDFs that are associated with the entrained particulate matter (in particular, that which is adsorbed on unburned carbon containing particulates).
- **Use of Activated Carbon**: Activated carbon injection is used at some HWIs to collect (sorb) CDD/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, and insufficient emissions data are available to generalize about any minor differences. Consequently, for purposes of generating emission factors, it was decided not to subdivide this class on the basis of APCD type.

EPA compiled a data base summarizing the results of stack testing for CDDs and CDFs at 17 HWIs (U.S. EPA, 1996c). Most facilities were tested between 1993 and 1996. For purposes of this report, CDD/CDF emission factors were estimated based on the results of the emission tests contained in this data base. The breakdown of furnace types of tested HWI facilities is as follows: 10 rotary kiln incinerators, 4 liquid injection incinerators, 1 fluidized-bed incinerator, and 2 fixed-bed.

As stated earlier, EPA/ORD decided not to subclassify the dedicated HWI designs for purposes of deriving an emission factor (EF). Instead, the EF was derived as an average across all 17 tested facilties. First, an average emission factor was calculated for each of 17 HWIs with Equation 3-3.

$$EF_{hwi} = \frac{C \times F_v}{I_w} \qquad \text{(Eqn. 3-3)}$$

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).

After developing average emission factors for each HWI, the overall average congener-specific emission factor was derived for all 17 tested HWIs using Equation 3-4.

$$EF_{avgHWI_{n=1-18}} = \sum \left(EF_{HWI_1} + EF_{HWI_2} + EF_{HWI_3} \cdots\cdots EF_{HWI_{18}} \right) \qquad \text{(Eqn. 3-4)}$$

Where:

EF_{HWI} = Average emission factor of 18 tested MWIs, ng/kg

Table 3-6 presents the average emission factors developed for specific congeners, total CDDs/CDFs, and TEQs for operating HWIs. The average congener emission profiles for the 17 HWIs are presented in Figure 3-10. The average TEQ emission factor for the 17 tested HWIs is 3.8-ng TEQ/kg of waste feed (assuming not detected values are zero).

3.2.4. Emission Estimates for Dedicated Hazardous Waste Incinerators

Although emissions data on a relatively high number of dedicated HWIs were available (i.e., 17 of 162 have been tested), the emission factor estimate is assigned a "medium" confidence rating due to uncertainties resulting from:

- *Extreme heterogeneity 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 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 Destruction Rated Efficiency of principal hazardous organic constituents in the waste. During trial burns, a prototype waste is burned, which 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 dedicated HWIs during 1987. The best estimate of the amount of hazardous waste combusted in 1995 is 1.5-million metric tons (Federal Register, 1996b). The activity level estimate for 1995 is assigned a "high" confidence rating, because it is based on a thorough review 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. A confidence rating of "medium" is assigned to the activity level estimate for 1987.

The annual TEQ emissions for the reference years 1995 and 1987 were estimated using Equation 3-5.

$$E_{HWI} = EF_{HWI} \times A_{HWI} \qquad \text{(Eqn. 3-5)}$$

Where:

E_{HWI} = Annual emissions from all HWIs, tested and non-tested (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 emission factor for dedicated HWIs (3.8-ng TEQ/kg waste) to these production estimates yields estimated emissions of 5.7-g TEQ in 1995 and 5.0-g TEQ in 1987 for HWIs. The "medium" confidence rating assigned to the emission factor, combined with the high confidence rating for the 1995 activity level and medium

confidence rating for the 1987 activity level, yields an overall medium confidence rating for both years. Accordingly, the estimated range of annual emissions is assumed to vary by a factor of five between the low and high ends of the range. For 1995, the range of TEQ emissions is estimated to be 2.6- to 12.8-g TEQ/yr. For 1987, the range of TEQ emissions is estimated to be 2.2- to 11.2-g TEQ/yr.

EPA/OSW has also developed estimates of the CDD/CDF emissions from dedicated HWIs as part of the development of the Hazardous Waste Incineration Rule (U.S. EPA, 1997d). Like ORD, OSW also decided not to subdivide the dedicated HWIs on the basis of design. Instead of an emission factor approach, OSW used an imputation method to estimate emissions at untested facilites. This procedure involved randomly selecting measured CDD/CDF flue gas concentrations (ng/dscm) from the pool of tested HWI facilities and assigning them to the untested facilites. With this procedure, all non-tested HWIs have an equal chance of being assigned any flue gas concentration from the pool of measured values. The flue gas concentrations were combined with flue gas flow rates for each facility to estimate the emission rate. A key difference in these approaches is that ORD uses waste feed rate directly in the calculation of emissions and the OSW approach is independent of waste feed rate. Both procedures are reasonable ways to deal with the broad range of uncertainties and both yield similar emission estimates. ORD has not identified any inherent advantage of one approach over the other and elected to use the emission factor approach primarily because it is consistent with the methods used in this document to characterize CDD/CDF emissions from all other source categories.

3.2.5. Industrial Boilers and Furnaces Burning Hazardous Waste

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

The national data base contains congener-specific emission concentrations for two tested boilers burning liquid hazardous waste as supplemental fuel. The average congener

and congener group emission profiles for the industrial boiler data set are presented in Figure 3-11. The average congener and TEQ emission factors are presented in Table 3-6. The limited set of emissions data prevented subdividing this class for the purpose of deriving an emission factor. The equation used to derive the emission factor is the same as Equation 3-4 above. The average TEQ emission factor for the two industrial boilers is 0.64-ng TEQ/kg of waste feed. This emission factor is assigned a "low" confidence rating, because it reflects testing at only 2 of the 136 hazardous waste boilers/furnaces.

Dempsey and Oppelt (1993) estimated that approximately 1.2-billion kg of hazardous waste were combusted in industrial boilers/furnaces in 1987. EPA estimates that in 1995 approximately 0.6-billion kg of hazardous waste were combusted in industrial boilers/furnaces (Federal Register, 1996b). The activity level estimate for 1995 is assigned a "high" confidence rating, because it is based on a thorough review 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 (Federal Register, 1996b). A confidence rating of "medium" is assigned to the estimated activity level for 1987. The 1987 estimate was largely based on a review of State permits (Dempsey and Oppelt,1993).

Equation 3-5, 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 factor of 0.64-ng TEQ/kg of waste feed by the total estimated kg of liquid hazardous waste burned in 1995 and 1987 yields the 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 0.38-g TEQ/yr in 1995 and 0.77-g TEQ/yr in 1987. Because of the low confidence rating for the emission factor, the overall confidence rating is low for both the 1987 and 1995 emission estimates. Accordingly, it is assumed that the uncertainty range around the best estimate varies by a factor of 10 between the low and high ends of the range. Thus, the uncertainty ranges are 0.12- to 1.2-g TEQ/yr for 1995 and 0.24- to 2.4-g TEQ/yr for 1987.

3.3. MEDICAL WASTE INCINERATION

Medical waste incineration (MWI) is the controlled burning of solid wastes generated primarily by hospitals, veterinary, and medical research facilities. The U.S. 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 MWI 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 MWI designs used to incinerate medical waste, review the distribution of APCDs used on MWIs, summarize the derivation of dioxin TEQ emission factors for MWIs, and summarize the national dioxin TEQ emission estimates for reference years 1995 and 1987.

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 percent are modular furnaces using controlled-air, 2 percent are modular furnaces using excess air, and 1 percent 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" or "starved-air." With sub-stoichiometric conditions, combustion occurs at relatively low temperatures (i.e., 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 (i.e., 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 the organic contaminants entrained in the combustion gases emanating from the primary combustion chamber. Combustion air at 100 to 300 percent in excess of stoichiometric requirement is usually added to the secondary chamber. Gases exiting the secondary chamber are directed to an incinerator stack (U.S. EPA, 1997b; U.S. EPA, 1991d; Buonicore, 1992b). Figure 3-12 displays a schematic of a typical modular furnace using controlled-air. Because of their low cost and good combustion performance, this design has been the most popular

choice for MWIs and has accounted for more than 95 percent of systems installed over the past two decades (U.S. EPA, 1990d; U.S. EPA, 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 percent to 300 percent 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 are typically smaller in capacity than controlled-air units and 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.

Rotary Kiln MWI: This technology is similar in terms of design and operational features to the rotary kiln technology 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; U.S. EPA, 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, loaded continuously and frequently with small waste batches, operate less than 24 hours per day, usually on a shift-type basis. Either manual or automated charging systems can be used, but the incinerator must be shut down for ash removal. Continuous incinerators are operated 24 hours per day and use automatic charging systems to charge waste into the unit in small, frequent batches. All continuous incinerators operate using a mechanism to automatically remove the ash from the incinerator (U.S. EPA, 1990d; U.S. EPA, 1991d).

3.3.2. Characterization of MWIs for Reference Years 1995 and 1987

MWI remains a poorly characterized industry in the United States in terms of knowing the exact number of facilities operational over time, the types of APCDs installed on these units, and the aggregate volume and weight of medical waste that is combusted in any given year (U.S. EPA, 1997b). The primary reason for this is that permits were not generally required for the control of pollutant stack emissions from MWIs until the early 1990s when State regulatory agencies began setting limits on emissions of particulate

matter and other contaminants (Federal Register, 1997b). Prior to that timeframe, only opacity was controlled.

The information available to characterize MWIs comes from national telephone surveys, stack emission permits, and data gathered by EPA during public hearings (Federal Register, 1997b). This information suggests the following:

- The number of MWIs in operation was approximately 5,000 in 1987 (U.S. EPA, 1987) and 2,375 in 1995 (Federal Register, 1997b).
- 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 percent. Certain activities caused this to occur, including more stringent air pollution control requirements by State regulatory agencies and the development of less expensive medical waste treatment technologies, such as autoclaving (Federal Register, 1997b). Because many MWIs have small waste charging capacity (i.e., about 50 metric tons per day), the installation of even elementary APCDs proved not to be cost effective. Thus, a large number of facilities elected to close rather than retrofit.

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

EPA estimates that about two-thirds of medical waste burned in MWIs in 1995 went to facilities equipped with some method of air pollution control (Federal Register, 1997b). The types of APCDs installed and the methods used on MWIs include: dry sorbent injection,

fabric filters, electrostatic precipitators (ESPs), wet scrubbers, and fabric filters combined with packed-bed scrubbers (composed of granular activated carbon). Some organic constituents in the flue gases can be adsorbed by the packed bed. Within the uncontrolled class of MWIs, about 12 percent of the waste were combusted in facilities with design capacities of <200 lbs/hr, with the majority of waste burned facilities >200 lb/hr. The estimated breakdown of controlled facilities is: 70 percent of the aggregate activity level are associated with facilities equipped with either wet scrubbers, fabric filters, or ESPs; 29.9 percent are associated with facilities utilizing dry sorbent injection, combined with fabric filters, and less than 1 percent is associated with facilities having the fabric filter/packed-bed APCD (AHA, 1995; Federal Register, 1997b).

3.3.3. Estimation of CDD/CDF Emissions From MWIs

Only 1 percent of existing facilities (i.e., 24 MWIs) has been stack sampled for CDD/CDFs. Consequently, most facilities have unmeasured emission levels of dioxin-like compounds. Because so few have been evaluated, the estimation of annual air emissions of CDD/CDFs from MWIs is quite dependent on extrapolations, engineering judgement, and the use of assumptions. In addition, the information about the activity levels of these facilities is also quite limited. With these data limitations, two approaches have been used in the past to estimate CDD/CDF emissions from MWIs, and a third is proposed here. These three approaches are as follows:

1. **EPA/OAQPS Approach**: EPA's Office of Air Quality Planning and Standards used this approach in support of the promulgation of final air emission standards for hospital/medical/infectious waste incinerators (Federal Register, 1997b).

2. **AHA Approach**: The American Hospital Association proposed an approach in its comments on drafts of this document and on the proposed MWI emissions regulations (AHA, 1995).

3. **EPA/ORD Approach**: In preparation of this document, EPA's Office of Research and Development (ORD) has developed a third approach.

Given the limitations with existing information, both the EPA/OAQPS and AHA approaches are reasonable methods for calculating annual releases of CDD/CDFs from MWIs. Both methods relied heavily on a series of assumptions to account for missing information. In developing a third approach, EPA/ORD built upon the other two approaches by utilizing the

most logical features of each. Because of the uncertainties with 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 four. As discussed below, the EPA/ORD approach used the strengths of the other two approaches, and represents some improvement in estimating CDD/CDF emissions.

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

On September 15, 1997, EPA promulgated final standards of performance for new and existing MWIs under the Clean Air Act Amendments (Federal Register, 1997b). CDD/CDF stack emission limits for existing MWIs were established as follows: 125 ng/dscm of total CDD/CDF (at 7 percent O_2, 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. *EPA/OAQPS Approach for Estimating Activity Level*

As a starting point for deriving the 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 American Hospital Association (AHA, 1995), supplemented with additional information compiled by EPA. This created a listing of 2,375 MWIs in the United States. Next a series of assumptions were used to derive activity level estimates, as follows:

1. The analysis divided MWIs into three design types based on the mode of daily operation: batch, intermittent, and 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 three to one.

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

3-7 is a summary of the OAQPS estimated annual operating hours per MWI design type.

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

Based on information obtained from AHA and State regulatory agencies, one-third of the population of MWIs operating in 1995 was etimated to have had no APCDs (i.e., were uncontrolled), and two-thirds had some type of APCD. CDD/CDF TEQ emission factors were then developed for uncontrolled and controlled MWIs. The procedure was as follows:

Estimating TEQ Emission Factors for Uncontrolled Facilities: The uncontrolled category of facilities was subdivided by residence time of the secondary combustion chamber. Based on tests at three MWIs, OAQPS concluded that stack emissions of CDD/CDFs from uncontrolled facilities were dependent on the residence time (i.e., the duration 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 (i.e., < 1 sec), the stack emissions of CDDC/CDFs would increase; conversely, the longer the residence time (i.e., > 1 sec), the CDD/CDF emissions decrease. The emissions testing at these MWIs provided the basis for the derivation of CDD/CDF TEQ emission factors for residence times of 1/4-sec, 1-sec and 2-sec. Table 3-8 is a summary of 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 approximately corresponds with the particulate matter (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 3-8 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 a TEQ 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 previously discussed, APCDs typically used by MWIs consist of one or more of the following: wet scrubber, dry scrubber,

and fabric filter combined with a packed bed. The EPA/OAQPS approach also included the addition of activated carbon to the flue gases as a means of emissions control (i.e., dry scrubbers combined with carbon injection). TEQ emission factors were developed for these control systems based on 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 3-9.

3.3.4.3. *EPA/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 Equation 3-6.

$$Em_{mwi} = (C \times H \times C_1) \times F_{TEQ} \qquad \text{(Eqn. 3-6)}$$

Where:

Em_{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 of the individual MWIs. The following equation is applied to estimate annual TEQ emissions from all MWIs.

$$Em_{mwi}(nationwide) = \sum (Em_{mwi_1}) + (Em_{mwi_2}) + \ldots\ldots (Em_{mwi_{2375}}) \qquad \text{(Eqn. 3-7)}$$

Where:

Em_{mwi}(nationwide) = Nationwide MWI TEQ emissions (g/yr)

Table 3-9 is a summary of annual CDD/CDF TEQ emissions for 1995 estimated using the EPA/OAQPS Approach.

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

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

From a national telephone survey of member hospitals conducted between September and November 1994, the AHA developed what is generally considered as the first attempt to systematically inventory MWIs in the United States. Approximately 6 percent 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 (1995) then developed CDD/CDF emission factors for each category of MWIs. Test reports of 19 MWIs were collected and evaluated. Average CDD/CDF TEQ flue gas concentrations (i.e., ng/dscm @7 percent O_2) 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/10^6 lbs of medical waste incinerated (equation for conversion not given). Table 3-10 is a summary of TEQ emission factors calculated by Doucet (1995) for each level of assumed APCDs on MWIs.

Similar to the EPA/OAQPS Approach (Section 3.3.4), the distribution of the APCD categories was derived by assuming that State particulate emission (PM) limits would indicate the APCD on any individual MWI (Doucet, 1995). Table 3-11 displays the AHA assumptions of air pollution control (APC) utilized on MWIs based upon 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 TEQ emissions (g/yr) from MWIs,

nationwide. Although no equation is given, it is presumed that the emissions were estimated by multiplying the activity level for each MWI size and APCD category by the associated TEQ emission factor. The sum of these calculations for each designated class yields the estimated annual TEQ emissions for all MWIs, nationwide. Doucet (1995) indicates that these computations are appropriate for TEQ emissions in 1995. Table 3-12 summarizes the nationwide annual TEQ emissions from MWIs using the AHA Approach.

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

Because of limitations in emissions data and on activity levels, the EPA/ORD approach used many of the logical assumptions developed in the EPA/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. *EPA/ORD Approach for Classifying MWIs and Estimating Activity Levels*

As with the EPA/OAQPS and AHA approaches, the EPA/ORD approach divided the MWIs into controlled and uncontrolled classes. The decisions about further dividing these two classes are described below:

Uncontrolled MWIs: For purposes of assigning CDD/CDF emission factors and activity levels to the uncontrolled class of MWIs, the EPA/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 CDD/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 EPA/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 percent of the waste incinerated at MWIs with 1/4-sec residence time; 26 percent of the waste incinerated at MWIs with 1-sec residence time; and 68 percent of the waste incinerated at MWIs with 2-sec residence time. Thus, about two-thirds of the activity level within the uncontrolled class were assumed in the EPA/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 (i.e., <200 lb/hr) are likely to have higher emissions, because they are more likely to be operating in a batch mode. The batch mode results in infrequent operation with more start-up and shut-down cycles. Thus, the batch-operated MWI usually spends more time outside of the ideal range of operating conditions. In support of this approach, the AHA presented limited empirical evidence indicating that CDD/CDF emission factors calculated from emission test reports for the low capacity units were about a factor of two higher than the emission factors for the high capacity units (Doucet, 1995).

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

Next, the available emission testing data for small and high capacity units (i.e., less than and greater than 200 lb/hr) were evaluated to determine if, as posited in the AHA approach, smaller capacity units have greater emission factors than large capacity units. This evaluation indicated a distinct difference in the emission factors between the two capacity categories, although the difference in the set of data evaluated was not as great as the difference observed in the data set evaluated in the AHA approach. The EPA/ORD approach, therefore, adopted the subcategorization scheme used in the AHA approach.

Controlled MWIs: Both the EPA/OAQPS approach and the AHA approach subcategorized the controlled MWIs on the basis of APCD equipment. However, the two approaches differed in the subcategories developed. The AHA approach divided the controlled class into two groups: facilities equipped with wet scrubbers (alone, with an ESP, or with a fabric filter), and facilities equipped with dry sorbent injector and a fabric filter (Doucet, 1995). The EPA/OAQPS approach divided the controlled class into three groups: facilities equipped with wet scrubbers, facilities equipped with dry scrubbers (with or without carbon injection), and facilities equipped with fabric filters and packed bed

scrubbers. This third category is comprised of a few facilities primarily located in the Northeast United States (O'Rourke, 1996). The EPA/ORD approach adopted the two subcategories of the AHA approach and the third subcategory of the EPA/OAQPS approach. For 1995, ORD used the activity levels for each facility as determined by the EPA/OAQPS inventory; the activity levels were then summed across facilities for each APCD subclass.

For 1987, the EPA/ORD approach assumed that every MWI was uncontrolled on the basis of a EPA study of MWI incineration conducted at that time (U.S. EPA, 1987d). This study indicates 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. The activity level estimates were derived from additional EPA studies (U.S. EPA, 1987d). This approach resulted in the following activity level assumptions for 1987: (a) 15 percent of the activity level (i.e., 0.2-billion kg medical waste) were incinerated/yr by MWIs with capacities less than or equal to 200 lb/hr, and (b) 85 percent of the activity level (i.e., 1-billion kg/yr) were incinerated by facilities with capacities greater than 200 lb/hr.

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

EPA/ORD collected the engineering reports of 24 tested MWIs. After reviewing these test reports, 19 met the criteria for acceptability. (See Section 3.1.3 for further details on the criteria.) 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.

The EPA stack testing method (EPA Method 23) produces a measurement of CDD/CDFs in units of mass concentration (i.e., nanograms per dry standard cubic meter of combustion gas (ng/dscm)) at standard temperature and pressure and one atmosphere and adjusted to a measurement of 7 percent 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 MWIs was calculated using the following equation:

$$EF_{mwi} = \frac{C \ x \ F_v}{I_w} \qquad \text{(Eqn. 3-8)}$$

Where:

EF_{mwi} = Emission Factor per MWI (average ng TEQ per kg of medical waste burned).

C = Average TEQ concentration in flue gases of tested MWIs (ng TEQ/dscm) (20°C, 1 atm; adjusted to 7% O_2).

F_v = Average volumetric flue gas flow rate (dscm/hr) (20°C, 1 atm; adjusted to 7% O_2).

I_w = Average medical waste incineration rate of the tested MWI (kg/hr).

The emission factor estimate for each design class and the number of stack tests used to derive it are shown in Table 3-14. Figures 3-12 and 3-13 present congener and congener group profiles for air emissions from MWIs lacking APCDs and for MWIs equipped with a wet scrubber/baghouse/fabric filter APCD system, respectively.

3.3.7. Summary of CDD/CDF Emissions From MWIs

Because the stack emissions from so few facilities have been tested (i.e., 19 test reports) relative to the number of facilities in this industry (i.e., 2,375 facilities in 1995 and 5,000 facilities in 1987) and because several tested facilities are no longer in operation or have installed new APCD after testing, the EPA/ORD approach did not calculate nationwide CDD/CDF emissions by calculating emissions from the tested facilities and adding those to calculated emissions for the non-tested facilities. Rather, the EPA/ORD approach (as well as the EPA/OAQPS and AHA approaches) calculated nationwide CDD/CDF emissions by multiplying the emission factor and activity level developed for each design class and then summing the calculated emissions for all classes. Tables 3-14 and 3-15 summarize the resulting national TEQ air emissions for the reference years 1995 and 1987, respectively. In addition, the Tables indicate the activity level and the TEQ emission factor used in estimating annual TEQ emissions.

In estimating annual TEQ emissions in both reference years, a "low" confidence rating was assigned to the estimate of the activity level. The primary reason for the low confidence rating is that very limited information is available on a facility level basis for characterizing MWIs in terms of the frequency and duration of operation, the actual waste

volume handled, and the level of pollution control. The 1987 inventory of facilities was based on very limited information. Although the 1995 EPA/OAQPS inventory was more comprehensive than the 1987 inventory, it was still based on a fairly limited survey of operating facilities (i.e., approximately 6 percent).

The emission factor estimates were given a "low" confidence rating, because only the reports of 19 tested MWI facilities could be used to derive emissions factors representing the 2,375 facilities operating in 1995 (i.e., less than 1 percent of estimated number of operating facilities). Even fewer tested facilities could be used to represent the larger number of facilities operating in 1987 (i.e., 8 tested facilities were used to represent 5,000 facilities). The limited emission tests available do cover all design categories used here to develop emission factors. However, because of the large number of facilities in each of these classes, it is very uncertain whether the few tested facilities in each class capture the true variability in emissions.

- **Reference Year 1995:** Based on the low confidence ratings for both the activity level and the emission factor, the estimated range of potential annual TEQ emissions from MWIs in 1995 is assumed to vary by a factor of 10 (between the low and high ends of the range). From Table 3-14, the central estimate of TEQ emissions in 1995 is estimated to be 477 g/yr, with a range of 151 to 1,510 g TEQ/yr.

- **Reference Year 1987:** Based on the low confidence ratings for both the activity level and the emission factor, the estimated range of potential annual TEQ emissions from MWIs in 1987 is assumed to vary by a factor of 10 (between the low and high ends of the range). From Table 3-15, the central estimate of TEQ emissions in 1987 is estimated to be 2,470 g/yr, with a range of 781- to 7,810-g TEQ/yr.

As explained above, the EPA/ORD approach to estimating national CDD/CDF TEQ emissions is a 'hybridization' of the EPA/OAQPS and AHA approaches. Table 3-16 compares the main features of each of the three approaches. The 1995 TEQ emissions estimated here (477-g TEQ/yr) are about 3.5 times higher than those of OAQPS and AHA (141- and 138-g TEQ/y, respectively). Most of this difference is due to differences in the emission estimates for the uncontrolled facilities (ORD - 436-g TEQ/yr, OAQPS - 136-g

TEQ/yr, AHA - 120-g TEQ/yr). An analysis of the differences in how these groups estimated emissions from the uncontrolled facilities are presented below:

- **Differences between the EPA/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 use similar emission factors for facilities with design capacities less than or equal to 200 lbs/h, but the emission factor for MWIs > 200 lbs/hr used in the EPA/ORD approach was higher than that used in the AHA approach by a factor of three. This results from the fact that the two approaches used different sets of emission tests to derive their emission factors.

- **Differences between the EPA/ORD and EPA/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 EPA/OAQPS approach assigned 68 percent of the total activity to the class with the lowest emission factor (i.e., those with >2-sec residence time). The emission factor for this class, 74-ng TEQ/kg, is considerably lower than either emission factor used in the EPA/ORD approach (1,700- and 1,860-ng TEQ/kg).

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

Regardless of the approach taken to estimate what the CDD/CDF emissions from 2,375 MWIs were in 1995, the National Emission Standards promulgated by EPA in September 1997 (Federal Register, 1997b) require substantial reductions of CDD/CDF air

emissions from MWIs. As a result of these standards, MWI emissions will be thoroughly assessed for purposes of compliance with the CDD/CDF standard. Compliance testing will allow the development of a more comprehensive emissions data base and more accurate characterization of this industry.

3.4. CREMATORIA

Bremmer et al. (1994) categorized crematoria into two basic operating types: a "cold" type and a "warm" type. In the "cold" type furnaces, the coffin is placed inside at a temperature of about 300°C. Using a burner, the temperature of the chamber is increased to 800-900°C and kept at that temperature for 2 to 2.5 hours. In the "warm" type furnace, the coffin is placed in a chamber preheated to 800°C or higher for 1.2 to 1.5 hours. The chamber exhausts from both furnace types are incinerated in an after burner at a temperature of about 850°C. Flue gases are then discharged to the atmosphere either: (a) directly without cooling; (b) after mixing with ambient air using an air blast to a temperature of about 200-350°C; or (c) after mixing with ambient air as in "b," followed by further cooling to about 150°C in an air cooler and passage through a fabric filter.

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 2.4-μg TEQ per body. The second furnace, a warm type with cooling of flue gases to 220°C prior to discharge, was calculated to yield 4.9-μg TEQ per body. The higher emission rate for the warm-type furnace was attributed by Bremmer et al. (1994) to the formation of CDD/CDF 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-μg TEQ per body for a crematorium in Berlin, Germany. No operating process information was provided by Bremmer et al. (1994) for the facility.

In the United States, CDD/CDF emissions were measured at one crematorium (CARB, 1990c) classified as a warm-type facility using the criteria of Bremmer et al. (1994). The combusted material at this facility was comprised of the body, as well as 4 pounds of cardboard, up to 6 pounds of wood, and an unquantified amount of unspecified plastic wrapping. The three emission tests conducted at this facility yielded an average emission factor of 0.5-μg TEQ/body. Although this emission factor is very similar to the emission factors reported by Bremmer et al. (1994), a "low" confidence rating is assigned to the factor, because it represents testing at only one U.S. facility. Table 3-17 presents

the congener-specific emission factors for this facility. Figure 3-14 presents CDD/CDF congener and congener group emission profiles based on these emission factors.

In 1995, 1,155 crematories were reported in the United States (Springer, 1997). However, there are no readily available data on the number of "cold" versus "warm" crematoria furnaces. In 1995, 21.1 percent of the deceased bodies were cremated (i.e., 488,224 cremations), and 15.2 percent of the deceased were cremated in 1987 (i.e., 323,371 cremations) (Springer, 1997). Cremations are projected to increase to 25 percent in the year 2000 and 37 percent in the year 2010 (Springer, 1997). A high confidence rating is assigned to these activity level estimates, because they are based on recent data provided by the Crematoria Association of North America.

Combining the emission rate of 0.5-μg TEQ/body with the number of cremations in 1995 (488,224) yields an estimated annual release of 0.24-g TEQ per year. Based on the low confidence rating assigned to the emission factor of 0.5-μg TEQ/body, the estimated range of potential emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the best estimate of annual emissions (0.24-g TEQ/yr) is the geometric mean of this range, then the range is calculated to be 0.07- to 0.75-g TEQ/yr. Combining the emission rate of 0.5-μg TEQ/body with the number of cremations in 1987 (323,371) yields an estimated release of 0.16-g (range 0.05- to 0.51-g TEQ/yr).

3.5. SEWAGE SLUDGE INCINERATION

The three principal combustion technologies used to incinerate sewage sludge in the United States are the multiple-hearth incinerator, fluidized-bed incinerator, and the electric furnace (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). Over 80 percent of operating sludge incinerators are multiple-hearth design. About 15 percent are fluidized-bed incinerators, and 3 percent are electric incinerators. Other types of technologies not widely used in the United States are single-hearth cyclones, rotary kilns, and high-pressure wet-air oxidation (U.S. EPA, 1997b).

Multiple-hearth Incinerator: This consists 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 the furnace. Moisture is evaporated from the sludge cake in the upper hearths of the furnace. The center hearths are the burning zone, where gas temperatures reach 871°C. The

bottom hearths are the burn-out zone, where the sludge solids become ash. A waste-heat boiler is usually included in the burning zone, where steam is produced to provide supplemental energy at the sewage treatment plant. Air pollution control measures typically include a venturi scrubber, an impingement tray scrubber, or a combination of both. Wet cyclones and dry cyclones are also used (U.S. EPA, 1995b).

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

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

EPA measured CDD/CDF emissions at two multiple-hearth incinerators and one fluidized-bed incinerator as part of Tier 4 of the National Dioxin Survey (U.S. EPA, 1987a). The results of these tests include congener group concentrations in stack gas, but lack measurement results for specific congeners other than 2,3,7,8-TCDD and 2,3,7,8-TCDF. In 1995, the Association of Metropolitan Sewerage Agencies (AMSA) submitted to EPA the results of stack tests conducted at an additional 15 sewage sludge incinerators (Green et al., 1995). Two of these data sets were considered not useable by EPA, because either detection limits or feed rates and stack flow were not provided. The average congener and congener group emission factors are presented in Table 3-18 for the three facilities from U.S. EPA (1987a) and the 13 AMSA facilities from Green et al. (1995). A wide variability was observed in the emission factors for the tested facilities. The total CDD/CDF emission

factor for the three U.S. EPA (1987a) facilities ranged from 90 to 3,400 ng/kg. For the 13 facilities reported in Green et al. (1995), a similarly large variability in emission factors was observed. Figure 3-15 presents the average congener and congener group profiles based on these data.

The average TEQ emission factor based on the data for the 13 AMSA facilities is 6.94-ng TEQ/kg of dry sludge combusted, assuming nondetected values are 0 and 7.19-ng TEQ/kg of dry sludge, assuming nondetected values are present at one-half the detection limit. Other countries have reported similar results. Bremmer et al. (1994) reported an emission rate of 5-ng TEQ/kg for a fluidized-bed sewage sludge incinerator, equipped with a cyclone and wet scrubber, in The Netherlands. Cains and Dyke (1994) measured CDD/CDF emissions at two sewage sludge incinerators in the United Kingdom. The emission rate at an incinerator equipped with an electrostatic precipitator and wet scrubber ranged from 2.75-ng TEQ/kg to 28.0-ng TEQ/kg. The emission rate measured at a facility equipped with only an electrostatic precipitator was 43.0-ng TEQ/kg.

In 1992, approximately 199 sewage sludge incineration facilities combusted about 0.865-million metric tons of dry sewage sludge (Federal Register, 1993b). No comparable data are available for the 1987 and 1995 reference time periods. For purposes of this report, it is assumed that 0.865-million metric tons of dry sewage sludge were incinerated during the two time periods. Given this mass of sewage sludge incinerated/yr, the estimate of TEQ emissions to air is 6.0-g TEQ per year, using the average AMSA TEQ emission factor of 6.94-ng TEQ/kg.

A "medium" confidence rating is assigned to the average TEQ emission factor for the AMSA facilities (6.94-ng TEQ/kg), because it was derived from stack testing at 13 sewage sludge incinerators. The activity level estimate is assigned a "high" confidence rating, because it is based on an extensive EPA survey to support rulemaking activities. Based on these confidence ratings, the estimated range of potential annual emissions is assumed to vary by a factor of five between the low and high ends of the range. Assuming that the estimate of annual emissions (6.0-g TEQ/yr) is the geometric mean of this range, then the range is calculated to be 2.7- to 13.4-g TEQ/yr.

3.6. TIRE COMBUSTION

Emissions of dioxin-like compounds from the incineration of automobile tires were measured from a tire incinerator stack tested by the State of California Air Resources Board

(CARB, 1991a). The facility consists of two excess air furnaces equipped with steam boilers to recovery the energy from the heat of combustion. Discarded whole tires were fed to the incineration units at rates ranging from 2,800 to 5,700 kg/hr during the 3 test days. The furnaces are equipped to burn natural gas as auxiliary fuel. The steam produced from the boilers is used to drive electrical turbine generators that produce 14.4 megawatts of electricity. The facility is equipped with a dry acid gas scrubber and fabric filter for the control of emissions prior to exiting the stack.

Emission factors for CDD/CDF and TEQ in units of ng/kg of tires combusted were derived as average values from the one facility stack tested in California (CARB, 1991a). Table 3-19 presents the congener-specific emission factors for this facility. Figure 3-16 presents CDD/CDF congener and congener group profiles based on these emission factors. From these data, the average emission factor is estimated to be 0.282-ng TEQ/kg of tires incinerated when all not detected values are treated as zero. Cains and Dyke (1994) reported much higher emission rates for two tire incinerators equipped only with simple grit arrestors in the United Kingdom, 188- and 228-ng TEQ/kg of combusted tire.

EPA estimated that approximately 0.50 million metric tons of tires were incinerated in 1990 in the United States (U.S. EPA, 1992a). This activity level estimate is given a "medium" confidence rating, because it is based on both published data and professional judgement. The use of scrap tires as a fuel was reported to have increased significantly during the late 1980s; however, no quantitative estimates were provided in U.S. EPA (1992a) for this period. In 1990, 10.7 percent of the 242-million scrap tires generated were burned for fuel. This percentage is expected to continue to increase (U.S. EPA, 1992a). Of the tires burned for energy recovery purposes, approximately 46 percent were utilized by pulp and paper facilities, 23 percent were utilized by cement kilns, and 19 percent were utilized by one tire-to-energy facility (U.S. EPA, 1995c).

If it is assumed that 500-million kilograms of discarded tires are incinerated annually in the United States, then, using the emission factors derived from stack data from the one tested facility, an average of 0.14 grams of TEQ per year are estimated to be emitted to the air. It must be noted that these may be underestimates of emissions from this source category, because the one facility tested in California is equipped with a dry scrubber combined with a fabric filter for air pollution control. These devices are capable of greater than 95 percent reduction and control of dioxin-like compounds prior to discharge from the stack. It is not know to what extent other tire incineration facilities operating in the U.S.

are similarly controlled. If such facilities are not so equipped, then the uncontrolled emission of CDD/CDF and TEQ could be much greater than the estimates developed above. Therefore, the estimated emission factor of dioxin from tire incineration is given a "low" confidence rating. Based on these confidence ratings, the estimated range of potential annual emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the best estimate of annual emissions (0.14-g TEQ/yr) is the geometric mean of this range, then the range is calculated to be 0.04- to 0.45-g TEQ/yr.

3.7. COMBUSTION OF WASTEWATER SLUDGE AT BLEACHED CHEMICAL PULP MILLS

Approximately 20.5 percent of the wastewater sludges generated at bleached chemical pulp mills are dewatered and burned in the facilities' bark burners. These sludges can contain CDD/CDFs and fairly significant levels of chloride. However, the level of heat input from sludge in the mixed feed rarely exceeds 10 percent in most bark boilers (NCASI, 1995).

NCASI (1995) provided congener-specific test results for four wood residue/sludge boilers tested between 1987 to 1993. The congener-specific emission factors derived from the stack test results obtained from one of these facilities (a spreader stoker equipped with an ESP) are presented in Table 3-20. During testing, the sludge feed rate averaged 3.2 tons per hour, and the feed rate for wood residue averaged 30.3 tons per hour. The average TEQ emission factors derived from the test results are 0.001 ng/kg of feed (i.e., sludge and wood residue), assuming nondetected values are 0 and 0.005 ng/kg of feed, assuming nondetected values are present at one-half the detection limit. The average TEQ concentration in the stack gas reported for this facility by NCASI (1995) was 1.4E-04 ng/dscsm (at 12 percent CO_2). The results of testing of stack emissions at the other three boilers burning sludge, wood residue, and coal were reported by NCASI (1995) to have significantly higher (i.e., factors of 41 to 207 times greater) average TEQ concentrations in the stack gases. However, reliable emission factors for these facilities could not be derived, because stack gas flow rates and sludge feed rates were not available.

NCASI (1995) also presented stack emission test results for five other bark boilers, at least one of which normally fires bark in combination with sludge and coal. Although stack gas flow rates were obtained during these tests, accurate measurements of the amounts of bark/wood fired were not measured and thus had to be estimated by NCASI (1995). The average congener and congener group emission factors derived from the test

results at these facilities are also presented in Table 3-20. Figure 3-17 presents the congener and congener group profiles based on these data. The average TEQ emission factor for these facilities is 0.4 ng/kg of feed or 80 to 400 times greater than the emission factor derived for the sole facility burning sludge and wood for which complete test results and operating parameters are available. This average TEQ emission factor is very similar to the average emission factor for industrial wood combustion derived in Section 4.2.2 of this report from testing by the California Air Resources Board of four industrial wood combustors (0.82 ng/kg of feed).

The available emissions test results for combustion of bleached Kraft mill wastewater sludge are not adequate to enable derivation of CDD/CDF emission factors specific to these bark/sludge combustors. However, the emissions test data presented in NCASI (1995), and discussed above, indicate that the CDD/CDF emission factors for bark/sludge combustors are similar to the emission factor developed in Section 4.2.2 for industrial facilities burning only wood residues/scrap. Thus, based on this conclusion about the applicability of the industrial wood combustor emission factor, and the fact that wood residues comprise a far greater fraction of the feed to these burners than does sludge, the national TEQ emission estimates derived in Section 4.2.2 of this report for industrial wood burning facilities are assumed to include emissions from these bark/sludge combustion units.

3.8. BIOGAS COMBUSTION

Schreiner et al. (1992) measured the CDD/CDF content of a flare combusting exhaust gases from an anaerobic sewage sludge digestor in Germany. The CDD/CDF content at the bottom of the flare was 1.4-pg TEQ/Nm^3, 3.3. pg TEQ/Nm^3 at the top of the flare, and 13.1 pg TEQ/Nm^3 in the middle of the flare. Congener-specific results were not reported. Using the theoretical ratio of flare gas volume to digestor gas volume combusted, 78.6:1, and the average CDD/CDF content of the three measurements, 5.9-pg TEQ/Nm^3, an emission rate of 0.46-ng TEQ/Nm^3 of digestor gas combusted is yielded.

During 1996, POTWs in the United States treated approximately 122-billion liters 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 percent of the total sludge generated (i.e., the sludge generated from treatment of about 30-trillion liters per day of wastewater).

An estimated 196 kg of sludge solids are generated for every million liters of wastewater subjected to primary and secondary treatment (Water Pollution Control Federation, 1990). Thus, multiplying 30-billion liters per day (i.e., 25 percent of 122-billion liters) by 196 kg/million liters and 365 days/yr yields an annual estimate of 2-million metric tons of sludge solids that may be anaerobically digested in POTWs annually.

The volume of sludge digestor gas combusted in flares annually can be estimated using operation parameters for a "typical" anaerobic digestor system as described in Water Pollution Control Federation (1990). Multiplying the annual amount of sludge solids of 2-million metric tons by the following parameters and appropriate conversion factors yields an annual flared digestor gas volume of 467-million Nm^3:

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

Because there are no direct measurements of CDD/CDF emissions from U.S. anerobic sludge digestor flares and because of uncertainties about the activity level for biogas combustion, no national emission estimate has been developed for inclusion in the national inventory. However, a preliminary order of magnitude estimate of the potential annual TEQ emissions from this source can be obtained by multiplying the emission factor of 0.46-ng TEQ/Nm^3 of digestor gas flared by the estimated volume of gas flared annually in the United States, 467-million Nm^3. This calculation yields an annual potential release of 0.22 grams, which, when rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, results in a value of 0.1-g TEQ/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

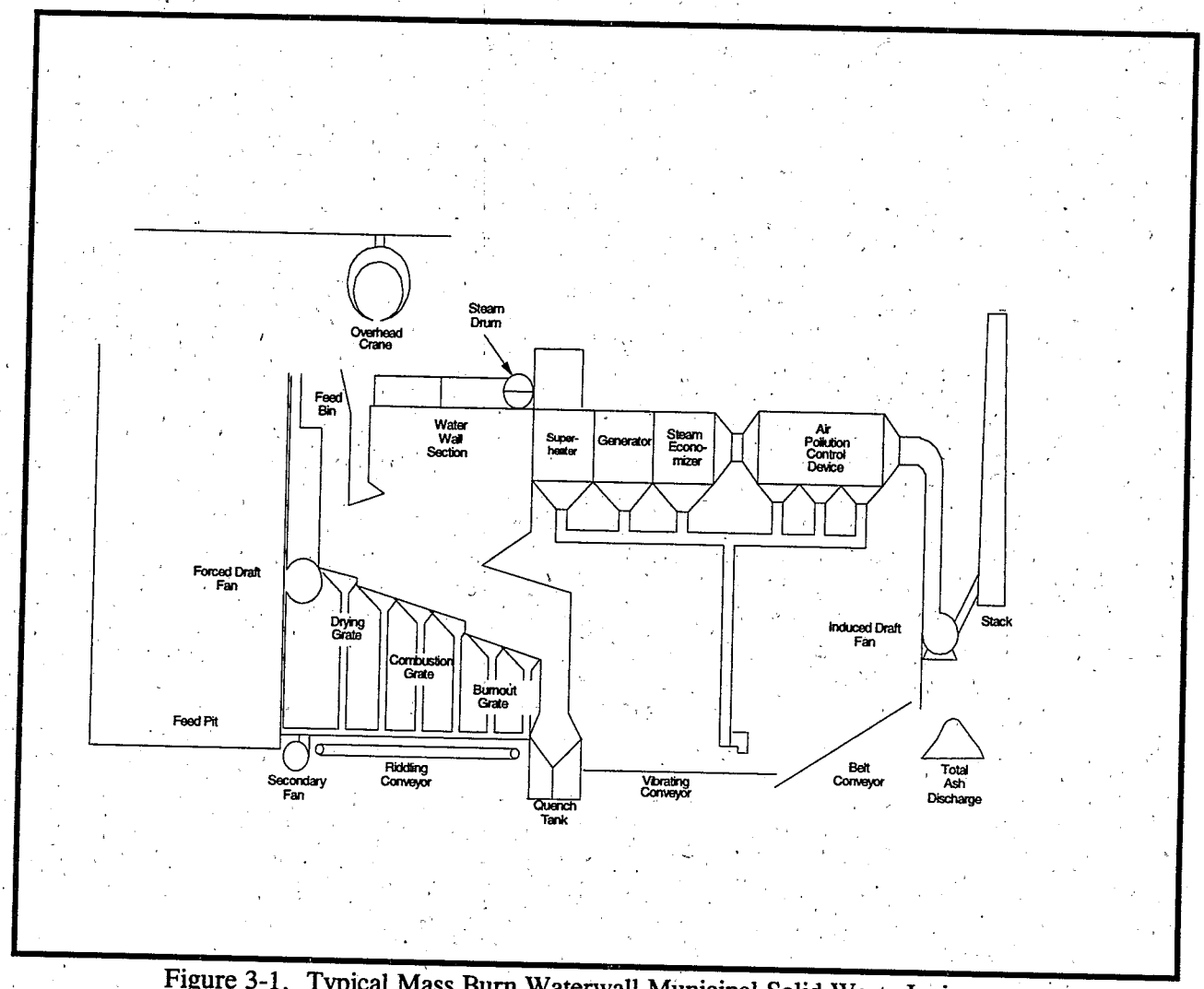


Figure 3-1. Typical Mass Burn Waterwall Municipal Solid Waste Incinerator

Source: U.S. EPA (1997b)

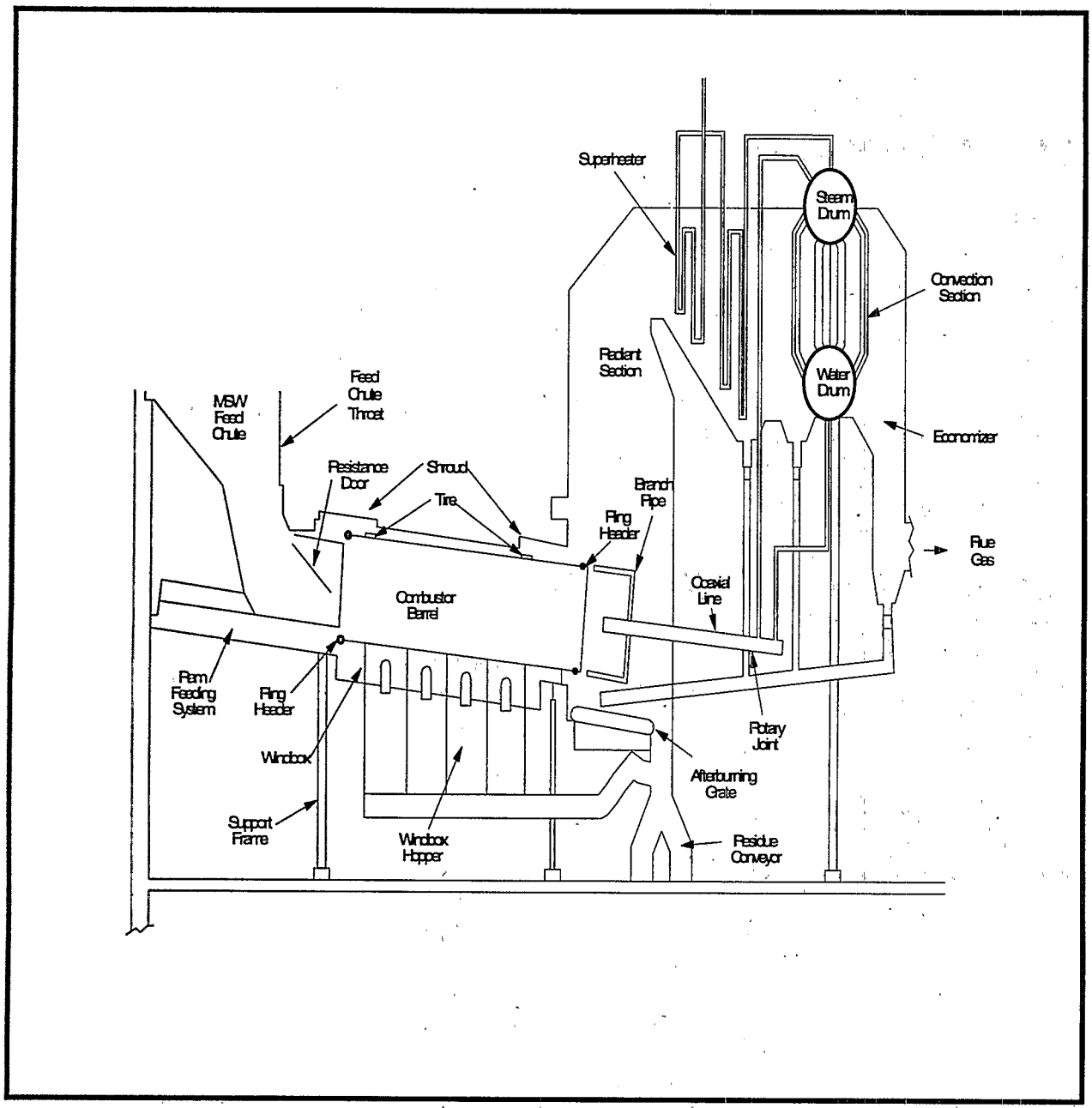


Figure 3-2. Typical Mass Burn Rotary Kiln Combustor

Source: U.S. EPA (1997b)

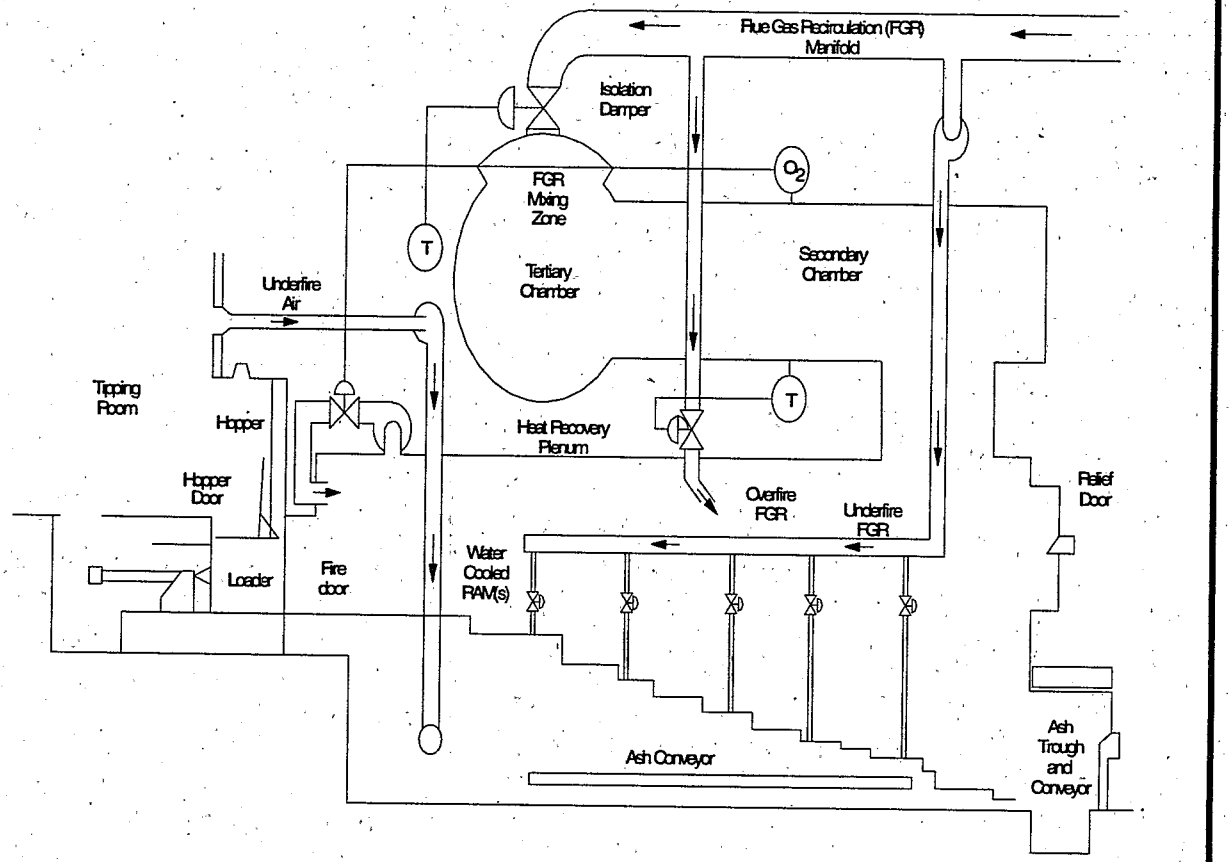


Figure 3-3. Typical Modular Excess-Air Combustor
Source: U.S. EPA (1997b)

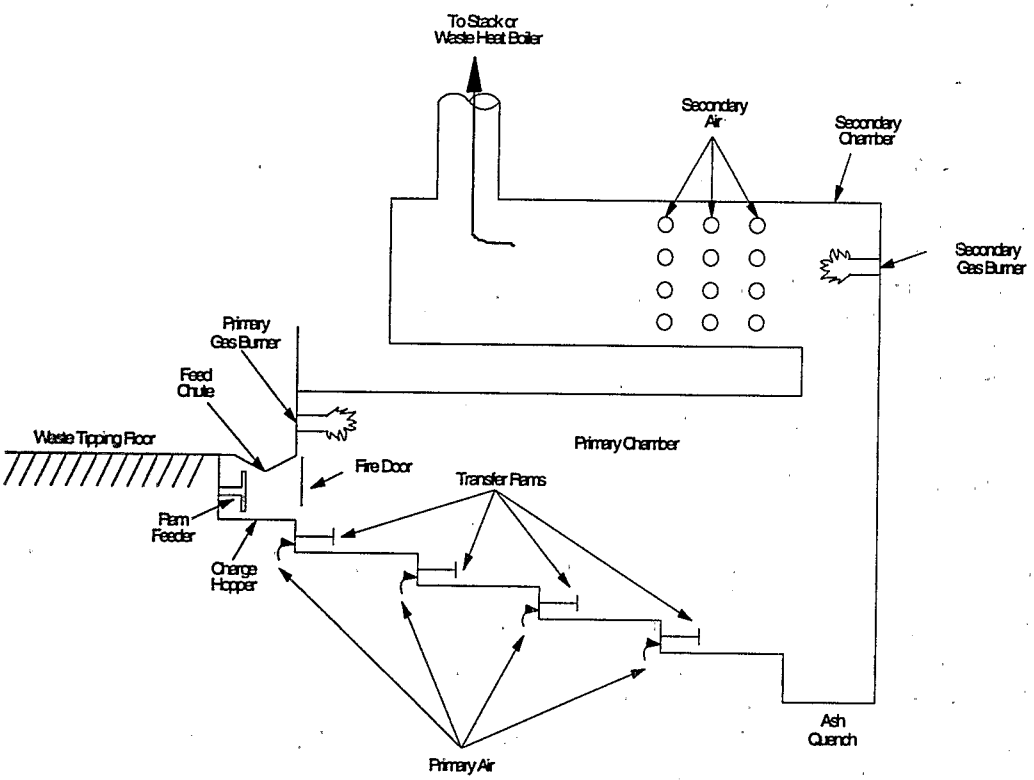


Figure 3-4. Typical Modular Starved-Air Combustor with Transfer Rams
Source: U.S. EPA (1997b)

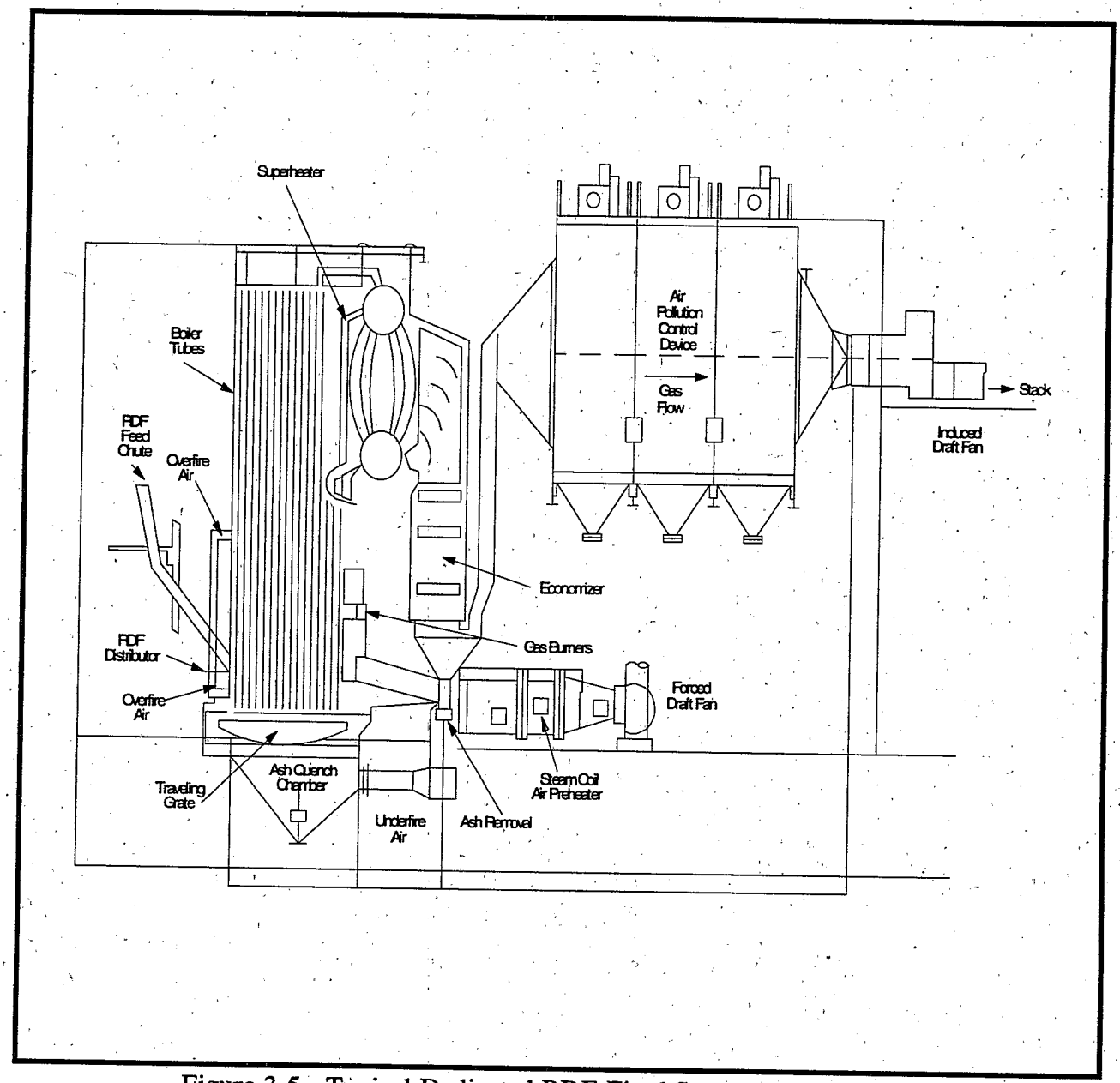


Figure 3-5. Typical Dedicated RDF-Fired Spreader Stoker Boiler
Source: U.S. EPA (1997b)

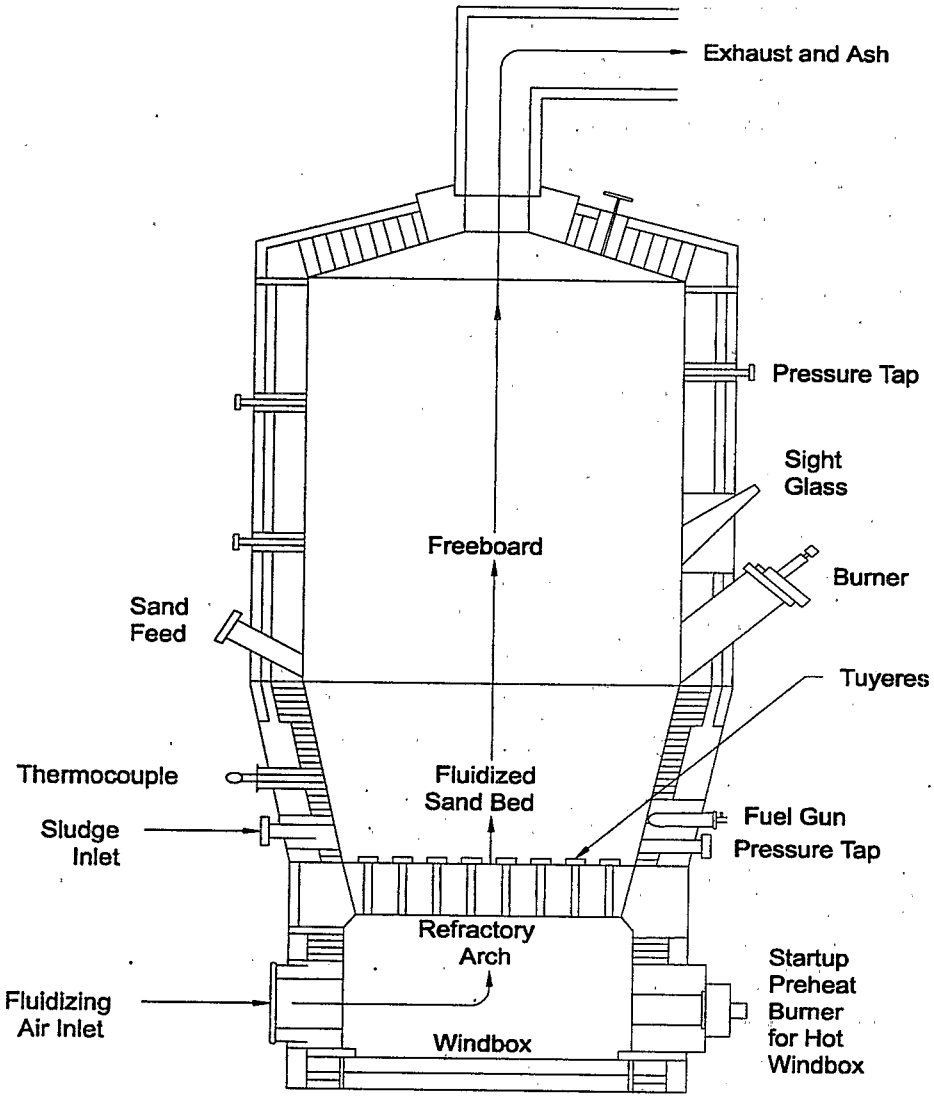
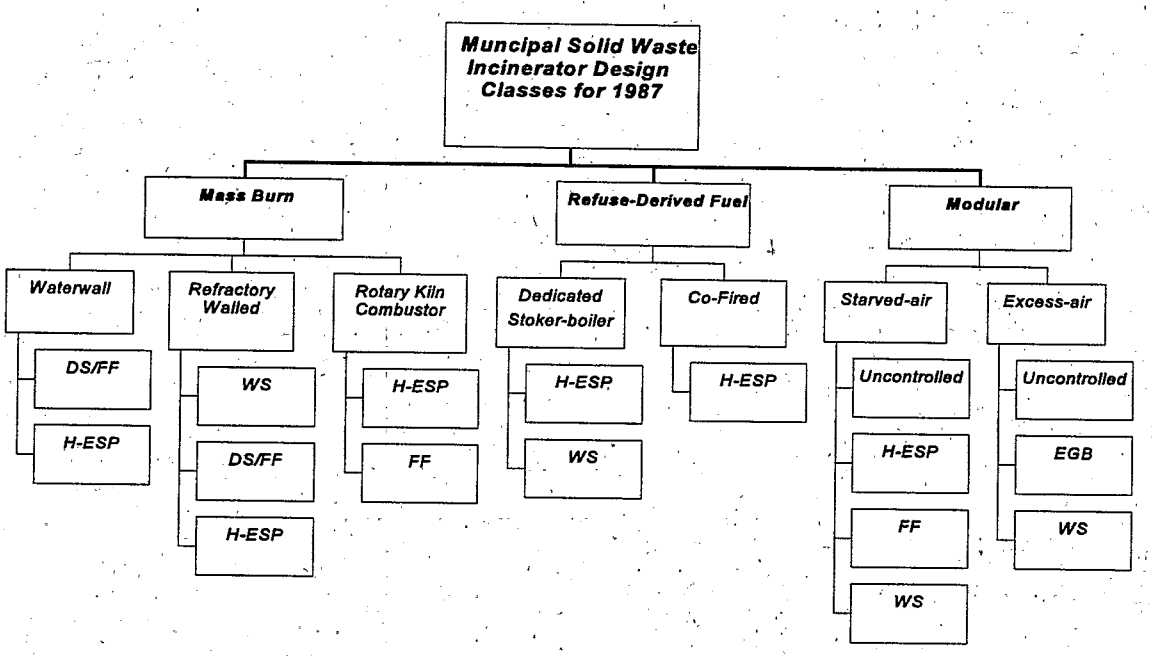
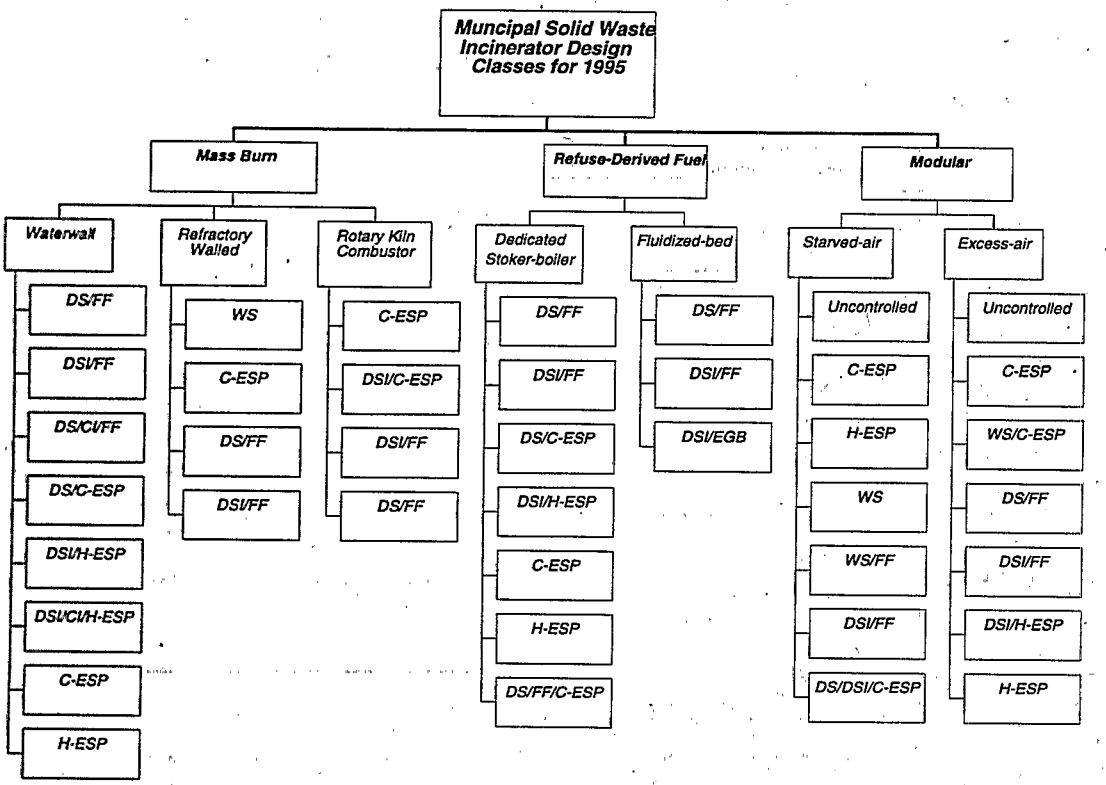


Figure 3-6. Fluidized-Bed RDF Incinerator
Source: U.S. EPA (1997b)



Key: DS/FF = Dry Scrubber combined with a Fabric Filter
H-ESP = Hot-side Electrostatic Precipitator (Temperature at control device is ≥230°C)
WS = Wet Scrubber
UNC = Uncontrolled (no APCD)
EGB = Electro Granular Activated Carbon Bed
FF = Fabric Filter

Figure 3-7. MSWI Design Classes for 1987



Key: DS/FF = Dry Scrubber combined with a Fabric Filter
DSI/FF = Dry Sorbent Injection coupled with a Fabric Filter
DS/CI/FF = Dry Scrubber -Carbon Injection-Fabric Filter
C-ESP = Cold-side Electrostatic Precipitator (Temperature at control device is below $\leq$230°C)
H-ESP = Hot-side Electrostatic Precipitator (Temperature at control device is $\geq$230°C)
WS = Wet Scrubber
UNC = Uncontrolled (no APCD)
EGB = Electro Granular Activated Carbon Bed

Figure 3-8. MSWI Design Classes for 1995

Table 3-1. Inventory of MSWIs in 1995 by Technology, APCD, and Activity Level

MSWI		UNC	Hot ESP	Cold ESP	DSI/H-ESP	DS/FF	DS/CI/FF	DS/FF/ C-ESP	WS/FF	WS C-ESP	DS/C-ESP	DS/DSI/ C-ESP	DSI/ CI/ H-ESP	DSI/ C-ESP	DSI/ FF	DSI/ EGB	WS	Total
MB/RC	No. Facilities	0	0	2	0	2	0	0	0	0	0	0	0	6	2	0	0	12
	Activity Level, kg/yr	0	0	2.00E+08	0	1.14E+09	0	0	0	0	0	0	0	5.07E+08	2.59E+08	0	0	2.10E+09
MB/REF	No. Facilities	0	0	1	0	2	0	0	0	0	1	0	0	0	1	0	2	7
	Activity Level, kg/yr	0	0	1.69E+08	0	2.68E+08	0	0	0	0	4.22E+08	0	0	0	1.13E+08	0	2.04E+08	1.18E+09
MB/WW	No. Facilities	0	6	8	1	28	3	0	0	0	8	0	1	0	2	0	0	57
	Activity Level, kg/yr	0	1.04E+09	2.81E+09	4.22E+08	8.57E+09	1.17E+09	0	0	0	2.31E+09	0	2.75E+08	0	1.97E+08	0	0	1.68E+10
FB/RDF	No. Facilities	0	0	0	0	1	0	0	0	0	0	0	0	0	1	1	0	3
	Activity Level, kg/yr	0	0	0	0	1.69E+08	0	0	0	0	0	0	0	0	8.45E+07	1.13E+08	0	3.66E+08
RDF/Ded	No. Facilities	0	1	4	1	7	0	1	0	0	4	0	0	0	1	0	0	19
	Activity Level, kg/yr	0	4.22E+07	1.81E+09	2.00E+08	2.51E+09	0	5.63E+08	0	0	1.75E+09	0	0	0	4.22E+08	0	0	7.30E+09
MOD -SA	No. Facilities	9	4	4	0	0	0	0	1	0	0	1	0	0	1	0	3	23
	Activity Level, kg/yr	1.87E+08	1.82E+08	1.25E+08	0	0	0	0	2.82E+07	0	0	7.60E+07	0	0	3.24E+07	0	4.90E+07	6.80E+08
MOD-EA	No. Facilities	1	1	3	1	1	0	0	0	1	0	0	0	0	1	0	0	9
	Activity Level, kg/yr	1.41E+07	1.97E+07	8.28E+07	1.41E+07	1.18E+08	0	0	0	6.76E+07	0	0	0	0	1.01E+08	0	0	4.18E+08
Total	No. Facilities	10	12	22	3	41	3	1	1	1	13	1	1	6	9	1	5	130
Total	Activity Level, kg/yr	2.01E+08	1.29E+09	5.19E+09	6.37E+08	1.28E+10	1.17E+09	5.63E+08	2.82E+07	6.76E+07	4.49E+09	7.60E+07	2.75E+08	5.07E+08	1.21E+09	1.13E+08	2.53E+08	2.88E+10

Table 3-1. Inventory of MSWIs in 1995 by Technology, APCD, and Activity Level (continued)

MB/RC = Mass Burn Rotary Kiln MB/REF = Mass Burn Refractory Walled MB/WW = Mass Burn Waterwalled RDF/Ded = Dedicated Refuse-Derived Fuel FB/RDF = Fluidized Bed Refuse-Derived Fuel MOD/SA = Modular Starved Air MOD/EA = Modular Excess Air	UNC = Uncontrolled Hot ESP = Hot side Electrostatic Precipitator Cold ESP = Cold side Electrostatic Precipitator DS/FF = Dry Scrubber with Fabric Filter FF = Fabric Filter EGB = Electro Gravel Bed WS = Wet Scrubber	DSI/FF = Dry Sorbent Injection with Fabric Filter DS/CI/FF = Spray Dryer - Carbon Injection - Fabric Filter DSI/EGB = Dry Sorbent Injection - Electro Gravel Bed

Table 3-2. Inventory of MSWIs in 1987 by Technology, APCD, and Annual Activity Level

	MSWI Type	UNC	Hot ESP	DS/FF	FF	EGB	WS	Total
MB/RC	No. of Facilities	0	3	0	1	0	0	4
	Activity Level,kg/yr	0	3.94E+08	0	1.58E+07	0	0	4.10E+08
MB/REF	No. of Facilities	0	12	1	0	0	7	20
	Activity Level,kg/yr	0	2.00E+09	1.41E+07	0	0	9.01E+08	3.04E+09
MB/WW	No. of Facilities	0	19	1	0	0	0	20
	Activity Level,kg/yr	0	5.20E+09	1.55E+08	0	0	0	5.35E+09
RDF/Dedicated	No. of Facilities	0	7	0	0	0	2	9
	Activity Level,kg/yr	0	3.01E+09	0	0	0	3.38E+08	3.35E+09
RDF/cofired	No. of Facilities	0	3	0	0	0	0	3
	Activity Level,kg/yr	0	2.53E+08	0	0	0	0	2.53E+08

Table 3-2. Inventory of MSWIs in 1987 by Technology, APCD, and Annual Activity Level (continued)

	MSWI Type	UNC	Hot ESP	DS/FF	FF	EGB	WS	Total
MOD/SA	No. of Facilities	36	2	0	3	0	4	53
	Activity Level,kg/yr	5.73E+08	1.17E+08	0	1.43E+08	0	5.30E+07	1.15E+09
MOD/EA	No. of Facilities	2	0	0	0	1	1	4
	Activity Level,kg/yr	4.17E+07	0	0	0	6.76E+07	1.27E+08	2.36E+08
	Total No. of Facilities	38	54	2	4	1	14	113
	Total Activity Level,kg/yr	6.15E+08	1.12E+10	2.96E+08	1.59E+08	6.76E+07	1.42E+09	1.38E+10

MB/RC = Mass Burn Rotary Kiln
MB/REF = Mass Burn Refractory Walled
MB/WW = Mass Burn Waterwalled
RDF/Ded = Dedicated Refuse-Derived Fuel
RDF/cofired = RDF cofired with coal
MOD/SA = Modular Starved Air
MOD/EA = Modular Excess Air

UNC = Uncontrolled
Hot ESP = Hot side Electrostatic Precipitator
DS/FF = Dry Scrubber with Fabric Filter
FF = Fabric Filter
EGB = Electro Gravel Bed
WS = Wet Scrubber
kg/y = kilogram per year

Table 3-3 Dioxin TEQ Emission Factors (ng TEQ per kg waste) for Municipal Solid Waste Incineration

Municipal Solid Waste Incinerator Design	Air Pollution Control Device	Average TEQ Emission Factor (ng/kg)	Basis and Rationale
Mass Burn Waterwall	C-ESP	6.1	Based on MB-WW; DS/C-ESP, same furnace and most similar APCD temperature
	DS/C-ESP	6.1	Based on direct tests
	DS/CI/FF	1.5	Based on direct tests
	DS/FF	0.63	Based on direct tests
	DSI/CI/H-ESP	7.74	Based on direct tests
	DSI/FF	1.91	Based on direct tests
	DSI/H-ESP	7.74	Based on MB-WW; DSI/CI/H-ESP, same furnace and most similar APCD temperature
	H-ESP	473	Based on direct tests
Mass Burn Refractory	C-ESP	236	Based on direct tests
	DS/C-ESP	51.1	Based on direct tests
	DS/FF	0.63	Based on MB-WW; DS/FF, most similar furnace and same APCD
	DSI/FF	1.91	Based on MB-WW; DSI/FF, most similar furnace and same APCD
	H-ESP	473	Based on MB-WW; H-ESP, most similar furnace and same APCD
	WS	236	Based on MB-Ref;C-ESP, same furnace and similar APCD temperature
Mass Burn Rotary Kiln	C-ESP	47	Based on MB-RK; DSI/FF, same furnace and similar emission control
	DS/FF	0.646	Based on direct tests
	DSI/C-ESP	47	Based on MB-RK; DSI/FF, same furnace and similar emission control
	DSI/FF	47	Based on direct tests
	FF	47	Based on MB-RK; DSI/FF, same furnace and similar emission control
	H-ESP	285	Based on direct tests
RDF Dedicated	C-ESP	231	Based on direct tests
	DS/C-ESP	0.527	Based on direct tests
	DS/FF	0.24	Based on direct tests
	DS/FF/C-ESP	0.24	Based on RDF-Ded; DS/FF, same furnace and similar APCD
	DSI/FF	231	Based on RDF-Ded; C-ESP, same furnace and similar emission control
	DSI/H-ESP	231	Based on RDF-Ded; C-ESP, same furnace and similar emission control
	H-ESP	1490	Based on direct tests
	WS	231	Based on RDF-Ded; C-ESP, same furnace and similar APCD temperature

Table 3-3 Dioxin TEQ Emission Factors (ng TEQ per kg waste) for Municipal Solid Waste Incineration (continued)

Municipal Solid Waste Incinerator Design	Air Pollution Control Device	Average TEQ Emission Factor (ng/kg)	Basis and Rationale
Modular Starved-air	C-ESP	16	Based on Mod-EA; C-ESP, similar furnace (modular design) and same APCD
	DS/DSI/C-ESP	16	Based on Mod-EA; C-ESP, similar furnace (modular design) and similar emission control
	DSI/FF	0.0247	Based on direct tests
	FF	16	Based on Mod-EA; C-ESP, similar furnace (modular design) and similar emission control
	H-ESP	79	Based on direct tests
	UNC	0.0247	Based on Mod-SA; DSI/FF, same furnace and most similar expected emissions
	WS	16	Based on Mod-EA; C-ESP, similar furnace (modular design) and similar APCD temperature
	WS/FF	16	Based on Mod-EA; C-ESP, similar furnace (modular design) and similar APCD temperature
Modular Excess-air	C-ESP	16	Based on direct tests
	DS/FF	16	Based on Mos-EA; C-ESP, same furnace and similar temperature in APCD - may over-estimate emissions
	DSI/FF	0.0247	Based on Mod-SA; DSI/FF, similar (modular design) furnace and same APCD
	DSI/H-ESP	118	Based on Mod-EA; H-ESP, same furnace and similar emissions
	EGB	0.0247	Based on Mod-SA; DSI/FF, same furnace and most similar expected emissions
	H-ESP	118	Based on direct tests
	UNC	0.0247	Based on Mod-SA; DSI/FF, same furnace and most similar expected emissions
	WS	16	Based on Mod-EA; C-ESP, same furnace and similar APCD temperature
	WS/C-ESP	16	Based on Mod-EA; C-ESP, same furnace and similar APCD
Fluidized-bed RDF	DS/FF	0.63	Based on MB-WW; DS/FF, similar furnace and same APCD
	DSI/EGB	0.63	Based on MB-WW; DS/FF, similar furnace - may under-estimate emissions
	DSI/FF	0.63	Based on MB-WW; DS/FF, similar furnace - may under-estimate emissions

Key:
- ng/kg = Nanograms TEQ per kilograms waste
- DS/FF = Dry scrubber combined with a fabric filter
- DSI/FF = Dry sorbent injection coupled with a fabric filter
- DS/CI/FF = Dry scrubber coupled with carbon injection and a fabric filter
- C-ESP = Cold-sided electrostatic precipitator (temperature at control device is below 220°C
- H-ESP = Hot-sided electrostatic precipitator (temperature at control device is above 220°C
- WS = Wet scrubber
- UNC = Uncontrolled (no APCD)
- EGB = Electro-granular activated carbon bed

Table 3-4 Annual TEQ Emissions (g/yr) From MSWIs Operating in 1995

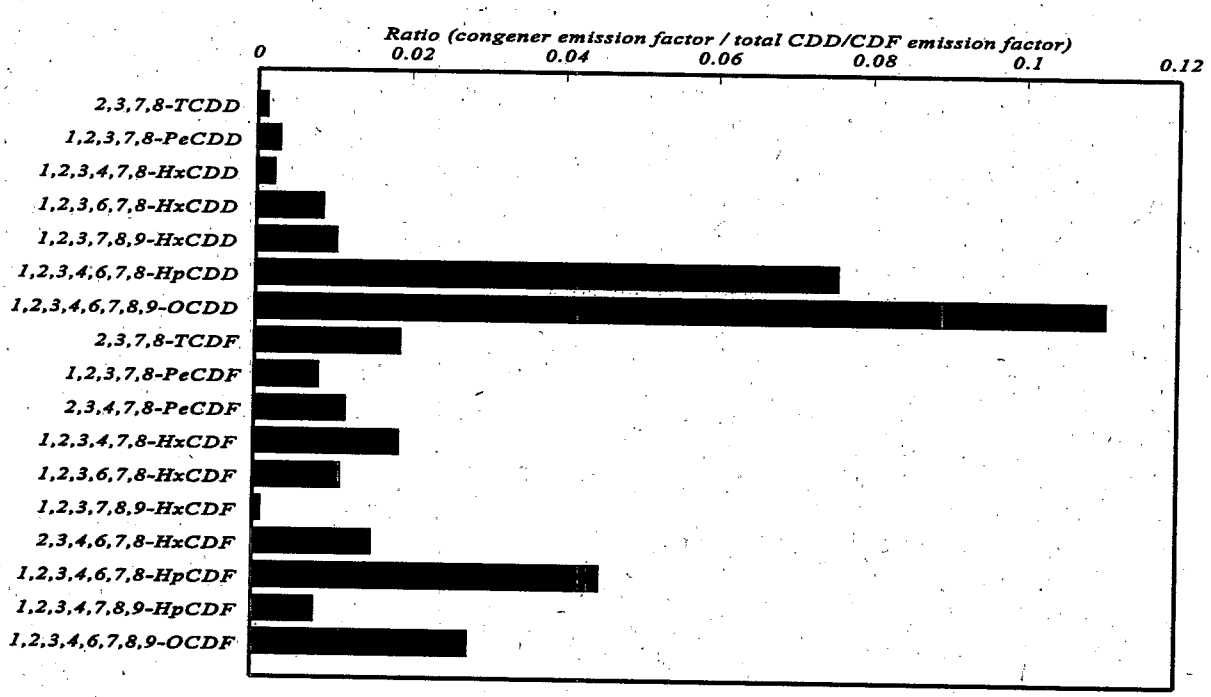
Municipal Solid Waste Incinerator Design	Air Pollution Control Device	Emissions From Tested Facilities (g TEQ/yr)	Average TEQ Emission Factor (ng/kg)	Activity Level Non-Tested Facilities (kg/yr)	Emissions From Non-Tested Facilities (g TEQ/yr)	Total Emissions From All Facilities (g TEQ/yr)
Mass Burn Waterwall	C-ESP	0	6.1	2.81e+09	17.1	17.1
	DS/C-ESP	2.09	6.1	1.88e+09	11.4	13.5
	DS/CI/FF	0.635	1.5	7.44e+08	1.12	1.75
	DS/FF	2.01	0.63	5.98e+09	3.77	5.77
	DSI/CI/H-ESP	2.12	-	0	0	2.12
	DSI/FF	0.279	-	0	0	0.279
	DSI/H-ESP	0	7.74	4.22e+08	3.27	3.27
	H-ESP	163	473	1.79e+08	84.5	247
	Subtotal	170			121	291
Mass Burn Refractory	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
Mass Burn Rotary Kiln	C-ESP	0	47	2.00e+08	9.4	9.4
	DS/FF	0.245	0.646	7.57e+08	0.489	0.734
	DSI/C-ESP	0	47	5.07e+08	23.8	23.8
	DSI/FF	5.29	47	1.46e+08	6.85	12.1
	Subtotal	5.54			40.6	46.1
RDF Dedicated	C-ESP	32.5	231	1.67e+09	385	418
	DS/C-ESP	0.321	0.527	1.14e+09	0.603	0.924
	DS/FF	0.0975	0.24	1.58e+09	0.379	0.477
	DSI/FF	0	231	4.22e+08	97.6	97.6
	DSI/H-ESP	0	231	2.00e+08	46.2	46.2
	H-ESP	0	1490	4.22e+07	63	63
	DS/FF/C-ESP	0	0.24	5.63e+08	0.135	0.135
	Subtotal	33			593	626
Modular Starved-air	C-ESP	0	16	1.25e+08	2	2
	DSI/FF	0.000801	-	0	0	0.000801
	H-ESP	8.01	79	8.03e+07	6.34	14.4
	UNC	0	0.0247	1.87e+08	0.00463	0.00463
	WS	0	16	4.90e+07	0.785	0.785
	WS/FF	0	16	2.82e+07	0.451	0.451
	DS/DSI/C-ESP	0	16	7.60e+07	1.22	1.22
	Subtotal	8.01			10.8	18.8
Modular Excess-air	C-ESP	0.0643	16	6.25e+07	1	1.07
	DS/FF	0	16	1.18e+08	1.9	1.9
	DSI/FF	0	0.0247	1.01e+08	0.00251	0.00251
	DSI/H-ESP	0	118	1.41e+07	1.66	1.66
	H-ESP	2.32	-	0	0	2.32
	UNC	0	0.0247	1.41e+07	0.000348	0.000348
	WS/C-ESP	0	16	6.76e+07	1.08	1.08
	Subtotal	2.39			5.64	8.03
Fluidized-bed RDF	DS/FF	0	0.63	1.69e+08	0.106	0.106
	DSI/EGB	0	0.63	1.13e+08	0.0709	0.0709
	DSI/FF	0	0.63	8.45e+07	0.0532	0.0532
	Subtotal	0			0.231	0.231
Total		280			820	1,100

Key: DS/FF = Dry Scrubber combined with a Fabric Filter
DSI/FF = Dry Sorbent Injection coupled with a Fabric Filter
DS/CI/FF = Dry Scrubber -Carbon Injection-Fabric Filter
C-ESP = Cold-side Electrostatic Precipitator (Temperature at control device is below ≤230°C)
H-ESP = Hot-side Electrostatic Precipitator (Temperature at control device is ≥230°C)
WS = Wet Scrubber
UNC = Uncontrolled (no APCD)
EGB = Electro Granular Activated Carbon Bed
ng/kg = nanogram per kilogram
kg/yr = kilograms per year

Table 3-5. Annual TEQ Emissions to the Air From MSWIs Operating in 1987

Municipal Solid Waste Incinerator Design	Air Pollution Control Device	Emissions From Tested Facilities (g TEQ/yr)	Average TEQ Emission Factor (ng/kg)	Activity Level Non-Tested Facilities (kg/yr)	Emissions From Non-Tested Facilities (g TEQ/yr)	Total Emissions From All Facilities (g TEQ/yr)
Mass Burn Waterwall	DS/FF	0.0373	-	0	0	0.0373
	H-ESP	433	473	3.27e+09	1550	1980
	Subtotal	433			1550	1980
Mass Burn Refractory	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			1,160	1,160
Mass Burn Rotary Kiln	FF	0	47	1.58e+07	0.741	0.741
	H-ESP	48.2	285	2.25e+08	64.2	112
	Subtotal	48.2			65	113
RDF Dedicated	H-ESP	840	1490	2.45e+09	3660	4500
	WS	0	231	3.38e+08	78.1	78.1
	Subtotal	840			3730	4570
RDF Cofired	H-ESP	0	231	2.53e+08	58.6	58.6
Modular Starved-air	FF	0	16	1.43e+08	2.29	2.29
	H-ESP	0.0643	79	3.61e+08	28.5	28.5
	UNC	0	0.0247	5.73e+08	0.0142	0.0142
	WS	0	16	5.30e+07	0.848	0.848
	Subtotal	0.0643			31.6	31.7
Modular Excess-air	EGB	0	0.0247	6.76e+07	0.00167	0.00167
	UNC	0	0.0247	4.17e+07	0.00103	0.00103
	WS	0	16	1.27e+08	2.03	2.03
	Subtotal	0			2.03	2.03
Totals		1,320			6,590	7,915

Key: DS/FF = Dry Scrubber combined with a Fabric Filter
DSI/FF = Dry Sorbent Injection coupled with a Fabric Filter
DS/CI/FF = Dry Scrubber -Carbon Injection-Fabric Filter
C-ESP = Cold-side Electrostatic Precipitator (Temperature at control device is below ≤230°C)
H-ESP = Hot-side Electrostatic Precipitator (Temperature at control device is ≥230°C)
WS = Wet Scrubber
UNC = Uncontrolled (no APCD)
EGB = Electro Granular Activated Carbon Bed
ng/kg = nanogram per kilogram
kg/yr = kilograms per year



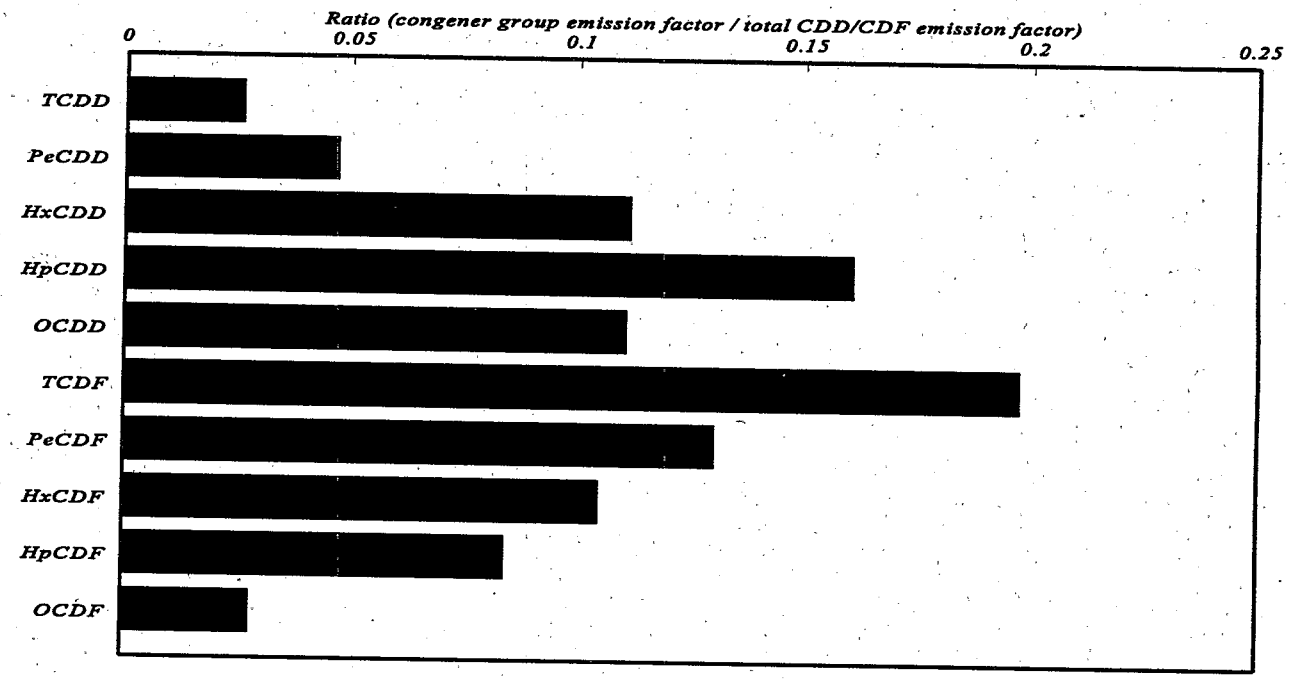


Figure 3-9. Congener and Congener Group Profiles for Air Emissions from a Mass-Burn Waterwall MSWI, Equipped with a Dry Scrubber and Fabric Filter

Table 3-6. CDD/CDF Emission Factors for Hazardous Waste Incinerators and Boilers

Congener/Congener Group	Incinerator Average Mean emission factor (17 facilities) (ng/kg feed)		Hot-Side ESP Boilers Mean emission factor (2 facilities) (ng/kg feed)	
	Nondetects Set to 1/2 Det. Limit	Nondetects Set to Zero	Nondetects Set to 1/2 Det. Limit	Nondetects Set to Zero
2,3,7,8-TCDD	0.44	0.14	0.10	0.00
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	0.20	0.18
1,2,3,7,8,9-HxCDD	0.49	0.48	0.22	0.20
1,2,3,4,6,7,8-HpCDD	1.77	1.75	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	3.96	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	2.70	2.70	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	13.78	13.46	0.70	0.70
Total TEQ (nondetects = 0)		3.83		0.64
Total TEQ (nondetects = 1/2 DL)	4.22		0.78	
Total TCDD			0.77	0.77
Total PeCDD			1.15	0.77
Total HxCDD			1.67	1.62
Total HpCDD			2.34	2.34
Total OCDD			5.24	5.24
Total TCDF			5.47	5.47
Total PeCDF			5.50	5.51
Total HxCDF			4.04	4.04
Total HpCDF			1.94	1.94
Total OCDF			0.70	0.70
Total CDD/CDF (nondetects = 0)		137.36		28.83
Total CDD/CDF (nondetects = 1/2 DL)	137.36		28.83	

ng/kg = nanograms per kilogram

Source: U.S. EPA (1996c).

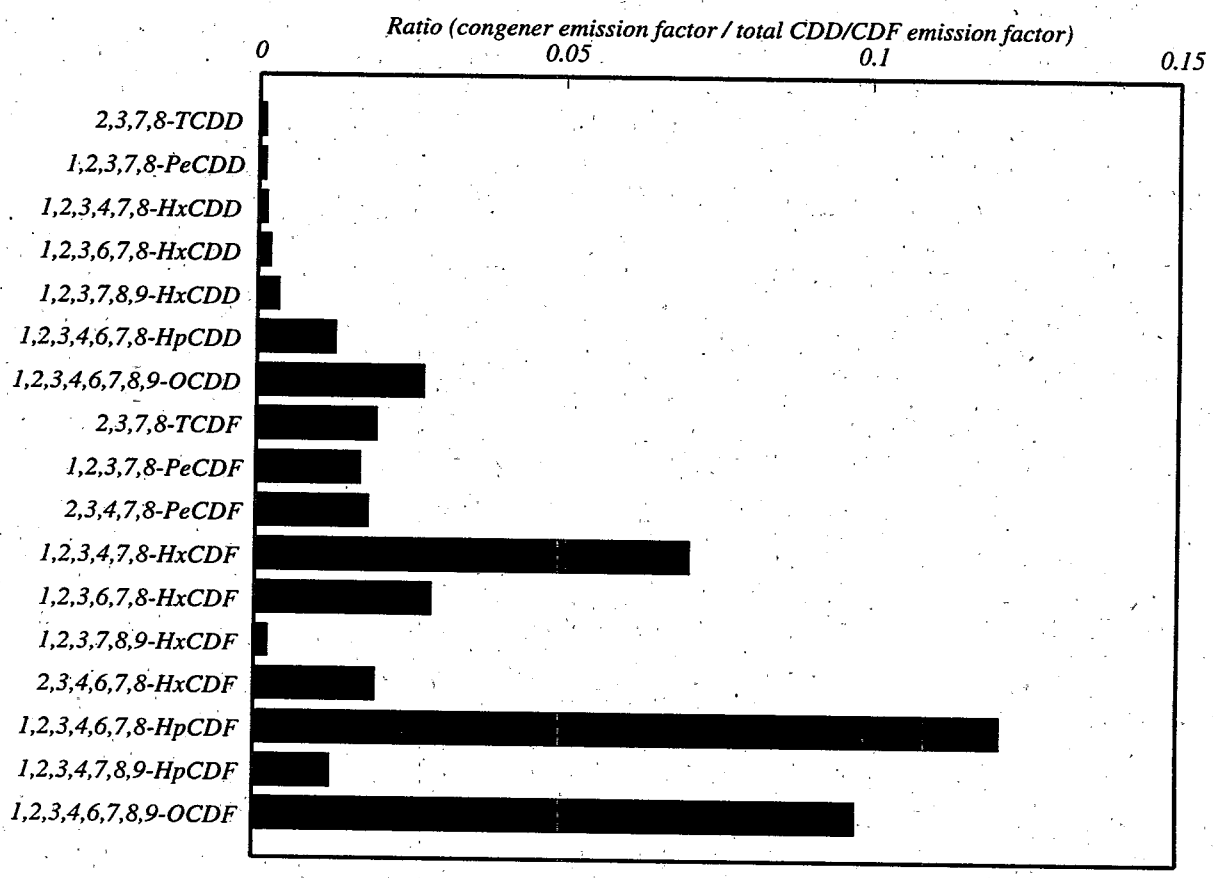
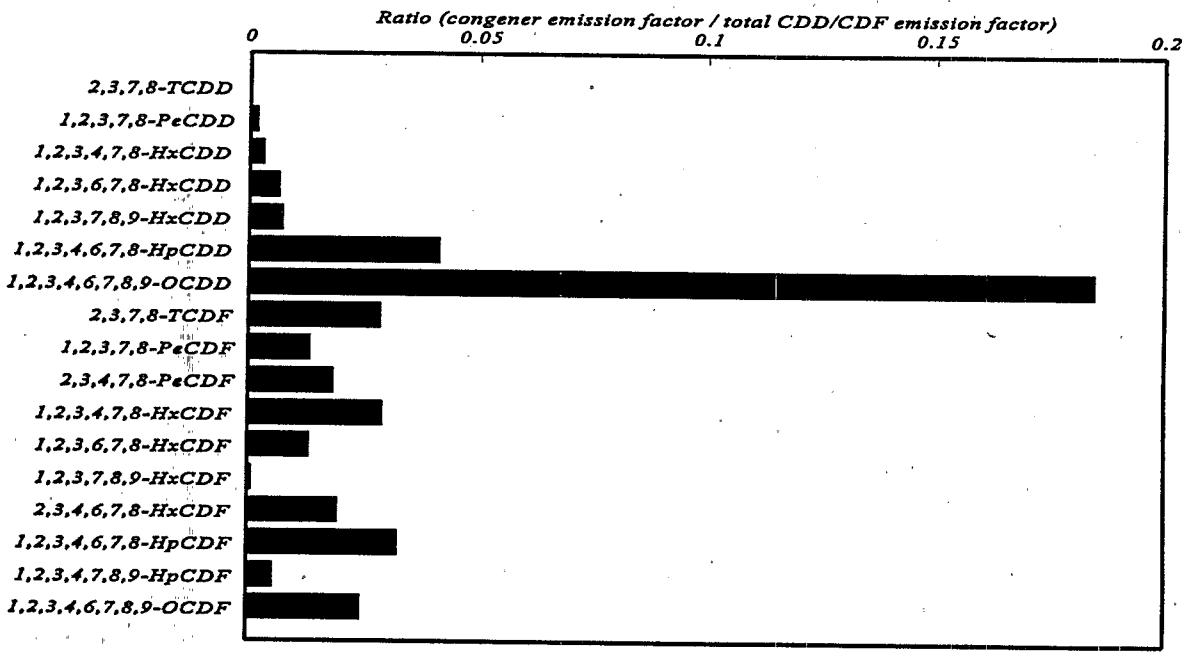


Figure 3-10. Congener Profile for Air Emissions from Hazardous Waste Incinerators



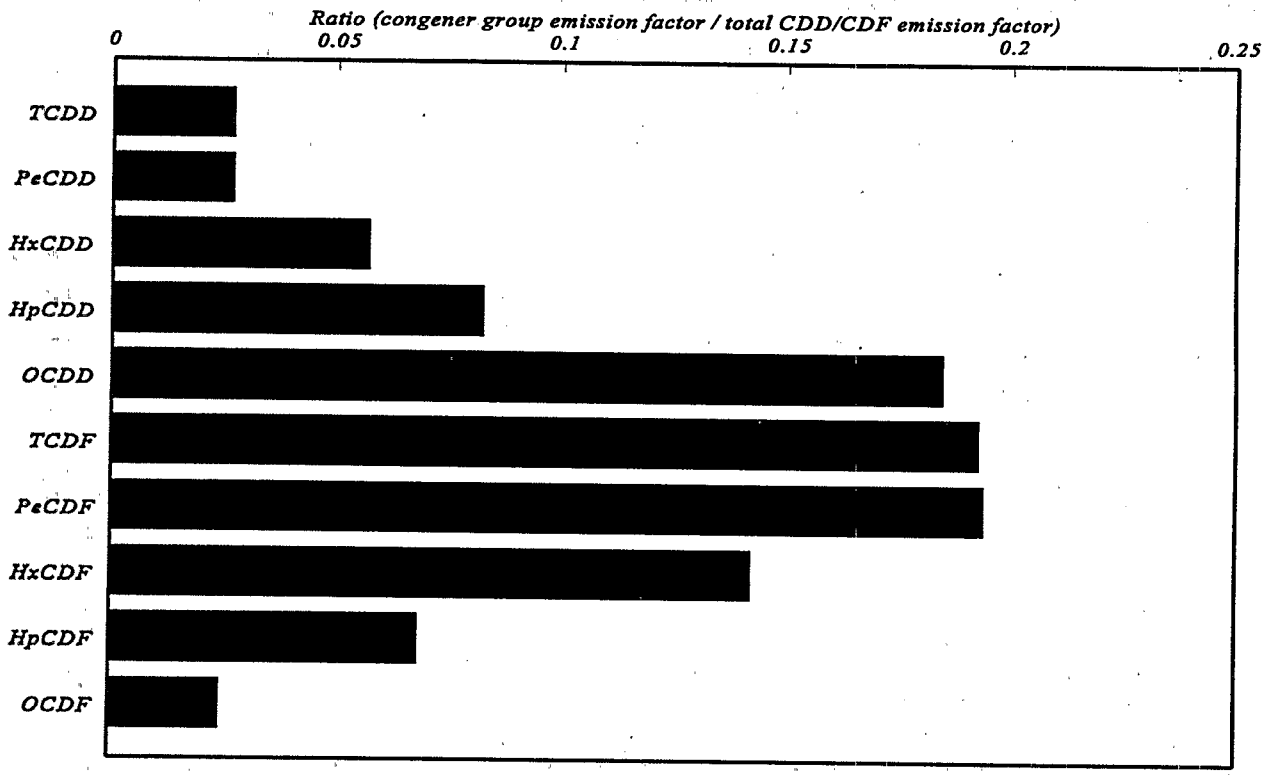


Figure 3-11. Congener and Congener Group Profiles for Air Emissions from Boilers and Industrial Furnaces Burning Hazardous Waste

Table 3-7. Summary of Annual Operating Hours for Each MWI Type

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

lb/hr = pounds per hour
hr/yr = hours per year

Table 3-8. OAQPS Approach: PM Emission Limits for MWIs and Corresponding Residence Times in the Secondary Combustion Chamber

MWI Type	PM Emission Limit[a] (gr/dscf)	Residence Time in 2° Chamber (seconds)	TEQ Emission Factor (kg TEQ/kg waste)
Intermittent and Continuous	≥0.3	0.25	3.96 e-9
	0.16 to < 0.30	1.0	9.09 e-10
	0.10 to ≤0.16	2.0	7.44 e-11
Batch	≥0.079	0.25	3.96 e-9
	0.042 to <0.079	1.0	9.09 e-10
	0.026 to <0.042	2.0	7.44 e-11

[a] gr/dscf = grains per dry standard cubic foot at standard temperature and pressure.

Table 3-9. OAQPS Approach: Estimated Nationwide CDD/CDF TEQ Emissions (g/yr) for 1995

MWI Type	Residence Time or APCD	CDD/CDF EF (ng/kg)	TEQ EF (ng/kg)	Activity Level (kg/yr)	CDD/CDF Emissions (g/yr)	TEQ Emissions (g/yr)
Batch	0.25 sec 1.00 sec 2.00 sec	1.94e+05 4.45e+04 3.65e+03	3.96e+03 9.09e+02 7.40e+01	5.95e+06 4.20e+05 2.14e+05	1.15e+03 1.87e+01 7.82e-01	2.35e+01 3.82e-01 1.60e-02
Continuous	0.25 sec 1.00 sec 2.00 sec	1.94e+05 4.45e+04 3.65e+03	3.96e+03 9.09e+02 7.40e+01	1.20e+06 5.10e+06 3.01e+07	2.34e+02 2.27e+02 1.10e+02	4.77 4.64 2.24
Continuous/ Intermittent	0.25 sec 1.00 sec 2.00 sec	1.94e+05 4.45e+04 3.65e+03	3.96e+03 9.09e+02 7.40e+01	4.54e+06 4.24e+07 9.79e+07	8.80e+02 1.88e+03 3.57e+02	1.80e+01 3.85e+01 7.29
Intermittent	0.25 sec 1.00 sec 2.00 sec	1.94e+05 4.45e+04 3.65e+03	3.96e+03 9.09e+02 7.40e+01	4.18e+06 1.83e+07 NA	8.11e+02 8.12e+02 NA	1.65e+01 1.66e+01 NA
Subtotal: Uncontrolled				2.53e+08	6.65e+03	1.36e+02
Batch	Wet Scrubber	4.26e+02	10	2.42e+04	1.00e-02	2.00e-04
Continuous	Wet Scrubber	4.26e+02	10	1.88e+08	8.01e+01	1.90
Intermittent	Wet Scrubber	4.26e+02	10	6.04e+07	2.58e+01	6.11e-01
Subtotal: Controlled w/Wet Scrubber				3.71e+08	1.58e+02	3.74
Continuous	Dry Scrubber no carbon	3.65e+02	7	9.94e+07	3.63e+01	7.39e-01
Continuous on-site/ Intermittent	Dry Scrubber with no carbon	3.56e+02	7	7.86e+06	2.87	5.80e-02
Continuous	Dry Scrubber with Carbon	7.00e+01	2	1.43e+07	1.00	2.40e-02
Continuous on-site/ Intermittent	Dry Scrubber with Carbon	7.00e+01	2	3.70e+06	2.61e-01	6.00e-03
Subtotal: Controlled w/Dry Scrubber				1.46e+08	4.80e+01	9.82e-01
Intermittent	Fabric Filter/ Packed Bed	3.34e+04	6.81e+02	6.99e+05	2.34e+01	4.76e-01
Total MWI				3.71e+08	6.88e+03	1.41e+02

NA = Not applicable
ng/kg = nanograms per kilogram
kg/yr = kilograms per year
g/yr = grams per year

Table 3-10. AHA Approach: TEQ Emission Factors Calculated for Air Pollution Control

APC Category	TEQ Emission Factor ($lb/10^6$ lbs waste)	Number of MWI Test Reports Used[a]
Uncontrolled		
MWIs up to 200 lb/hr	1.53e-03	4
MWIs > 200 lb/hr	5.51e-04	13
Wet scrubber/BHF/ESP[b]	4.49e-05	11
Dry sorbent injection/Fabric Filter	6.95e-05	8

[a] The same MWI may have been used more than once in deriving emission factors.

[b] Wet scrubbers-bag house filters-electrostatic precipitators. Bag house is also called Fabric Filter.

Source: Doucet (1995).

Table 3-11. AHA Assumptions of the Percent Distribution of Air Pollution Control on MWIs Based on PM Emission Limits

PM Emission Limits[a] (gr/dscf)	Percent MWIs Uncontrolled[b]	Percent MWIs with Wet Scrubbers/ BHFs/ESPs[c]	Percent MWIs DI/FF[d]
≥ 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%

a Particulate matter (PM) emission limits at the stack, grains per dry standard cubic foot (gr/dscf).

b Uncontrolled means there is no air pollution control device installed on the MWI.

c Scrubbers/BHFs/EDPs means wet scrubbers-bag house filters-electrostatic precipitators.

d DI/FF means dry sorbent injection combined with fabric filters.

Table 3-12. AHA Approach: Estimated Annual Nationwide CDD/CDF TEQ Emissions

APCD[a]	MWI Capacity[b] (lb/hr)	CDD/CDF TEQ Emission Factor[c] (g/kg waste)	MWI Activity Level[d] (kg/yr)	Annual TEQ Emissions (g/yr)
Uncontrolled	≤ 200 > 200	1.54 e-06 5.51 e-07	2.28 e+07 1.54 e+08	3.51e+01 8.48e+01
Subtotal: Uncontrolled			1.77 e+08	1.20e+02
WS/BHF/ESP	>200	4.49 e-08	3.51 e+08	1.58e+01
DI/FF	>200	6.95 e-08	2.60 e+07	1.81
Subtotal: Controlled			3.77 e+08	1.76e+01
Total			5.54 e+08	1.38e+02

a APCD = Air Pollution Control Device assumed by AHA. Uncontrolled means there is no air pollution control device installed on the MWI. WS/BHF/ESP = Wet scrubber-bag house filter-electrostatic precipitator. DI/FF = Dry sorbent injection-fabric filter.

b MWI capacity is the design capacity of the primary combustion chamber.

c TEQ Emission Factor derived from tested facilities.

d Activity Level is the annual amount of medical waste incinerated by each APCD class.

lb/hr = pounds per hour
g/kg = grams per kilogram
kg/yr = kilograms per year
g/yr = grams per year

Table 3-13. Comparison Between Predicted Residence Times and Residence Times Confirmed by State Agencies from EPA/ORD Telephone Survey

State	Residence Time Categories	Percentage of Uncontrolled MWIs Predicted by PM Method	Percentage of Uncontrolled MWIs Confirmed by State Agency
Michigan	1/4 second 1.0 second 2.0 seconds	2% (6/280 MWIs) 2% (5/280) 96% (269/280)	96% (269/280 MWIs) 3% (9/280) 1% (1/280)
Massachusetts	1/4 second 1.0 second 2.0 seconds	6% (6/94 MWIs) 0% (0/94) 94% (88/94)	Unknown Unknown 4% (2/50)
Virginia	1/4 second 1.0 second 2.0 seconds	11% (6/56) 0 % (0/50) 89% (50/56)	4.5% (1/22) 91% (20/22) 4.5% (1/22)
New Jersey	1/4 second 1.0 second 2.0 seconds	0% (0/53 MWIs) 0% (0/53) 100% (53/53)	Unknown Unknown Unknown

Source: O'Rourke (1996).

Table 3-14. EPA/ORD Approach: Annual TEQ Emissions from Medical Waste Incineration (MWI) for Reference Year 1995

MWI Class (APCD)	MWI Subclass (Capacity or APCD)	No. of Tested Facilities	Emission Factor Total CDD/CDF (ng/kg)	TEQ Emission Factor (ng/kg)	Activity Level (kg/yr)	Annual CDD/F Emissions (g/yr)	Annual TEQ Emissions (g/yr)
Uncontrolled	≤200 lb/hr	3	9.25e+04	1.86e+03	3.06e+07	2.83e+03	5.71e+01
	>200 lb/hr	5	6.02e+04	1.70e+03	2.23e+08	1.34e+04	3.79e+02
Controlled	Wet Scrubber/ Fabric Filter/ ESP	8	4.65e+03	7.2e+01	3.71e+08	1.72e+03	2.68e+01
	Dry Sorbent Injection/ Fabric Filter	2	2.85e+02	7	1.46e+08	4.16e+01	9.90e-01
	Fabric Filter/ Packed Bed Scrubber	1	1.10e+05	1.35e+03	6.99e+05	7.73e+01	9.50e-01
Total					7.71e+08	2.02e+04	4.77e+02

APCD = Air Pollution Control Devices
ng/kg = nanograms per kilogram
kg/yr = kilograms per year
g/yr = grams per year
lb/hr = pounds per hour

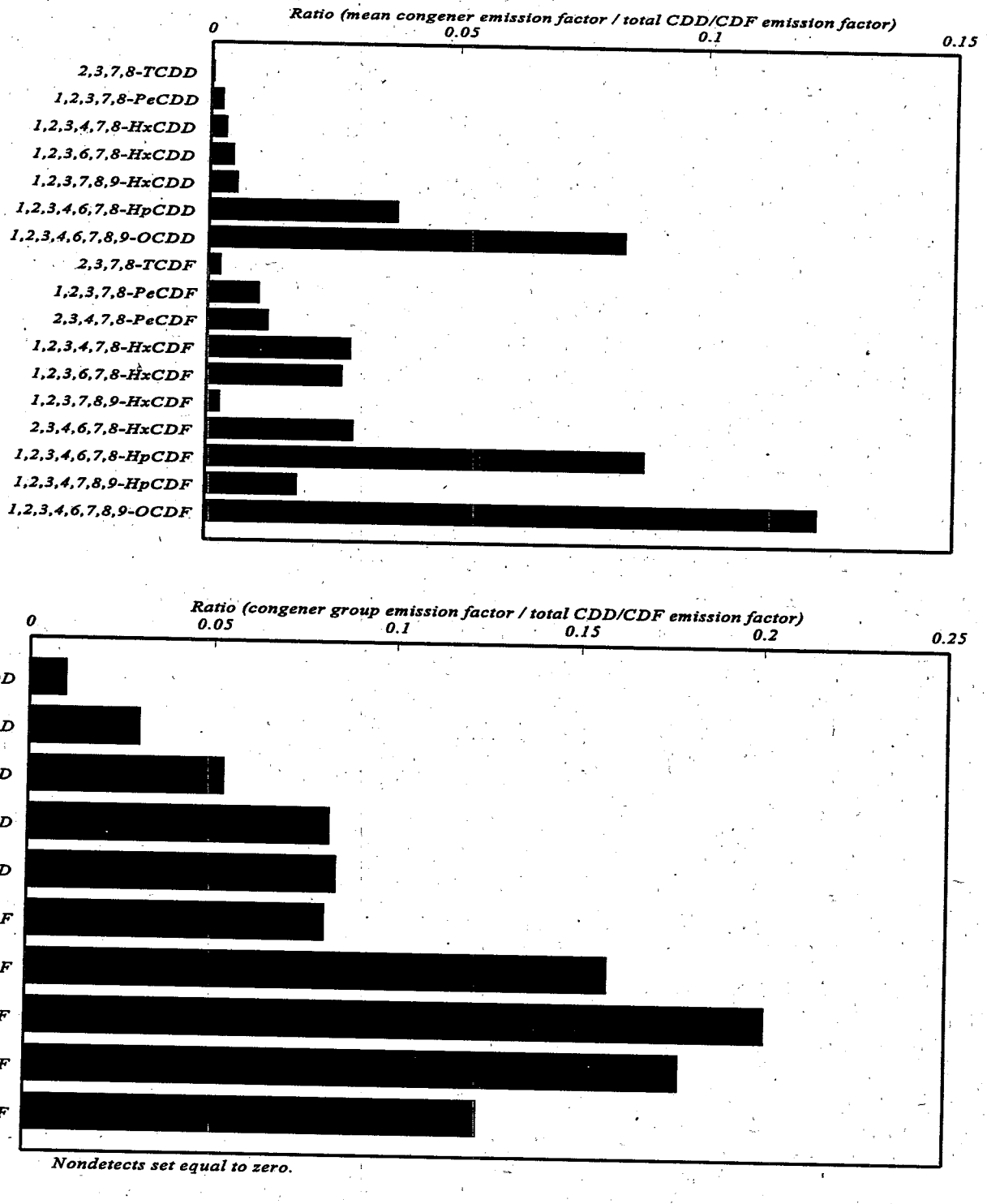


Figure 3-12. Congener and Congener Group Profiles for Air Emissions from Medical Waste Incinerators without APCD

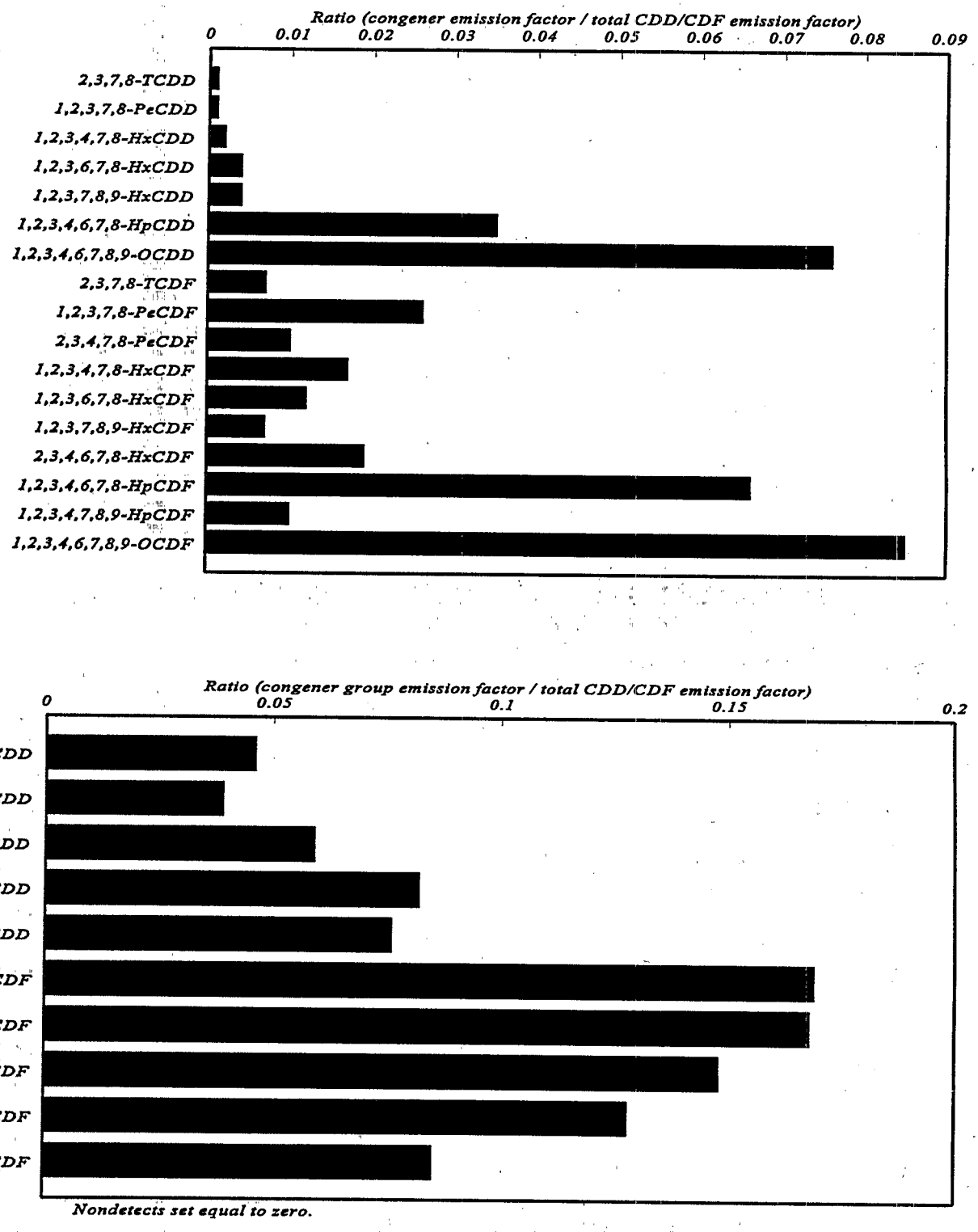


Figure 3-13. Congener and Congener Group Profiles for Air Emissions from Medical Waste Incinerators Equipped with a Wet Scrubber, Baghouse, and Fabric Filter

Table 3-15. Summary of Annual TEQ Emissions from Medical Waste Incineration (MWI) for Reference Year 1987

MWI Class[a]	No of Tested Facilities	Activity Level (kg/yr)	Total CDD/F Emission Factor[b] (g/kg)	TEQ Emission Factor (g/kg)	Annual CDD/F Emissions (g/yr)	Annual TEQ Emissions (g/yr)
≤ 200 lb/hr	3	2.19 e+08	9.25 e-05	1.86 e-06	2.02e+04	4.08e+02
> 200 lb/hr	5	1.21 e+09	6.02 e-05	1.70 e-06	7.31e+04	2.06e+03
Total	8	1.43 e+09			9.33e+04	2.47e+03

[a] This uses the categorization scheme of the AHA Approach (Doucet, 1995).

kg/yr = kilograms per year
g/kg = grams per kilogram
g/yr = grams per year
lb/hr = pounds per hour

Table 3-16. Comparisons of Basic Assumptions Used in the EPA/ORD, the EPA/OAQPS, and the AHA Approaches to Estimating Nationwide CDD/CDF TEQ Emissions from MWIs in 1995

Assumptions	EPA/ORD Approach	EPA/OAQPS Approach	AHA Approach
Reference Year	1995	1995	1995
Number of MWIs	2,375	2,375	2,233
Estimated Activity Level	7.71 e+08 kg/yr	7.71 e+08 kg/yr	5.54 e+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 (RT) in secondary chamber	By design capacity
Assumed Distribution of Uncontrolled Class	Same as AHA assumption	By RT of 0.25, 1.0 and 2.0 sec by State PM emission limits	By estimated annual hrs of operation of < 200 lb/hr and > 200 lb/hr design capacity
APCDs Assumed for Controlled Class	WS/FF/ESP DI/FF FF/Packed Bed Scrub	WS DS-no Carbon DS-Carbon FF/Packed Bed Scrub	WS/FF/ESP DI/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 TEQ Emission Factors (ng/kg)	1,865 = ≤200 lb/hr 1,701 = >200 lb/hr	a/ 3,960 = 0.25 s RT b/ 909 = 1.0 s RT c/ 200 lb/hr 74 = 2.0 s RT	d/ 1,540 = ≤200 lb/hr e/ 551 = > 200 lb/hr
Controlled TEQ Emission Factors (ng/kg)	f/ WS/FF/ESP: 72 g/ DSI/FF: 7 h/ FF/PBS: 1,352	i/ WS: 10 j/ DS no carbon: 7 k/ DS with carbon: 2 l/ FF/PBS: 681	m/ WS/FF/ESP: 44.9 n/ DSI/FF: 69.5

WS = Wet Scrubber; FF = Fabric Filter; ESP = Electrostatic Precipitator; DSI = Dry Sorbent Injection; DS = Dry Scrubber; no carbon = without the addition of activated carbon; with carbon = with the addition of activated carbon; PBS = Packed Bed Scrubber.

a 0.25 seconds residence time (RT) in the secondary chamber.
b 1.0 seconds residence time (RT) in the secondary chamber.
c 2.0 seconds residence time (RT) in the secondary chamber.
d design capacities less than or equal to 200 lbs/hr.
e design capacities greater than 200 lbs/hr.

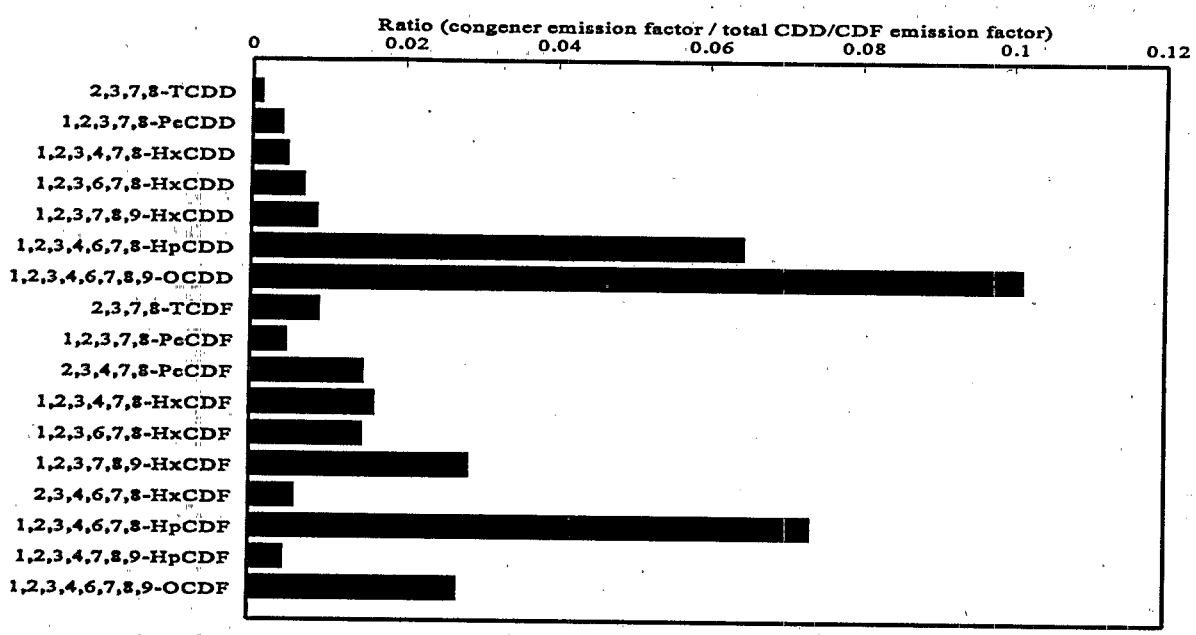
lb/hr = pounds per hour
kg/yr = kilograms per year

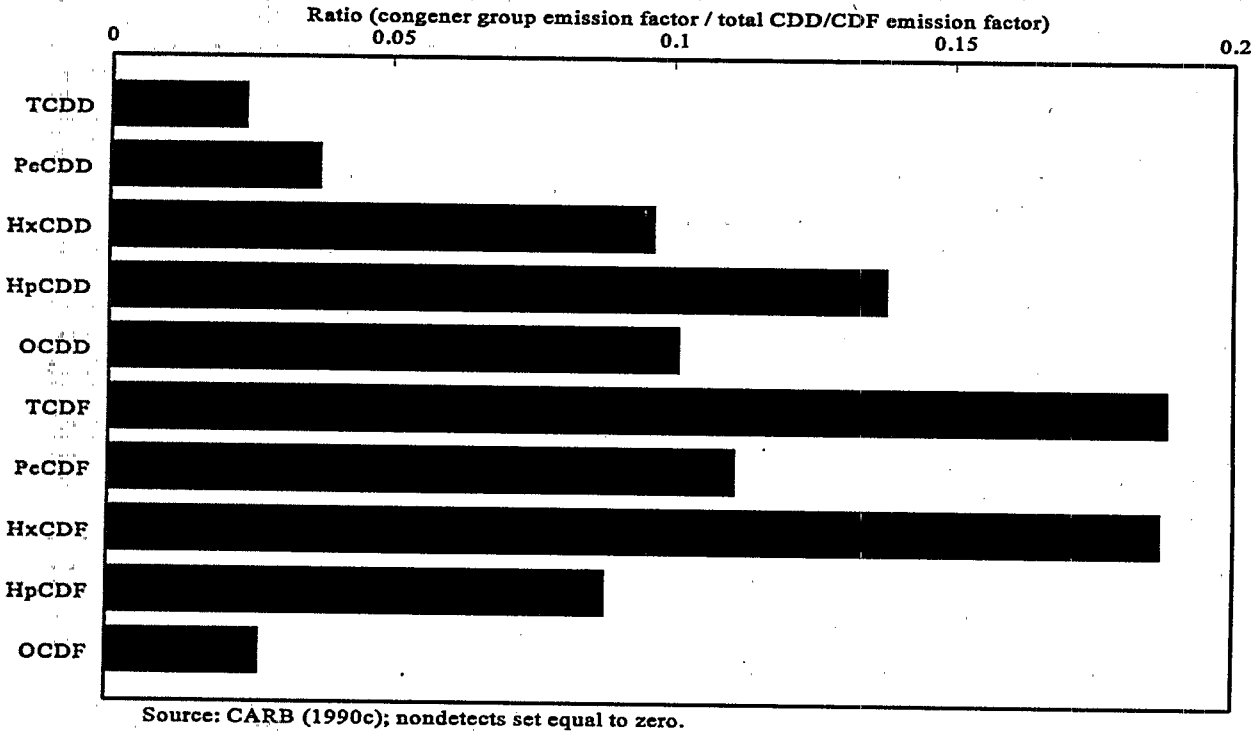
Table 3-17. CDD/CDF Air Emission Factors for a Crematorium

Congener/Congener Group	Mean Facility Emission Factor	
	Assuming ND = zero (ng/body)	Assuming ND = 1/2 det 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 TEQ	501	508
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

ng/body = nanograms per body

Source: CARB (1990c)





Source: CARB (1990c); nondetects set equal to zero.

Figure 3-14. Congener and Congener Group Profiles for Air Emissions from a Crematorium

Table 3-18. CDD/CDF Emission Factors for Sewage Sludge Incinerators

Congener	U.S. EPA (1987a) - 3 facilities Mean Emission Factor (ng/kg)		Green et al. (1995) - 13 facilities Mean Emission Factor (ng/kg)	
	Nondetects Set to Zero	Nondetects Set to 1/2 Det. Limit	Nondetects Set to Zero	Nondetects Set to 1/2 Det. Limit
2,3,7,8-TCDD	0.39	0.44	0.12	0.23
1,2,3,7,8-PeCDD	NR	NR	0.23	0.32
1,2,3,4,7,8-HxCDD	NR	NR	0.03	0.11
1,2,3,6,7,8-HxCDD	NR	NR	0.10	0.16
1,2,3,7,8,9-HxCDD	NR	NR	0.29	0.36
1,2,3,4,6,7,8-HpCDD	NR	NR	2.55	2.70
OCDD	46.2	46.2	13.60	14.00
2,3,7,8-TCDF	179	179	26.60	26.63
1,2,3,7,8-PeCDF	NR	NR	1.98	2.08
2,3,4,7,8-PeCDF	NR	NR	6.84	6.89
1,2,3,4,7,8-HxCDF	NR	NR	2.17	2.24
1,2,3,6,7,8-HxCDF	NR	NR	0.79	0.83
1,2,3,7,8,9-HxCDF	NR	NR	0.03	0.08
2,3,4,6,7,8-HxCDF	NR	NR	1.26	1.46
1,2,3,4,6,7,8-HpCDF	NR	NR	1.46	1.64
1,2,3,4,7,8,9-HpCDF	NR	NR	0.17	0.27
OCDF	109	109	1.22	1.62
Total TCDD	37.6	37.7	35.80	37.81
Total PeCDD	2.66	2.81	0.82	1.63
Total HxCDD	16.6	16.9	1.74	2.25
Total HpCDD	53.9	54.0	4.39	5.03
Total OCDD	46.2	46.2	13.60	14.00
Total TCDF	528	528	123.85	124.10
Total PeCDF	253	253	59.94	60.16
Total HxCDF	75.4	75.9	12.69	13.50
Total HpCDF	144	144	2.63	3.12
Total OCDF	109	109	1.22	1.62
Total TEQ	NR	NR	6.94	7.19
Total CDD/CDF	1,266	1,268	257	263

ng/kg = nanograms per kilogram
NR = not reported
Sources: U.S. EPA (1987a); Green et al. (1995)

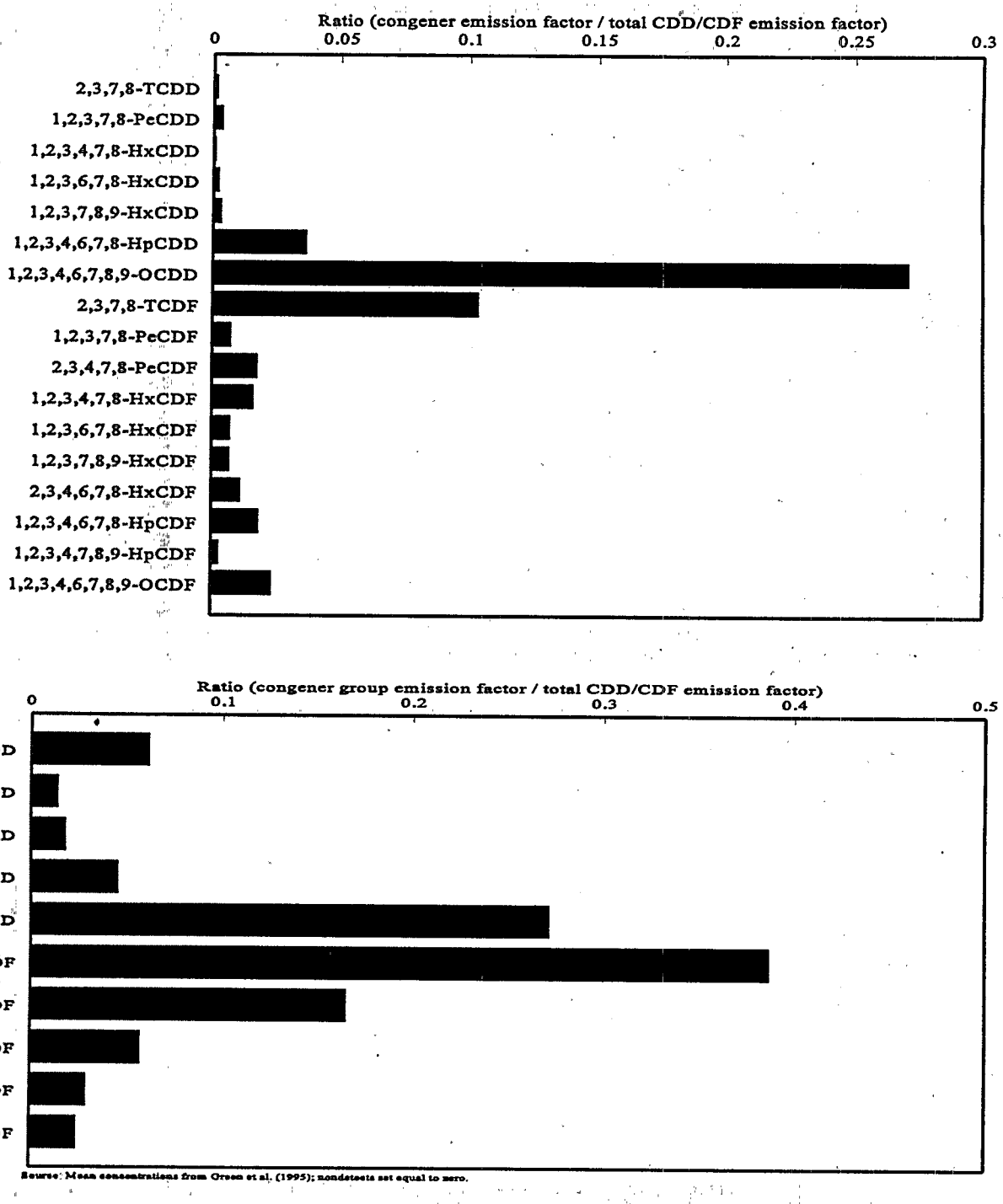


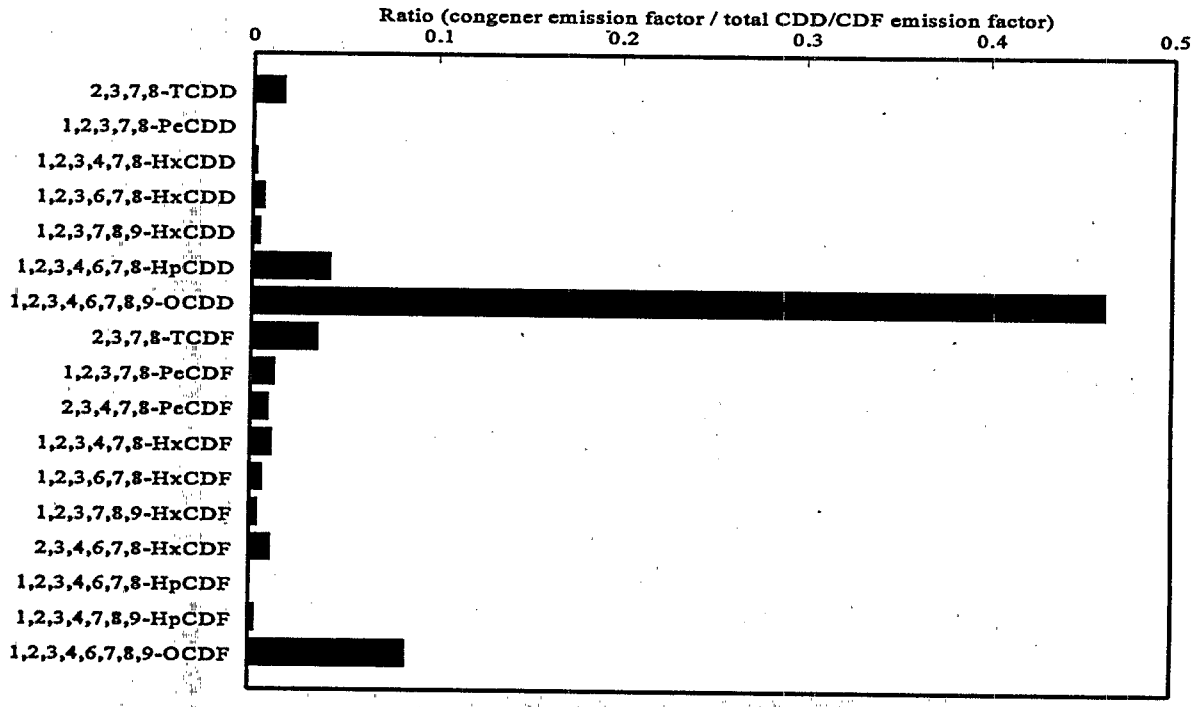
Figure 3-15. Congener and Congener Group Profiles for Air Emissions from Sewage Sludge Incinerators

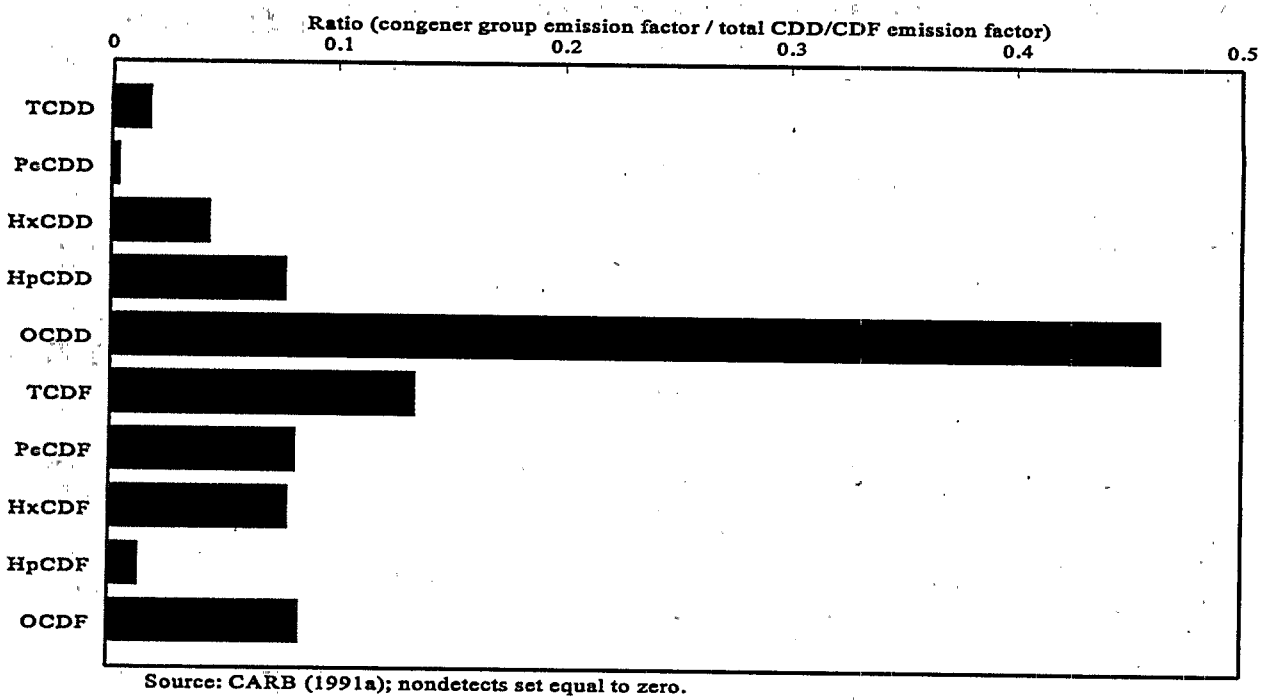
Table 3-19. CDD/CDF Air Emission Factors for Tire Combustion

Congener/Congener Group	Mean Facility Emission Factor	
	Assuming ND = zero (ng/kg)	Assuming ND = 1/2 det limit (ng/kg)
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	0.090
1,2,3,7,8,9-HxCDF	0.036	0.068
2,3,4,6,7,8-HxCDF	0.100	0.148
1,2,3,4,6,7,8-HpCDF	0.000	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	1.600	1.962
Total TEQ	0.282	0.310
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	0.710	0.710
Total HpCDF	0.119	0.186
Total OCDF	0.756	0.756
Total CDD/CDF	8.953	9.021

ng/kg = nanograms per kilogram
ND = not detected

Source: CARB (1991a)





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

Figure 3-16. Congener and Congener Group Profiles for Air Emissions from a Tire Combustor

Table 3-20. CDD/CDF Emission Factors for Combustion of Bleached-Kraft Mill Sludge in Wood Residue Boilers

Congener	Sludge and Wood - 1 facility Mean Emission Factors (ng/kg feed)		Wood Residue Only - 5 facilities Mean Emission Factors (ng/kg feed)	
	Nondetects Set to Zero	Nondetects Set to 1/2 Det. Limit	Nondetects Set to Zero	Nondetects Set to 1/2 Det. Limit
2,3,7,8-TCDD	0	0.001	0.066	0.068
1,2,3,7,8-PeCDD	0	0.001	0.110	0.112
1,2,3,4,7,8-HxCDD	0	0.001	0.179	0.183
1,2,3,6,7,8-HxCDD	0	0.001	0.191	0.193
1,2,3,7,8,9-HxCDD	0	0.001	0.522	0.524
1,2,3,4,6,7,8-HpCDD	0	0.003	0.635	0.637
OCDD	0.025	0.025	1.317	1.317
2,3,7,8-TCDF	0.005	0.005	0.707	0.719
1,2,3,7,8-PeCDF	0	0.003	0.145	0.149
2,3,4,7,8-PeCDF	0	0.003	0.159	0.164
1,2,3,4,7,8-HxCDF	0	0.001	0.108	0.111
1,2,3,6,7,8-HxCDF	0	0.001	0.071	0.073
1,2,3,7,8,9-HxCDF	0	0.001	0.064	0.067
2,3,4,6,7,8-HxCDF	0	0.001	0.015	0.017
1,2,3,4,6,7,8-HpCDF	0	0.001	0.072	0.074
1,2,3,4,7,8,9-HpCDF	0	0.000	0.017	0.020
OCDF	0	0.001	0.049	0.060
Total TCDD	0	0.002	1.628	1.629
Total PeCDD	0	0.001	1.958	1.980
Total HxCDD	0	0.002	1.792	1.796
Total HpCDD	0	0.003	1.120	1.132
Total OCDD	0.025	0.025	1.317	1.317
Total TCDF	0.094	0.094	4.532	4.552
Total PeCDF	0	0.003	1.548	1.549
Total HxCDF	0	0.001	0.536	0.543
Total HpCDF	0	0.001	0.111	0.116
Total OCDF	0	0.001	0.049	0.060
Total TEQ	0.001	0.005	0.401	0.409
Total CDD/CDF	0.119	0.134	14.593	14.674

ng/kg = nanograms per kilogram

Source: NCASI (1995)

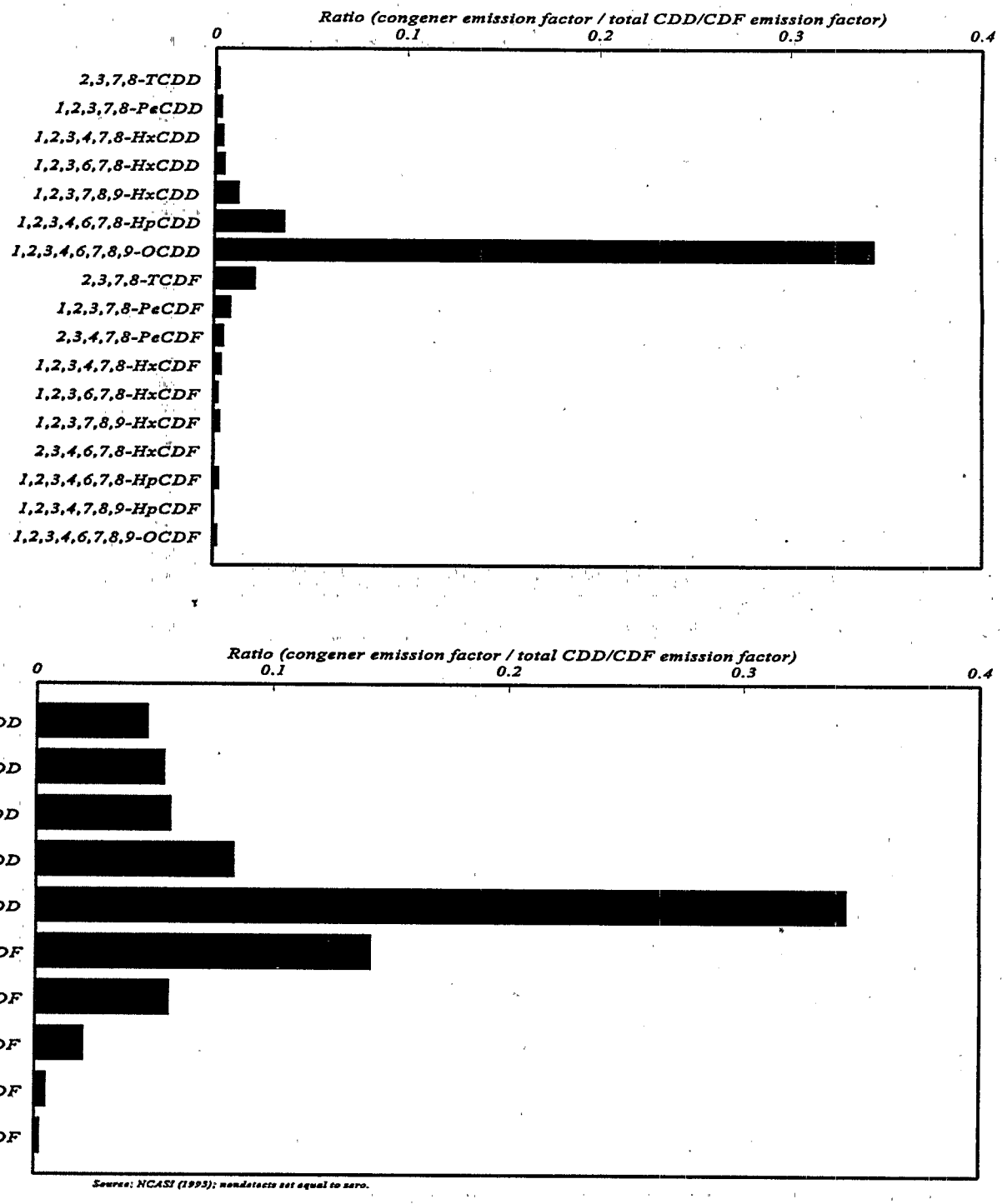


Figure 3-17. Congener and Congener Group Profiles for Air Emissions from Bleached Kraft Mill Combustors

4. COMBUSTION SOURCES OF CDD/CDF: POWER/ENERGY GENERATION

4.1. MOTOR VEHICLE FUEL COMBUSTION

Ballschmiter et al. (1986) reported detecting CDD/CDFs in used motor oil and thus provided some of the first evidence that CDD/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 in the oil or the fuel (such as dichloroethane or pentachlorophenate) were speculated to lead to the formation of CDDs and CDFs. The congener patterns found in the used oil samples were characterized by Ballschmiter et al. (1986) as 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 CDD/CDFs in vehicle exhausts, researchers have developed and implemented several measurement approaches for collecting and analyzing vehicle exhausts. Other researchers have estimated vehicle exhaust emissions of CDD/CDFs indirectly from studies of tunnel air. The results of these two types of studies are summarized in chronological order in the following Section 4.1.1 and Section 4.1.2. Estimates of national annual CDD/CDF TEQ emissions from on-road motor vehicles fueled with leaded gasoline, unleaded gasoline, and diesel fuel are presented in Section 4.1.3 based on the results of these studies. National emission estimates have not been generated for off-road vehicles (i.e., construction and farm vehicles) or stationary sources using these fuel types because of lack of emission factor data.

4.1.1. Tailpipe Emission Studies

Marklund et al. (1987) provided the first direct evidence of the presence of CDDs and CDFs in car emissions based on tailpipe measurements on Swedish cars. Approximately 20 to 220 pg of TEQ from tetra- and penta-CDD/CDFs were reported per kilometer driven for four cars running on leaded gasoline. For this study, an unleaded gasoline was used to which was added tetramethyl lead (0.15 grams of lead per liter [g/L] or 0.57 grams per gallon) and dichloroethane (0.1 g/L as a scavenger). The fuel used may not accurately represent commercial fuels, which typically contain a mixture of chlorinated

and brominated scavengers (Marklund et al., 1990). Also, the lead content of the fuel used (0.15 g lead/L), although the normal lead content for Swedish fuels at the time (Marklund et al., 1990), was higher than the lead content of leaded gasoline in the United States during the late 1980s (lowered to 0.10 g lead/gallon or 0.026 g lead/L effective January 1, 1986). Marklund et al. (1987) reported a striking similarity in the TCDF and PeCDF congener profiles in the car exhausts and those found in emissions from municipal waste incinerators. For two cars running on unleaded gasoline, CDD/CDF emissions were below the detection limit, which corresponded to approximately 13 pg of TEQ per kilometer driven.

Table 4-1 presents a summary description of the results of the Marklund et al. (1987) study and subsequent studies (presented in chronological order) discussed below. Tables 4-2 and 4-3 present the results of tailpipe emission studies reported for diesel-fueled cars and trucks, respectively. Table 4-4 presents the results of studies using leaded gasoline-fueled cars, and Tables 4-5 and 4-6 present results of studies with cars fueled by unleaded gasoline. Figures 4-1, 4-2, and 4-3 present congener and congener group profiles from diesel-fueled vehicles, leaded gasoline-fueled vehicles, and unleaded gasoline-fueled vehicles, respectively.

Virtually no testing of vehicle emissions in the United States for CDD/CDFs has been reported. In 1987, the California Air Resources Board (CARB) produced a draft report on the testing of the exhausts of four gasoline-powered cars and three diesel fuel-powered vehicles (one truck, one bus, and one car) (CARB, 1987a). However, CARB indicated to EPA that the draft report should not be cited or quoted to support general conclusions about CDD/CDFs in motor vehicle exhausts because of the small sample size of the study and because the use of low rather than high resolution mass spectrometry in the study resulted in high detection limits and inadequate selectivity in the presence of interferences (Lew, 1993). CARB did state that the results of a single sample from the heavy-duty diesel truck could be reported, because congeners from most of the homologue groups were present in the sample at levels that could be detected by the analytical method and there were no identified interferences in this sample. This test was conducted under steady state conditions (50 km/hr) for 6 hours with an engine with a fuel economy of 5.5 km/L. The TEQ emission factor of this one sample was equivalent to 7,290 pg/L of fuel burned (or 1,300 pg/km driven) if nondetected values are treated as one-half the detection limit.

Treating nondetected values as zeros yields a TEQ concentration equivalent to 3,720 pg/L of fuel burned (or 663 pg/km driven) (Lew, 1996).

Haglund et al. (1988) sampled exhaust gases from three different vehicles (two cars fueled with leaded and unleaded gasoline, respectively, and a heavy-duty diesel truck) for the presence of brominated dibenzo-p-dioxins (BDD) and brominated dibenzofurans (BDF). The authors concluded that the dibromoethane scavenger added to the tested gasoline probably acted as a halogen source. TBDF emissions measured 23,000 pg/km in the car with leaded gasoline and 240 pg/km in the car with unleaded gasoline. TBDD and PeBDF emissions measured 3,200 and 980 pg/km, respectively, in the car with leaded gasoline. All BDD/Fs were below detection limits in the diesel truck emissions.

Bingham et al. (1989) also analyzed 2,3,7,8-substituted CDD/CDFs in automobile exhausts. Four cars using leaded gasoline (0.45 g/L tetramethyllead, 0.22 g/L dichloroethane, and 0.2 g/L dibromoethane) were tested, and one car using unleaded gasoline was tested. Only HpCDD and OCDD were detected in the exhaust from the vehicle using unleaded fuel. The total TEQ emission rate for this car, based on these detected congeners, was 1 pg/km; the detection limit for the other 2,3,7,8-substituted CDD/CDFs was a combined 28 pg TEQ/km. 2,3,7,8-TCDF was detected in the exhaust of two of four cars using leaded fuel. OCDD was detected in the exhaust from three of the cars, and PeCDF and HpCDD were each detected in the exhaust from one car. TEQ emission rates for the cars using leaded fuel, based on detected congeners only, were 5 to 39 pg/km.

Marklund et al. (1990) tested cars fueled with commercial fuels, measuring CDD/CDF emissions before and/or after the muffler of Swedish vehicles (including new and old vehicles). Three cars were tested using unleaded gasoline, and two cars were tested with leaded gasoline (0.15 g Pb/L and dichloroethane and dibromoethane scavengers). CDD/CDFs were not detected in the fuels at a detection limit of 2 pg TEQ/L, but were detected at a level of 1,200 pg TEQ/L in the new semi-synthetic engine lube oil used in the engines. The test driving cycle employed (i.e., 31.7 km/hr as a mean speed; 91.2 km/hr as a maximum speed; and 17.9 percent of time spent idling) yielded a fuel economy of approximately 9 to 10 km/L or 22 to 24 miles/gallon. Marklund et al. (1990) reported the following emission results in units of pg TEQ/L of fuel consumed and also in units of pg TEQ/km driven during the test:

- Leaded gas/before muffler: 2.4 to 6.3 pg TEQ/km (or 21 to 60 pg TEQ/L of fuel consumed);
- Leaded gas/in tailpipe: 1.1 to 2.6 pg TEQ/km (or 10 to 23 pg TEQ/L);
- Unleaded gas/catalyst-equipped/in tailpipe: 0.36 pg TEQ/km (or 3.5 pg TEQ/L); and
- Unleaded gas/before muffler: 0.36 to 0.39 pg TEQ/km (or 3.5 pg TEQ/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 after the muffler. No muffler-related difference in new cars running on leaded gasoline or in old or new cars running on unleaded gasoline was observed.

Marklund et al. (1990) also analyzed the emissions from a heavy-duty diesel-fueled truck for CDD/CDFs. None were detected; however, the authors pointed out that the test fuel was a reference fuel and may not be representative of commercial diesel fuel. Also, due to analytical problems, a much higher detection limit (about 100 pg TEQ/L) was employed in the diesel fuel test than in the gasoline tests (5 pg TEQ/L). Further uncertainty was introduced by the fact that diesel emission samples were only collected prior to 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: 1,083 pg TEQ/L;
- Unleaded fuel (catalyst-equipped): 7 pg TEQ/L;
- Unleaded fuel (not catalyst-equipped): 51 pg TEQ/L; and
- Diesel fuel: 24 pg TEQ/L.

The major findings of a German study of emissions of halogenated dibenzodioxins and dibenzofurans from internal combustion engines running on commercial fuels were published in 1991 (Schwind et al., 1991), and the full detailed 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 TEQ per liter of fuel consumed are presented below. The results from those tests conducted under normal operating conditions with commercial fuels and for which congener-specific emission results were presented in Hutzinger et al. (1992) are listed in Tables 4-2 through 4-6.

- Leaded fuel: 52 to 1,184 pg TEQ/L;
- Unleaded fuel (not catalyst-equipped): 57 to 177 pg TEQ/L;
- Unleaded fuel (catalyst-equipped): 15 to 26 pg TEQ/L;
- Diesel fuel (cars): 10 to 130 pg TEQ/L; and
- Diesel fuel (trucks): 70 to 81 pg TEQ/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 CDD/CDF present at a detection limit of 1 pg/L of fuel consumed for individual congeners.

Gullett and Ryan (1997) recently reported the results of the first program to sample diesel engine emissions for CDD/CDFs during actual highway and city driving. The exhaust emissions from a 1991 Freightliner diesel tractor with a 10.3 L, 6-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 driving routes. The average emission factor for the three highway tests conducted (15.1 pg TEQ/km; range 11.7-18.7 pg TEQ/km; standard deviation of 3.5 pg TEQ/km) was a factor of three below the average of the two city driving tests (49.9 pg TEQ/kg; range 3.0-96.8 pg TEQ/km). Detection limits were considered as zeros in the calculation of these emission factors. The average of all five tests was 29.0 pg TEQ/km with a standard deviation of 38.3 pg TEQ/km; this standard deviation reflects the 30-fold variation in the two city driving route tests.

4.1.2. Tunnel Emission Studies

Several European studies and one recent U.S. study evaluated CDD/CDF emissions from vehicles by measuring the presence of CDD/CDFs in tunnel air. This approach has the advantage that it allows random sampling of large numbers of cars, including 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 unknown uncertainties 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 rather than the transient driving cycle and cold engine starts that are typical of urban driving conditions and that may affect emission levels. Each of these studies is summarized below in chronological order.

Rappe et al. (1988) reported the CDD/CDF content of two air samples (60 m^3 per sample) collected from a tunnel in Hamburg, Germany, during January of 1986 to be 0.42 and 0.58 pg TEQ/m^3. Each sample was collected for a period of about 60 hours. Rappe et al. (1988) reported that the tunnel handles 65,000 vehicles per day of which 17 percent were classified as "heavy traffic." The congener-specific results of the two samples are presented in Table 4-7. Rappe et al. (1988) concluded that the results clearly show that traffic (with leaded gasoline and halogenated additives) is a source of CDD/CDFs in ambient air. Measurement of ambient air conducted in September of 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 Olso, Norway, performed during April/May of 1988. Oehme et al. (1991) 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 vs. 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, in units of Nordic TEQ, estimated in this study are:

- Light-duty vehicles using gasoline (approximately 70-75 percent using leaded gas): uphill = 520 pg TEQ/km; downhill = 38 pg TEQ/km; mean = 280 pg TEQ/km; and
- 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 percent incline at an average speed of 37 miles per hour and vehicles moving downhill on a 3.5 percent decline at an average speed of 42 miles per hour. Although Oehme et al. (1991) reported results in units of Nordic TEQs rather than I-TEQs, the results in I-TEQ should be nearly identical (i.e., about 3 to 6 percent higher), because the only difference between the two TEQ schemes is the toxic equivalency factor assigned to 1,2,3,7,8-PeCDF (0.1 in Nordic and 0.05 in I-TEQ), a minor component of the toxic CDD/CDFs measured in the tunnel air. Table 4-7 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 plug (PUF). The TEQ concentration in the air sampled with the filter/PUF device was 74 to 78 percent of the value obtained with only the high volume sampler only device. However, the results obtained from both sets of devices indicated that the tunnel air had a dioxin TEQ concentration about twice as high as the outside air (filter/PUF: 80.3 fg TEQ/m^3 for tunnel air vs. 35 fg TEQ/m^3 for outside air; filter only: 100 fg TEQ/m^3 for tunnel air vs. 58 fg TEQ/m^3 for outside air). Wevers et al. (1992) presented the congener-specific results for only one tunnel air measurement; these results are presented in Table 4-7 From these data, Bremmer et al. (1994) calculated an emission factor of 65 pg TEQ/km driven for all road traffic collectively.

During October/November 1995, Gertler et al. (1996; 1998) conducted a study at the Fort McHenry Tunnel in Baltimore, Maryland, with the stated objective of measuring 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 services most of the heavy-duty vehicles (i.e., approximately 25 percent of the vehicles using the bore are heavy-duty) was measured, and the air was sampled for CDD/CDFs during 7 sampling periods of 12-hour duration. Three of the samples were collected during daytime (i.e., 6 am to 6 pm) and four samples were collected during the night (i.e., 6 pm to 6 am). 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. Heavy-duty vehicles accounted for 21.2 to 28.8 percent of all vehicles passing through the tunnel for the seven sample runs. The emission factors calculated, assuming that all CDD/CDF emitted in the tunnel were from heavy-duty vehicles, are presented in Table 4-8. The average TEQ emission factor was reported to be 172 pg TEQ/km. The major uncertainties in the study were tunnel air volume measurement, sampler flow volume control, and analytical measurement of CDD/CDF (Gertler et al., 1996; 1998).

EPA's Office of Mobile Sources (OMS) has reviewed the Gertler et al. (1996) study (Lorang, 1996). Overall, OMS found the study to be technologically well done, with no major criticisms or comments on the test methodology or protocol. OMS found no reason to doubt the validity of the emission factor determined by the study. OMS did note that the particulate emission rate for heavy-duty vehicles measured in the study (0.32 g/mile) is lower than the general particulate emission rate used by EPA (i.e., about 1 g/mile) and, thus, may underestimate CDD/CDF emissions under different driving conditions. OMS 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 miles/hour with the entering traffic slightly higher and 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). 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. (1988), Wevers et al. (1992), and Gertler et al. (1996) 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. (1991). The Oehme et al. (1991) study also differs from the other two studies in that the total of 2,3,7,8-substituted CDFs dominates total 2,3,7,8-substituted CDDs (by a factor of 2), whereas just the opposite is observed in Rappe et al. (1988), Wevers et al. (1992), and Gertler et al. (1996).

4.1.3. National Emission Estimates

Estimates of national CDD/CDF TEQ emissions are presented in this section only for on-road vehicles utilizing gasoline or diesel fuel. Because emission factors are lacking for off-road uses (i.e., construction vehicles, farm vehicles, and stationary industrial equipment), no emission estimates could be developed at this time.

Activity Information: The U.S. Federal Highway Administration, as reported in U.S. Department of Commerce (DOC) (1997), reports that 1,586-billion total vehicle miles (2,552 billion km) were driven in the United States during 1994 by automobiles and motorcycles. Because 1994 is the last year for which data are available, these data are used as a surrogate for 1995 activity levels. Trucks accounted for 840-billion vehicle miles (1,351-billion km), and buses accounted for 6.4-billion vehicle miles (10-billion km) (U.S. DOC, 1997). In 1992, diesel-fueled trucks accounted for 14.4 percent of total truck vehicle km driven; gasoline-fueled trucks accounted for the remaining 85.6 percent (U.S. DOC, 1995b). Applying this factor (i.e., 14.4 percent) to the 1994 truck km estimate (i.e., 1,351-billion km) indicates that an estimated 195-billion km were driven by diesel-fueled trucks in 1994. It is assumed that all other vehicle km driven (3,718-billion km) were those of gasoline-powered vehicles. It is further assumed that all of these km were driven by unleaded gasoline-powered vehicles because in 1992, only 1.4 percent of the gasoline supply were leaded fuel (EIA, 1993); usage should have further declined by 1995, because use of leaded fuel in motor vehicles for highway use in the United States was prohibited as of December 31, 1995 (Federal Register, 1985a).

Similar information for 1987 is as follows. 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 percent of total truck km driven (U.S. DOC, 1995b). Applying this factor (i.e., 17.2 percent) to the 1987 truck km estimate (i.e., 887-billion km) indicates that an estimated 153-billion km were driven by diesel-fueled trucks. It is assumed that all other vehicle km driven (2,939-billion km) were those of gasoline-powered vehicles. Leaded gasoline accounted for 24.1 percent of the gasoline supply in 1987 (EIA, 1993). Thus, it can be estimated that 708-billion km (i.e., 24.1 percent of 2,939-billion km) were 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 on the basis that they are based on recent U.S. Bureau of the Census transportation studies.

Emission Estimates: Using the results of the studies discussed in Section 4.1.1, separate annual national emission estimates are developed below for vehicles burning leaded gasoline, unleaded gasoline, and diesel fuel. Estimates are provided for the years 1987 and 1995. The emission estimates for reference year 1995 are based on activity data (i.e., kilometers driven) for calendar year 1994.

Leaded Gasoline: Literature indicates that CDD/CDF emissions do occur from 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 TEQ/km from four cars fueled with a reference unleaded fuel to which lead (0.5 gplg) and a chlorinated scavenger were added. Marklund et al. (1990) reported much lower emissions in the exhaust of cars (1.1 to 6.3 pg TEQ/km) using a commercial leaded fuel (0.57 gplg) containing both dichloroethane and dibromoethane as scavengers. Marklund et al. (1990) attributed the difference in the emission measurements of the 1987 and 1990 studies 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 1,083 pg/L of fuel (or approximately 108 pg TEQ/km) from a car fueled with a commercial leaded fuel (lead content not reported). Bingham et al. (1989) reported emissions from four cars using

gasoline with a lead content of 1.7 gplg in New Zealand to range from 5 to 39 pg TEQ/km. The German study reported by Schwind et al. (1991) and Hutzinger et al. (1992) measured emissions of 52 to 1,184 pg TEQ/L (or approximately 5.2 to 118 pg TEQ/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 (i.e., 70 to 75 percent of the cars) ranged from 38 to 520 pg Nordic TEQ/km.

As shown in Table 4-4, the average emission factor reported for the tailpipe emission studies performed using commercial leaded fuel (i.e., Marklund et al., 1990; Hagenmaier et al., 1990; and Schwind et al., 1991) is 457 pg TEQ/L (or 45.7 pg/km assuming an average fuel economy of 10 km/L). A "low" confidence rating is assigned to this factor because it is based on European fuels and emission control technologies, which may have differed from U.S. leaded-fuels and engine technology, and also because the factor is based is based on tests with only nine cars.

Combining the average emission factor developed above (45.7 pg TEQ/km) with the estimate for km driven by leaded fuel-powered vehicles in 1987 (708-billion km) suggests that 32.4 g TEQ/yr were emitted from vehicles using leaded fuels in 1987. Based on the low confidence rating assigned to the emission factor estimate, the estimated range of potential emissions is assumed to have varied by a factor of 10 between the low and high ends of the range. Assuming that the mean estimate of emissions in 1987 (32.4 g TEQ/yr) is the geometric mean of the actual range, then the range is calculated to be 10.2 to 102 g TEQ/yr. Although there likely was minor use of unleaded 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).

Unleaded Gasoline: The literature documenting results of European studies indicates that CDD/CDF emissions are less from vehicles burning unleaded fuels than are the 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 noncatalyst-equipped cars. Marklund et al. (1987) did not detect CDD/CDF in emissions from two catalyst-equipped cars running on unleaded gasoline at a detection limit of 13 pg TEQ/km. Marklund et al. (1990) reported emission factors of 0.36 and 0.39 pg TEQ/km for two noncatalyst-equipped cars and an emission factor of 0.36 pg TEQ/km for

one catalyst-equipped car. Hagenmaier et al. (1990) reported an emission factor of 5.1 pg TEQ/km for one noncatalyst-equipped car and 0.7 pg TEQ/km for one catalyst-equipped car. Schwind et al. (1991) and Hutzinger et al. (1992) reported emission factors of 5.7 to 17.7 pg TEQ/km for several noncatalyst-equipped cars tested under various conditions; the reported emission factor range for catalyst-equipped cars was 1.5 to 2.6 pg TEQ/km.

All automobiles running on unleaded gasoline in the United States are equipped with catalysts. As shown in Table 4-6, the average emission factor reported for the tailpipe emission studies performed on catalyst-equipped cars (i.e., Hagenmaier et al. 1990; Schwind et al., 1991; and Hutzinger et al., 1992) is 17 pg TEQ/L (or 1.7 pg TEQ/km assuming an average fuel economy of 10 km/L). A "low" confidence rating is assigned to this emission factor because the European fuels and emission control technology used may differ from current U.S. fuels and technology and also because the emission factor range is based on tests with only three catalyst-equipped cars.

Combining the calculated mean emission factor of 1.7 pg TEQ/km with the estimate derived above for vehicle km driven in 1995 by unleaded gasoline-powered vehicles (3,718 billion km) suggests that 6.3 g of TEQ were emitted from vehicles using unleaded fuels in 1995. Based on the low confidence rating for the emission factor, the estimated range of potential annual emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the mean estimate of annual emissions (6.3 g TEQ/yr) is the geometric mean of the actual range, the range is calculated to be 2.0 to 20 g TEQ/yr.

Applying the same emission factor (1.7 pg/km) to the estimate derived above for vehicle km driven in 1987 by unleaded gasoline-powered vehicles (2,231-billion km), suggests that 3.8 g of TEQ may have emitted in 1987. Assuming that this estimate is the geometric mean of the actual range yields a range of 1.2 to 12 g TEQ/yr.

Diesel Fuel: Few data are available upon which to base an evaluation of the extent of CDD/CDF emissions resulting from diesel fuel combustion. The limited data available address emissions only from on-road vehicles; no emissions data are available for off-road diesel uses (i.e., construction vehicles, farm vehicles, and stationary equipment). Two U.S. tailpipe studies are available: CARB (1987a) and Gullett and Ryan (1997). CARB (1987a) reported a relatively high emission factor of 663 pg TEQ/km (not detected values assumed to be zero) for one tested heavy-duty truck with a fuel economy at 50 km/hr of 5.5 km/L.

Gullett and Ryan (1997) reported a range of emission factors for one diesel truck tested on six highway or city driving routes, 3.0 to 96.8 pg TEQ/km (mean of 29.0 pg TEQ/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 TEQ/L (or 18 pg TEQ/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 TEQ/L (or 6 to 15 pg TEQ/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 TEQ/L (or approximately 2.4 pg TEQ/km) for one tested car. Schwind et al. (1991) and Hutzinger et al. (1992) reported emission factors of 5 to 13 pg TEQ/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. (1991) to enable an exact calculation of emission in units of I-TEQ. However, based on the information that was provided, the mean emission factor in units of I-TEQ is approximately 5,250 to 5,400 pg I-TEQ/km. These indirectly estimated emission factors are considerably larger than those reported from 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 were collected in this study representing several thousand heavy duty diesel vehicles, several characteristics of this study introduce considerable uncertainty with regard to using the study's results as a basis for estimating emissions in the United States. These factors include: (1) heavy-duty vehicles comprised only 3 to 19 percent of total vehicle traffic in the tunnel; (2) the majority of the light-duty vehicles were fueled with leaded gasoline the combustion of which, as noted above in Table 4-4, can release considerable amounts of CDD/CDFs; and (3) technology differences likely existed between the 1988 Norwegian and the 1987 and 1995 U.S. vehicle fleets.

The recent tunnel study conducted in Baltimore, Maryland, by Gertler et al. (1996; 1998) has the same disadvantages shared by all tunnel studies relative to tailpipe studies.

Specifically, tunnel studies rely on indirect measurements (rather than tailpipe measurements), which may introduce unknown uncertainties, and the emission factors calculated from these studies reflect driving conditions by the vehicle fleet using the tunnel and not necessarily the overall vehicle fleet under other driving conditions. However, the Gertler et al. (1996; 1998) study does have strengths lacking in the Oehme et al. (1991) tunnel study. Also, the Gertler et al. (1996; 1998) study has benefits over the two U.S. diesel truck taipipe studies. These include: (1) the study is a recent study conducted in the United States and thus reflects current U.S. fuels and technology; (2) virtually no vehicle using the tunnel used leaded gasoline; (3) the tunnel walls and streets were cleaned 1 week prior to the start of sampling and, in addition, the study analyzed road dust and determined that resuspended road dust contributed only about 4 percent of the estimated emission factors; (4) heavy-duty vehicles comprised, on average, a relatively large percentage (25.7 percent) of vehicles using the tunnel; and (5) a large number of heavy-duty vehicles, approximately 33,000, passed through the tunnel during the sampling period, which generates confidence that the emission factor is representative of interstate trucks.

In consideration of the strengths and weaknesses of the available emission factor data from the tailpipe and tunnel studies, the mean TEQ emission factor reported by Gertler et al. (1996; 1998), 172 pg TEQ/km, is assumed to represent the best current estimate of the average emission factor for on-road diesel-fueled trucks. Because it may not be representative of emission rates for the entire fleet of diesel-fueled trucks under the wide array of driving conditions encountered on the road, this emission factor is assigned a "low" confidence rating.

Combining the calculated mean emission factor from Gertler et al. (1996; 1998) with the above estimate for vehicle kms driven in 1995 in the United States by diesel-fueled trucks (195-billion km) suggests that 33.5 g of TEQ were emitted from trucks using diesel fuel in 1995. Based on the "low" confidence rating assigned to this emission factor, the estimated range of potential annual emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the mean estimate of annual emissions (33.5 g TEQ/yr) is the geometric mean of the actual range, then the range is calculated to be 10.6 to 106 g TEQ/yr.

Combining the same emission factor (172 pg TEQ/km) to the estimate derived above for vehicle km driven in 1987 by diesel-fueled trucks (153-billion km) suggests that 26.3 g

of TEQ were emitted from diesel-fueled trucks in 1987; the range is calculated (8.3 to 83.2 g TEQ/yr).

4.2. WOOD COMBUSTION

In 1995, wood fuel provided about 2.6 percent (or 2,350-trillion Btu) of the total primary energy consumed in the United States (EIA, 1997b). During 1987, wood energy consumption is estimated to have been 2,437-trillion Btu, or 3.2 percent of total primary energy consumed (EIA, 1997b). The industrial sector is the largest consumer of wood fuel, accounting for almost 72 percent of total wood fuel consumption in 1995 and 65 percent in 1987. The residential sector accounted for 25 percent of consumption in 1995 and 35 percent in 1987. The electric utility sector accounted for less than 1 percent of total consumption in both years. There are no accurate sources to provide reliable estimates of commercial wood energy use; consumption is thought to be between 20- and 40-trillion Btu, or 2 to 4 percent of total wood consumption (EIA, 1994; EIA, 1997b).

These energy consumption estimates, however, appear to include the energy value of black liquor solids, which are combusted in recovery boilers by wood pulp mills. In 1987 and 1995, the energy value of combusted black liquor solids were 950-trillion Btu and 1,078-trillion Btu, respectively (American Paper Institute, 1992; American Forest & Paper Association, 1997). Subtracting these black liquor energy value estimates from the national totals for wood fuel yields 1,487-trillion Btu in 1987 and 1,272-trillion Btu in 1995. Assuming that 1 kg of oven-dried wood (i.e., 2.15 kg of green wood) provides approximately 19,000 Btu (EIA, 1994), then an estimated 66.9-million and 78.3-million metric tons of oven-dried wood equivalents were burned for energy purposes in 1995 and 1987, respectively. Of these totals, an estimated 31.4-million metric tons and 44.8-million metric tons were consumed by the residential sector in 1995 and 1987, respectively. An estimated 35.5-million metric tons and 33.5-million metric tons were consumed by the industrial sector in 1995 and 1987, respectively.

The following two subsections discuss the results of relevant emission studies for the residential and industrial sectors and present annual emission estimates.

4.2.1. Residential Wood Combustion

The measurement of CDDs and CDFs in chimney soot and bottom ash from wood-burning stoves and fireplaces has been reported by several researchers (Bumb et al., 1980; Nestrick and Lamparski, 1982 and 1983; Clement et al., 1985b; Bacher et al., 1992; Van Oostam and Ward, 1995; and Dumler-Gradl et al., 1995a). Two studies have provided direct measurement of CDD/CDFs in flue gas emissions from wood stoves (Schatowitz et al., 1993; Vikelsoe et al., 1993). The findings of each of these studies are summarized in the following paragraphs.

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

Nestrick and Lamparski (1982; 1983) expanded the research of Bumb et al. (1980) by conducting a survey of CDD concentrations in chimney soot from residential wood-burning units in three different rural areas of the United States. Samples were collected from the base of six chimneys in each of the three study areas. Results of a pilot study at one residential chimney site had determined that this location provided the highest CDD concentrations in soot. Samples were not collected from units where any type of treated or manufactured wood had been burned. For lack of a suitable analytical method, analysis was not performed for PeCDDs. The results of this survey are summarized in Table 4-9. There was wide variation in the results across soot samples with standard deviations for congeners and congener groups often equal to or exceeding the mean value; however, CDDs in each congener group were detected in the soot from almost all sampled units. Nestrick and Lamparski (1982; 1983) concluded that the results do not appear to present any easily discernible patterns with respect to geographic region, furnace operational parameters, or wood fuel type. Nestrick and Lamparski (1982; 1983) attribute the wide variability observed to differences in design of the different units, which affected the sampling point and/or the conditions at the sampling point, and/or possible contamination of the fuel wood.

Clement et al. (1985b) analyzed chimney soot and bottom ash from residential woodstoves and fireplaces in Canada. The CDD/CDF congener concentrations are

presented in Table 4-9 (soot) and Table 4-10 (bottom ash). CDD/CDF congeners were detected in all samples analyzed, although the relative amounts of the different congener groups varied considerably and inconsistently within the type of wood burning unit and between ash and soot samples from the same unit.

Bacher et al. (1992) characterized the full spectrum (i.e., mono- through octa-substitution) of chlorinated and brominated dibenzo-p-dioxin and dibenzofuran congeners in the soot from an old farmhouse in southern Germany. The chimney carries smoke from an oven that had used untreated wood at the rate of about 5 m^3 per year for more than 10 years. 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 detection limit of 20 ng/kg. The results for the tetra- through octa- CDDs and CDFs are presented in Table 4-9. The results indicate that CDFs dominate the CDDs in each congener group except octa. Also, the lower chlorinated congener groups dominate the higher chlorinated congener groups for both the CDDs and CDFs. The TEQ content of the chimney soot was 720 ng/kg of which less than 30 percent was due to CDDs.

Van Oostdam and Ward (1995) analyzed soot from two wood stoves in British Columbia, Canada, and found TEQ concentrations of 86 and 335 ng TEQ/kg. The congener-specific results are presented in Table 4-9. The soot from a wood stove burning salt-laden wood in a coastal area was found to have a TEQ content of 7,706 ng TEQ/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 4-11. As was observed by Nestrick and Lamparski (1982; 1983) and Clement et al. (1985b), CDD/CDFs were detected in all samples; however, there was wide variability in total TEQ concentrations within and across unit type/fuel type combinations.

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/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 volume% oxygen) for the household stove were reported by Schatowitz et al. (1993):

- Open door burn of beech wood sticks: 0.77 ng TEQ/kg (0.064 ng TEQ/Nm^3);
- Closed door burn of beech wood sticks: 1.25 ng TEQ/kg (0.104 ng TEQ/Nm^3); and
- Closed door burn of household waste: 3,230 ng TEQ/kg (114.4 ng TEQ/Nm^3).

Vikelsoe et al. (1993) studied emissions of CDD/CDF congener groups from residential wood stoves in Denmark. The wood fuels used in the experiments were seasoned birch, beech, and spruce, equilibrated to 18 percent absolute moisture. Four different types of stoves (including one experimental stove) were evaluated under both normal and optimal (i.e., well controlled with CO emission as low as possible) operating conditions. Widely varying total CDD/CDF emissions were found for the 24 different fuel/stove type/operating condition combinations. The emissions from spruce were about twice as high as the emissions 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 (considering wood and stove types) emission rate and emission factor for wood stoves were reported to be 1.9 ng Nordic-TEQ/kg and 0.18 ng Nordic-TEQ/Nm^3, respectively. Because Vickelsoe et al. (1993) 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.

Based on the results reported by Schatowitz et al. (1993) and Vickelsoe et al. (1993), 2 ng TEQ/kg appear to be a reasonable average emission factor for residential wood burning. A "low" confidence rating was assigned to this estimate on the basis that it

is derived from only two direct measurement studies. Although the studies were conducted in Europe, residential wood burning practices are probably sufficiently similar to apply to the United States.

In 1987, 22.5-million households in the United States burned wood (EIA, 1991). Of these households, wood was used in 1987 as the primary heating fuel in 5-million households and as a secondary source for aesthetic purposes (i.e., fireplaces) in 17.4-million households (EIA, 1991; EIA, 1997b). Lower numbers were reported for 1995; wood was reported to be used as the primary fuel in 3.53-million households (EIA, 1997b). More rural low-income households consume wood as a primary heating fuel than do other sectors of the population. The majority of these households use wood-burning stoves as the primary heating appliance. Although fireplaces are the most common type of wood-burning equipment in the residential sector, only 7 percent of fireplace users report use of fireplaces for heating an entire home (EIA, 1991; EIA, 1994).

Residential wood consumption in 1995 was 596-trillion Btu (31.4-million metric tons), or 25 percent of total U.S. wood energy consumption (EIA, 1997b). In 1987, residential wood consumption was 852-trillion Btu (44.8-million metric tons), or 35 percent of total U.S. consumption (EIA, 1997b). These production estimates are given "high" confidence ratings because they are based on recent government survey data.

Combining the best estimate of the emission factor (2 ng TEQ/kg wood) with the mass of wood consumed by residences in the years 1995 and 1987 indicates that the annual TEQ air emissions from this source were approximately 62.8 grams in 1995 and 89.6 grams in 1987. Based on the "low" confidence rating assigned to the emission factor, the estimated range of potential annual emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the best estimate of annual emissions in 1995 (62.8 g TEQ/yr) is the geometric mean of this range, then the range is calculated to be 19.8 to 198 g TEQ/yr. For 1987, the range is calculated to be 28.3 to 283 g TEQ/yr.

4.2.2. Industrial Wood Combustion

Congener-specific measurements of CDD/CDFs in stack emissions from industrial wood-burning furnaces were measured by the California Air Resources Board at four facilities in 1988 (CARB, 1990b; CARB, 1990e; CARB, 1990f; CARB, 1990g).

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) (1995) presented congener-specific emission factors for five boilers tested during burns of bark/wood residue. The average congener emission factors derived from the four CARB studies are presented in Table 4-12. Congener and congener group profiles are presented in Figure 4-5.

In CARB (1990b), CDD/CDFs were measured 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 gas passed through a multicyclone before entering the stack. From this study, average emission factors for total CDD/CDF and total TEQ are calculated to be 48.1 and 0.64 ng/kg of wood burned, respectively.

In CARB (1990e), CDD/CDFs were measured in the emissions from two spreader stoker wood-fired boilers operated in parallel by an electric utility for generating electricity. The exhaust gas stream from each boiler is passed through a dedicated ESP after which the gas streams are combined and emitted to the atmosphere through a common stack. Stack tests were conducted both when the facility burned fuels allowed by existing permits and when the facility burned a mixture of permitted fuel supplemented by urban wood waste at a ratio of 70:30. From this study, average emission factors for total CDD/CDF and total TEQ are calculated to be 29.2 and 0.82 ng/kg of wood burned, respectively.

In CARB (1990f), CDD/CDFs were measured in the emissions from a twin fluidized bed combustors designed to burn wood chips for the generation of electricity. The air pollution control device (APCD) system consisted of ammonia injection for controlling nitrogen oxides, and a multiclone and electrostatic precipitator for controlling particulate matter. During testing, the facility burned wood wastes and agricultural wastes allowed by existing permits. From this study, average emission factors for total CDD/CDF and total TEQ are calculated to be 47.9 and 1.32 ng/kg of wood burned, respectively.

In CARB (1990g), CDD/CDFs were measured in the emissions from a quad-cell wood-fired boiler. During testing, the fuel consisted of wood chips and bark. The flue gases passed through a multicyclone and an ESP before entering the stack. From this study, average emission factors for total CDD/CDF and total TEQ are calculated to be 27.4 and 0.50 ng/kg of wood burned, respectively.

The facility tested by EPA was located at a lumber products plant that manufactures overlay panels and other lumber wood products. The wood-fired boiler tested was a three-cell dutch oven equipped with a waste heat boiler. The feed wood was a mixture of bark, hogged wood, and green and dry planar shavings. Nearly all the wood fed to the lumber plant had been stored in sea water adjacent to the facility and, therefore, had a significant concentration of inorganic chloride. The exhausted gases from the boiler passed through a cyclone and fabric filter prior to discharge from the stack. From this study, an average emission factor for total CDD/CDF of 1,020 ng/kg of wood burned (range: 552 to 1,410 ng/kg) was reported. An average emission factor for TEQ of 17.1 ng/kg of wood burned (range: 7.34 to 22.8 ng/kg) was estimated by EPA using measured congener group concentrations and concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF. These emission factors from the burning of salt wood are significantly higher than those measured in the four CARB studies. This finding was consistent with the conclusion of NCASI (1995) that CDD/CDF emissions from facilities burning salt-laden wood residue may be considerably higher than from those burning salt-free wood.

NCASI (1995) presented stack emission test results for five boilers burning bark or wood residues. One of these facilities, equipped with a multicyclone, normally burns bark in combination with sludge and coal. One other facility, equipped with an ESP, normally fires pulverized coal. The other three facilities were spreader stokers equipped with multicyclones or ESPs. Although stack gas flow rates were obtained during these tests, accurate measurements of the amounts of bark/wood fired were not made and had to be estimated by NCASI (1995) from steam production rates. The average TEQ emission factor for these facilities was 0.4 ng/kg of feed.

The mean of the emission factors derived from the four CARB studies, 0.82 ng TEQ/kg wood (assuming nondetected values are zero), is used in this report as most representative of industrial wood combustion. The results of the EPA study were not used in the derivation of this mean emission factor because congener-specific measurements for most 2,3,7,8-substituted congeners were not made. Because congener-specific test data were available for these four facilities and because the mean TEQ emission factor derived from these test data is very similar to that estimated by NCASI (1995) for five wood-fired boilers, this emission factor was assigned a "medium" confidence rating.

It should be noted, however, that this emission factor (0.82 ng TEQ/kg wood) may not be an appropriate emission factor to apply to the combustion of waste wood containing elevated chlorine content. Umweltbundesamt (1996) reported the results of stack gas testing at approximately 30 facilities of varying design type as well as type of wood fuel combusted. Elevated CDD/CDF emissions were observed when the combustion conditions were poor, as evidenced by elevated carbon monoxide emissions, and/or when the fuel contained elevated chlorine levels. Umweltbundesamt (1996) attributed the correlation between elevated CDD/CDF emissions and elevated chlorine content of the fuel to the fire retardant effects of chlorine, which may have inhibited complete combustion. The chlorine content of untreated wood and bark were reported to range from 0.001 to 0.01 percent by weight and 0.01 to 0.02 percent by weight, respectively. Chipboard can contain up to 0.2 percent chlorine by weight because of binding agents used to manufacture the chipboard. Preservative-treated wood and PVC-coated wood were reported to contain chlorine contents as high as 1.2 and 0.3 percent by weight, respectively.

As discussed in Section 4.2, industrial wood consumption in 1995 totaled 35.5-million metric tons. The majority of wood fuel consumed in the industrial sector consists of wood waste (i.e., chips, bark, sawdust, and hogged fuel). Consumption in the industrial sector is dominated by two industries: the "Paper and Allied Products" industry - SIC 26 and the "Lumber and Wood Products" industry - SIC 24 (EIA, 1994). A similar amount, 33.5-million metric tons, was burned for fuel in industrial furnaces in 1987 (EIA, 1994). These activity level estimates are assigned a "high" confidence rating because they are based on recent government survey data.

Applying the average TEQ emission factor from the four CARB studies (0.82 ng TEQ/kg wood) to the estimated quantities of wood burned by industrial facilities in 1995 and 1987 yields estimated TEQ emissions to air of 29.1 g TEQ in 1995 and 27.5 g TEQ in 1987. Based on the "medium" confidence rating given to the TEQ emission factor, the estimated range of potential annual emissions is assumed to vary by a factor of five between the low and high ends of the range. Assuming that the estimates of annual emissions to air for these 2 years are the geometric means of the respective ranges, then the ranges are calculated to be 13.0 to 65.0 g TEQ in 1995 and 12.3 to 61.5 g TEQ in 1987.

4.3. OIL COMBUSTION

Two major categories of fuel oil are burned by combustion sources: distillate oils and residual oils. These oils are further distinguished by grade numbers, with Nos. 1 and 2 being distillate oils; Nos. 5 and 6 being residual oils; and No. 4 either distillate oil or a mixture of distillate and residual oils. No. 6 fuel oil is sometimes referred to as Bunker C. Distillate oils are more volatile and less viscous than residual oils. They have negligible nitrogen and ash contents and usually contain less than 0.3 percent sulfur (by weight). Distillate oils are used mainly in domestic and small commercial applications. Being more viscous and less volatile than distillate oils, the heavier residual oils (Nos. 5 and 6) must be heated for ease of handling and to facilitate proper atomization. Because residual oils are produced from the residue remaining after the lighter fractions (gasoline, kerosene, and distillate oils) are removed from the crude oil, they contain significant quantities of ash, nitrogen, and sulfur. Residual oils are used mainly in utility, industrial, and large commercial application (U.S. EPA, 1995b).

4.3.1. Residential/Commercial Oil Combustion

No testing of the CDD/CDF content of air emissions from residential/commercial oil-fired combustion units in the United States could be located. However, U.S. EPA (1997b) has estimated CDD/CDF congener group and TEQ emission factors based on 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 in U.S. EPA (1997b) was derived using the calculated emission factors for 2,3,7,8-TCDD, 2,3,7,8-TCDF, and the 10 congener groups. These emission factors are presented in Table 4-13, and the congener group profile is presented in Figure 4-6.

Because there are no direct measurements of CDD/CDF emissions in stack gases from U.S. residential oil-fired combustors and because of uncertainties associated with using chimney soot data to estimate stack emissions, no national emission estimates for this category are proposed at this time. However, a preliminary order of magnitude estimate of national TEQ emissions from this source category can be derived using the emission factor presented in Table 4-13 (150 pg TEQ/L of oil combusted). Distillate fuel oil sales to the residential/commercial sector totaled 39.7 billion liters in 1995 (EIA, 1997a).

Application of the TEQ emission factor of 150 pg TEQ/L to this fuel oil sales estimate results in estimated TEQ emissions of 6.0 g TEQ in 1995, which, when rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, results in a value of 10 g TEQ/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of the emissions.

4.3.2. Utility Sector and Industrial Oil Combustion

Preliminary CDD/CDF emission factors for oil-fired utility boilers developed from boiler tests conducted over the past several years are reported in U.S. EPA (1995c). The data are a composite of various furnace configurations and APCD systems. Table 4-14 lists the median emission factors presented in U.S. EPA (1995c; 1997b). The congener and congener group profiles based on these data are presented in Figure 4-7. The median TEQ emission factor was reported to be 314 pg/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. This project, the Field Chemical Emissions Measurement (FCEM) project, included testing of two cold side 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 also presented in Table 4-14. The average TEQ emission factor is 95.5 pg/L of oil burned when nondetected values are treated as zero (170 pg/L when nondetected values are treated as one-half the detection limit).

The TEQ emission factor reported in EPRI (1994) is a factor of three less than the median TEQ emission factor reported in U.S. EPA (1995c; 1997b). For purposes of this assessment, an emission factor of 200 pg/L (i.e., the average of 95.5 and 314 pg/L) is assumed to be current best estimate of the average TEQ emission factor for utility/industrial oil burning. This estimate is assigned a "low" confidence rating.

TEQ emission factors an order of magnitude larger were reported by Bremmer et al. (1994), based on measurements of CDD/CDF emission from three stationary used oil combustion units and from a ferry fired with a blend of used and virgin oil. Flue gases from a garage stove consisting of an atomizer fueled by spent lubricating oil from diesel engines (35 mg Cl^-/kg) were reported to contain 0.1 ng TEQ/Nm^3 (or 2 ng TEQ/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^-/kg) contained 0.2 ng TEQ/Nm^3 (or 4.8 ng TEQ/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^-/kg) contained 0.3 ng TEQ/Nm^3 (or 6.0 ng TEQ/kg of oil burned). The emission rate from the ferry (heavy fuel oil containing 11 ng/kg organic chlorine) was 3.2 to 6.5 ng TEQ/kg of oil burned. From these data, Bremmer et al. (1994) derived an average emission factor for combustion of used oil of 4 ng TEQ/kg of oil burned.

Bremmer et al. (1994) also reported measuring CDD/CDF emissions from a river barge and a container ship fueled with gas oil (less than 2 ng/kg of organic chlorine). The exhaust gases contained from 0.002 to 0.2 ng TEQ/Nm^3. From these data, Bremmer et al. (1994) derived an average emission factor for inland oil-fueled vessels of 1 ng TEQ/kg oil burned.

Residual fuel oil sales totaled 46.6-billion liters in 1995 and 77.3 billion liters in 1987 (EIA, 1992; 1997a). Vessel bunkering was the largest consumer (48 percent 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 200 pg/L to these residual fuel oil sales results in estimated TEQ emissions of 9.3 g TEQ in 1995 and 15.5 g TEQ in 1987. Based on the "low" confidence rating assigned to the emission factors, the estimated range of potential emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the estimate of TEQ emissions in 1995 (i.e., 9.3 g TEQ) is the geometric mean of the range, then the range is calculated to be 2.9 to 29 g TEQ/yr. For the year 1987, the range is calculated to be 4.9 to 49 g TEQ/yr.

4.4. COAL COMBUSTION

During 1995, coal consumption accounted for approximately 22 percent of the energy consumed from all sources in the United States (U.S. DOC, 1997). In 1995, 872-million metric tons of coal were consumed in the United States. Of this total, 88.4 percent (or 771-million metric tons) were consumed by electric utilities, 11.0 percent (or 96-million metric tons) were consumed by the industrial sector (including consumption of 30 million metric tons by coke plants), and 0.6 percent (or 5.3-million metric tons) were consumed by

residential and commercial sources (EIA, 1997b). Comparable figures for 1987 are: total consumption, 759-million metric tons; consumption by electric utilities, 651-million metric tons; consumption by coke plants, 33.5-million metric tons; consumption by other industries, 68.2-million metric tons; and consumption by the residential and commercial sectors, 6.3-million metric tons (EIA, 1995c). These production estimates are assigned a "high" confidence rating because they are based on detailed studies specific to the United States.

The following two subsections discuss the results of relevant emission studies for the utility/industrial and residential sectors and present annual emission estimates.

4.4.1. Utilities and Industrial Boilers

Until recently, few studies had been performed to measure CDD/CDF concentrations in emissions from coal-fired plants, and several of these studies did not have the congener specificity and/or detection limits necessary to fully characterize this potential source (U.S. EPA, 1987a; NATO, 1988; Wienecke et al., 1992). Recently, the results of testing of coal-fired utility and industrial boilers have been reported for facilities in The Netherlands, the United Kingdom, and the United States.

Bremmer et al. (1994) reported the results of emission measurements at two coal-fired facilities in The Netherlands. The emission rate from a pulverized coal electric power plant equipped with an ESP and a wet scrubber for sulfur removal was reported as 0.02 ng TEQ/Nm^3 (at 11 percent O_2) (or 0.35 ng TEQ/kg of coal fired). The emission rate for a grass drying chain grate stoker equipped with a cyclone APCD was reported to be 0.16 ng TEQ/Nm^3 (at 11 percent O_2) (or 1.6 ng TEQ/kg of coal fired). Cains and Dyke (1994) recently reported an emission rate of 102 to 109 ng TEQ/kg of coal at a small-scale facility in the United Kingdom that was equipped with an APCD consisting only of a grit arrestor. Umweltbundesamt (1996) reported that the TEQ content of stack gases from 16 coal-burning facilities in Germany ranged from 0.0001 to 0.04 ng TEQ/m^3; the data provided in this report did not enable emission factors to be calculated.

The U.S. Department of Energy sponsored a project in 1993 to assess emissions of hazardous air pollutants at coal-fired power plants. As part of this project, CDD/CDF stack emissions were measured at seven U.S. coal-fired power plants. The preliminary results of this project (i.e., concentrations in stack emissions) were reported by Riggs et al. (1995)

and are summarized in Table 4-15. The levels reported for individual 2,3,7,8-substituted congeners were typically not detected or very low (i.e., ≤0.033 ng/Nm^3). In general, CDF levels were higher than CDD levels. OCDF and 2,3,7,8-TCDF were the most frequently detected congeners (i.e., at four of the seven plants). Table 4-16 presents characteristics of the fuel used and APCD employed at each plant. Variation in emissions between plants could not be attributed by Riggs et al. (1995) to any specific fuel or operational characteristic.

During the early 1990s, EPRI also sponsored a project to gather information of consistent quality on power plant emissions. This project, the Field Chemical Emissions Measurement (FCEM) project, included testing of four cold-side ESP-equipped coal-fired power plants for CDD/CDF emissions. Two plants burned bituminous coal and two burned subbituminous coal. The final results of the DOE project discussed above were integrated with the results of the EPRI testing and published in 1994 (EPRI, 1994). The average congener and congener group emission factors derived from this 11 facility data set, as reported in EPRI (1994), are presented in Table 4-17. Congener and congener group profiles for the data set are presented in Figure 4-8. The average TEQ emission factor, assuming nondetected values are zero, is 0.087 ng/kg of coal combusted. The average TEQ emission rate, assuming nondetected values are one-half the detection limit, is 0.136 ng/kg of coal combusted. A "medium" confidence rating is assigned to these emission factors because they are based on recent testing at U.S. facilties.

As stated above, consumption of coal by the U.S. utility and industrial sectors (excluding consumption at coke plants) was 837-million metric tons in 1995 and 719-million metric tons in 1987. Applying the TEQ emission factor of 0.087 ng TEQ/kg of coal combusted to these production factors yields estimated annual emissions of 72.8 g TEQ in 1995 and 62.6 g TEQ in 1987.

Based on the "medium" confidence rating assigned to the estimated TEQ emission factor, the estimated range of potential emissions is assumed to vary by a factor of five between the low and high ends of the range. Assuming that the estimated emissions (assuming nondetected values are zero) of 72.8 g TEQ in 1995 and 62.6 g TEQ in 1987 are the geometric means of these ranges for these years, then the ranges are calculated to be 32.6 to 163 g TEQ in 1995 and 28 to 140 g TEQ in 1987.

4.4.2. Residential/Commercial Coal Combustion

Coal is usually combusted in underfeed or hand-stoked furnaces in the residential sector. 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 are 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 and CDD/CDF; therefore, the potential for CDD/CDF formation exists. Typically, coal-fired residential furnaces are not equipped with particulate matter or gaseous pollutant control devices that may limit emissions of any CDD/CDFs formed (U.S. EPA, 1997b). No testing of the CDD/CDF content of 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 CDD/CDF from a household heating system in Germany, fired either with "salt" lignite coal (i.e., total chlorine content of 2,000 ppm) or "normal" lignite coal (i.e., total chlorine content of 300 ppm). CDD/CDFs were detected in the flue gases generated by combustion of both fuel types. (See Table 4-18.) 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 for the "salt" coal (0.109 ng TEQ/m^3 or 2.74 ng TEQ/kg of coal) by a factor of eight than for the "normal" coal (0.015 ng TEQ/m^3 or 0.34 ng TEQ/kg of coal).

Eduljee and Dyke (1996) used the results of testing performed by the Coal Research Establishment in the United Kingdom to estimate emission factors for residential coal combustion units as follows:

- Anthracite coal: 2.1 ng TEQ/kg of coal; and
- Bituminous coal: 5.7 to 9.3 ng TEQ/kg of coal (midpoint of 7.5 ng TEQ/kg).

CDD/CDF emission factors for coal-fired residential furnaces were estimated in U.S. EPA (1997b) based on average particulate CDD/CDF concentrations from chimney soot samples collected from seven coal ovens, and particulate matter emission factors specific to anthracite and bituminous coal combustion obtained from AP-42 (U.S. EPA, 1995b). The TEQ emission factors estimated in U.S. EPA (1997b) (i.e., 68.0 and 98.5 ng TEQ/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) stated that the estimated factors should be considered to represent maximum emission factors, because soot may not be representative of the particulate matter actually emitted to the atmosphere. These emission factors are presented in Table 4-18, and congener group profiles are presented in Figure 4-9.

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

Because there are no direct measurements of CDD/CDF emissions from U.S. residential coal-fired combustors and because of uncertainties regarding the comparability of U.S. and German and British coal and combustion units, no national emission estimate for this category is proposed at this time. However, a preliminary order of magnitude estimate of national TEQ emissions from this source category can be derived using the emission factors of Eduljee and Dyke (1996). As noted above, 5.3-million metric tons of coal were consumed by the residential/commercial sector in 1995 (U.S. DOC, 1997). U.S. EPA (1997b) reports that 72.5 percent of the coal consumed by the residential sector in 1990 were bituminous and 27.5 percent were anthracite. Assuming that these relative proportions reflect the actual usage in 1995, then application of the emission factors from Eduljee and Dyke (1996) (i.e., 2.1 ng TEQ/kg of anthracite coal and 7.5 ng TEQ/kg of bituminous coal) to the consumption value of 5.3-million metric tons results in an estimated TEQ emission of 32.0 g TEQ in 1995, which, when rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, results in a value of 10 g TEQ/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

Table 4-1. Descriptions and Results of Vehicle Emission Testing Studies for CDDs and CDFs

Study	Country	Fuel Type	Scavenger[a]	Catalyst Equipped	Number of Test Vehicles	Emission Factor (pg TEQ/km driven)	Driving Cycle; Sampling Location
CARB (1987a); Lew (1996)	United States	Diesel (truck)	No	NR	1	663-1,300	6-hr dynamometer test at 50 km/hr
Marklund et al. (1987)	Sweden	Unleaded	No	Yes	2	not detected (<13)	A10 (2 cycles); muffler exhaust
		Leaded	Yes	No	4	approx. 20-220	A10 (2 cycles); muffler exhaust
Bingham et al. (1989)	New Zealand	Unleaded	No	NR	1	1	A10 (3 or 4 cycles); muffler exhaust
		Leaded	Yes	NR	4	5-39	A10 (3 or 4 cycles); muffler exhaust
Marklund et al. (1990)	Sweden	Unleaded	No	No	2	0.36-0.39	FTP-73 test cycle; before muffler
		Leaded	Yes	No	2	2.4-6.3	FTP-73 test cycle; before muffler
		Unleaded	No	Yes	1	0.36	FTP-73 test cycle; in tailpipe
		Leaded	Yes	No	2	1.1-2.6[e]	FTP-73 test cycle; in tailpipe
		Diesel (truck)	No	NR	1	not detected (<18)[b]	U.S. Federal mode 13 cycle; before muffler
Hagenmaier et al. (1990)	Germany	Unleaded	No	No	1	5.1[b]	Comparable to FTP-73 test cycle; in tailpipe
		Unleaded	No	Yes	1	0.7[b]	Comparable to FTP-73 test cycle; in tailpipe
		Leaded	Yes	No	1	108[b]	Comparable to FTP-73 test cycle; in tailpipe
		Diesel (car)	No	NR	1	2.4[b]	Comparable to FTP-73 test cycle; in tailpipe
Oehme et al. (1991) (tunnel study)	Norway	---	---	---	(c)	520[d]	Cars moving uphill (3.5% incline) at 60 km/hr
						38[d]	Cars moving downhill (3.5% decline) at 70 km/hr
						avg = 280	
						9,500[d]	Trucks moving uphill (3.5% incline) at 60 km/hr
						720[d]	Trucks moving downhill (3.5% decline) at 70 km/hr
						avg = 5,100	
Schwind et al. (1991) Hutzinger et al. (1992)	Germany	Leaded	Yes	No	1	5.2-118[b]	Various test conditions (i.e., loads and speeds)
		Unleaded	No	No	1	5.7-17.7[b]	Various test conditions (i.e., loads and speeds)
		Unleaded	No	Yes	1	1.5-2.6[b]	Various test conditions (i.e., loads and speeds)
		Diesel (car)	No	No	1	5.0-13[b]	Various test conditions (i.e., loads and speeds)
		Diesel (truck)	No	No	1	13-15[b]	Various test conditions (i.e., loads and speeds)
Gertler et al. (1996) (tunnel study)	United States	Diesel (truck)	---	---	(f)	mean = 172	Mean of seven 12-hour samples
Gullett and Ryan (1997)	United States	Diesel (truck)	No	---	1	mean - 29.0	Mean of five sample routes

[a] Dichloroethane and dibromoethane, except for Marklund et al. (1987), used as scavengers.

[b] Results reported were in units of pg TEQ/liter of fuel. For purposes of this table, the fuel economy factor used by Marklund et al. (1990), 10 km/L or 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 (or 13.2 miles/gal), was used.

[c] Tests were conducted over portions of 4 days, with traffic rates of 8,000-14,000 vehicles/day. Heavy duty vehicles (defined as vehicles over 7 meters in length) ranged from 4-15% of total.

[d] Emission factors are reported in units of pg Nordic TEQ/km driven; the values in units of I-TEQ/km are expected to be about 3 to 6 percent higher.

[e] 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 TEQ/km.

[f] Tests were conducted over 5 days with heavy-duty vehicle rates of 1,800-8,700 vehicles per 12-hour sampling event. Heavy-duty vehicles accounted for 21-28 percent of all vehicles.

NR = Not Reported

Table 4-2. Diesel-Fueled Automobile CDD/CDF Congener Emission Factors

Congener/Congener Group	Automobile Tailpipe Emission Study Results				Mean Emission Factors	
	63 km/hr (Ref. A) (pg/L)	Idling (test no. 25) (Ref. B) (pg/L)	57 km/hr (test no. 24) (Ref. B) (pg/L)	57 km/hr (full load) (test no. 28) (Ref. B) (pg/L)	Assuming ND = zero (pg/L)	Assuming ND = 1/2 det limit (pg/L)
2,3,7,8-TCDD	7.9	13.1	2.4	22	11.4	11.4
1,2,3,7,8-PeCDD	9.0	6.3	4.1	23	10.6	10.6
1,2,3,4,7,8-HxCDD	ND (5.1)	21.4	1.0	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	2.0	10	10.0	10.6
1,2,3,4,6,7,8-HpCDD	44.1	107	22.9	166	85.0	85.0
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	71.0	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	3.0	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	501.0	846.8	558.8	809.8	679.1	681.0
Total 2,3,7,8-CDF	184.4	958.7	158.2	1117.5	604.7	606.7
Total TEQ (ND = zero)	20.8	100.7	10.4	129.6	65.4	
Total TEQ (ND = 1/2 det limit)	22.2*	100.7	10.4	129.6		65.7
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	3093	916	916
Total PeCDF	39.3	821	36	1205	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 (ND = zero)	926.3	3,957	968	7,018	3,217	
Total CDD/CDF (ND = 1/2 det limit)	926.3	3,957	968	7,018		3,217

ND = Not detected; value in parentheses is the detection limit.
* = A TEQ of 23.6 pg/L is reported in Ref. A; however, a TEQ of 22.2 pg/L is calculated based on reported congener levels.

Ref. A: Hagenmaier et al. (1990)
Ref. B: Schwind et al. (1991); Hutzinger et al. (1992)

Table 4-3. Diesel-Fueled Truck CDD/CDF Congener Emission Factors

Congener/Congener Group	Truck Tailpipe Study Results			Mean Emission Factors	
	50 km/hr (test no. 40) (Ref. A) (pg/L)	90 km/hr (full load) (test no. 42) (Ref. A) (pg/L)	50 km/hr (Ref. B) (pg/L)	Assuming ND = zero (pg/L)	Assuming ND = 1/2 det lim (pg/L)
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	14.0	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	1,355	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)	23.0	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 TEQ (ND = zero)	81	70	3,720	1,290	
Total TEQ (ND = 1/2 det limit)	81	70	7,290		2,480
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	1355	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 (ND = zero)	4,340	2,778	1,080,500	362,538	
Total CDD/CDF (ND = 1/2 det limit)	4,340	2,778	1,104,700		370,596

ND = Not detected; value in parentheses is the detection limit.

Ref. A: Schwind et al. (1991); Hutzinger et al. (1992)
Ref. B: Lew (1993; 1996)

Table 4-4. Leaded Gasoline-Fueled Automobile CDD/CDF Congener Emission Factors

Congener/Congener Group	Automotive Tailpipe Emission Study Results							Mean Emission Factors	
	FTP cycle (Ref. A) (pg/L)	63 km/hr (Ref. B) (pg/L)	Idling (test no. 12) (Ref. C) (pg/L)	Full load (test no. 13) (Ref. C) (pg/L)	64 km/hr (test no. 14) (Ref. C) (pg/L)	Rated power (test no. 15) (Ref. C) (pg/L)	FTP cycle (test no. 22) (Ref. C) (pg/L)	Assuming ND = zero (pg/L)	Assuming ND = 1/2 det limit (pg/L)
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	1166	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	1857	1861
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 TEQ (ND = zero)	65.9	1,075	≥ 52	≥ 300	≥ 1,184	≥ 56	419	≥ 450	
Total TEQ (ND = 1/2 det limit)	102	1,083	≥ 52	≥ 300	≥ 1,184	≥ 56	419		≥ 457
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 (ND = zero)	22,950	85,937	6,199	≥ 36,326	94,597	74,160	19,480	≥ 49,066	
Total CDD/CDF (ND = 1/2 det limit)	23,940	85,937	6,199	≥ 36,326	94,597	74,160	19,480		≥ 49,212

NR = Not reported.
ND = Not detected; value in parentheses is the reported detection limit.

Ref. A: 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).
Ref. B: Hagenmaier et al. (1990)
Ref. C: Schwind et al. (1991); Hutzinger et al. (1992)

Table 4-5. Unleaded Gasoline-Fueled (Without Catalytic Converters) Automobile CDD/CDF Congener Emission Factors

Congener/Congener Group	Automotive Tailpipe Emission Study Results						Mean Emission Factors	
	FTP cycle (Ref. A) (pg/L)	63 km/hr (Ref. B) (pg/L)	FTP cycle (test no. 21) (Ref. C) (pg/L)	64 km/hr (test no. 17) (Ref. C) (pg/L)	64 km/hr (test no. 20) (Ref. C) (pg/L)	64 km/hr (test no. 31/2) (Ref. C) (pg/L)	Assuming ND = zero (pg/L)	Assuming ND = 1/2 det limit (pg/L)
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	18.0	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	17.0	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	44.0	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	418.0	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	909	936
Total TEQ (ND = zero)	6.4	50.9	96.4	122	144	177	99.5	
Total TEQ (ND = 1/2 det limit)	26.2	50.9	96.4	122	144	177		103
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	1540	1540
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 (ND = zero)	183	3,963	5,076	6,431	4,421	15,176	5875	
Total CDD/CDF (ND = 1/2 det limit)	249	3,963	5,076	6,431	4,421	15,176		5886

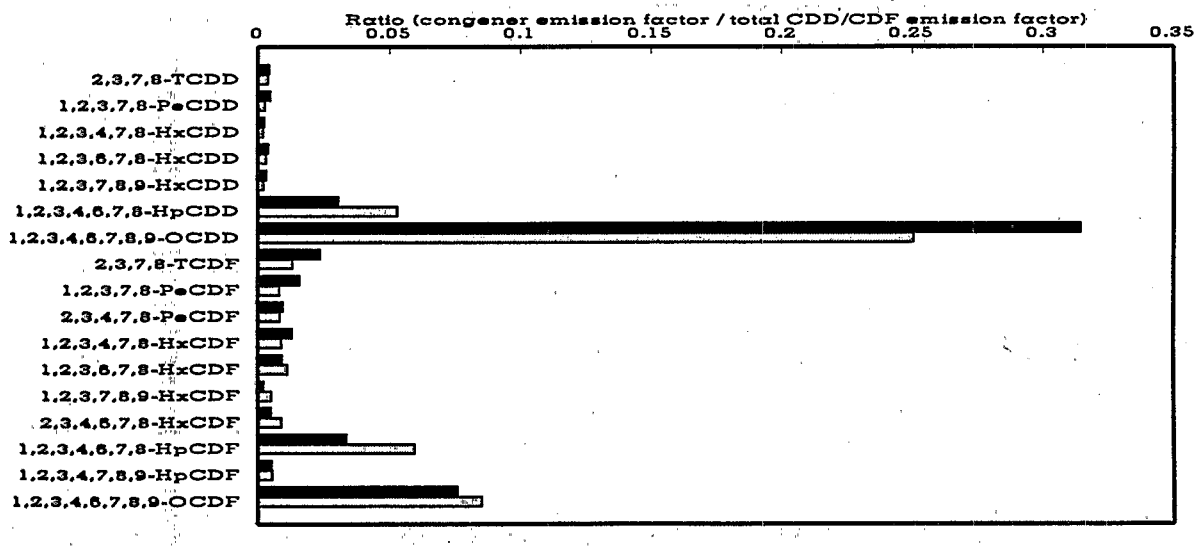
ND = Not detected; value in parentheses is the reported detection limit.

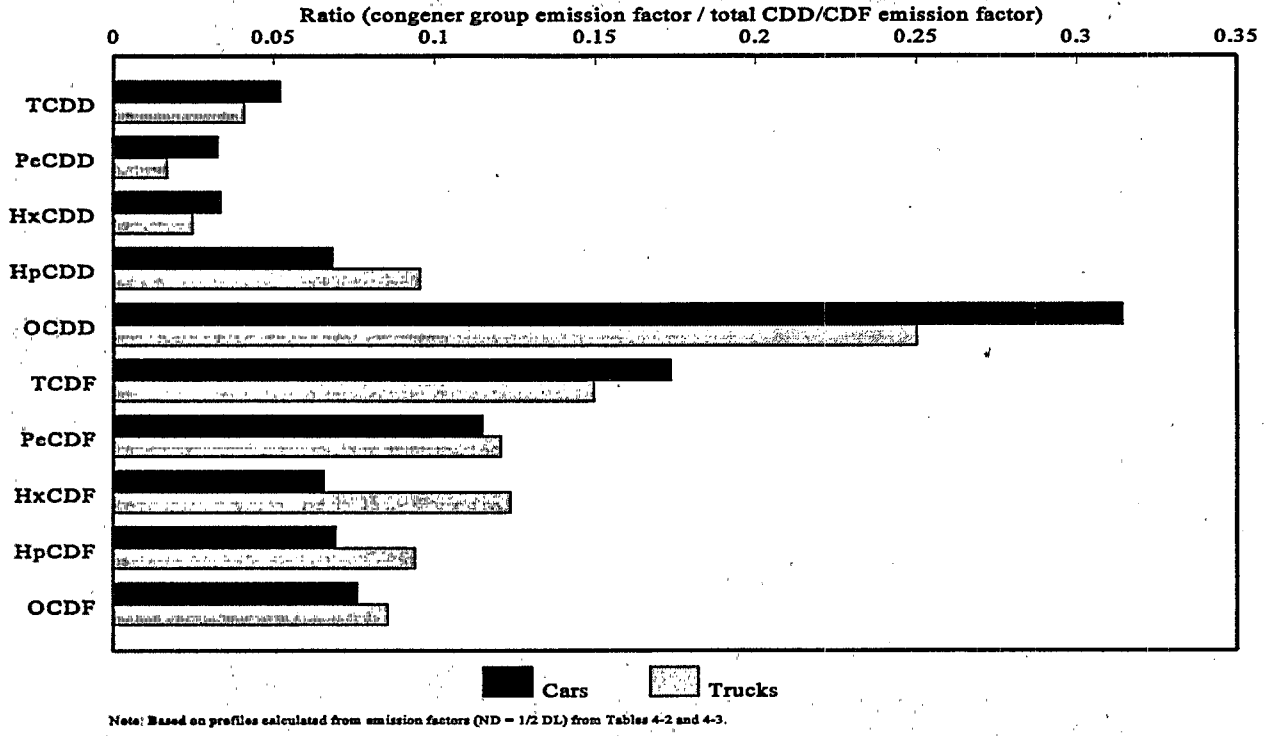
Ref. A: Marklund et al. (1990); values in the table were calculated from the reported units of pg/km to pg/L assuming a fuel economy of 10 km/L for unleaded gas.
Ref. B: Hagenmaier et al. (1990)
Ref. C: Schwind et al. (1991); Hutzinger et al. (1992)

Table 4-6. Unleaded Gasoline-Fueled (With Catalytic Converters) Automobile CDD/CDF Congener Emission Factors

Congener/Congener Group	Automotive Tailpipe Emission Study Test Results				Mean Emission Factors	
	63 km/hr (Ref. A) (pg/L)	64 km/hr (test no. 29I) (Ref. B) (pg/L)	64 km/hr (test no. 30/2) (Ref. B) (pg/L)	64 km/hr (test no. 18) (Ref. B) (pg/L)	Assuming ND = zero (pg/L)	Assuming ND = 1/2 det limit (pg/L)
2,3,7,8-TCDD	1.6	3.0	ND (7.9)	14	4.7	5.6
1,2,3,7,8-PeCDD	1.6	2.6	ND (7.9)	4	2.1	3.0
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	6.0	6.4	2	4.5	4.5
1,2,3,7,8,9-HxCDD	3.1	6.0	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	69.0	69.0
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	78.0	78.0
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 TEQ (ND = zero)	7.2	16	10	26	15	
Total TEQ (ND = 1/2 det limit)	7.2	16	17	26		17
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	78.0	78.0
Total CDD/CDF (ND = zero)	483.4	928	1,095	1,133	910	
Total CDD/CDF (ND = 1/2 det limit)	483.4	928	1,087	1,133		945

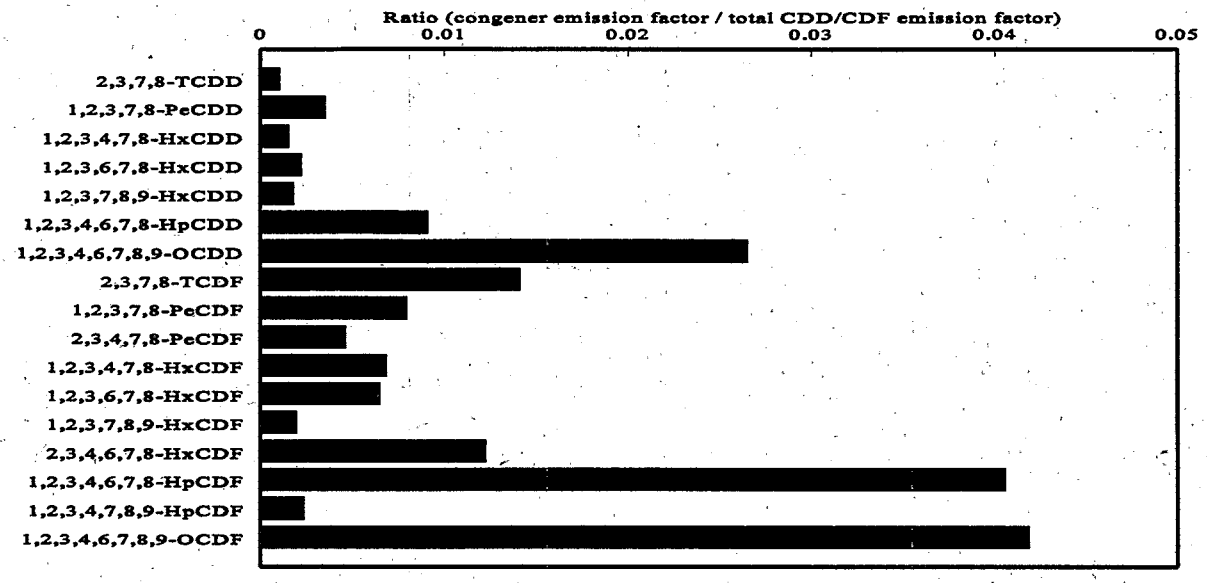
ND = Not detected; value in parentheses is the reported detection limit.
Ref. A: Hagenmaier et al. (1990)
Ref. B: Schwind et al. (1991); Hutzinger et al. (1992)

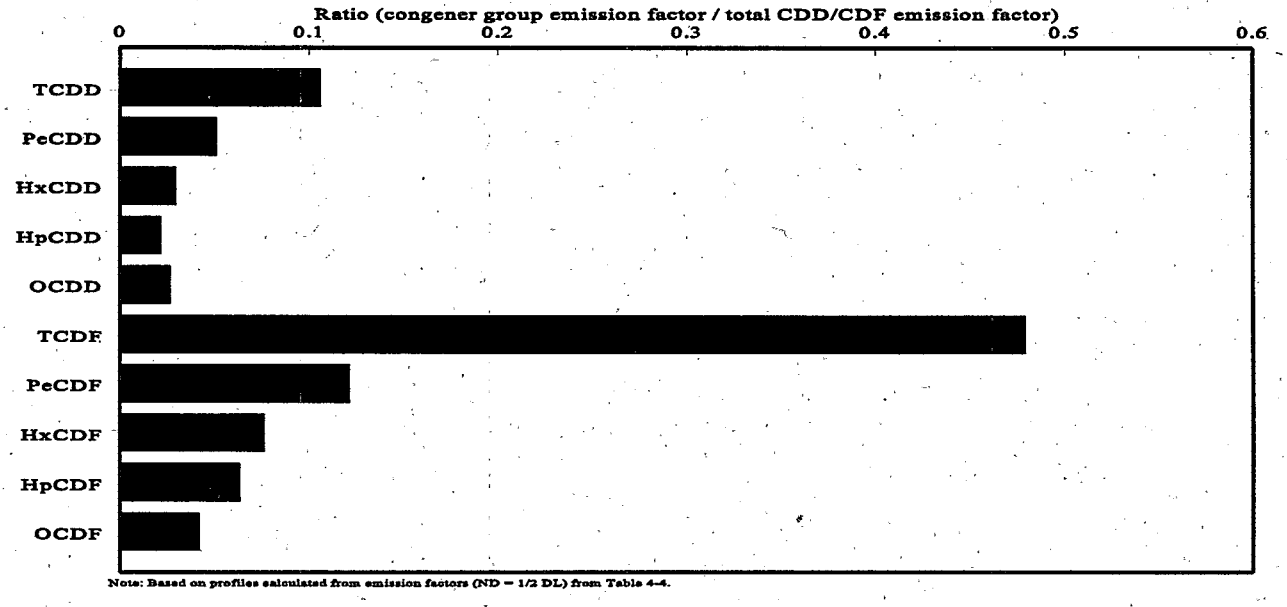




Note: Based on profiles calculated from emission factors (ND = 1/2 DL) from Tables 4-2 and 4-3.

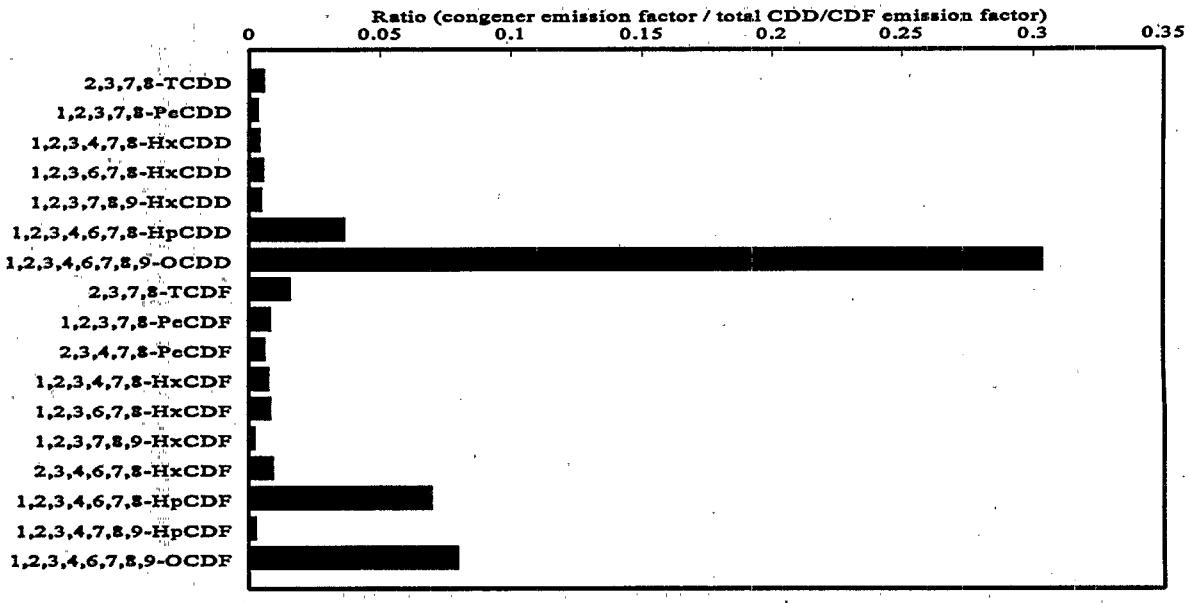
Figure 4-1. Congener and Congener Group Profiles for Air Emissions from Diesel-fueled Vehicles

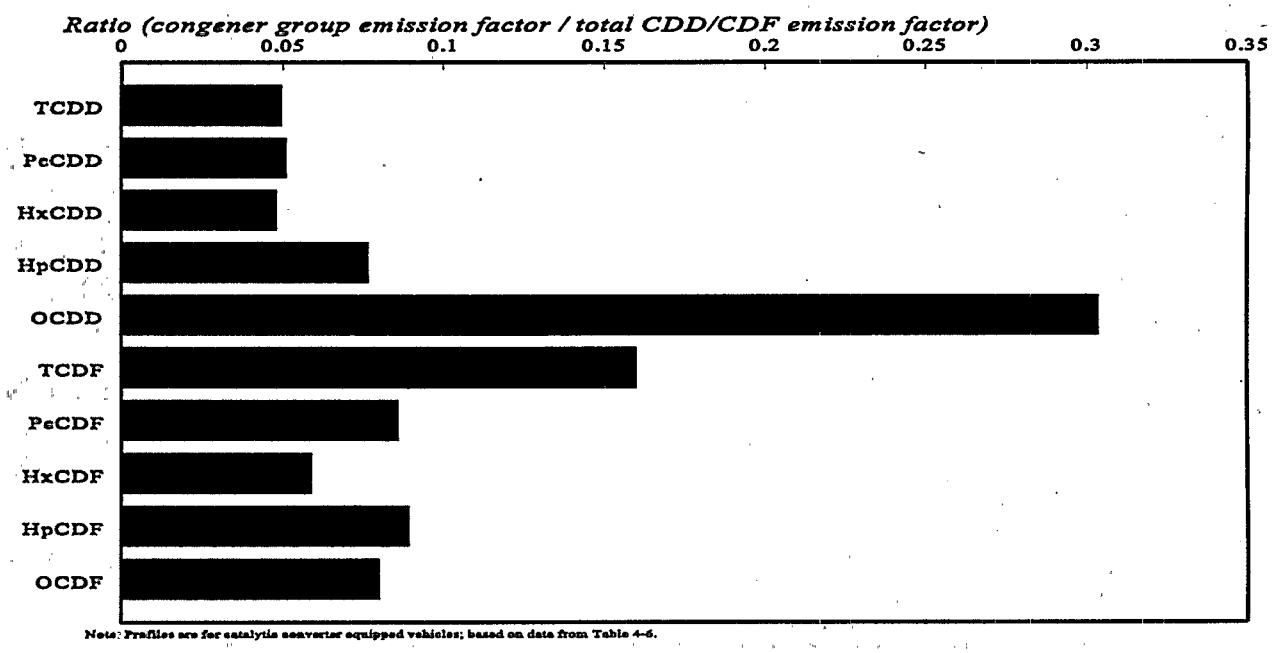




Note: Based on profiles calculated from emission factors (ND = 1/2 DL) from Table 4-4.

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

Table 4-7. European Tunnel Study Test Results

Congener/Congener Group	Tunnel Air Germany (Ref. A) (pg/m3)	Tunnel Air Germany (Ref. A) (pg/m3)	Tunnel Air Belgium (Ref. B) (pg/m3)	Tunnel Air Norway (workdays)[a] (Ref. C) (pg/m3)	Tunnel Air Norway (weekend)[a] (Ref. C) (pg/m3)
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)	0.030	0.25	0.06
1,2,3,4,6,7,8-HpCDD	1.9	2.0	0.468	1.41	0.16
OCDD	6.3	6.4	2.190	0.10	0.50
2,3,7,8-TCDF	0.17	0.72	0.013	0.58	0.07
1,2,3,7,8-PeCDF	0.40	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)	0.250	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	2.50	2.34	1.330	7.98	5.82
Total TEQ	0.58	0.42	0.096	0.91	0.48
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	0.10	0.50
Total TCDF	3.5	6.2	NR	13.20	1.70
Total PeCDF	3.6	4.1	NR	10.17	7.91
Total HxCDF	2.0	1.1	NR	6.42	2.08
Total HpCDF	1.9	1.2	NR	2.62	1.41
Total OCDF	ND (1.3)	ND (1.0)	NR	1.62	2.54
Total CDD/CDF	31.2	26.6	NR	38.80	17.06

ND = Not detected; value in parentheses is the detection limit.

Ref. A: Rappe et al. (1988)
Ref. B: Wevers et al. (1992)
Ref. C: Oehme et al. (1991)

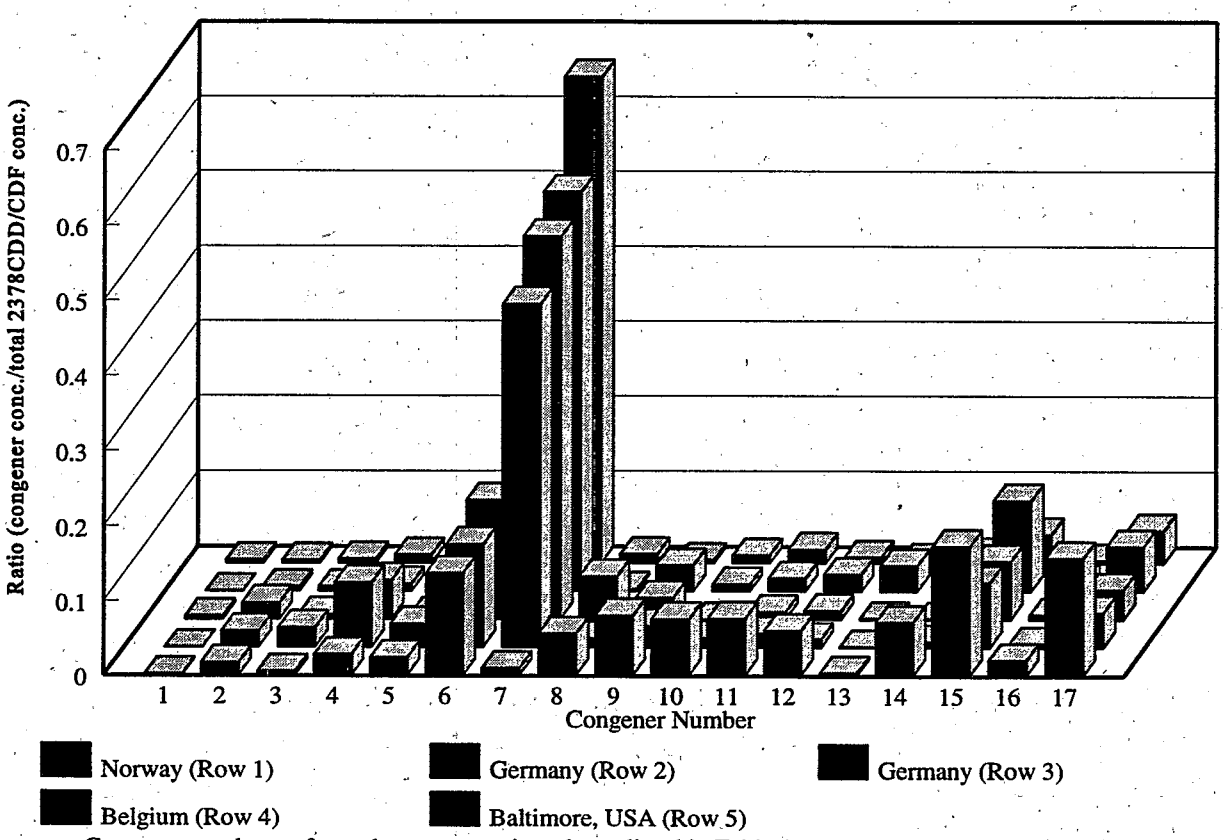
[a] Listed values are the differences between the concentrations at the inlet and outlet of the northbound tunnel lanes.

Table 4-8. Baltimore Harbor Tunnel Study: Estimated Emission Factors for Heavy-Duty (HD) Diesel Vehicles

Congener/Congener Group	Run-Specific Emission Factors							Mean Emission Factors (pg/km)
	Run No. 2 (pg/km)	Run No. 3 (pg/km)	Run No. 5 (pg/km)	Run No. 6 (pg/km)	Run No. 8 (pg/km)	Run No. 9 (pg/km)	Run No. 10 (pg/km)	
2,3,7,8-TCDD	24.5	61.6	0.0	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	0.0	83.0	29.0
1,2,3,4,7,8-HxCDD	18.2	25.2	46.5	8.3	64.5	0.0	123	40.8
1,2,3,6,7,8-HxCDD	37.5	28.2	64.3	19.6	153	71.1	186	80.0
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	0.0	43.3	34.5
2,3,4,7,8-PeCDF	24.5	75.7	131	46.6	85.0	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	51.0	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	93.0	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	25.0	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	1,335	12,743	7,028	10,515	5,725
Total 2,3,7,8-CDF	95.7	1,108	1,684	784	1,347	1,371	1,362	1,107
Total TEQ	73.8	175	170	96	235	153	303	172
Total TCDD	245	0	140	165	311	109	97.3	152
Total PeCDD	110	21.9	83.3	35.6	174	0.0	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	3361	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
HD vehicles as % of total vehicles	21.2	22.0	22.6	34.0	28.8	24.2	27.4	25.7

Source: Gertler et al. (1996)

Notes:
1) Listed values are based on the difference between the calculated chemical mass entering the tunnel and the mass exiting the tunnel.
2) All calculated negative emission factors were set equal to zero.
3) All CDD/CDF emissions were assumed to result from heavy-duty diesel fueled vehicles. The table presents in the last row the percent of total traffic that was heavy-duty vehicles.



Congener numbers refer to the congeners in order as listed in Table 4-7.

Figure 4-4. Tunnel Air Concentrations

Table 4-9. CDD/CDF Concentrations in Residential Chimney Soot from Wood Stoves and Fireplaces

Congener/Congener Group	U.S. East Region (Ref. A) (ng/kg)	U.S. West Region (Ref. A) (ng/kg)	U.S. Central Region (Ref. A) (ng/kg)	German Farmhouse (Ref. B) (ng/kg)	Canadian Wood Stove (Ref. C) (ng/kg)	Canadian Fireplace (Ref. C) (ng/kg)	Canadian Wood Stove (Ref. D) (ng/kg)
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*	522*	1,831*	35	NR	NR	ND (10)
1,2,3,6,7,8-HxCDD	250*	522*	1,831*	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 TEQ	126	112	459	720	NR	NR	211
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	8,783

NR = Not reported.
* = Analytical method could not distinguish between congeners; listed value is the sum of both congeners.

Ref. A: Nestrick and Lamparski (1982; 1983); mean values listed - six samples collected in each Region.
Ref. B: Bacher et al. (1992)
Ref. C: Clement et al. (1985b)
Ref. D: Van Oostdam and Ward (1995); mean of two samples - nondetected values assumed to be zero.

Table 4-10. CDD/CDF Concentrations in Residential Bottom Ash from Wood Stoves and Fireplaces

Congener/Congener Group	Canadian Wood Stove (Ref. A) (ng/kg)	Canadian Wood Stove (Ref. A) (ng/kg)	Canadian Wood Stove (Ref. A) (ng/kg)	Canadian Fireplace (Ref. A) (ng/kg)
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.
Ref. A: Clement et al. (1985b)

Table 4-11. CDD/CDF Concentrations in Chimney Soot (Bavaria, Germany)

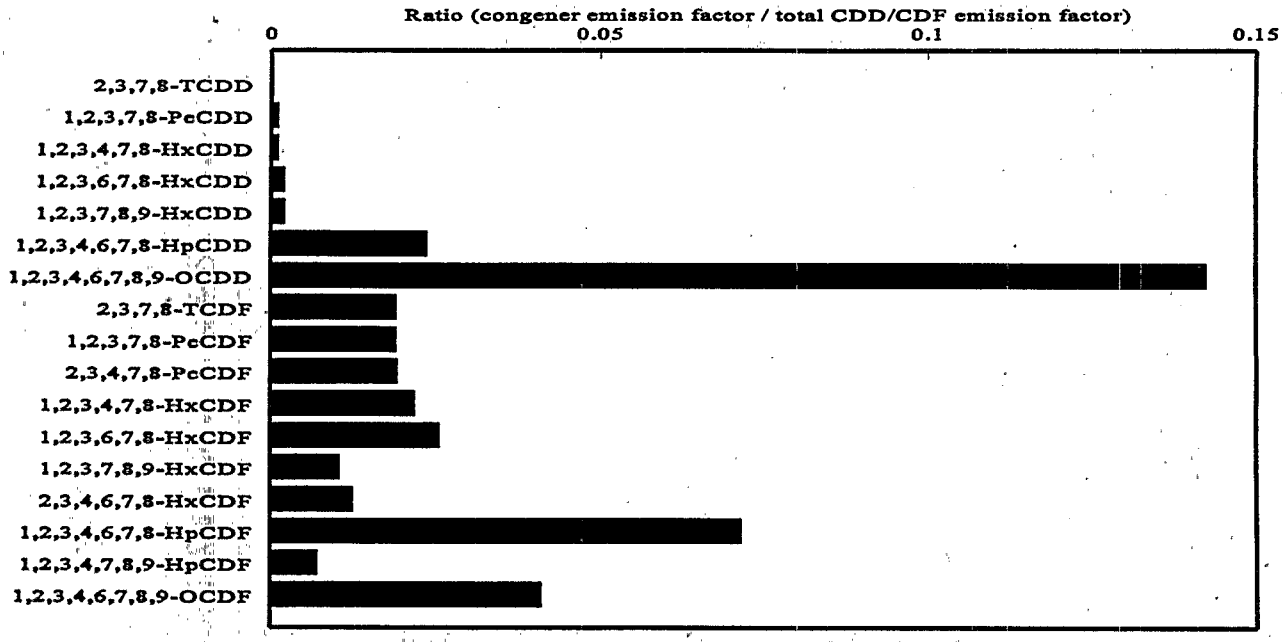
Unit Type	Fuel Type	Number of Samples	CDD/CDF Concentrations in Soot (ng TEQ/kg)		
			Minimum	Mean	Maximum
Oven	Wood	33	10.4	2,015	15,849
Tiled Stove	Wood	39	4.0	3,453	42,048
Heating System	Wood	9	16.9	1,438	20,450
Oven	Wood/coal	27	77.3	2,772	10,065
Tiled Stove	Wood/coal	5	53.1	549	4,911
Oven	Wood, wood/coal, waste	5	116.3	6,587	10,652

Source: Dumler-Gradl et al. (1995a).

Table 4-12. CDD/CDF Emission Factors for Industrial Wood Combustors

Congener	Four facilities tested by CARB Mean Emission Factors (ng/kg wood)	
	Nondetects Set to Zero	Nondetects Set to 1/2 Det. Limit
2,3,7,8-TCDD	0.007	0.016
1,2,3,7,8-PeCDD	0.044	0.054
1,2,3,4,7,8-HxCDD	0.042	0.055
1,2,3,6,7,8-HxCDD	0.086	0.096
1,2,3,7,8,9-HxCDD	0.079	0.132
1,2,3,4,6,7,8-HpCDD	0.902	0.905
OCDD	6.026	6.026
2,3,7,8-TCDF	0.673	0.672
1,2,3,7,8-PeCDF	0.790	0.790
2,3,4,7,8-PeCDF	0.741	0.741
1,2,3,4,7,8-HxCDF	0.761	0.768
1,2,3,6,7,8-HxCDF	0.941	0.941
1,2,3,7,8,9-HxCDF	0.343	0.350
2,3,4,6,7,8-HxCDF	0.450	0.491
1,2,3,4,6,7,8-HpCDF	2.508	2.749
1,2,3,4,7,8,9-HpCDF	0.260	0.344
OCDF	1.587	1.590
Total TCDD	0.151	0.154
Total PeCDD	1.039	1.039
Total HxCDD	1.748	1.748
Total HpCDD	2.936	2.936
Total OCDD	6.026	6.026
Total TCDF	4.275	4.275
Total PeCDF	9.750	9.750
Total HxCDF	7.428	7.428
Total HpCDF	3.747	3.988
Total OCDF	1.588	1.590
Total TEQ	0.82	0.85
Total CDD/CDF	38.69	38.93

Sources: CARB (1990b); CARB (1990e); CARB (1990f); CARB (1990g)



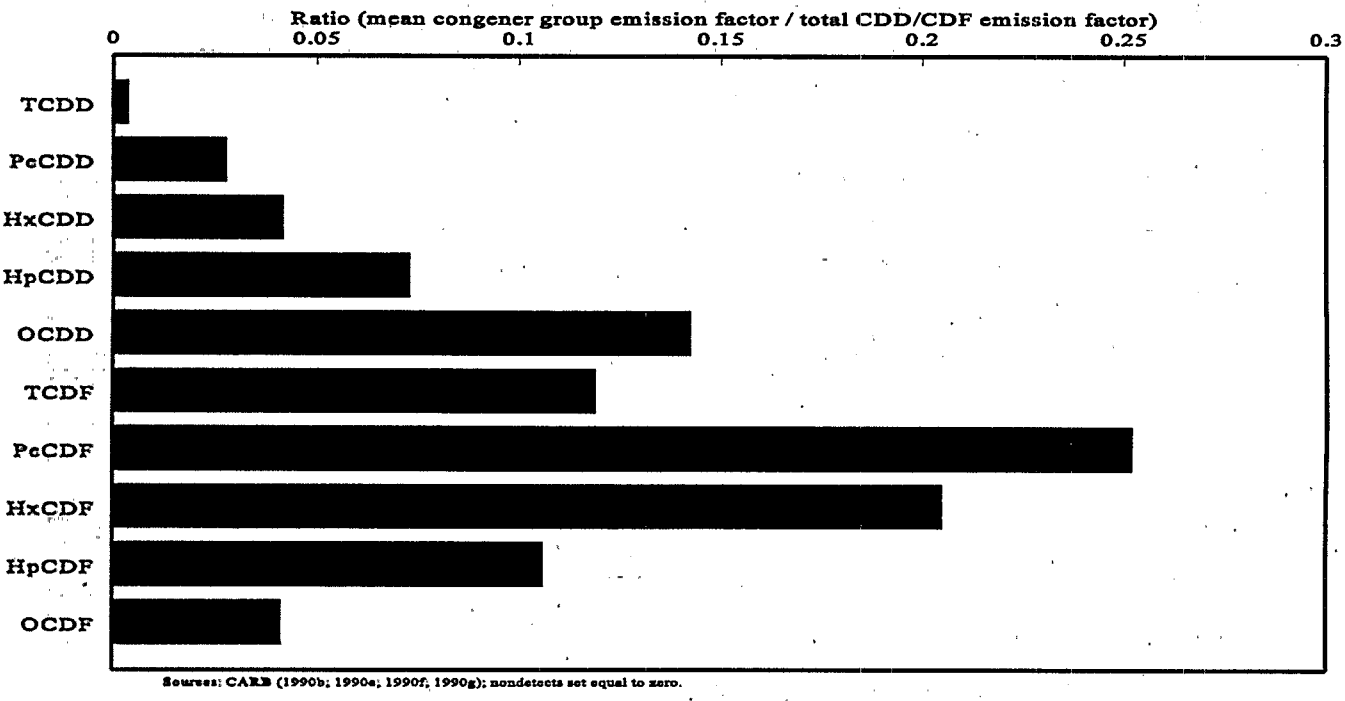


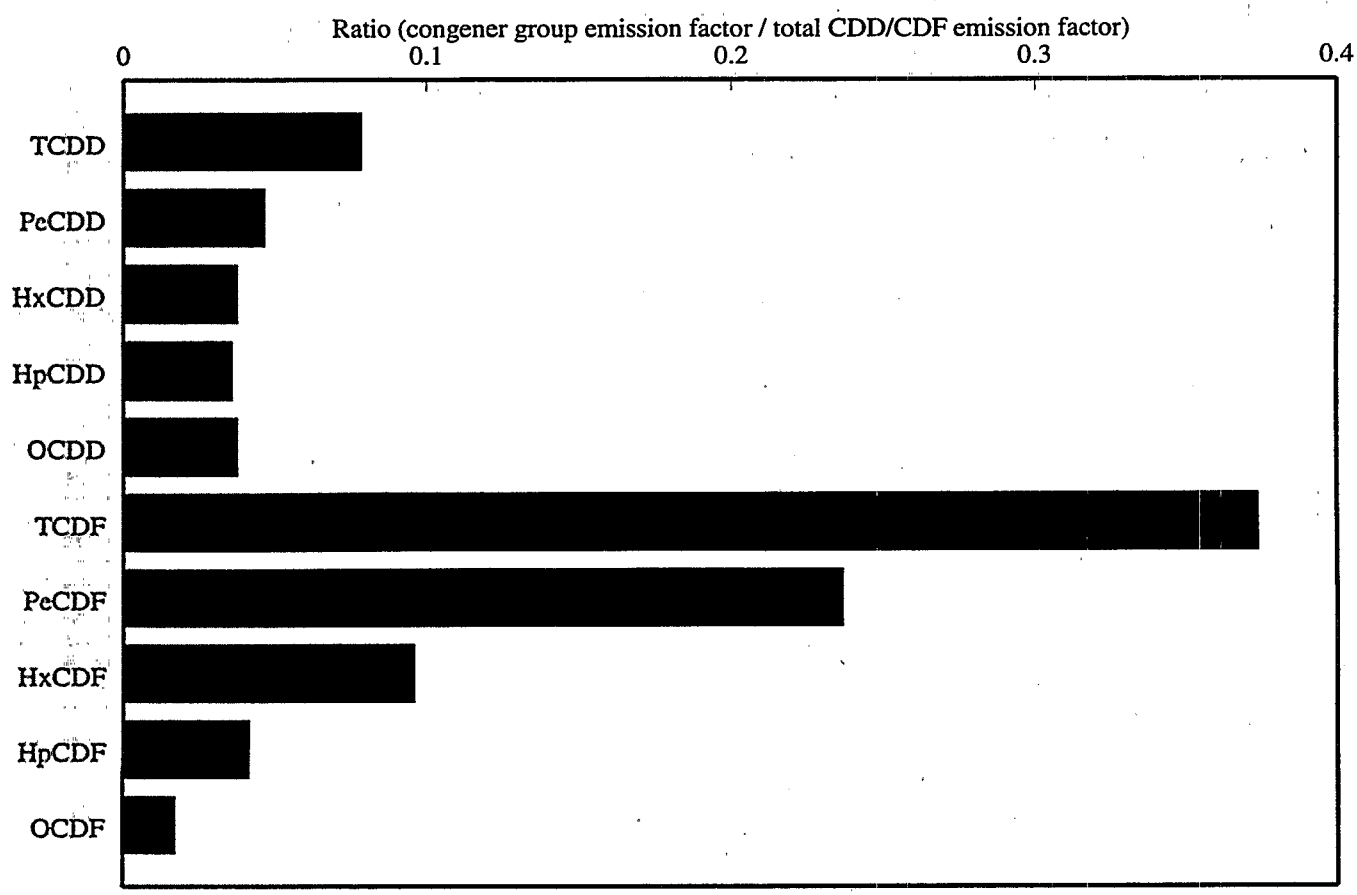
Figure 4-5. Congener and Congener Group Profiles for Air Emissions from Industrial Wood Combustors

Table 4-13. Estimated CDD/CDF Emission Factors for Oil-Fired Residential Furnaces

Congener/Congener Group	Mean Facility Emission Factor (pg/L oil)
2,3,7,8-TCDD	56
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	66
2,3,7,8-TCDF	53
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	30
Total 2,3,7,8-CDD	NR
Total 2,3,7,8-CDF	NR
Total TEQ	150
Total TCDD	139
Total PeCDD	82
Total HxCDD	66
Total HpCDD	63
Total OCDD	66
Total TCDF	663
Total PeCDF	420
Total HxCDF	170
Total HpCDF	73
Total OCDF	30
Total CDD/CDF	1,772

Source: U.S. EPA (1997b)

NR = Not reported.



Source: U.S. EPA (1995c)

Figure 4-6. Congener Group Profile for Air Emissions from Residential Oil-fueled Furnaces

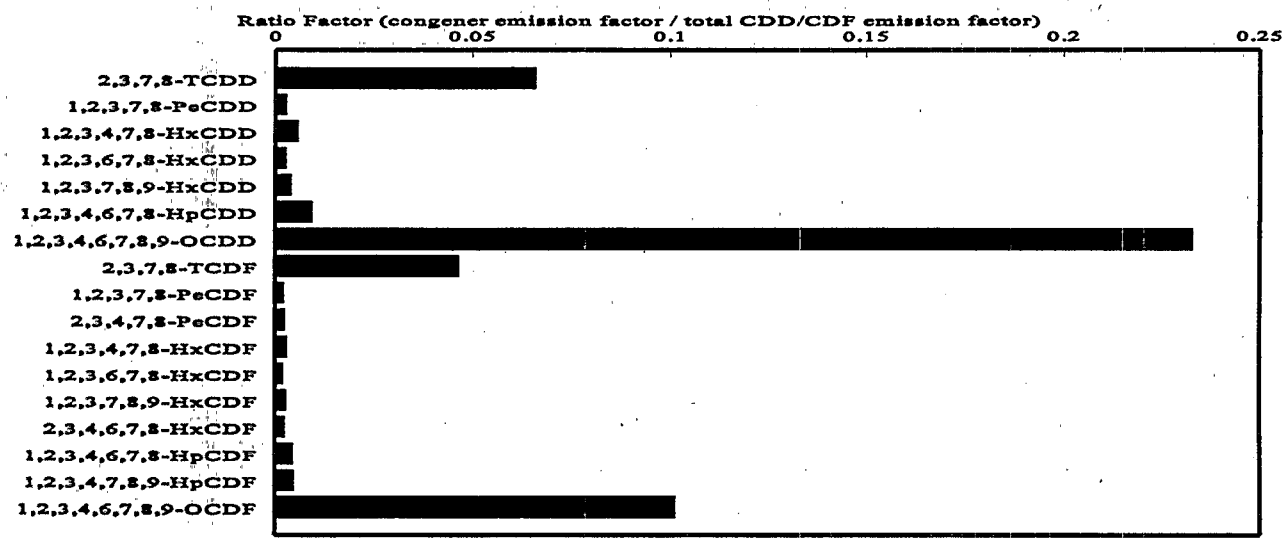
Table 4-14. CDD/CDF Emission Factors for Oil-Fired Utility/Industrial Boilers

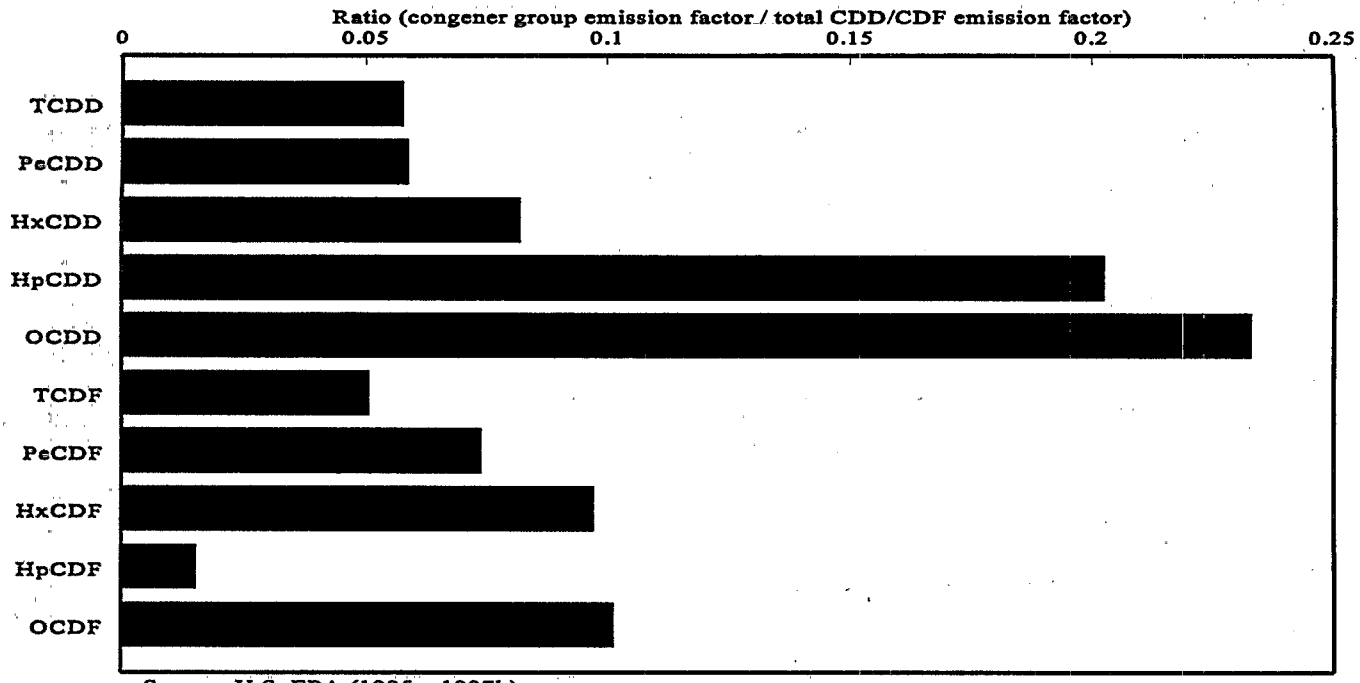
Congener/Congener Group	U.S. EPA (1997b) Median Emission Factor (pg/L oil)	EPRI (1994) Mean Emission Factor	
		ND = zero (pg/L oil)	ND = 1/2 DL (pg/L oil)
2,3,7,8-TCDD	117	0	26.6
1,2,3,7,8-PeCDD	104	24.7	43.1
1,2,3,4,7,8-HxCDD	215	63.3	108
1,2,3,6,7,8-HxCDD	97	65.8	79.3
1,2,3,7,8,9-HxCDD	149	79.7	102
1,2,3,4,6,7,8-HpCDD	359	477	546
OCDD	413	2055	2141
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 TEQ	314	95.5	170
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

Sources:

U.S. EPA (1997b) - number of facilities not reported.
EPRI (1994) - based on two cold side ESP-equipped power plants.

Note: Assumes a density for residual fuel oil of 0.87 kg/L.





Source: U.S. EPA (1995c; 1997b)

Figure 4-7. Congener and Congener Group Profiles for Air Emissions from Industrial Oil-fueled Boilers

Table 4-15. CDD/CDF Concentrations in Stack Emissions from U.S. Coal-Fired Power Plants

Congener/Congener Group	Plant 1 (pg/Nm^3)	Plant 2 (pg/Nm^3)	Plant 3 (pg/Nm^3)	Plant 4 (pg/Nm^3)	Plant 5 (pg/Nm^3)	Plant 6 (pg/Nm^3)	Plant 7 (pg/Nm^3)
2,3,7,8-TCDD	ND (3.5)	ND (3.5)	1.0	ND (2.0)	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 (2.0)
1,2,3,6,7,8-HxCDD	ND (0.44)	5.0	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 (2.0)	ND (3.3)	13	0.7
1,2,3,7,8-PeCDF	ND (1.0)	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 (5.0)	2.9	ND (10)	ND (5.8)	ND (4.0)	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 (2.0)	ND (4.2)	3.0	ND (10)	ND (16.4)	ND (2.5)	ND (2.0)
1,2,3,4,6,7,8-HpCDF	2.0	29	6.0	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 (5.0)	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 (1.0)	4.4	6.0	ND (10)	ND (4.7)	ND (3.2)	ND (32)
Total HxCDD	1.3	18	2.7	ND (10)	ND (26.3)	ND (4.0)	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	3.0
Total HxCDF	7.6	39	29	ND (10)	ND (16.4)	ND (5.0)	ND (27)
Total HpCDF	4.3	34	9.0	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 parentheses is the detection limit.
NR = Not reported; suspected contamination problem.
Source: Riggs et al. (1995)

Table 4-16. Characteristics of U.S. Coal-Fired Power Plants Tested by DOE

Plant No.	Coal Type	Coal Chlorine Content (mg/kg)	Temperature (°C) at:			
			Pollution Control Device[a]			Stack
			ESP	Bag	FGD	
1	Bituminous	800	160	--	--	160
2	Bituminous	1,400	130	--	--	130
3	Subbituminous	300	--	150	--	150
4	Subbituminous	390	--	70	130	75
5	Bituminous	1,400	130	--	120	40
6	Lignite	400	170	--	170	110
7	Bituminous	1,000	150	--	--	150

[a] ESP = Electrostatic precipitator, Bag = Baghouse, FGD = Flue gas desulfurization system.

Source: Riggs et al. (1995).

Table 4-17. CDD/CDF Emission Factors for Coal-Fired Utility/Industrial Power Plants

Congener/Congener Group	Mean Emission Factor	
	ND = zero (ng/kg coal)	ND = 1/2 DL (ng/kg coal)
2,3,7,8-TCDD	0.007	0.020
1,2,3,7,8-PeCDD	0	0.018
1,2,3,4,7,8-HxCDD	0	0.038
1,2,3,6,7,8-HxCDD	0.005	0.031
1,2,3,7,8,9-HxCDD	0.005	0.039
1,2,3,4,6,7,8-HpCDD	0.216	0.241
OCDD	0.517	0.648
2,3,7,8-TCDF	0.109	0.117
1,2,3,7,8-PeCDF	0.008	0.025
2,3,4,7,8-PeCDF	0.075	0.085
1,2,3,4,7,8-HxCDF	0.110	0.136
1,2,3,6,7,8-HxCDF	0.016	0.031
1,2,3,7,8,9-HxCDF	0.015	0.043
2,3,4,6,7,8-HxCDF	0.054	0.075
1,2,3,4,6,7,8-HpCDF	0.354	0.385
1,2,3,4,7,8,9-HpCDF	0.097	0.126
OCDF	0.159	0.281
Total 2,3,7,8-CDD	0.750	1.035
Total 2,3,7,8-CDF	0.997	1.304
Total TEQ	0.087	0.136
Total TCDD	0.076	0.078
Total PeCDD	0.027	0.029
Total HxCDD	0.060	0.060
Total HpCDD	0.106	0.120
Total OCDD	0.517	0.648
Total TCDF	0.230	0.250
Total PeCDF	0.347	0.223
Total HxCDF	0.209	0.209
Total HpCDF	0.127	0.133
Total OCDF	0.159	0.281
Total CDD/CDF	1.86	2.03

Source: EPRI (1994) - 11 facility data set.

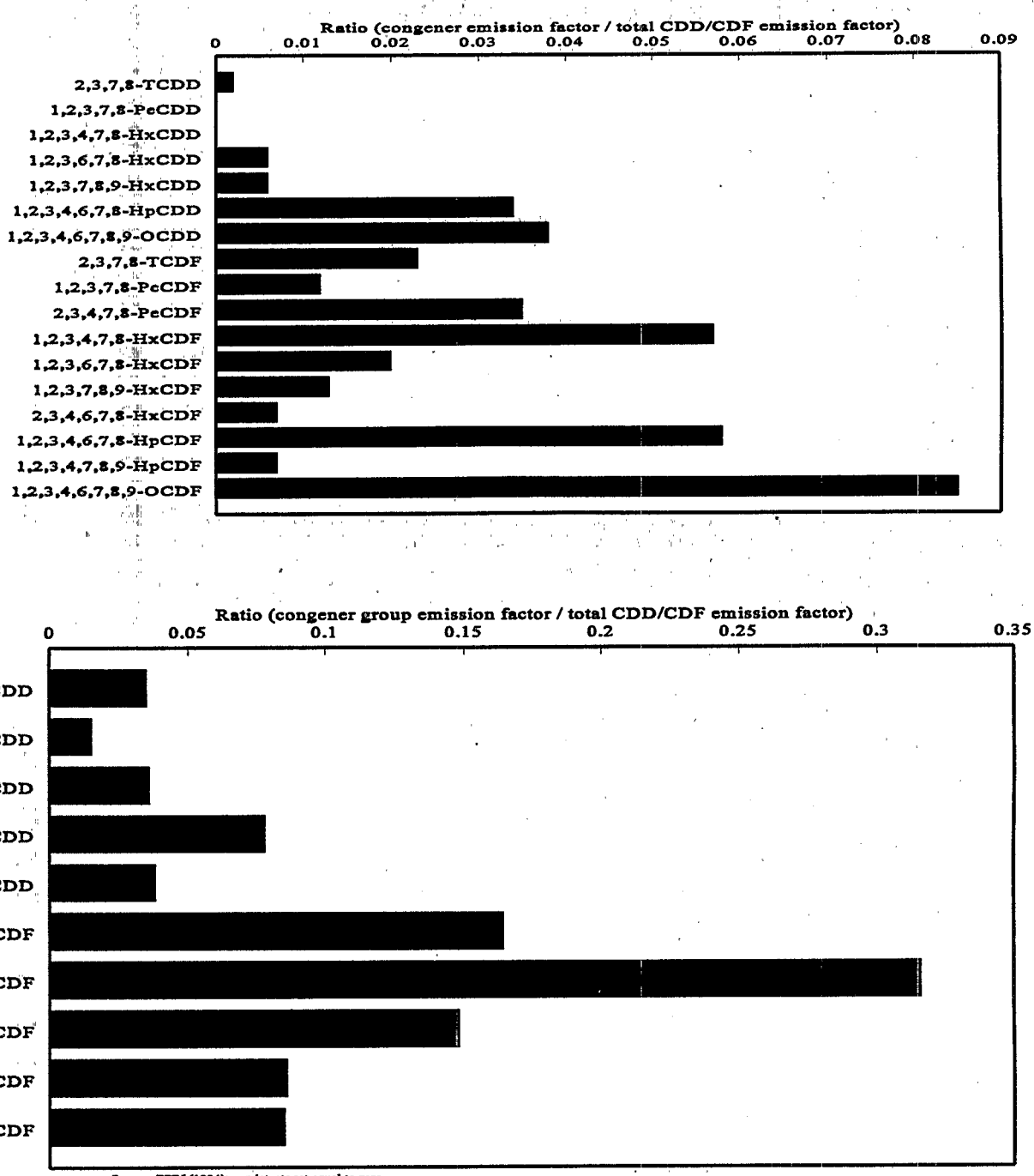


Figure 4-8. Congener and Congener Group Profiles for Air Emissions from Industrial/Utility Coal-fueled Combustors

Table 4-18. CDD/CDF Emission Factors from Residential Coal Combustors

Congener/Congener Group	"Salt" Lignite Ref. A (ng/kg coal)	"Normal" Lignite Ref. A (ng/kg coal)	Anthracite Ref. B (ng/kg coal)	Bituminous Ref. B (ng/kg coal)
2,3,7,8-TCDD	0.58	0.06	1.60	2.40
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	0.60	0.09	NR	NR
1,2,3,7,8,9-HxCDD	0.40	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	0.50	42.0	63.0
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	0.30	4.2	6.3
Total 2,3,7,8-CDD	22.37	3.38	NR	NR
Total 2,3,7,8-CDF	13.60	3.20	NR	NR
Total TEQ	2.74	0.34	60.0	98.5
Total TCDD	14.23	9.00	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	0.30	4.2	6.3
Total CDD/CDF	189.5	50.93	1,205	1,841

Sources: Ref A: Thub et al. (1995); listed results represent means of three flue gas samples.
Ref B: 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.

NR = not reported.

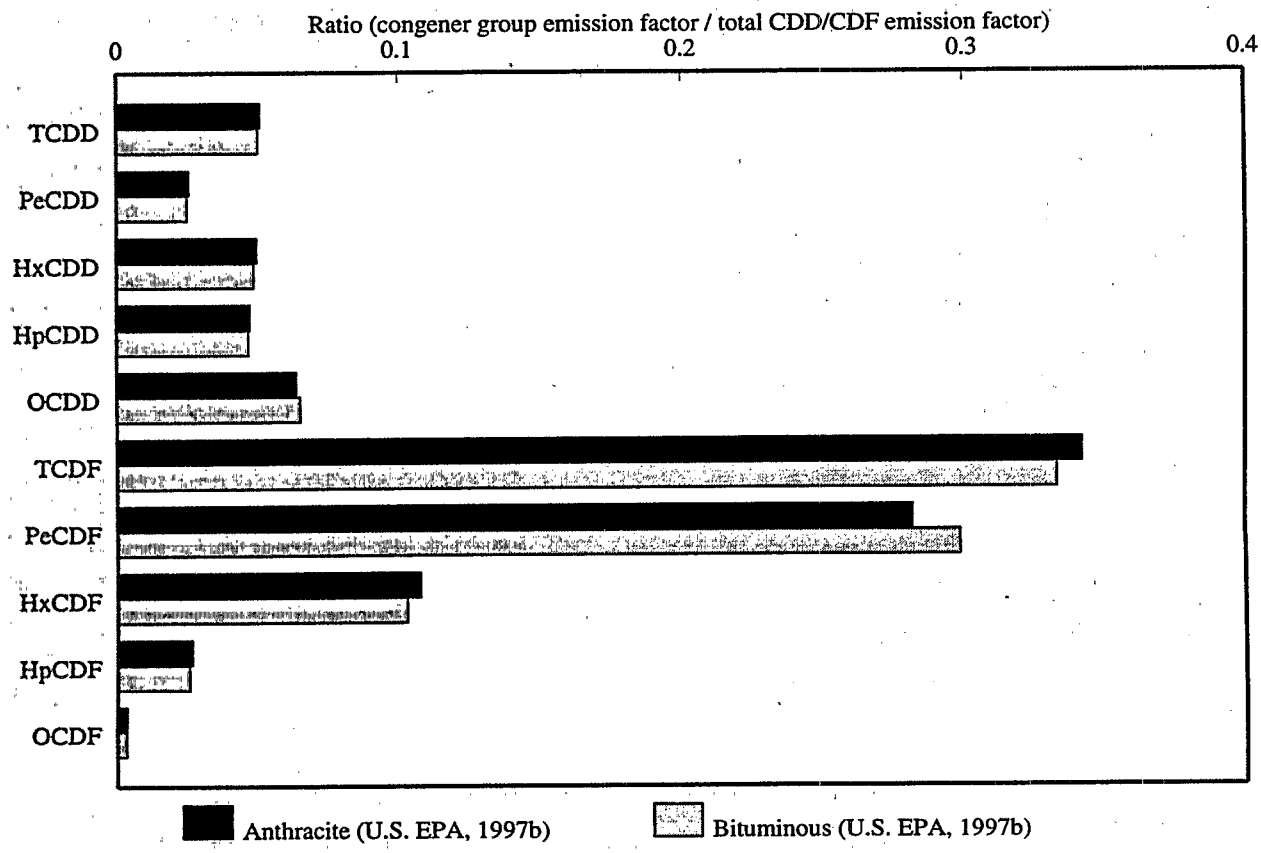


Figure 4-9. Congener Group Profile for Air Emissions from Residential Coal-fueled Combustors

5. COMBUSTION SOURCES OF CDD/CDF: OTHER HIGH TEMPERATURE SOURCES

5.1. CEMENT KILNS

This section addresses CDD/CDF emissions from Portland cement kilns. These facilities use high temperature to convert mineral feed stocks into Portland cement and other types of construction materials. For purposes of this analysis, cement kilns have been subdivided into two categories: those that burn hazardous waste and those that do not. Lightweight aggregate kilns are not addressed in this report. The following sections describe cement kiln technology, review the derivation of TEQ emission factors for cement kilns that do burn and do not burn hazardous waste as supplemental fuel, and derive annual TEQ air emissions (g/yr) for 1995 and 1987.

5.1.1. Process Description of Portland Cement Kilns

In the United States, the primary cement product is called Portland cement. Portland cement is a fine, grayish 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 further ground into a fine powder and mixed with gypsum to form the Portland cement. The cement kiln is a large, rotating steel cylindrical furnace lined with refractory material. The kiln is aligned on a slight angle, usually a slope of 3° - 6°. This allows for the materials to pass through the kiln by gravity. The upper end of the kiln is known as the 'cold' end. This is where the raw materials, or meal, is fed into the kiln. The lower end of the kiln is known as the "hot" end. The hot end is where the combustion of primary fuels (usually coal and petroleum coke) transpires to produce a high temperature. The cement kiln is operated in a counter-current configuration. This means that the hot combustion gases are convected up through the kiln while the raw materials are passing down toward the lower end. The kiln rotates about 50 to 70 revolutions per hour, and the rotation induces mixing and the forward progress of mixed materials. As the meal moves through the cement kiln and is heated by the hot combustion gases, water is vaporized and pyroprocessing of materials occurs.

When operating, the cement kiln can be viewed as consisting of three temperature zones necessary to produce cement clinker. Zone 1 is at the upper end of the kiln where the raw meal is added. Temperatures in this zone typically range from ambient up to 600°C. In this area of the kiln, moisture is evaporated from the raw meal. The second thermal zone is known as the calcining zone. Calcining occurs when the hot combustion gases from the combustion of primary fuels dissociates calcium carbonate from the limestone to form calcium oxide. In this region of the kiln, temperatures are in a range of 600°C to 900°C. The third region of the kiln is known as the burning or sintering zone. The burning zone is the hottest region of the kiln. Here temperatures in excess of 1,500°C induce the calcium oxide to react with silicates, iron and aluminum in the raw materials to form cement clinker. The formation of clinker actually occurs near the lower end of the kiln (close to the combustion of primary fuel) where temperatures are the hottest. The chemical reactions that occur here are referred to as pyroprocessing.

The cement clinker that is formed and that leaves the kiln at the hot end is a gray-colored, glass-hard material comprised of dicalcium silicate, tricalcium silicate, calcium aluminate, and tetracalcium aluminoferrite. At this point, the clinker has a temperature of about 1,100°C. The hot clinker is then dumped onto a moving grate where it is cooled by passing under a series of cool air blowers. Once cooled to ambient temperature, the clinker is ground into a fine powder and mixed with gypsum to produce the Portland cement product.

Cement kilns can be either wet or dry processes. In the wet process, the raw materials are ground and mixed with water to form a slurry. The meal-water slurry is fed into the kiln through a pump. This is an older process. A greater amount of heat energy is needed in the wet process than in other types of kilns. These kilns consume about 5 to 7 trillion BTUs per ton of clinker product to evaporate the additional water.

In the dry process, a pre-heater is used to pre-dry the raw meal. A typical pre-heater consists of a vertical tower containing a series of cyclone-type vessels. Raw meal is added at the top of the tower, and hot kiln exhaust flue gases from the kiln operation are used to preheat the meal prior to being loaded into the kiln. Pre-heating the meal has the advantage of lowering fuel consumption of the kiln. Therefore, dry kilns are now the most popular cement kiln type. EPA estimates that Portland cement clinker production in the United States was 67.6-billion kg in 1995 and 52-billion kg in 1987 (U.S. DOC, 1996).

5.1.2. Cement Kilns Burning Hazardous Waste

The high temperatures achieved in cement kilns make cement kilns an attractive technology for combusting hazardous waste as supplemental fuel. Sustaining the relatively high combustion temperatures (1,100°C to 1,500°C) that are needed to form cement clinker requires the burning of a fuel with a high energy output. Therefore, coal or petroleum coke is typically used as the primary fuel source. Because most of the cost of operating the cement kiln at high temperatures is associated with the consumption of fossil fuels, some cement kiln operators have elected to burn hazardous liquid and solid waste as supplemental fuel. Currently about 75 percent of the primary fuel is coal. Organic hazardous waste may have a similar energy output as coal (9,000 to 12,000 Btu/lb for coal). The strategy of combusting the waste as supplemental fuel is to off-set the amount of coal/coke that is purchased and burned by the kiln. The operator may charge a disposal fee to the waste generator for the right to combust the hazardous waste at the kiln, which also offsets the cost of kiln operation. Much of the high energy and ignitable wastes are primarily comprised of such diverse substances as waste oils, spent organic solvents, sludges from the paint and coatings industry, waste paints and coatings from the auto and truck assembly plants, and sludges from the petroleum refining industry (Greer et al., 1992).

The conditions inherent in the cement kiln mimic conditions of hazardous waste incineration. For example, the gas residence time in the burning zone is typically three seconds while at temperatures in excess of 1,500°C (Greer et al., 1992). In addition, trial burns have consistently shown that 99.99 to 99.9999 percent destruction and removal efficiencies for the very stable organic wastes can be achieved in cement kilns (Greer et al., 1992). Although the combustion of hazardous waste as supplemental or substitute fuel does have apparent advantages, only 16 percent of the Portland cement kilns (34 of the 212 kilns) combusted hazardous waste in 1995 (Federal Register, 1996b). Other types of supplemental fuel used by these facilities include automobile tires, used motor oil, and sawdust, and scrap wood chips.

The method of introducing liquid and solid hazardous waste into the kiln is a key factor to the complete consumption of the waste during the combustion of the primary fuel. Liquid hazardous waste is either injected separately or blended with the primary fuel (coal). Solid waste is mixed and burned along with the primary fuel.

5.1.3. Air Pollution Control Devices Used on Cement Kilns

The pyroprocessing of raw meal in a cement kiln produces fine particulates. This is referred to as cement kiln dust. Cement kiln dust is collected and controlled with fabric filters and/or electrostatic precipitators. Acid gases such as SO_2 can be formed during pyroprocessing of the sulfur-laden minerals, but the minerals have high alkalinity which neutralizes SO_2 gases. Most PM control devices used at cement kilns in 1995 and 1987 were considered to be hot-side control devices. A hot side control device is one that operates at flue gas temperatures above 150°C (note that some EPA rules use different definitions for hot side devices for different industries). This has been identified as the critical temperature at or above which CDD/CDFs are formed.

Reducing the flue gas temperature in the PM control device is one factor shown to have a significant impact on limiting dioxin formation and emissions at cement kilns (U.S. EPA, 1997d). Recent emissions testing at a Portland cement kiln showed that CDD/CDFs were almost entirely absent at the inlet to a hot-sided ESP, but CDDs and CDFs were measured at the exit to the ESP (U.S. EPA, 1997d). This conclusively showed that dioxins were formed within the hot-side ESP. Reducing the flue gas temperature in the PM control device to below 150°C has been shown to substantially limit CDD/CDF formation at cement kilns. This is believed to be due to preventing the post-combustion catalytic formation of CDD/CDFs. Consequently a number of cement kilns have added flue gas quenching units upstream of the APCD to reduce the inlet APCD temperature, thereby reducing CDD/CDF stack concentrations. A quench usually consists of a water spray system within the flue duct. Thus, cement kilns tested after 1995 have substantially reduced CDD/CDF emissions as compared to cement kilns used to derive emission estimates in this report.

5.1.4. CDD/CDF Emission Factors for Cement Kilns

The source emissions data base contains test reports of CDD/CDF emissions from 12 cement kilns burning hazardous waste and 11 cement kilns not burning hazardous waste (U.S. EPA,1996c) 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 not burning hazardous waste were derived from testing during normal operations.

For purposes of deriving emission factors, the general strategy used in this document is to consider subdividing each source category on the basis of design and operation. However, cement kilns are relatively uniform in terms of kiln design, raw feed material, temperatures of operation, and APCDs. Therefore, no subdivisions were made on these bases. An important difference among kilns, however, is the whether or not hazardous waste is burned as a supplementary fuel. The average TEQ emission factors are 24.34 ng TEQ per kg clinker produced and 0.29 ng TEQ kg clinker produced for cement kilns burning and not burning hazardous waste, respectively. Accordingly, the average emission factor for kilns burning hazardous waste is about 80 times greater than that for kilns not burning hazardous waste. As discussed in Section 5.1.6 (Cement Kiln Dust), a comparison of CDD/CDF concentrations in cement kiln dust samples from cement kilns burning and not burning hazardous waste show a similar relationship (i.e., the cement kiln dust from kilns burning hazardous waste had about 100 times higher CDD/CDF TEQ concentration than dust from nonhazardous waste burning kilns).

It is possible that differences other than the use of hazardous waste are contributing to the observed differences in emissions. Although the average emission factors for the two groups of kilns differ substantially, the emission factors for individual kilns in the two groups overlap. The five lowest emission factors for kilns burning hazardous waste span the same range as the five highest emission factors for kilns not burning hazardous waste. Accordingly, other aspects of the design and operation of the kilns may be affecting CDD/CDF emissions. Possibilities include procedures for preheating the meal, type of primary fuel, type of secondary fuel, and the characteristics of the raw meal. All tested kilns were operating with hot-side ESPs during the stack tests.

Attempts to understand this issue through parametric testing of cement kilns have yielded mixed results. EPA conducted a limited comparison of CDD/CDF TEQ stack gas concentrations (ng TEQ/dscm) between cement kilns burning hazardous wastes and not burning hazardous wastes (U.S. EPA, 1997d). These comparisons were made at 14 cement kilns. Operating conditions (e.g., APCD temperature), with the exception of the fuel being burned, were the same or similar for each set of comparisons. Baseline conditions used coal as the only primary fuel. The results of these comparisons showed:

- Seven kilns in which the baseline (i.e., no combustion of hazardous waste) CDD/CDF TEQ stack gas concentrations were about the same as that for the burning of hazardous wastes;
- Two kilns in which the baseline CDD/CDF TEQ stack gas concentrations were about double that for the burning of hazardous wastes; and
- Five kilns in which the hazardous waste CDD/CDF TEQ stack gas concentrations were substantially greater (from 3 to 29 times greater) than that for the baseline operating conditions.

Currently no satisfactory explanation exists for the apparent differences in the emission factors. Given the strong empirical evidence that real differences may exist, EPA/ORD has decided to treat the kilns burning hazardous waste separately from those not burning hazardous waste for the purposes of developing a CDD/CDF emissions inventory.

The average emission factor (EF) for each cement kiln was calculated using Equation 5-1.

$$EF_{ck} = \frac{C \times F_v}{I_{cl}} \qquad \text{(Eq. 5-1)}$$

Where:

EF_{ck} = Cement kiln emission factor (burning or not burning hazardous waste), (ng TEQ per kg of clinker produced).

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_{cl} = Average cement kiln clinker production rate (kg/hr).

After developing average emission factors for each tested cement kiln, the overall average congener-specific emission factor was derived for all tested HWIs using Equation 5-2 below.

$$EF_{avgCK} = \frac{\sum [EF_{CK_1} + EF_{CK_2} + EF_{CK_3} \ldots\ldots EF_{CK}]}{N} \qquad \text{(Eq. 5-2)}$$

Where:

Ef_{avgCK} = Average emission factor of tested cement kilns either burning or not burning hazardous waste as supplemental fuel (ng TEQ/kg clinker)

N = Number of cement kilns tested

The average emission factors representative of the cement kilns burning and not burning hazardous waste are summarized in Table 5-1. Because the same test reports were used, the emission factors are the same for both the 1995 and 1987 reference years. Congener and congener group profiles for cement kilns burning hazardous waste are presented in Figure 5-1 and for cement kilns not burning hazardous wastes in Figure 5-2.

5.1.5. National Estimates of CDD/CDF Emissions from Cement Kilns

National estimates of CDD/CDF air emissions (grams TEQ per year) from all Portland cement kilns operating in 1995 and 1987 were made by multiplying the average TEQ emission factor by the annual activity level (cement clinker produced) for cement kilns burning and not burning hazardous waste, respectively.

Nonhazardous waste burning cement kilns produced 61.3-billion kg of cement clinker in 1995 (Heath,1995). Since a total of 67.6-billion kg of cement clinker were produced in the United States in 1995 (U.S. DOC, 1996), it follows that cement kilns burning hazardous waste produced 6.3-billion kg of clinker (or 9.3 percent of the clinker produced). Approximately 52-billion kg of cement clinker were produced in 1987 (U.S. DOC, 1996). If it is assumed that 9.3 percent of this total clinker production was from hazardous waste burning kilns, then about 4.8 billion kg of clinker were produced in hazardous waste burning kilns in 1987. These activity level estimates are given a "high" confidence rating, because they are based on recent survey data (U.S. EPA, 1996c).

The TEQ emission factors are given a "low" confidence rating for both cement kilns burning and not burning hazardous waste. The TEQ EF for nonhazardous waste burning kilns were given a low rating because only 11 out of 178 (6 percent) have been tested for CDD/CDF emissions. These data may not be representative of routine CDD/CDF emissions from all kilns not burning hazardous waste. Emission factors for the 11 tested kilns ranged

from not detected up to a maximum of 2.6 ng TEQ/kg clinker. Although a higher percentage of the kilns burning hazardous waste had been tested (12 out of 34 or 35 percent of the kilns were tested in 1995) greater uncertainty exists about whether the emissions are representative of normal operations due to trial burn procedures. Accordingly, a low confidence rating was also assigned to the kilns burning hazardous waste.

The low confidence rating for the emission factors and high confidence rating for the activity levels combine to produce an overall low confidence rating. Accordingly, the estimated ranges of potential emissions are assumed to vary by a factor of 10 between the low and high ends of the range:

- 1995: For cement kilns not burning hazardous waste, the central estimate is 17.8 g TEQ/yr with a range of 5.6 g TEQ/yr to 56.3 g TEQ/yr. For cement kilns burning hazardous waste, the central estimate is 153 g TEQ/yr with a range of 48.4 g TEQ/yr to 484 g TEQ/yr.
- 1987: For cement kilns not burning hazardous waste, the central estimate is 13.7 g TEQ/yr with a range of 4.3 g TEQ/yr to 43.3 g TEQ/yr. For cement kilns burning hazardous waste, the central estimate is 117 g TEQ/yr with a range of 37.0 g TEQ/yr to 370 g TEQ/yr.

An alternative way to estimate CDD/CDF emissions would be to make no distinction between kilns burning and not burning hazardous waste. If the test data are combined to develop a single emission factor for all cement kilns, the average emission factor would then be 12.84 ng TEQ/kg of clinker. Multiplying this average emission factor by the 67.6 billion kg of total cement clinker produced in 1995 would yield an emission estimate of 868 g TEQ/yr. Applying the same procedure to the 52-billion kg of clinker produced in 1987 yields an emission estimate of 668 g TEQ/yr. The central estimates using this approach exceed the upper estimates derived above using the approach of separating kilns burning and not burning hazardous waste.

On April 19, 1996, EPA proposed revised emission standards for cement kilns and lightweight aggregate kilns burning hazardous waste (Federal Register, 1996b). These standards, including emission standards for CDD/CDF (0.20 ng TEQ/dscm at 7 percent O_2), were proposed under joint authority of the Clean Air Act (CAA) and the Resource

Conservation and Recovery Act (RCRA). The proposed standards reflect the performance of Maximum Achievable Control Technologies (MACT) as specified by the CAA. These standards should lead to lower CDD/CDF emissions than those estimated above for 1995.

5.1.6. Cement Kiln Dust

EPA characterized cement kiln dust (CKD) in a Report to Congress (U.S. EPA, 1993g). The report was based in part on a 1991 survey of cement manufacturers conducted by the Portland Cement Association (PCA). Survey responses were received from 64 percent of the active cement kilns in the United States. Based on the survey responses, EPA estimated that in 1990 the U.S. cement industry generated about 12.9-million metric tons of gross CKD and 4.6-million metric tons of "net CKD," of which 4.2-million metric tons were land disposed. The material collected by the APCD system is called "gross CKD" (or "as generated" CKD). The gross CKD is either recycled back into the kiln system or is removed from the system for disposal (i.e., "net CKD" or "as managed" CKD) (U.S. EPA, 1993g).

Also in support of the Report to Congress, EPA conducted sampling and analysis during 1992 and 1993 of CKD and clinker. The purposes of the sampling and analysis efforts were: (1) to characterize the CDD/CDF content of clinker and CKD ; (2) to determine the relationship, if any, between the CDD/CDF content of CKD and the use of hazardous waste as fuel; and (3) to determine the relationship, if any, between the CDD/CDF content of CKD and the use of wet versus dry process cement kilns. Clinker samples were collected from 9 kilns not burning hazardous waste and 11 kilns burning hazardous waste (U.S. EPA, 1993g).

CDD/CDFs were not detected in any cement kiln clinker samples. Tetra- through octa-chlorinated CDDs and CDFs were detected in the "gross CKD" samples obtained from 10 of the 11 kilns and in the "net CKD" samples obtained from 8 of the 11 kilns. The CDD/CDF content of "gross CKD" ranged from 0.008 to 247 ng TEQ/kg and from 0.045 to 195 ng TEQ/kg for "net CKD." Analyses for seven PCB congeners were also conducted, but no congeners were detected in any clinker or CKD sample. The mean CDD/CDF concentrations in "net CKD" generated by the kilns burning hazardous waste are higher (35 ng TEQ/kg) than in "net CKD" generated by the facilities not burning hazardous waste (3.0E-02 ng TEQ/kg). These calculations of mean values treated nondetected values as

zero. If the nondetected values had been excluded from the calculation of the means, the mean value for "net CKD" from kilns burning hazardous waste would increase by a factor of 1.2, and the mean value for "net CKD" from kilns not burning hazardous 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 was considered atypical of the industry (U.S. EPA, 1993g) and was not included in the calculation, then the mean "net CKD" concentration for hazardous waste burning kilns decreases to 2.9 ng/kg.

All CKD is normally disposed in engineered landfills and consequently not categorized as an environmental release as defined in this emission inventory. The amount of CDD/CDF associated with these materials is calculated for informational purposes. The estimate of land-disposed CKD from the 1991 PCA Survey (4.2-million metric tons per year [basis year is 1990]) was divided among kilns burning hazardous waste (34 kilns) and those that do not (178 kilns) on the basis of the number of kilns in each category. The average TEQ concentration in the net CKD from kilns burning hazardous waste (including the high value discussed above) was 35 ng TEQ/kg. For kilns that do not have hazardous waste, the average concentration in the "net CKD" was 3.0E-02. Multiplying these average concentrations by the annual "net CKD" production yields estimates of 24-g TEQ/yr for kilns burning hazardous waste and 0.1-g TEQ/yr for kilns not burning hazardous waste, yielding a total of 24.1-g TEQ/yr for all kilns.

5.2. 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 components of the aggregate are dried, heated, and mixed/coated with the bitumen at an asphalt mixing installation. "Old" asphalt (i.e., asphalt from dismantled bridges and roads) can be disaggregated to its original components through heating and reused in the manufacture of new asphalt.

No data are available on CDD/CDF emissions, if any, from U.S. asphalt mixing operations. However, limited data are available for facilities in The Netherlands and Germany.

Bremmer et al. (1994) measured CDD/CDF content in air emissions from an asphalt mixing plant in The Netherlands to be 47-ng TEQ per metric ton of produced asphalt. No congener-specific emission factors were reported by Bremmer et al. (1994). The tested facility heated old asphalt in an individual recycling drum to about 150°C with flue gases that were mixed with ambient air to a temperature of 300-400°C. Parallel to this recycling drum, the "main drum" dried and heated the aggregate (sand and gravel/granite chippings) to a temperature of about 220°C. The flue gases leaving the recycling drum are led along the main burner of the main drum for incineration. The old asphalt, the minerals from the main drum, and new bitumen from a hot storage tank (about 180°C) were mixed in a mixer to form new asphalt. Natural gas fueled the tested facility during the sample collection period and used old asphalt as 46 percent of the feed. The facility's APCD system consisted of cyclones and a fabric filter.

Umweltbundesamt (1996) reported lower emission factors for three tested facilities in Germany that were also equipped with fabric filters. These three facilities were fueled by oil and/or butane gas and used old asphalt at usage rates ranging from 30 to 60 percent of the feed. The emission factors calculated from the stack gas concentrations, gas flow rates, and hourly thruputs for these three facilities were 0.2, 3.5, and 3.8 ng TEQ/metric ton of asphalt produced.

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 percent 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.

Because there are no direct measurements of CDD/CDF emissions from U.S. asphalt plants and because of uncertainties regarding the comparability of U.S. and Dutch asphalt plant technologies and feed materials, no national emission estimate for this category is proposed at this time. However, a preliminary order of magnitude estimate of the potential 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 (i.e., 14 ng TEQ/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 TEQ/yr, which, when rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, results in a value of 10 g TEQ/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

5.3. PETROLEUM REFINING CATALYST REGENERATION

Regeneration of spent catalyst for use in the petroleum refinery reforming process is a potential source of CDDs and CDFs based on 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). The available data indicate that CDD/CDFs can be generated during the catalyst regeneration process. However, the available data indicate that releases to water (i.e., treated wastewater) and in solid waste are minimal. Releases to air could result from untreated vented flue gases at some facilities, and the CDD/CDFs formed could possibly be reintroduced into other refining operations (e.g., the coker) and resulting products. However, the available data are not adequate to support even order of magnitude release estimates for air and product releases. The following paragraphs summarize 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 750 to 850°F and then reactivating the catalyst at elevated temperatures (850 to 1,000°F) using chlorine or chlorinated compounds (e.g., methylene chloride, 1,1,1-trichloroethane, and ethylene dichloride). Burning of the coke produces flue gases that can contain CDDs and CDFs along with other combustion

products. Because flue gases, if not vented directly to the atmosphere, may be scrubbed with caustic or water, internal effluents may become contaminated with CDD/CDFs (Kirby, 1994; SAIC, 1994).

In 1988, the Canadian Ministry of the Environment detected concentrations of CDDs in an internal wastestream of spent caustic in a petroleum refinery that ranged from 1.8 to 22.2 μgL, 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 CDD/CDFs in the final combined refinery plant effluent was below the detection limits.

Amendola and Barna (1989) reported detecting trace levels of hexa- to octa-CDDs and CDFs in untreated wastewaters (up to 2.9 pg TEQ/L) and wastewater sludges (0.26 to 2.4 ng TEQ/kg) at a refinery in Ohio. The levels of detected total CDD/CDFs in the wastewater and sludge were much lower (<3 ng/L and <1 μg/kg, respectively) than the levels reported by Maniff and Lewis (1988). No CDD/CDFs were detected in the final treated effluent (i.e., less than 0.2 ng TEQ/L). The data collected in the study were acknowledged to be too limited to enable identifying the source(s) of the CDD/CDFs within the refinery. Amendola and Barna (1989) also present in an appendix to their report the results of analyses of wastewater from the reformer catalyst regeneration process units at two other U.S. refineries. In both cases, untreated wastewaters contained CDDs and CDFs at levels ranging from high pg/L to low ng/L (results were reported for congener group totals, not specific congeners). However, CDD/CDFs were not detected in the only treated effluent sample collected at one refinery.

Thompson et al. (1990) reported total CDD and CDF concentrations of 8.9 ng/m^3 and 210 ng/m^3, respectively, in stack gas samples from a Canadian petroleum refinery reforming operation. Thompson et al. (1990) also observed CDDs and CDFs in the internal wash water from a scrubber of a periodic/cyclic regenerator in the pg/L to ng/L range.

Beard et al. (1993) conducted a series of benchtop experiments to investigate the mechanism(s) of CDD/CDF formation in the catalytic reforming process. A possible pathway for the formation of CDFs was found, but the results could not explain the formation of CDDs. Analyses of the flue gas from burning coked catalysts revealed the presence of unchlorinated dibenzofuran (DBF) in quantities up to 220 μg/kg of catalyst.

Chlorination experiments indicated that dibenzofuran and possibly biphenyl and similar hydrocarbons act as CDF precursors and can become chlorinated in the catalyst regeneration process. Corrosion products on the steel piping of the process plant seem to be the most likely chlorinating agent.

In May 1994, EPA's Office of Water conducted a sampling and analytical study of catalytic reforming regeneration wastewater for CDD/CDFs at three petroleum refining plants (Kirby, 1994). The study objectives were to determine the analytical method best suited for determining CDD/CDFs in refinery wastewater matrices and to screen/characterize wastewater discharges from several types of reforming operations for CDD/CDFs. The report for this study (Kirby, 1994) also presented results submitted voluntarily to EPA by two other facilities. The sampled untreated wastewaters and spent caustics were found to contain a wide range of CDD/CDF concentrations, 0.1 pg TEQ/L to 57.2 ng TEQ/L. The study results also showed that 90 percent of the TEQ is contained in the wastewater treatment sludges generated during the treatment of wastewater and caustic from the regeneration process.

EPA recently issued a notice of its proposed intent not to designate spent reformer catalysts as a listed hazardous waste under RCRA (Federal Register, 1995b). The primary oil/water/solids sludges at petroleum refineries are listed as hazardous wastes (K048, K051, F037, and F038) (Federal Register, 1995b). The Agency's assessment of current management practices associated with recycling reforming catalyst found no significant risks to human health or the environment. The Agency estimated that 94 percent of the approximately 3,600 metric tons of spent reformer catalyst generated annually are currently recycled for their precious metal content. However, EPA made no determination of the "listability" of spent caustic residuals formed during regeneration of spent reforming catalysts. The Agency did identify potential air releases from the combustion of the reforming catalyst prior to reclamation as possibly of concern. The Agency requested comments on: (1) opportunities for removing dioxin prior to discharge of scrubber water into the wastewater treatment system; (2) opportunities to segregate this wastestream; and (3) potential health risk associated with insertion of dioxin-contaminated media back into the refinery process (such as the coker). In this proposed rulemaking, EPA also noted the possibility of dioxin releases to air during regeneration operations, but indicated that EPA is scheduled to assess the need for development of MACT standards under the CAA

for petroleum refining refiner units in 1996. As part of its regulatory investigation under RCRA, EPA's OSW commissioned a study to analyze and discuss existing data and information concerning CDD/CDF formation in the treatment of catalytic reformer wastes. This report (SAIC, 1994) also identified potential process modifications that may prevent the formation of CDD/CDFs.

5.4. 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 recent 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 CDD/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 the following paragraphs.

No studies published to date have demonstrated a complete and thorough mass balance, and it is not known whether the CDD/CDFs measured in cigarette smoke are the result of formation during tobacco combustion, volatilization of CDD/CDFs present in the unburned tobacco, or a combination of these two sources. The combustion processes operating during cigarette smoking are complex and could be used to justify both proposed 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 CDD/CDFs initially present in the tobacco. Both solid and gas phase temperatures rapidly decline to 200 to 400°C within 2 mm of the char line. Formation of CDD/CDFs has been reported in combustion studies with other media in this temperature range of 200 to 900°C. However, it is known that a process likened by Guerin et al. (1992) to steam distillation takes place in the region behind the char line because of high localized concentrations of water and temperatures of 200 to 400°C. At least 1,200 tobacco constituents (e.g., nicotine, n-paraffin, some terpenes) are transferred intact from the tobacco into the smoke stream by distillation in this area, and it is plausible that CDD/CDFs present in the unburned tobacco would be subject to similar distillation.

Bumb et al. (1980), using low resolution mass spectrometry, analyzed the CDD content of mainstream smoke from the burning of a U.S. brand of unfiltered cigarette. A package of 20 cigarettes was combusted in each of two experiments. Approximately 20 to 30 puffs of 2 to 3 seconds duration were collected from each cigarette on a silica column. Hexa-, hepta-, and octa-CDD were detected at levels of 0.004-0.008, 0.009, and 0.02-0.05 ng/g, respectively.

Muto and Takizawa (1989) employed a continuous smoking apparatus to measure CDD congener concentrations in the mainstream smoke generated from the combustion of one kind of filtered cigarette (brand not reported). The apparatus pulled air at a constant continuous rate (rather that a pulsed rate) through a burning cigarette and collected the smoke on a series of traps (glass fiber filter, polyurethane foam, and XAD-II resin). The CDD content of the smoke, as well as the CDD content of the unburned cigarette and the ash from the burned cigarettes, were also analyzed using low-resolution mass spectrometry. The results for all three media are presented in Table 5-2, and the congener group profiles for the three media are presented in Figure 5-3. Table 5-3 and Figure 5-4 present the mainstream smoke results on a mass per cigarette basis to enable comparison with the results of other studies. The major CDD congener group found was HpCDD, which accounted for 84 percent of total CDDs found in the cigarette, 94 percent of total CDDs found in smoke, and 99 percent of total CDDs found in the ash. The 2,3,7,8-HpCDDs also accounted for the majority of the measured TEQ in the cigarettes and smoke; however, none were measured in the ash. Although no PeCDDs were detected in the cigarette, PeCDDs were detected at low levels in the smoke, indicating probable formation during combustion. Based on the similarities in the congener group profiles for the three media, Muto and Takizawa (1989) concluded that most of the CDDs found in the cigarette smoke appear to be the result of volatilization of CDD/CDFs present in the unburned cigarette rather than resulting from formation 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 (i.e., 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 with a large collection device. The average TEQ content 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 (1989) 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 (i.e., 1 puff/min; puff flow rate of 35 mL/2 sec) was utilized, 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 5-3. The TEQ content in mainstream smoke, normalized to a mass per cigarette basis, was 0.90 pg/cigarette (i.e., about 2 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 was reported by Muto and Takizawa (1989) and in Ball et al. (1990) study, the dominant congener groups were HpCDDs and OCDD; however, HpCDFs were also relatively high compared to the other congener group totals. The sidestream smoke contained about 2-pg TEQ per 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, United States, Taiwan, China, United Kingdom, Germany, and Denmark. Table 5-4 presents the study results. The total CDD/CDF content and total TEQ content ranged from 109 to 1,136 pg/pack and from 1.4 to 12.6 pg/pack, respectively. The Chinese cigarette brand contained significantly less CDD/CDFs and TEQs than any other brand of cigarette. Figure 5-5 depicts the congener group profiles for the average results for each country. A high degree of similarity is shown in the CDF congener group profiles between the tested cigarette brands. The Japanese and Taiwanese cigarettes show CDD congener group profiles different from the other countries' cigarettes.

In 1995, approximately 487-billion cigarettes were consumed in the United States and by U.S. overseas armed forces personnel. In 1987, approximately 575-billion cigarettes were consumed. Per-capita U.S. cigarette consumption, based on total U.S. population aged 16 and over, declined to 2,415 in 1995; the record high was 4,345 in 1963 (The Tobacco Institute, 1995; USDA, 1997). These activity level estimates are assigned a "high" confidence rating.

The available emission factor data presented above enable estimates of the amount of TEQs that may have been released to the air in 1994 from the combustion of cigarettes estimated by two methods. The confidence rating assigned to the emission factor is "low" based on the very limited amount of testing performed to date. First, an annual emission estimate for 1995 of 0.21-g TEQ is obtained if it is assumed that: (1) the average TEQ content of seven brands of U.S. cigarettes reported by Matsueda et al. (1994), 8.60 pg/pack (or 0.43 pg/cigarette) are representative of cigarettes smoked in the United States; (2) CDD/CDFs are not formed, and the congener profile reported by Matsueda et al. (1994) is not altered during combustion of cigarettes; and (3) all CDD/CDFs contributing to the TEQ are released from the tobacco during smoking. The second method is to assume that the TEQ emission rates for a common Swedish brand of cigarette reported by Löfroth and Zebühr (1992) for mainstream smoke (0.90 pg/cigarette) and sidestream smoke (2.0 pg/cigarette) are representative of the emission rates for U.S. cigarettes. This second method yields an annual emission estimate of 1.41 g TEQ. For 1987, the two methods yield estimates of 0.25 g TEQ and 1.67 g TEQ.

Because of the "low" confidence rating assigned to the emission factor, the estimated range of potential air emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the average of the annual emissions estimated by the two methods for 1995 (i.e., 0.8 g TEQ) and 1987 (i.e., 1.0 g TEQ) are the geometric means of the ranges for these years, the ranges are calculated to be 0.25 to 2.5 g TEQ for 1994 and 0.31 to 3.1 g TEQ for 1987. Although these emission quantities are relatively small when compared to the emission quantities estimated for various industrial combustion source categories, these emissions assume significance because humans are directly exposed to cigarette smoke.

5.5. 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 percent of the decabromobiphenyl ether were converted to BDFs in samples that were irradiated with ultraviolet light for 16 hours.

Thoma and Hutzinger (1989) observed the formation of BDFs during combustion experiments with polybutylene-terephthalate polymers containing 9 to 11 percent decabromodiphenyl ether. Maximum formation of BDFs occurred at 400 to 600°C, with a BDF yield of 16 percent. Although Thoma and Hutzinger (1989) 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 BDD/BDFs during the compounding/ 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 upon which to derive annual BDD/BDF emission estimates from this source.

5.6. CARBON REACTIVATION FURNACES

Granular activated carbon (GAC) is an adsorbent that is widely used to remove organic pollutants from wastewater and in the treatment of finished drinking water at water treatment plants. Activated carbon is manufactured from the heat treatment of nut shells and coal under pyrolytic conditions (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 (e.g., 600 - 1600 m^2/g), combined with the extremely small pore diameter of the particles (e.g., 15-25 Angstroms) increases the adsorption characteristics (Buonicore, 1992a). GAC will eventually become saturated, and the adsorption properties will 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 utilize 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, 1995c; 1997b).

The used GAC can contain compounds that are precursors to the formation of CDD/CDFs during the thermal treatment process. EPA measured precursor compounds in spent GAC 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. U.S. EPA (1995c; 1997b) reported results of testing performed at a county water facility in California during 1990.

The industrial carbon regeneration plant processed 36,000 kg/day of spent GAC used in the treatment of industrial wastewater effluents. Spent carbon was reactivated in a multiple-hearth furnace, cooled in a water quench, and stored and shipped back to primary chemical manufacturing facilities for reuse. The furnace fired 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 a fabric filter. Temperatures in the afterburner were about 930°C. From the results of this testing, a TEQ emission factor of 2.98 ng TEQ/kg carbon processed can be derived. The emission factor for total CDD/CDF was 58.6 ng/kg.

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. Off-gasses from the reactivation/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/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.

From the results of testing the regeneration unit at the county water facility reported by U.S. EPA (1995c; 1997b), a TEQ emission factor of 1.73 ng TEQ/kg of carbon processed can be derived. The emission factor for total CDD/CDF was 47 ng/kg. The report did not provide the configuration and type of furnace tested. However, the report did state that the emissions from the furnace were controlled by an afterburner and a scrubber.

The industrial GAC reaction furnace test data indicate that an average of 2.98 ng TEQ per kg of GAC may be released to the air during an industrial operation. The TEQ emission rate for the regeneration unit at the county water treatment facility was 1.73 ng TEQ/kg carbon. "Low" confidence ratings are given to these emission factors, because only one industrial GAC reactivation furnace in each category was stack tested.

The mass of GAC that is reactivated annually in carbon reactivation furnaces is not known. However, a rough estimate, to which a "low" confidence rating is assigned, is the mass of virgin GAC shipped each year by GAC manufacturers. According to U.S. DOC (1990c), 48,000 metric tons of GAC were shipped in 1987. Data for 1995 are not yet available for GAC shipments from U.S. DOC (1996). However, U.S. EPA (1995c; 1997b) reports water and wastewater treatment operations consumed 65,000 metric tons of GAC in 1990. An estimated 50 percent of this volume were used for industrial uses, and 50 percent were used for municipal uses. Industrial facilities potentially regenerated 24,000 metric tons and 32,500 metric tons of GAC in 1987 and 1990, respectively. In 1987 and 1990 municipal facilities potentially regenerated 24,000 metric tons and 32,500 metric tons, respectively.

Applying the TEQ emission factor of 2.98 ng TEQ/kg of reactivated carbon to the estimates of potential GAC reactivation volume by industrial facilities yields annual release estimates of 0.072 g TEQ in 1987 and 0.097 g TEQ in 1990. Using the TEQ emission factor of 1.73 ng/kg of reactivated carbon yields estimated annual emissions by municipal facilities of 0.042 g TEQ in 1987 and 0.056 g TEQ in 1990. Based on the "low" confidence ratings assigned to the activity level and emission factors, the estimated range of potential annual emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the total releases estimated for 1990 (i.e., 0.15 g TEQ) and for 1987 (i.e., 0.11 g TEQ) are the geometric means of the ranges for those 2 years, the ranges are calculated to be 0.05 to 0.47 g TEQ in 1990 and 0.03 to 0.34 g TEQ in 1987.

5.7. KRAFT BLACK LIQUOR RECOVERY BOILERS

Kraft black liquor recovery boilers are associated with the production of pulp in making of paper using the Kraft process. In this process, wood chips are cooked in large vertical vessels called digesters at elevated temperatures and pressures in an aqueous solution of sodium hydroxide and sodium sulfide (Someshwar and Pinkerton, 1992). Wood is broken down into two phases: a soluble phase containing primarily lignin, and an insoluble phase containing the pulp. The spent liquor (called black liquor) from the digester contains sodium sulfate and sodium sulfide that the industry finds beneficial in recovering for reuse in the Kraft process. In the recovery of black liquor chemicals, weak black liquor is first concentrated in multiple-effect evaporators to about 65 percent solids. The concentrated black liquor also contains 0.5 to 4 percent chlorides by weight (U.S. EPA, 1987a). Recovery of beneficial chemicals is accomplished through combustion in a Kraft black liquor recovery furnace. The concentrated black liquor is sprayed into a 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 (Someshwar and Pinkerton, 1992). The combustion gas is usually passed through an electrostatic precipitator that collects particulate matter prior to being vented out the stack. The particulate matter can be processed to further recover and recycle sodium sulfate.

In 1987, the U.S. 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. 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 the 1990 to 1993 time period. 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 5-5 for the three facilities from U.S. EPA (1987a) and the six facilities from NCASI (1995). Figure 5-6 presents the average congener and congener group profiles based on the test results presented in 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/kg of black liquor solids, assuming nondetected values are zero and 0.068 ng TEQ/kg and are present at one-half the detection limit. The results for the three facilities reported in U.S. EPA (1987a) 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. A "medium" confidence rating is assigned to these emission factors, because the emission factors 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.

The amounts of black liquor solids burned in Kraft black liquor recovery boilers in the United States during 1987 and 1995 were 69.8-million metric tons and 80.8-million metric tons, respectively (American Paper Institute, 1992; American Forest & Paper Association, 1997). These activity level estimates are assigned a confidence rating of "high," because they are based on recent industry survey data. Combining the emission factor of 0.028 ng TEQ/kg of solids combusted with the activity level estimates of 69.8- and 80.8-million metric tons in 1987 and 1995, respectively, indicates that annual emissions from this source were approximately 2.0 grams in 1987 and 2.3 grams in 1995. Based on the confidence ratings assigned to the emission factor and activity level estimates, the estimated range of potential annual emissions is assumed to vary by a factor of five between the low and high ends of the range. Assuming that the best estimate of annual TEQ emissions in 1987 (2.0 g TEQ/yr) is the geometric mean of this range, then the range

is calculated to be 0.9 to 4.5 g TEQ/yr. For 1995, the range is calculated to be 1.0 to 5.0 g TEQ/yr.

5.8. OTHER IDENTIFIED SOURCES

Several manufacturing processes are identified as potential sources of CDD/CDF formation, because the processes use chlorine-containing components and/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.

Burning of Candles - Schwind et al. (1995) analyzed the wicks and waxes of uncolored candles, as well as the fumes of burning candles, for CDD/CDF, total chlorophenol, and total chlorobenzene content. The results are presented in Table 5-6. As shown in Table 5-6, beeswax contained the highest levels of CDD/CDF and total chlorophenols. In contrast, the concentration of total chlorobenzenes in stearin wax was a factor of 2 to 3 times higher than in paraffin or beeswax. The concentrations of the three analyte groups were significantly lower in the wicks than in the waxes. Emissions of CDD/CDF from all three types of candles were very low during burning. In fact, comparison of the emission factor to the original CDD/CDF concentration in the wax indicates a net destruction of the CDD/CDF originally presented in the wax.

Information is not readily available on the volume of candles consumed annually in the United States. However, the value of U.S. candle wholesale shipments in 1992 was nearly $360 million (U.S. DOC, 1996). Assuming that average wholesale cost per kg of candle is $1, then the volume of candles shipped was 360-million kg. If it is further assumed that 75 percent of the candle volume are actually burned and that the CDD/CDF emissions rate is 0.015 ng/kg, then a rough "what if" estimate of the annual emission from combustion of candles is 4 mg TEQ/yr.

Glass Manufacturing - Bremmer et al. (1994) and Douben et al. (1995) estimated annual emissions of less that 1 gram TEQ/yr from glass manufacturing facilities in The Netherlands and the United Kingdom, respectively. Glass is manufactured by heating to a temperature of 1,400 to 1,650°C a mixture of sand and, depending on the type of glass, lime, sodium carbonate, dolomite, clay, or feldspar. In addition, various coloring and clarifying agents may be added. Chlorine enters the process as a contaminant (i.e., 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 TEQ/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 DeFre (1995) and Douben et al. (1995), respectively. However, the emission factors used to generate these estimates were not provided. Umweltbundesamt (1996) reported low emissions (0.016 to 0.028 ng TEQ/kg) during tests at two lime kilns in Germany.

Ceramics and Rubber Manufacturers - Similarly, Douben et al. (1995) estimated annual emissions from ceramic manufacturers and rubber manufacturers in the United Kingdom. Lexen et al. (1993) had previously detected high concentrations of CDD/CDF in emissions from a ceramic manufacturer in Sweden, which occasionally glazed ceramics by volatilization of sodium chloride in a coal-fired oven. Lexen et al. (1993) also detected high pg/L levels of TEQ in the scrubber water from the vulcanization process at a Swedish rubber manufacturer.

Table 5-1. CDD/CDF Emission Factors for Cement Kilns

Congener/Congener Group	Kilns Burning Hazardous Waste Mean Emission Factor (12 facilities) (ng/kg clinker produced)		Kilns Not Burning Hazardous Waste Mean Emission Factor (11 facilities) (ng/kg clinker produced)	
	Nondetects Set to 1/2 Det. Limit	Nondetects Set to Zero	Nondetects Set to 1/2 Det. Limit	Nondetects Set to Zero
2,3,7,8-TCDD	1.22	1.21	0.020	0.013
1,2,3,7,8-PeCDD	3.68	3.67	0.050	0.038
1,2,3,4,7,8-HxCDD	3.90	3.89	0.044	0.031
1,2,3,6,7,8-HxCDD	4.54	4.54	0.058	0.045
1,2,3,7,8,9-HxCDD	6.37	6.36	0.067	0.053
1,2,3,4,6,7,8-HpCDD	14.58	14.58	0.471	0.466
OCDD	4.35	4.34	0.751	0.751
2,3,7,8-TCDF	18.17	18.17	0.793	0.792
1,2,3,7,8-PeCDF	10.96	10.87	0.118	0.108
2,3,4,7,8-PeCDF	27.38	27.26	0.253	0.243
1,2,3,4,7,8-HxCDF	16.97	16.84	0.211	0.202
1,2,3,6,7,8-HxCDF	7.22	7.18	0.067	0.058
1,2,3,7,8,9-HxCDF	1.46	1.43	0.021	0.007
2,3,4,6,7,8-HxCDF	10.52	10.45	0.094	0.089
1,2,3,4,6,7,8-HpCDF	6.68	6.68	0.168	0.159
1,2,3,4,7,8,9-HpCDF	1.44	1.42	0.022	0.006
OCDF	1.02	1.00	0.281	0.255
Total TEQ (nondetects = 0)		24.34		0.29
Total TEQ (nondetects = 1/2 DL)	24.45		0.32	
Total TCDD	NR	NR	2.14	2.14
Total PeCDD	NR	NR	2.26	2.26
Total HxCDD	NR	NR	6.50	6.50
Total HpCDD	NR	NR	0.92	0.92
Total OCDD	NR	NR	0.75	0.75
Total TCDF	NR	NR	7.22	7.22
Total PeCDF	NR	NR	2.13	2.13
Total HxCDF	NR	NR	0.64	0.64
Total HpCDF	NR	NR	0.27	0.26
Total OCDF	NR	NR	0.28	0.26
Total CDD/CDF (nondetects = 0)		≥1,443		23.08
Total CDD/CDF (nondetects = 1/2 DL)	≥1,443		23.11	

NR = Not reported

Source: U.S. EPA (1996c)

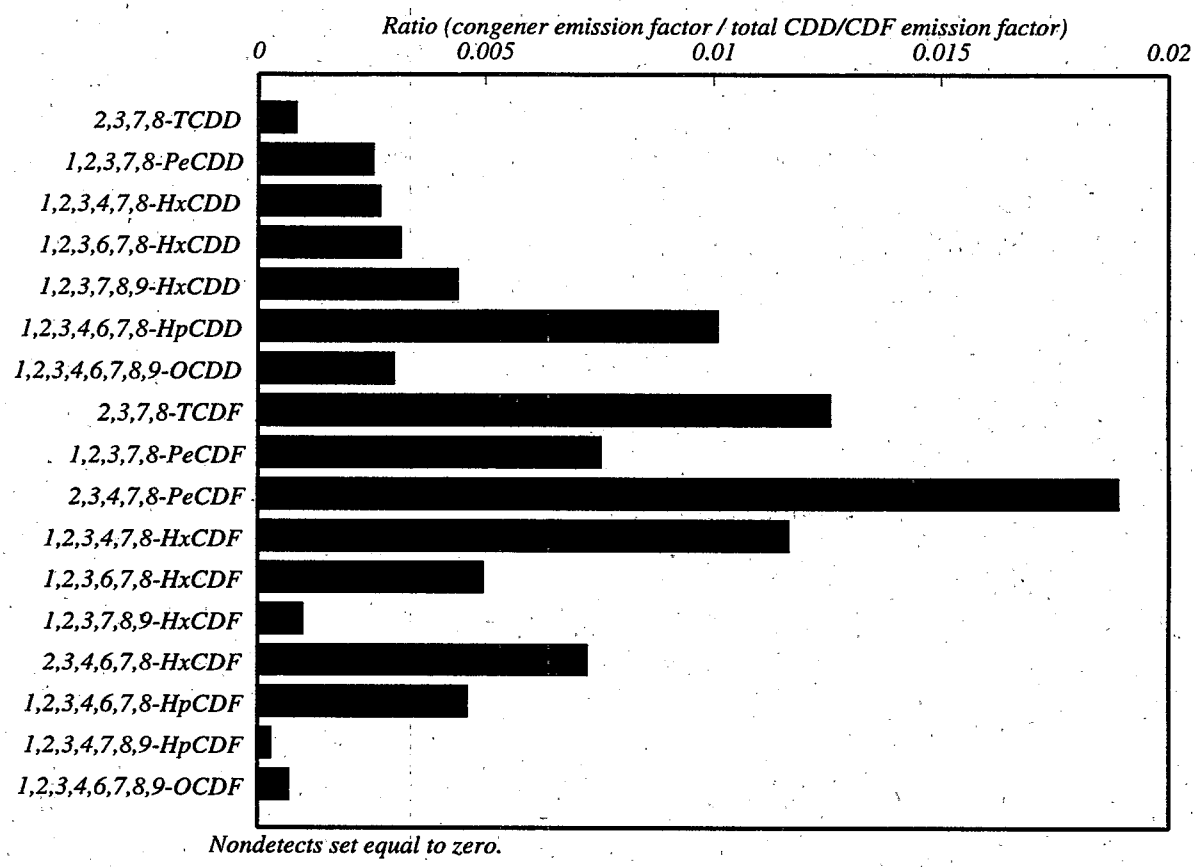
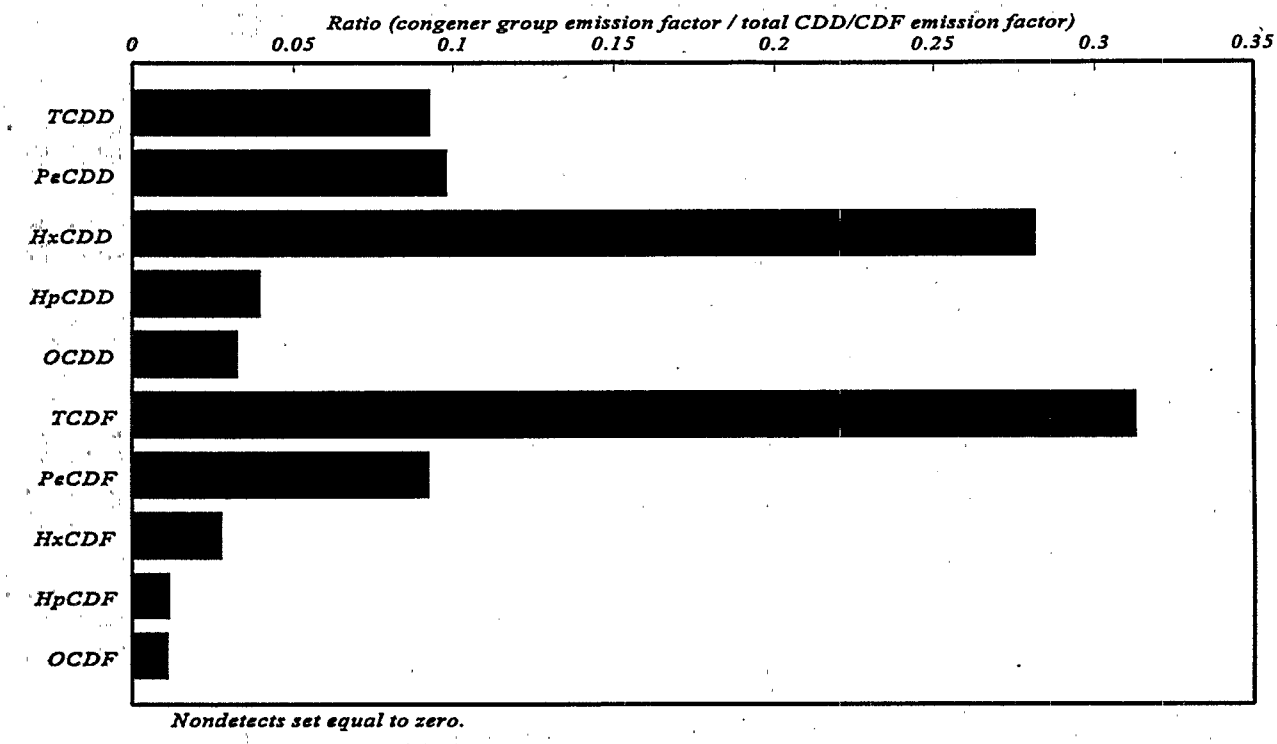


Figure 5-1. Congener Profile for Air Emissions from Cement Kilns Burning Hazardous Waste



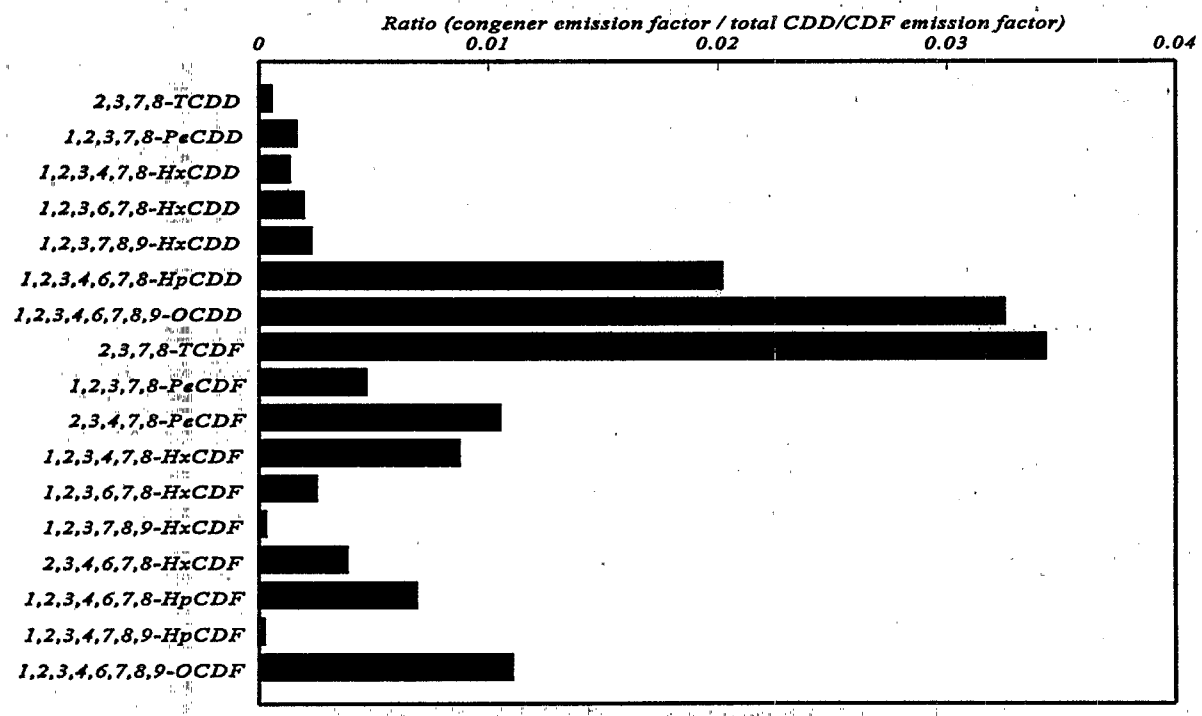


Figure 5-2. Congener and Congener Group Profiles for Air Emissions from Cement Kilns Not Burning Hazardous Waste

Table 5-2. CDD Concentrations in Japanese Cigarettes, Smoke and Ash

Congener/Congener Group	Cigarette (pg/g)	Concentrations	
		Mainstream smoke (ng/m3)	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	2.15	0.56
1,2,3,6,7,8-HxCDD	a	a	a
1,2,3,7,8,9-HxCDD	a	a	a
1,2,3,4,6,7,8-HpCDD	1,343	783	ND(0.5)
OCDD	257	240	ND(0.5)
2,3,7,8-TCDF	--	--	--
1,2,3,7,8-PeCDF	--	--	--
2,3,4,7,8-PeCDF	--	--	--
1,2,3,4,7,8-HxCDF	--	--	--
1,2,3,6,7,8-HxCDF	--	--	--
1,2,3,7,8,9-HxCDF	--	--	--
2,3,4,6,7,8-HxCDF	--	--	--
1,2,3,4,6,7,8-HpCDF	--	--	--
1,2,3,4,7,8,9-HpCDF	--	--	--
OCDF	--	--	--
Total 2,3,7,8-CDD	1,602	1,026	0.56
Total 2,3,7,8-CDF	--	--	--
Total TEQ	13.88	8.50	0.056
Total TCDD	44.9	68.0	4.63
Total PeCDD	ND(0.5)	1.51	ND(0.5)
Total HxCDD	13.41	7.51	5.01
Total HpCDD	1,629	4,939	3,211
Total OCDD	257	240	ND(0.5)
Total TCDF	--	--	--
Total PeCDF	--	--	--
Total HxCDF	--	--	--
Total HpCDF	--	--	--
Total OCDF	--	--	--
Total CDD/CDF	1,944	5,256	3,221

ND = Nondetected (detection limit is in parentheses).
-- = Not reported.

a = Value reported only for total 2,3,7,8-substituted HxCDDs.
c = Concentrations listed include the contribution of a coeluting non-2,3,7,8-substituted congener.

Source: Muto and Takizawa (1989)

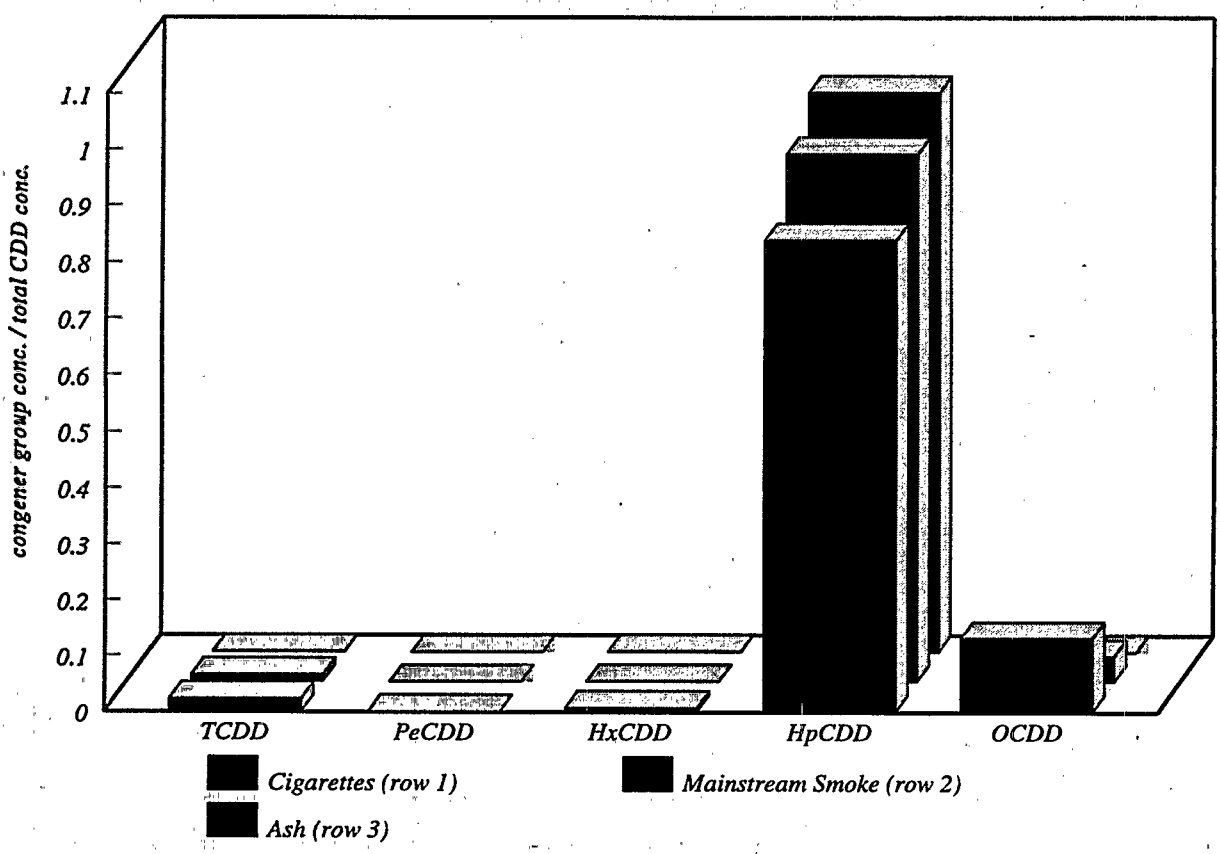


Figure 5-3. CDD Profiles for Japanese Cigarettes, Smoke, and Ash

Table 5-3. CDD/CDF Emissions in Cigarette Smoke

Congener/Congener Group	Ref. A (1 Japanese brand) (mainstream smoke)	Concentrations - Normalized to a per Cigarette Basis (pg/cig)		
		Ref. B (Avg of 10 German brands) (mainstream smoke)	Ref. C (1 Swedish brand) (mainstream smoke)	Ref. C (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	0.10	0.19
1,2,3,6,7,8-HxCDD	b	0.05	0.34	0.60
1,2,3,7,8,9-HxCDD	b	0.04	0.25	0.55
1,2,3,4,6,7,8-HpCDD	137	1.3	6.05	12.2
OCDD	42	3.4	22.1	38.8
2,3,7,8-TCDF	--	0.19	1.2	2.1
1,2,3,7,8-PeCDF	--	0.13	0.34	0.80
2,3,4,7,8-PeCDF	--	0.04	0.34	0.60
1,2,3,4,7,8-HxCDF	--	ND(0.03)	1.3	3.8
1,2,3,6,7,8-HxCDF	--	0.03	0.48	1.2
1,2,3,7,8,9-HxCDF	--	0.03	0.14	0.39
2,3,4,6,7,8-HxCDF	--	0.05	0.21	0.50
1,2,3,4,6,7,8-HpCDF	--	0.16	10.0	23.5
1,2,3,4,7,8,9-HpCDF	--	0.03	2.6	5.0
OCDF	--	0.11	3.2	10.7
Total 2,3,7,8-CDD	179	4.85	29.0	52.7
Total 2,3,7,8-CDF	--	0.77	19.8	48.6
Total TEQ	1.49	0.09	0.9	2.0
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	--	1.41	4.5	5.75
Total PeCDF	--	0.83	3.23	6.35
Total HxCDF	--	0.35	5.30	12.9
Total HpCDF	--	0.27	19.8	47.8
Total OCDF	--	0.11	3.2	10.7
Total CDD/CDF	919	10.5	74.5	152

Ref. A: Muto and Takizawa (1989)
Ref. B: Ball et al. (1990)
Ref. C: Löfroth and Zebühr (1992)
Ref. D: Muto and Takizawa (1992)

ND = Nondetected (detection limit is in parentheses).
-- = Not reported.
a = Emissions calculated assuming 0.0035 m^3 of smoke are inhaled per 20 cigarettes smoked (Ref. D).
b = Ref. A reported a value only for total 2,3,7,8-HxCDDs (0.38 pg/cig).
c = Concentrations listed include the contribution of a coeluting non-2,3,7,8-substituted congener.

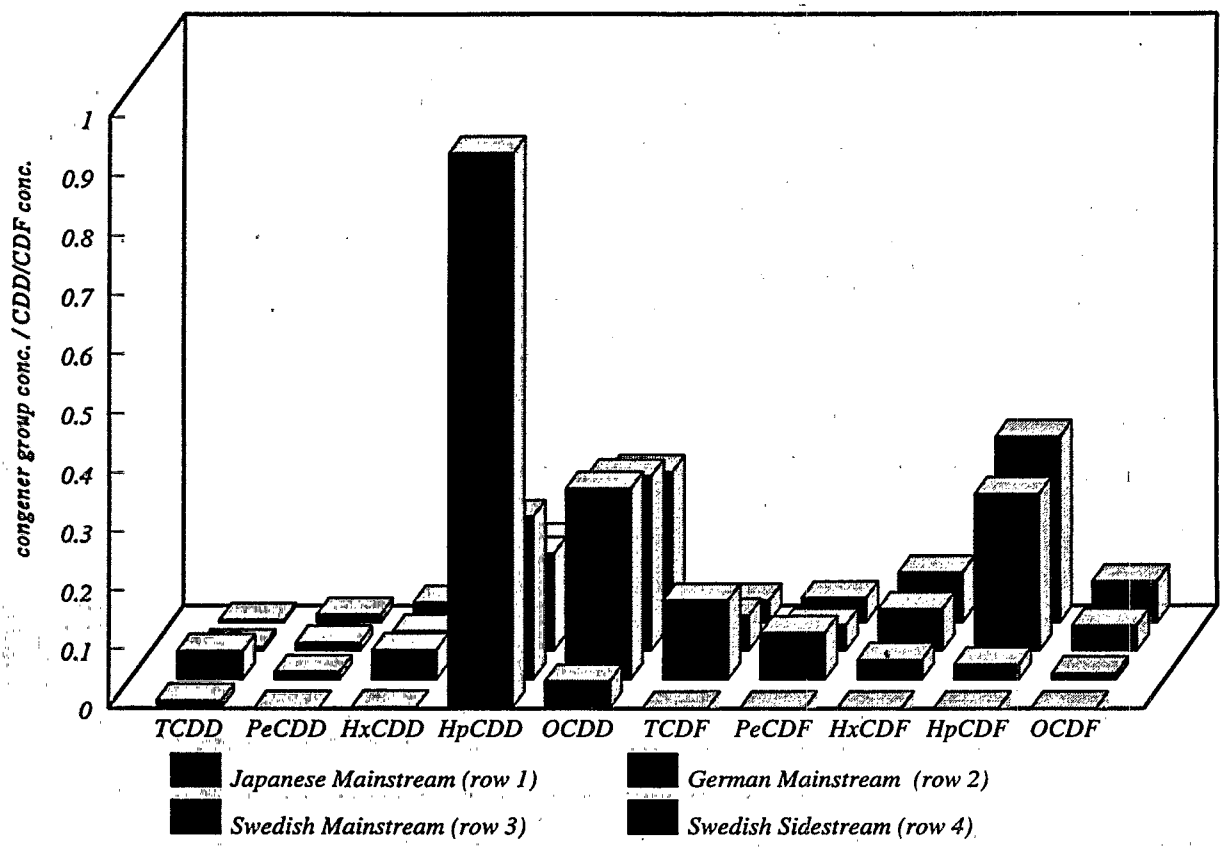


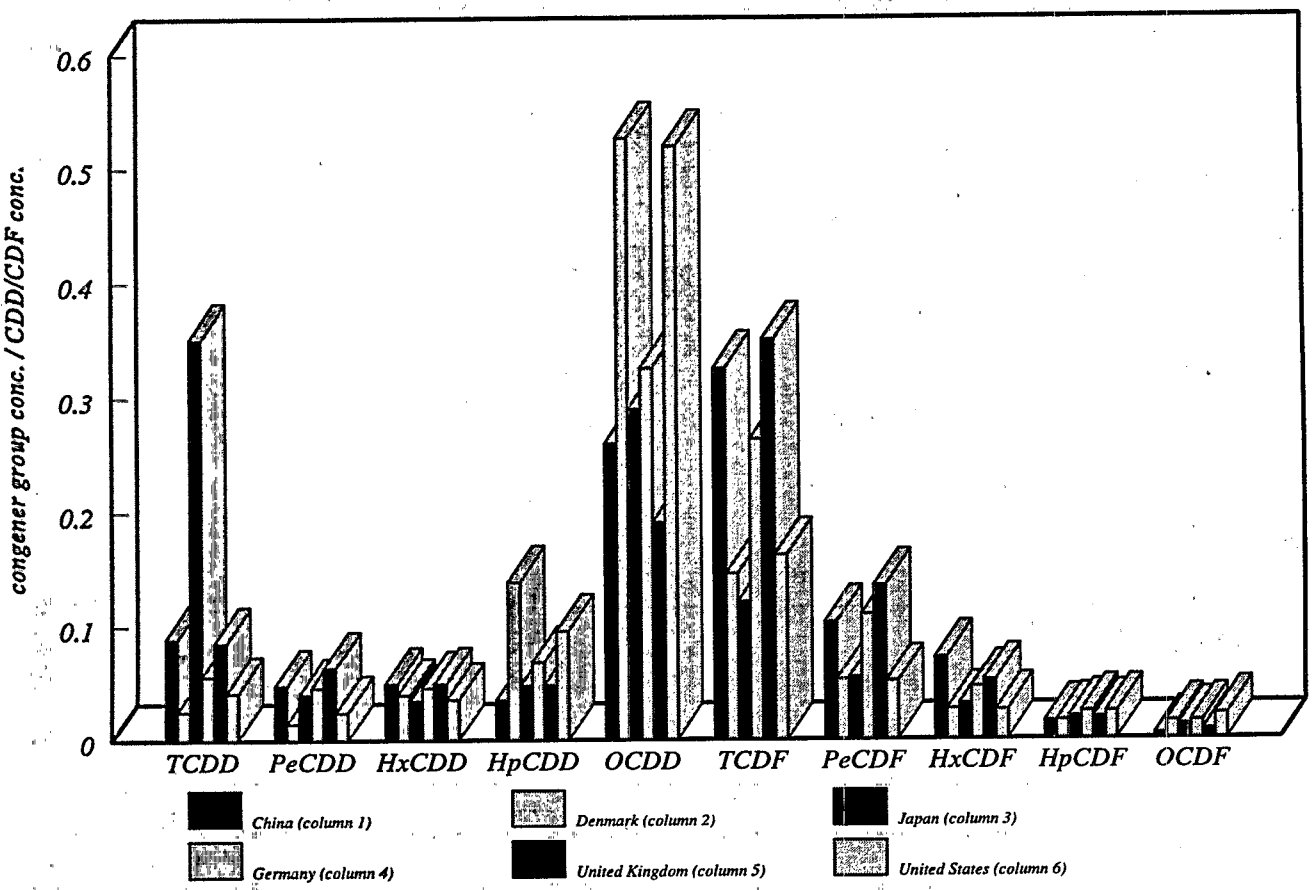
Figure 5-4. Congener Group Profiles for Mainstream and Sidestream Cigarette Smoke

Table 5-4. CDD/CDF Concentrations in Cigarette Tobacco

Congener/Congener Group	U.S. Brands (Avg of 7 brands)	Japan (Avg of 6 brands)	Concentrations in brands from various countries (pg/pack)				
			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	1.0	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	244.0	189.5	272.7	28.2	354.3	288.6
2,3,7,8-TCDF	18.2	4.8	15.6	11.0	1.2	2.2	7.9
1,2,3,7,8-PeCDF	8.7	5.3	21.2	16.0	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	17.0	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	7.0	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	652	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 TEQ	8.6	4.6	12.6	9.3	1.4	3.8	9.1
Total TCDD	47.1	296.3	85.1	329	9.7	17.0	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	40.0	47.7	62.0	3.8	93.1	60.2
Total OCDD	589.3	244.0	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	19.0	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	1136	845	996	1513	109	674	887

Source: Matsueda et al. (1994)

a = Value reported only for total 2,3,7,8-substituted HxCDDs.
b = Value reported only for total 2,3,7,8-substituted PeCDFs.
c = Value reported only for total 2,3,7,8-substituted HxCDFs.
d = Value reported only for total 2,3,7,8-substituted HpCDFs.



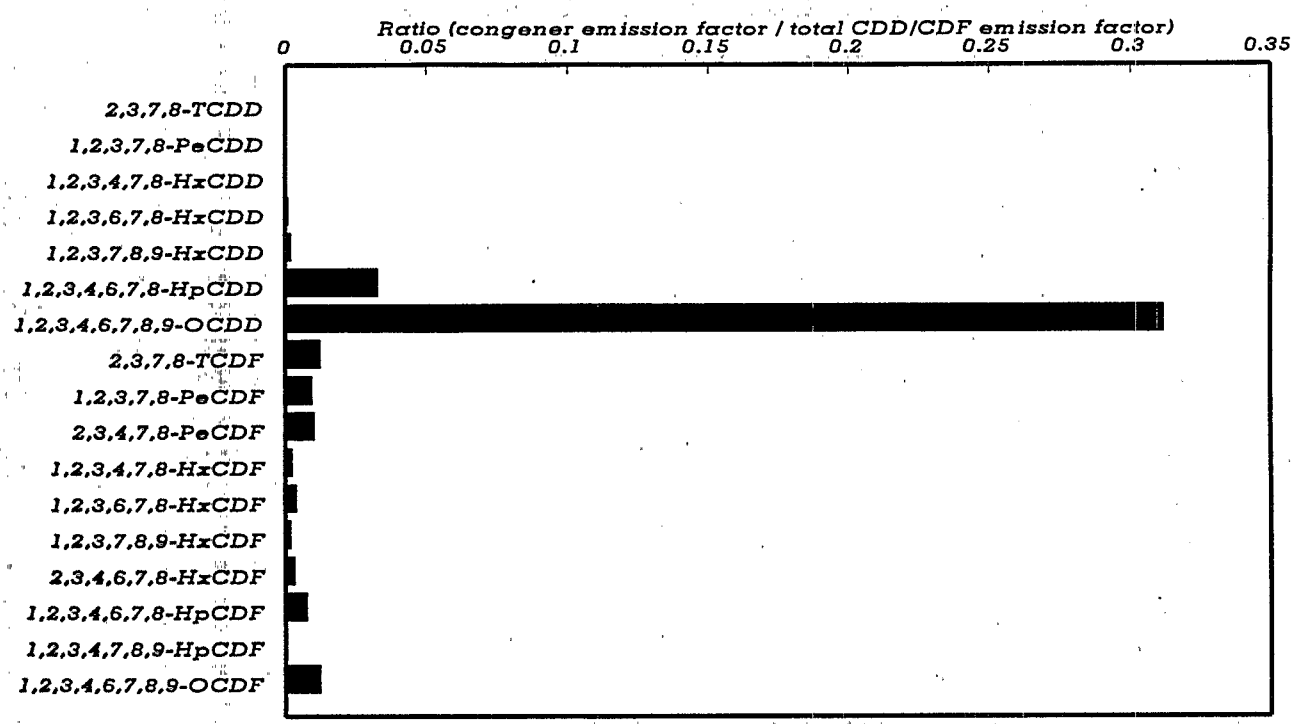
Source: Matsueda et al. (1994)

Figure 5-5. Congener Group Profiles for Cigarette Tobacco from Various Countries

Table 5-5. CDD/CDF Emission Factors for Black Liquor Recovery Boilers

Congener	U.S. EPA (1987) - 3 Facilities Mean Emission Factors (ng/kg feed)		NCASI (1995) - 6 Facilities Mean Emission Factors (ng/kg feed)	
	Nondetects Set to Zero	Nondetects Set to 1/2 Det. Limit	Nondetects Set to Zero	Nondetects Set to 1/2 Det. Limit
2,3,7,8-TCDD	0	0.04	0	0.017
1,2,3,7,8-PeCDD	NR	NR	0	0.019
1,2,3,4,7,8-HxCDD	NR	NR	0.001	0.021
1,2,3,6,7,8-HxCDD	NR	NR	0.003	0.016
1,2,3,7,8,9-HxCDD	NR	NR	0.006	0.020
1,2,3,4,6,7,8-HpCDD	NR	NR	0.108	0.140
OCDD	4.24	4.24	1.033	1.054
2,3,7,8-TCDF	0.04	0.06	0.040	0.053
1,2,3,7,8-PeCDF	NR	NR	0.030	0.036
2,3,4,7,8-PeCDF	NR	NR	0.033	0.038
1,2,3,4,7,8-HxCDF	NR	NR	0.007	0.022
1,2,3,6,7,8-HxCDF	NR	NR	0.012	0.022
1,2,3,7,8,9-HxCDF	NR	NR	0.005	0.017
2,3,4,6,7,8-HxCDF	NR	NR	0.010	0.024
1,2,3,4,6,7,8-HpCDF	NR	NR	0.024	0.037
1,2,3,4,7,8,9-HpCDF	NR	NR	0	0.018
OCDF	0.35	0.35	0.040	0.066
Total TCDD	0.21	0.36	0.106	0.123
Total PeCDD	0.27	0.13	0.013	0.089
Total HxCDD	0.80	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	1.00	1.270	1.275
Total PeCDF	0.64	0.77	0.370	0.377
Total HxCDF	1.16	1.20	0.102	0.109
Total HpCDF	1.05	1.05	0.024	0.040
Total OCDF	0.35	0.35	0.040	0.066
Total TEQ	NR	NR	0.028	0.068
Total CDD/CDF	11.71	12.17	3.314	3.535

Sources: U.S. EPA (1987a); NCASI (1995)



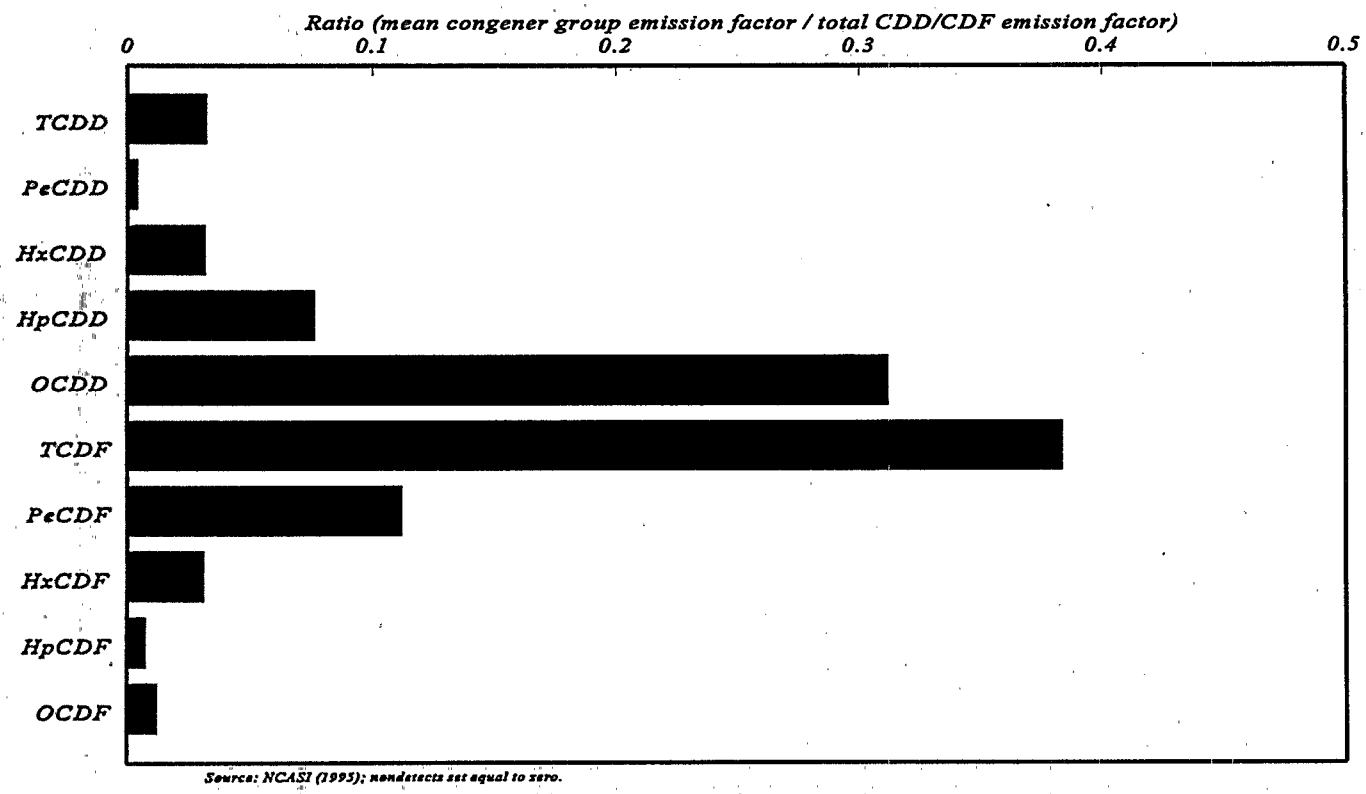


Figure 5-6. Congener and Congener Group Profiles for Air Emissions from Kraft Black Liquor Recovery Boilers

Table 5-6. Concentrations of CDD/CDF in Candle Materials and Emissions

Wax Material	Candle Component	Concentration			Emission Factor
		CDD/CDF (ng TEQ/kg)	ΣChlorophenol (μg/kg)	ΣChlorobenzenes (μg/kg)	CDD/CDF (ng TEQ/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	--
Stearin	Wick	0.12	0.94	0.34	--
Beeswax	Wick	0.08	0.74	0.35	--

Source: Schwind et al. (1995)

6. COMBUSTION SOURCES OF CDD/CDF: MINIMALLY CONTROLLED AND UNCONTROLLED COMBUSTION SOURCES

6.1. COMBUSTION OF LANDFILL GAS

The U.S. EPA recently promulgated emission standards/guidelines to control emissions of landfill gas from existing and future landfills under the Clean Air Act (Federal Register, 1996a). These regulations require the relatively largest landfills (i.e., largest on the basis of design capacity) in the United States (approximately 312 landfills) to periodically measure and determine their annual emission of landfill gas. Those landfills that emit more than 50 metric tons of nonmethane organic compounds (NMOC) annually must collect landfill gas and reduce the NMOC content by 98 weight percent through use of a control device. EPA estimates that when implemented, these controls will reduce NMOC annual 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 this mass reduction is achieved by flares, the corresponding volume of landfill gas that will be burned is approximately 14-billion m^3/yr (based on an assumed default NMOC concentration in landfill gas of 1,532 ppmv and a conversion factor of 3.545 mg/m^3 of NMOC per 1 ppmv of NMOC [Federal Register, 1993d]). EPA estimated that over 100 landfills had some form of collection and/or control systems in place in 1991 (Federal Register, 1991b). Thus, a rough approximation of the volume of landfill gas that is currently combusted is 4.7-billion m^3/yr (or 33 percent of future expected reductions). This estimate is similar to the 2.0- to 4.0-billion m^3 of landfill gas that were estimated in EIA (1994) as collected and consumed for energy recovery purposes in 1992. EIA (1992) estimated that between 0.9- and 1.8-billion m^3 of landfill gas were collected and burned in 1990 for energy recovery purposes.

Only one study of CDD/CDF emissions from a landfill flare was reported for a U.S. landfill (CARB, 1990d). The TEQ emission factor calculated from the results of this study is approximately 2.4 ng TEQ/m^3 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 TEQ/m^3, from the incineration of untreated landfill gas in a flare at a facility located in The Netherlands. No congener-specific emission factors were provided in

Bremmer et al. (1994). The average TEQ emission factor for the CARB (1990d) and Bremmer et al. (1994) studies is 1.4 ng TEQ/m^3 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 TEQ/m^3 with most values below 0.1 ng TEQ/m^3. However, Bremmer et al. (1994) also reported an emission factor of 0.5 ng TEQ/m^3 from a landfill-gas fired engine in The Netherlands.

The limited emission factor data available were thus judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary order of magnitude estimate of the annual TEQ release from this source category can be obtained using the estimated volume of combusted gas and the available emission factors. Combining the estimate of current landfill gas volume that is combusted (4.7-billion m^3/yr) with the emission factor of 1.4 ng TEQ/m^3 of flare-combusted gas yields an annual emission estimates of 6.6 g TEQ, which, when rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, results in a value of 10 g TEQ/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

6.2. ACCIDENTAL FIRES

Accidental fires occurring in buildings and vehicles are uncontrolled combustion processes that typically result in relatively high emissions of incomplete combustion products because of poor combustion conditions (Bremmer et al., 1994). The incomplete combustion products 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 demonstrate the presence of CDD/CDF concentrations in soot deposits and residual ashes from such fires, few direct measurements of CDD/CDFs in the fumes/smoke of fires have been attempted. The results of several of these studies are described below, followed by an evaluation of the available data.

6.2.1. Soot/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 grams 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 minutes in either an air atmosphere or a nitrogen atmosphere. The combustion experiments yielded CDD/CDF concentrations in soot of 110 μg TEQ/kg for a low molecular weight PVC, 450 μg TEQ/kg for a high molecular weight PVC, and 270 μg TEQ/kg of PVC cable. The pyrolysis experiments in the air atmosphere yielded lower CDD/CDF concentrations in soot: 24.4 μg TEQ/kg for a low molecular weight PVC, 18.7 μg TEQ/kg for a high molecular weight PVC, and up to 41 μg TEQ/kg for PVC cable. In general, CDFs were predominantly formed over CDDs. The lower chlorinated CDF congeners were dominant in the combustion experiments; however, the HpCDF and OCDF congeners were dominant in the pyrolysis experiments. No CDD/CDFs were detected in pyrolysis experiments under a nitrogen atmosphere. Also, no CDD/CDFs were detected when chlorine-free polyethylene samples were subjected to the same combustion and pyrolysis conditions.

Deutsch and Goldfarb (1988) reported finding CDD/CDF concentrations ranging from 0.04 to 6.6 μg/kg in soot samples collected after a 1986 fire in a State University of New York lecture hall. The fire consumed or melted plastic furnishings, cleaning products containing chlorine, wood, and paper.

Funcke et al. (1988) (as reported in Bremmer et al., 1994 and Rotard, 1993) analyzed 200 ash and soot samples from sites of accidental fires in which PVC was involved. CDD/CDFs were detected in more than 90 percent of the samples at concentrations in the ng TEQ/kg to μg TEQ/kg range. Fires involving the combustion of materials containing relatively large amounts of PVC and other chlorinated organic substances resulted in the highest levels of CDD/CDFs with CDD/CDF concentrations ranging from 0.2 to 110 μg TEQ/kg of residue.

Thiesen et al. (1989) analyzed residues from surfaces of PVC-containing materials that were partially burned during accidental fires at sites in Germany that manufactured or stored plastics. CDD/CDF concentrations in residues were reported as 0.5 μg TEQ/kg for

soft PVC, 4.6 μg TEQ/kg for PVC fibers, and 28.3 μg TEQ/kg for a hard PVC. The ratio of total CDFs to total CDDs in the three samples ranged from 4 to 7. The dominant 2,3,7,8-substituted CDF and CDD congeners in all three samples were 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,6,7,8-HpCDD.

Following an accidental fire at a Swedish carpet factory in 1987, 200 metric tons of PVC and 500 metric tons of PVC-containing carpet burned. Marklund et al. (1989) analyzed snow samples within 1,500 meters downwind from the fire site and found CDD/CDF concentrations in the top 2 cm ranging from 0.32 μg TEQ/m^2 at 10 meters from the site to 0.01 μg TEQ/m^2 at 1,500 meters downwind of the site. Because of an atmospheric inversion and very light wind at the time of the fire, the smoke from the fire remained close to the ground. The soot deposited onto the snow was thus assumed to be representative of the soot generated and released from the fire. Wipe samples of soot from interior posts of the plant (5 and 20 meters from the fire) contained EADON TEQ concentrations of 0.18 and 0.05 μg/m^2. On the basis of these deposition measurements, Marklund et al. (1989) estimated the total CDD/CDF emission from the fire to be less than 3 mg TEQ.

Carroll (1996) estimated a soot-associated CDD/CDF emission factor (i.e., does not include volatile emissions) of 28 to 138 ng TEQ/kg of PVC burned for this fire using the following assumptions: (1) the PVC carpet backing was one-half the weight of the carpet; (2) the carpet backing contained 30 percent by weight PVC resin; and (3) 20 to 100 percent of the PVC and PVC carpet backing present in the warehouse actually burned. Carroll (1996) also estimated a similar soot-associated emission factor (48 to 240 ng TEQ/kg of PVC burned) for a fire at a plastics recycling facility in Lengerich, Germany. Carroll (1996) used the results of wipe samples collected at downwind distances of up to 6,300 meters from the fire to estimate the emission factor.

Fiedler et al. (1993) presented a case study of CDD/CDF contamination and associated remedial actions taken at a kindergarten in Germany following a fire, which destroyed parts of the roof, windows, and furnishings. Soot collected from the building contained CDD/CDFs at a concentration of 45 μg TEQ/kg (or 15 μg TEQ/m^2). Fiedler et al. (1993) attributed the CDD/CDFs detected to the combustion of plastic and wooden toys, floors, and furnishings; however, no information was provided on the quantities of these materials that burned.

Wichmann et al. (1993; 1995) measured the CDD/CDF content of ash/debris and deposited surface residues that resulted from experimental test burns of two cars (a 1974 Ford Taurus and a 1988 Renault Espace), one subway car, and one railway coach in a tunnel in Germany. Based on the measurements obtained from sampled ash/debris and from soot collectors placed at regular spacing up to 420 meters downwind of the burn site, the total amounts of CDD/CDF in the ash/debris and tunnel surface residues from each vehicle burn experiment were estimated to be: 1974 model car - 0.044 mg TEQ; 1988 model car - 0.052 mg TEQ; subway car - 2.6 mg TEQ; and railway coach - 10.3 mg TEQ. Of these total amounts of TEQ, 73 to 89 percent were accounted for by the tunnel surface residues and 11 to 27 percent by ash/debris. The average CDD/CDF content of the ash/debris from each experimental burn was as follows: new car - 0.14 μg TEQ/kg; old car - 0.30 μg TEQ/kg; subway car - 3.1 μg TEQ/kg; and railway coach - 5.1 μg TEQ/kg.

6.2.2. Fume/Smoke Studies

Merk et al. (1995) collected fume/smoke generated during the burning of 400 kg of wood and 40 kg of PVC in a closed building (4,500 m^3 volume) over a 45-minute time 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 CDD/CDFs. The particulates and gas phase showed the same congener pattern, decreasing concentration with increasing degree of chlorination, thus indicating no preferential sorption of higher chlorinated congeners to smoke particulates. However, the CDD/CDF found in the gas phase (about 5 ng TEQ/m^3) accounted for more than 90 percent of the detected CDD/CDFs. Merk et al. (1995) also reported that the soot deposited from this fire resulted in surface contamination of 0.050 μg TEQ/m^2.

Dyke and Coleman (1995) reported a four-fold increase in CDD/CDF TEQ concentrations in the ambient air during "bonfire" night in Oxford, England. Bonfire night (November 5) is an annual event in England 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 TEQ/m^3. The air concentration during the bonfire night was 0.65 pg TEQ/m^3. The dominant congeners in all samples were the hepta- and octa- CDDs. The study was not designed to collect data that would enable calculation of an emission rate nor 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

Structural Fires - The limited data available were judged inadequate for developing national emission estimates that could be included in the national inventory. This conclusion was also reached in national emission inventories developed for The Netherlands (Bremmer et al., 1994) and the United Kingdom (UK Department of the Environment, 1995). Most cited studies involved situations (i.e., 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, etc. likely to be found in accidental fires cannot be accounted for by the factors that can be derived from these studies. Also, most of these studies addressed only soot and/or ash residues and did not address potential volatile emissions of CDD/CDFs which, according to Merk et al. (1995), may represent 90 percent of the CDD/CDFs generated during burning of PVC.

Two recent 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 the Federal Republic of Germany. The estimates derived in these three studies are presented below, following a brief summary of the number of accidental fires reported annually in the United States.

In 1995, approximately 574,000 structural fires were reported in the United States (U.S. DOC, 1997). Of these, 426,000 were reported for residential structures, which consist of 320,000 fires in 1-2 family units, 94,000 fires in apartments, and 12,000 fires in "other" residential settings. The remaining 148,000 structural fires consist of 15,000 - public assembly; 9,000 - educational; 9,000 - institutional; 29,000 - stores and offices; 29,000 - special structures; 39,000 - storage; and 18,000 - industry, utility, and defense. The latter two categories may be under reported as some incidents were handled by private fire brigades or fixed suppression systems, which do not report (U.S. DOC, 1997).

Carroll (1996) estimated the total CDD/CDF content of soot and ash generated from the 358,000 fires reported in U.S. DOC (1995a) for 1993 in 1-2 family unit residential structural fires. The estimated soot/ash content ranged from 0.47 to 22.8 g TEQ with

0.07 to 8.6 g TEQ in soot and 0.4 to 14.2 g TEQ in ash. Carroll (1996) then developed detailed estimates of the PVC content of typical homes (including plumbing, wiring, siding and windows, wallpaper, blinds and shades, and upholstery), and, using statistical data on fire loss (i.e., dollar value), the typical loss per recorded fire (9.5 percent) was assumed to represent the typical percentage of PVC present that is burned. Extrapolating to all 358,000 1-2 family unit fires yielded an annual mass of PVC burned of 2,470 metric tons. Carroll (1996) then developed TEQ emission factors from the results of Thiesen et al. (1989) and Marklund et al. (1989) using a soot emission factor (i.e., grams of soot produced per gram of PVC combusted) derived by Carroll (1996) based on assumptions regarding the surface area of the soot collection funnel used by Marklund et al. (1989) and the soot deposition rate on that funnel. These TEQ emission factors were then applied by Carroll (1996) to the estimated 2,470 metric tons of PVC burned annually in 1-2 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 (i.e., 0.48 to 22.8 g TEQ/yr). If the conclusion of Merk et al. (1995) that 90 percent of the CDD/CDFs formed in fires are in the gaseous phase rather than particulate phase (i.e., greater than 0.5 μm diameter) is assumed to be correct, then the volatile CDD/CDF emissions corresponding to the range of soot/ash emissions estimated by Carroll (1996) total 4.3 to 205 g TEQ/yr. There is very low confidence in these estimated emissions because of the numerous assumptions employed in their derivation.

Thomas and Spiro (1995) estimated that 20 g of TEQ may be released annually to air from structural fires. This estimate assumed an emission factor of 4 ng TEQ/kg of material combusted (i.e., the emission rate for "poorly controlled" wood combustion), an assumed material combustion factor of 6,800 kg/fire, and 688,000 structural fires/yr.

Lorenz et al. (1996) estimated annual generation of CDD/CDF TEQs in the Federal Republic of 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 TEQ generation was estimated to be 78 to 212 grams.

Vehicle Fires - The limited data available were judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary order of magnitude estimate of the range of potential CDD/CDF emissions that may result from vehicle fires can be estimated using the results reported by Wichmann, et al. (1993; 1995) for controlled vehicle fires in a tunnel (0.044 mg TEQ for an old car to 2.6

mg TEQ for a subway car). Although Wichmann et al. (1993; 1995) did not measure volatile CDD/CDFs (which were reported by Merk et al. (1995), to account for the majority of CDD/CDFs formed during a fire), the study was conducted in a tunnel, and it is likely that a significant fraction of the volatile CDD/CDFs sorbed to tunnel and collector surfaces and were thus measured as surface residues. In 1995, approximately 406,000 vehicle fires were reported in the United States (U.S. DOC, 1997). If it is assumed that 99 percent of the 406,000 reported vehicle fires in 1995 involved cars and trucks (i.e., approximate percentage of in-service cars and trucks to total of all motor vehicles, U.S. DOC (1995a) and that the applicable emission rate is 0.044 mg/TEQ per incident, then the annual TEQ formation is 17.7 g TEQ. The emission factor of 2.6 mg TEQ/fire is assumed to be applicable to the remaining 1 percent of vehicle fires, thus yielding an emission of 10.6 g TEQ/yr. The total TEQ annual emission is roughly estimated to be 28.3 g TEQ/yr, which, when rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, results in a value of 10 g TEQ/yr. This estimate sould be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

6.3. LANDFILL FIRES

In the late 1980s, two serious fires occurred in landfills near Stockholm, Sweden. The first involved a fire in a large pile of refuse-derived fuel. Based on 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 10s of grams based on the assumption that the ratio of CDD/CDFs to chlorobenzenes in landfill fire emissions is similar to the ratio observed in stack gases of municipal waste incinerators. 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 impacted by smoke from the fire. The discharge of CDD/CDF necessary to cause the CDD/CDF concentrations measured on the leaves was estimated to be several 10s of grams (Persson and Bergström, 1991).

In response to these incidents, Persson and Bergström (1991) 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 TEQ emissions in Sweden from landfill fires to be 35 grams. The estimate was based on the emission rate of 1 μg Nordic TEQ/kg waste burned, an assumed average density of landfill waste of 700 kg/m^3, an assumed waste burn of 150 m^3 for each surface landfill fire (167 fires in Sweden per year), and an assumed waste burn of 500 m^3 for each deep landfill fire (50 fires in Sweden per year). The estimates of waste burn mass for each type of fire were the average values obtained from a survey of 62 surface fires and 25 deep fires. The estimated number of fires per year was based on the results of a survey of all Swedish municipalities for fires reported during the years 1988 and 1989. Sweden has an estimated 400 municipal landfills (Persson and Bergström, 1991).

Ruokojärvi et al. (1995) measured the ambient air concentrations of CDD/CDF 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 50-70 g Nordic TEQ (Aittola, 1993 - as reported by Ruokojärvi et al., 1995).

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 are expected to be similar between the United States and Sweden. However, 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 order of magnitude 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 county. Both countries are Western, 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 1995 population of

Sweden is 8,822,000 (U.S. DOC, 1995a). Thus, the per capita landfill fire-associated TEQ emission factor is 4.0 μg TEQ/person/year (i.e., 35 grams/8,822,000 people). Applying this factor to the U.S. population (263,814,000) (U.S. DOC, 1995a) results in an estimated annual emission of 1,050 g of TEQ. When rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, the estimated annual emission is 1,000 g TEQ/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions. An annual emission of similar size is obtained if it is assumed that the ratio of annual TEQ emissions to number of landfills in Sweden, 87.5 mg TEQ/landfill (i.e., 35 grams/400 landfills), is applicable to the United States, which has 3,558 landfills (U.S. EPA, 1996b). The resulting annual emission estimate is 311 g TEQ/yr.

6.4. FOREST AND BRUSH FIRES

Because CDD/CDFs have been detected both in the soot from residential wood burning (Bumb et al.; 1980; Nestrick and Lamparski, 1982 and 1983; Bacher et al., 1992), and in the flue gases from residential wood burning (Schatowitz et al.; 1993; Vickelsoe et al., 1993) [Section 4.2 contains details on these studies], it is reasonable to presume that wood burned in forest and brush fires may also be a source of CDD/CDFs.

Only one study could be found that reported direct measurements of CDD/CDFs in the emissions from forest fires. This study, by Tashiro et al. (1990), reported detection of total CDD/CDFs in air at levels ranging from about 15 to 400 pg/m^3. The samples were collected from fixed collectors 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), reported total CDD/CDF levels in the smoke of about 20 pg/m^3. The authors concluded that CDD/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 CDD/CDFs.

Although not designed to directly assess whether CDD/CDFs are formed during brush fires, Buckland et al. (1994) measured the 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 2-cm deep surface soil cores 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 TEQ content in the three unburnt area soil sample composites were 3.0 ng/kg, 8.7 ng/kg, and 10.0 ng/kg. The TEQ content in the three burnt area soil sample composites were 2.2 ng/kg, 3.1 ng/kg, and 36.8 ng/kg. Total CDD/CDF content ranged from 1,050 to 7,700 ng/kg in the unburnt area soil samples and from 1,310 to 27,800 ng/kg in the burnt area soil samples. OCDD accounted for 94 to 97 percent of the total CDD/CDF content in all samples.

Similarly, a survey of controlled straw field burning in the United Kingdom (Walsh et al., 1994) indicated that the straw burning did not increase CDD/CDF burden in the soil; however, a change in congener distribution was observed. Soils from three fields were sampled immediately before and after burning, along with ash from the fire. The mean TEQ concentrations in the pre-burn soil, post-burn soil, and field burn ash were 1.79 ng/kg, 1.72 ng/kg, and 1.81 ng/kg, respectively. Concentrations of 2,3,7,8-TCDF were lower in the post-burn soils than in the pre-burn soils. Conversely, the concentrations of OCDD were higher in the post-burn soils indicating possible formation of OCDD during the combustion process.

Van Oostdam and Ward (1995) reported finding no detectable levels of 2,3,7,8-substituted CDD/CDFs in three soil samples and four ash samples following a forest fire in British Columbia. The detection limits on a congener-specific basis (unweighted for TEQ) ranged from 1 to 2 ng/kg. Nondetected values were also reported by Van Oostdam and Ward (1995) for ashes at a slash and burn site; the soil contained about 0.05 ng TEQ/kg, whereas background soil contained about 0.02 ng TEQ/kg.

The concentrations presented by Clement and Tashiro (1991) cannot accurately be converted to an emission factor, because the corresponding rates of combustion gas production and wood consumption are not known. As a result, three alternative approaches were considered to develop these emission factors:

- Soot-Based Approach: This approach assumes that the level of CDD/CDFs in chimney soot are representative of the CDD/CDFs in emissions, and estimates the CDD/CDF emission rate as the product of the soot level and the total particulate emission rate. This involves first assuming that the CDD/CDF levels measured by Bacher et al.

(1992) in chimney soot (720 ng TEQ/kg) are representative of the CDD/CDF concentrations of particles emitted during forest fires. Second, the total particulate generation rate must be estimated. Ward et al. (1976) estimated the national average particulate emission factor for wildfires as 150 lb/ton biomass dry weight based primarily on data for head fires. Ward et al. (1993) estimated the national average particulate emission factor for prescribed burning as 50 lb/ton biomass dry weight. Combining the total particulate generation rates with the CDD/CDF levels in soot yields emission factor estimates of 54 μg of TEQ and 18 μg of TEQ/metric ton of biomass burned in wildfires and prescribed burning, respectively. This corresponds to a range of 54 to 18 ng TEQ/kg of biomass. This estimate is likely to be an overestimate, because the levels of CDD/CDF measured in chimney soot by Bacher et al. (1992) may represent accumulation/enrichment of CDD/CDFs measured in chimney soot over time, leading to much higher levels than what is actually on emitted particles.

- Carbon Monoxide (CO) Approach: CO is a general indicator of the efficiency of combustion and the emission rate of many emission products can be correlated to the CO emission rate. The Schatowitz et al. (1993) data for emissions during natural wood burning in open stoves suggest an emission rate of 10 μg TEQ/kg of CO. Combining this factor with the CO production rate during forest fires (roughly 0.1 kg CO/kg of biomass - Ward et al. (1993)) yields an emission factor of 1,000 ng TEQ/kg biomass. This factor appears unreasonably high, because it is even higher than the soot-based factor discussed above. Although the formation kinetics of CDD/CDF during combustion are not well understood, it appears that CDD/CDF emissions do not correlate well with CO emissions.

- Wood Stove Approach: This approach assumes that the emission factor for residential wood burning (using natural wood and open door, i.e., uncontrolled draft) applies to forest fires. As discussed in Section 4.2.1, this approach suggests an emission factor of about 2 ng TEQ/kg of wood burned. This value appears more reasonable than the factors suggested by the soot and CO approaches. However, forest fire conditions differ significantly from combustion conditions in wood stoves. For example, forest fire combustion does not occur in an enclosed chamber, and the biomass consumed in forest fires is usually green and includes underbrush, leaves, and grass. Given these differences

and the uncertainties about the formation kinetics of CDD/CDF during combustion, it is difficult to determine whether CDD/CDF emissions would be higher or lower from forest fires than from wood stoves. Thus, although an emission factor of 2 ng TEQ/kg appears to be the best estimate that can be made currently, it must be considered highly uncertain; therefore, a "low" confidence rating was assigned to this estimate.

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 burnings are not readily available for the reference years 1995 and 1997. An estimated 5.1-million acres of biomass were burned in 1989 during prescribed burns (Ward et al., 1993). Prescribed burning is also known as managed or controlled burning and is used as a forest management tool under exacting weather and fuel conditions. This value of 5.1-million acres is assumed to be an appropriate value to use for reference years 1987 and 1995.

Combining these acreage estimates with biomass consumption rates of 9.43 metric tons/acre in areas consumed by wildfires (Ward et al., 1976) and 7.44 metric tons/acre in areas consumed in prescribed burns (Ward et al., 1993), indicates that 47-million metric tons of biomass were consumed in 1987 by wildfires, 66-million metric tons of biomass were consumed in 1995 by wildfires, and 38-million metric tons of biomass were consumed in 1987 and in 1995 by prescribed burns. These estimates were assigned a "medium" confidence rating, because they are based on a combination of estimates involving historical data on acres burned but less certain estimates of biomass burned/acre.

Combining the emission factor developed using the "wood stove" approach (i.e., 2 ng TEQ/kg biomass) with the amount of biomass consumed annually in wildfires and prescribed fires (total of 85-million metric tons in 1987 and 104-million metric tons in 1995) indicates that the TEQ emissions from this source were 170 g in 1987 and 208 g in 1995. Based on the low confidence rating given to the emission factor, the estimated range of potential annual emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the best estimate of emissions in 1987 (170 g TEQ/yr) is the geometric mean of this range, then the range is calculated to be 53.8 to 538 g TEQ/yr. The range for 1995 is calculated to be 64.5 to 645 g TEQ/yr.

6.5 BACKYARD TRASH BURNING

In many rural areas of the United States, disposal of residential solid waste may take place via open backyard burning in barrels or similar home-made devices. Although no national statistics on the prevalence of this practice have been reported, the results of a telephone survey conducted in the early 1990s of residents in five central Illinois counties indicate that about 40 percent of the residents in a typical rural Illinois county burn household waste (Two Rivers Region Council of Public Officials and Patrick Engineering, 1994). The survey also found that, on average, those households that burn waste dispose of approximately 63 percent of their household waste through burning in barrels (Two Rivers Region Council of Public Officials and Patrick Engineering, 1994).

The low combustion temperatures and oxygen-starved conditions associated with these devices may result in incomplete combustion and increased pollutant emissions (Lemieux, 1997). EPA's Control Technology Center, in cooperation with the New York State Departments of Health (NYSDOH) and Environmental Conservation (NYSDEC), recently 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 based on the typical percentages of various waste materials disposed by New York State residents; hazardous wastes (i.e., chemicals, paints, oils, etc.) were not included in the test waste. A variety of compounds, including CDD/CDFs, were measured in the emissions from the simulated open burning. The measured CDD/CDF TEQ emission factor for waste, which has not been separated for recycling purposes, was 0.14 μg TEQ/kg of waste burned (setting not detected values equal to zero) and 0.3 μg TEQ/kg (setting not detected values equal to one-half the detection limit).

The limited emission factor and activity level data available were judged inadequate for developing national emission estimates that could be included in the national inventory. The number of households nationwide burning waste in barrels is unknown. The emission factor was developed on the basis of just two experiments. The representativeness of the trash and burning conditions used in the experiments to rural conditions nationwide are unknown. However, combining the emission factor of 0.14 μg TEQ/kg of waste burned with the following information/assumptions, allows a preliminary order of magnitude

estimate to be made of potential national CDD/CDF TEQ emissions from backyard household trash burning.

- Forty percent of the rural population in the United States are assumed to burn their household waste in a barrel (Two Rivers Region Council of Public Officials and Patrick Engineering, 1994).

- On average, each U.S. citizen generates 3.72 pounds of solid waste (excluding yard waste) per day (or 616 kg/person-yr) (U.S. EPA, 1996b).

- On average, for those individuals burning household waste, approximately 63 percent of waste generated are burned (i.e., 63 percent of 616 kg/person-yr = 388 kg/person-year) (Two Rivers Region Council of Public Officials and Patrick Engineering, 1994).

- In 1992, 51.8-million people lived in nonmetropolitan areas (U.S. DOC, 1997).

Emissions = $(51.8 \times 10^6$ people)(40%)(388 kg/person-yr)(0.14 μg TEQ/kg)(10^{-6} g/μg)
= 1,125 g TEQ/yr

When rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, the estimate of 1,125 g TEQ/yr results in a value of 1,000 g TEQ/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

6.6. UNCONTROLLED COMBUSTION OF POLYCHLORINATED BIPHENYLS (PCBS)

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 and CDFs. At elevated temperatures, such as in transformer fires, PCBs can undergo reactions to form CDF and other by-products. More than 30 accidental fires and explosions involving PCB transformers and capacitors in the United States and Scandinavia, which involved the combustion of PCBs and the generation of CDDs and 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 with 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 percent) and

chlorobenzene (35 percent). Laboratory analyses of soot samples from a PCB transformer fire, which 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 percent, and a residence time of 0.8 seconds or longer. Combusting mineral oil and silicone oil containing 5, 50, and 500 ppm of Aroclor 1254 at these conditions for 0.8 seconds yielded PCB to CDF conversion efficiencies as high as 4 percent. Up to 3 percent conversion efficiency was observed when an askarel (70 percent 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 (TSCA).

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 to support even an order of magnitude estimate of annual CDD/CDF emissions. 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: (1) a TEQ emission rate of 20 μg/kg of PCB burned; (2) 74,000 metric tons of PCB are still in use in various electrical equipment; and (3) 1 percent of the in-use PCBs is burned during the course of structural fires annually.

6.7. VOLCANOES

To date, no studies demonstrating formation of CDD/CDFs by volcanoes have been published. Gribble (1994) summarized some of the existing information on the formation of chlorinated compounds by natural sources, including volcanoes. Gribble (1994) reported that several studies had demonstrated the presence of chlorofluorocarbons and simple halogenated aliphatic compounds (one and two carbon chain length) in volcanic gases. In addition, several chlorinated monoaromatic compounds as well as three PeCB congeners were reported as having been detected in the ash from the 1980 eruption of Mt. St.

Helens. The formation of these PCB compounds was hypothesized by Gribble (1994) to be the result of rapid, incomplete high temperature combustion of chloride-containing plant material in the eruption zone. However, Gribble (1994) presented no information indicating formation of CDD/CDFs by volcanoes.

Lamparski et al. (1990) analyzed groundfall ash samples collected at various distances and locations from Mt. St. Helens following the eruption in 1980. The findings of this study indicate that volcanic particulate emissions were free of detectable PCBs and nearly free of detectable CDDs (0.8 ng/kg HpCDD detected) upon exiting the volcano and remained so throughout their period of deposition in the blast zone. However, upon transport through the atmosphere, measurable and increasing levels of CDDs and PCBs were detected in deposited ash as the ash passed from rural to urban environments. The authors hypothesized that CDDs and PCBs in the atmosphere became associated with the volcanic ash particulates through gas-phase sorption or particulate agglomeration.

Takizawa et al. (1994) sampled the dust fall from the active volcano, Fugendake, as well as the volcanic ash from the active volcano, Sakurajima, for CDD and CDF congener group concentrations. The study was not designed to determine whether the CDD/CDFs observed were formed by the volcanoes or were scavenged from the atmosphere by the falling dust and ash. The dust fall was collected for 1-month periods during July and October 1992; two samples of the volcanic ash were collected in 1992. The results of the sample analyses for 2,3,7,8-substituted CDDs and CDFs, presented in Table 6-2, show that no 2,3,7,8-substituted congeners with less than 7 chlorines were detected; Takizawa et al. (1994), however, did report that non-2,3,7,8-substituted congeners in the lower chlorinated congener groups were detected.

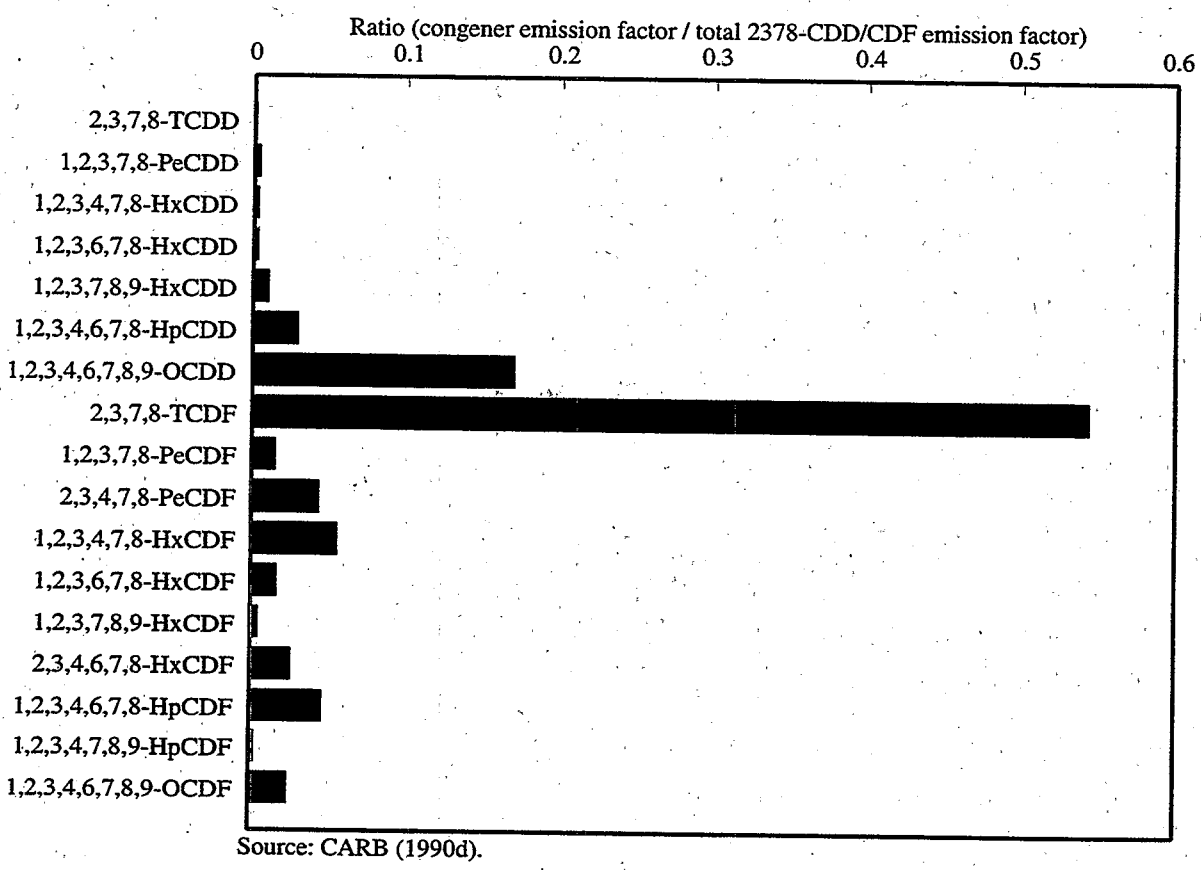
Based on the available information from the studies discussed above, it is concluded that volcanoes do not appear to be sources of CDD/CDF release to the environment.

Table 6-1. CDD/CDF Emission Factors for a Landfill Flare

Congener/Congener Group	Mean Facility Emission Factor*
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	0.110
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 TEQ	2.392
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

Source: CARB (1990d)

* Assumes heat content of 1.86E+07 J/m^3 for landfill gas (Federal Register, 1996a).
NR = Not reported.



Source: CARB (1990d).

Figure 6-1. Congener Profile for Landfill Flare Air Emissions

Table 6-2. CDD/CDF in Dust Fall and Ashes from Volcanoes

2,3,7,8-Substituted Congener Group	Dust Fall (mg/km^2/month)[a]		Volcanic Ash (ng/kg)[b]	
	July 1992	Oct. 1992	Ash No. 1	Ash No.2
TCDD	<0.5	<0.5	<0.1	<0.1
PeCDD	<0.5	<0.5	<0.1	<0.1
HxCDD	<0.5	<0.5	<0.1	<0.1
HpCDD	9.2	5.2	2.5	1.8
OCDD	14	11	1.7	2.2
TCDF	<0.5	<0.5	<0.1	<0.1
PeCDF	<0.5	<0.5	<0.1	<0.1
HxCDF	<0.5	<0.5	<0.1	<0.1
HpCDF	1.9	2.8	1.2	1.2
OCDF	4.2	1.8	<0.5	<0.5

Source: Takizawa et al. (1994).

[a] Dust fall measured from the active volcano, Fugendake.

[b] Volcanic ash measured from active volcano, Sakurajima.

7. METAL SMELTING AND REFINING SOURCES OF CDD/CDF

7.1. PRIMARY NONFERROUS METAL SMELTING/REFINING

Nonferrous metals include copper, magnesium, nickel, and aluminum. The potential for formation and release of CDD/CDFs by primary copper smelters has been addressed by Environmental Risk Sciences (1995). Although European investigators (Oehme et al., 1989; Lexen et al., 1993) have reported the presence of CDD/CDFs in the wastestreams of magnesium, nickel, and aluminum refining facilities, insufficient information is available for evaluating CDD/CDF emissions, if any, from the smelting/refining of these nonferrous metals in the United States. The findings of these studies are discussed in the following paragraphs.

Environmental Risk Sciences (1995) recently prepared an analysis for the National Mining Association on the potential for dioxin emissions from the primary copper smelting industry. The analysis included a detailed review of the process chemistry and technology of primary copper smelting, collection of operating conditions, and process stream compositions from seven of the eight U.S. primary copper smelters, and stack testing for CDD/CDFs at two facilities. The stack testing (Secor International, Inc., 1995a and 1995b) involved the principal process off-gas streams for copper smelters: main stack, plant tail gas stack, and the vent fume exhaust. The two tested facilities were assumed to be representative of the other facilities in the industry due to similarities in process chemistry, process stream composition, and process stream temperatures.

The results of the analyses of the process chemistry/technology and the operating parameters and process stream compositions indicated a very low potential for CDD/CDF emissions. The results of this conclusion are supported by the stack test data from the two tested facilities. CDD/CDFs were not detected in the emissions from either facility. If it is conservatively assumed that all nondetected values were present at one-half the detection limits, the annual TEQ emission rate for the copper smelting industry would be less than 1 gram (g).

Oehme et al. (1989) reported that the production of magnesium leads to the formation of CDDs and CDFs. Oehme et al. (1989) estimated that 500 g of TEQ are released in wastewater to the environment and 6-g TEQ are released to air annually from a magnesium production facility studied in Norway; CDFs predominated with a CDF to CDD

concentration ratio of 10 to 1. The magnesium production process involves a step in which $MgCl_2$ is produced by heating MgO/coke pellets in a pure chlorine atmosphere to about 700 to 800°C. The $MgCl_2$ is then electrolyzed to metallic magnesium and Cl_2. The Cl_2 excess from the $MgCl_2$ process and the Cl_2 formed during electrolysis are collected by water scrubbers and discharged to the environment.

Oehme et al. (1989) also reported that certain primary nickel refining processes generate CDDs and CDFs, primarily CDFs. Although the current low temperature process used at the Norwegian facility studied is estimated to release only 1-g TEQ per year, a high temperature $NiCl_2$/NiO conversion process that had been used for 17 years at the facility is believed to have resulted in much more significant releases based on the ppb levels of CDFs detected in aquatic sediments downstream of the facility (Oehme et al., 1989).

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 CDD/CDF.

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/refining processes for some metals (e.g., aluminum, copper, and magnesium) utilize chemicals such as NaCl, KCl, 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 and CDFs, as evidenced by the detection of CDDs and CDFs in the stack emissions of secondary aluminum, copper, and lead smelters (Aittola et al., 1992; U.S. EPA, 1987a; U.S. EPA 1997b).

7.2.1. Secondary Aluminum Smelters

Secondary aluminum smelters reclaim aluminum from scrap containing aluminum. This recycling involves 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 contaminates 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.

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 the addition of chlorine gas. The molten aluminum is transferred to a holding furnace and alloyed to final specifications.

CDD/CDF emission factors for secondary aluminum operations can be derived from results of testing performed in 1995 at four secondary aluminum smelters. Three of the tests were conducted by EPA in conjunction with the Aluminum Association for the purpose of identifying emission rates from facilities with potentially MACT-grade operations and APCD equipment.

The first facility tested was a top charge melt furnace (Advanced Technology Systems, Inc., 1995). During testing, the charge material to the furnace was specially formatted to contain no oil, paint, coatings, rubber, or plastics (other than incidental amounts). The CDD/CDF emissions from such a clean charge, 0.26-ng TEQ/kg charge material, would be expected to represent the low end of the normal industry range.

The second facility operates a sweat furnace to preclean the scrap and a reverberatory furnace to smelt the pre-cleaned aluminum (U.S. EPA, 1995h). Stack emissions are controlled by an afterburner operated at 1,450° F. The TEQ emission factor for this facility was 3.22-ng TEQ/kg aluminum produced.

The third facility employs a crusher/roasting dryer as a precleaning step followed by a reverberatory furnace (Galson Corporation, 1995). The emissions from the two units are vented separately. The exhaust from the crusher/dryer is treated with an afterburner and a baghouse. The exhaust from the furnace passes through a baghouse with lime injection.

Both stack exhausts were tested and the combined TEQ emission factor was 12.95-ng TEQ/kg aluminum produced. Because the activity level of the facility at the time of sampling was treated as confidential business information, the calculated emission factor was based on the reported typical production rates of the two operations, 26,000 lbs/hr for the crusher/dryer and 6,700 lbs/hr for the furnace.

The fourth facility operates a scrap roasting dryer followed by a sidewell reverberatory furnace (Envisage Environmental, Inc., 1995). The emissions from the two units are vented separately. Exhaust from the dryer passes through an afterburner and a lime-coated baghouse. The exhaust from the furnace passes through a lime-coated baghouse. Both stack exhausts were tested and the combined TEQ emission factor was 36.03-ng TEQ/kg of charge material. Problems with the scrap dryer were discovered after the testing was completed. Also, operating conditions during testing were reported to represent more worst case than typical operations.

The congener and congener group emission factors derived from this testing are presented in Table 7-1. The average congener and congener group profiles are presented in Figure 7-1. The average of the TEQ emission factors measured at the four facilities is 13.1-ng TEQ/kg of scrap feed. [Note: Although the emission factors at two of the facilities are based on the output rather than input rate, the two rates are assumed, for purposes of this report, to be roughly equivalent.] Although the testing was recently conducted at U.S. facilities, a "low" confidence rating is assigned to this average emission factor, because it is based on the results of testing at only four facilities, several of which may have more effective APCD than the other facilities in the industry. For example, two facilities tested by CARB in 1992 and reported in two confidential reports (CARB, 1992a, as reported in U.S. EPA, 1997b; CARB, 1992b, as reported in U.S. EPA, 1997b) were reported to have TEQ emission factors of 52.2- and 21.7-ng TEQ/kg scrap aluminum consumed.

Umweltbundesamt (1996) reported stack testing results for 25 aluminum smelters/ foundries in Germany. Sufficient data were provided in Umweltbundesamt (1996) to enable calculation of TEQ emission factors for 11 of the tested facilities. The calculated emission factors ranged from 0.01- to 167-ng TEQ/kg of scrap feed. Three facilities had emission factors exceeding 100-ng TEQ/kg, and two facilities had emission factors less than 1-ng TEQ/kg. The mean emission factor for the 11 facilities was 42-ng TEQ/kg,

which is very similar to the mean emission factor for the two CARB studies (i.e., 37-ng TEQ/kg).

A total of approximately 727,000 metric tons of scrap aluminum were consumed by 67 secondary aluminum smelters in 1987 (U.S. DOC, 1995c). In 1995, consumption of scrap aluminum by the 76 facilities comprising the secondary aluminum smelting industry had nearly doubled to a quantity of 1.3-million metric tons (U.S. Geological Survey, 1997a; The Aluminum Association, 1997). A "high" confidence rating is assigned to these production estimates, because they are based on government survey data. Applying the TEQ emission factor of 13.1-ng TEQ/kg of scrap feed to these consumption values yields estimated annual emissions of 9.5-g TEQ in 1987 and 17.0-g TEQ in 1995.

Based on the "low" confidence rating assigned to the estimated TEQ emission factor, the estimated range of potential emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the estimated emissions of 9.5-g TEQ in 1987 and 17.0-g TEQ in 1995 are the geometric means of the ranges for these years, then the ranges are calculated to be 3.0- to 30.0-g TEQ in 1987 and 5.4- to 53.8-g TEQ in 1995.

It should be noted that a significant amount of scrap aluminum is consumed by other segments of the aluminum industry. Integrated aluminum companies consumed 1.4-million metric tons of scrap aluminum in 1995, and independent mill fabricators consumed 0.68-million metric tons (U.S. Geological Survey, 1997a).

7.2.2. Secondary Copper Smelters/Refiners

Stack emissions of CDD/CDFs from a secondary copper smelter were measured by EPA during the National Dioxin Study (U.S. EPA, 1987a). The tested facility recovers copper and precious metals from copper and iron-bearing scrap and was chosen for testing by EPA because the process technology and air pollution control equipment in place were considered typical for the source category. The copper and iron-bearing scrap are fed in batches to a cupola blast furnace, which produces a mixture of slag and black copper. Four 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 percent 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 comprised 22 percent 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 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 controlled particulate emissions, and the flue gas then was discharged into a common stack. The estimated emission factors derived for this site are presented in Table 7-2. The emission factors are based on the total weight of scrap fed to the furnace. The TEQ emission factor estimated in U.S. EPA (1997c), based on the measured congener and congener group emission factors, is 779 ng/kg of scrap metal smelted. Figure 7-2 presents the congener group profile based on these emission factors.

Approximately 390,000 metric tons of scrap copper were consumed by U.S. secondary copper smelters/refiners in 1987 (U.S. DOC, 1990a). In 1995, approximately 695,000 metric tons of scrap copper were consumed by the 24 operating U.S. copper smelters, refiners, and ingot makers (U.S. Geological Survey, 1997a). If the TEQ emission rate derived above (779 ng/kg of scrap consumed) is assumed to be representative of the 24 copper facilities, then the estimated air emissions of CDD/CDF TEQ by secondary copper operations in the United States in 1987 were 304 grams, and the estimated TEQ emissions in 1995 were 541 grams. A "high" confidence rating is assigned to the production estimates, because they are based on government survey data. A "low" confidence rating is assigned to the TEQ emission estimate, because it is based on direct measurements at only one U.S. copper smelter. Based on these confidence ratings, the estimated range of potential annual emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the estimates of annual emissions (304-g TEQ in 1987 and 541-g TEQ in 1995) are the geometric means of these ranges for those years, then the ranges are calculated to be 96- to 960-g TEQ in 1987 and 171- to 1,710-g TEQ in 1995.

It should be noted that a significant amount of scrap copper is consumed by other segments of the copper industry. In 1995, brass mills and wire-rod mills consumed

886,000 metric tons of copper-base scrap; foundries and miscellaneous manufacturers consumed 71,500 metric tons (U.S. Geological Survey, 1997a).

7.2.3. Secondary Lead Smelters/Refiners

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 comprise 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 one 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, 1994a).

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 percent 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 the emissions of a blast furnace (U.S. EPA, 1994a).

Historically, many lead-acid batteries contained PVC plastic separators between the battery grids. These separators are not removed from the lead-bearing parts of the battery during the battery breaking and separation process. When the PVC is burned in the smelter furnace, the chlorides are released as HCl, Cl_2, and chlorinated hydrocarbons (Federal Register, 1995d). The source of CDD/CDFs at secondary lead smelters is the PVC separator (U.S. EPA, 1995c). In 1990, about 1 percent of scrap batteries processed at lead smelters contained PVC separators. In 1994, less than 0.1 percent of scrap batteries contained PVC separators. This trend is expected to continue because no U.S. manufacturer of lead-acid automotive batteries currently uses PVC in production (U.S. EPA, 1995c; Federal Register, 1995d).

The total current annual production capacity of the 23 companies currently comprising the U.S. lead smelting industry is 1.36-million metric tons. Blast furnaces not co-located with reverberatory furnaces account for 21 percent of capacity (or 0.28-million metric tons). Reverberatory furnaces and blast and electric furnaces co-located with reverberatory furnaces account for 74 percent of capacity (or 1.01-million metric tons). Rotary furnaces account for the remaining 5 percent of capacity (or 0.07-million metric tons). Actual production volume statistics by furnace type are not available. However, if it is assumed that the total actual production volume of the industry, 0.97-million metric tons in 1995 (U.S. Geological Survey, 1997a) and 0.72-million metric tons in 1987 (U.S. EPA, 1994a), are reflective of 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 0.20-, 0.72-, and 0.05-million metric tons, respectively, in 1995, and 0.15-, 0.53-, and 0.04-million metric tons, respectively, in 1987. In 1987, the industry consisted of 24 facilities.

CDD/CDF emission factors can be estimated for lead smelters based on the results of emission tests recently performed by EPA at three smelters (a blast furnace, a co-located blast/reverberatory furnace, and a rotary kiln furnace) (U.S. EPA, 1992e; 1995d; 1995e). The air pollution control systems at the three tested facilities consisted of both baghouses and scrubbers. Congener-specific measurements were made at the exit points of both APCD exit points at each facility. Table 7-3 presents the congener and congener group emission factors from the baghouse and the scrubber for each site. Figure 7-3 presents the corresponding profiles for the baghouse emissions from the tested blast furnace and reverberatory furnace. Although all 23 smelters employ baghouses, only 9 employ scrubber technology. Facilities that employ scrubbers account for 14 percent of the blast furnace (not co-located) production capacity, 52 percent of the reverberatory and co-located furnace production capacity, and 57 percent of the rotary furnace production capacity. From the reported data, TEQ emission factors (ng TEQ/kg lead processed) for each of the three furnace configurations are presented below as a range reflecting the presence or absence of a scrubber.

Emission factors when nondetected values are set equal to zero:

- Blast furnace: 0.63- to 8.31-ng TEQ/kg lead produced.

- Reverberatory/co-located furnace: 0.051- to 0.41-ng TEQ/kg lead produced.
- Rotary furnace: 0.24- to 0.66-ng TEQ/kg lead produced.

If it is assumed that these emission rate ranges are representative of the range of emission rates at the non-tested facilities with the same basic furnace configuration and presence or absence of scrubbers, then combining these emission rate ranges with the estimates derived above for secondary lead production volumes and the percents of each configuration type that utilize or do not utilize scrubbers yields the following estimated air emissions in units of grams TEQ per year:

	Estimated Annual TEQ Emissions (g TEQ)*	
Configuration	Ref. Year 1995	Ref. Year 1987
Blast furnaces w/scrubbers	0.018	0.013
Blast furnaces w/o scrubbers	1.429	1.072
Reverberatory furnaces w/ scrubbers	0.019	0.014
Reverberatory furnaces w/o scrubbers	0.142	0.104
Rotary furnaces w/ scrubbers	0.019	0.015
Rotary furnaces w/o scrubbers	0.005	0.004
	1.632	1.223

* Calculated using emission factors based on nondetected values set equal to zero.

A "medium" confidence rating is ascribed to the emission factors derived above, because stack test data were available for 3 of the 23 smelters 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.

Based on these confidence ratings, the estimated range of potential annual emissions is assumed to vary by a factor of 5 between the low and high ends of the range. Assuming that the estimates of annual emissions (1.63-g TEQ in 1995 and 1.22-g TEQ in 1987) are the geometric means of these ranges for these years, then the ranges are calculated to be 0.73- to 3.65-g TEQ in 1995 and 0.55- to 2.73-g TEQ in 1987.

As discussed above, the PVC separators used historically in lead-acid batteries are believed to be the source of the CDD/CDFs observed in emissions from secondary lead smelters. PVC separators are no longer used in the United States in the manufacture of lead-acid batteries, and less than 0.1 percent of the scrap batteries in 1994 contained PVC separators (U.S. EPA, 1995c; Federal Register, 1995c). EPA predicts that by the time existing smelters demonstrate compliance in 1997 with the National Emission Standards for Hazardous Air Pollutants (NESHAP) for secondary lead smelters promulgated by EPA (Federal Register, 1995c), batteries containing PVC will only be present in the scrap battery inventory in trace amounts, resulting at most, in only trivial amounts of HCl or Cl_2 air emissions.

7.3. PRIMARY FERROUS METAL SMELTING/REFINING

Iron is manufactured from its ores (i.e., 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 production of iron and steel involves several operations identified by European researchers as potential emission sources of CDD/CDFs: sinter production, coke production, and electric arc furnaces. Each of these potential sources is discussed in the following subsections.

7.3.1 Sinter Production

During iron manufacturing, iron ores undergo sintering to enable better processing in the blast furnace. In the sintering process, iron ore fines are mixed with coke fines, and the mixture is placed on a grate, which is then heated to a temperature of 1,000-1,400°C. The heat generated during combustion sinters the small particles. Also, iron-bearing dusts and slags from other processes in the steel plant are recycled as a feed mix for the sinter plant (Knepper, 1981; Capes, 1983; U.S. EPA, 1995b).

No testing of CDD/CDF emissions from U.S. sinter plants has been reported. However, several European investigators have reported that iron ore sinter plants are major sources of airborne emissions CDD/CDFs (Rappe, 1992b; Lexen et al., 1993; Lahl, 1993; Lahl, 1994). Lahl (1993; 1994) reports that the management practice of recycling dusts and scraps from other processes in the steel plant into the sintering plant introduces traces of chlorine and organic compounds that generate the CDD/CDFs found in these plants. The

comparability of recycling practices at U.S. and European sinter plants has not been determined.

Sinter plants in Sweden were reported to emit up to 3-ng TEQ/Nm^3 stack gas or 2- to 4-g TEQ/yr per plant to the air (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 had an emission factor of 1.8-ng TEQ/dscm (at 11 percent O_2). The other two facilities, both equipped with cyclones, had emission factors of 6.3- and 9.6-ng TEQ/dscm (at 7 percent O_2). Lahl (1993; 1994) reports stack emissions for sintering plants in Germany (after passage through mechanical filters and electrostatic precipitators) ranging from 3- to 10-ng TEQ/Nm^3. A recent compilation of emission measurements by the German Federal Environmental Agency indicates stack emission concentrations ranging from 1.2- to 60.6-ng TEQ/m^3 (at 7 percent O_2); the majority of current emissions lie around 3-ng TEQ/m^3 (Umweltbundesamt, 1996).

In 1996, 11 sintering plants were operating in the United States, with a total annual production capacity of about 17.6-million metric tons (Metal Producing, 1996). Over the past 15 years, the size of this industry decreased dramatically. In 1982, 33 facilities operated with a combined total capacity of 48.3-million metric tons (U.S. EPA, 1982b). In 1987, sinter consumption was 14.5-million metric tons (AISI, 1990); in 1994, consumption was 12.2-million metric tons (AISI, 1995) or approximately 77 percent of production capacity assuming that production capacity in 1994 was the same as in 1996.

No testing of CDD/CDF emissions from U.S. sinter plants has been reported upon which to base an estimate of national emissions, and the comparability between dust/scrap recycling practices at U.S. and European sinter plants has not been determined. The limited data available were thus judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary order of magnitude estimate of potential TEQ annual emissions from U.S. sintering plants can be made using European emission test results and the following assumptions based on the data presented in Table 7-4: (1) the total strand surface area of U.S. plants is 1,685 m^2; (2) on average, an estimated 5,877 m^3 of exhaust gas are emitted per hour per m^2 of strand; (3) on average, sinter plants are operating at 77 percent capacity for 350 operating days per year (i.e., 6,486 hrs/yr); and (4) the TEQ emission factor is about 4-ng TEQ/m^3 of exhaust gas (i.e., the approximate midpoint of the emission factors reported by Rappe (1992b), Lexen et

al. (1993), Bremmer et al. (1994), Lahl (1994), and Umweltbundesamt, 1996)). Applying these assumptions yields an estimated total annual current emission of 256-g TEQ/yr, which, when rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, results in a value of 100-g TEQ/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

7.3.2 Coke Production

Coke is the principal fuel used in the manufacture of iron and steel. Coke 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 produced hot coke of 0.23-ng TEQ/kg of coal consumed. Minimal CDD/CDF air emissions, 0.002-ng TEQ/kg of coal, were estimated by Bremmer et al. (1994) for flue gases generated during charging and emptying the coke ovens.

In 1995, an estimated 30-million metric tons of coal were consumed by coke plants in the United States (EIA, 1997b). No testing of CDD/CDF emissions from U.S. coke plants has been reported upon which to base an estimate of national emissions. The limited data available were thus judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary order of magnitude estimate of potential TEQ annual emissions from U.S. coke plants can be made by combining the consumption value of 30-million metric tons and the emission factor reported by Bremmer et al. (1994) for a Dutch coke plant (0.23-μg TEQ/kg of coke). This calculation yields an annual emission of 6.9-g TEQ in 1995, which, when rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, results in a value of 10-g TEQ/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

7.3.3 Electric Arc Furnaces

Electric arc furnaces (EAFs) are used to produce carbon and steel alloys. The production of steel in an EAF is a batch process, and the input material is typically 100 percent scrap. Scrap, alloying agents, and fluxing materials are loaded into the cylindrical, refractory-lined EAF, and then carbon electrodes are lowered into the EAF. The current of the opposite polarity electrodes generates heat between the electrodes and through the scrap. A batch ranges from about 1.5 to 5 hours to produce carbon steel and from 5 to 10 hours to produce alloy steel (U.S. EPA, 1995b).

The melting of scrap ferrous material contaminated with metalworking fluids and plastics containing chlorine provides the conditions conducive to formation of CDD/CDFs. Tysklind et al. (1989) studied the formation and releases of CDD/CDFs at a pilot 10-ton electric furnace in Sweden. Scrap ferrous metal feedstocks containing varying amounts of chlorinated compounds (i.e., PVC plastics, cutting oils, or $CaCl_2$) were charged into the furnace under different operational conditions (i.e., 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^3 (i.e., after a bag house filter) were observed with a feedstock comprised of scrap metal with PVC plastics (1.3 g of chlorine per kg of feedstock). This emission equates to 7.7-ng Nordic TEQ/kg of feedstock. The highest emissions during batch charging also occurred when the scrap metal with PVC plastic was combusted (0.3-ng Nordic TEQ/dry Nm^3 or 1.7-ng Nordic TEQ/kg of feedstock). Much lower emissions (0.1-ng Nordic TEQ/dry Nm^3 or 0.6-ng Nordic TEQ/kg of feedstock) were observed when scrap metal with cutting oils containing chlorinated additives (0.4 g of chlorine per kg of feedstock) was melted. Although these cutting oil-related emissions were not significantly different than the emissions observed from the melting of "no-chlorine" scrap metal, relatively high levels of CDD/CDF (i.e., 110-ng Nordic TEQ/dry Nm^3) were detected in flue gases prior to the bag house. The congener profiles of raw flue gas samples (i.e., prior to APCD) showed that CDFs, rather than CDDs, were predominant in all three feedstock types. The congener profile from the test burn with PVC-containing feedstock showed a higher chlorinated congener content than was observed with the other feedstocks.

Eduljee and Dyke (1996) used a range of 0.7- to 10-ng TEQ per kg of scrap feed to estimate national emissions for the United Kingdom. The range was assumed to be

representative of "no chlorine" and "high chlorine" operations. However, little information was provided in Eduljee and Dyke (1996) on the supporting emission test studies (i.e., tested facility operational materials, feed rates, congener-specific emission rates).

Umweltbundesamt (1996) reported stack testing results for a variety of EAFs in Germany. Sufficient data were provided in Umweltbundesamt (1996) to enable calculation of TEQ emission factors for six of the tested facilities. Two facilities had emission factors exceeding 1-ng TEQ/kg of scrap processed, and two facilities had emission factors less than 0.1-ng TEQ/kg of scrap. The mean emission factor was 1.15-ng TEQ/kg of scrap. The TEQ concentrations in the stack gases at these facilities (corrected to 7 percent O_2) ranged from less than 0.1- to 1.3-ng TEQ/m^3.

In 1995, electric arc furnaces accounted for 40.4 percent of U.S. steel production (or 38.4 of the total 95.2-million metric tons of raw steel produced) (Fenton, 1996). No testing of CDD/CDF emissions from U.S. electric arc furnaces has been reported upon which to base an estimate of national emissions, and the limited European data available were thus judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary order of magnitude rough estimate of potential TEQ annual emissions from U.S. electric arc furnaces can be made by combining the production estimate of 38.4-million metric tons and the average emission factor derived from the data reported in Umweltbundesamt (1996) for six EAFs (i.e., 1.15-ng TEQ/kg scrap). This calculation yields an annual emission estimate of 44.3 g of TEQ in 1995, which, when rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, results in a value of 10-g TEQ/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

7.4 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 is performed primarily in cupola (or blast) furnaces and to a lesser extent in electric arc furnaces (EAF). About 70 percent of all iron castings are produced using cupolas, while steel foundries rely almost exclusively on EAFs or induction furnaces for melting. The cupola is typically a vertical, cylindrical steel shell with either a refractory-lined or 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. (EAFs are discussed in Section 7.3.3.) 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 EAFs, 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 percent (or 18-million metric tons) were used by ferrous foundries. The other 75 percent were used by primary ferrous metal smelters (principally those using EAFs) (U.S. Geological Survey, 1997b). Thus, foundries face the same potential for CDD/CDF emissions as EAFs because of use of scrap containing chlorinated solvents, plastics, and cutting oils. (See Section 7.3.3.) The potential for formation and release of CDD/CDFs during the casting process (i.e., pouring of molten metal into molds and cores comprised of sand and various organic binders and polymers) is not known.

The results of emissions testing have been reported for only one 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 a baghouse. The congener and congener group emission factors derived from the testing are presented in Table 7-5. The congener and congener group profiles are presented in Figure 7-4. The calculated TEQ emission factor for this set of tests is 0.37 ng/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 in Umweltbundesamt (1996) to enable calculation of TEQ emission factors for eight of the tested facilities. Three facilities had emission factors exceeding 1 ng/kg of metal charge, and four facilities had emission

factors less than 0.1 ng TEQ/kg of metal charge; the emission factors span more than four orders of magnitude. The mean emission factor was 1.26-ng TEQ/kg of metal feed.

Based on the wide range of emissions for the tested German foundries reported in Umweltbundesamt (1996), the confidence in the degree to which the one tested U.S. facility represents the mean emission factor for the approximate 1,000 U.S. foundries is considered very low. Therefore, the limited data available were thus judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary order of magnitude estimate of potential TEQ annual emissions from U.S. ferrous foundries can be made by combining the mean emission factor derived from the data reported in Umweltbundesamt (1996) for eight foundries (1.26-ng TEQ/kg of metal feed) with an activity level for U.S. foundries. In 1995, U.S. shipments from the approximate 1,000 U.S. ferrous foundries were 13.9-million metric tons of which about 90 percent were iron castings and 10 percent were steel castings (Fenton, 1996). This calculation yields an annual emission estimate of 17.5 g of TEQ in 1995, which, when rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, results in a value of 10-g TEQ/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

7.5. SCRAP ELECTRIC WIRE RECOVERY

The objective of wire recovery is to remove the insulating material and reclaim the metal (e.g., copper, lead, silver, and gold) comprising the electric wire. The reclaimed metal is then sold by the recovery facility to a secondary metal smelter. Wire insulation commonly consists of a variety of plastics, asphalt-impregnated fabrics, or burlap. In ground cables, chlorinated organics are used to preserve the cable casing. 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 treated via thermal processing to burn off the insulating material, industry and trade association representatives state that current recovery operations typically no longer involve thermal treatment, but instead involve mechanical chopping the scrap electric wire into fine particles. The

insulating material is then removed by air blowing and gravitational settling of the heavier metal fraction (telephone conversation between R. Garino, Institute of Scrap Recycling Industries, and T. Leighton, Versar, Inc. on March 2, 1993; telephone conversation between J. Sullivan, Triple F. Dynamics, and T. Leighton, Versar, Inc., on March 8, 1993).

Dioxin-like compounds emitted to the air from a scrap wire reclamation incinerator were measured from a facility during EPA's National Dioxin Study of combustion sources (U.S. EPA, 1987a). The tested facility was determined to be typical of this industrial source category at that time. Insulated wire and other metal-bearing scrap material were fed to the incinerator on a steel pallet. The incinerator was operated in a batch mode, with the combustion cycles for each batch of scrap feed lasting between 1 and 3 hours. Incineration of the material occurred by burning natural gas. Although most of the wire had a tar-based insulation, PVC-coated wire was also fed to the incinerator. Temperatures during combustion in the primary chamber furnace were about 570°C. The tested facility was equipped with a high temperature natural gas-fired afterburner (980 to 1,090°C). Emission factors estimated for this facility are presented in Table 7-6. The TEQ emission factor (based only on 2,3,7,8-TCDD, 2,3,7,8-TCDF, OCDD, and OCDF) is 2.5-ng TEQ/kg scrap feed. Figure 7-5 presents a congener group profile based on these emission factors.

These emission factors from the U.S. EPA (1987a) study are in general agreement with those reported by Bremmer et al. (1994) for three facilities in The Netherlands, which have subsequently ceased operations. Emission rates at a facility burning underground cables and cables containing PVC ranged from 3.7-ng TEQ/kg to 14-ng TEQ/kg. The emission rate at a second facility ranged from 21-ng TEQ/kg of scrap (when burning copper core coated with greasy paper) to 2,280-ng TEQ/kg of scrap (when burning lead cable). The third facility, which burned motors, was reported to have an emission rate of 3,300-ng TEQ/kg of scrap. Based on these measurements, Bremmer et al. (1994) used emission rates of 40-ng TEQ/kg of scrap and 3,300-ng TEQ/kg of scrap for estimating national emissions in The Netherlands for facilities burning wires/cables and those burning motors.

Although limited emission testing has been conducted at one U.S. facility, the activity level for this industry sector in reference years 1987 and 1995 is unknown; therefore, an estimate of national emissions cannot be made. It is uncertain how many facilities still combust scrap wire in the United States. Trade association and industry representatives state that only minimal quantities of scrap wire are still burned by U.S.

scrap wire recovery facilities. However, a recent inventory of CDD/CDF sources in the San Francisco Bay area noted that two facilities in the Bay area thermally treat 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; the current magnitude of small-scale, unregulated burning of scrap wire in the United States is not known. For example, Harnly et al. (1995) analyzed soil/ash mixtures from three closed metal recovery facilities and from three closed sites of open burning for copper recovery near a California desert town. The geometric mean of the total CDD/CDF concentrations at the facility sites and the open burning sites was 86,000 and 48,500 ng/kg, respectively. The geometric mean TEQ concentrations were 2,900- and 1,300-ng TEQ/kg, respectively. A significantly higher geometric mean concentration (19,000-ng TEQ/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 7-7. The results show that the five dominant congeners in the soil/ash samples at both the facility and 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 dominant congeners.

Van Wijnen et al. (1992) reported similar results for soil samples collected from unpermitted former scrap wire and car incineration sites 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 CDD/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 TEQ/kg of scrap for illegal, unregulated burning of cables in The Netherlands.

7.6. DRUM AND BARREL RECLAMATION FURNACES

Hutzinger and Fiedler (1991b) reported detecting CDD/CDFs in stack gas emissions from drum and barrel reclamation facilities at levels ranging from 5 to 27 ng/m^3. EPA measured dioxin-like compounds in the stack gas emissions of a drum and barrel reclamation furnace as part of the National Dioxin Study (U.S. EPA, 1987a).

Drum and barrel reclamation furnaces operate a burning furnace to thermally clean used steel 55-gallon drums of residues and coatings. The drums processed at these facilities come from a variety of sources in the petroleum and chemical industries. The thermally cleaned drums are then repaired, repainted, relined, and sold for reuse. The drum burning process subjects used drums to an elevated temperature in a tunnel furnace for a sufficient time so that the paint, interior linings, and previous contents are burned or disintegrated. The furnace is fired by auxiliary fuel. Used drums are loaded onto a conveyor that moves at a fixed speed. As the drums pass through the preheat and ignition zone of the furnace, additional contents of the drums drain into the furnace ash trough. A drag conveyor moves these sludges and ashes to a collection pit. The drums are air cooled as they exit the furnace. Exhaust gases from the burning furnace are typically drawn through a breeching fan to a high-temperature afterburner.

The afterburner at the facility tested by EPA operated at an average of 827°C during testing and achieved a 95 percent reduction in CDD/CDF emissions (U.S. EPA, 1987a). Emission factors estimated for this facility are presented in Table 7-8. Based on the measured congener and congener group emissions, the average TEQ emission factor was estimated in U.S. EPA (1997b) to be 49.4-ng TEQ per drum. The congener group profile is presented in Figure 7-6.

Approximately 2.8- to 6.4-million 55-gallon drums are incinerated annually in the United States (telephone conversation between P. Rankin, Association of Container Reconditioners, and C. D'Ruiz, Versar, Inc., December 21, 1992). This estimate is based on the following assumptions: (1) 23 to 26 incinerators are currently in operation; (2) each incinerator, on average, handles 500 to 1,000 drums per day; and (3) on average, each incinerator operates 5 days per week, with 14 days downtime per year for maintenance activities. The weight of 55-gallon drums varies considerably; however, on average, a drum weighs 38 lbs (or 17 kg); therefore, an estimated 48- to 109-million kg of drums are estimated to be incinerated annually. Assuming that 4.6-million drums are burned each year (i.e., the midpoint of the range) and applying the mean emission factor developed above (i.e., 49.4-ng TEQ per drum), the estimated annual emission of TEQ is 0.23 grams per year of TEQ. No activity level data are available that would enable annual emission estimates to be made specifically for reference years 1987 and 1995.

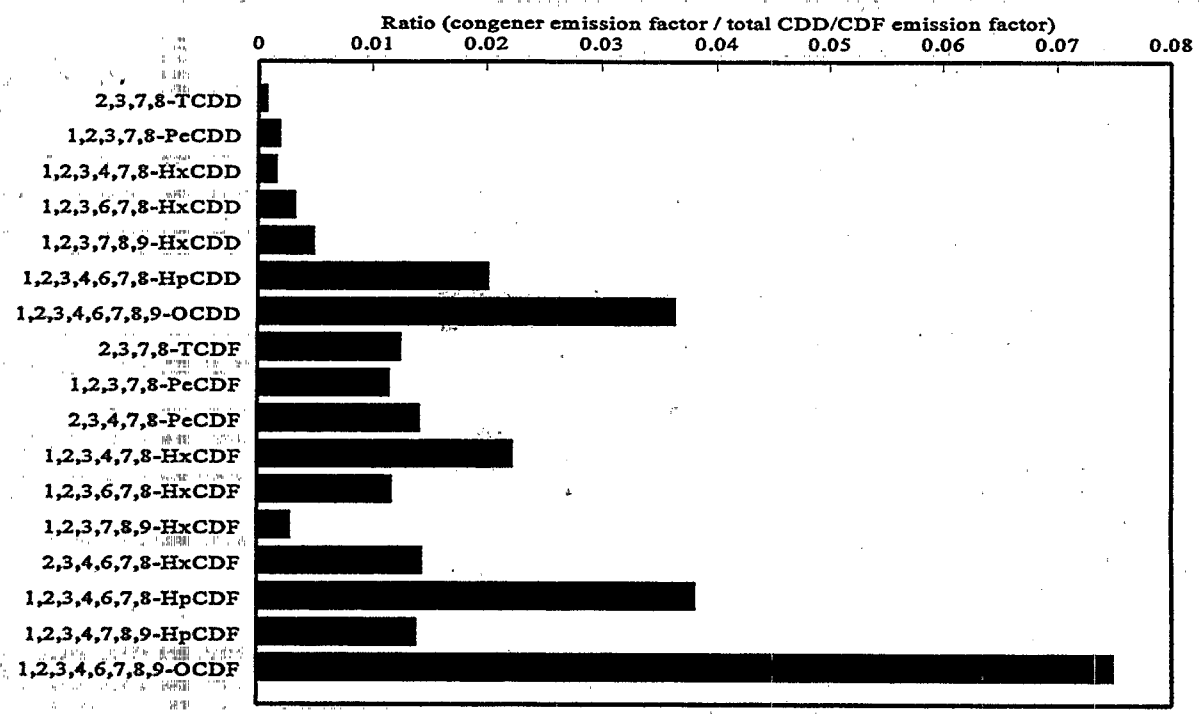
A "low" confidence rating is assigned to the activity level estimate because it is based an expert judgement rather than a published reference. A "low" confidence rating is also assigned to the emission factor, because it was developed from stack tests conducted at just one U.S. drum and barrel furnace and, thus, may not represent average emissions from current operations in the United States. Based on these confidence ratings, the estimated range of potential annual emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the best estimate of annual emissions (0.23-g TEQ/yr) is the geometric mean of this range, then the range is calculated to be 0.07- to 0.73-g TEQ/yr.

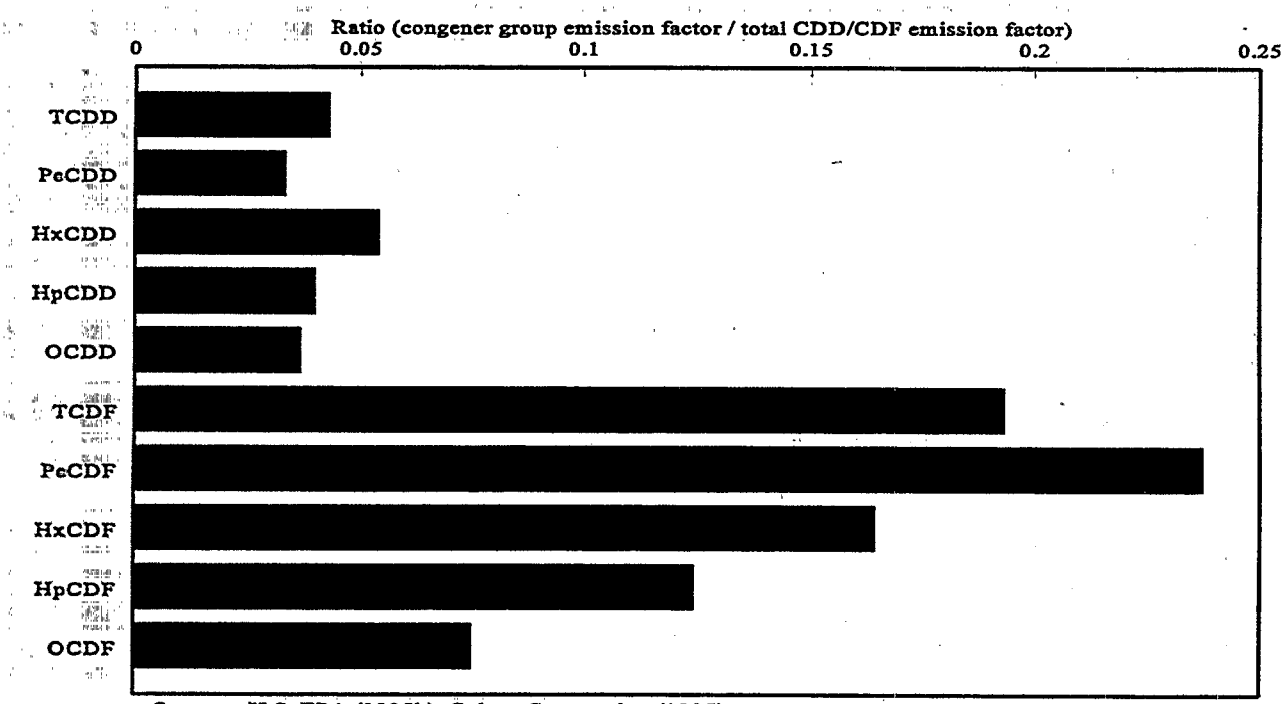
Table 7-1. CDD/CDF Emission Factors for Secondary Aluminum Smelters

Congener/Congener Group	Mean Facility Emission Factor (ng/kg scrap feed) (Ref. 1)	Mean Facility Emission Factor (ng/kg scrap feed) (Ref. 2)	Mean Facility Emission Factor (ng/kg scrap feed) (Ref. 3)	Mean Facility Emission Factor (ng/kg scrap feed) (Ref. 4)
2,3,7,8-TCDD	<0.01	0.13	0.51	2.17
1,2,3,7,8-PeCDD	0.02	0.39	1.19	3.84
1,2,3,4,7,8-HxCDD	0.05	0.24	1.35	2.88
1,2,3,6,7,8-HxCDD	0.13	0.86	1.52	5.39
1,2,3,7,8,9-HxCDD	0.15	1.26	2.51	7.22
1,2,3,4,6,7,8-HpCDD	0.51	7.67	2.60	18.01
OCDD	0.42	14.97	1.01	NR
2,3,7,8-TCDF	0.44	0.74	14.20	47.12
1,2,3,7,8-PeCDF	0.06	1.51	10.47	20.01
2,3,4,7,8-PeCDF	0.17	2.44	11.06	29.60
1,2,3,4,7,8-HxCDF	0.32	2.44	21.84	52.32
1,2,3,6,7,8-HxCDF	0.11	2.69	7.10	16.31
1,2,3,7,8,9-HxCDF	0.02	1.02	0.47	1.20
2,3,4,6,7,8-HxCDF	0.30	3.82	7.09	22.96
1,2,3,4,6,7,8-HpCDF	0.07	11.39	14.61	35.29
1,2,3,4,7,8,9-HpCDF	0.03	5.50	1.21	5.17
OCDF	0.30	30.40	3.15	18.77
Total TEQ	0.26	3.22	12.95	36.03
Total TCDD	NR	3.30	46.03	NR
Total PeCDD	NR	4.91	28.07	NR
Total HxCDD	NR	11.45	35.51	NR
Total HpCDD	NR	14.71	6.01	NR
Total OCDD	0.42	14.97	1.01	NR
Total TCDF	NR	29.67	161.80	NR
Total PeCDF	NR	28.73	222.75	NR
Total HxCDF	NR	32.23	115.32	NR
Total HpCDF	NR	39.44	39.94	NR
Total OCDF	0.30	30.40	3.15	18.77
Total CDD/CDF	NR	209.81	659.60	NR

NR = Not reported.

Sources: Ref. 1: Advanced Technology Systems, Inc. (1995)
Ref. 2: U.S. EPA (1995h)
Ref. 3: Galson Corporation (1995)
Ref. 4: Envisage Environmental, Inc. (1995)





Sources: U.S. EPA (1995h); Galson Corporation (1995)

Figure 7-1., Congener and Congener Group Profiles for Air Emissions from Secondary Aluminum Smelters

Table 7-2. CDD/CDF Emission Factors for a Secondary Copper Smelter

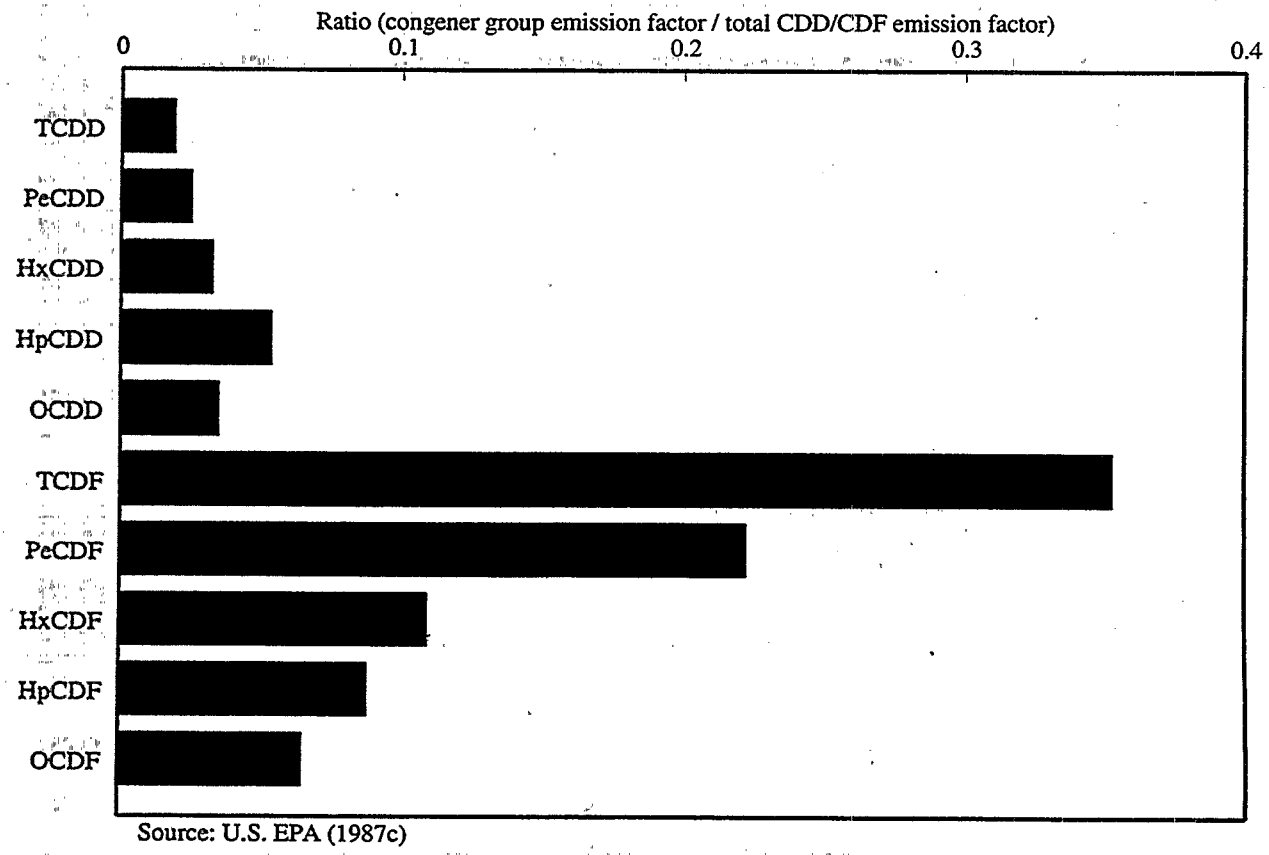
Congener/Congener Group	Mean Facility Emission Factor[a] (ng/kg scrap feed)
2,3,7,8-TCDD	127
1,2,3,7,8-PeCDD	NR
1,2,3,4,7,8-HxCDD	NR
1,2,3,6,7,8-HxCDD	NR
1,2,3,7,8,9-HxCDD	NR
1,2,3,4,6,7,8-HpCDD	NR
OCDD	1,350
2,3,7,8-TCDF	2,720
1,2,3,7,8-PeCDF	NR
2,3,4,7,8-PeCDF	NR
1,2,3,4,7,8-HxCDF	NR
1,2,3,6,7,8-HxCDF	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	2,520
Total 2,3,7,8-CDD	NR
Total 2,3,7,8-CDF	NR
Total TEQ	779[b]
Total TCDD	736
Total PeCDD	970
Total HxCDD	1,260
Total HpCDD	2,080
Total OCDD	1,350
Total TCDF	13,720
Total PeCDF	8,640
Total HxCDF	4,240
Total HpCDF	3,420
Total OCDF	2,520
Total CDD/CDF	38,890

NR = Not reported.

[a] No nondetected values were reported for 2,3,7,8-TCDD, 2,3,7,8-TCDF, or any congener group in the three test runs.

[b] Estimated in U.S. EPA (1995c) based on the measured congener and congener group emissions.

Source: U.S. EPA (1987a).



Source: U.S. EPA (1987c)

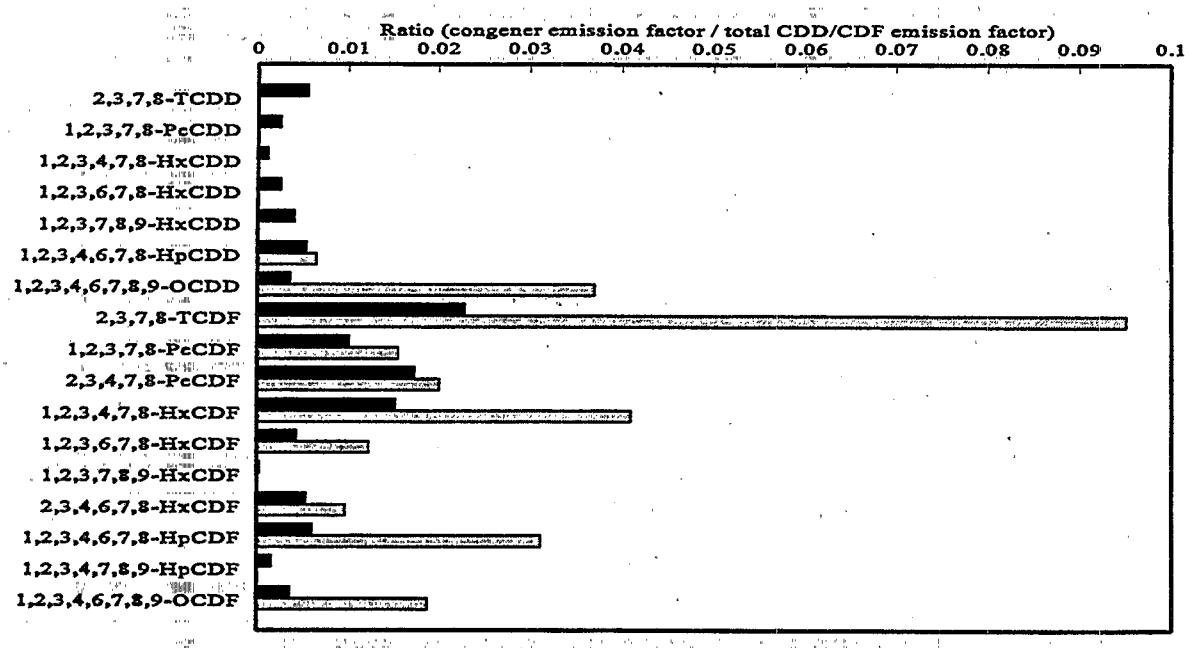
Figure 7-2. Congener Group Profile for Air Emissions from a Secondary Copper Smelter/Refiner

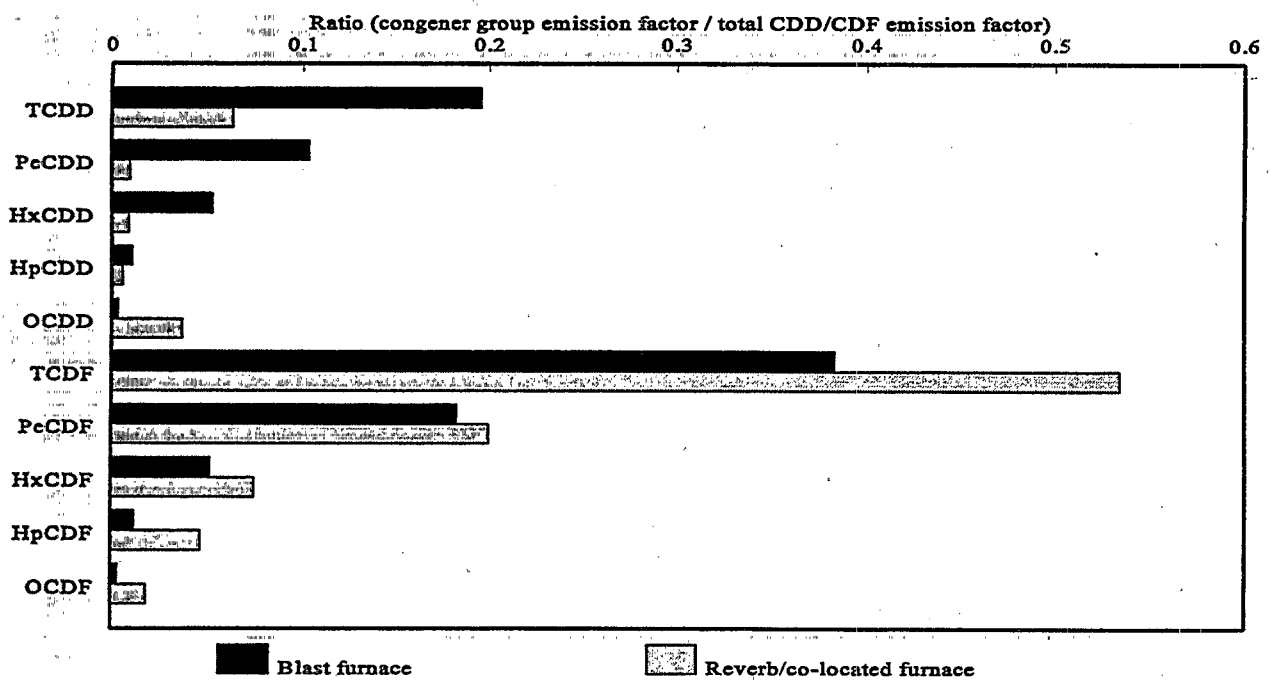
Table 7-3. CDD/CDF Emission Factors for Secondary Lead Smelters

Congener/Congener Group	Blast Furnace (Ref. A) (ng/kg lead produced)		Blast/reverb (Ref. B) (ng/kg lead produced)		Rotary kiln (Ref. C) (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	0.00	0.00	0.10	0.24
1,2,3,7,8-PeCDD	0.99	0.03	0.00	0.00	0.01	0.00
1,2,3,4,7,8-HxCDD	0.43	0.00	0.00	0.00	0.00	0.00
1,2,3,6,7,8-HxCDD	0.99	0.03	0.00	0.00	0.00	0.00
1,2,3,7,8,9-HxCDD	1.55	0.03	0.00	0.00	0.00	0.00
1,2,3,4,6,7,8-HpCDD	2.06	0.08	0.10	0.06	0.00	0.22
OCDD	1.40	0.39	0.57	0.55	0.24	2.41
2,3,7,8-TCDF	8.73	0.93	1.46	0.49	0.40	1.20
1,2,3,7,8-PeCDF	3.88	0.43	0.24	0.02	0.14	0.40
2,3,4,7,8-PeCDF	6.65	0.36	0.31	0.00	0.14	0.46
1,2,3,4,7,8-HxCDF	5.83	0.37	0.63	0.00	0.11	0.27
1,2,3,6,7,8-HxCDF	1.67	0.11	0.19	0.00	0.02	0.10
1,2,3,7,8,9-HxCDF	0.11	0.00	0.00	0.00	0.04	0.13
2,3,4,6,7,8-HxCDF	2.06	0.11	0.15	0.00	0.00	0.00
1,2,3,4,6,7,8-HpCDF	2.34	0.19	0.48	0.00	0.03	0.13
1,2,3,4,7,8,9-HpCDF	0.63	0.06	0.00	0.00	0.00	0.00
OCDF	1.39	0.18	0.29	0.00	0.00	0.00
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 TEQ (nondetects = 0)	8.31	0.63	0.41	0.05	0.24	0.66
Total TEQ (nondetects = 1/2 DL)	8.32	0.71	0.44	0.10	0.25	0.69
Total TCDD	74.33	7.39	0.97	1.58	3.40	7.90
Total PeCDD	39.29	1.73	0.15	0.16	0.29	0.27
Total HxCDD	20.05	0.81	0.14	0.02	0.10	0.23
Total HpCDD	4.20	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	0.00	0.00
Total CDD/CDF (nondetects = 0)	380.43	41.92	15.36	7.66	16.76	45.57
Total CDD/CDF (nondetects = 1/2 DL)	380.44	42.27	15.36	7.74	16.80	45.62

Sources: Ref. A: U.S. EPA (1995e); Ref. B: U.S. EPA (1992e); Ref. C: U.S. EPA (1995d)

Note: Except where noted, emission factors were calculated assuming nondetected values are zero.





Source: U.S. EPA (1992e); U.S. EPA (1995d); U.S. EPA (1995e)

Note: Profiles are for emissions from baghouses; nondetected values set equal to zero.

Figure 7-3. Congener and Congener Group Profiles for Air Emissions from Secondary Lead Smelters/Refiners

Table 7-4. Operating Parameters for U.S. Iron Ore Sinter Plants

Company	Location	Capacity (1,000 MT/yr)	Grate Area (sq. m.)	Waste Gas Fan Capacity (1,000 m^3/hr)	Volumetric Flow Rate (m^3/m^2-hr)
A.K. Steel Corp.	Middleton, OH	907	71.3	517	7,251
A.K. Steel Corp.	Ashland, KY	816	75.0	289	3,852
Bethlehem Steel	Burns Harbor, IN	2,676	187.7	1,160	6,184
Bethlehem Steel	Sparrows Point, MD	3,856	353.0	3,398	9,625
Geneva Steel	Provo, UT	816	113.7	805	7,082
Inland Steel	East Chicago, IN	1,089	124.9	748	5,987
LTV Steel	East Chicago, IN	1,270	124.9	NA	NA
U.S. Steel	Gary, IN	3,992	361.2	722	1,999
Weirton Steel	Weirton, WV	1,179	163.9	668	4,074
Wheeling-Pittsburgh Steel	East Steubenville, WV	519	49.7	340	6,837
WCI Steel	Warren, OH	477	59.9*	NA	NA
TOTALS		17,597	1,685	961	Avg = 5,877

* = Grate area for WCI Steel was calculated using the average ratio of capacity to grate area for the Geneva Steel and Inland Steel facilities both of which were constructed by the same builder (i.e., Dwight Lloyd).

NA = Not avaiable.

Sources: Metal Producing (1991; 1996)

Table 7-5. CDD/CDF Emission Factors for a Ferrous Foundry

Congener/Congener Group	Mean Facility Emission Factor (ng/kg scrap feed) (CARB, 1993a)
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	0.520
1,2,3,7,8-PeCDF	0.305
2,3,4,7,8-PeCDF	0.350
1,2,3,4,7,8-HxCDF	0.190
1,2,3,6,7,8-HxCDF	0.170
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 TEQ	0.372
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	884.3

NR = Not reported.

Source: CARB (1993a) (as reported in U.S. EPA, 1997b)

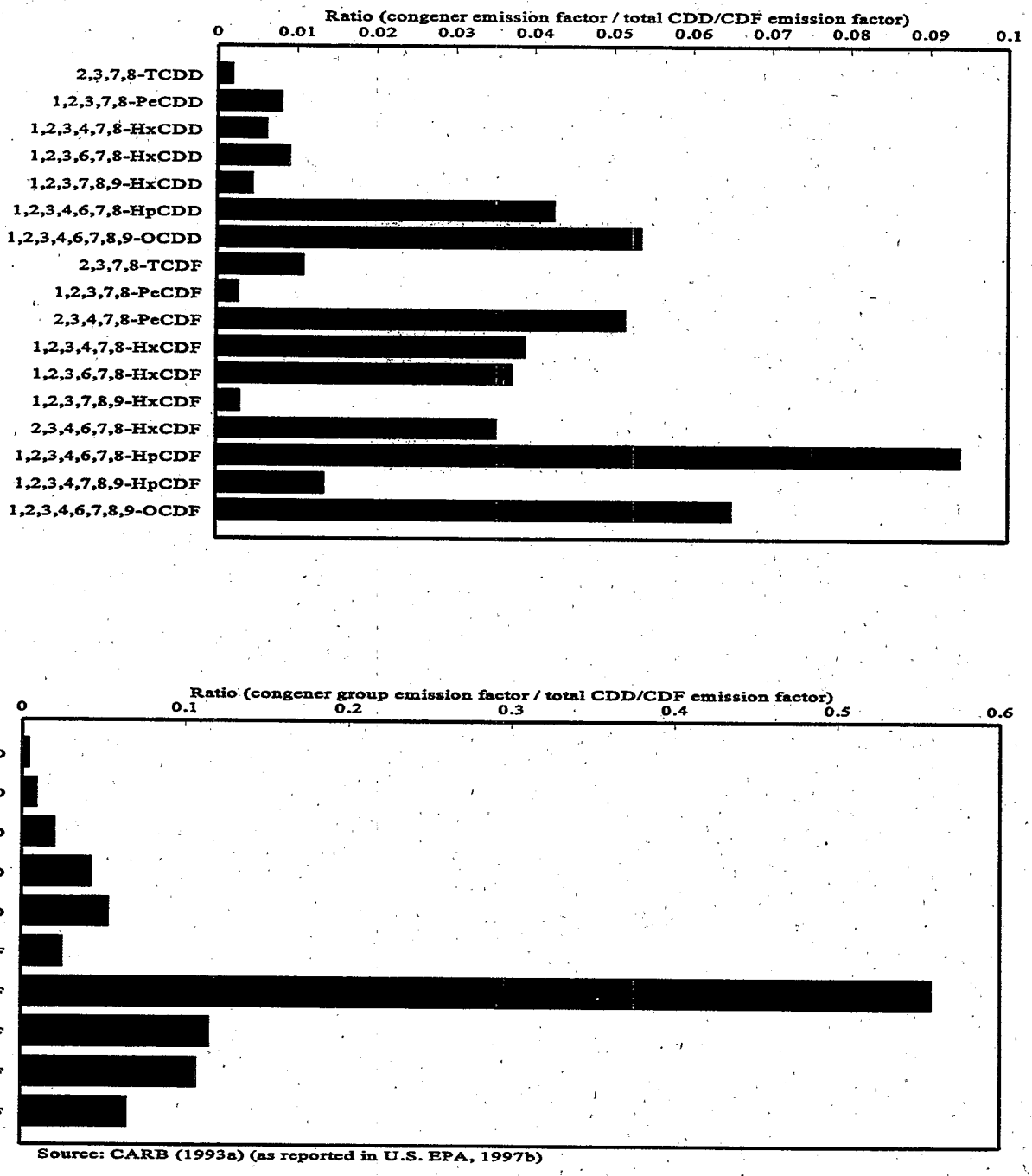


Figure 7-4. Congener and Congener Group Profiles for Air Emissions from a Ferrous Foundry

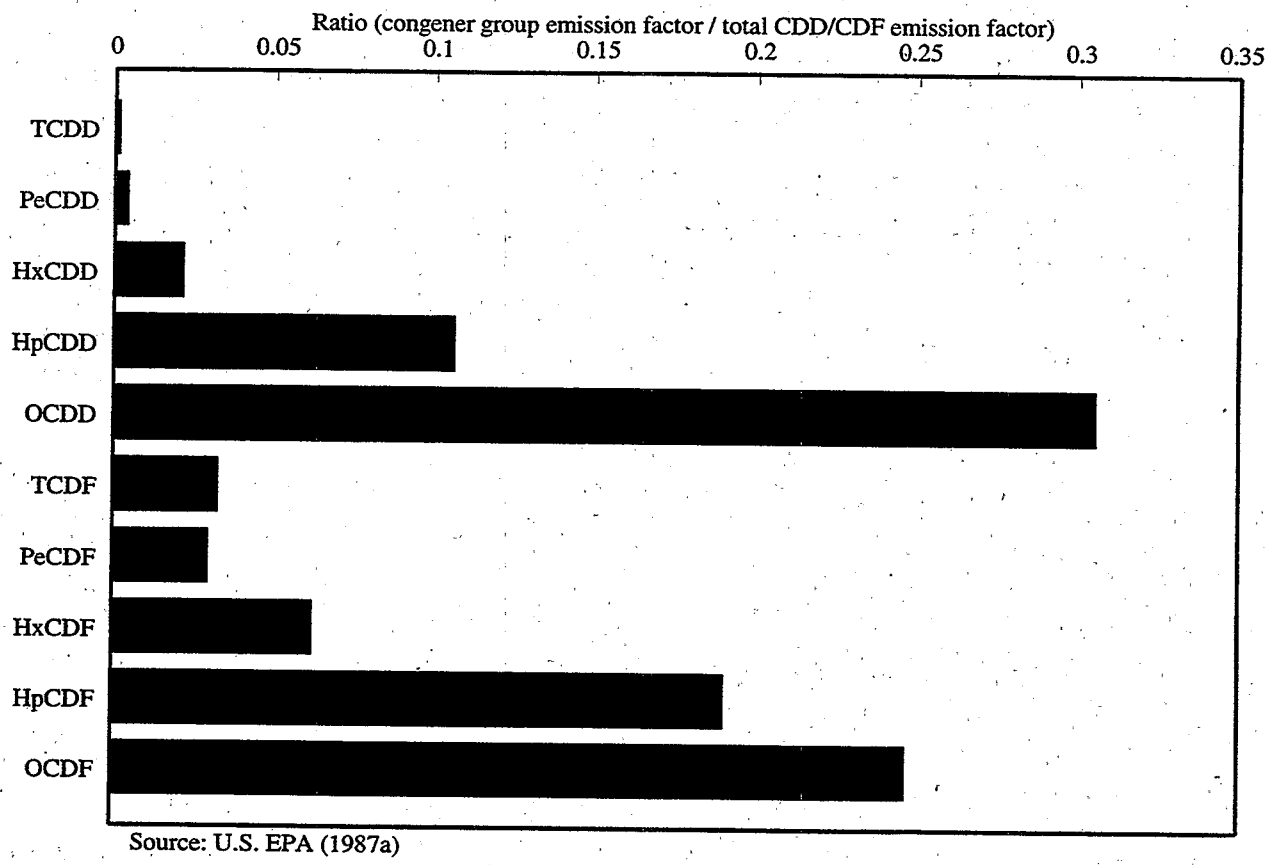
Table 7-6. CDD/CDF Emission Factors for a Scrap Wire Incinerator

Congener/Congener Group	Mean Facility Emission Factor [a] (ng/kg scrap feed)
2,3,7,8-TCDD	0.374
1,2,3,7,8-PeCDD	NR
1,2,3,4,7,8-HxCDD	NR
1,2,3,6,7,8-HxCDD	NR
1,2,3,7,8,9-HxCDD	NR
1,2,3,4,6,7,8-HpCDD	NR
OCDD	1,000
2,3,7,8-TCDF	2.67
1,2,3,7,8-PeCDF	NR
2,3,4,7,8-PeCDF	NR
1,2,3,4,7,8-HxCDF	NR
1,2,3,6,7,8-HxCDF	NR
1,2,3,7,8,9-HxCDF	NR
2,3,4,6,7,8-HxCDF	NR
1,2,3,4,6,7,8-HpCDF	NR
1,2,3,4,7,8,9-HpCDF	NR
OCDF	807
Total 2,3,7,8-CDD	NR
Total 2,3,7,8-CDF	NR
Total TEQ	NR
Total TCDD	4.42
Total PeCDD	13.7
Total HxCDD	71.1
Total HpCDD	347
Total OCDD	1,000
Total TCDF	107
Total PeCDF	97.4
Total HxCDF	203
Total HpCDF	623
Total OCDF	807
Total CDD/CDF	3,273

NR = Not reported

[a] No nondetected values were reported for 2,3,7,8-TCDD, 2,3,7,8-TCDF, or any congener group in the three test runs.

Source: U.S. EPA (1987a)



Source: U.S. EPA (1987a)

Figure 7-5. Congener Group Profile for Air Emissions from a Scrap Wire Incinerator

Table 7-7. Geometric Mean 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)	
	Geom. mean (μg/kg)	Relative % of Total CDD/CDF	Geom. mean (μg/kg)	Relative % of Total CDD/CDF	Geom. mean (μg/kg)	Relative % of Total CDD/CDF
2,3,7,8-TCDD	*		*		*	
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	7.0%
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	2.0%	1.4	1.6%	0.66	1.4%
1,2,3,4,7,8-HxCDF	46,000	9.0%	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%	0.92	1.1%	0.66	1.4%
2,3,4,6,7,8-HxCDF	5,000	1.0%	1.6	1.9%	0.49	1.0%
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	*	*	*	*	*	*
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	2.0%
Total HpCDD	24,000	4.7%	4.1	4.8%	2.0	4.1%
Total OCDD	18,000	3.5%	7.2	8.5%	3.4	7.0%
Total TCDF	23,000	4.5%	14	16.5%	5.6	11.5%
Total PeCDF	110,000	21.6%	12	14.1%	7.0	14.4%
Total HxCDF	88,000	17.3%	12	14.1%	7.6	15.7%
Total HpCDF	110,000	21.6%	17	20.0%	7.4	15.3%
Total OCDF	100,000	19.6%	14	16.5%	6.6	13.6%
Total TEQ	19,000		2.9		1.3	
Total CDD/CDF	510,000		85		48.5	

* = Analytical method utilized had low sensitivity for TCDDs; results were not reported.

Source: Hamly et al. (1995)

Table 7-8. CDD/CDF Emission Factors for a Drum and Barrel Reclamation Furnace

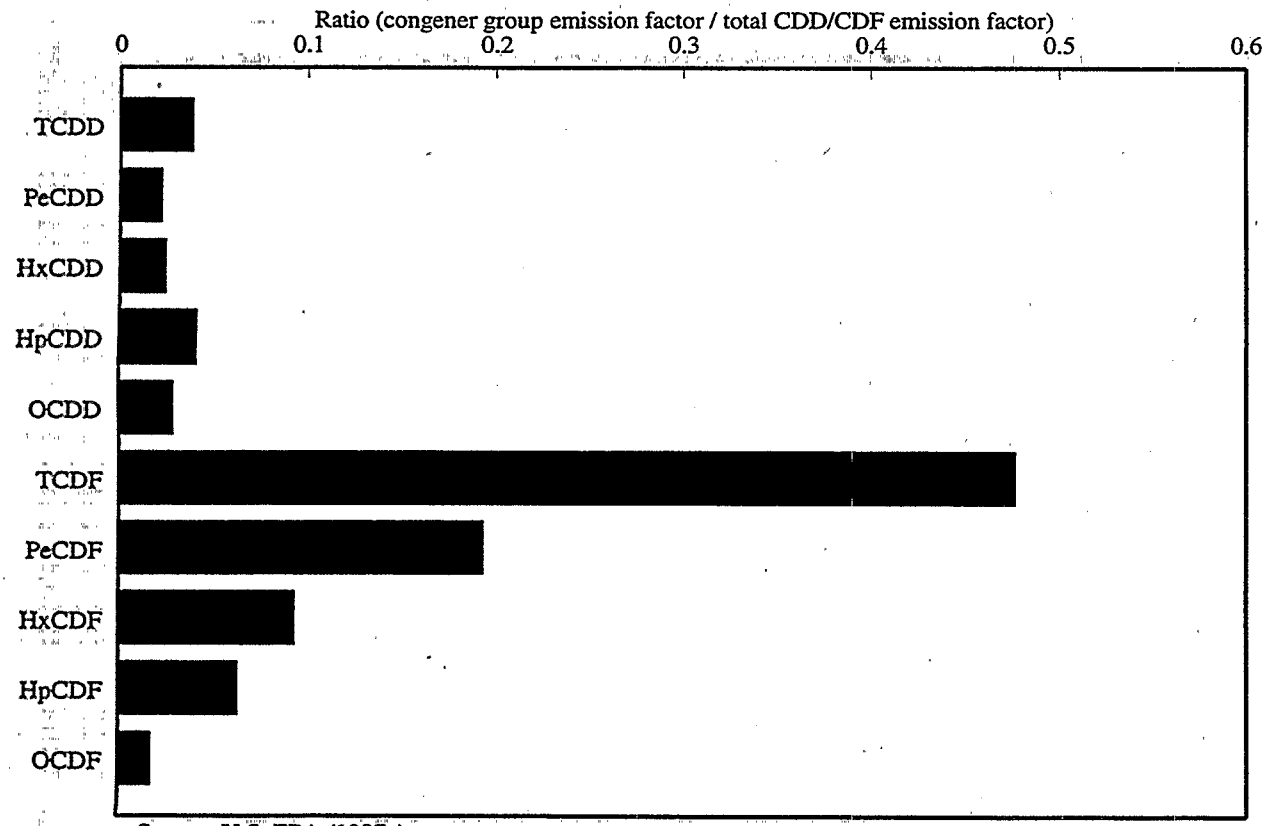
Congener/Congener Group	Mean Facility Emission Factor[a] (ng/drum)
2,3,7,8-TCDD	2.09
1,2,3,7,8-PeCDD	NR
1,2,3,4,7,8-HxCDD	NR
1,2,3,6,7,8-HxCDD	NR
1,2,3,7,8,9-HxCDD	NR
1,2,3,4,6,7,8-HpCDD	NR
OCDD	37.5
2,3,7,8-TCDF	36.5
1,2,3,7,8-PeCDF	NR
2,3,4,7,8-PeCDF	NR
1,2,3,4,7,8-HxCDF	NR
1,2,3,6,7,8-HxCDF	NR
1,2,3,7,8,9-HxCDF	NR
2,3,4,6,7,8-HxCDF	NR
1,2,3,4,6,7,8-HpCDF	NR
1,2,3,4,7,8,9-HpCDF	NR
OCDF	22.4
Total 2,3,7,8-CDD	NR
Total 2,3,7,8-CDF	NR
Total TEQ	49.4[b]
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

NR = Not reported.

[a] No nondetected values were reported for 2,3,7,8-TCDD, 2,3,7,8-TCDF, or any congener group in the three test runs.

[b] Estimated in U.S. EPA (1995c) based on the measured congener and congener group emissions.

Source: U.S. EPA (1987a).



Source: U.S. EPA (1987a)

Figure 7-6. Congener Group Profile for Air Emissions from a Drum Incinerator

8. CHEMICAL MANUFACTURING AND PROCESSING SOURCES

8.1. BLEACHED CHEMICAL WOOD PULP AND PAPER MILLS

In March of 1988, EPA and the U.S. pulp and paper industry jointly released the results from a screening study that provided the first comprehensive data on formation and discharge of CDDs and CDFs from pulp and paper mills (U.S. EPA, 1988a). This early screening study of five bleached kraft mills ("Five Mill Study") confirmed that the pulp bleaching process was primarily responsible for the formation of the CDDs and CDFs. The study results showed that 2,3,7,8-TCDD was present in seven of nine bleach 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 and 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 (U.S. EPA, 1990a). This 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 U.S. mills where chemically produced wood pulps were bleached with chlorine or chlorine derivatives. The final study report was released in July 1990 (U.S. EPA, 1990a).

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 and 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 and CDFs found in pulp, wastewater sludge, and wastewater effluent on a toxic equivalents basis. Although at the time of this 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 based upon 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 (i.e., pulp, sludge, and effluent). Figures 8-1 through 8-3 present congener profiles for each matrix

(normalized to total CDD/CDF and to total TEQ) using the median reported concentrations. Based on examination of the raw, mill-specific data, EPA (1990a) concluded that the congener profiles were fairly consistent across matrices within mills and that 2,3,7,8-TCDD and 2,3,7,8-TCDF account for the majority of TEQ in the samples. Using the median concentrations and treating nondetected values as either zero or the detection limit, EPA (1990a) demonstrated that 2,3,7,8-TCDD and 2,3,7,8-TCDF accounted for 92.8 to 99.0 percent of the total TEQ found in pulp, 92.7 to 95.8 percent of the TEQ in sludge, and 72.7 to 91.7 of the TEQ in effluent.

A similar full-congener analysis study was reported by NCASI for samples collected from eight mills during the mid-1990s (Gillespie, 1997). The results of these analyses are presented in Table 8-2. The frequencies of detection of 2,3,7,8-TCDD and 2,3,7,8-TCDF were significantly lower than in the previous 1988 study. Therefore, deriving meaningful summary statistics concerning the relative importance of 2,3,7,8-TCDD and 2,3,7,8-TCDF to the total TEQ is difficult. Treating all nondetected values as zero indicates that 2,3,7,8-TCDD and 2,3,7,8-TCDF may account for 91 percent of the total effluent TEQ, 46 percent of the total sludge TEQ, and 87 percent of the total pulp TEQ. Because of the high frequency of nondetects, treating all nondetected values as the detection limits indicates that 2,3,7,8-TCDD and 2,3,7,8-TCDF account for only 12 percent of the total effluent TEQ, 14 percent of the total sludge TEQ, and 12 percent of the total pulp TEQ.

In 1992, the pulp and paper industry conducted its own NCASI-coordinated survey of 2,3,7,8-TCDD and 2,3,7,8-TCDF emissions. The collected data were summarized and analyzed in a report entitled *Summary of Data Reflective of the Pulp and Paper Industry Progress in Reducing the TCDD/TCDF Content of Effluents, Pulps, and Wastewater Treatment Sludges* (NCASI, 1993). Ninety-four mills participated in the NCASI study, and NCASI assumed that the remaining 10 (of 104) operated at the same levels as measured in the 1988 104 Mill Study. All nondetected values were counted as half the detection limit. If detection limits were not reported, they were assumed to be 10 ppq for effluent and 1 ppt for sludge or bleached pulp. The data used in the report were provided by individual pulp and paper companies that had been requested by NCASI to generate the data using the same protocols used in the 104-Mill Study. NCASI (1993) reported that the pulp and paper industry had taken numerous steps to reduce CDD/CDF releases since 1988, and that

the 1992 survey results were more reflective of releases at the end of 1992 than the data generated in the 104-Mill Study.

As part of its ongoing efforts to develop revised effluent guidelines and standards for the pulp, paper, and paperboard industry, EPA in 1993 published the Development Document for the guidelines and standards being proposed for this industry (U.S. EPA, 1993d). The Development Document presents estimates of the 2,3,7,8-TCDD and 2,3,7,8-TCDF annual discharges in wastewater from the mills in this industry as of January 1, 1993. EPA used the most recent information about each mill from four data bases (104-Mill Study, EPA short-term monitoring studies at 13 mills, EPA long-term monitoring studies at 8 mills, and industry self-monitoring data submitted to EPA) to estimate these discharges. The 104-Mill Study data were used only for those mills that did not report making any process changes subsequent to the 104-Mill Study and did not submit any more recent effluent monitoring data.

Gillespie (1994; 1995) reported the results of 1993 and 1994 updates, respectively, to the 1992 NCASI survey. As was the case in the 1992 survey, companies were requested to follow the same protocols for generating data used in the 104-Mill Study. Gillespie (1994; 1995) reported that less than 10 percent of mills had 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in effluent above the nominal detection limits of 10 ppq and 100 ppq, respectively. Similar results were obtained in the short- and long-term sampling reported for 18 mills in U.S. EPA (1993d); 2,3,7,8-TCDD was detected at four mills, and 2,3,7,8-TCDF was detected at nine mills. Gillespie (1994) reported that wastewater sludges at most mills (i.e., 90 percent) contained less than 31 ppt of 2,3,7,8-TCDD and less than 100 ppt of 2,3,7,8-TCDF. Gillespie (1995) also reported that 90 percent of the mills reported 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in sludge of less than 17 ppt and 76 ppt, respectively, in 1994. U.S. EPA (1993d) reported similar results but found detectable levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF in sludges from 64 percent and 85 percent of the facilities sampled, respectively. Gillespie (1994) reported that nearly 90 percent of the bleached pulps contained less than 2 ppt of 2,3,7,8-TCDD and less than 160 ppt of 2,3,7,8-TCDF. Gillespie (1995) reported that 90 percent of the bleached pulps contained 1.5 ppt or less of 2,3,7,8-TCDD and 5.9 ppt or less of 2,3,7,8-TCDF. The final levels in white paper products would correspond to levels in bleached pulp, so bleached paper products would also be expected to contain less than 2 ppt of 2,3,7,8-TCDD.

Overall, a 92 percent reduction in TEQ generation from 1988 to 1993 was reported by Gillespie (1994), with an additional 2 percent reduction reported in 1994 by Gillespie (1995).

Estimates of National Emissions in 1987 and 1995 - The U.S. annual discharges of 2,3,7,8-TCDD, 2,3,7,8-TCDF, and TEQs due to these two compounds are summarized in Table 8-3 for each of the five surveys discussed above. The release estimates for 1994 from Gillespie (1995) and 1988 from U.S. EPA (1990a) are believed to best represent emissions in the reference years 1995 and 1987, respectively. During the period between the conduct of the 104-Mill Study and the issuance of the U.S. EPA Development Document (U.S. EPA, 1993d), the U.S. pulp and paper industry reduced releases of CDD/CDFs primarily by instituting numerous process changes to reduce the formation of CDD/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). Because most of the reduction between 1988 and 1994 can be attributed to process changes of a pollution prevention nature, it should be expected that the percentage reduction observed in effluent, sludge, and pulp emissions over this time period should be very similar, which is indeed the case. Observed percentage reductions in emissions are 92 percent, 89 percent, and 93 percent for effluent, sludge, and pulp, respectively.

The confidence ratings for these release estimates were judged to be high based on the fact that direct measurements were made at virtually all facilities, indicating a high level of confidence in both the production and emission factor estimates. Based on these high confidence ratings, the estimated ranges of potential annual emissions for effluent, sludge, and pulp are assumed to vary by a factor of 2 between the low and high ends of the ranges. Assuming that the best estimates of annual emissions in 1995 (i.e., the 1994 estimates presented in Table 8-3) are the geometric means of the likely ranges, then the ranges are calculated to be 13.8- to 27.6-g TEQ/yr for effluent, 20.0- to 40.0-g TEQ/yr for sludge, and 17.0- to 34.0-g TEQ/yr for pulp (i.e., TEQs that will enter the environment in the form of paper products). Assuming that the best estimates of annual emissions in 1987 (i.e., the 1988 estimates presented in Table 8-3) are the geometric means of the likely ranges, then the ranges are calculated to be 252- to 504-g TEQ/yr for effluent, 243- to 485-g TEQ/yr for sludge, and 375- to 714-g TEQ/yr for pulp.

In 1990, the majority of the wastewater sludge generated by these facilities was landfilled or placed in surface impoundments (75.5 percent), with the remainder incinerated (20.5 percent), applied to land directly or as compost (4.1 percent), or distributed as a commercial product (less than 1 percent) (U.S. EPA, 1993e). No more recent (i.e., 1995) or earlier (i.e., 1987) data on disposition of wastewater sludges are available. Using these statistics, the best estimate of TEQ applied to land (i.e., not incinerated or landfilled) in 1995 was 1.4 g (i.e., 4.1 percent of 28.4 g), and the range is 1.0- to 2.0-g TEQ/yr. The central estimate and range for 1987 are 14.1-g TEQ (i.e., 4.1 percent of 343 g) and 10- to 20-g TEQ, respectively.

8.2. MANUFACTURE OF CHLORINE, CHLORINE DERIVATIVES, AND METAL CHLORIDES

No testing of CDD/CDF emissions to air, land, or water from U.S. manufacturers of chlorine, chlorine derivatives, and metal chlorides have been reported upon which to base estimates of national emissions. 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, mercury cells containing graphite electrodes were the primary type of electrolytic process used in the chloralkali industry to produce chlorine. As shown in Table 8-4, high levels of CDFs have been found in several samples of graphite electrode sludge from facilities in Europe. The CDFs dominate the CDDs 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; Rappe et al., 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, Strandell et al. (1994) reported the results of an analysis of a metal electrode sludge from a facility in Sweden, analyzed as part of the Swedish Dioxin Survey. As with the graphite electrode sludge, this sludge contained high levels of CDFs (similar to those of the graphite sludge) and primarily nondetectable levels of CDDs. 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 PAHs present in the rubber linings of the electrolytic cell may have formed the CDFs found in the one sample analyzed.

Although not regulated specifically for CDD/CDFs, EPA issued restrictions under the Resource Conservation and Recovery Act (RCRA) on the land disposal of wastewater and sludges generated by chlorine manufacturers utilizing the mercury cell process and the diaphragm process (with graphite electrodes) (Waste Codes K071, K073, and K106) (40 CFR 268). In addition, EPA is currently evaluating whether to regulate the chlorine manufacturing industry as a major source of hazardous air pollutants (HAPs) under Section 112(b) of the Clean Air Act (CAA). As part of this investigation, monitoring of air emissions for HAPs (including CDD/CDFs) is being performed; preliminary results of the investigation indicate no detectable emissions of CDD/CDFs (telephone conversation between G. Schweer, Versar, Inc., and I. Rosario, U.S. EPA, Office of Air Quality Planning and Standards, April 11, 1996).

8.2.2. Manufacture of Chlorine Derivatives and Metal Chlorides

The limited sampling of chlorine-derivative products indicates that these products contain very low, if any, concentrations of CDD/CDFs. Rappe et al. (1990c) analyzed a sample of chlorine bleach consisting of 4.4 percent 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 TEQ/L. Hutzinger and Fiedler (1991a) reported finding no CDD/CDFs at a detection limit of 4 μg/kg in chlorine

gas or in samples of 10 percent sodium hypochlorite, 13 percent sodium hypochlorite, and 31-33 percent hydrochloric acid at a detection limit of 1 μg/kg.

Hutzinger and Fiedler (1991a) reported the results of analyses of samples of $FeCl_2$, $AlCl_3$, $CuCl_2$, CuCl, $SiCl_4$, and $TiCl_4$ for their content of HpCDF, OCDF, HpCDD, and OCDD. The sample of $FeCl_3$ contained HpCDF and OCDF in the low μg/kg range, but no HpCDD or OCDD were detected at a detection limit of 0.02 μg/kg. One of the two samples of $AlCl_3$ analyzed also contained a low μg/kg concentration of OCDF. The samples of $CuCl_2$ and CuCl contained sub μg/kg concentrations of HpCDF, OCDF, and OCDD. The results are presented in Table 8-5.

8.3. MANUFACTURE OF HALOGENATED ORGANIC CHEMICALS

Several chemical production processes generate CDDs and CDFs (Versar, 1985; Hutzinger and Fiedler, 1991a). CDDs and 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 and CDFs to the environment. Also, the products themselves may contain these compounds, and when used/consumed, may result in additional releases to the environment. CDD and CDF congener distribution patterns indicative of noncombustion sources have been observed in sediments in southwest Germany and The Netherlands. The congener patterns found suggest that wastes from the production of chlorinated organic compounds may be important sources of CDD and CDF contamination in these regions (Ree et al., 1988). The production and use of many of the chlorophenols, chlorophenoxy herbicides, and PCB products are 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 based on limited use and disposal conditions (Rappe, 1992a).

8.3.1. Chlorophenols

Chlorophenols have been widely used for a variety of pesticidal applications. The higher chlorinated phenols (i.e., tetrachlorophenol and pentachlorophenol) and their sodium salts have been primarily used for wood preservation. The lower chlorinated phenols have been used primarily as chemical intermediates in the manufacture of other pesticides. For

example, 2,4-dichlorophenol is used to produce the herbicides 2,4-Dichlorophenoxyacetic acid (2,4-D), 4-(2,4-Dichlorophenoxy)butanoic acid (2,4-DB), 2-(2,4-Dichlorophenoxy)-propanoic acid (2,4-DP), Nitrophen, Genite, and Zytron, while 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). [See Sections 8.3.7 and 8.3.8 for information on EPA actions to control CDD/CDF contamination of pesticides (including pentachlorophenol 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 benzenesulphonic acids, followed by the removal of the sulphonic 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, CDD/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, CDD/CDFs can form through chlorophenate 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 and 1978b) are presented in Table 8-6. Typically, CDD/CDFs were not detected in monochlorophenols (MCP) 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 8-7 and 8-8 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.

Regulatory Actions - 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 promulgated land disposal restrictions on wastes under RCRA (i.e., wastewaters and nonwastewaters) resulting from the manufacture of chlorophenols (40 CFR 268). Table 8-9 lists all wastes in which CDDs and CDFs are specifically regulated as hazardous constituents by EPA, 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 detection limits in the waste extract listed in Table 8-9 for each of the following congener groups: TCDDs, PeCDDs, HxCDDs, TCDFs, PeCDFs, and HxCDFs. Wastes from PCP-wood preserving operations (waste codes K001 and F032) are also regulated as hazardous wastes under RCRA (40 CFR 261).

EPA's Office of Water promulgated effluent limitations for facilities that manufacture chlorinated phenols and discharge treated wastewater (40 CFR 414.70). These effluent limitations do not specifically regulate CDDs and CDFs; however, the treatment processes required to control the chlorinated phenols that are regulated (2-chlorophenol and 2,4,-dichlorophenol) are also expected to reduce releases of any CDDs and CDFs that may be present in the untreated wastewater. The effluent limitations for the individual regulated chlorinated phenols are less than or equal to 39 μg/L for facilities that utilize biological end-of-pipe treatment.

DCPs and TrCPs are subject to reporting under the Dioxin/Furan Test Rule, which is discussed in Section 8.3.7 of this report. On the effective date of that rule (i.e., June 5, 1987) and since that date, only the 2,4-DCP isomer has been commercially produced (or imported) in the United States, and as noted in Table 8-6, no CDD/CDFs were detected in the product. Testing is required for the other DCPs and TrCPs, if manufacture or importation resumes. Similarly, TeCPs were subject to reporting under the Dioxin/Furan Pesticide Data Call-In (DCI) (discussed in Section 8.3.8 of this report). Since issuance of

the DCI, the registrants of TeCP-containing pesticide products have elected to no longer support the registration of their products in the United States.

In January 1987, EPA entered into a Settlement Agreement with pentachlorophenol (PCP) manufacturers, which set limits on allowed uses of PCP and its salts and set maximum allowable concentrations of 2,3,7,8-TCDD and HxCDDs effective in February 1989. Section 8.3.8 discusses the 1987 PCP Settlement Agreement and estimates current releases of CDD/CDFs associated with use of PCP in the United States.

Since the late 1980s, U.S. commercial production of chlorophenols has been limited to 2,4-dichlorophenol (2,4-DCP) and PCP. As noted above, disposal of wastes generated during the manufacture of chlorophenols are strictly regulated and thus releases to the environment are expected to be negligible. With regards to releases associated with the use of 2,4-DCP, no CDD/CDFs have been detected in 2,4-DCP. Releases associated with the use of PCP are presented in Sections 8.3.8.

8.3.2. Chlorobenzenes

Chlorobenzenes have been produced in the United States since 1909. U.S. production operations were developed primarily to provide chemical raw materials for the production of phenol, aniline, and various pesticides based on the higher chlorinated benzenes. Due to changes over time in the processes used to manufacture phenol and aniline, and to the phase-out of highly chlorinated pesticides such as DDT and hexachlorobenzene, U.S. production of chlorobenzenes decreased in 1988 to 50 percent 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 150-300°C in the presence of a metal salt catalyst; and (3) dehydrohalogenation of hexachlorocyclohexane wastes at 200-240°C with a carbon catalyst to produce trichlorobenzene, which can be further chlorinated to produce higher chlorinated benzenes (Ree et al., 1988; Hutzinger and Fiedler, 1991a; Bryant, 1993).

All chlorobenzenes currently manufactured in the United States are produced using 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 MCBz and DCBz. The finished product is a mixture of chlorobenzenes, and refined products must be obtained by distillation and crystallization (Bryant, 1993).

CDD/CDFs can be inadvertently produced during the manufacture of chlorobenzenes by nucleophilic substitution and pyrolysis mechanisms (Ree et al., 1988). The criteria required for production of CDD/CDFs via nucleophilic substitution are: (1) oxygen as a nuclear substituent (i.e., presence of chlorophenols) and (2) production and/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 any of these criteria. Although Ree et al. (1988) and Hutzinger and Fiedler (1991a) state that the criteria for formation of CDD/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 8-10 summarizes the very limited published information on CDD/CDF contamination of chlorobenzene products. The presence of CDD/CDFs has been reported in TCBz, PeCBz, and HCBz. No CDD/CDFs have been reported in monochlorobenzene (MCBz) and DCBz. Conflicting data exist concerning the presence of CDD/CDFs in TCBz. One study (Villanueva et al., 1974) detected no CDD/CDFs in one sample of 1,2,4-TCBz at a detection limit 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 percent 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).

Regulatory Actions - EPA has determined, as part of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Pesticide Data Call-In (discussed in Section 8.3.8), that the 1,4-DCBz manufacturing processes used in the United States are not likely to form CDD/CDFs. MCBz, DCBz, and TCBz are also listed as potential precursor chemicals under the TSCA Dioxin/Furan Test Rule and are subject to reporting. (See Section 8.3.7.) In addition, a Significant New Use Rule (SNUR) was issued by EPA under Section 5(a)(2) of

TSCA on December 1, 1993, with an effective date of January 14, 1994, for PeCBz and 1,2,4,5-TeCBz (Federal Register, 1993c). This rule requires persons to submit a significant new use 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).

EPA's Office of Solid Waste promulgated land disposal restrictions on wastes (i.e., wastewaters and nonwastewaters) resulting from the manufacture of chlorobenzenes (40 CFR 268). Table 8-9 lists all solid wastes in which CDDs and CDFs are specifically regulated as hazardous constituents by EPA, including chlorobenzene wastes. The regulations prohibit the land disposal of these wastes until they are treated to a level below the routinely achievable detection limits in the waste extract listed in Table 8-7 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). Although these effluent limitations do not specifically address CDDs and CDFs, the treatment processes required to control the chlorinated benzenes that are regulated (chlorobenzene; 1,2-dichlorobenzene; 1,3-dichlorobenzene; 1,4-dichlorobenzene; 1,2,4-trichlorobenzene; and hexachlorobenzene) are expected to reduce releases of any CDDs and CDFs that may be present in the untreated wastewater. The effluent limitations for the individual regulated chlorinated benzenes are less than or equal to 77 μg/L for facilities that utilize biological end-of-pipe treatment and are less than or equal to 196 μg/L for facilities that do not employ 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 expected under the normal operating conditions of the processes currently used in the United States to produce these four chemicals. No tetra-, penta-, or hexachlorinated benzenes are now intentionally produced or used in the United States (Bryant, 1993). Thus, releases of CDD/CDFs from manufacture of chlorobenzenes in 1995 were estimated as negligible. Because the available information on CDD/CDF content of MCBz to PeCBz is very limited and is based primarily on unpublished European data and because information

on the chlorobenzene manufacturing processes in place during 1987 is not readily available, no emission estimates can be made for 1987.

8.3.3. Chlorobiphenyls

PCBs are manufactured by the direct batch chlorination of molten biphenyl in the presence of a catalyst followed by separation and purification of the desired chlorinated biphenyl fractions. During the manufacture of PCBs, the inadvertent production of CDFs also occurred. The purpose of this section is to address potential releases of CDD/CDFs associated with leaks and spills of PCBs. CDFs have been shown to form when PCB-containing transformers and capacitors undergo malfunctions or are subjected to fires that result in accidental combustion of the dielectric fluid. This combustion source of PCB-associated CDFs is discussed in Section 6.6. Section 11.2 addresses releases of dioxin-like PCBs.

Production of PCBs is believed to have been confined to 10 countries. The total amount of PCBs produced worldwide since 1929 (i.e., the first year of known production) is estimated to total 1.5-billion kg. Initially, PCBs were primarily used as dielectric fluids in transformers. After World War II, PCBs found steadily increasing use as dielectric fluids in capacitors, as heat-conducting fluids in heat exchangers, and as heat-resistant hydraulic fluids in mining equipment and vacuum pumps. PCBs also were used in a variety of "open" applications (i.e., uses from which PCBs cannot be re-collected) including: plasticizers, carbonless copy paper, lubricants, inks, laminating agents, impregnating agents, paints, adhesives, waxes, additives in cement and plaster, casting agents, dedusting agents, sealing liquids, fire retardants, immersion oils, and pesticides (DeVoogt and Brinkman, 1989).

PCBs were manufactured in the United States from 1929 until 1977. U.S. production peaked in 1970, with a volume of 85-million pounds. Monsanto Corporation, the major U.S. producer, voluntarily restricted the use of PCBs in 1971, and annual production fell to 40-million pounds in 1974. Monsanto 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: 1,400-million pounds produced; 3-million pounds imported (primarily from Japan, Italy, and France); 1,253-million pounds sold in the United States; and 150-million pounds exported (ATSDR, 1993; DeVoogt 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 percent. Listed below are the percentages of total Aroclor production during the years 1957 to 1977 by Aroclor mixture as reported by Brown (1994).

Aroclor	1957-1977 U.S. Production (%)
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 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 were similar in terms of chlorine content (by weight percent and average number of chlorines per molecule) to those of various Aroclors. Listed below are comparable mixtures in terms of chlorine content marketed under several trade names.

Aroclor	Clophen	Pyralene	Phenoclor	Fenclor	Kanechlor
1232		2000			200
1242	A-30	3000	DP-3	42	300
1248	A-40		DP-4		400
1254	A-50		DP-5	54	500
1260	A-60		DP-6	64	600

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 2.0 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 8-11 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/CDFs congeners in commercial PCB mixtures (Bowes et al., 1975b; Brown et al. 1988; Hagenmaier, 1987; Malisch, 1994). Only the Hagenmaier (1987) and Malisch (1994) studies, however, reported the concentrations of all 2,3,7,8-substituted CDDs and CDFs. Table 8-12 presents the results of these four studies. 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 unused samples and used samples (i.e., samples from previously used capacitors and transformers) of Aroclors 1016, 1242, 1254, and 1260. The concentration ranges reported for the used and unused Aroclors were similar, leading Brown et al. (1988) to conclude that CDFs are not formed during the normal use of PCBs in electrical equipment.

Estimates of the amounts of CDD/CDF TEQ that may have been released to the environment during 1987 and 1995 from spills and leaks can be made using the release data reported by manufacturing facilities to EPA's Toxics Release Inventory (TRI). Table 11-6 in Section 11.2.2 lists the amounts of PCBs reported to TRI to be released to the

environment during the years 1988 through 1993. These TRI data include emissions to the air, discharges to bodies of water, and releases to land. Based on these data, annual emissions of PCBs to air during 1988 and 1993 could have been as high as 2.7 kg and as low as 0 kg, respectively. If it is further assumed that the ratio of TEQ to total PCB in the air emissions was 0.17:1,000,000 (i.e., the average of the TEQ contents for Clophen A-30 and Clophen A-50 [i.e., 170 μg/kg] reported by Hagenmaier (1987) and presented in Table 8-12), then annual emissions of TEQs to air in 1988 and 1993 could have been 0.5 and 0 mg, respectively. Similar assumptions for PCB releases to water of 4.5 kg in 1988 and 0 kg in 1993 yield estimated TEQ emissions during 1988 and 1993 of 0.8 and 0 mg, respectively. For land releases of 341 kg in 1988 and 120 kg in 1993, estimated TEQ emissions during 1988 and 1993 are 58 and 20 mg, respectively. All of these estimated releases are considered to be negligible (i.e., less than 1 gram per year).

8.3.4. Polyvinyl Chloride

Although it is recognized that CDD/CDFs are formed during the manufacture of ethylene dichloride (EDC) and vinyl chloride monomer (VCM), polyvinyl chloride (PVC) manufacturers and environmental public interest groups disagree as to the quantity of CDD/CDFs formed and released to the environment in wastes and possibly PVC products. Insufficient information is available at this time to enable EPA to make definitive release estimates. Although EPA regulates emissions from EDC/VC production facilities under the Clean Water Act (40 CFR 61), the Clean Air Act (40 CFR 414), and RCRA (40 CFR 268 - Waste Codes F024, K019, and K020), CDD/CDFs are not specifically regulated pollutants; as a consequence, monitoring data for CDD/CDFs in emissions are generally lacking. The Interim Phase I Report addressing products and treated wastewater was submitted to EPA in November 1996 (The Vinyl Institute, 1996). The remainder of this section summarizes the available information and presents the release estimates made by various interested parties.

In 1993, Greenpeace International issued a report on dioxin emissions associated with the production of EDC/VCM (Greenpeace, 1993). Greenpeace estimated that 5- to 10-g TEQ are released to the environment (air, water, and ground combined) annually for every 100,000 metric tons of VCM produced. This emission factor was based on data gathered by Greenpeace on four European plants. The Vinyl Institute responded with a

critique of the Greenpeace report (ChemRisk, 1993). Miller (1993) summarized the differing views of the two parties. According to Miller (1993), European PVC manufacturers claim the emission factor is 0.01- to 0.5-g TEQ/100,000 metric tons of VCM. Although Greenpeace (1993) and ChemRisk (1993) used basically the same monitoring information to develop their emission factors, Greenpeace adjusted the emission factor to account for unquantified fugitive emissions and waste products containing unspecified amounts of CDD/CDFs.

In 1995, Greenpeace issued another study reiterating the organization's concern that the generation and emissions of CDD/CDFs may be significant and urging that further work be initiated to quantify and prevent emissions (Stringer et al., 1995). However, this study acknowledged that because EDC/VCM production technologies and waste treatment/disposal practices are very site-specific, the limited information currently available on CDD/CDF generation and emissions makes it difficult to quantify amounts of CDD/CDFs generated and emitted.

Tiernan et al. (1995) reported the results of testing two samples of ethylene dichloride, two samples of vinyl chloride monomer, and two samples from each of two different batches of powdered PVC pipe resin. The PVC resin analyses were performed using an extraction procedure that results in complete dissolution of the PVC resin, followed by liquid-liquid extraction of the dissolved material. With the exception of OCDD, no CDD/CDFs were detected in any of the samples at detection limits ranging from less than 1 ng/kg for the tetra- and hexa- congener groups and 0.5 to 4.6 ng/kg for hexa- through octa-CDDs and CDFs. The OCDD levels detected (6 to 8 ng/kg) were of the same magnitude as the OCDD levels detected in the blank samples implying background contamination.

Stringer et al. (1995) presented the results of analyses of three samples of chlorinated wastes obtained from U.S. EDC/VCM manufacturing facilities. The three wastes were characterized according to EPA hazardous waste classification numbers as follows: (1) an F024 waste (i.e., waste from the production of short chain aliphatics by free radical catalyzed processes); (2) a K019 waste (i.e., heavy ends from the distillation of ethylene from EDC production); and a probable K020 waste (i.e., heavy ends from distillation of VC in VCM manufacture). Table 8-13 presents the analytical results reported by Stringer et al. (1995). The reported CDD/CDF concentrations in the three wastes were

20-μg TEQ/kg, 5,928-μg TEQ/kg, and 3.2-μg TEQ/kg for the F024, K019, and K020 waste, respectively. Stringer et al. (1995) stated that the concentration found in the K020 waste was similar to levels found in comparable waste from a VCM manufacturing facility in the United Kingdom (3.1 to 7.6 μg/kg).

In response to the lack of definitive studies and at the request of EPA, U.S. PVC manufacturers initiated an extensive monitoring program to evaluate the extent of any CDD/CDF releases to air, water, land, as well as product contamination. Emission and product testing are being performed at various facilities representative of various manufacturing and process control technologies. An independent peer review panel has been formed and is reviewing the results of all monitoring studies prior to their public release. The Interim Phase I Report from this study has been submitted to EPA, and the results are summarized in Table 8-14.

The Interim Phase I Report (The Vinyl Institute, 1996) presented results for treated wastewater samples from six sites that manufacture only PVC and from four sites that manufacture EDC/VCM or EDC/VCM/PVC (range: ND - 2.2-pg TEQ/L; mean = 0.60-pg TEQ/L assuming NDs = 0 and 4.5-pg TEQ/L assuming NDs = 1/2 DL). The method detection limit was 10 pg/L for all congeners, except OCDD and OCDF (50 pg/L). Based on these sample data and facility-specific production data, The Vinyl Institute estimated that total TEQ releases to waters from U.S. EDC, VCM, and PVC production facilities are in the range of 0.043 to 0.36 grams/year.

The Vinyl Institute (1996) presented results for 22 samples from 14 of the 24 U.S. facilities manufacturing suspension and mass PVC resins (i.e., pipe, bottle, and packaging resins). CDD/CDFs were detected in only one sample (0.043-ng TEQ/kg), which upon resampling showed nondetect (ND) as well. The method detection limit was 2 ng/kg for all congeners except OCDD and OCDF (6 ng/kg). The Vinyl Institute (1996) also presented results for six samples from four of the seven U.S. facilities manufacturing dispersion PVC resins. The results ranged from ND to 0.008-pg TEQ/g (mean = 0.001-pg TEQ/g assuming NDs = 0, and 0.4-pg TEQ/g assuming NDs = 1/2 DL). The method detection limit was 2 pg/g for all congeners except OCDD and OCDF (4 pg/g). The Vinyl Institute (1996) also presented results for 5 samples from 5 of the 15 U.S. facilities manufacturing EDC. CDD/CDFs were detected in only one sample (0.03-pg TEQ/g). The method detection limit for all congeners was 1 pg/g. Based on 1995 production data and the average TEQ

observed for the samples analyzed, total releases of CDD/CDF TEQs from suspension/mass PVC resins, emulsion PVC resins, and "sales" EDC were estimated by The Vinyl Institute (1996) to be 0.0 to 3.0 grams, 0.004 to 0.1 grams, and 0.008 to 0.29 grams, respectively.

The estimated PVC production in the United States during 1995 was 5.656-million metric tons per year (The Vinyl Institute, 1996). Applying the worldwide emission factors discussed above to the U.S. PVC industry, gives a range of dioxin emissions of 0.56- to 28.3-g TEQ/yr (based on the ChemRisk (1993) emission factors) to 283- to 565-g TEQ/yr (based on the 1993 Greenpeace emission factors). It is anticipated that the Vinyl Institute will be completing and releasing the full report on PVC resin, wastewater treatment solids, waste water, and incinerator stack releases in the spring of 1998. EPA anticipates that this information, along with the information from previously cited sources, should be adequate to make a reasonable emission estimate for this inventory.

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. ITC, 1946-1994). The production of 1,2-dichloroethane and vinyl chloride accounted for 82 percent of this total production. Highly chlorinated CDDs and CDFs (i.e., 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 Promochem (Hutzinger and Fiedler, 1991a; Heindl and Hutzinger, 1987). No CDD/CDFs were detected in two samples of ally chloride, three samples of 1,1,1-trichloroethane, and four samples of trichloroethylene (detection limit 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). Although these effluent limitations do not specifically address CDDs and CDFs, the treatment processes required to control the chlorinated aliphatic compounds that are regulated (e.g., 68 μg/L for 1,2-dichloroethane and 22 μg/L for tetrachloroethylene) are expected to reduce releases of any CDDs and CDFs that may be present in the untreated wastewater. Similarly, EPA's Office of Solid Waste promulgated restrictions on land disposal of wastes generated during manufacture of many chlorinated aliphatics (40 CFR 268); however, these restrictions do not specifically regulate CDD/CDFs.

8.3.6. Dyes, Pigments, and Printing Inks

Several researchers analyzed various dyes, pigments, and printing inks obtained in Canada and Germany for the presence of CDDs and CDFs (Williams et al., 1992; Hutzinger and Fiedler, 1991a; Santl et al., 1994c). The following paragraphs discuss the findings of these studies.

Dioxazine Dyes and Pigments - Williams et al. (1992) analyzed the CDD/CDF content in dioxazine dyes and pigments available in Canada. As shown in Table 8-15, OCDD and OCDF concentrations in the μg/g range, and HpCDD, HxCDD, and PeCDD concentrations in the ng/g range were found in Direct Blue 106 dye (3 samples), Direct Blue 108 dye (1 sample), and Violet 23 pigments (6 samples) (Williams et al., 1992). These dioxazine pigments are derived from chloranil, which has been found to contain high levels of CDD/CDFs and has been suggested as the source of contamination among these dyes (Christmann et al., 1989a; Williams et al., 1992; U.S. EPA, 1992b). In May 1990, EPA received test results showing that chloranil was heavily contaminated with dioxins; levels as high as 3,065-μg TEQ/kg were measured in samples from four importers (mean value of 1,754-μg TEQ/kg) (U.S. EPA, 1992b; Remmers et al., 1992). (See Section 8.3.7 for analytical results.)

In the early 1990s, EPA learned that dioxin TEQ levels in chloranil could be reduced by more than two orders of magnitude (to less than 20 μg/kg) through manufacturing feedstock and process changes. EPA's Office of Pollution Prevention and Toxics (OPPT) subsequently began efforts to complete an industry-wide switch from the use of contaminated chloranil to low-dioxin chloranil. Although chloranil is not manufactured in

the United States, significant quantities are imported. As of May 1992, EPA had negotiated agreements with all chloranil importers and domestic dye/pigment manufacturers known to EPA that use chloranil in their products to switch to low-dioxin chloranil. In May 1993, when U.S. stocks of chloranil with high levels of CDD/CDFs had been depleted, EPA proposed a significant new use rule (SNUR) under Section 5 of TSCA that requires industry to notify EPA at least 90 days prior to the manufacture, import, or processing, for any use, of chloranil containing total CDD/CDFs at a concentration greater than 20 μg/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 (ITC) 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 the CDD/CDF contamination level was 1,754-μg TEQ/kg, then the maximum release into the environment via processing wastes and finished products was 64.0 g of TEQ. If it is assumed that the import volume in 1995 was also 36,500 kg, but that the imported chloranil contained 10-μg TEQ/kg on average, then the total potential annual CDD/CDF release associated with chloranil in 1995 was 0.36 g of TEQ. Given the low confidence in the estimates of import volumes in 1987 and 1995, the estimated range of potential annual emissions for both years is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that 64.0-g TEQ/yr was the geometiric mean of this range for 1987, then the range is calculated to be 20- to 200-g TEQ/yr. Assuming that 0.36-g TEQ/yr was the geometric mean of this range in 1995, then the range is calculated to be 0.11- to 1.1-g TEQ/yr.

Phthalocyanine Dyes and Printing Inks - Hutzinger and Fiedler (1991a) found CDD/CDFs (tetra-, penta-, and hexachlorinated congeners) in the μg/kg range in a sample of a Ni-phthalocyanine dye. No CDD/CDFs were detected (detection limit of 0.1 to 0.5 μg/kg) in two samples of Cu-phthalocyanine dyes and in one Co-phthalocyanine dye (Hutzinger and Fiedler, 1991a).

Santl et al. (1994c) 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 8-16. The TEQ content of the inks ranged from 17.5 to 90.1 ng/kg. Primarily non-2,3,7,8-substituted

congeners were found. The identities of the dyes/pigments in these inks were not reported.

8.3.7. TSCA Dioxin/Furan Test Rule

Based on 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 chlorinated and brominated dioxins and furans 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 8-17. The specific dioxin and furan congeners that require quantitation and the target limits of quantitation (LOQ) are specified in the Rule are listed in Table 8-18. 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 29 precursor chemicals listed in Table 8-19. 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.

Sixteen sampling and analytical protocols and test data for 10 of the 12 chemicals that required testing were submitted to EPA (Holderman and Cramer, 1995). Data from 15 submissions were accepted; one submission is under review. Manufacture/import of two substances (tetrabromobisphenol-A-bis-2,3-dibromopropylether and tetrabromobisphenol-A-diacrylate) have stopped since the test rule was promulgated. [NOTE: All data and reports in the EPA TSCA Docket are available for public review/inspection at EPA Headquarters in Washington, DC.]

Table 8-20 presents the results of analytical testing for dioxins and furans for the eight chemicals with data available in the TSCA docket. Five of these 10 chemicals contained dioxin/furans. 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 8-21 presents the quantitative analytical results for the four submitted chloranil samples, as well as the

results of analysis by EPA of a sample of carbazole violet, which is manufactured from chloranil.

It should be noted that 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 (detection limits 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 and CDFs in the environment. Up to that time, CDD and CDF levels were not regulated in end-use pesticide products. Certain pesticide active ingredients, particularly chlorinated phenols and their derivatives, were known or suspected, however, to be contaminated with CDDs and CDFs (e.g., pentachlorophenol (PCP), Silvex, and 2,4,5-T). During the 1980s, EPA took several actions to investigate and control CDD/CDF contamination of pesticides.

In 1983, EPA cancelled the sale of Silvex and 2,4,5-T for all uses (Federal Register, 1983). Earlier, in 1979, EPA 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.

EPA entered into a Settlement Agreement in 1987 with PCP manufacturers to allow continued registrations for wood uses (Federal Register, 1987a) under a restricted use basis but which set tolerance levels for HxCDD and 2,3,7,8-TCDD. TCDD levels were not allowed to exceed 1.0 ppb in any product, and after February 2, 1989, (a gradually phased in requirement), any manufacturing-use PCP released for shipment could not contain HxCDD levels that exceeded an average of 2 ppm over a monthly release or a batch level of

4 ppm. On January 21, 1987, EPA issued a Final Determination and Intent to Cancel and Deny Applications for Registrations of Pesticide Products Containing Pentachlorophenol (Including but not limited to its salts and esters) for Nonwood Uses, which prohibited the registration of PCP and its salts for most nonwood uses (Federal Register, 1987b). EPA deferred action on several uses (i.e., uses in pulp/paper mills, oil wells, and cooling towers) pending receipt of additional exposure, use, and ecological effects data. On January 8, 1993, EPA issued a press advisory stating that the EPA Special Review of these deferred nonwood uses was being terminated, because all of these uses either had been voluntarily cancelled by the registrants or had been cancelled by EPA for failure of the registrants to pay the required annual maintenance fees (U.S. EPA, 1993f).

An estimated 8,400 metric tons of PCP were used for wood preservation in the United States in 1994 (Micklewright, 1994); for purposes of this report, it is assumed that an identical amount was used in 1995. An estimated 12,000 metric tons were used in 1987 (WHO, 1991). Historically, PCP has contained about 3-mg TEQ/kg, based on data presented in Table 8-7. Figure 8-4 presents congener and congener group profiles, respectively, for PCP, based on the results of those studies presented in Table 8-7 that provided complete congener and congener group measurements. Combining these two estimates indicates that 25,000 g and 36,000 g of TEQ may have entered the environment in the form of PCP-treated wood products in 1995 and 1987, respectively. These release estimates are assigned a H/H confidence rating, indicating high confidence in both the activity and emission factor estimates. Based on this high confidence rating, the estimated range of potential release in the form of treated wood products is assumed to vary by a factor of 2 between the low and high ends of the range. Assuming that the estimated releases of 25,000 g and 36,000 g of TEQ are the geometric means of these ranges, then the ranges are calculated to be 17,700- to 35,400-g TEQ for 1995 and 25,500 to 51,000 for 1987.

In addition to the pesticide cancellations and product standards, EPA's Office of Pesticide Programs (OPP) issued two Data Call-Ins (DCIs) in 1987. Pesticide manufacturers are required to register their products with EPA in order to market them commercially in the United States. Through the registration process, mandated by FIFRA, EPA can require that the manufacturer of each active ingredient generate a wide variety of scientific data through several mechanisms. The most common process is the five-phase reregistration

effort to which the manufacturers (i.e., registrants) of older pesticide products must comply. In most registration activities, registrants must generate data under a series of strict testing guidelines, 40 CFR 158--Pesticide Assessment Guidelines (U.S.EPA, 1988b). Some pesticide active ingredients may require additional data, outside of the norm, to adequately develop effective regulatory policies for those products. Therefore, EPA can require additional data, where needed, through various mechanisms, including the DCI process.

The purpose of the first DCI (dated June and October 1987), Data Call In Notice for Product Chemistry Relating to Potential Formation of Halogenated Dibenzo-p-dioxin or Dibenzofuran Contaminants in Certain Active Ingredients, was to identify through an analysis of raw materials and process chemistry, those pesticides that may contain halogenated dibenzo-p-dioxin and dibenzofuran contaminants. The list of 93 pesticides (76 pesticide active ingredients) to which this DCI applied, along with their corresponding Shaughnessey and Chemical Abstract code numbers, are presented in Table 8-22. [Note: the Shaughnessey code is an internal EPA tracking system--it is of interest because chemicals with similar code numbers are similar in chemical nature (e.g., salts, esters, and acid forms of 2,4-D).] All registrants supporting registrations for these chemicals were subject to the requirements of this DCI, unless their product qualified for a Generic Data Exemption (i.e., a registrant exclusively used a FIFRA-registered pesticide product(s) as the source(s) of the active ingredient(s) identified in Table 8-22 in formulating their product(s)). Registrants whose products did not meet the Generic Data Exemption were required to submit the types of data listed below to enable EPA to assess the potential for formation of tetra- through hepta-halogenated dibenzo-p-dioxin or dibenzofuran contaminants during manufacture. Registrants, however, had the option to voluntarily cancel their product or "reformulate to remove an active ingredient," described in Table 8-22, to avoid compliance with the DCI.

- Product Identity and Disclosure of Ingredients: EPA required submittal of a Confidential Statement of Formula (CSF), based on the requirements specified in 40 CFR 158.108 and 40 CFR 158.120 - Subdivision D: Product Chemistry. Registrants who had previously submitted still current CSFs were not required to resubmit this information.

- Description of Beginning Materials and Manufacturing Process: Based on the requirements mandated by 40 CFR 158.120 - Subdivision D, EPA required submittal of a manufacturing process description for each step of the manufacturing process, including specification of the range of acceptable conditions of temperature, pressure, or pH at each step.
- Discussion of the Formation of Impurities: Based on the requirements mandated by 40 CFR 158.120 - Subdivision D, EPA required submittal of a detailed discussion/assessment of the possible formation of halogenated dibenzo-p-dioxins and dibenzofurans.

The second DCI (dated June and October 1987), Data Call-In for Analytical Chemistry Data on Polyhalogenated Dibenzo-p-Dioxins/Dibenzofurans (HDDs and HDFs), was issued for 68 pesticides (16 pesticide active ingredients) suspected to be contaminated by CDD/CDFs. (See Table 8-23.) All registrants supporting registrations for these pesticides were subject to the requirements of this DCI, unless the product qualified for various exemptions or waivers. Pesticides covered by the second DCI were strongly suspected by EPA to contain detectable levels of HDD/HDFs.

Under the second DCI, registrants whose products did not qualify for an exemption or waiver were required to generate and submit the following types of data in addition to the data requirements of the first DCI:

- Quantitative Method For Measuring HDDs or HDFs: Registrants were required to develop an analytical method for measuring the HDD/HDF content of their products. The DCI established a regimen for defining the precision of the analytical method (i.e., for internal standard--precision within +/- 20 percent and recovery range of 50 to 150 percent, also a signal to noise ratio of at least 10:1 was required). Target quantification limits were established in the DCI for specific HDD and HDF congeners. (See Table 8-24.)
- Certification of Limits of HDDs or HDFs: Registrants were required to submit a "Certification of Limits" in accordance with 40 CFR 158.110 and 40 CFR 158.120 - Subdivision D. Analytical results were required that met the guidelines described above.

Registrants could select one of two options to comply with the second DCI. The first option was to submit relevant existing data, develop new data, or share the cost to develop new data with other registrants. The second option was to alleviate the DCI requirements through several exemption processes including a Generic Data Exemption, voluntary cancellation, reformulation to remove the active ingredient of concern, an assertion that the data requirements do not apply, or the application/award of a low-volume, minor-use waiver.

The data contained in CSFs, as well as any other data generated under Subdivision D, are typically considered Confidential Business Information (CBI) under the guidelines prescribed in FIFRA, because they usually contain information regarding proprietary manufacturing processes. In general, all analytical results submitted to EPA in response to both DCIs are considered CBI and cannot be released by EPA into the public domain. Summaries based on the trends identified in that data, as well as data made public by EPA, are summarized below.

The two DCIs included 161 pesticides. Of these, 92 are no longer supported by registrants. Based on evaluations of the process chemistry submissions required under the DCIs, OPP determined that formation of CDD/CDFs was not likely during the manufacture of 43 of the remaining 69 pesticides; thus, analysis of samples of these 43 pesticides was not required by OPP. Evaluation of process chemistry data is ongoing at OPP for an additional seven pesticides. Tables 8-22 and 8-23 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 in OPP (U.S. EPA, 1995a).

OPP required that analysis of production samples be performed on the remaining 19 pesticides. (See Table 8-25.) The status of the analytical data generation/evaluation to date is summarized as follows: (1) no detection of CDD/CDFs above the LOQs in registrant submissions for 13 active ingredients; (2) detection of CDD/CDFs above the LOQs for 2,4-D acid (two submissions) and 2,4-D 2-ethyl hexyl acetate (one submission); and (3) ongoing data generation or evaluation for four pesticides.

Table 8-24 presents a summary of results recently obtained by EPA for CDDs and 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 8-24.

Schecter et al. (1997) recently reported the results of analyses of samples of 2,4-D manufactured in Europe, Russia, and the United States. (See Table 8-26.) The total TEQ concentrations measured in the European and Russian samples are similar to those measured in the EPA DCI samples; however, the levels reported by Schecter et al. (1997) for U.S. samples are significantly lower.

An estimated 26,300 metric tons of 2,4-D were consumed in the United States in 1995, making it one of the top 10 pesticides in terms of quantity used (U.S. EPA, 1997a). An estimated 30,400 metric tons were consumed during 1987 (U.S. EPA, 1988c). Based on the average CDD/CDF congener concentrations in 2,4-D presented in Table 8-24 (i.e., not including OCDD and OCDF), the corresponding TEQ concentration is 0.70 μg/kg. Combining this TEQ concentration with the activity level estimates for 1995 and 1987 indicates that 18.4 g and 21.3 g of TEQ may have entered the environment in 1995 and 1987, respectively. These release estimates are assigned a H/H confidence rating indicating high confidence in both the production and emission factor estimates. Based on this high confidence rating, the estimated range of potential release is assumed to vary by a factor of 2 between the low and high ends of the range. Assuming that the estimated releases of 18.4 g and 21.3 g of TEQ are the geometric means of these ranges, then the ranges are calculated to be 13.0- to 26.0-g TEQ in 1995 and 15.1- to 30.2-g TEQ in 1987.

8.4. OTHER CHEMICAL MANUFACTURING AND PROCESSING SOURCES

8.4.1. Municipal Wastewater Treatment Plants

Sources - CDD/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 CDD/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, 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 and 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; 1993b) and Horstmann and McLachlan (1994a; 1994b; 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 to contribute measurably, the total contribution of TEQ from household wastewater was eight times greater than that from surface runoff at the study city.

Horstmann et al. (1992) provided initial evidence that household wastewater could be a significant source. Horstmann et al. (1993a) measured CDD/CDF levels in the effluent from four different loads of laundry from two different domestic washing machines. The concentrations of total CDD/CDF in the four samples ranged from 3,900 to 7,100 pg/L and were very similar in congener profile, with OCDD being the dominant congener followed by the hepta- and hexa-CDDs. Based on the similar concentrations and congener profiles found, Horstmann et al. (1993a) concluded that the presence of CDD/CDF in washing machine wastewater is widespread. A simple mass balance performed using the results showed that the CDD/CDFs found in the four washing machine wastewater samples could account for 27 to 94 percent of the total CDD/CDF measured in the sludge of the local wastewater treatment plant (Horstmann and McLachlan, 1994a).

Horstmann et al. (1993a) also performed additional experiments that showed that detergents, commonly used bleaching agents, and the washing cycle process itself were not responsible for the observed CDD/CDFs. To determine if the textile fabric or fabric finishing processes could account for the observed CDD/CDFs, Horstmann et al. (1993b), Horstmann and McLachlan (1994a; 1994b), and Klasmeier and McLachlan (1995) 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), as well as over 100 new textile finished products. Low concentrations were found in most products (i.e., less than 50 ng/kg of total CDD/CDF), but a small percentage contained high concentrations up to 290 μg/kg of total CDD/CDF. Based on the concentrations and patterns found, the authors concluded that neither unfinished new fabrics nor common cotton finishing processes can explain the CDD/CDF levels found in wastewater. Rather, the use of CDD/CDF-containing textile dyes and pigments and the use in some developing countries of pentachlorophenol to treat unfinished cotton appear to be the sources of the detected CDDs/CDFs.

Horstmann and McLachlan (1994a; 1994b; 1995) reported the results of additional experiments that demonstrated that the small percentage of clothing items with high CDD/CDF levels could be responsible for the quantity of CDD/CDFs observed in household wastewater and sewage sludge. They demonstrated that the CDD/CDFs can be gradually removed from the fabric during washing, can be transferred to the skin, subsequently transferred back to other textiles, and then washed out, or can be transferred to other textiles during washing and then removed during subsequent washings.

Releases to Water - The presence of CDD/CDFs in sewage sludge suggests that CDD/CDFs may also be present in the wastewater effluent discharges of POTWs; however, few studies reporting the results of effluent analyses for CDD/CDFs have been published.

Rappe et al. (1989a) tested the effluent from two Swedish POTWs for all 2,3,7,8-substituted CDD/CDF congeners. OCDD was detected in the effluents from both facilities at concentrations ranging from 14 to 39 pg/L. 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF were detected in the effluent of one facility at concentrations of 2.8 and 2.0 pg/L, respectively. No 2,3,7,8-substituted tetra-, penta-, and hexa-CDDs and CDFs were detected (detection limits of 0.2 to 20 pg/L).

Ho and Clement (1990) reported the results of sampling during the late 1980s of 37 POTWs in Ontario, Canada, for each of the five CDD/CDF congener groups with four to eight chlorines. The sampled facilities included 27 secondary treatment facilities, 7 primary treatment facilities, 1 tertiary plant, and 2 lagoons. The facilities accounted for about 73 percent of the sewage discharged by POTWs in Ontario. No CDDs/CDFs were detected (detection limit in low ng/L range) in the effluents from the lagoons and the tertiary treatment facility. Only OCDD and TCDF were detected in the effluents from the primary treatment facilities (two and one effluent samples, respectively). HpCDD, OCDD, TCDF,

and OCDF were detected in the effluents from the secondary treatment facilities (detected in four or fewer samples at levels ranging from 0.1 to 11 ng/L).

Gobran et al. (1995) analyzed the raw sewage and final effluent of an Ontario, Canada, wastewater treatment plant for CDD/CDF congeners over a 5-day period. Although HpCDD, OCDD, HpCDF, and OCDF were detected in the raw sewage (12 to 2,300 pg/L), no CDD/CDFs were detected in the final effluent at congener-specific detection limits ranging from 3 to 20 pg/L.

The California Regional Water Quality Control Board (CRWQCB, 1996) reported the results of effluent testing at nine POTWs in the San Francisco area. A total of 30 samples were collected during 1992-1995; 1 to 6 samples were analyzed for each POTW. Table 8-27 summarizes the sampling results. With the exception of OCDD, most 2,3,7,8-substituted CDD/CDF congeners were seldom detected.

The CRWQCB (1996) data were collected to be representative of effluent concentrations in the San Francisco area; these data cannot be considered to be representative of CDD/CDF effluent concentrations at the 16,000+ POTWs nationwide. Therefore, the data can only be used to generate a preliminary estimate of the potential mass of CDD/CDF TEQ that may be released annually by U.S. POTWs. Approximately 122-billion liters of wastewater are treated daily by POTWs in the United States (U.S. EPA, 1997c). Multiplying this value by 365 days/year and by the "overall mean" TEQ concentrations listed in Table 8-27 (i.e., 0.29 pg/L, assuming not detected values are zero, and 3.66 pg/L, assuming not detected values are one-half the detection limit) yields annual TEQ release estimates of 13 to 163 grams/year.

Sewage Sludge Land Disposal - EPA conducted the National Sewage Sludge Survey in 1988 and 1989 to obtain national data on sewage sludge quality and management. As part of this survey, EPA analyzed sludges from 174 POTWs that employed at least secondary wastewater treatment for more than 400 analytes including CDD/CDFs. Although sludges from only 16 percent of the POTWs had detectable levels of 2,3,7,8-TCDD, all sludges had detectable levels of at least one CDD/CDF congener (U.S. EPA, 1996a). TEQ concentrations as high as 1,820-ng TEQ/kg dry weight were measured. The congener-specific results of the survey are presented in Table 8-28. If all nondetected values found in the study are assumed to be zero, then the mean and median CDD/CDF concentrations of the sludges from the 174 POTWs are 50- and 11.2-ng TEQ/kg (dry

weight basis), respectively. If the nondetected values are set equal to the detection limit, then the mean and median CDD/CDF concentrations are 86- and 50.4-ng TEQ/kg, respectively (U.S. EPA, 1996a; Rubin and White, 1992).

Green et al. (1995) and Cramer et al. (1995) reported the results of analyses of 99 samples of sewage sludge collected from 75 wastewater treatment plants across the United States during the summer of 1994. These data are summarized in Table 8-29. For the calculation of results in units of TEQ, results from all samples collected from the same facility were averaged by Green et al. (1995) to ensure that results were not biased towards the concentrations found at facilities from which more than one sample were collected. If all nondetected values are assumed to be zero, then the POTW mean and median CDD/CDF concentrations were 47.7- and 30.0-ng TEQ/kg (dry weight basis), respectively (standard deviation of 45.0-ng TEQ/kg). If the nondetected values are set equal to the detection limits, then the POTW mean and median CDD/CDF concentrations were 64.6- and 49.1-ng TEQ/kg, respectively (standard deviation of 50.6-ng TEQ/kg). The mean and median results reported by Green et al. (1995) and Cramer et al. (1995) are very similar in terms of total TEQ to those reported by EPA for samples collected 5 years earlier (U.S. EPA, 1996a; Rubin and White, 1992). The predominant congeners in both data sets are the octa- and hepta CDDs and CDFs. Although not present at high concentrations, 2,3,7,8-TCDF was commonly detected.

The CDD/CDF concentrations and congener group patterns observed in these two U.S. surveys are similar to the results reported for sewage sludges in several other Western countries. Stuart et al. (1993) reported mean CDD/CDF concentrations of 23.3-ng TEQ/kg (dry weight) for three sludges from rural areas, 42.3-ng TEQ/kg for six sludges from light industry/domestic areas, and 52.8-ng TEQ/kg for six sludges from industrial/domestic areas collected during 1991-1992 in England and Wales. Näf et al. (1990) reported CDD/CDF concentrations ranging from 31- to 40-ng TEQ/kg (dry weight) in primary and digested sludges collected from the POTW in Stockholm, Sweden, during 1989. Gobran et al. (1995) reported an average CDD/CDF concentration of 15.7-ng TEQ/kg in anaerobically digested sludges from an industrial/domestic POTW in Ontario, Canada. In all three studies, the congener group concentrations increased with increasing degree of chlorination, with OCDD the dominant congener. Figure 8-6 presents congener profiles, using the mean concentrations reported by Green et al. (1995).

Approximately 5.4-million dry metric tons of sewage sludge are estimated by EPA to be generated annually in the United States based on the results of the 1988/1989 EPA National Sewage Sludge Survey (Federal Register, 1993b). Table 8-30 lists the volume of sludge disposed annually by use and disposal practices. No more recent comprehensive survey data to characterize sludge generation and disposal practices during 1995 are available. For this reason, and because the median TEQ concentration values reported in the 1988/1989 survey (U.S. EPA, 1996a) and the 1995 survey (Green et al., 1995; Cramer et al., 1995) were nearly identical, the estimated amounts of TEQs that may have been present in sewage sludge and been released to the environment in 1987 and 1995 were assumed to be the same. These values, presented in Table 8-30, were estimated using the average (i.e., 50-ng TEQ/kg) of the median TEQ concentration values (nondetected values set at detection limits) reported by U.S. EPA (1996a) (i.e., 50.4-ng TEQ/kg) and by Green et al. (1995) and Cramer et al. (1995) (i.e., 49.1-ng TEQ/kg). Multiplying this mean total TEQ concentration by the sludge volumes generated, yields an annual potential total release of 208 grams of TEQ for nonincinerated sludges. Of this 208 grams of TEQ, 3.6 grams enter commerce as a product for distribution and marketing. The remainder is applied to land (105.5 grams) or is landfilled (98.8 grams).

These release estimates are assigned a H/H confidence rating indicating high confidence in both the production and emission factor estimates. The high rating was based on the judgement that the 174 facilities tested by EPA (U.S. EPA, 1996a), and the 75 facilities tested by Green et al. (1995) and Cramer et al. (1995) were reasonably representative of the variability in POTW technologies and sewage characteristics nationwide. Based on this high confidence rating, the estimated range of potential annual emissions is assumed to vary by a factor of 2 between the low and high ends of the range. Assuming that the best estimate of annual emission to land (105.5-g TEQ/yr) is the geometric mean of this range, then the range is calculated to be 74.6- to 149-g TEQ/yr. Assuming that the best estimate of 3.6-g TEQ annual emissions in product (i.e., the fraction of sludge that is distributed and marketed as a product) is the geometric mean of the range, then the range is calculated to be 2.5- to 5.0-g TEQ/yr.

8.4.2. Drinking Water Treatment Plants

There is no strong evidence that chlorination of water for drinking purposes results in the formation of CDD/CDFs. Few surveys of finished drinking water for CDD/CDF content have been conducted. The few that have been published only rarely report the presence of any CDD/CDF even at low pg/L detection limits, and in those cases, the CDD/CDFs were also present in the untreated water.

Rappe et al. (1989b) reported the formation of CDFs (tetra- through octa-chlorinated CDFs) when tap water and double-distilled water were chlorinated using chlorine gas. The CDF levels found in the single samples of tap water and double-distilled water were 35- and 7-pg TEQ/L, respectively. No CDDs were detected at detection limits ranging from 1 to 5 pg/L. However, the water samples were chlorinated at a dosage rate of 300 mg of chlorine per liter of water, which is considerably higher (by a factor of one to two orders of magnitude) than the range of dosage rates typically used to disinfect drinking water. Rappe et al. (1989b) hypothesized that the CDFs or their precursors are present in chlorine gas. Rappe et al. (1990a) analyzed a 1,500-liter sample of drinking water from a municipal drinking water treatment plant in Sweden. Although the untreated water was not analyzed, a sludge sample from the same facility was analyzed. The large sample volume enabled Rappe et al. (1990a) to detect CDD/CDFs at concentrations on the order of 0.001 pg/L. The TEQ content of the water and sludge was 0.0029-pg TEQ/L and 1.4 ng/kg, respectively. The congener patterns of the drinking water and sludge sample were very similar, suggesting that the CDD/CDFs detected in the finished water were present in the untreated water.

8.4.3. Soaps and Detergents

As discussed in Section 8.4.1, CDD/CDFs were detected in nearly all sewage sludges tested whether obtained from industrialized areas or rural areas. Because of their ubiquitous presence in sewage sludge, several studies have been conducted to determine the source(s) of the CDD/CDFs. A logical category of products to test because of their widespread usage are detergents, particularly those that contain or release chlorine during use (i.e., hypochlorite-containing and dichloroisocyanuric acid-containing detergents). The results of studies conducted to date, which are summarized below, indicate that CDD/CDFs are not formed during use of chlorine-free detergents, chlorine-containing or chlorine-

releasing detergents, and chlorine bleach during household bleaching operations. Although few results of testing of detergents for CDD/CDFs were reported, low levels of CDD/CDFs were reported only in a sample of a Swedish dichloroisocyanurate-containing detergent. CDD/CDFs were also detected in a sample of a Swedish "soft soap," manufactured from tall oil.

Sweden's Office of Nature Conservancy (1991) reported that the results of a preliminary study conducted at one household indicated that CDD/CDFs may be formed during use of dichloroisocyanurate-containing dish washing machine detergents. A more extensive main study was then conducted using standardized food, dishes, cutlery, etc. and multiple runs. Testing of laundry washing, fabric bleaching, and actual testing of the CDD/CDF content of detergents was also performed. The study examined: (1) hypochlorite- and dichloroisocyanurate-containing dish washing machine detergents; (2) sodium hypochlorite-based bleach (4.4 percent 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. CDD/CDFs were nondetected in either the chlorine-free detergent or the detergent with hypochlorite; 0.6-pg TEQ/g was detected in the detergent containing dichloroisocyanurate. The results of all dish and laundry washing machine tests showed very low levels of CDD/CDFs, often nondetected values. There was no significant difference between the controls and test samples. In fact, the control samples contained higher TEQ content than some of the experimental samples. The drain water from the dish washing machine tests contained <1.0- to <3.0-pg TEQ/L (the water only control sample contained <2.8-pg TEQ/L). The CDD/CDF content of the laundry drain water samples ranged from <1.1- to <4.6-pg TEQ/L (the water only control sample contained <4.4-pg TEQ/L).

Thus, under the test conditions examined by Sweden's Office of Nature Conservancy (1991), CDD/CDFs are not formed during dish washing and laundry washing nor during bleaching with hypochlorite-containing bleach. No definitive reason could be found to explain the difference in results between the preliminary study and the main study for dish washing 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.

Hagenmaier and Brunner (1993) also conducted a laundry study in Germany and obtained results similar to those reported by Sweden's Office of Nature Conservancy (1991) main study. Hagenmaier and Brunner (1993) used a popular detergent with bleach and one without bleach. The total volume of laundry wastewater (approximately 85 to 90 L) from the experiment with the bleach-containing detergent contained 390 ng of total CDD/CDF, while the bleach-free wastewater contained 460 ng.

Rappe et al. (1990c) analyzed a sample of a Swedish commercial soft soap, as well as a sample of tall oil and a sample of tall resin for CDD/CDF content. Tall oil and tall resin, byproducts 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 280-290°C, yielding tall oil and tall resin. The measured TEQ content of the liquid soap was 0.447-ng TEQ/L. PeCDDs were the dominant congener group followed by HpCDDs, HxCDDs, PeCDFs, and OCDD with some tetra- CDFs and CDDs also present. The TEQ content of the tall oil (9.5 ng/kg) and tall resin (200 ng/kg) was significantly higher than the level found in the liquid soap. The tall oil contained primarily tetra- and penta- CDDs and CDFs, while the tall resin contained primarily HpCDDs, HxCDDs, and OCDD. Rappe et al. (1990c) compared the congener patterns of the three samples and noted that although the absolute values for the tetra- and penta- CDFs and CDDs differed between the tall oil/tall resin and liquid soap samples, the same congeners were present in the samples. The congener patterns for the more chlorinated congeners were very similar. Table 8-31 presents the results reported by Rappe et al. (1990c).

In 1987, 118-million liters of liquid household soaps were shipped in the United States (U.S. DOC, 1990b); shipment quantity data are not available for liquid household soap 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), only a very preliminary estimate of the annual release of CDD/CDF TEQ from liquid soap can be made. If it is assumed that an average 118-million liters of liquid soap contain 0.447-ng TEQ/L, then the resulting estimate is 0.05-g TEQ/yr.

8.4.4. Textile Manufacturing and Dry Cleaning

As discussed in Section 8.4.1, CDD/CDFs have been detected in nearly all sewage sludges tested whether obtained from industrialized areas or rural areas. To determine if

the textile fabric or fabric finishing processes could account for the observed CDD/CDFs, several studies were conducted in Germany. These studies, summarized in the following paragraphs, indicate that, although some finished textile products do contain detectable levels of CDD/CDFs and that these CDD/CDFs can be released from the textile during laundering or dry cleaning, 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 pentachlorophenol to treat unfinished cotton appear to be the sources of the detected CDD/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. Based on the concentrations found, the authors concluded that neither unfinished new fabrics nor common cotton finishing processes can explain the CDD/CDF levels found in laundry wastewater.

Fuchs et al. (1990) reported that dry cleaning solvent redistillation residues collected from 12 commercial and industrial dry cleaning operations contained considerable amounts of CDD/CDFs. The reported TEQ content ranged from 131 to 2,834 ng/kg with the dominant congeners always OCDD and the HpCDDs. Towara et al. (1992) demonstrated that neither the use of chlorine-free solvents nor variation of the dry cleaning process parameters lowered the CDD/CDF content of the residues.

Umlauf et al. (1993) conducted a study to characterize the mass balance of CDD/CDFs in the dry cleaning process. The soiled clothes (containing 16-pg total CDD/CDF per kg) accounted for 99.996 percent of the CDD/CDF input. Input from indoor air containing 0.194 pg/m^3 accounted for the remainder (i.e., 0.004 percent). The dry cleaning process removed 82.435 percent of the CDD/CDF in the soiled clothing. Most of the input CDD/CDF (82.264 percent) was found in the solvent distillation residues. Air

emissions (at 0.041 pg/m^3) accounted for 0.0008 percent of the total input, which is less than the input from indoor air. The fluff (at a concentration of 36 ng/kg) accounted for 0.1697 percent, and water effluent (at a concentration of 0.07 pg/L) accounted for 0.0000054 percent.

Horstmann and McLachlan (1994a; 1994b; 1995) analyzed 35 new textile samples (primarily cotton products) obtained in Germany for CDD/CDFs. Low levels were found in most cases (total CDD/CDF less than 50 ng/kg). The dominant congeners found were OCDD and the HpCDDs. However, several colored T-shirts from a number of clothing producers had extremely high levels, with concentrations up to 290,000 ng/kg. Because the concentrations in identical T-shirts purchased at the same store varied by up to a factor of 20, the authors concluded that the source of CDD/CDFs is not a textile finishing process, because a process source would have resulted in a more consistent level of contamination. Klasmeier and McLachlan (1995) subsequently analyzed 68 new textile products obtained in Germany for OCDD and OCDF. Most samples had nondetectable levels (42 samples $<$60 ng/kg). Only four samples had levels exceeding 500 ng/kg.

Horstmann and McLachlan (1994a; 1994b) reported finding two different congener group patterns in the more contaminated of the 35 textile products. One pattern agreed well with the congener pattern for PCP reported by Hagenmaier and Brunner (1987), while the other pattern was similar to that reported by Remmers et al. (1992) for chloranil-based dyes. The authors hypothesize that the use of PCP to preserve cotton, particularly when it is randomly strewn on bales of cotton as a preservative during sea transport, is the likely source of the high levels occasionally observed. As discussed in Section 8.3.8, the use of PCP for nonwood uses was prohibited in the United States in 1987. However, Horstmann and McLachlan (1994a) comment that PCP is still used in developing countries, especially to preserve cotton during sea transport.

Horstmann and McLachlan (1994a; 1994b) conducted additional experiments that demonstrated that the small percentage of clothing items with high CDD/CDF levels could be responsible for the quantity of CDD/CDFs observed in household wastewater. They demonstrated that the CDD/CDFs can be gradually removed from the fabric during washing, can be transferred to the skin, and subsequently transferred back to other textiles and then washed out, or can be transferred to other textiles during washing and then removed during subsequent washings.

Table 8-1. CDD/CDF Concentrations in Pulp and Paper Mill Bleached Pulp, Wastewater Sludge, and 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 1,150	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)	0	ND (6.2)	ND (2.5) to ND (15)	0
2,3,4,6,7,8-HxCDF	ND (0.3)	ND (0.2) to ND (0.4)	0	ND (1.7)	ND (0.9) to 34	1	ND (8.2)	ND (4.8) to ND (15)	0
1,2,3,4,6,7,8-HpCDF	ND (0.6)	ND (0.1) to 0.8	3	6.6	ND (3.6) to 70	7	ND (23)	ND (13) to 44	3
1,2,3,4,7,8,9-HpCDF	ND (0.6)	ND (0.1) to ND (2.1)	0	ND (1.6)	ND (1.2) to 10	1	ND (22)	ND (6.4) to ND (41)	0
OCDF	2.2	ND(2.8) to 4.3	8	22	ND (54) to 168	8	190	ND (180) to 230	8
Total 2,3,7,8-CDD[a,b]	55.7			798			3,212		
Total 2,3,7,8-CDF[a,b]	18			272.5			310		
Total TEQ (ND = zero)[b]	8.28			90.1			59		
Total TEQ (ND = DL)[b]	8.83			93.1			73		
Total CDD/CDF[b]	120			1,695			4,013		

ND = not detected; values in parentheses are detection limits (DL).
[a] Calculated assuming nondetected values are zero.
[b] Sum of median values.
ng/kg = nanograms per kilogram
pg/L = picograms per liter
Source: U.S. EPA (1990a).

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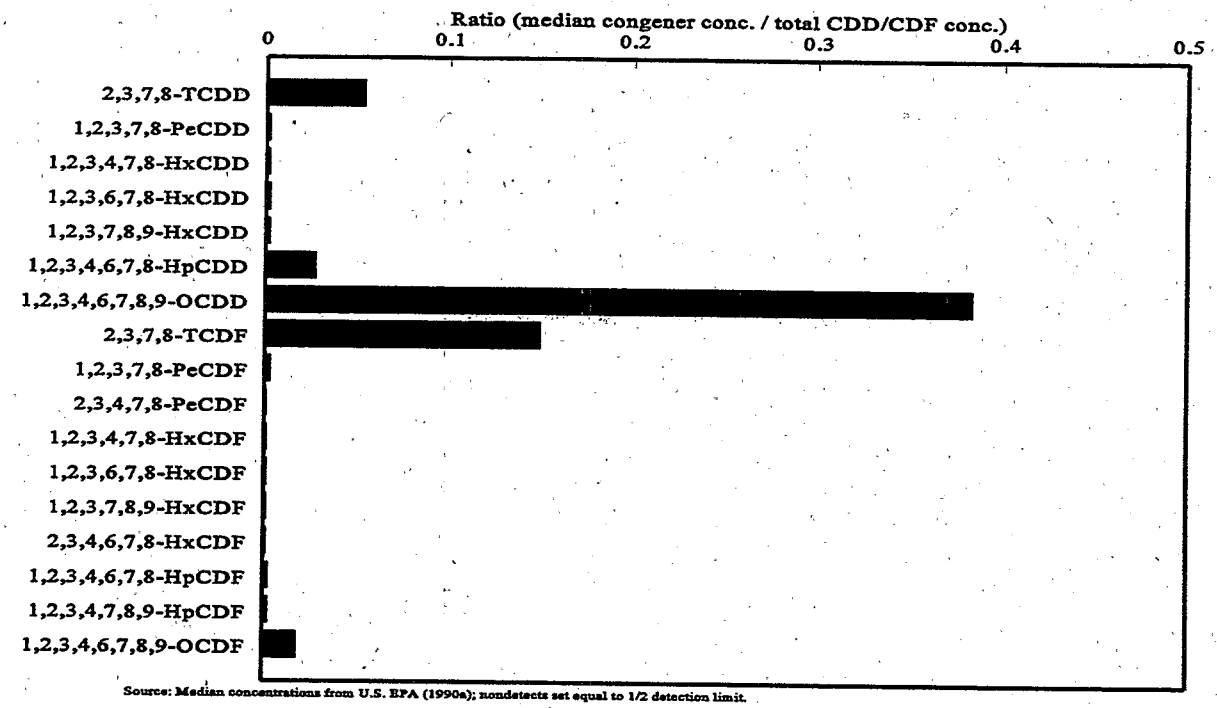
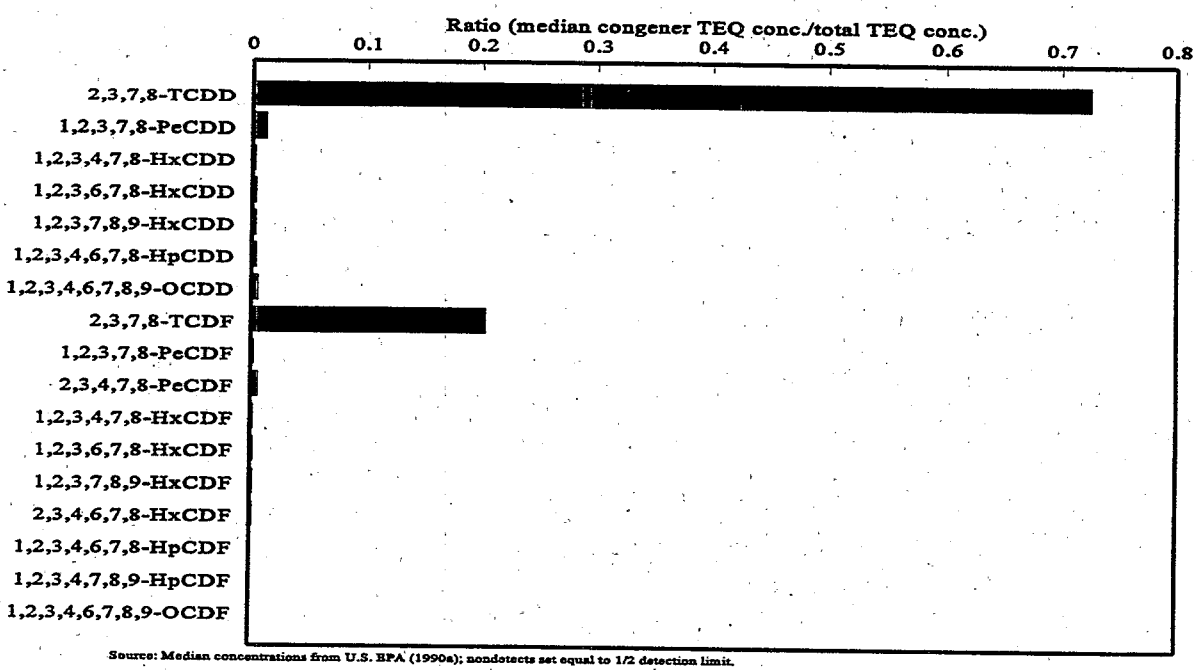
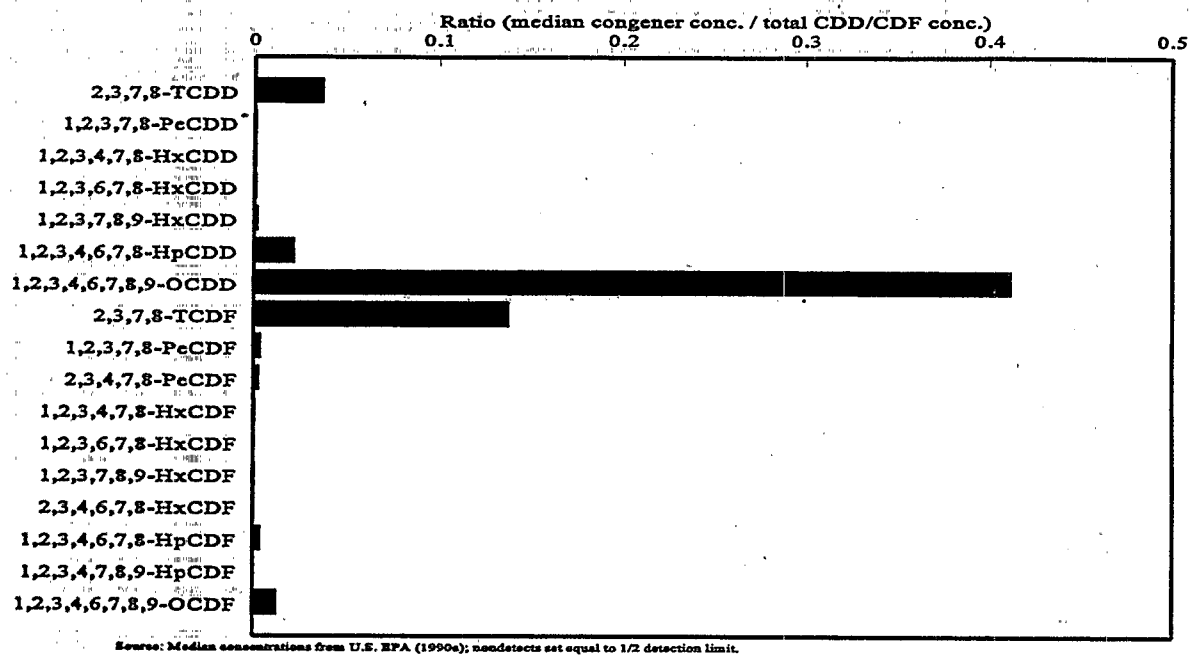


Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.

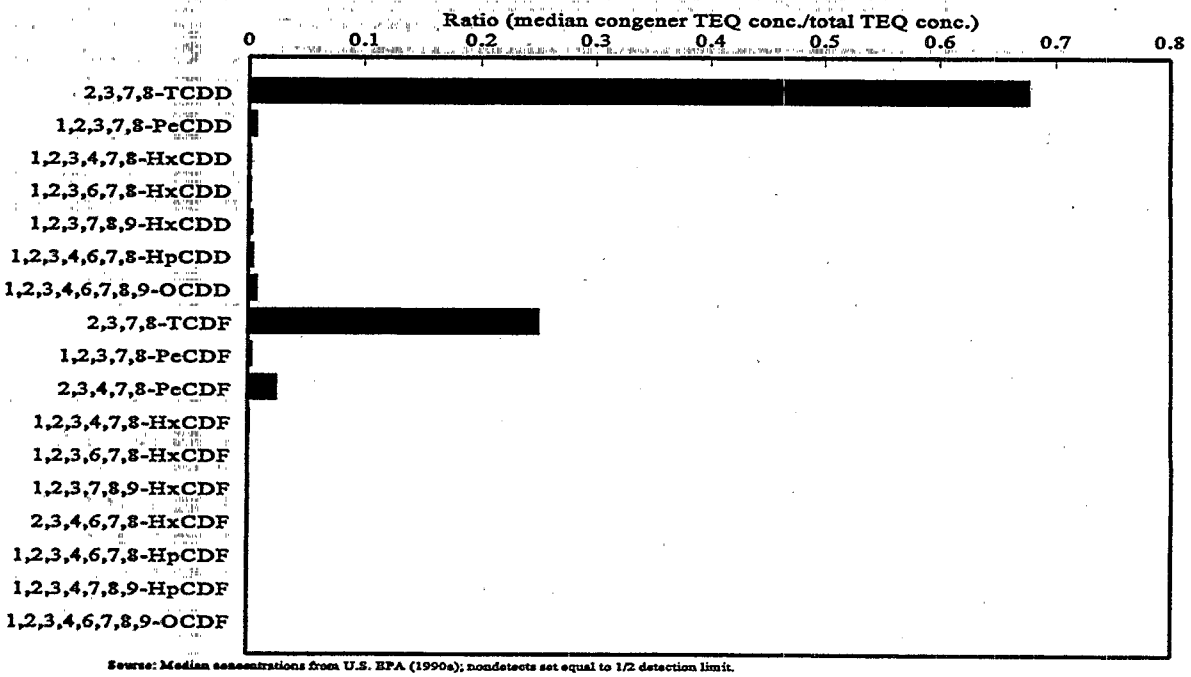


Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.

Figure 8-1. 104-Mill Study Full Congener Analysis Results for Pulp

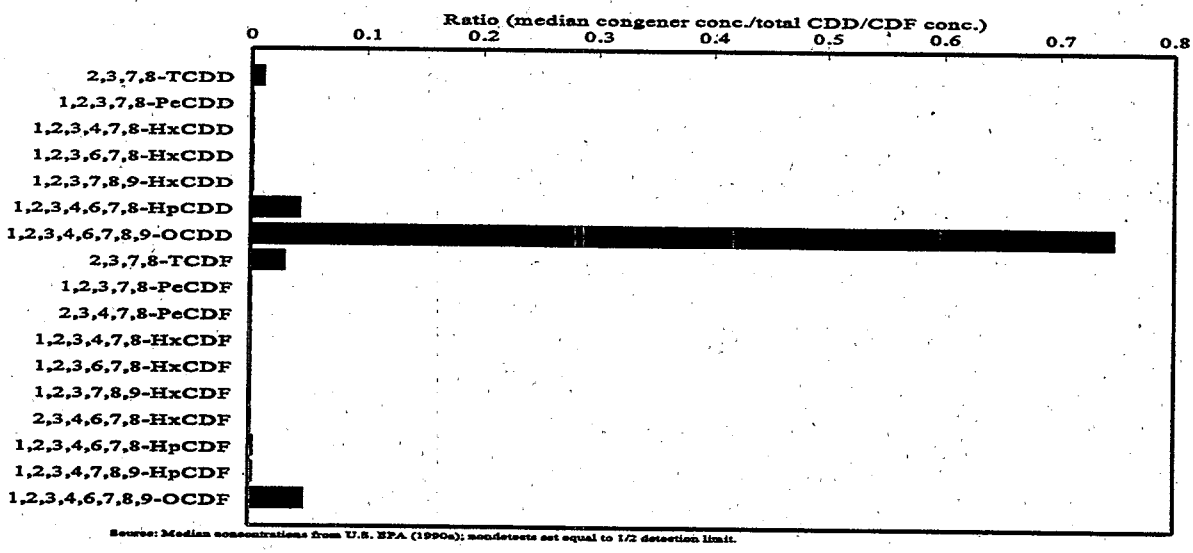


Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.

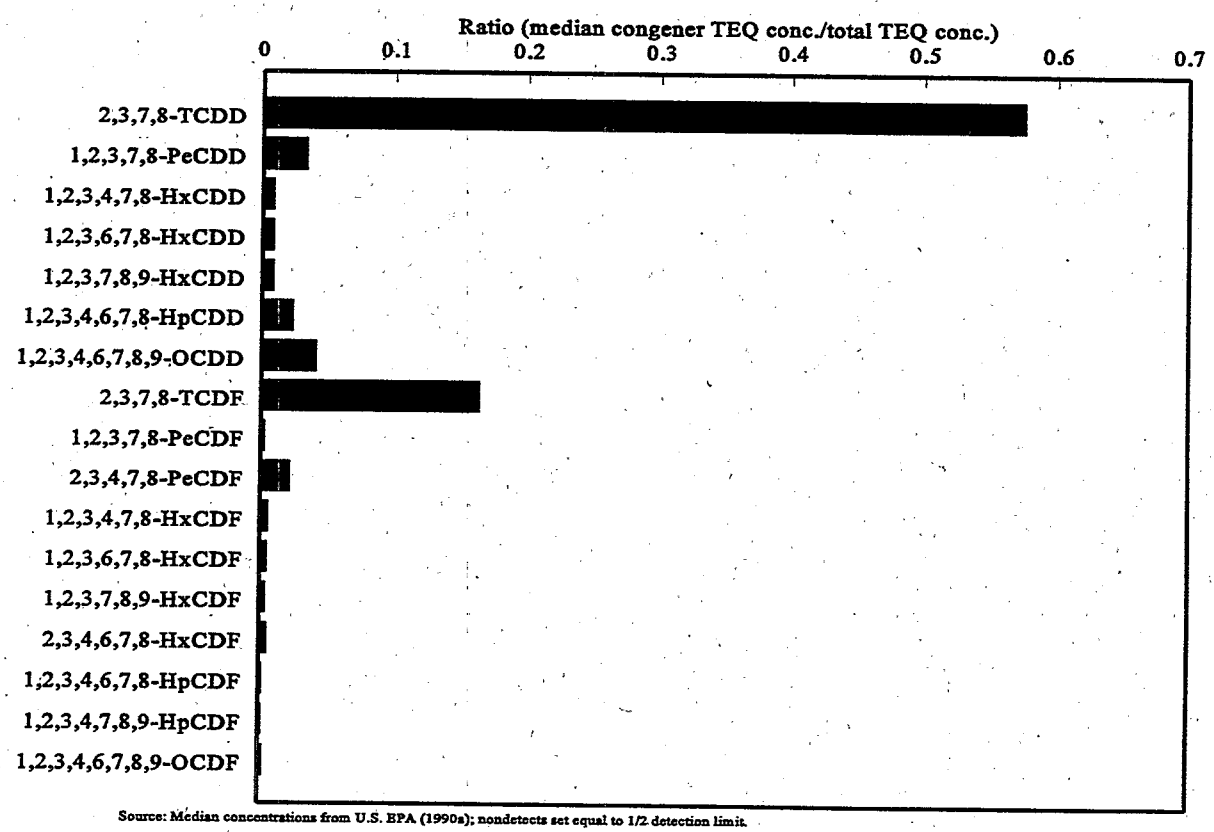


Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.

Figure 8-2. 104-Mill Study Full Congener Analysis Results for Sludge



Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.



Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.

Figure 8-3. 104-Mill Study Full Congener Analysis Results for Effluent

Table 8-2. CDD/CDF Concentrations in Pulp and Paper Mill Bleached Pulp, Wastewater Sludge, and Effluent (circa 1996)

Congener/Congener Group	Bleached Pulp				Wastewater Sludge				Wastewater Effluent			
	Mean ND = 0 (ng/kg)	Median (ng/kg)	Range (ng/kg)	No. of Detects/ No. of Samples	Mean ND = 0 (ng/kg)	Median (ng/kg)	Range (ng/kg)	No. of Detects/ No. of Samples	Mean ND = 0 (pg/L)	Median (ng/kg)	Range (pg/L)	No. of Detects/ No. of 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	99.0	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	0	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	0	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	0	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	0	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	0	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	0	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	0	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	0	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	0	ND(106)	ND(104) to ND(110)	0/18
Total 2,3,7,8-CDD[a]	2.7				492				103			
Total 2,3,7,8-CDF[a]	10.7				8.4				2.3			
Total TEQ (ND = zero)[a]	1.5				3.0				1.5			
Total TEQ (ND = DL)[a]	11.3				22.9				105			

ND = not detected; values in parentheses are detection limits (DL).

[a] Sum of mean values.

ng/kg = nanograms per kilogram
pg/L = picograms per liter

Source: Gillespie (1997).

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Table 8-3. Summary of Bleached Chemical Pulp and Paper Mill Discharges of 2,3,7,8-TCDD and 2,3,7,8-TCDF

Matrix	Congener	1988 Discharge[a] (g/year)	1992 Discharge[b] (g/year)	1992 Discharge[c] (g/year)	1993 Discharge[b] (g/year)	1994 Discharge[b] (g/year)
Effluent	2,3,7,8-TCDD	201	22	71	19	14.6
	2,3,7,8-TCDF	1,550	99	341	76	49.0
	TEQ	356	32	105	27	19.5
Sludge[d]	2,3,7,8-TCDD	210	33	NR	24	18.9
	2,3,7,8-TCDF	1,320	118	NR	114	95.2
	TEQ	343	45	100	35	28.4
Pulp	2,3,7,8-TCDD	262	24	NR	22	16.2
	2,3,7,8-TCDF	2,430	124	NR	106	78.8
	TEQ	505	36	150	33	24.1

NR = Not reported.

[a] 104-Mill Study (U.S. EPA, 1990a): Total discharge rate of congener or TEQ (based only on 2,3,7,8-TCDD and 2,3,7,8-TCDF concentration) summed across all 104 mills.

[b] NCASI 1992 Survey (NCASI, 1993), 1993 Update (Gillespie, 1994), and 1994 Update (Gillespie, 1995): Total discharge rate of congener or TEQ (based only on 2,3,7,8-TCDD and 2,3,7,8-TCDF concentration) summed across all 104 mills. The daily discharge rates reported in NCASI (1993), Gillespie (1994), and Gillespie (1995) were multiplied by a factor of 350 days/yr to obtain estimates of annual discharge rates.

[c] The discharge in effluent was estimated in U.S. EPA (1993d) for January 1, 1993. The TEQ discharges in sludge and pulp were estimated by multiplying the 1988 discharge estimates for each by the ratio of the 1993 and 1988 effluent discharge estimates (i.e., the estimate of the reduction in 1988 discharges achieved by pollution prevention measures taken by the industry between 1988 and 1993).

[d] Approximately 20.5 percent of the sludge generated in 1990 were incinerated. The remaining 79.5 percent were predominantly landfilled (56.5 percent) or placed in surface impoundments (18.1 percent); 4.1 percent were land-applied directly or as compost, and 0.3 percent were distributed/marketed (U.S. EPA, 1993e).

g/year = grams per year

Sources: Gillespie (1995); Gillespie (1994); NCASI (1993); U.S. EPA (1993d); U.S. EPA (1993e).

Table 8-4. CDD/CDF Concentrations in Graphite Electrode Sludge from Chlorine Production

Congener/Congener Group	Sludge 1 (μg/kg)	Sludge 2 (μg/kg)	Sludge 3 (μg/kg)	Sludge 4 (μg/kg)
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	2.0	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	2.0	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*	1.015	2.21	2.45	0.705
Total 2,3,7,8-CDF*	152.37	341.7	339.6	303
Total TEQ*	13.5	30.2	30.2	27.7
Total TCDD	ND (0.006)	ND (0.009)	ND (0.009)	NR
Total PeCDD	ND (0.070)	ND (0.009)	ND (0.009)	NR
Total HxCDD	ND (0.046)	ND (0.064)	ND (0.074)	NR
Total HpCDD	0.22	0.48	0.56	NR
Total OCDD	0.92	2	2.2	0.65
Total TCDF	64	150	140	NR
Total PeCDF	75	240	240	NR
Total HxCDF	68	140	140	NR
Total HpCDF	24	53	54	NR
Total OCDF	31	76	71	81
Total CDD/CDF*	263.14	661.48	647.76	NR

ND = Nondetected (values in parentheses are the reported detection limits)
NR = Not reported
* = Calculated assuming not detected values were zero.
μg/kg = micrograms per kilogram

Sources: Rappe et al. (1991); Rappe (1993)

Table 8-5. CDD/CDF Concentrations in Metal Chlorides

Congener Group	$FeCl_3$ (μg/kg)	$AlCl_3$ (μg/kg)	$AlCl_3$ (μg/kg)	$CuCl_2$ (μg/kg)	CuCl (μg/kg)	$TiCl_4$ (μg/kg)	$SiCl_4$ (μg/kg)
Total TCDD	NR	NR	NR	NR	NR	NR	NR
Total PeCDD	NR	NR	NR	NR	NR	NR	NR
Total HxCDD	NR	NR	NR	NR	NR	NR	NR
Total HpCDD	ND	ND	ND	0.03	ND	ND	ND
Total OCDD	ND	ND	0.1	0.6	0.03	ND	ND
Total TCDF	NR	NR	NR	NR	NR	NR	NR
Total PeCDF	NR	NR	NR	NR	NR	NR	NR
Total HxCDF	NR	NR	NR	NR	NR	NR	NR
Total HpCDF	12	ND	ND	0.1	0.08	ND	ND
Total OCDF	42	ND	34	0.5	0.2	ND	ND

NR = Not reported.
ND = Nondetected (detection limit of 0.02 μg/kg)
μg/kg = micrograms per kilogram

Source: Hutzinger and Fiedler (1991a)

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Table 8-6. CDD/CDF Concentrations in Mono- through Tetra-Chlorophenols

Congener/ Congener Group	2-CP (Ref. A) (mg/kg)	2,4-DCP (Ref. A) (mg/kg)	2,6-DCP (Ref. A) (mg/kg)	2,4,5-TrCP (Na salt) (Ref. A) (mg/kg)	2,4,5-TrCP (Ref. A) (mg/kg)	2,4,6-TrCP (Ref. A) (mg/kg)	2,4,6-TrCP (Na salt) (Ref. B & C) (mg/kg)	2,3,4,6-TeCP (Ref. A) (mg/kg)	2,3,4,6-TeCP (Na salt) (Ref. B & C) (mg/kg)
Total TCDD	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02) - 14	ND (0.02) - 6.5	ND (0.02) - 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) - 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) - 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) - 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) - 0.17	0.7
Total TCDF	+	ND	ND	ND	ND	+	1.5	+	0.5
Total PeCDF	ND	ND	ND	ND	ND	+	17.5	+	10
Total HxCDF	ND	ND	ND	ND	ND	+	36	+	70
Total HpCDF	ND	ND	ND	ND	ND	ND	4.8	+	70
Total OCDF	ND	ND	ND	ND	ND	ND	--	+	10
Total CDD/CDF	--	--	--	--	--	--	--	--	--

ND = Not detected; value in parentheses is the detection limit, if reported.
+ = Detected but not quantified.
-- = Not reported.
mg/kg = milligrams per kilogram
Ref. A: Firestone et al. (1972); because of poor recoveries, authors stated that actual CDD/CDF levels may be considerably higher than those reported.
Ref. B: Rappe et al. (1978a); common Scandinavian commercial chlorophenols.
Ref. C: Rappe et al. (1978b); common Scandinavian commercial chlorophenols.

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Table 8-7. Historical CDD/CDF Concentrations in Historical and Current Technical Pentachlorophenol Products

Congener/ Congener Group	PCP (Ref. B) (1973) (μg/kg)	PCP (Ref. C) (1978) (μg/kg)	PCP (Ref. A) (1979) (μg/kg)	PCP (Ref. D) (1984) (μg/kg)	PCP (Ref. I) (1985) (μg/kg)	PCB (Ref. I) (1986) (μg/kg)	PCP (Ref. E) (1987) (μg/kg)	PCP (Ref. F) (1987) (μg/kg)	PCP (Ref. I) (1985-88) (μg/kg)	PCP (Ref. G) (1991) (μg/kg)	PCP (Ref. H) (1987-96) (μg/kg)	PCP (Ref. J) (1987-96) (μg/kg)	PCP (Ref. K) (unknown) (μg/kg)
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	99,960	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*	--	--	--	712,300	1,687,615	1,037,568	811,860	891,435	2,812,621	--	--	--	334,130
Total 2,3,7,8-CDF*	--	--	--	--	260,159	268,238	130,076	158,230	262,469	--	--	--	22,280
Total TEQ*	--	--	--	1,970	4,445	2,736	1,853	2,321	4,173	>1,270	--	--	811
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)	ND	--
Total HxCDD	5,500	--	10,100	4,500	4,694	2,925	1,700	3,300	912	8,900	1,530	1,686	--
Total HpCDD	98,000	--	296,000	135,000	283,000	134,000	154,000	198,000	117,000	130,000	62,900	61,083	--
Total OCDD	220,000	--	1,386,000	610,000	1,475,000	930,000	733,000	790,000	2,723,000	1,100,000	--	231,755	--
Total TCDF	40	900	--	ND (10)	6	ND	0.8	0.4	ND	ND (10)	ND (10)	54	--
Total PeCDF	250	4,000	1,400	--	10	3	141	343	200	ND (10)	ND (10)	509	--
Total HxCDF	22,000	32,000	9,900	--	1,982	1,407	4,300	13,900	1,486	14,000	2,500	15,534	--
Total HpCDF	150,000	120,000	88,000	62,000	125,000	146,000	74,000	127,000	99,000	36,000	38,600	93,377	--
Total OCDF	160,000	130,000	43,000	130,000	222,000	233,000	118,000	137,000	237,000	170,000	--	156,451	--
Total CDD/CDF*	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	--	560,448	--

ND = Not detected; value in parentheses is the detection limit.
-- = Not reported.
* = Calculated assuming not detected values are zero.
μg/kg = micrograms per kilogram

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Table 8-7. Historical CDD/CDF Concentrations in Historical and Current Technical Pentachlorophenol Products (continued)

Sources:

Ref. A: U.S. DHHS (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).
Ref. B: Buser and Bosshardt (1976); mean of 10 samples of "high" CDD/CDF content PCP received from Swiss commercial sources in 1973.
Ref. C: Rappe et al. (1978b); sample of U.S. origin "presumably prepared by alkaline hydrolysis of hexachlorobenzene."
Ref. D: 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).
Ref. E: Hagenmaier and Brunner (1987); sample of Witophen P (Dynamit Nobel - Lot no. 7777) (obtained in Germany).
Ref. F: Hagenmaier and Brunner (1987); sample of PCP produced by Rhone Poulenc (obtained in Germany).
Ref. G: Harrad et al. (1991); PCP-based herbicide formulation from NY State Dept. Environm. Conservation.
Ref. H: Pentachlorophenol Task Force (1997); average of monthly batch samples for the period Jan. 1987 to Aug. 1996.
Ref. I: Pentachlorophenol Task Force (1997); samples of "penta" manufactured in 1985, 1986, and 1988.
Ref. J: KMG-Bermuth, Inc. (1997); average of monthly batch samples for the period Feb. 1987 to Dec. 1996 (excluding the following months for which data were not available: Feb. 1993, Jan. 1992, Dec. 1991, Sept. 1991, Dec. 1988, and Sept. 1988).
Ref. K: Schecter et al. (1997); sample found stored in a barn in Vermont.

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Table 8-8. Historical CDD/CDF Concentrations in Pentachlorophenol-Na

Congener/Congener Group	PCP-Na (Ref. A) (1969) (μg/kg)	PCP-Na (Ref. B) (1973) (μg/kg)	PCP-Na (Ref. C) (1973) (μg/kg)	PCP-Na (Ref. D) (1987) (μg/kg)	PCP-Na (Ref. E) (1987) (μg/kg)	PCP-Na (Ref. F) (1992) (μg/kg)	PCP-Na (Ref. G) (1980s) (μg/kg)
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	53.0	4,410	4,050
1,2,3,7,8,9-HxCDD	--	--	--	282	19.0	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 (1.0)	149
1,2,3,7,8-PeCDF	--	--	--	8.2	1.9	ND (4.0)	319
2,3,4,7,8-PeCDF	--	--	--	6.6	1.1	ND (4.0)	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*	--	--	--	53,063	35,289	1,059,253	118,878
Total 2,3,7,8-CDF*	--	--	--	38,795	4,499	126,492	43,841
Total TEQ*	--	--	--	452	79.5	3,374	1,201
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	1200
Total PeCDF	--	60	40	137	27	88.4	6400
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*	--	15,980	235,990	117,859	43,752	1,348,751	378,742

ND = Not detected; value in parentheses is the detection limit.
-- = Not reported.
* = Calculated assuming not detected values are zero.
μg/kg = micrograms per kilogram.

Sources:
Ref. A: Firestone et al. (1972); mean of two samples of PCP-Na obtained in the United States between 1967 and 1969.
Ref. B: Buser and Bosshardt (1976); mean of five samples of "low" CDD/CDF content PCP-Na received from Swiss commercial sources.
Ref. C: Buser and Bosshardt (1976); sample of "high" CDD/CDF content PCP-Na received from a Swiss commercial source.
Ref. D: Hagenmaier and Brunner (1987); sample of Dowicide-G purchased from Fluka; sample obtained in Germany.
Ref. E: Hagenmaier and Brunner (1987); sample of Preventol PN (Bayer AG); sample obtained in Germany.
Ref. F: Santl et al. (1994c); 1992 sample of PCP-Na from Prolabo, France.
Ref. G: Palmer et al. (1988); sample of a PCP-Na formulation collected from a closed sawmill in California in the late 1980s.

Table 8-9. Summary of Specific Dioxin-Containing Wastes That Must Comply with Land Disposal Retrictions

EPA Hazardous Waste Number	Waste Description	Land Disposal Restriction Effective Date	Regulated Waste Constitutent	Treatment Standard[a] (ppb)	
				Wastewaters (μg/L)	Nonwastewaters (μg/kg)
F020	Wastes (except wastewater and spent carbon from hydrogen chloride 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	0.063 0.063 0.063 0.063 0.035 0.063	1 1 1 1 1 1
F021	Wastes (except wastewater and spent carbon from hydrogen chloride 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	0.063 0.063 0.063 0.063 0.035 0.063	1 1 1 1 1 1
F022	Wastes (except wastewater and spent carbon from hydrogen chloride 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	0.063 0.063 0.063 0.063 0.035 0.063	1 1 1 1 1 1
F023	Wastes (except wastewater and spent carbon from hydrogen chloride 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	0.063 0.063 0.063 0.063 0.035 0.063	1 1 1 1 1 1
F026	Wastes (except wastewater and spent carbon from hydrogen chloride 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	0.063 0.063 0.063 0.063 0.035 0.063	1 1 1 1 1 1
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	0.063 0.063 0.063 0.063 0.035 0.063	1 1 1 1 1 1

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Table 8-9. Summary of Specific Dioxin-Containing Wastes That Must Comply with Land Disposal Retrictions (continued)

EPA Hazardous Waste Number	Waste Description	Land Disposal Restriction Effective Date	Regulated Waste Constitutent	Treatment Standard[a] (ppb)	
				Wastewaters (μg/L)	Nonwastewaters (μg/kg)
F028	Residues resulting from the incineration or thermal treatment of soil contaminated with EPA Hazardous Waste Nos. F020-F023, F026, and F027	November 8, 1988	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1
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 (non-wastewater)	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1
K043	2,6-dichlorophenol waste from the production of 2,4-D.	June 8, 1989	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1
K099	Untreated wastewater from the production of 2,4-D.	August 8, 1988	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1

[a] Treatment standards (i.e., maximum allowable concentration in waste extraact) are based on incineration to 99.9999 percent destruction and removal efficiency.
μg/L = micrograms per liter
μg/kg = micrograms per kilogram
Source: 40 CFR 268

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Table 8-10. CDD/CDF Concentrations in Chlorobenzenes

Congener/ Congener Group	MCBz (Ref. A) (μg/kg)	1,2-DCBz (for synthesis) (Ref. A) (μg/kg)	1,2,4-TrCBz ("pure") (Ref. B) (μg/kg)	Mixed TrCBz (47%) (Ref. A) (μg/kg)	1,2,4,5-TeCBz (99%) (Ref. A) (μg/kg)	PeCBz (98%) (Ref. A) (μg/kg)	HCBz (97%) (Ref. A) (μg/kg)	HCBz (Ref. B) (μg/kg)
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)	0.140	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)	0.030	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	--	--	--	--

ND = Nondetected; value in parentheses is the detection limit, if reported.
-- = Not reported.
μg/kg = micrograms per kilogram.

Ref. A: Hutzinger and Fiedler (1991a); unpublished results of tests performed at the Univ. of Bayreuth, Germany and by Dr. H. Hagenmaier.
Ref. B: Villanueva et al. (1974); range of three samples of commercially available HCBz.

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Table 8-11. Concentrations of CDD/CDF Congener Groups in Unused Commercial PCB Mixtures

PCB Mixture	Year of Manufacture	CDF Congener Group Concentrations (mg/kg)						CDD Congener Group Concentrations (mg/kg)						Reference Number
		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	0.030	d
Aroclor 1248	1969	0.5	1.2	0.3	--	--	2.0	--	--	--	--	--	--	b
Clophen A-40	--	1.289	0.771	0.144	0.020	0.011	2.235	ND	ND	ND	0.012	0.030	0.042	d
Kanechlor 400	--	--	--	--	--	--	20.0	--	--	--	--	--	--	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	1.0	1.10	1.35	--	3.8	--	--	--	--	--	--	b, c
Aroclor 1260	1969	0.1	0.4	0.5	--	--	1.0	--	--	--	--	--	--	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	--	16.340	21.164	7.630	2.522	1.024	48.681	ND	ND	ND	0.014	0.032	0.046	d
Clophen A-60	--	1.4	5.0	2.2	--	--	8.6	--	--	--	--	--	--	a
Phenoclor DP-6	--	0.7	10.0	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	--	--	2.0	--	--	--	--	--	--	b

ND = Nondetected
-- = Not reported
mg/kg = milligram per kilogram

References

a: Bowes et al. (1975a)
b: Erickson (1986)
c: ATSDR (1993)
d: Hagenmaier (1987)
e: Malisch (1994)

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Table 8-12. 2,3,7,8-Substituted Congener Concentrations in Unused PCB Mixtures

Congener	Congener Concentrations in Clophens (μg/kg)						Congener Concentrations in Aroclors (μg/kg)									
	A-30 (Ref. A)	A-30 (Ref. B)	A-40 (Ref. B)	A-50 (Ref. B)	A-60 (Ref. A)	A-60 (Ref. B)	1016 (Ref. C)	1242 (Ref. C)	1248 (Ref. D)	1254 (Ref. C)	1254 (Ref. C)	1254 (Ref. C)	1254 (Ref. D)	1260 (Ref. C)	1260 (Ref. C)	1260 (Ref. C)
2,3,7,8-TCDD	ND	ND	ND	ND	ND	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,7,8-PeCDD	ND	ND	ND	ND	0.1	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,4,7,8-HxCDD	ND	ND	ND	ND	0.2	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,6,7,8-HxCDD	0.8	ND	ND	ND	ND	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,7,8,9-HxCDD	ND	ND	ND	ND	ND	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,4,6,7,8-HpCDD	5.6	2.4	4.4	5.3	2.5	6.8	--	--	--	--	--	--	--	--	--	--
OCDD	31.1	24.7	30.3	26.9	14.9	32.3	--	--	--	--	--	--	--	--	--	--
2,3,7,8-TCDF	1032.6	36.9	250.2	1005.7	2287.7	3077.2	0.10	40.1	330	28.0	20.9	55.8	110	63.5	6.88	29.0
1,2,3,7,8-PeCDF	135.8	14.9	52.7	155.2	465.2	1750.8	--	--	--	--	--	--	--	--	--	--
2,3,4,7,8-PeCDF	509.2	13.1	171.3	407.5	1921.9	2917	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	1604.2	2324.1	--	--	--	--	--	--	--	--	--	--
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	408.3	--	--	--	--	--	--	--	--	--	--
1,2,3,4,6,7,8-HpCDF	43.7	0.6	7	205.5	480.6	1126.1	--	--	--	--	--	--	--	--	--	--
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	1024.3	--	--	--	--	--	--	--	--	--	--
Total TCDD	0.7	ND	ND	ND	0.4	ND	--	--	--	--	--	--	--	--	--	--
Total PeCDD	ND	ND	ND	ND	2.0	ND	--	--	--	--	--	--	--	--	--	--
Total HxCDD	1.2	ND	ND	ND	1.8	ND	--	--	--	--	--	--	--	--	--	--
Total HpCDD	5.6	5.4	11.6	11.0	3.0	13.5	--	--	--	--	--	--	--	--	--	--
Total OCDD	31.1	24.7	30.3	26.9	14.9	32.3	--	--	--	--	--	--	--	--	--	--
Total TCDF	6376.6	713	1289.4	5402.3	15785.7	16340	--	--	--	--	--	--	--	--	--	--
Total PeCDF	2402.4	136.5	770.8	2153.7	11654.6	21164	--	--	--	--	--	--	--	--	--	--
Total HxCDF	804.8	5.1	143.6	2213.8	4455.8	7630.2	--	--	--	--	--	--	--	--	--	--
Total HpCDF	108.3	0.8	19.5	478.8	1517.0	2522.3	--	--	--	--	--	--	--	--	--	--
Total OCDF	15.7	ND	11.4	69.2	639.2	1024.3	--	--	--	--	--	--	--	--	--	--
Total CDD/CDF*	9746.4	885.5	2276.6	10355.7	34074.4	48726.5	--	--	--	--	--	--	--	--	--	--
Total I-TEQ*	407.2	14.70	71.71	327.11	1439.2	1444.2	--	--	--	--	--	--	--	--	--	--

ND = Nondetected.
-- = Not reported.
* = Calculated asumming not detected values are zero.
μg/kg = micrograms per kilogram.

References:
A = Malisch (1994)
B = Hagenmaier (1987)
C = Brown et al. (1988)
D = Bowes (1975b)

Table 8-13. Reported CDD/CDF Concentrations in Wastes from PVC Manufacture

Congener/Congener Group	F024 Waste (μg/kg)	K019 Waste (μg/kg)	K020 Waste (μg/kg)
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	0.30	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	4.20	920	0.89
OCDD	15.00	1,060	3.00
2,3,7,8-TCDF	0.91	680	0.44
1,2,3,7,8-PeCDF	9.5	975	1.80
2,3,4,7,8-PeCDF	1.6	1,050	0.58
1,2,3,4,7,8-HxCDF78	110	10,100	11.0
	24.0	9,760	2.4
1,2,3,6,7,8-HxCDF	9.5	21,800	1.3
1,2,3,7,8,9-HxCDF	3.1	930	0.89
2,3,4,6,7,8-HxCDF	250	13,400	38.0
1,2,3,4,6,7,8-HpCDF	51.0	1,340	6.0
1,2,3,4,7,8,9-HpCDF	390	43,500	650
OCDF			
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 TEQ	19.98	5,928	3.19
Total TCDD	3.1	1,230	1.9
Total PeCDD	3.6	3,540	1.7
Total HxCDD	1.3	3,950	NR
Total HpCDD	5.0	1,270	1.7
Total OCDD	15.0	1,060	3.0
Total TCDF	15.0	20,600	6.0
Total PeCDF	65.0	45,300	11.0
Total HxCDF	300	63,700	27.0
Total HpCDF	450	16,600	58.0
Total OCDF	390	43,500	650
Total CDD/CDF	1,248	200,750	760.3

NR = Congener group concentration reported in source is not consistent with reported congener concentrations.
μg/kg = micrograms per kilogram

Source: Stringer et al. (1995)

Table 8-14. CDD/CDF Measurements in Products and Treated Wastewater from U.S. PEDC/VCM/PVC Manufacturers

Congener and Congener Groups	Suspension and Mass PVC Resins			Dispersion PVC Resins			Ethylene Dichloride (EDC)			Treated Wastewater		
	No. Detects/ No. Samples	Range of Detected Conc. (ng/kg)		No. Detects/ No. Samples	Range of Detected Conc. (ng/kg)		No. Detects/ No. Samples	Range of Detected Conc. (ng/kg)		No. Detects/ No. Samples	Range of Detected Conc. (pg/L)	
		Min.	Max.		Min.	Max.		Min.	Max.		Min.	Max
2,3,7,8-TCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,7,8-PeCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,4,7,8-HxCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,6,7,8-HxCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,7,8,9-HxCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,4,6,7,8-HpCDD	1/22	nd	0.64	1/6	nd	0.8	0/5	nd	nd	3/10	nd	26
OCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	2/10	nd	260
2,3,7,8-TCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,7,8-PeCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
2,3,4,7,8-PeCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,4,7,8-HxCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	1/10	nd	5.8
1,2,3,6,7,8-HxCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	1/10	nd	3.8
1,2,3,7,8,9-HxCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
2,3,4,6,7,8-HxCDF	1/22	nd	0.37	0/6	nd	nd	0/5	nd	nd	2/10	nd	6.5
1,2,3,4,6,7,8-HpCDF	0/22	nd	nd	0/6	nd	nd	1/5	nd	1.1	4/10	nd	78
1,2,3,4,7,8,9-HpCDF	0/22	nd	nd	0/6	nd	nd	1/5	nd	0.40	3/10	nd	20
OCDF	0/22	nd	nd	2/6	nd	0.38	1/5	nd	11	0/10	nd	3.2
Mean TEQ (ND = zero)		0.002			0.001			0.0005			0.60	
Mean TEQ (ND = 1/2 DL)			0.65			0.35			0.21			4.5
Total TCDD	0/22	nd	nd	1/6	nd	0.24	0/5	nd	nd	0/10	nd	nd
Total PeCDD	0/22	nd	nd	1/6	nd	0.32	0/5	nd	nd	0/10	nd	nd
Total HxCDD	0/22	nd	nd	5/6	nd	0.97	0/5	nd	nd	0/10	nd	nd
Total HpCDD	1/22	nd	0.64	1/6	nd	1.3	0/5	nd	nd	3/10	nd	48
Total OCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	2/10	nd	260
Total TCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
Total PeCDF	0/22	nd	nd	1/6	nd	0.3	0/5	nd	nd	0/10	nd	nd
Total HxCDF	1/22	nd	0.37	0/6	nd	nd	0/5	nd	nd	2/10	nd	30
Total HpCDF	0/22	nd	nd	0/6	nd	nd	1/5	nd	2.02	3/10	nd	140
Total OCDF	0/22	nd	nd	2/6	nd	0.38	1/5	nd	11	5/10	nd	900

nd = not detected.
ng/kg = nanograms per kilogram
pg/L = picograms per liter
Source: The Vinyl Institute (1996)

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Table 8-15. CDD/CDF Concentrations in Dioxazine Dyes and Pigments (Canada)

Congener/Congener Group	Blue 106 (μg/kg)			Blue 108 (μg/kg)	Violet 23 (μg/kg)					
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	*	*	*	*	*	*	*	*	*	*
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 TEQ **	56.4	30.2	19.5	0.1	16.0	1.4	18.9	12.7	2.7	2.7
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**	54,533	30,012	19,112	47	8,275	957	14,882	9,540	1,787	1,880

ND = Nondetected; value in parenthesis is the detection limit.
-- = Not reported.
* = Results listed for 1,2,3,4,7,8-HxCDF include concentrations for 1,2,3,6,7,8-HxCDF.
** = Nondetected values were assumed to be zero for calculation of Total TEQs and Total CDD/CDF.
μg/kg = micrograms per kilogram
Source: Williams et al. (1992)

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Table 8-16. CDD/CDF Concentrations in Printing Inks (Germany)

Congener/Congener Group	Rotogravure (2-color) (ng/kg)	Rotogravure (4-color) (ng/kg)	Offset (4-color) (ng/kg)	Offset (4-color) (ng/kg)
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	1320	249
Total TEQ *	90.1	66.2	38.2	17.5
Total TCDD	4	ND (2)	77	38
Total PeCDD	58	145	35	25
Total HxCDD	2,679	2,485	660	246
Total HpCDD	5,630	3,460	1,100	445
Total OCDD	5,810	2,350	890	230
Total TCDF	5.5	28	90	35
Total PeCDF	13	ND (4)	340	110
Total HxCDF	29	45	95	94
Total HpCDF	64	14	566	63
Total OCDF	129	ND (10)	960	165
Total CDD/CDF	14,422	8,527	4,813	1,451

ND = Nondetected; value in parenthesis is the detection limit.
-- = Not reported.
* = Calculation of TEQ values assumes nondetected congeners are present at half of their detection limits.
ng/kg = nanograms per kilogram.

Source: Santl et al. (1994c).

Table 8-17. Chemicals Requiring TSCA Section 4 Testing Under the Dioxin/Furan Rule

Currently Manufactured or Imported as of June 5, 1987[a]	
CAS No.	Chemical Name
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	[a]Tetrabromobisphenol-A-bis-2,3-dibromopropylether
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	[a]Tetrabromobisphenol-A-diacrylate
Not Currently Manufactured or Imported as of June 5, 1987[b]	
CAS No.	Chemical Name
79-95-8	Tetrachlorobisphenol-A
87-10-5	3,4',5-Tribromosalicylanide
87-65-0	2,6-Dichlorophenol
95-77-2	3,4-Dichlorophenol
95-95-4	2,4,5-Trichlorophenol
99-28-5	2,6-Dibromo-4-nitrophenol
120-36-5	2[2,4-(Dichlorophenoxy)]-propanoic acid
320-72-9	3,5-Dichlorosalicyclic acid
488-47-1	Tetrabromocatechol
576-24-9	2,3-Dichlorophenol
583-78-8	2,5-Dichlorophenol
608-71-9	Pentabromophenol
615-58-7	2,4-Dibromophenol
933-75-5	2,3,6-Trichlorophenol
1940-42-7	4-Bromo-2,5-dichlorophenol
2577-72-2	3,5-Dibromosalicylanide
3772-94-9	Pentachlorophenyl laurate
37853-61-5	Bismethylether of tetrabromobisphenol-A
-	Alkylamine tetrachlorophenate
-	Tetrabromobisphenol-B

a Tetrabromobisphenol-A-bis-2,3-dibromopropylether and tetrabromobisphenol-A-diacrylate are no longer manufactured in or imported into the United States (Cash, 1993).

b As of August 5, 1995, neither manufacture nor importation of any of these chemicals had resumed in the United States (Holderman, 1995).

Table 8-18. Congeners and Limits of Quantitation (LOQ) for Which Quantitation is Required Under the Dioxin/Furan Test Rule and Pesticide Data Call-In

Chlorinated Dioxins and Furans	Brominated Dioxins and Furans	LOQ (μg/kg)
2,3,7,8-TCDD	2,3,7,8-TBDD	0.1
1,2,3,7,8-PeCDD	1,2,3,7,8-PeBDD	0.5
1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-HxBDD	2.5
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxBDD	2.5
1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-HxBDD	2.5
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpBDD	100
2,3,7,8-TCDF	2,3,7,8-TBDF	1
1,2,3,7,8-PeCDF	1,2,3,7,8-PeBDF	5
2,3,4,7,8-PeCDF	2,3,4,7,8-PeBDF	5
1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxBDF	25
1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-HxBDF	25
1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-HxBDF	25
2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-HxBDF	25
1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpBDF	1,000
1,2,3,4,7,8,9-HpCDF	1,2,3,4,7,8,9-HpBDF	1,000

μg/kg = microgram per kilogram.

Table 8-19. Precursor Chemicals Subject to Reporting Requirements Under TSCA Section 8(a)

CAS No.	Chemical Name
85-22-3	Pentabromoethylbenzene
87-61-6	1,2,3-Trichlorobenzene
87-84-3	1,2,3,4,5-Pentabromo-6-chlorocyclohexane
89-61-2	1,4-Dichloro-2-nitrobenzene
89-64-5	4-Chloro-2-nitrophenol
89-69-0	2,4,5-Trichloronitrobenzene
92-04-6	2-Chloro-4-phenylphenol
97-74-6	4-Chloro-o-toloxy acetic acid
94-81-5	4-(2-Methyl-4-chlorophenoxy) butyric acid
95-50-1	o-Dichlorobenzene
95-56-7	o-Bromophenol
95-57-8	o-Chlorophenol
95-88-5	4-Chlororesorcinol
95-94-3	1,2,4,5-Tetrachlorobenzene
95-50-7	5-Chloro-2,4-dimethoxyaniline
99-30-9	2,6-Dichloro-4-nitroaniline
99-54-7	1,2-Dichloro-4-nitrobenzene
106-37-6	Dibromobenzene
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

Table 8-20. Results of Analytical Testing for Dioxins and Furans in the Chemicals Tested To-Date Under Section 4 of the Dioxin/Furan Test Rule

CAS Number	Chemical Name	No. of Chemical Companies That Submitted Data	No. of Positive Studies	Congeners Detected (detection range: µg/kg)
79-94-7	Tetrabromobisphenol-A	3	0	ND[a]
118-75-2	2,3,5,6-Tetrachloro-2,5-cyclohexadiene-1,4-dione (chloranil)	4	4	See Table 8-21
118-79-6	2,4,6-Tribromophenol	1	0	ND[a]
120-83-2	2,4-Dichlorophenol	1	0	ND[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	ND[a]
32536-52-0	Octabromodiphenyl oxide	3	3	2,3,7,8-TBDD (ND-0.71) 1,2,3,7,8-PeBDD (ND-0.1) 2,3,7,8-TBDF (ND-12.6) 1,2,3,7,8-PeBDF (ND-6.3) 2,3,4,7,8-PeBDF (ND-83.1) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (ND-67.8) 1,2,3,7,8,9-HxBDF (ND-56.0) 1,2,3,4,6,7,8-HpBDF (ND-330)
378-53-59-1	1,2-Bis(tribromo-phenoxy)-ethane	1	1	2,3,7,8-TBDF (ND-0.04) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (ND-0.03) 1,2,3,4,6,7,8-HpBDF (ND-0.33)
32534-81-9	Pentabromodiphenyl oxide	2	2	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	ND[a]

[a] No 2,3,7,8-substituted dioxins and furans detected above the Test Rule target limits of quantitation (LOQ). (See Table 8-18.)
[b] Third study is currently undergoing EPA review.
[c] Study is currently undergoing EPA review.
µg/kg = micrograms per kilogram
Source: Holderman and Cramer (1995).

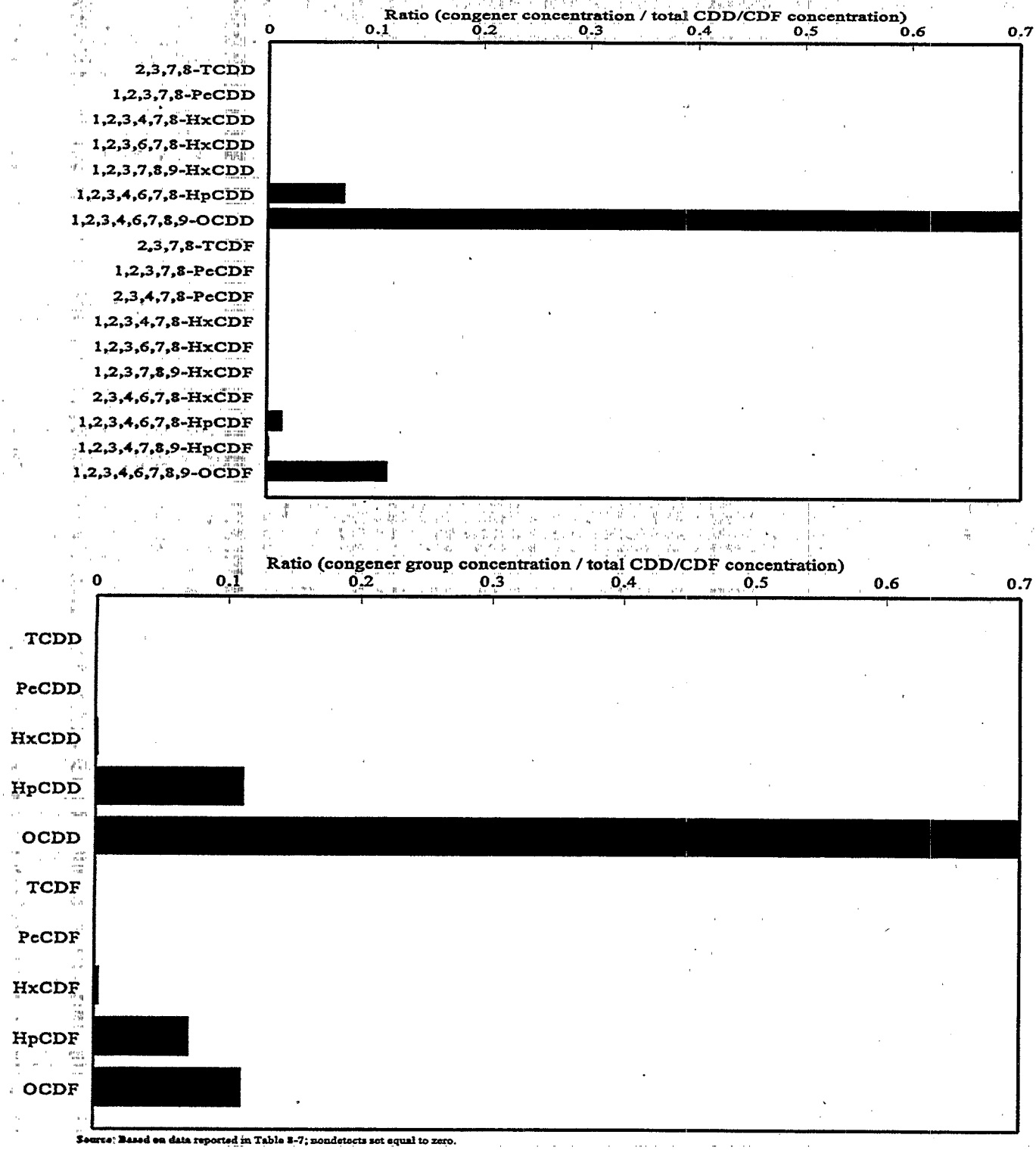
Table 8-21. CDDs and CDFs in Chloranil and Carbazole Violet Samples Analyzed Pursuant to the EPA Dioxin/Furan Test Rule

Congener	Concentration (μg/kg) in Chloranil				Concentration (μg/kg) in 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 TEQ*	263	2,874	814	3,065	211

Source: Remmers et al. (1992).

nd = nondetected; minimum limit of detection shown in parenthesis.
μg/kg = micrograms per kilogram.

* = Calculated assuming not detected values are zero.



Source: Based on data reported in Table 8-7; nondetects set equal to zero.

Figure 8-4. Congener and Congener Group Profiles for Technical PCP

Table 8-22. 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-triiodobenzoate	17601-49-9	Yes	--
012001	Neburon	555-37-3	Yes	--
012101	Crufomate	299-86-5	Yes	--
019201	MCPB, 4-butyric acid [4-(2-Methyl-4-chlorophenoxy)butyric acid]	94-81-5	No	Yes
019202	MCPB, Na salt [Sodium 4-(2-methyl-4-chlorophenoxy)butyrate]	6062-26-6	No	No
019401	4-Chlorophenoxyacetic acid	122-88-3	No	Yes
025501	Chloroxuron	1982-47-4	Yes	--
027401	Dichlobenil	1194-65-6	No	Yes
028201	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	--
029601	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	--
035505	Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea]	330-54-1	No	No

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Table 8-22. 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
035506	Linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea]	330-55-2	No	No
035901	Metobromuron [3-(p-bromophenyl)-1-methoxy-1-methylurea]	3060-89-7	Yes	--
053501	Methyl parathion [O,O-Dimethyl O-p-nitrophenyl phosphorothioate]	298-00-0	No	No
055001	Dichlorophene [Sodium 2,2'-methylenebis(4-chlorophenate)]	97-23-4	Yes	--
055005	Dichlorophene, sodium salt [Sodium 2,2'-methylenebis(4-chlorophenate)]	10254-48-5	Yes	--
055201	1,2,4,5-Tetrachloro-3-nitrobenzene	117-18-0	Yes	--
057501	Ethyl Parathion [O,O-diethyl O-p-nitrophenyl phosphorothioate]	56-38-2	No	No
058102	Carbophenothion [S-(((p-chlorophenyl)thio)methyl) O,O-diethyl phosphorodithioate]	786-19-6	Yes	--
058301	Ronnel [O,O-dimethyl O-(2,4,5-trichlorophenyl) phosphorothioate]	229-84-3	Yes	--
058802	Mitin FF [Sodium 5-chloro-2-(4-chloro-2-(3-(3,4-dichlorophenyl)ureido)phenoxy) benzenesulfonate]	3567-25-7	No	No
059401	Orthodichlorobenzene	95-50-1	Yes	--
061501	Paradichlorobenzene	106-46-7	No	No
062201	Chlorophene [2-Benzyl-4-chlorophenol]	120-32-1	No	No
062202	Potassium 2-benzyl-4-chlorophenate	35471-49-9	No	In review
062203	Sodium 2-benzyl-4-chlorophenate	3184-65-4	No	In review
062204	2-Chlorophenol	95-57-8	Yes	--
062206	2-Chloro-4-phenylphenol	92-04-6	Yes	--
062207	Potassium 2-chloro-4-phenylphenate	18128-16-0	Yes	--
062208	4-Chloro-2-phenylphenol	not available	Yes	--
062209	4-Chloro-2-phenylphenol, potassium salt	53404-21-0	Yes	--
062210	6-Chloro-2-phenylphenol	85-97-2	Yes	--
062211	6-Chloro-2-phenylphenol, potassium salt	18128-17-1	Yes	--
062212	4-Chloro-2-phenylphenol, sodium salt	10605-10-4	Yes	--
062213	6-Chloro-2-phenylphenol, sodium salt	10605-11-5	Yes	--

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Table 8-22. 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
062214	4 and 6-Chloro-2-phenylphenol, diethanolamine salt	53537-63-6	Yes	--
062215	2-Chloro-4-phenylphenol, sodium salt	31366-97-9	Yes	--
064202	4-Chloro-2-cyclopentylphenol	13347-42-7	Yes	--
064208	Fentichlor [2,2'-Thiobis(4-chloro-6-methylphenol)]	4418-66-0	Yes	--
064209	Fentichlor [2,2'-Thiobis(4-chlorophenol)]	97-24-5	Yes	--
064214	4-Chloro-2-cyclopentylphenol, potassium salt of	35471-38-6	Yes	--
064218	4-Chloro-2-cyclopentylphenol, sodium salt	53404-20-9	Yes	-
067707	Chlorophacinone	3691-35-8	No	No
069105	ADBAC [Alkyl* dimethyl benzyl ammonium chloride *(50% C14, 40% C12, 10% C16)]	68424-85-1	No	No
069144	ADBAC [Alkyl* dimethyl 3,4-dichlorobenzyl ammonium chloride *(61% C12, 23% C14, 11% C16, 5% C18)]	not available	No	No
077401	Niclosamide [2-Aminoethanol salt of 2',5-dichloro-4'-nitrosalicylanilide]	1420-04-8	No	No
077406	5-Chlorosalicylanilide	4638-48-6	Yes	--
078780	2-Methyl-4-isothiazolin-3-one	not available	Yes	--
079202	Tetradifon [4-chlorophenyl 2,4,5-trichlorophenyl sulfone]	116-29-0	Yes	--
079301	Chloranil [tetrachloro-p-benzoquinone]	118-75-2	Yes	--
080403	6-Chlorothymol	89-68-9	Yes	--
080811	Anilazine [2,4-Dichloro-6-(o-chloroanilino)-s-triazine]	101-05-3	Yes	--
081901	Chlorothalonil [tetrachloroisophthalonitrile]	1897-45-6	No	Yes
082602	Sodium 2,3,6-Trichlorophenylacetate	2439-00-1	Yes	--
084101	Chlorfenvinphos	470-90-6	Yes	--
084901	O-(2-Chloro-1-(2,5-dichlorophenyl)vinyl) O,O-diethyl phosphorothioate	1757-18-2	Yes	--
086801	PCMX [4-Chloro-3,5-xylenol]	88-04-0	No	No
097003	Piperalin [3-(2-Methylpiperidino)propyl 3,4-dichlorobenzoate]	3478-94-2	No	No

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Table 8-22. 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
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	Diflubenzuron [N-(((4-chlorophenyl)amino)carbonyl)-2,6-difluorobenzamide]	35367-38-5	No	Yes
109001	Oxadiazon [2-tert-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)- delta 2 -1,3,4- oxadiazoline-5-one]	19666-30-9	No	Yes
109301	Fenvalerate	51630-58-1	No	In review
109302	Fluvalinate [N-2-Chloro-4-trifluoromethyl)phenyl-DL-valine (+-)-cyano(3-phenoxy- phenyl)methyl ester]	69409-94-5	No	No
109801	Iprodione [3-(3,5-Dichlorophenyl)-N-(1-methylethyl)-2,4-dioxo-1-imidazolidinecarboxamide (9CA)]	36734-19-7	No	No
109901	Triadimefon [1-(4-Chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone]	43121-43-3	No	No
110902	Diclofop - methyl [methyl 2-(4-(2,4-dichlorophenoxy)phenoxy)propanoate]	51338-27-3	No	Yes
111401	Profenofos [O-(4-Bromo-2-chlorophenyl)-O-ethyl S-propyl phosphorothioate]	41198-08-7	No	In review
111601	Oxyfluorfen [2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene]	42874-03-3	No	In review
111901	Imazalil [1-(2-(2,4-Dichlorophenyl)-2-(2-propenyloxy)ethyl)-1H-imidazole]	35554-44-0	No	No
112802	Bromothalin [N-Methyl-2,4-dinitro-n-(2,4,6-tribromophenyl)-6-(trifuloromethyl)benzenamine]	63333-35-7	No	No
113201	Vinclozolin [3-(3,5-Dichlorophenyl)-5-ethenyl-5-methyl-2,4-oxazolidinedione (9CA)]	50471-44-8	No	No
119001	Fenridazon [Potassium 1-(p-chlorophenyl)-1,4-dihydro-6-methyl-4-oxo- pyridazine- 3-carboxylate]	83588-43-6	No	In review
123901	Tridiphane [2-(3,5-Dichlorophenyl)-2-(2,2,2-trichloroethyl) oxirane]	58138-08-2	No	No
125601	Paclobutrazol	76738-62-0	No	No
128838	Linalool	78-70-6	No	In review
206600	Fenarimol [a-(2-chlorophenyl)-a-(4-chlorophenyl)-5-pyrimidinemethanol]	60168-88-9	No	No

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Table 8-23. Status of Second Pesticide Data-Call-In: Pesticides Suspected of Being Contaminated with Dioxins

Shaughnessy Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
029801	Dicamba [3,6-dichloro-o-anisic acid]	1918-00-9	No	Yes
029802	Dicamba dimethylamine [3,6-dichloro-o-anisic acid]	2300-66-5	No	Yes
029803	Diethanolamine dicamba [3,6-dichloro-2-anisic acid]	25059-78-3	Yes	--
030001	2,4-Dichlorophenoxyacetic acid	94-75-7	No	Yes
030002	Lithium 2,4-dichlorophenoxyacetate	3766-27-6	No	No
030003	Potassium 2,4-dichlorophenoxyacetate	14214-89-2	Yes	--
030004	Sodium 2,4-dichlorophenoxyacetate	2702-72-9	No	No
030005	Ammonium 2,4-dichlorophenoxyacetate	2307-55-3	Yes	--
030010	Alkanol* amine 2,4-dichlorophenoxyacetate *(salts of the ethanol and ispropanol series)	not available	Yes	--
030011	Alkyl* amine 2,4-dichlorophenoxyacetate *(100% C12)	2212-54-6	Yes	--
030013	Alkyl* amine 2,4-dichlorophenoxyacetate *(100% C14)	28685-18-9	Yes	--
030014	Alkyl* amine 2,4-dichlorophenoxyacetate *(as in fatty acids of tall oil)	not available	Yes	--
030016	Diethanolamine 2,4-dichlorophenoxyacetate	5742-19-8	No	No
030017	Diethylamine 2,4-dichlorophenoxyacetate	20940-37-8	Yes	--
030019	Dimethylamine 2,4-dichlorophenoxyacetate	2008-39-1	No	No
030020	N,N-Dimethyloleylamine 2,4-dichlorophenoxyacetate	53535-36-7	Yes	--
030021	Ethanolamine 2,4-dichlorophenoxyacetate	3599-58-4	Yes	--
030023	Heptylamine 2,4-dichlorophenoxyacetate	37102-63-9	Yes	--
030024	Isopropanolamine 2,4-dichlorophenoxyacetate	6365-72-6	Yes	--
030025	Isopropylamine 2,4-dichlorophenoxyacetate	5742-17-6	No	No
030028	Morpholine 2,4-dichlorophenoxyacetate	6365-73-7	Yes	--
030029	N-Oleyl-1,3-propylenediamine 2,4-dichlorophenoxyacetate	2212-59-1	Yes	--
030030	Octylamine 2,4-dichlorophenoxyacetate	2212-53-5	Yes	--
030033	Triethanolamine 2,4-dichlorophenoxyacetate	2569-01-9	Yes	--
030034	Triethylamine 2,4-dichlorophenoxyacetate	2646-78-8	No	No

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Table 8-23. Status of Second Pesticide Data-Call-In: Pesticides Suspected of Being Contaminated with Dioxins (continued)

Shaughnessy Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
030035	Triisopropanolamine 2,4-dichlorophenoxyacetate	32341-80-3	No	No
030039	N,N-Dimethyl oleyl-linoleyl amine 2,4-dichlorophenoxyacetate	55256-32-1	Yes	--
030052	Butoxyethoxypropyl 2,4-dichlorophenoxyacetate	1928-57-0	Yes	--
030053	Butoxyethyl 2,4-dichlorophenoxyacetate	1929-73-3	No	No
030055	Butoxypropyl 2,4-dichlorophenoxyacetate	1928-45-6	Yes	--
030056	Butyl 2,4-dichlorophenoxyacetate	94-80-4	Yes	--
030062	Isobutyl 2,4-dichlorophenoxyacetate	1713-15-1	Yes	--
030063	Isooctyl(2-ethylhexyl) 2,4-dichlorophenoxyacetate	1928-43-4	No	Yes
030064	Isooctyl(2-ethyl-4-methylpentyl) 2,4-dichlorophenoxyacetate	25168-26-7	Yes	--
030065	Isooctyl(2-octyl) 2,4-dichlorophenoxyacetate	1917-97-1	Yes	--
030066	Isopropyl 2,4-dichlorophenoxyacetate	94-11-1	No	No
030072	Propylene glycol butyl ether 2,4-dichlorophenoxyacetate	1320-18-9	Yes	--
030801	4-(2,4-Dichlorophenoxy)butyric acid	94-82-6	No	Yes
030804	Sodium 4-(2,4-dichlorophenoxy)butyrate	10433-59-7	No	No
030819	Dimethylamine 4-(2,4-dichlorophenoxy)butyrate	2758-42-1	No	No
030853	Butoxyethanol 4-(2,4-dichlorophenoxy)butyrate	32357-46-3	Yes	--
030856	Butyl 4-(2,4-dichlorophenoxy)butyrate	6753-24-8	Yes	--
030863	Isooctyl 4-(2,4-dichlorophenoxy)butyrate	1320-15-6	Yes	--
031401	2-(2,4-Dichlorophenoxy)propionic acid	120-36-5	No	Yes
031419	Dimethylamine 2-(2,4-dichlorophenoxy)propionate	53404-32-3	No	No
031453	Butoxyethyl 2-(2,4-dichlorophenoxy)propionate	53404-31-2	No	No
031463	Isooctyl 2-(2,4-dichlorophenoxy)propionate	28631-35-8	No	No
031501	MCPP acid [2-(2-Methyl-4-chlorophenoxy)propionic acid]	7085-19-0	No	Yes

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Table 8-23. Status of Second Pesticide Data-Call-In: Pesticides Suspected of Being Contaminated with Dioxins (continued)

Shaughnessy Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
031519	MCPP, DMA [Dimethylamine 2-(2-methyl-4-chlorophenoxy)propionate]	32351-70-5	No	No
035301	Bromoxynil [3,5-dibromo-4-hydroxybenzonitrile]	1689-84-5	No	Yes
044901	Hexachlorophene [2,2'-Methylenebis(3,4,6-trichlorophenol)]	70-30-4	Yes	--
044902	Hexachlorophene, Na salt [Monosodium 2,2'-methylenebis(3,4,6-trichlorophenate)]	5736-15-2	Yes	--
044904	Hexachlorophene, K salt [Potassium 2,2'-methylenebis(3,4,6-trichlorophenate)]	67923-62-0	Yes	--
054901	Irgasan [5-Chloro-2-(2,4-dichlorophenoxy)phenol]	3380-34-5	No	Yes
063004	Tetrachlorophenols	25167-83-3	Yes	--
063005	Tetrachlorophenols, sodium salt	25567-55-9	Yes	--
063006	Tetrachlorophenols, alkyl* amine salt*(as in fatty acids of coconut oil)	not available	Yes	--
063007	Tetrachlorophenols, potassium salt	53535-27-6	Yes	--
064203	Bithionolate sodium [Disodium 2,2'-thiobis(4,6-dichlorophenate)]	6385-58-6	Yes	--
064212	Phenachlor [2,4,6-Trichlorophenol]	88-06-2	Yes	--
064219	Potassium 2,4,6-trichlorophenate	2591-21-1	Yes	--
064220	2,4,6-Trichlorophenol, sodium salt	3784-03-0	Yes	--
064501	Phenothiazine	92-84-2	Yes	--
078701	Dacthal-DCPA [Dimethyl tetrachloroterephthalate]	1861-32-1	No	Yes
079401	Endosulfan [hexachlorohexahydromethano-2,4,3-benzodioxathiepin-3-oxide]	115-29-7	No	No
082501	Silvex [2-(2,4,5-trichlorophenoxy)propionic acid]	93-72-1	Yes	--
083701	Tetrachlorvinphos [2-Chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate]	961-11-5	No	Yes
104101	Edolan [Sodium 1,4',5'-trichloro-2'-(2,4,5-trichlorophenoxy) methanesulfonanilide]	69462-14-2	Yes	--

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Table 8-24. Summary of Results for CDDs and CDFs in Technical 2,4-D and 2,4-D Ester Herbicides

Congener	EPA LOQ[a] (μg/kg)	Total Number of Technicals	Number of Technicals Greater Than LOQ	Observed Maximum Concentration (μg/kg)	Average Concentration[b] (μg/kg)
2,3,7,8-TCDD	0.1	8	2	0.13	0.06
1,2,3,7,8-PeCDD	0.5	8	3	2.6	0.78
1,2,3,4,7,8-HxCDD	2.5	8	0	0.81	0.31
1,2,3,6,7,8-HxCDD	2.5	8	0	0.77	0.39
1,2,3,7,8,9-HxCDD	2.5	8	0	0.68	0.24
1,2,3,4,6,7,8-HpCDD	100	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	1000	8	0	8.3	2.17
1,2,3,4,7,8,9-HpCDF	1000	8	0	1.2	0.18
OCDF	--	--	--	--	--
				TOTAL[c]	5.60 (0.70 TEQ)

Source: U.S. EPA Office of Pesticide Program file

a Limit of quantitation required by EPA in the Data Call-In.

b Average of the mean results for multiple analyses of four technical 2,4-D and/or 2,4-D ester products for which detectable CDD/CDF congener concentrations less than the LOQs were quantified; not detected values were assumed to be zero.

c Total equals the sum of the individual congener averages.

μg/kg = micrograms per kilogram.

"--" indicates analyses not performed.

Table 8-25. Summary of Analytical Data Submitted to EPA in Response to Pesticide Data Call-Ins

Shaughnessey Code	Pesticide		Number of Positive Submissions[a] To-Date
	Common Name	Chemical Name	
019201	MCPB, 4-butyric acid	4-(2-methyl-4-chlorophenoxy)butyric acid	0
019401	4-CPA	4-Chlorophenoxyacetic acid	0
027401	Dichlobenil	2,6-Dichlorobenzonitrile	0
029801	Dicamba	3,6-Dichloro-o-anisic acid	0
029802	Dicamba, dimethylamine	3,6-Dichloro-o-anisic acid, dimethylamine salt	0
030001	2,4-D	2,4-Dichlorophenoxy acetic acid	2
030063	2,4-D, 2EH	Isooctyl(2-ethylhexyl)2,4-dichlorophenoxyacetate	1
030801	2,4-DB	4-(2,4-Dichlorophenoxy)butyric acid	0
031301	DCNA	2,6-Dichloro-4-nitroaniline	Pending
031401	2,4-DP	2-(2,4-Dichlorophenoxy)propionic acid	0
031501	Mecoprop (MCPP)	2-(2-methyl-4-chlorophenoxy)propionic acid	0
035301	Bromoxynil	3,5-Dibromo-4-hydroxybenzonitrile	0
054901	Irgasan	5-Chloro-2-(2,4-dichlorophenoxy)phenol	0
078701	Dacthal (DCPA)	Dimethyl tetrachloroterephthalate	Pending
081901	Chlorothalonil	Tetrachloroisophthalonitrile	Pending
083701	Tetrachlorvinphos	2-Chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate	0
108201	Diflubenzuron	N-(((4-chlorophenyl)amino)carbonyl)-2,6-difluorobenzamide	0
109001	Oxadiazon	2-Tert-butyl-4(2,4-dichloro-5-isopropoxyphenyl)-delta2-1,3,4-oxadiazoline-5-one	Pending
110902	Dichlofop-methyl	Methyl-2-(4-(2,4-dichlorophenoxy)phenoxy) propanoate	0

Source: U.S. EPA (1995a); personal communication with S. Funk (EPA/OPP/HED) on March 27, 1996.

[a] "Positive" is defined as the detection of any congener at a concentration greater than or exceeding the LOQs listed in Table 8-24

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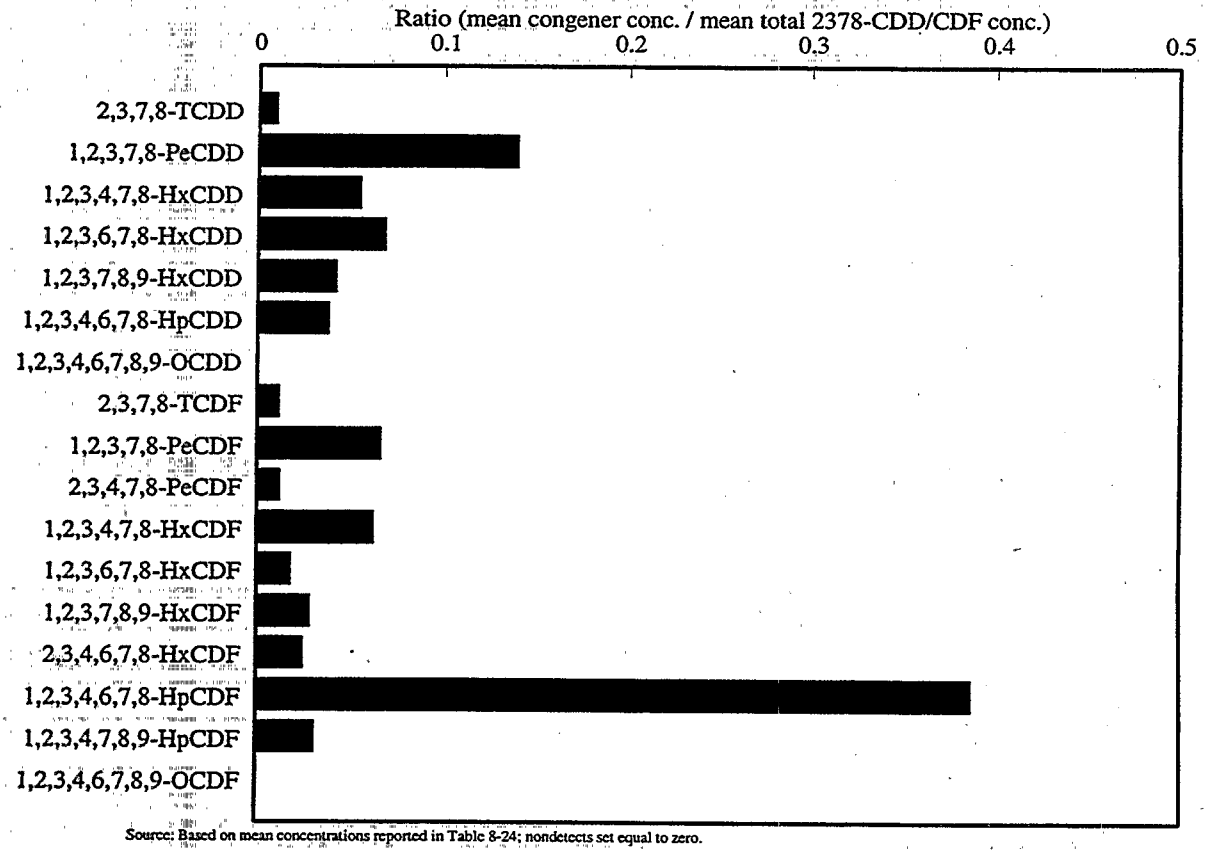

Source: Based on mean concentrations reported in Table 8-24; nondetects set equal to zero.

Figure 8-5. Congener Profile for 2,4-D (salts and esters)

Table 8-26. CDD/CDF Concentrations in Samples of 2,4-D and Pesticide Formulations Containing 2,4-D

Congener/Congener Group	Acbar Super (Gaza City*) (μg/kg)	Amco Super (Gaza City*) (μg/kg)	(Bethlehem)* (μg/kg)	Chimprom (Russia) (μg/kg)	Dragon Lawn Weed Killer (μg/kg)	KGRO (U.S.) (μg/kg)	Pro Care Premium (U.S.) (μg/kg)	Ortho Weed-B-Gone (U.S.) (μg/kg)	Sigma Co. (U.S.) (μg/kg)	American Brand Chemical Co. (U.S.) (μg/kg)
2,3,7,8-TCDD	ND (0.1)	ND (0.1)	ND (0.1)	ND (0.02)	ND (0.001)	--	--	--	--	--
1,2,3,7,8-PeCDD	0.1	ND (0.1)	1.2	0.03	0.0014	--	--	--	--	--
1,2,3,4,7,8-HxCDD	ND (0.1)	ND (0.1)	ND (0.1)	0.02	ND (0.001)	--	--	--	--	--
1,2,3,6,7,8-HxCDD	ND (0.1)	0.2	0.6	0.05	0.0024	--	--	--	--	--
1,2,3,7,8,9-HxCDD	ND (0.1)	ND (0.1)	0.4	ND (0.02)	0.0010	--	--	--	--	--
1,2,3,4,6,7,8-HpCDD	0.1	1.2	0.3	0.23	0.0017	--	--	--	--	--
OCDD	0.1	2.6	0.1	0.85	0.0063	--	--	--	--	--
2,3,7,8-TCDF	0.3	ND (0.1)	ND (0.1)	ND (0.1)	0.0036	--	--	--	--	--
1,2,3,7,8-/1,2,3,4,8-PeCDF	ND (0.1)	0.2	0.7	1.2	0.0010	--	--	--	--	--
2,3,4,7,8-PeCDF	ND (0.1)	ND (0.1)	0.1	0.06	0.0011	--	--	--	--	--
1,2,3,4,7,8-/1,2,3,4,7,9-HxCDF	ND (0.1)	0.1	0.4	0.08	0.0013	--	--	--	--	--
1,2,3,6,7,8-HxCDF	ND (0.1)	ND (0.1)	0.1	0.11	ND (0.001)	--	--	--	--	--
1,2,3,7,8,9-HxCDF	ND (0.1)	ND (0.1)	ND (0.1)	ND (0.02)	ND (0.001)	--	--	--	--	--
2,3,4,6,7,8-HxCDF	ND (0.1)	ND (0.1)	0.1	0.05	0.0011	--	--	--	--	--
1,2,3,4,6,7,8-HpCDF	0.1	0.8	0.1	0.24	0.0016	--	--	--	--	--
1,2,3,4,7,8,9-HpCDF	ND (0.1)	ND (0.1)	ND (0.1)	0.02	ND (0.001)	--	--	--	--	--
OCDF	0.2	3.8	0.4	0.46	0.0039	--	--	--	--	--
Total 2,3,7,8-CDD (ND = 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 (ND = 0)	0.6	4.9	1.9	2.22	0.0136	0.1628	0.4253	0.1095	3.0507	0.0822
Total TEQ (ND = 0)	0.082	0.066	0.850	0.142	0.0023	0.0009	0.0012	0.0014	0.0013	0.0019
Total TEQ (ND = 1/2 det. limit)	0.195	0.197	0.915	0.159	0.0029	0.0016	0.0018	0.0029	0.0040	0.0046
Total TCDD	--	--	--	--	--	--	--	--	--	--
Total PeCDD	--	--	--	--	--	--	--	--	--	--
Total HxCDD	--	--	--	--	--	--	--	--	--	--
Total HpCDD	--	--	--	--	--	--	--	--	--	--
Total OCDD	--	--	--	--	--	--	--	--	--	--
Total TCDF	--	--	--	--	--	--	--	--	--	--
Total PeCDF	--	--	--	--	--	--	--	--	--	--
Total HxCDF	--	--	--	--	--	--	--	--	--	--
Total HpCDF	--	--	--	--	--	--	--	--	--	--
Total OCDF	--	--	--	--	--	--	--	--	--	--
Total CDD/CDF	--	--	--	--	--	--	--	--	--	--

* 2,4-D manufactured in Europe and packaged in Palestine.
-- = Not reported.
μg/kg = micrograms per kilogram.

Source: Schecter et al. (1997)

Table 8-27. Mean CDD/CDF Measurements in Effluents from Nine U.S. POTWs

Congener/Congener Group	No. Detections/ No. Samples	Range of Detection Limits	Range of Detected Concentrations (POTW mean basis)		Overall Means*	
			Minimum Detected Conc. (pg/L)	Maximum Detected Conc. (pg/L)	Mean Conc. (ND = 0) (pg/L)	Mean Conc. (ND = 1/2DL) (pg/L)
2,3,7,8-TCDD	0/30	0.31 - 8.8	nd	nd	0.00	0.98
1,2,3,7,8-PeCDD	0/30	0.45 - 15	nd	nd	0.00	1.32
1,2,3,4,7,8-HxCDD	0/30	0.43 - 9.8	nd	nd	0.00	1.38
1,2,3,6,7,8-HxCDD	0/30	0.81 - 10	nd	nd	0.00	1.42
1,2,3,7,8,9-HxCDD	0/30	0.42 - 9.7	nd	nd	0.00	1.31
1,2,3,4,6,7,8-HpCDD	3/30	0.75 - 18	nd	5.0	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	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	0.22	1.72
2,3,4,6,7,8-HxCDF	1/30	0.25 - 7.9	nd	nd	0.00	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	0.00	1.18
OCDF	1/30	0.86 - 28	nd	3.2	0.36	3.40
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 TEQ			nd	2.32	0.29	3.66
Total TCDD	4/27	1.2 - 8.8	nd	9.7	1.23	2.61
Total PeCDD	0/27	0.62 - 200	nd	nd	0.00	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	25.0	6.61	7.70
Total PeCDF	1/30	0.64 - 25	nd	20.0	2.22	4.72
Total HxCDF	1/30	0.93 - 17	nd	13.0	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	3.40
Total CDD/CDF			nd	99.75	42.00	71.96

nd = not detected.
* = The "overall means" are the means of the individual POTW mean concentrations.
pg/L = picograms per liter.

Source: California Regional Water Quality Control Board (1996).

Table 8-28. CDD/CDF Concentrations Measured in EPA's National Sewage Sludge Survey

Congener	Percent Detected	Maximum Concentration (ng/kg)	Median Concentration (ng/kg)		Mean Concentration (ng/kg)	
			Nondetects Set to Det. Limit	Nondetects Set to Zero	Nondetects Set to Det. Limit	Nondetects Set to Zero
2,3,7,8-TCDD	16	116	6.86	0	NR	NR
1,2,3,7,8-PeCDD	18	736	9.84	0	NR	NR
1,2,3,4,7,8-HxCDD	25	737	22.5	0	NR	NR
1,2,3,6,7,8-HxCDD	49	737	27.3	0	NR	NR
1,2,3,7,8,9-HxCDD	39	737	28.0	0	NR	NR
1,2,3,4,6,7,8-HpCDD	98	52,500	335	335	NR	NR
OCDD	100	905,000	3,320	3,320	NR	NR
2,3,7,8-TCDF	65	337	17.0	3.90	NR	NR
1,2,3,7,8-PeCDF	22	736	9.60	0	NR	NR
2,3,4,7,8-PeCDF	26	736	10.4	0	NR	NR
1,2,3,4,7,8-HxCDF	43	1,500	28.0	0	NR	NR
1,2,3,6,7,8-HxCDF	35	737	18.0	0	NR	NR
1,2,3,7,8,9-HxCDF	16	1,260	18.0	0	NR	NR
2,3,4,6,7,8-HxCDF	27	737	18.0	0	NR	NR
1,2,3,4,6,7,8-HpCDF	71	7,100	57.0	36.0	NR	NR
1,2,3,4,7,8,9-HpCDF	26	842	23.0	0	NR	NR
OCDF	80	69,500	110	80.0	NR	NR
Total TEQ		1,820	50.4	11.2	86*	50*
Total 2,3,7,8-CDD/CDF		NR	NR	NR	NR	NR

Source: U.S. EPA (1996a); for POTWs with multiple samples, the pollutant concentrations were averaged before the summary statistics presented in the table were calculated. All concentrations are in units of ng/kg dry weight.

NR = Not reported.
* = Values presented by Rubin and White (1992) for 175 rather than 174 POTWs.
ng/kg = nanograms per kilogram.

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Table 8-29. CDD/CDF Concentrations Measured in 99 Sludges Collected from 75 U.S. POTWs During 1994

Congener	Percent Detected	Maximum Concentration Detected (ng/kg)	Median Concentration (ng/kg)		Mean Concentration (ng/kg)	
			Nondetects Set to Det. Limit	Nondetects Set to Zero	Nondetects Set to Det. Limit[1]	Nondetects Set to Zero[1]
2,3,7,8-TCDD	40	12.3	1.95	0	2.72 (2.40)	1.71 (2.86)
1,2,3,7,8-PeCDD	23	37.5	8.23	0	10.9 (7.80)	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)	17.0 (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	9.70	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)	14.0 (25.9)
1,2,3,6,7,8-HxCDF	17	200	14.0	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 (41.0)
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)	15.0 (33.4)
OCDF	93	11,200	286	281	786 (1,503)	775 (1,506)
Total TEQ (facility basis)[2]		246	49.1	30.0	64.6 (50.6)	47.7 (45.0)
Total 2,3,7,8-CDD/CDF		73,520	7,916	7,881	14,110 (14,390)	13,880 (14,200)

Source: Green et al. (1995); Cramer et al. (1995).

[1] Values in parentheses are standard deviations.

[2] For POTWs with multiple samples, the sample TEQ concentrations were averaged by Green et al. (1995) to POTW averages before calculation of the total TEQ mean and median values presented in the table.

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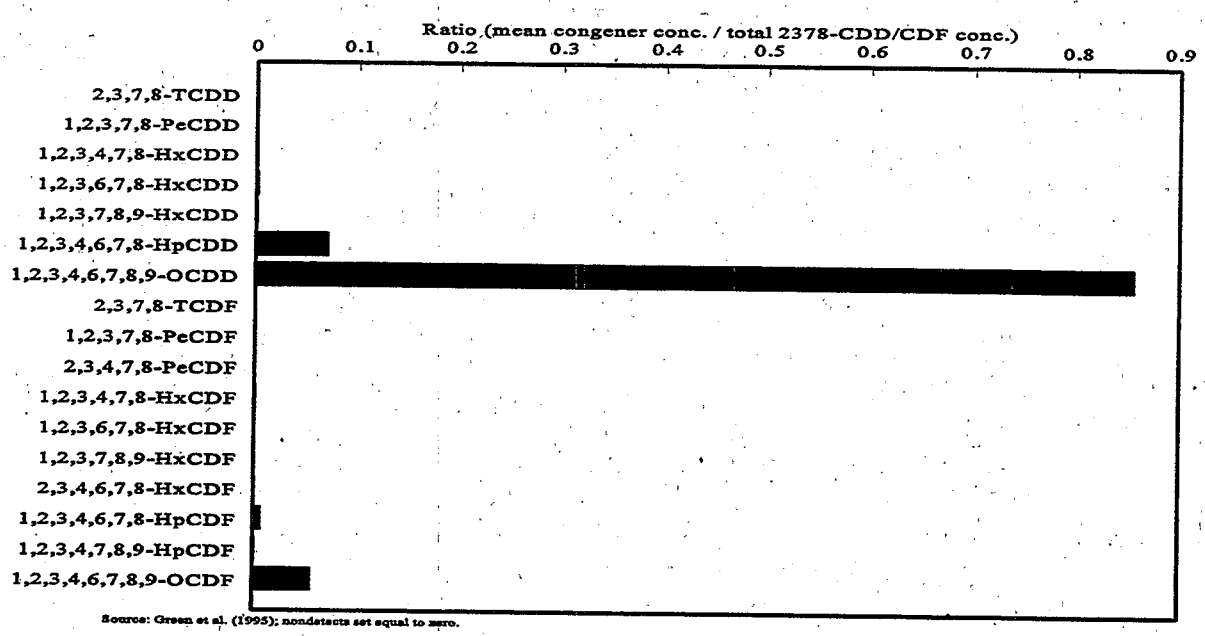
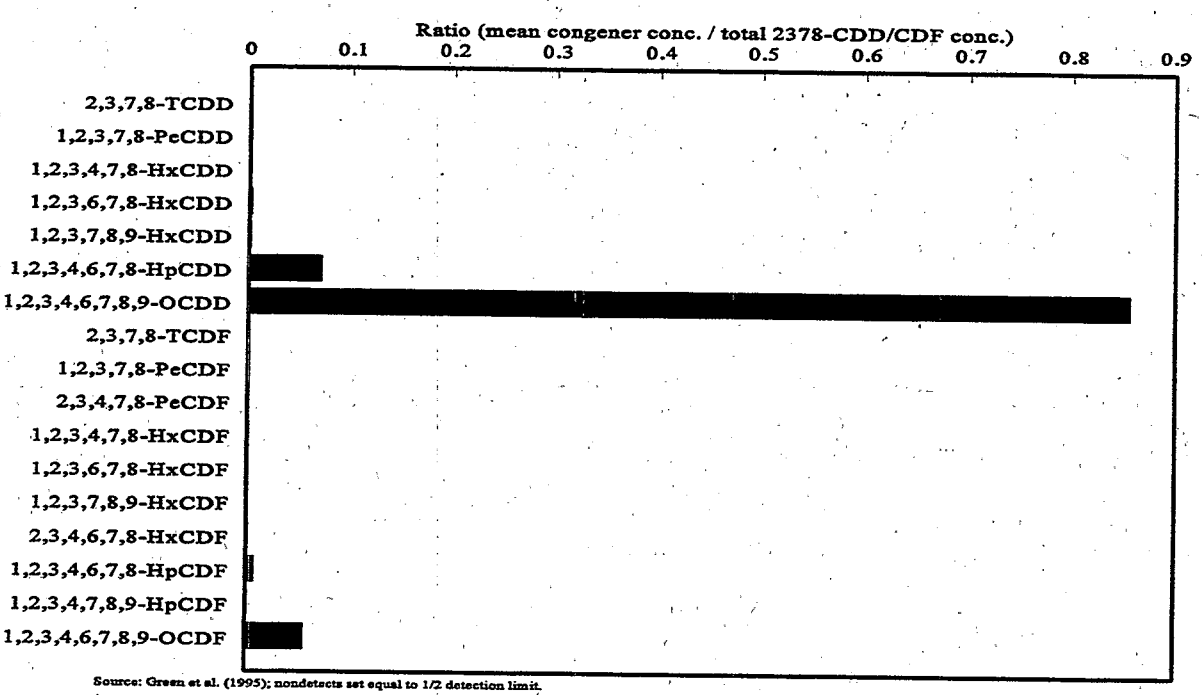


Source: Green et al. (1995); nondetects set equal to zero.



Source: Green et al. (1995); nondetects set equal to 1/2 detection limit.

Figure 8-6. Congener Profiles for Sewage Sludge

Table 8-30. Quantity of Sewage Sludge Disposed Annually by Primary, Secondary, or Advanced Treatment POTWs and Potential Dioxin TEQ Releases

Use/Disposal Practice	Volume Disposed (thousands of dry metric tons/year)	Percent of Total Volume	Potential Dioxin Release[c] (g of TEQ/yr)
Land Application	1,714	32.0[e]	85.7
Distribution and Marketing	71	1.3	3.6
Surface Disposal Site/Other	396	7.4	19.8
Sewage Sludge Landfill	157	2.9	7.8
Co-Disposal Landfills[a]	1,819	33.9	91.0
Sludge Incinerators and Co-Incinerators[b]	865	16.1	(f)
Ocean Disposal	(336)[d]	(6.3)[d]	(0)[d]
TOTAL	5,357	100.0	207.9

a Landfills used for disposal of sewage sludge and solid waste residuals.

b Co-incinerators treat sewage sludge in combination with other combustible waste materials.

c Potential dioxin TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (i.e., column 2) by the average of the median dioxin TEQ concentrations in sludge reported by Rubin and White (1992) (i.e., 50.4-ng/kg dry weight) and Green et al. (1995) and Cramer et al. (1995) (i.e., 49.1-ng TEQ/kg).

d 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 in the oceans in 1988 has not been determined.

e Includes 21.9 percent applied to agricultural land, 2.8 percent applied as compost, 0.6 percent applied to forestry land, 3.1 percent applied to "public contact" land, 1.2 percent applied to reclamation sites, and 2.4 percent applied in undefined settings.

f See Section 3.6.5 for estimates of CDD/CDF releases to air from sewage sludge incinerators.

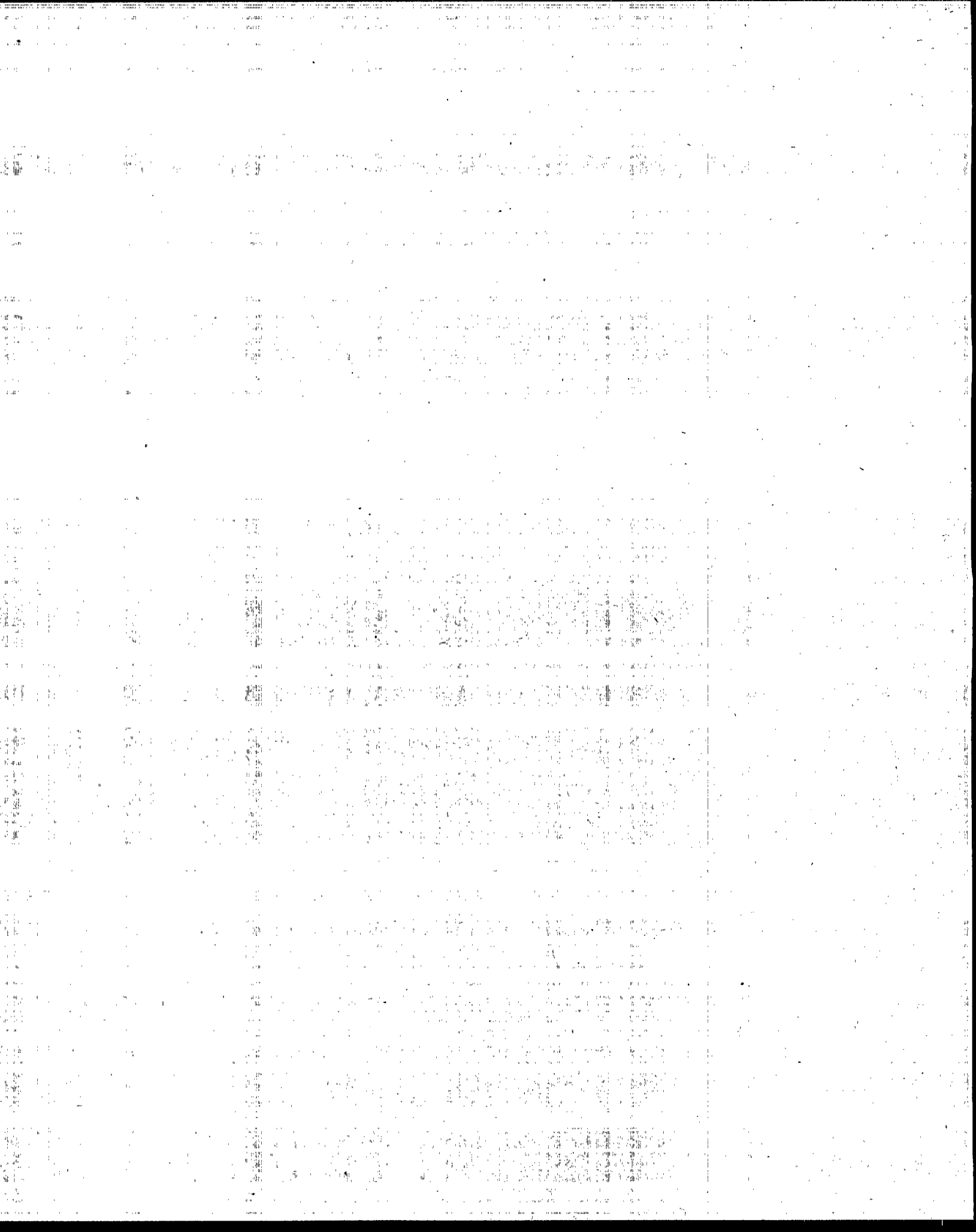
Sources: Federal Register (1990); Federal Register (1993b); Rubin and White (1992); Green et al. (1995); Cramer et al. (1995).

Table 8-31. CDD/CDF Concentrations in Swedish Liquid Soap, Tall Oil, and Tall Resin

Congener/Congener Group	Liquid Soap (ng/L)	Tall Oil (ng/kg)	Tall Resin (ng/kg)
2,3,7,8-TCDD	ND (0.009)	3.6	ND (1)
1,2,3,7,8-PeCDD	0.400	5.3	3.1
1,2,3,4,7,8-HxCDD	ND (0.020)	ND (2)	ND (4)
1,2,3,6,7,8-HxCDD	0.320	ND (2)	810
1,2,3,7,8,9-HxCDD	0.180	ND (2)	500
1,2,3,4,6,7,8-HpCDD	1.900	ND (1)	5,900
OCDD	1.000	5.3	6,000
2,3,7,8-TCDF	0.620	17	ND (2)
1,2,3,4,8-/1,2,3,7,8-PeCDF	0.290	4.2	ND (0.4)
2,3,4,7,8-PeCDF	0.200	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 (0.010)	ND (2)	9.0
OCDF	NA	NA	NA
Total 2,3,7,8-CDD	3.8	14.2	13213.1
Total 2,3,7,8-CDF	1.123	25.2	43
Total TEQ	0.447	9.5	200
Total TCDD	0.120	31	ND (1)
Total PeCDD	15.000	380	25
Total HxCDD	3.400	3.3	6,800
Total HpCDD	3.600	ND (1)	11,000
Total OCDD	1.000	5.3	6,000
Total TCDF	1.000	26	ND (2)
Total PeCDF	1.300	41	ND (0.5)
Total HxCDF	0.150	4.9	56
Total HpCDF	ND (0.010)	ND (2)	19
Total OCDF	NA	NA	NA
Total CDD/CDF	25.57	491.5	23,900

Source: Rappe et al. (1990c).

ND = Nondetected; value in parenthesis is the detection limit.
NA = Not analyzed.
-- = Not reported.
ng/kg = nanograms per kilogram.



9. BIOLOGICAL SOURCES OF CDD/CDF

Recent laboratory and field research studies demonstrate that biochemical formation of CDD/CDFs from chlorophenol precursors is possible and that, under certain conditions, some CDD/CDFs can be biodegraded to form less chlorinated congeners. Both of these formation routes are discussed in this chapter.

Also, CDD/CDFs were recently discovered in ball clay deposits. The origin of these CDD/CDFs is not yet determined, and natural occurrence is still considered a possibility.

9.1. BIOTRANSFORMATION OF CHLOROPHENOLS

Several researchers demonstrated under laboratory conditions that biochemical formation of CDD/CDFs from chlorophenol precursors is possible. These studies are described below. However, the extent to which CDD/CDFs are formed in the environment via this mechanism cannot be estimated at this time.

In 1991, Lahl et al. (1991) reported finding CDD/CDFs in all 22 samples of various types of composts analyzed. The hepta- and octa-substituted CDDs and CDFs were typically the dominant congener groups found. The TEQ content of the composts ranged from 0.8- to 35.7-ng TEQ/kg. Similarly, CDD/CDFs are frequently detected in sewage sludges. (See Section 8.4.1.) The CDD/CDFs found in compost may primarily be the result of atmospheric deposition onto plants which are subsequently composted and also by uptake of CDD/CDFs from air by the active compost (Krauss et al., 1994). The CDD/CDFs found in sewage sludge may primarily be due to the sources identified in Section 8.4.1. However, laboratory studies with solutions of trichlorophenols and pentachlorophenol (PCP) in the presence of peroxidase enzymes and hydrogen peroxide (Svenson et al., 1989; Oberg et al., 1990; Wagner et al., 1990; Oberg and Rappe, 1992; Morimoto and Kenji, 1995) and with sewage sludge spiked with PCP (Oberg et al., 1992) indicate that biochemical formation of CDD/CDFs, particularly the higher chlorinated congeners, from chlorophenol precursors is possible.

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 actual conversion efficiency of chlorinated phenols to CDD/CDFs observed in these studies was low, however. In the solution studies, Oberg and Rappe (1992) reported

a conversion efficiency of PCP to OCDD of about 0.01 percent; Morimoto and Kenji (1995) reported a conversion efficiency of PCP to OCDD of 0.8 percent; and Wagner et al. (1990) reported a conversion efficiency of trichlorophenol to HpCDD of about 0.001 percent. Oberg et al. (1990) reported a conversion efficiency of trichlorophenols to CDD/CDFs of about 0.001 percent. In the sewage sludge study (Oberg et al. 1992), a conversion efficiency of PCP to total CDDs of 0.0002 to 0.0004 percent was reported.

Several researchers recently conducted both laboratory and field studies in an attempt to better understand the extent and factors affecting the fate and/or formation of CDD/CDFs in composts and sewage sludges. The findings of several of these studies are discussed in the following paragraphs. The findings are not always consistent in terms of the congener profiles/patterns detected and the extent, if any, of CDD/CDF "formation," which may be due in part to variations in the compost materials studied, 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 TEQ/kg (mean of 31-ng TEQ/kg). The concentrations in the five active compost samples (1 to 30 days in age) ranged from 7.7- to 54-ng TEQ/kg (mean of 21-ng TEQ/kg). The observation that CDD/CDF concentrations measured in two soil samples from the immediate vicinity of the composting (1.0- and 1.3-ng TEQ/kg) facility were significantly lower than the levels found in the composts, suggested to the authors that the source(s) of CDD/CDFs in the composts was different than the source(s) affecting local soils. A strong similarity between the congener profiles observed in the composts with 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) indicated to the authors that leaching of CDD/CDFs from PCP-treated wood in the compost piles was the likely source of the observed CDD/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 TEQ/kg; mean of 30-ng TEQ/kg), two municipal solid waste composting facilities (19- to 96-ng TEQ/kg;

mean of 48-ng TEQ/kg), and one municipal facility composting solid waste and dewatered sewage sludge (37- to 87-ng TEQ/kg; mean of 56-ng TEQ/kg). All facilities were located in the United States. Two general trends were observed. First, an increase was observed in analyte levels, with an increasing degree of chlorination for each compound type (i.e., CDDs, CDFs, chlorophenols, and chlorobenzenes). Second, an increase in concentration of each congener or homologue group, with a progression from yard waste to solid waste to solid waste/sewage sludge composts, was observed. As noted above, 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 the exclusive contributor of the observed CDD/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. The two PCP-spiked composts were monitored for periods of 55 days and 286 days, respectively. 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 a period of 49 days. Oberg et al. (1993) state that for a "typical" composting event, a two- to threefold increase in TEQ content corresponds to an elevation by 0.2- to 0.5-ng TEQ/kg dry weight.

Weber (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 tetra-chlorobenzenes (4 to 40 mg/kg). In nearly all of the digestion experiments, the addition of these precursors did not lead to any significant changes in CDD/CDF concentrations. The initial CDD/CDF concentrations in the two sludges were 9- and 20-ng TEQ/kg. 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).

9.2. BIOTRANSFORMATION OF HIGHER CDD/CDFS

Several recent studies examining 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) CDD/CDFs. However, the extent to which more toxic CDD/CDFs are formed in the environment via this mechanism cannot be estimated at this time. The following paragraphs discuss those studies that examined the products of biodegradation in sediments, compost, and sewage sludge.

Several recent 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 utilizing 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, attributed to biologically mediated reductive dechlorination, with net disappearance rates ranging from 0.0031 wk^{-1} to 0.0175 wk^{-1} (i.e., half-lives of approximately 1 to 4 years). However, Adriaens et al. (1995) conclude that the actual half-lives may be orders of magnitude higher. The experiment with 1,2,3,4,6,7,8-HpCDD yielded formation of two HxCDD (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 lesser chlorinated congeners were identified from incubations with the other tested congeners. 1,2,4,6,8-PeCDF was also examined in

dichlorophenol-enriched cultures. After 6 months 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 ± 4 μg/L) decreased by 30 percent to 14 ± 2 μg/L over a period of 7 months with the consecutive appearance and disappearance of tri-, di-, and mono-CDDs. Experiments were also conducted by spiking the sediment with HxCDDs, HpCDDs, and OCDD. Up to 10 percent of the spiked OCDD were converted to hepta-, hexa-, penta-, tetra-, tri-, di-, and monochlorinated 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 reported that CDD/CDFs can be formed during composting operations through biological action on chlorophenols present in the compost feed material. The results of studies that specify likely involvement of chlorophenols are described in Section 9.1. Another possible formation mechanism was suggested by Vickelsoe et al. (1994), who reported that higher chlorinated CDD/CDF congeners are formed when humic acid is reacted with a peroxidase enzyme, hydrogen peroxide, and sodium chloride. It is expected that some organic material in compost and sewage sludge has a humic-like structure. Several additional studies are described below in which the potential involvement of chlorophenols could not be assessed, because chlorophenol concentrations in the composts were not reported.

Schäfer et al. (1993) monitored the seasonal changes in the CDD/CDF content, as well as the extent of CDD/CDF formation, in the composts from a vegetable and garden waste compost operation in Germany. Finished compost samples were collected and analyzed every 2 months for 1 year. An annual cycle was observed in TEQ concentrations, with peak concentrations in the summer (approximately 8.5-ng TEQ/kg) that were 2.5 times higher than the lowest concentrations observed in the winter (approximately 3.5-ng

TEQ/kg). No seasonal source was apparent that could explain the observed differences in seasonal levels. The CDD/CDF contents of the starting waste materials for two compost cycles (March and September) were measured to monitor the extent of CDD/CDF formation during composting. For the March cycle sample, most 2,3,7,8-substituted CDD/CDF congeners decreased in concentration during composting. Four CDF congeners showed a slight increase in concentration (i.e., less than 10 percent). For the September cycle sample, OCDD and HpCDD concentrations increased 300 percent during composting. Less than 10 percent increases were observed for HxCDDs and OCDF; all other 2,3,7,8-substituted CDD/CDF congeners showed decreases in concentrations during composting.

Krauss et al. (1994) measured the extent of CDD/CDF formation during the composting of household waste using a laboratory compost reactor. After 11 weeks, the TEQ content of the compost increased from 3.0 to 4.5 ng. The largest increases in mass content were observed for HpCDD (primarily 1,2,3,4,6,7,8-HpCDD) and OCDD. TCDD, PeCDD, and HxCDD showed no change in mass content. All CDF congener groups showed decreases in mass content; however, the concentrations in both the starting and finished compost were close to the analytical detection limits.

Oberg et al. (1994) reported the results of monitoring of two household waste composts and two garden composts. For the two household waste composts, total CDD/CDF content decreased in both composts over the 12-week test period. Total CDD content and PCB content decreased, but total CDF content increased in contrast to the findings of Krauss et al. (1994). A small increase in OCDD content in both composts, however, was observed. The two garden composts were monitored by Oberg et al. (1994) for a 60-week period. Total CDD/CDF concentration increased, with the largest increases observed for OCDD and HpCDDs. The lower chlorinated CDFs decreased in concentration.

As a followup 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 TEQ concentrations in the raw sludges were 20- and 200-ng TEQ/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 (i.e., greater than 40 percent) were observed for TCDF, PeCDF, HxCDF, TCDD, and PeCDD in the sludge initially containing 20-ng TEQ/kg and for TCDF, TCDD, HpCDD, and OCDD in the initially high content sludge. The greatest percentage decreases in congener concentrations (i.e., greater than 40 percent) were observed for non-2,3,7,8-substituted congeners.

10. PHOTOCHEMICAL SOURCES OF CDD/CDF

10.1. PHOTOTRANSFORMATION OF CHLOROPHENOLS

Several researchers demonstrated that CDD/CDFs can be formed via photolysis of pentachlorophenol (PCP) under laboratory conditions. These studies are described below. However, the extent to which CDD/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 percent 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 due to an apparent 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 utilized methylene chloride as the carrier. Results were reported only for OCDD. The OCDD concentration increased by a maximum factor of 1.5 for EC-7 and technical PCP, and by a factor of 88 for purified PCP. The results suggested to the authors 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 containing PCP under conditions simulating those used to purify water with ultraviolet (UV) radiation (i.e., 5-hour exposure to 254-nm radiation from low pressure mercury lamps). The three solutions tested contained approximately 1 mg/L of PCP or PCP-Na before irradiation, but the CDD/CDF content varied dramatically (1.5-, 2066-, and 2071-pg TEQ/L). Irradiation resulted in nearly total destruction of PCP (greater than 99 percent loss) in all three experiments. An overall net increase in TEQ content was observed in the initially low TEQ content water, but a net decrease was observed for the two initially high TEQ content waters.

- Irradiation of laboratory water containing purified PCP showed an increase in TEQ concentration from 1.5 pg/L to 214.5 pg/L. The increase in TEQ was due entirely to the formation of 1,2,3,4,6,7,8-HpCDD, OCDD, and 1,2,3,4,6,7,8-HpCDF. Formation of non-2,3,7,8-substituted HpCDDs and HpCDFs was also observed. The ratios of the concentrations of these non-2,3,7,8-congeners to the concentrations of the 2,3,7,8-congeners were 0.6 for HpCDDs and 5.0 for HpCDFs. The HpCDD and HpCDF congeners formed indicated that the operative mechanism is photoinduced dechlorination of OCDD at a peri position and dechlorination of OCDF at only the 1- and 9-peri positions.

- Irradiation of water containing technical PCP-Na (Dowicide-G) resulted in a net loss in CDD/CDF TEQ content from 2,065.5 pg/L to 112.7 pg/L. The only 2,3,7,8-substituted congener showing an increased concentration was 1,2,3,6,7,8-HxCDD. The other congeners originally present in the technical PCP-Na showed reductions of 80.6 to 100 percent.

- The TEQ content of seepage water from a landfill (2,071 pg TEQ/L) was reduced by a factor of two to 1,088 pg TEQ/L. However, several 2,3,7,8-substituted congeners did increase in concentration (1,2,3,6,7,8-HxCDD; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,8-HpCDF; and OCDF).

Waddell et al. (1995) also studied the effect of irradiating distilled laboratory water containing PCP under conditions simulating those used to purify water with UV radiation. The results obtained were similar to those of Vollmuth et al. (1994). Analytical grade PCP at a concentration of 10 mg/L was exposed for 12 minutes to 200-300-nm radiation from a medium pressure mercury lamp. All CDD/CDF congener groups increased in concentration over the 12-minute exposure period, with the greatest increases observed for OCDD (75-fold increase) and HpCDDs (34-fold increase). The TEQ content of the solution increased from 4.2-pg TEQ/L to 137-pg TEQ/L over the 12-minute period. The dominant congeners

formed in terms of both concentration and contribution to TEQ were 1,2,3,4,6,7,8-HpCDD, OCDD, and 1,2,3,7,8,9-HxCDD.

10.2. PHOTOLYSIS OF HIGHER CDD/CDFS

Photolysis appears to be one of the few environmentally significant degradation mechanisms for CDD/CDFs in water, air, and soil. Although, in most studies, good mass balances were not obtained and the photolytic pathways for CDD/CDFs were not fully identified, a major photolysis pathway appears to be photodechlorination, resulting in formation of lower chlorinated CDD/CDFs. A preferential loss of chlorines from the peri positions (i.e., chlorines at the 1, 4, 6, and 9 positions) rather than from the lateral positions (i.e., chlorines at the 2, 3, 7, and 8 positions) was reported for some congener groups when irradiated as dry films, sorbed to soil, and as gas-phase CDD/CDFs (Choudry and Webster, 1989; Kieatiwong et al., 1990; Sivils et al., 1994 and 1995; Tysklind et al., 1992). Several researchers reported that carbon-oxygen cleavage and other mechanisms may be similarly or more important pathways for CDD/CDFs containing four or fewer chlorines.

Because of the difficulties inherent in controlling experimental variables for nonvolatile and highly lipophilic compounds like CDD/CDFs, few photolysis studies have been performed with natural waters, on soil, or particulate matrices, and in the gas phase to examine the rates and products of photolysis under environmentally relevant conditions. Thus, it is not possible at this time to quantitatively estimate the mass of various CDD/CDF congeners formed in the environment annually via photolytic mechanisms. The following paragraphs summarize the key findings of recent environmentally significant studies for the water, soil, and air media.

10.2.1 Photolysis in Water

Numerous studies demonstrate that CDD/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 CDD/CDFs using natural waters and sunlight.

Choudry and Webster (1989) experimentally determined the sunlight photolysis half-life of 1,3,6,8-TCDD in pond water to be 3.5 days (i.e., 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 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 of the 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF in the water:acetonitrile solution were 6.5 and 46 days, respectively, and 1.2 and 0.19 days in lake water, respectively. 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 the river and lake water (half-lives of about 4 to 6 hours) were double the rates observed in pure water (half-lives of about 8 to 11 hours). Dung and O'Keefe (1992) attribute the difference in rates to the presence of natural organics in the river and lake water that may be acting as sensitizers.

10.2.2 Photolysis on Soil

Photolysis of CDD/CDFs on soil has not been well characterized. Based on the data generated to date, however, photolysis is an operative degradation process only in the near-surface soil where UV light penetrates (i.e., the top few millimeters or less of soil), and dechlorination of peri-substituted chlorines appears to occur preferentially.

Miller et al. (1989) studied the CDD degradation products resulting from irradiation of ^{13}C-labeled OCDD on two soil types using sunlamps. Approximately 38 to 42 percent of the OCDD were degraded by day 5 of the experiment; no significant further loss of OCDD

was observed over the following 10 days. Although determined not to be the dominant photolysis pathway, photodechlorination was observed in both soils; approximately 10 to 30 percent of the lower chlorinated congeners were produced from the immediate higher chlorinated congeners. The HpCDD and HxCDD congeners observed as degradation products were present in approximately similar proportions to the number of congeners in each congener group. However, Miller et al. (1989) found that 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were observed in greater yields 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 similar experiments to those of Miller et al. (1989) using natural sunlight rather than sunlamps for irradiation of ^{13}C-labeled OCDD on soils. Photodechlorination was estimated to account for approximately 10 percent 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. The findings of Miller et al. (1989) and Kieatiwong et al. (1990) 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 in good agreement with 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 percent; PeCDD - 40 percent; and TCDD - 75 percent. The sunlight photolysis of OCDF on soil was also studied by Tysklind et al. (1992). 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 CDD/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 hours 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 CDD/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 an UV-light transmission of greater than 50 percent in the 280-320 mm range. In both the summer and autumn exposure periods, the concentrations of CDD/CDFs (on a congener group basis) were similar in the grass exposed to UV-light and the grass that was not exposed. Welsch-Pausch and McLachlan (1995) concluded that if photodegradation is occurring, it is a relatively insignificant factor in the accumulation of CDD/CDF in pasture grass.

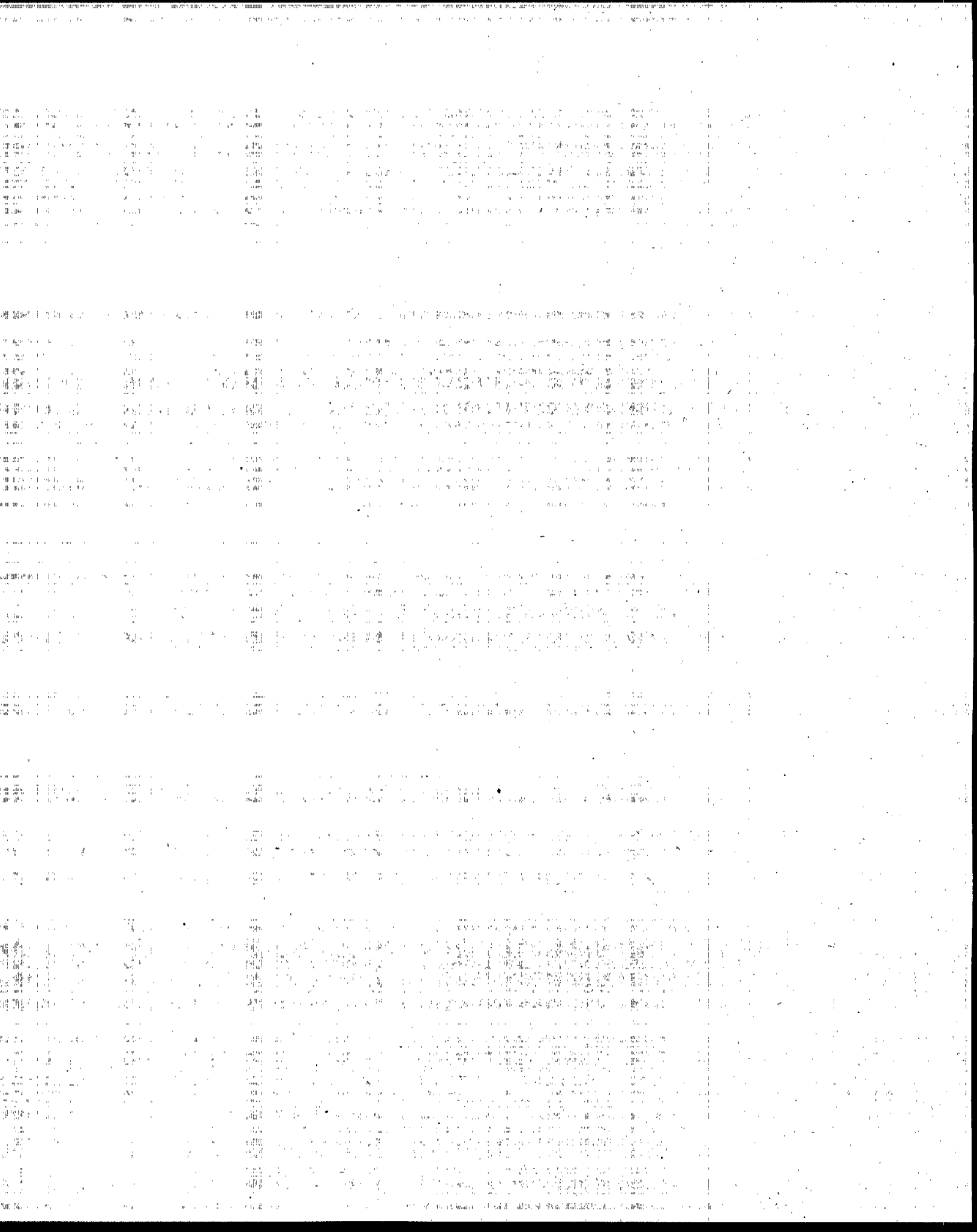
10.2.4 Photolysis in Air

Photolysis of CDD/CDFs in the atmosphere has not been well-characterized. Based on the data generated to date, however, photolysis appears to be a significant mechanism for degradation (i.e., principally dechlorination of the peri-substituted chlorines) of those CDD/CDFs present in the atmosphere in the gas phase. For airborne CDD/CDFs sorbed to particulates, photolysis appears to proceed very slowly, if at all. Because of the low volatility of CDD/CDFs, few studies have been attempted to measure actual rates of photodegradation of gaseous-phase CDD/CDF, and only recently studies have examined the relative importance of photolysis to particulate-bound CDD/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 time up to 20 minutes. 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 exists 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 indicated that laterally-substituted congeners (i.e., chlorines at the 2, 3, 7, and 8 positions) degrade at a slower rate than the peri-substituted congeners (i.e., chlorines at the 1, 4, 6, and 9 positions). Although the rate constants were not presented in Sivils et al. (1994), the degradation rate for 2,3,7,8-TCDD (30 percent loss in 20 minutes) was reported to be slower than the rates for all other tested CDDs. Also, 1,2,4,7,8-PeCDD (with 2 peri-chlorines) degraded significantly faster than 1,2,3,7,8-PeCDD (with only 1 peri-chlorine).

The photolysis of 2,3,7,8-TCDD sorbed onto small diameter fly ash particulates suspended in air was studied by Mill et al. (1987). The results indicated that fly ash appears to confer photostability on 2,3,7,8-TCDD. Little (8 percent) to no loss was observed on the two fly ash samples after 40 hours of illumination. Similar results were in photolysis studies with fly ash reported by Tysklind and Rappe (1991) and Koester and Hites (1992). Tysklind and Rappe (1991) subjected fly ashes from two German incinerators under various simulated environmental conditions. The fraction of photolytically degradable CDD/CDF after 288 hours of exposure was in the range of 20 to 40 percent of the extractable CDD/CDF. However, a 10 to 20 percent 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 CDD/CDFs naturally adsorbed to five fly ashes collected from electrostatic precipitators. No significant degradation was observed in 11 photodegradation experiments performed on the ashes for periods ranging from 2 to 6 days. Koester and Hites (1992) concluded that: (1) the absence of photodegradation was not due to the absence of a hydrogen-donor organic substance; (2) other molecules or the ash, as determined by a photolysis experiment with an ash extract, inhibit photodegradation either by absorbing light and dissipating energy or by quenching the excited states of the CDD/CDFs; and (3) the surface of the ash itself may hinder photolysis by shielding the CDD/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 biphenyls (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 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 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

Tables 11-1 and 11-2 present emission estimates for the major known or suspected sources that could release dioxin-like PCBs to the environment. Table 11-1 presents estimated annual releases for the time period 1990 to 1995. Table 11-2 presents estimated annual releases for the time period 1985 to 1989. For each source listed in Tables 11-1and 11-2, estimated emissions to air, water, land, and product are listed where appropriate and where data are adequate to enable an estimate to be made. The term "product" in Tables 11-1 and 11-2 is defined to include substances or articles (e.g., sewage sludge that is distributed/marketed commercially) that are known to contain dioxin-like PCBs and whose subsequent use may result in releases to the environment.

Releases of "old" dioxin-like PCBs (i.e., dioxin-like PCBs manufactured prior to the ban) to the environment can occur from ongoing use and disposal practices. Prior to regulations enacted beginning in the late 1970s that limited the manufacture/use/disposal of PCBs, significant quantities of PCBs were released to the environment in association with: (1) the manufacture of PCBs; (2) the manufacture of products containing PCBs; and (3) the use and disposal of products containing PCBs, as well as materials that may have been contaminated with trace levels of PCBs from prior PCB use or disposal. Following the ban on PCB production, releases from these first two categories ceased to exist. The third type of releases, those associated with product use and disposal, will continue in at least three ways:

- Products containing greater than 2 pounds of PCBs (e.g., dielectric fluids in transformers and large capacitors) are controlled by disposal regulations that have minimized environmental releases;

- Disposal of products containing small quantities of PCBs (e.g., small capacitors, fluorescent lighting fixtures) or trace quantities of PCBs (e.g., wastepapers) are subject to disposal as municipal solid waste but may result in some release to the general environment;

- Leaks and spills of still in-service PCBs; and

- Illegal disposal of PCBs.

Although no estimates of emissions of "old" dioxin-like PCBs from reservoir sources (i.e., soils and sediments) have been made, the widespread occurrence of PCBs is most likely due to the re-release of these compounds from reservoir sources. Sediments act as a reservoir whereby dioxin-like PCBs can become resuspended in the water column and volatilize from the water body into the atmosphere. Soils act as a reservoir accumulating dioxin-like PCBs from aerial deposition and then reintroducing them to the atmosphere through windblown soil or as vapors. It is reasonable to assume that the quantities of dioxin-like PCBs available for release from reservoir sources are significantly larger than the quantities of dioxin-like PCBs available for release from current use and disposal of dioxin-like PCB-containing material.

Insufficient information is currently available to enable a determination as to whether any significant release of newly formed dioxin-like PCBs is occurring in the United States. Unlike CDD/CDFs, PCBs were intentionally manufactured in the United States in large quantities from 1929 until production was banned in 1977. Although no strong evidence exists that the dioxin-like PCBs are produced in other than trace quantities as byproducts during combustion or chemical processes, most research on formation of dioxin-like compounds has, to date, focused on CDD/CDFs rather than PCBs. Thus, there are currently insufficient empirical data upon which to estimate emission factors for any potential source category. Congener-specific measurements in discharges from potential sources are needed.

11.2 RELEASES OF COMMERCIAL PCBs

PCBs were commercially manufactured by the direct batch chlorination of molten biphenyl with anhydrous chlorine in the presence of a catalyst, followed by separation and purification of the desired chlorinated biphenyl fractions. The degree of chlorination was controlled by the chlorine contact time in the reactor. Commercial PCBs production is believed to have been confined to 10 countries. Total PCBs produced worldwide since 1929 (i.e., the first year of known production) has been estimated to total 1.5-million metric tons. Initially, PCBs were primarily used as dielectric fluids in transformers. After World War II, PCBs found steadily increasing use as dielectric fluids in capacitors, as heat-conducting fluids in heat exchangers, and as heat-resistant hydraulic fluids in mining equipment and vacuum pumps. PCBs also were used in a variety of "open" applications (i.e, uses from which PCBs cannot be recollected) including: plasticizers, carbonless copy paper, lubricants, inks, laminating agents, impregnating agents, paints, adhesives, waxes, additives in cement and plaster, casting agents, dedusting agents, sealing liquids, fire retardants, immersion oils, and pesticides (DeVoogt and Brinkman, 1989).

PCBs were manufactured in the United States from 1929 until 1977. U.S. production peaked in 1970 with a volume of 39,000 metric tons. In 1971, Monsanto Corporation, the major U.S. producer, voluntarily restricted the sales of PCBs to all applications with the exception of "closed electrical systems," and annual production fell to 18,000 metric tons in 1974. Monsanto ceased PCB manufacture in mid-1977 and shipped the last inventory in October 1977. Regulations issued by EPA beginning in 1977, principally under the Toxic Substances Control Act (TSCA) (40 CFR 761), have strictly limited the production, import, use, and disposal of PCBs. The estimated cumulative production and consumption volumes of PCBs in the United States from 1930 to 1975 were: 635,000 metric tons produced; 1,400 metric tons imported (primarily from Japan, Italy, and France); 568,000 metric tons sold in the United States; and 68,000 metric tons exported (Versar, 1976). The reliability of these values is +5 percent and -20 percent (Versar, 1976).

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 hexa-chlorinated

congeners with an average chlorine content of 41 percent. From 1957 until 1972, Monsanto also manufactured several blends of PCBs and polychlorinated terphenyls (PCTs) under the trade names Aroclor 2565 and Aroclor 4465; manufacture and sales volumes are not available for these blends. Listed below are the percentages of total Aroclor production during the years 1957 to 1977 by Aroclor mixture as reported by Brown (1994).

Aroclor	1957-1977 U.S. Production (%)
1016	12.88
1221	0.96
1232	0.24
1242	51.76
1248	6.76
1254	15.73
1260	10.61
1262	0.83
1268	0.33

The trade names of the major commercial PCB technical grade mixtures manufactured in other countries included: *Clophen* (Germany), *Fenclor* and *Apirolio* (Italy), *Kanechlor* (Japan), *Phenoclor* and *Pyralene* (France), *Sovtel* (USSR), *Delor* and *Delorene* (Czechoslovakia), and *Orophene* (German Democratic Republic) (DeVoogt and Brinkman, 1989). The mixtures marketed under these trade names had similar chlorine content (by weight percent and average number of chlorines per molecule) to those of various Aroclors. Listed below are comparable mixtures in terms of chlorine content marketed under several trade names.

Aroclor	Clophen	Pyralene	Phenoclor	Fenclor	Kanechlor
1232		2000			200
1242	A-30	3000	DP-3	42	300
1248	A-40		DP-4		400
1254	A-50		DP-5	54	500
1260	A-60		DP-6	64	600

Major advances in analytical separation and resolution techniques during the 1980s and 1990s enabled various researchers to identify and quantify PCB congeners present in Aroclors, Clophens, and Kanechlors (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; and Schwartz et al., 1993). 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 (i.e., Aroclor 1248, Clophen A-40, and Kanechlor 400 comprise one mixture group) reported by these researchers. Table 11-3 also presents calculation of the corresponding 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) attribute 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. 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 will differ from the commercial mixtures. This is because after release to the environment, the composition of PCB mixtures changes over time, through partitioning, chemical transformation, and preferential bioaccumulation (U.S. EPA, 1996g). Dioxin-like PCB congeners differ by up to one to two orders of magnitude in their water solubilities, vapor pressures, K_{ow} values, and Henry's Law constants. Thus, although all the dioxin-like PCB congeners are poorly soluble in water and have very low vapor pressures, they will volatilize and leach at different rates. Similarly, because the congeners differ somewhat in their rates of biodegradation, bioaccumulation, and photodegradation, the congener

patterns found in environmental media and biota will vary from those found in commercial mixtures.

Although environmental mixtures are often characterized in terms of Aroclors, this characterization can be both imprecise and inappropriate. Qualitative and quantitative errors can arise from judgements in comparing GC/MS peaks for a sample with the characteristic peak patterns for different Aroclors, particularly for environmentally altered patterns (U.S. EPA, 1996g). For the same reason, it can be both imprecise and inappropriate to infer concentrations of dioxin-like PCB congeners in an environmental sample based on characterization of the sample's Aroclor content and knowledge of the dioxin-like congener content in the commercial Aroclor. Safe (1994) wrote, "Regulatory agencies and environmental scientists have recognized that the composition of PCBs in most enviromental extracts does not resemble the compositions of the commercial product." Similarly, ATSDR (1993) stated, "It is important to recognize that the PCBs to which people may be exposed are likely to be different from the original PCB source because of changes in congener and impurity composition resulting from differential partitioning and transformation in the environment and differential metabolism and retention."

11.2.1. Approved PCB Disposal/Destruction Methods

In 1978, EPA began regulating the disposal of PCBs and PCB-contaminated waste under the TSCA, PL 94-469. The disposal regulations, published in the Code of Federal Regulations, 40 CFR, Part 761, state that the preferred disposal method is incineration at 1,200°C or higher. If the waste contains material that can not be destroyed by incineration, EPA clearance must be obtained to dispose of the waste in a chemical waste landfill, or in another approved manner.

The PCB disposal regulations describe disposal of three distinct types of PCB waste: PCBs, PCB articles (i.e., items containing PCBs), and PCB containers. Within these categories of PCB waste, further distinctions are made based on the PCB concentration in the waste. The acceptable disposal methods are based on the PCB concentrations in the specific waste to be destroyed. The acceptable disposal methods are: Annex I incinerators, high-efficiency boilers, Annex II chemical waste landfills, and other approved methods. The following subsections and Table 11-4 provide brief descriptions of these

disposal methods. More complete descriptions of the specific methodologies are provided in the Code of Federal Regulations, 40 CFR, Part 761.

Approved Incinerators/High Efficiency Boilers - PCB Annex I incinerators must meet the specific technical standards and criteria listed in Annex I of EPA's PCB regulations. The minimum operating requirements for disposal of liquid wastes are 2 seconds at 1,200°C (2,190°F) with 3 percent excess oxygen (measured in the stack gas), or 1.5 seconds at 1,600°C (2,910°F) and 2 percent excess oxygen (measured in the stack gas). Monitoring requirements, approval conditions, and trial burn requirements are prescribed in Annex I. Commercial or industrial incinerators intending to destroy liquid PCB wastes must demonstrate compliance with the Annex I requirements through a comprehensive trial burn program. Annex I incinerators operating at optimum performance level should destroy 99.997 percent of liquid PCB waste with a resulting maximum emission factor of 0.03 grams per kilogram (g/kg).

Criteria for Annex I incinerators were established for the destruction of liquid PCB wastes; however, these incinerators also may be used for disposal of nonliquid PCB items (such as capacitors), provided that a destruction and removal efficiency of 99.9999 percent and a maximum emission factor of 0.001 g/kg are met.

High-efficiency boilers may be used to destroy PCBs and PCB-contaminated waste with PCB concentrations not exceeding 500 ppm. Conventional industrial and utility boilers may be designated as high-efficiency boilers, if they are operated under the prescribed combustion conditions defined in the PCB disposal regulations. The PCB regulations do not specify a minimum PCB destruction efficiency for high-efficiency boilers; however, EPA-approved boilers operated according to the regulations have reported destruction efficiencies in excess of 99.9 percent, with a corresponding emission factor of 0.1 g/kg (U.S. EPA, 1987c).

Approved Chemical Waste Landfills - Approved chemical waste landfills can be used for the disposal of some, but not all, PCB wastes. PCB-contaminated materials acceptable for land disposal in an approved landfill include PCB mixtures (e.g., certain PCB-contaminated soil/solid debris, PCB-contaminated dredged materials, and PCB-contaminated municipal sewage sludge), PCB articles that cannot feasibly be incinerated (e.g., drained and flushed transformers), and drained PCB containers. EPA must issue written approval 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 in these landfills are placed in sealed containers, thereby, minimizing any PCB emissions.

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. Subsequent to April 29, 1983, all other PCB disposal technologies (thermal and nonthermal) that are to be used in more than one EPA Region must 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.

Emission Estimates - Table 11-5 lists the amounts of PCBs reported in EPA's Toxics Release Inventory (TRI) as transferred offsite for treatment, energy recovery, or disposal during the years 1988 through 1993. 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 percent, then annual emissions of PCBs to air during 1988 and 1993 could have been as high as 26,422 kg and 4,635 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.

11.2.2. Accidental Releases of In-Service PCBs

EPA banned PCB production and use in open systems in 1977. Subsequent to the 1977 ban, releases of commercially produced PCB 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 incomplete combustion occurring during accidental fires involving PCB-containing equipment. These two types of accidental releases are discussed in this section.

Leaks and Spills - PCBs that remain in active service at this time are those contained in "closed system" (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 percent 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, 1988).

The number of each of these items owned by the utility industry, the quantity of PCBs each contains, 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 were reported in the April 22, 1982, Federal Register relative to a proposed modification to the PCB regulations (Federal Register, 1982a). The findings indicated that over 99 percent of the total quantity of PCBs contained in utility-owned electrical equipment in 1981 (73,700 metric tons) were in 40,000 PCB transformers (those containing > 500 ppm of PCBs) and large PCB capacitors (those containing > 3 lbs 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 percent of the estimated releases were the result of leaks from large PCB capacitors (Federal Register, 1982a). Leaks/spills typically occur in transformers when the gasket joining the top to the body corrodes, tears, or physically fails. PCBs can then leak past this failed section and potentially spill onto the surrounding ground. PCB capacitors typically fail by rupturing, exposing the contained PCBs to the environment. Failure is caused by environmental and weathering effects (e.g., lightning) or material failures (e.g., metal fatigue).

As of mid-1988, the total population of in-service PCB transformers and large PCB capacitors was estimated to have decreased from 140,000 to 110,000 and from 3.3 million to 1.9 million, respectively (Versar, 1988). PCB transformers have normal operating lifetimes of 30 years and 40 years, respectively. The accelerated retirement rate over this

7-year time period was attributed to EPA's PCB Electrical Use Rule (Federal Register, 1982b), which required the removal of 950 food/feed industry transformers by 1985 and removal of 1.1-million unrestricted-access large PCB capacitors by October 1988. In addition, EPA's PCB Transformer Fires Rule (Federal Register, 1985b) required the removal by 1990 of 7,600 480-volt network transformers. More recent inventories of PCB-containing electrical equipment are not available. However, a recent Information Collection Request submitted by EPA to the Office of Management and Budget for information on uses, locations, and conditions of PCB electrical equipment estimated that there may be 150,000 owners of PCB-containing transformers used in industry, utilities, government buildings, and private buildings (Federal Register, 1997a). It is expected (and is demonstrated by the reported PCB transfers in TRI - See Table 11-5) that many owners of PCB electrical equipment have removed PCB-containing equipment to eliminate potential liability.

The proportion of spilled PCB that enters the atmosphere, runs off to surface water, or remains in or on the surface depends on a variety of factors including the porosity of the surface onto which the PCBs are spilled (concrete, soil), the PCB isomers that are spilled, ambient conditions (i.e., temperature, wind speed, precipitation), and the cleanup schedule. The number and diversity of factors affecting PCB emissions from spills and leaks make estimation of an emission factor difficult. A rough approximation of the annual amount that may be released to the environment from spills and leaks can be made using the release data reported by manufacturing facilities to EPA's TRI. Table 11-6 lists the amounts of PCBs reported in TRI to be released to the environment during 1988 through 1993. These data include emissions to the air, discharges to bodies of water, releases at the facility to land, as well as contained disposal into underground injection wells.

Based on these TRI data, annual emissions of PCBs to air during 1988 and 1993 could be as high as 2.7 kg and 0 kg, respectively. For purposes of deriving a preliminary rough estimate of potential releases of dioxin-like PCBs, it can be assumed that the ratio of TEQ to total PCB in the air emissions was 84:1-million (i.e., the average of the estimated mean TEQ contents for Aroclors 1242 and 1254 presented in Table 11-3). Based on this assumption, annual emissions of PCB TEQs in 1988 and 1993 could have been 0.2 and 0 grams, respectively. Similar assumptions for releases to water listed in Table 11-6 yield estimated TEQ emissions during 1988 and 1993 of 0.4 and 0 grams, respectively. For

land, estimated TEQ emissions during 1988 and 1993 could have been 29 and 10 grams, respectively.

Accidental Fires - The available information is not adequate to support an estimate of potential annual releases of dioxin-like PCBs from accidental electrical equipment fires. For fires involving PCB transformers or capacitors, the amount of PCBs released is dependent upon the extensiveness of the fire and the speed at which it is extinguished. A number of these fires are documented. A New York fire, involving 200 gallons of transformer fluid containing some 65 percent by weight PCBs, resulted in a release of up to 1,300 pounds of PCBs. A capacitor fire that burned uncontrolled for 2 hours in Sweden resulted in the destruction of 12 large utility capacitors containing an estimated 25 pounds of PCBs each, for a total potential release of 300 pounds. However, data are incomplete on the exact amount of PCBs released as a result of these two fires.

EPA has imposed reporting requirements to ensure that the National Response Center is informed immediately of fires involving PCB transformers (40 CFR 761). The recordkeeping requirements are used to document the use, location, and condition of PCB equipment. Responses are mandatory, but 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 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.

11.2.3. 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 7 of the Aroclors. Sludges from 19 percent 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), Gutenmann et al. (1994) 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, 126, and 169. The sludge samples were collected from 75 wastewater treatment plants across the United States during the summer of 1994. These data are summarized in Table 11-8. For the calculation of results in units of TEQ, results from all samples collected from the same facility were averaged by Green et al. (1995) to ensure that results were not biased towards the concentrations found at facilities from which more than one sample were collected. If all nondetected values are assumed to be zero, then the POTW mean and median dioxin-like PCB TEQ concentrations were 47.5- and 22.6-ng TEQ/kg (dry weight basis), respectively (standard deviation of 89.4-ng TEQ/kg). If the nondetected values are set equal to the detection limits, then the POTW mean and median TEQ concentrations were 48.1- and 23.9-ng TEQ/kg, respectively (standard deviation of 89.2-ng TEQ/kg).

Approximately 5.4-million dry metric tons of sewage sludge are estimated by EPA to be generated annually in the United States based on the results of the 1988/1989 EPA National Sewage Sludge Survey (Federal Register, 1993b). Table 11-9 lists the volume of sludge disposed annually by use and disposal practices. Table 11-9 also lists the estimated amount of dioxin-like PCB TEQs that may be present in sewage sludge and potentially be released to the environment. These values were estimated using the mean/median (i.e., about 48-ng TEQ/kg) TEQ concentration reported by Green et al. (1995) and Cramer et al. (1995). Multiplying this TEQ concentration by the sludge volumes generated, yields an annual potential total release of 200 g of TEQ for nonincinerated sludges. Of this 200 g of TEQ, 3.4 grams enter commerce as a product for distribution and marketing. The remainder is applied to land (101.3 grams) or is landfilled (94.8 grams).

These release estimates are assigned a H/M confidence rating indicating "high" confidence in the production estimate and "medium" confidence in the emission factor estimates. The "medium" rating was based on the judgement that, although the 75 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. Based on this confidence rating, the estimated range of potential annual emissions is assumed to vary by a factor of 5 between the low and high ends of the range. Assuming that the best estimate of annual emission to land (101-g TEQ/yr) is the geometric mean of this range, then the range is calculated to be 45.2- to 226-g TEQ/yr. Assuming that the best estimate of 3.4-g TEQ annual emissions in product (i.e., the fraction of sludge that is distributed and marketed as a product) is the geometric mean of the range, then the range is calculated to be 1.5- to 7.5-g TEQ/yr.

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 banned 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 required manufacturers with processes inadvertently generating PCBs and importers of products containing 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 Solid Waste Incineration

Municipal solid waste incinerators have long been identified as potential PCB air emission sources. Stack gas concentrations of PCBs for three incinerators were reported in U.S. EPA (1987c), and the average test results yields an emission factor of 18-μg PCBs/kg refuse. Stack gas emissions of PCBs from the three incinerators were quantified without

determining the incinerator's PCB destruction efficiency. The PCB content of various consumer paper products was analyzed as part of the study. This study indicates that paper products such as magazine covers and paper towels contained up to 139 micrograms of PCB per kilogram of paper (μg/kg). These levels, which were reported in 1981, were attributed to the repeated recycle of waste paper containing PCBs. For example, carbonless copy paper manufactured prior to 1971 contained PCB levels as high as 7 percent. This copy paper then became a component of waste paper, which was recycled. The PCBs inevitably were introduced into other paper products, resulting in continued measurable levels in municipal refuse some 4 years after the PCB manufacturing ban was imposed. Refuse-Derived Fuel (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 in U.S. EPA (1987c) that municipal refuse does contain detectable levels of PCBs, and that some of these PCBs may enter the atmosphere when the refuse is incinerated.

Shane et al. (1990) analyzed fly ashes from five municipal solid waste (MSW) incinerators for PCB congener group content. Total PCB levels ranged from 99 to 322 μg/kg in these ashes with the tri-, tetra-, and penta-congener groups occurring in the highest concentrations. Shane et al. (1990) also analyzed seven bottom ashes and eight bottom ash/fly ash mixtures for total PCB measured as Aroclor 1254. The detection limit for this Aroclor analysis was 5 μg/kg. Aroclor 1254 was detected in two of the seven bottom ash samples (26 and 8 μg/kg) and in five of the eight fly ash/bottom ash mixtures (range of 6 to 33 μg/kg).

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 MSW incinerators (Sakai et al., 1993a; Sakai et al., 1993b; Boers et al., 1993; Schoonenboom et al., 1993; Sakai et al., 1994). 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 recently 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, not individual congeners, were measured during stack testing of two industrial wood burning facilities by the State of California Air Resources Board (CARB, 1990e; 1990f). Table 11-10 presents the average of the congener group (i.e., mono- through decachlorobiphenyl) emission factors for these two facilities. No tetra- or more chlorinated congeners (i.e., the congener groups containing the dioxin-like PCBs) were detected at either facility at detection limits corresponding to emission factors in the low ng/kg of wood combusted range.

In CARB (1990e), PCBs were measured in the emissions from two spreader stoker wood-fired boilers operated in parallel by an electric utility for generating electricity. The exhaust gas stream from each boiler is passed through a dedicated ESP after which the gas streams are combined and emitted to the atmosphere through a common stack. Stack tests were conducted both when the facility burned fuels allowed by existing permits and when the facility burned a mixture of permitted fuel supplemented by urban wood waste at a ratio of 70:30.

In CARB (1990f), PCBs were measured in the emissions from twin fluidized bed combustors designed to burn wood chips to generate electricity. The APCD system consisted of ammonia injection for controlling nitrogen oxides, and a multiclone and electrostatic precipitator for controlling particulate matter. During testing, the facility burned wood wastes and agricultural wastes allowed by existing permits.

11.4.3. Medical Waste Incineration

As discussed in Section 3.3, EPA recently issued nationally applicable emission standards and guidelines for medical waste incinerators (MWI) that address CDD/CDF emissions. Although PCBs are not addressed in these regulations, the data base of stack test results at MWIs compiled for this rulemaking does contain limited data on PCB congener group emission factors. Data are available for two MWIs lacking add-on APCD equipment and for two MWIs with add-on APCD equipment in place. The average congener group emission factors derived from these test data are presented in Table 11-11.

Because data are available for only 4 of the estimated 2,400 facilities that comprise this industry and because these data do not provide congener-specific emission factors, no national estimates of total PCB or dioxin-like PCB emissions are being made at this time.

11.4.4. Tire Combustion

Emissions of PCB congener groups, not individual congeners, were measured during stack testing of a tire incinerator by the State of California Air Resources Board (CARB, 1991a). The facility consists of two excess air furnaces equipped with steam boilers to recovery the energy from the heat of combustion. Discarded whole tires were fed to the incineration units at rates ranging from 2,800 to 5,700 kg/hr during the 3 testing days. The furnaces are equipped to burn natural gas as auxiliary fuel. The steam produced from the boilers drives electrical turbine generators that produce 14.4 megawatts of electricity. The facility is equipped with a dry acid gas scrubber and fabric filter for the control of emissions prior to exiting the stack. Table 11-12 presents the congener group (i.e., mono- through decachlorobiphenyl) emission factors for this facility. The emission factor for the total of the tetra- through hepta-chlorinated congener groups is about 1.2 μg/kg of tire processed.

EPA estimated that approximately 0.50-million metric tons of tires were incinerated in 1990 in the United States (U.S. EPA, 1992a). This production estimate is given a "medium" confidence rating, because it is based on both published data and professional judgement. The use of scrap tires as a fuel increased significantly during the late 1980s; however, no quantitative estimates were provided in U.S. EPA (1992a) for this period. In 1990, 10.7 percent of the 242-million scrap tires generated were burned for fuel. This percentage is expected to continue to increase (U.S. EPA, 1992a). Of the tires burned for energy recovery purposes, pulp and paper facilities used approximately 46 percent; cement kilns, 23 percent; and one tire-to-energy facility, 19 percent (U.S. EPA, 1997b).

If it is assumed that 500-million kg of discarded tires are incinerated annually in the United States, then, using the sum of the average emission factors for the total tetra- through hepta-chlorinated congener groups (1.2-μg/kg tire processed) derived from stack data from the one tested facility, yields a total emission of 610 g per year. However, it is not known what fraction of this emission is dioxin-like PCBs.

11.4.5. Cigarette Smoking

Using high-resolution mass spectrometry, Matsueda et al. (1994) analyzed tobacco from 20 brands of commercially available cigarettes collected in 1992 from Japan, the United States, Taiwan, China, the United Kingdom, Germany, and Denmark for the PCB congeners 77, 126, and 169. Table 11-13 presents the results of the study.

However, no studies have been reported which examined the tobacco smoke for the presence of these congeners. Thus, it is not known whether the PCBs present in the tobacco are destroyed or volatilized during combustion, or whether PCBs are formed during combustion. The combustion processes operating during cigarette smoking are complex and could be used to support either of these potential 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 CDD/CDFs initially present in the tobacco. Both solid and gas phase temperatures rapidly decline to 200 to 400°C within 2 mm of the char line. Formation of dioxin-like PCBs has been reported in combustion studies with other media in this temperature range (Sakai et al., 1994). However, it is known that a process likened by Guerin et al. (1992) to steam distillation takes place in the region behind the char line because of high localized concentrations of water and temperatures of 200 to 400°C. At least 1,200 tobacco constituents (e.g., nicotine, n-paraffin, some terpenes) are transferred intact from the tobacco into the smoke stream by distillation in this area, and it is plausible that PCBs present in the unburned tobacco would be subject to similar distillation.

In 1995, approximately 487-billion cigarettes were consumed in the United States and by U.S. Armed Forces personnel stationed overseas. Per-capita U.S. cigarette consumption in 1995, based on total U.S. population aged 16 and over, declined to 2,415 from a record high of 4,345 in 1963. In 1987, approximately 575-billion cigarettes were consumed domestically (The Tobacco Institute, 1995; USDA, 1997).

A preliminary rough estimate of potential emissions of dioxin-like PCBs can be made using the following assumptions: (1) the average dioxin-like PCB TEQ content of seven brands of U.S. cigarettes reported by Matsueda et al. (1994), 0.68 pg/pack (or 0.034 pg/cigarette) is representative of cigarettes smoked in the United States; (2) dioxin-like PCBs are neither formed nor destroyed, and the congener profile reported by Matsueda et

al. (1994) is not altered during combustion of cigarettes; and (3) all dioxin-like PCBs contributing to the TEQ are released from the tobacco during smoking. Based on these assumptions, the calculated annual emissions would be 0.020-g TEQ and 0.016-g TEQ for reference years 1987 and 1995, respectively.

11.4.6. Sewage Sludge Incineration

U.S. EPA (1996f) derived an emission factor of 5.4 μg of total PCBs per kg of dry sludge incinerated. This emission factor was based on measurements conducted at five multiple hearth incinerators controlled with wet scrubbers. In 1992, approximately 199 sewage sludge incineration facilities conbusted 0.865-million metric tons of dry sewage sludge (Federal Register, 1993b). Given this mass of sewage sludge incinerated, the estimated annual release of total PCBs to air annually is 4,670 g. However, it is not known what fraction of this annual emission is dioxin-like PCBs.

11.5. NATURAL SOURCES

11.5.1. Biotransformation of Other PCBs

Biologically mediated reductive dechlorination under anaerobic conditions to less chlorinated congeners followed by slow anaerobic and/or aerobic biodegradation is believed to be 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; and Schreiner et al., 1995) have revealed that more than two dozen strains of aerobic bacteria and fungi, which 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 the genus *Alcaligenes*. The major metabolic pathway involves addition of O_2 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.

However, 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-PCBs and higher chlorinated PCBs, the half-lives in fresh surface water and soil are likely to exceed 1 year. PCBs with all or most chlorines on one ring and PCBs with fewer than two chlorines in the ortho position tend to degrade more rapidly. For example, Gan and Berthouex (1994) monitored over a 5-year period the disappearance of PCB congeners applied to soil with sewage sludge. Three of the tetra- and penta-chlorinated 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-year period.

Until recent years, little investigation focused on anaerobic microbial dechlorination or degradation of PCBs even though most PCBs eventually accumulate in anaerobic sediments (Abramowicz, 1990; Risatti, 1992). Environmental dechlorination of PCBs via losses of meta and para chlorines has been reported in field studies for freshwater, estuarine, and marine anaerobic sediments including those from the Acushnet Estuary, the Hudson River, the Sheboygan River, New Bedford Harbor, Escambia Bay, Waukegan Harbor, the Housatonic River, and Woods Pond (Brown et al., 1987; Rhee et al., 1989; Van Dort and Bedard, 1991; Abramowicz, 1990; Bedard et al., 1995; and Bedard and May, 1996). The altered PCB congener distribution patterns found in these sediments (i.e., different patterns with increasing depth or distance from known sources of PCBs) have been interpreted as evidence that bacteria may dechlorinate PCBs in anaerobic sediment.

Results of laboratory studies reported recently confirm anaerobic degradation of PCBs. Chen et al. (1988) found that "PCB-degrading" bacteria from the Hudson River could significantly degrade the mono-, di-, and tri-PCB components of a 20-ppm Aroclor 1221 solution within 105 days. These congener groups make up 95 percent of Aroclor 1221. No degradation of higher chlorinated congeners (present at 30 ppb or less) was observed, and a separate 40-day experiment with tetra-PCB also showed no degradation.

Rhee et al. (1989) reported degradation of mono- to penta-substituted PCBs in contaminated Hudson River sediments held under anaerobic conditions in the laboratory (N_2 atmosphere) for 6 months at 25°C. Amendment of the test samples with biphenyl resulted in greater loss of PCB. No significant decreases in the concentrations of the more highly chlorinated (i.e., more than five chlorines) were observed. No evidence of degradation was

observed in samples incubated in CO_2/H_2 atmospheres. Abramowicz (1990) hypothesized that this result could be an indication that, in the absence of CO_2, a selection is imposed favoring organisms capable of degrading PCBs to obtain CO_2 and/or low molecular weight metabolites as electron receptors.

Risatti (1992) examined the degradation of PCBs at varying concentrations (10,000 ppm, 1,500 ppm, and 500 ppm) in the laboratory with "PCB-degrading" bacteria from Waukegan Harbor. After 9 months of incubation at 22°C, the 500-ppm and 1,500-ppm samples showed no change in PCB congener distributions or concentrations, thus indicating a lack of degradation. Significant degradation was observed in the 10,000-ppm sediment with at least 20 congeners ranging from TrCBs to PeCBs showing decreases.

Quensen et al. (1988) also demonstrated that microorganisms from PCB-contaminated sediments (Hudson River) dechlorinated most tri- through hexa-PCBs in Aroclor 1242 under anaerobic laboratory conditions. The Aroclor 1242 used to spike the sediment contained predominantly tri- and tetra-PCBs (85 mole percent). Three concentrations of the Aroclor, corresponding to 14-, 140-, and 700-ppm on a sediment dry-weight basis, were used. Dechlorination was most extensive at the 700-ppm test concentration; 53 percent of the total chlorine were removed in 16 weeks, and the proportion of TeCBs through HxCBs decreased from 42 to 4 percent. Much less degradation was observed in the 140-ppm sediment, and no observable degradation was found in the 14-ppm sediment. These results and those of Risatti (1992) suggest that the organism(s) responsible for this dechlorination may require relatively high levels of PCB as a terminal electron acceptor to maintain a growing population.

Quensen et al. (1990) reported that dechlorination of 500-ppm spike concentrations of Aroclor 1242, 1248, 1254, and 1260 by microorganisms from PCB-contaminated sediments in the Hudson River and Silver Lake occurred primarily at the meta- and para-positions; ortho-substituted mono- and di-PCBs increased in concentration. Significant decreases over the up to 50-week incubation period were reported for the following dioxin-like PCBs: 156, 167, 170, 180 and 189. Of the four dioxin-like TeCBs and PeCBs detected in the Aroclor spikes (i.e., IUPAC Nos. 77, 105, 114, and 118), all decreased significantly in concentration, with the possible exception of PeCB 114 in the Aroclor 1260-spiked sediment.

Nies and Vogel (1990) reported similar results with Hudson River sediments incubated anaerobically and enriched with acetone, methanol, or glucose. Approximately 300 ppm of Aroclor 1242 (31-mole percent TeCBs, 7-mole percent PeCBs, and 1-mole percent HxCBs) were added to the sediments prior to incubation for 22 weeks under an N_2 atmosphere. Significant dechlorination was observed, with dechlorination occurring primarily at the meta- and para-positions on the more highly chlorinated congeners (i.e., TeCBs, PeCBs, and HxCBs), resulting in the accumulation of less-chlorinated, primarily ortho-substituted mono- through tri-substituted congeners. No significant dechlorination was observed in the control samples (i.e., samples containing no added organic chemical substrate and samples that were autoclaved).

Bedard and May (1996) also reported similar findings in the sediments of Woods Pond, believed contaminated with Aroclor 1260. Significant decreases in the sediment concentrations of PCBs 118, 156, 170, and 180 (relative to their concentrations in Aroclor 1260) were observed. No increases or decreases were reported for the other dioxin-like PCBs.

Bedard et al. (1995) demonstrated that it is possible to stimulate substantial microbial dechlorination of the highly chlorinated PCB mixture Aroclor 1260 *in situ* with a single addition of 2,6-dibromobiphenyl. Bedard et al. (1995) added 365 g of 2,6-dibromobiphenyl to 6-foot diameter submerged caissons containing 400-kg sediment (dry weight) and monitored the change in PCB congener concentrations for a period of 1 year. At the end of the observation period, the hexa- through mono-chlorinated PCBs decreased 74 percent in the top of the sediment and 69 percent in the bottom. The average number of chlorines per molecule dropped 21 percent from 5.83 to 4.61, with the largest reduction observed in meta-chlorines (54 percent reduction) followed by para-chlorines (6 percent). The dechlorination stimulated by 2,6-dibromobiphenyl selectively removed meta-chlorines positioned next to other chlorines.

The findings of these latter studies are significant, because removal of meta- and para-chlorines from the dioxin-like PCBs should reduce their toxicity and bioaccumulative potential and also form less chlorinated congeners that are more amenable to aerobic biodegradation.

Van Dort and Bedard (1991) reported the first experimental demonstration of biologically-mediated ortho-dechlorination of a PCB and stoichiometric conversion of that

PCB congener (2,3,5,6-TeCB) to less chlorinated forms. In that study, 2,3,5,6-TeCB was incubated under anaerobic conditions with unacclimated methanogenic pond sediment for 37 weeks, with reported dechlorination to 2,5-DCB (21 percent); 2,6-DCB (63 percent); and 2,3,6-TrCB (16 percent).

11.5.2. Photochemical Transformation of Other PCBs

Photolysis and photo-oxidation may be major pathways for destruction of PCBs in the environment. Research reported to date and summarized below indicates that ortho-substituted chlorines are more susceptible to photolysis than are meta- and para-substituted congeners. Thus, photolytic formation of more toxic dioxin-like PCBs may occur. Oxidation by hydroxyl radicals, however, apparently occurs preferentially at the meta- and para-positions thus resulting in a net decrease rather than a net increase in the environmental load of dioxin-like PCBs.

Based on the data available in 1983, Leifer et al. (1983) concluded that all PCBs, especially the more highly chlorinated congeners and those that contain two or more chlorines in the ortho-position, photodechlorinate. In general, as the chlorine content increases, the photolysis rate increases. More recently, Lepine et al. (1992) exposed dilute solutions (4 ppm) of Aroclor 1254 in cyclohexane to sunlight for 55 days in December and January. Congener-specific analysis indicated that the amounts of many higher chlorinated congeners, particularly mono-ortho-substituted congeners decreased, while those of some lower chlorinated congeners increased. The results for the dioxin-like PCBs indicated a 43.5 percent decrease in the amount of PeCB 114; a 73.5 percent decrease in the amount of HxCB 156; and a 24.4 percent 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 percent and 0.43 percent, 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 gaseous-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 the measurements of Atkinson (1987) 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 increases with increasing degree of chlorination. Table 11-14 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 (i.e., 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 stearic hindrance effects. Based upon their kinetic measurements and reported steady-state aqueous system OH concentrations or estimates of OH radical production rates, Sedlak and Andren (1991) 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.

Table 11-1. Current Dioxin-Like PCB Emission Estimates for the United States (Reference Year 1995)

Emission Source	Emissions (g TEQ/yr) to Media															
	Air				Water				Land				Product			
	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]
Releases of Commercial PCBs																
Approved disposal					NA	NA	NA	NA					NA	NA	NA	NA
Accidental releases													NA	NA	NA	NA
Municipal Sludge Disposal																
Nonincinerated sludge	NA	NA	NA	NA	NA	NA	NA	NA	45.2	101	226	H/M	1.5	3.4	7.5	H/M
Chemical Manuf./Processing Sources																
All manuf./processing sources																
Combustion Sources																
Municipal waste incineration													NA	NA	NA	NA
Industrial wood combustion													NA	NA	NA	NA
Medical waste incineration													NA	NA	NA	NA
Tire combustion													NA	NA	NA	NA
Cigarettes					NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sewage sludge incineration																

[a] CR = Confidence rating. First letter is rating assigned to "production" estimate; second letter is rating assigned to "emission factor." (See Section 2.1 and Table 2-1 for details.)
H = High Confidence.
M = Medium Confidence.
L = Low Confidence.

NA = Not applicable.
NEG = Expected to be negligible or nonexistent.
BLANK = Insufficient data available upon which to base an estimate.
G TEQ/yr = grams toxic equivalent per year.

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Table 11-2. Current Dioxin-Like PCB Emission Estimates for the United States (Reference Year 1987)

Emission Source	Emissions (g TEQ/yr) to Media															
	Air				Water				Land				Product			
	Lower	Central	Upper	CR(a)	Lower	Central	Upper	Cr(a)	Lower	Central	Upper	CR(a)	Lower	Central	Upper	CR(a)
Releases of Commercial PCBs																
Approved disposal					NA	NA	NA	NA					NA	NA	NA	NA
Accidental releases													NA	NA	NA	NA
Municipal Sludge Disposal																
Nonincinerated sludge	NA	NA	NA	NA	NA	NA	NA	NA	88	197	440	H/M	1.5	3.4	7.5	H/M
Chemical Manuf./Processing Sources																
All manuf./processing sources																
Combustion Sources																
Municipal waste incineration													NA	NA	NA	NA
Industrial wood combustion													NA	NA	NA	NA
Medical waste incineration													NA	NA	NA	NA
Tire combustion													NA	NA	NA	NA
Cigarettes					NA	NA	NA	NA					NA	NA	NA	NA
Sewage sludge incineration																

[a] CR = Confidence rating. First letter is rating assigned to "production" estimate; second letter is rating assigned to "emission factor." (See Section 2.1 and Table 2-1 for details.)
H = High Confidence.
M = Medium Confidence.
L = Low Confidence.

NA = Not applicable.
NEG = Expected to be negligible or nonexistent.
BLANK = Insufficient data available upon which to base an estimate.
G TEQ/yr = grams toxic equivalent per year.

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Table 11-3. Weight Percent Concentrations of Dioxin-like PCBs in Aroclors, Clophens, and Kanechlors

Dioxin-Like PCB Congener	IUPAC Number	Number of Samples Analyzed	Number of Detections	Mean Conc. (ND = 0) (g/kg)	TEQ Conc. (ND = 0) (mg/kg)	Mean Conc.[a] (ND = 1/2DL) (g/kg)	TEQ Conc.[a] (ND = 1/2DL) (mg/kg)
AROCLOR 1016							
3,3',4,4'-TCB	77	2	0	0	0	0	0
2,3,3',4,4'-PeCB	105	1	0	0	0	0	0
2,3,4,4',5-PeCB	114	1	0	0	0	0	0
2,3',4,4',5-PeCB	118	1	0	0	0	0	0
2',3,4,4',5-PeCB	123	1	0	0	0	0	0
3,3',4,4',5-PeCB	126	1	0	0	0	0	0
2,3,3',4,4',5-HxCB	156	1	0	0	0	0	0
2,3,3',4,4',5'-HxCB	157	1	0	0	0	0	0
2,3',4,4',5,5'-HxCB	167	1	0	0	0	0	0
3,3',4,4',5,5'-HxCB	169	2	0	0	0	0	0
2,2',3,3',4,4',5-HpCB	170	1	0	0	0	0	0
2,2',3,4,4',5,5'-HpCB	180	1	0	0	0	0	0
2,3,3',4,4',5,5'-HpCB	189	1	0	0	0	0	0
				Total TEQ =	0	Total TEQ =	0
AROCLOR 1221							
3,3',4,4'-TCB	77	1	1	4.00	2.00	4.00	2.00
2,3,3',4,4'-PeCB	105	1	0	0	0	0	0
2,3,4,4',5-PeCB	114	1	0	0	0	0	0
2,3',4,4',5-PeCB	118	1	1	4.50	0.45	4.50	0.45
2',3,4,4',5-PeCB	123	1	0	0	0	0	0
3,3',4,4',5-PeCB	126	1	0	0	0	0	0
2,3,3',4,4',5-HxCB	156	1	0	0	0	0	0
2,3,3',4,4',5'-HxCB	157	1	0	0	0	0	0
2,3',4,4',5,5'-HxCB	167	1	0	0	0	0	0
3,3',4,4',5,5'-HxCB	169	1	0	0	0	0	0
2,2',3,3',4,4',5-HpCB	170	0	--	--	--	--	--
2,2',3,4,4',5,5'-HpCB	180	0	--	--	--	--	--
2,3,3',4,4',5,5'-HpCB	189	1	0	0	0	0	0
				Total TEQ =	2.45	Total TEQ =	2.45
AROCLOR 1242, Clophen A-30, and Kanechlor 300							
3,3',4,4'-TCB	77	12	12	3.14	1.57	3.14	1.57
2,3,3',4,4'-PeCB	105	8	8	3.66	0.37	3.66	0.37
2,3,4,4',5-PeCB	114	5	2	1.55	0.77	1.66	0.83
2,3',4,4',5-PeCB	118	6	6	8.26	0.83	8.26	0.83
2',3,4,4',5-PeCB	123	6	4	1.53	0.15	1.58	0.16
3,3',4,4',5-PeCB	126	11	8	0.06	6.29	0.11	11.29
2,3,3',4,4',5-HxCB	156	6	5	0.48	0.24	0.52	0.26
2,3,3',4,4',5'-HxCB	157	5	1	0.004	0.002	0.11	0.06
2,3',4,4',5,5'-HxCB	167	5	1	0.004	0.00004	0.11	0.00
3,3',4,4',5,5'-HxCB	169	11	2	0.00002	0.0002	0.05	0.54
2,2',3,3',4,4',5-HpCB	170	3	2	0.38	0.04	0.46	0.05
2,2',3,4,4',5,5'-HpCB	180	2	1	0.30	0.003	0.43	0.004
2,3,3',4,4',5,5'-HpCB	189	4	0	0	0	0	0
				Total TEQ =	10.26	Total TEQ =	15.94
AROCLOR 1248, Clophen A-40, and Kanechlor 400							
3,3',4,4'-TCB	77	10	10	4.56	2.28	4.56	2.28
2,3,3',4,4'-PeCB	105	6	6	7.83	0.78	7.83	0.78
2,3,4,4',5-PeCB	114	4	3	5.05	2.53	5.06	2.53
2,3',4,4',5-PeCB	118	5	5	20.01	2.00	20.01	2.00
2',3,4,4',5-PeCB	123	4	4	2.12	0.21	2.12	0.21
3,3',4,4',5-PeCB	126	8	6	0.15	14.51	0.18	18.26
2,3,3',4,4',5-HxCB	156	5	5	1.41	0.70	1.41	0.70
2,3,3',4,4',5'-HxCB	157	4	3	0.33	0.16	0.34	0.17
2,3',4,4',5,5'-HxCB	167	4	2	0.25	0.002	0.26	0.003
3,3',4,4',5,5'-HxCB	169	9	3	0.01	0.13	0.05	0.47
2,2',3,3',4,4',5-HpCB	170	2	2	2.05	0.21	2.05	0.21
2,2',3,4,4',5,5'-HpCB	180	1	1	2.60	0.03	2.60	0.03
2,3,3',4,4',5,5'-HpCB	189	3	1	0.004	0.0004	0.10	0.01
				Total TEQ =	23.54	Total TEQ =	27.65

Table 11-3. Weight Percent Concentrations of Dioxin-like PCBs in Aroclors, Clophens, and Kanechlors (continued)

Dioxin-Like PCB Congener	IUPAC Number	Number of Samples Analyzed	Number of Detections	Mean Conc. (ND = 0) (g/kg)	TEQ Conc. (ND = 0) (mg/kg)	Mean Conc.[a] (ND = 1/2DL) (g/kg)	TEQ Conc.[a] (ND = 1/2DL) (mg/kg)
AROCLOR 1254, Clophen A-50, and Kanechlor 500							
3,3',4,4'-TCB	77	12	9	0.59	0.30	0.64	0.32
2,3,3',4,4'-PeCB	105	9	9	26.67	2.67	26.67	2.67
2,3,4,4',5-PeCB	114	6	3	15.98	7.99	16.08	8.04
2,3',4,4',5-PeCB	118	8	8	66.33	6.63	66.33	6.63
2',3,4,4',5-PeCB	123	5	5	5.35	0.53	5.35	0.53
3,3',4,4',5-PeCB	126	11	9	1.23	122.95	1.26	125.68
2,3,3',4,4',5-HxCB	156	7	7	11.22	5.61	11.22	5.61
2,3,3',4,4',5'-HxCB	157	6	5	1.49	0.75	1.53	0.77
2,3',4,4',5,5'-HxCB	167	7	6	2.47	0.02	2.47	0.02
3,3',4,4',5,5'-HxCB	169	11	6	0.10	1.01	0.15	1.50
2,2',3,3',4,4',5-HpCB	170	5	5	5.80	0.58	5.80	0.58
2,2',3,4,4',5,5'-HpCB	180	4	4	6.63	0.07	6.63	0.07
2,3,3',4,4',5,5'-HpCB	189	4	1	0.07	0.01	0.21	0.02
				Total TEQ =	149.12	Total TEQ =	152.44
AROCLOR 1260, Clophen A-60, and Kanechlor 600							
3,3',4,4'-TCB	77	12	6	0.16	0.08	0.21	0.10
2,3,3',4,4'-PeCB	105	8	8	1.56	0.16	1.56	0.16
2,3,4,4',5-PeCB	114	6	3	1.00	0.50	1.10	0.55
2,3',4,4',5-PeCB	118	8	7	11.14	1.11	11.14	1.11
2',3,4,4',5-PeCB	123	5	1	0.00	0.00	0.11	0.01
3,3',4,4',5-PeCB	126	11	7	2.30	230.22	2.33	233.27
2,3,3',4,4',5-HxCB	156	8	8	7.53	3.77	7.53	3.77
2,3,3',4,4',5'-HxCB	157	5	5	2.28	1.14	2.28	1.14
2,3',4,4',5,5'-HxCB	167	7	6	3.23	0.03	3.23	0.03
3,3',4,4',5,5'-HxCB	169	11	5	0.21	2.09	0.24	2.37
2,2',3,3',4,4',5-HpCB	170	5	5	28.98	2.90	28.98	2.90
2,2',3,4,4',5,5'-HpCB	180	4	4	66.30	0.66	66.30	0.66
2,3,3',4,4',5,5'-HpCB	189	5	5	2.16	0.22	2.16	0.22
				Total TEQ =	242.87	Total TEQ =	246.29

[a] Calculated for a congener only when at least one sample contained detectable levels of that congener.

References:
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)

g/kg = grams per kilogram.
mg/kg = milligrams per kilogram.

Table 11-4. Disposal Requirements for PCBs and PCB Items

	Waste Characterization		Disposal Requirements
PCBs	Mineral oil dielectric fluids from PCB transformers	Those analyzing > 500 ppm PCB	Annex I incinerator[a]
	Mineral oil dielectric fluids from PCB-contaminated transformers	Those analyzing 50-500 ppm PCB	Annex I incinerator High efficiency boiler (40 CFR 761.10(a)(2)(iii)) Other approved incinerator[b] Annex II chemical waste landfill[c]
	PCB liquid wastes other than mineral oil dielectric fluid	Those analyzing > 500 ppm PCB	Annex I incinerator
		Those analyzing 50-500 ppm PCB	Annex I incinerator High efficiency boiler (40 CFR 761.10(a)(2)(iii)) Other approved incinerator[b] Annex II chemical waste landfill[c]
	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		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 per Annex I or Annex II
		Those not containing PCB fluids	Annex I incinerator or Annex II chemical waste landfill
PCB Containers	Those used to contain only PCBs at a concentration < 500 ppm		As municipal solid waste provided any liquid PCBs are drained prior to disposal
	Other PCB containers		Annex I incinerator Annex II, provided any liquid PCBs are drained prior to disposal Decontaminate per Annex IV

[a] Annex I incinerator defined in 40 CFR 761.40.
[b] Requirements for other approved incinerators are defined in 40 CFR 761.10(e).
[c] Annex II chemical waste landfills are described in 40 CFR 761.41. Annex II disposal is permitted if the PCB waste contains less than 500 ppm PCB and is not ignitable as per 40 CFR Part 761.41(b)(8)(iii).
[d] Disposal of containerized capacitors in Annex II landfills was permitted until March 1, 1981; thereafter, only Annex I incineration has been permitted.
ppm = parts per million

Source: U.S. EPA (1987c).

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Table 11-5. Offsite Transfers of PCBs Reported in TRI (1988-1993)

Year	No. of TRI Forms Filed	Reported Transfers (kg)		
		Transfers to POTWs	Transfers for Treatment/ Disposal	TOTAL TRANSFERS
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

kg = kilograms.
POTWs = publicly-owned treatment works.

Sources: U.S. EPA (1993h); U.S. EPA (1995g)

NA = Not available.

Table 11-6. Releases of PCBs Reported in TRI (1988-1993)

Year	No. of TRI Forms Filed	Reported Releases (kg)					
		Fugitive or Nonpoint Air Emissions	Stack or Point Air Emissions	Surface Water Discharges	Underground Injection	Releases to Land	TOTAL RELEASES
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

Sources: U.S. EPA (1993h); U.S. EPA (1995g)

NA = Not available.

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Table 11-7. Aroclor Concentrations Measured in EPA's National Sewage Sludge Survey

Aroclor	Percent Detected	Maximum Concentration (ng/kg)	Median Concentration (ng/kg)	
			Nondetects Set to Det. Limit	Nondetects Set to Zero
1016	0	--	--	0
1221	0	--	--	0
1232	0	--	--	0
1242	0	--	--	0
1248	9	5.20	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

Source: U.S. EPA (1996a); for POTWs with multiple samples, the pollutant concentrations were averaged before the summary statistics presented in the table were calculated. All concentrations are in units of nanograms per kilogram (ng/kg) dry weight.

Table 11-8. Dioxin-Like PCB Concentrations Measured in 99 Sludges Collected from 75 U.S. POTWs During 1994

Congener	IUPAC Number	Percent Detected	Maximum Concentration (ng/kg)	Median Concentration (ng/kg)		Mean Concentration (ng/kg)	
				Nondetects Set to Det. Limit	Nondetects Set to Zero	Nondetects Set to Det. Limit	Nondetects Set to Zero
3,3',4,4'-TCB	77	98	22,900	720	720	1,898 (3,648)	1,898 (3,648)
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	96	3,020	85.3	85.3	198 (404)	197 (404)
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	17	1,470	14.7	0	32.3 (146)	19.8 (147)
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*				23.9	22.6	48.1 (89.2)	47.5 (89.4)

Source: Green et al. (1995); Cramer et al. (1995)

* 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.
Ng/kg = nanograms per kilogram.

NOTE: Blank cells indicate that no measurements of these congeners were made.

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Table 11-9. Quantity of Sewage Sludge Disposed Annually by Primary, Secondary, or Advanced Treatment POTWs and Potential Dioxin-Like PCB TEQ Releases

Use/Disposal Practice	Volume Disposed (thousands of dry metric tons/year)	Percent of Total Volume	Potential TEQ Release[c] (g of TEQ/yr)
Land Application	1,714	32.0[e]	82.3
Distribution and Marketing	71	1.3	3.4
Surface Disposal Site/Other	396	7.4	19.0
Sewage Sludge Landfill	157	2.9	7.5
Co-Disposal Landfills[a]	1,819	33.9	87.3
Sludge Incinerators and Co-Incinerators[b]	865	16.1	(f)
Ocean Disposal	(336)[d]	(6.3)[d]	(0)[d]
TOTAL	5,357	100.0	199.5

[a] Landfills used for disposal of sewage sludge and solid waste residuals.

[b] Co-incinerators treat sewage sludge in combination with other combustible waste materials.

[c] Potential PCB TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (i.e., column 2) by the average of the mean dioxin TEQ concentrations in sludge reported by Green et al. (1995) and Cramer et al. (1995) (i.e., 48-ng TEQ/kg).

[d] 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 in the oceans in 1988 has not been determined.

[e] Includes 21.9 percent applied to agricultural land, 2.8 percent applied as compost, 0.6 percent applied to forestry land, 3.1 percent applied to "public contact" land, 1.2 percent applied to reclamation sites, and 2.4 percent applied in undefined settings.

[f] See Section 11.4.6 for for a discussion of dioxin-like PCB releases to air from sewage sludge incinerators.

Sources: Federal Register (1990); Federal Register (1993b); Green et al. (1995); Cramer et al. (1995).

Table 11-10. PCB Congener Group Emission Factors for Industrial Wood Combustors

Congener Group	Number of Sites	Number of Detections	Maximum Concentration Detected (ng/kg wood)	Mean Concentration (ng/kg)	
				Nondetects Set to Det. Limit	Nondetects Set to Zero
Monochlorobiphenyls	2	1	32.1	39.4	16.0
Dichlorobiphenyls	2	1	23.0	50.9	11.5
Trichlorobiphenyls	2	1	19.7	42.3	9.8
Tetrachlorobiphenyls	2	0	--	22.7	--
Pentachlorobiphenyls	2	0	--	17.6	--
Hexachlorobiphenyls	2	0	--	17.0	--
Heptachlorobiphenyls	2	0	--	17.9	--
Octachlorobiphenyls	2	0	--	15.8	--
Nonachlorobiphenyls	2	0	--	25.0	--
Decachlorobiphenyls	2	0	--	36.3	--

ng/kg = nanograms per kilogram.

Source: CARB (1990e; 1990f)

Table 11-11. PCB Congener Group Emission Factors for Medical Waste Incinerators (MWIs)

Congener Group	Mean Emission Factor (ng/kg) (2 MWIs without APCD)		Mean Emission Factor (ng/kg) (2 MWIs with APCD)	
	Nondetects Set to Det. Limit	Nondetects Set to Zero	Nondetects Set to Det. Limit	Nondetects Set to Zero
Monochlorobiphenyls	0.059	0.059	0.311	0
Dichlorobiphenyls	0.083	0.083	0.340	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

APCD = Air Pollution Control Device
ng/kg = nanograms per kilogram.
-- = Not reported.

Source: See Section 3.3 for details on tested facilities.

Table 11-12. PCB Congener Group Emission Factors for a Tire Combustor

Congener Group	Number of Samples	Number of Detections	Maximum Concentration Detected (ng/kg)	Mean Emission Factor (ng/kg)	
				Nondetects Set to Det. Limit	Nondetects Set to Zero
Monochlorobiphenyls	3	0	--	0.04	--
Dichlorobiphenyls	3	1	34.8	11.7	11.6
Trichlorobiphenyls	3	1	29.5	11.8	9.8
Tetrachlorobiphenyls	3	0	--	10.0	--
Pentachlorobiphenyls	3	2	2,724	1,092	1,092
Hexachlorobiphenyls	3	1	106.5	55.9	35.5
Heptachlorobiphenyls	3	1	298.6	107.7	99.5
Octachlorobiphenyls	3	0	--	20.9	--
Nonachlorobiphenyls	3	0	--	17.7	--
Decachlorobiphenyls	3	0	--	41.9	--

ng/kg = nanograms per kilogram.

Source: CARB (1991a)

Table 11-13. Dioxin-Like PCB Concentrations in Cigarette Tobacco

Congener	IUPAC Number	Concentrations in brands from various countries (pg/pack)						
		U.S. Brands (Avg of 7 brands)	Japan (Avg of 6 brands)	United Kingdom (Avg of 3 brands)	Taiwan (1 brand)	China (1 brand)	Denmark (1 brand)	Germany (1 brand)
3,3',4,4'-TCB	77	105.7	70.2	53.0	133.9	12.6	21.7	39.3
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*		0.68	0.82	0.64	1.54	0.25	0.24	0.76

Source: Matsueda et al. (1994)

NOTE: Blank cells indicate that no measurements of these congeners were made.

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Table 11-14. Estimated Tropospheric Half-Lives of Dioxin-Like PCBs with Respect to Gas-Phase Reaction with the OH Radical

Congener Group	Dioxin-Like Congener	Estimated OH Reaction Rate Constant (10^{-12} cm^3/molecule-sec)	Estimated Tropospheric Lifetime (days)[a]	Estimated Tropospheric Half-Life (days)[a]
TCB	3,3',4,4'-TCB	0.583	25	17
PeCB	2,3,3',4,4'-PeCB	0.299	48	34
	2,3,4,4',5-PeCB	0.383	38	26
	2,3',4,4',5-PeCB	0.299	48	34
	2',3,4,4',5-PeCB	0.482	30	21
	3,3',4,4',5-PeCB	0.395	37	25
HxCB	2,3,3',4,4',5-HxCB	0.183	79	55
	2,3,3',4,4',5'-HxCB	0.214	68	47
	2,3',4,4',5,5'-HxCB	0.214	68	47
	3,3',4,4',5,5'-HxCB	0.266	54	38
HpCB	2,2',3,3',4,4',5-HpCB	0.099	147	102
	2,2',3,4,4',5,5'-HpCB	0.099	147	102
	2,3,3',4,4',5,5'-HpCB	0.125	116	80

cm^3 = cubic centimeters.

[a] Calculated using a 24-hour average OH radical concentration of 8×10^5 molecule/cm^3.

Source: Atkinson (1995) [Based on Atkinson (1991) and Kwok et al. (1995)].

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REFERENCES

Abramowicz, D. (1990) Aerobic and anaerobic biodegradation of PCBs: A review. Critical Reviews in Biotechnology. 10(3):241-251.

Adriaens, P.; Grbic-Galic, D. (1992) Effect of cocontaminants and concentration on the anaerobic biotransformation of PCDD/F in methanogenic river sediments. Organohalogen Compounds 8:209-212.

Adriaens, P.; Grbic-Galic, D. (1993) Reductive dechlorination of PCDD/F by anaerobic cultures and sediments. Organohalogen Compounds 12:107-110.

Adriaens, P.; Fu, Q.; Grbic-Galic, D. (1995) Bioavailability and transformation of highly chlorinated dibenzo-p-dioxins and dibenzofurans in anaerobic soils and sediments. Environ. Sci. Technol. 29(9):2252-2260.

Advanced Technology Systems, Inc. (1995) Report on measurement of hazardous air pollutants from aluminum melt furnace operations at Ravenswood Aluminum Corporation. Monroeville, PA: Advanced Technology Systems, Inc.

AHA. American Hospital Association. (1995) Comments by the American Hospital Association in review of *Estimating Exposures to Dioxin-Like Compounds* (EPA/600/688/005Ca-c; June 1994; External Review Draft). Public Comment Number EXP-48-A1, received January 17, 1995.

AHA. American Hospital Association. (1997) Letter dated January 20, 1997, from V. James McLarney, Associate Vice President, American Hospital Association (AHA), Chicago, IL, to Mr. John Schaum, National Center for Environmental Assessment, U.S. Environmental Protection Agency, Washington, D.C. (with attachments).

Ahlborg, V.G.; Becking, G.C.; Birnbaum, L.S.; Brower, A.; Derks, H.J.G.M.; Feeley, M.; Golor, C.; Hanberg, A.; Larsen, J.C.; Liem, A.K.D.; Safe, S.H.; Schlatter, C.; Waern, F.; Younes, M.; Yränkeikki, E. (1994) Toxic equivalency factors for dioxin-like PCBs. Chemosphere 28(6):1049-1067.

AISI. American Iron and Steel Institute. (1990) Annual statistical report - 1989. Washington, D.C.: American Iron and Steel Institute.

AISI. American Iron and Steel Institute. (1995) Annual statistical report - 1994. Washington, D.C.: American Iron and Steel Institute.

Aittola, J.; Paasivirta, J.; Vattulainen, A. (1992) Measurements of organochloro compounds at a metal reclamation plant. Organohalogen Compounds 9:9-12.

Aittola, J.P. (1993) Environmental emissions from landfill fires, preliminary investigation. Viatek Topiola Og, Espoo, Finland.

Albro, P.W.; Parker, C.E. (1979) Comparison of the compositions of Aroclor 1242 and Aroclor 1016. Journal of Chromatography 169:161-166.

Albro, P.W.; Corbett, J.T.; Schroeder, J.L. (1981) Quantitative characterization of polychlorinated biphenyl mixtures (Aroclors® 1248, 1254, and 1260) by gas chromatography using capillary columns. Journal of Chromatography 205:103-111.

Amendola, G.A.; Barna, D.R. (1989) USEPA petroleum refinery dioxin screening survey: BP Oil-Lima, Ohio Refinery. Westlake, OH: U.S. Environmental Protection Agency, Region 5, Environmental Sciences Division.

American Forest & Paper Association (1997) Paper, paperboard & wood pulp statistics: data through 1996. Washington, DC: American Forest & Paper Association.

American Paper Institute (1992) Statistics of paper, paperboard & wood pulp: data through 1991. New York, NY: American Paper Institute.

Atkinson, R. (1987) Estimation of OH radical reaction rate constants and atmospheric lifetimes for polychlorobiphenyls, dibenzo-p-dioxins, and dibenzofurans. Environ. Sci. Technol. 21:305-307.

Atkinson, R. (1991) Atmospheric lifetimes of dibenzo-p-dioxins and dibenzofurans. The Science of the Total Environment. 104:17-33.

ATSDR. Agency for Toxic Substances and Disease Registry (1993) Toxicological profile for selected PCBs (Aroclor-1260, -1254, -1248, -1242, -1232, -1221, and -1016). Atlanta, GA: Public Health Service, ATSDR. NTIS Publication No. PB93-182517.

BAAQMD. Bay Area Air Quality Management District. (1996) Air emissions of dioxins in the Bay area. San Francisco, CA: Bay Area Air Quality Management District. March 27, 1996.

Bacher, R.; Swerev, M.; Ballschmiter, K. (1992) Profile and pattern of monochloro- through octachlorodibenzodioxins and -dibenzofurans in chimney deposits from wood burning. Environ. Sci. Technol. 26(8):1649-1655.

Ball, M.; Päpke, O.; Lis, A. (1990) Polychloridibenzodioxine und polychlordibenzofurane in cigaretterauch. Beiträge zur Tabakforschung International 14(6):393-402.

Ballschmiter, K.; Buchert, H.; Niemczyk, R.; Munder, A.; Swerev, M. (1986) Automobile exhausts versus municipal waste incineration as sources of the polychloro-dibenzodioxins (PCDD) and -furans (PCDF) found in the environment. Chemosphere 15(7):(901-915).

Barkovskii, A.L.; Adriaens, P. (1995) Reductive dechlorination of tetrachloro-dibenzo-p-dioxin partitioned from Passaic River sediments in an autochthonous microbial community. Organohalogen Compounds 24:17-21.

Barkovskii, A.L.; Adriaens, P. (1996) Microbial dechlorination of historically present and freshly spiked chlorinated dioxins and diversity of dioxin-dechlorinating populations. Applied and Environmental Microbiology 62(12):4556-4562.

Beard, A.; Krishnat, P.N.; Karasek, F.W. (1993) Formation of polychlorinated dibenzofurans by chlorination and de novo reactions with $FeCl_3$ in petroleum refining processes. Environ. Sci. Technol. 27(8):1505-1511.

Bedard, D.L.; Unterman, R.; Bopp, L.H.; Brennan, M.J.; Haberl, M.L.; Johnson, C. (1986) Rapid assay for screening and characterizing microorganisms for the ability to degrade polychlorinated biphenyls. Applied and Environmental Microbiology 51(4):761-768.

Bedard, D.L.; Smullen, L.A.; DeWeerd, K.A.; Dietrich, D.K.; Frame, G.M.; May, R.J.; Principe, J.M.; Rouse, T.O.; Fessler, W.A.; Nicholson, J.S. (1995) Chemical activation of microbially-mediated PCB dechlorination: a field study. Organohalogen Compounds 24:23-28.

Bedard, D.L.; May, R.J. (1996) Characterization of the polychlorinated biphenyls in the sediments of Woods Pond: evidence for microbial dechlorination of Aroclor 1260 in situ. Environ. Sci. Technol. 30(1):237-245.

Bergström, J.; Björner, B. (1992) Dioxiner ock bränder vid ovfallsuplag. Mamo, Miljökonsulterna i Studsvik AB. Stiftelsen reforsk. FoU nr 68. 94 p. (English summary).

Bingham, A.G.; Edmunds, C.J.; Graham, B.W.; Jones, M.T. (1989) Determination of PCDDs and PCDFs in car exhaust. Chemosphere 19(1-6):669-673.

Boers, J.P.; de Leer, E.W.B.; Gramberg, L.; de Koning, J. (1993) Levels of coplanar PCBs in flue gases of high temperature processes and their occurrence in environmental samples. Organohalogen Compounds 11:233-236.

Bowes, G.W.; Mulvihill, M.J.; Simoneit, B.R.T.; Burlingame, A.L.; Risebrough, R.W. (1975a) Identification of chlorinated dibenzofurans in American polychlorinated biphenyls. Nature 256:305-307.

Bowes, G.W.; Mulvihill, M.J.; DeCamp, M.R.; Kende, A.S. (1975b) Gas chromatographic characteristics of authentic chlorinated dibenzofurans; identification of two isomers in American and Japanese polychlorinated biphenyls. J. Agric. Food Chem. 23(6):1222-1223.

Bremmer, H.J.; Troost, L.M.; Kuipers, G.; DeKoning, J.; Sein, A.A. (1994) Emissions of dioxins in The Netherlands. National Institute of Public Health and Environmental Protection (RIVM) and Netherlands Organization for Applied Scientific Research (TNO). Report No. 770501018.

Brown, J.F. (1994) Determination of PCB metabolic, excretion, and accumulation rates for use as indicators of biological response and relative risk. Environ. Sci. Technol. 28(13):2295-2305.

Brown, J.F.; Bedard, D.L.; Brennan, M.J.; Carnahan, J.C.; Feng, H.; Wagner, R.E. (1987) Polychlorinated biphenyl dechlorination in aquatic sediments. Science 236:709-712.

Brown, J.F.; Carnahan, J.C.; Dorn, S.B.; Groves, J.T.; Ligon, W.V., May, R.J.; Wagner, R.E.; Hamilton, S.B. (1988) Levels of bioactive PCDF congeners in PCB dielectric fluids from capacitors and transformers. Chemosphere 17(9):1697-1702.

Brown, J.F.; Frame, G.M.; Olson, D.R.; Webb, J.L. (1995) The sources of the coplanar PCBs. Organohalogen Compounds 26:427-430.

Brunner, C.R. (1992) Sewage sludge. In: Buonicore, A.J., Davis, W.T., eds., Air pollution engineering manual. Air and Waste Management Association. New York, NY: Van Nostrand Reinhold. pp. 296-311.

Bruzy, L.P.; Hites, R.A. (1995) Estimating the atmospheric deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans from soil. Environ. Sci. Technol. 29:2090-2098.

Bryant, J.G. (1993) Chlorinated benzenes. In: Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. 6. pp. 87-100.

Buckland, S.J.; Dye, E.A., Leathem, S.V.; Taucher, J.A. (1994) The levels of PCDDs and PCDFs in soil samples collected from conservation areas following brush fires. Organohalogen Compounds. 20:85-89.

Bumb, R.R.; Crummett, W.B.; Cutie, S.S.; Gledhill, J.R.; Hummel, R.H.; Kagel, R.O.; Lamparski, L.L.; Luoma, E.V.; Miller, D.L.; Nestrick, T.J.; Shadoff, L.A.; Stehl, R.H.; Woods,J.S. (1980) Trace chemistries of fire: a source of chlorinated dioxins. Science 210(4468):385-390.

Buonicore, A.J. (1992a) Control of gaseous pollutants. In: Buonicore, A.J., Davis, W.T., eds., Air pollution engineering manual. Air and Waste Management Association. New York, NY: Van Nostrand Reinhold.

Buonicore, A.J. (1992b) Medical waste incineration. In: Buonicore, A.J., Davis, W.T., eds., Air pollution engineering manual, Air and Waste Management Association. New York, NY: Van Nostrand Reinhold.

Buser, H.R.; Bosshardt, H.P. (1976) Determination of polychlorinated dibenzo-p-dioxins and dibenzofurans in commercial pentachlorophenols by combined gas chromatography-mass spectrometry. Journal of the AOAC 59(3):562-569.

Cains, P.W.; Dyke, P. (1994) Emissions of chlorinated dibenzodioxins and dibenzofurans from waste combustion plants in the UK. Organohalogen Compounds 20:271-276.

California Regional Water Quality Control Board (CRWQCB) (1996) Memorandum to David Cleverly (U.S. Environmental Protection Agency) from Lila Tang (California Regional Water Quality Control Board).

Capes, C.E. (1983) Size enlargement. In: Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. 21:77-105. New York, NY: John Wiley and Sons.

CARB (California Air Resources Board) (1987a) Determination of PCDD and PCDF emissions from motor vehicles. Draft report. October 1987. Test Report No. C-86-029.

CARB (California Air Resources Board) (1990a) ARB evaluation test conducted on a hospital waste incinerator at Los Angeles Co. - USC Medical Center Los Angeles, California. Engineering Evaluation Branch, Monitoring and Laboratory Division. Test Report C-87-122.

CARB (California Air Resources Board) (1990b) Evaluation on a woodwaste fired incinerator at Koppers Company, Oroville,California. Test Report No. C-88-065. Engineering Evaluation Branch, Monitoring and Laboratory Division. May 29, 1990.

CARB (California Air Resources Board) (1990c) Evaluation test on two propane fired crematories at Camellia Memorial Lawn Cemetery. Test Report No. C-90-004. Engineering Evaluation Branch, Monitoring and Laboratory Division. Preliminary Draft.

CARB (California Air Resources Board) (1990d) Compliance testing for non-criteria pollutants at a landfill flare. Confidential Report No. ERC-2. Engineering Evaluation Branch, Monitoring and Laboratory Division. [As reported in U.S. EPA, 1997b.]

CARB (California Air Resources Board) (1990e) Evaluation test on a wood waste fired incinerator at Pacific Oroville Power Inc. Test Report No. C-88-050. Engineering Evaluation Branch, Monitoring and Laboratory Division. May 29, 1990.

CARB (California Air Resources Board) (1990f) Evaluation test on twin fluidized bed wood waste fueled combustors located in Cental California. Test Report No. C-87-042. Engineering Evaluation Branch, Monitoring and Laboratory Division. February 7, 1990.

CARB (California Air Resources Board) (1990g) Evaluation test on a wood waste fired incinerator at Louisiana Pacific Hardboard Plant, Oroville, CA. Test Report No. C-88-066. Engineering Evaluation Branch, Monitoring and Laboratory Division. [As reported in NCASI, 1995.]

CARB (California Air Resources Board) (1991a) Emissions test of the Modesto Energy Project tires-to-energy facility. Project No. C-87-072. Engineering Evaluation Branch, Monitoring and Laboratory Division. May 24, 1991.

CARB (California Air Resources Board) (1992a) Dioxin/furan estimates from a secondary aluminum facility. Confidential Report No. ERC-9. Engineering Evaluation Branch, Monitoring and Laboratory Division. [As reported in U.S EPA, 1997b.]

CARB (California Air Resources Board) (1992b) Emission measurements on delacquering system. Confidential Report No. ERC-32. Engineering Evaluation Branch, Monitoring and Laboratory Division. [As reported in U.S EPA, 1997b.]

CARB (California Air Resources Board) (1993a) Emissions measurement of toxic compounds from a cupola baghouse at a steel foundry. Confidential Report No. ERC-61. Engineering Evaluation Branch, Monitoring and Laboratory Division. [As reported in U.S. EPA, 1997b.]

Carpenter, C.; Schweer, G.; Stinnett, G.; Gabel, N. (1986) Exposure assessment for hexachlorobenzene. Washington, DC: U.S. Environmental Protection Agency, Office of Toxic Substances. EPA 560/5-86-019.

Carroll, W.F. (1996) Is PVC in house fires the great unknown source of dioxin? Fire and Materials. 20:161-166.

Cash, G. (1993) Document on dioxin/furan data call-ins [memorandum to John Schaum, U.S. EPA, Office of Research and Development]. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics. May 4, 1993.

CEQ (Council on Environmental Quality) (1997) Environmental Quality 1990. 25th Annual Report. Washington, DC: Council on Environmental Quality. Executive Office of the President of the United States.

ChemRisk (1993) Critique of dioxin factories. Prepared for: The Vinyl Institute, September 1993.

Chen, Y.R.; Chen, C.J.; Lee, C.C.; Chuong, C.Y. (1986) Reproductive effects of emissions from waste electrical products combustion. Presented at: Dioxin '86, 6th International Symposium on Chlorinated Dioxins and Related Compounds; Fukuoka, Japan.

Chen, M.; Hong, C.S.; Bush, B.; Rhee, G.Y. (1988) Anaerobic biodegradation of polychlorinated biphenyls by bacteria from Hudson River sediments. Ecotoxicol. and Environ. Safety 16:95-105.

Choudhry, G.G.; Webster, G.R.B. (1989) Environmental photochemistry of PCDDs. 2. Quantum yields of direct phototransformation of 1,2,3,7-tetra-, 1,3,6,8-tetra-, 1,2,3,4,6,7,8-hepta-, and 1,2,3,4,6,7,8,9-octachlorodibenzo-p-dioxin in aqueous acetonitrile and their sunlight half-lives. J. Agric. Food Chem. 37:254-261.

Christmann, W.; Klöppel, K.D.; Partscht, H.; Rotard, W. (1989a) Tetrachlorobenzoquinones, a source of PCDD/PCDF. Chemosphere 18(1-6):789-792.

Christmann, W.; Kasiske, D.; Klöppel, K.D.; Partscht, H.; Rotard, W. (1989b) Combustion of polyvinyl chloride - an important source for the formation of PCDD/PCDF. Chemosphere 19(1-6):387-392.

Clement, R.E.; Tosine, H.M; Osborne, J.; Ozvacic, V.; Wong, G. (1985a) Levels of chlorinated organics in a municipal incinerator. In: Keith, L.H.; Rappe, C.; Choudhary, G., eds., Chlorinated dioxins and dibenzofurans in the total environment II. Boston, MA: Butterworth Publishers.

Clement, R.E.; Tosine, H.M.; Ali, B. (1985b) Levels of polychlorinated dibenzo-p-dioxins and dibenzofurans in wood burning stoves and fireplaces. Chemosphere, 14:815-819.

Clement, R.E.; Tashiro, C. (1991) Forest fires as a source of PCDD and PCDF. Presented at: Dioxin '91, 11th International Symposium on Chlorinated Dioxins and Related Compounds; Research Triangle Park, NC; September 1991.

Cramer, P.H.; Heiman, J.; Horrigan, M.; Lester, R.; Armstrong, S. (1995) Results of a national survey for polychlorinated dibenzo-p-dioxins, dibenzofurans, and coplanar polychlorinated biphenyls in municipal biosolids. Organohalogen Compounds 24:305-308.

Cull, M.R.; Dobbs, A.J.; Goudot, M.; Schultz, N. (1984) Polychlorodibenzo-p-dioxins and dibenzofurans in technical pentachlorophenol-results of a collaborative analytical exercise. Chemosphere 13(10):1157-1165.

Curlin, L.C.; Bommaraju, T.V. (1991) Alkali & chlorine products. In: Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. pp. 938-1025.

deBoer, J. de; Stronck, C.J.N.; Traag, W.A.; van der Meer, J. (1993) Non-ortho and mono-ortho substituted chlorobiphenyls and chlorinated dibenzo-p-dioxins, and dibenzofurans in marine and freshwater fish and shellfish from The Netherlands. Chemosphere 26(10):1832-1842.

Dempsey, C.R.; Oppelt, E.T. (1993) Incineration of hazardous waste: A critical review update. Air & Waste 43: 25-73.

Deutsch, D.G.; Goldfarb, T.D. (1988) PCDD/PCDF contamination following a plastic fire in a university lecture hall building. Chemosphere 17(12):2423-2431.

DeVoogt, P.; Brinkman, U.A. (1989) Production, properties and usage of polychlorinated biphenyls. In: Halogenated biphenyls, terphenyls, napthalenes, dibenzodioxins and related products. Kimbrough, R.; Jensen, A.A., Eds. New York, NY: Elsevier Science Publishers.

Donnelly, J.R. (1992) Waste incineration sources: refuse. In: Buonicore, A.J.; Davis, W.T., eds, Air pollution engineering manual. Air and Waste Management Association. New York, NY: Van Nostrand Reinhold. pp. 263-275.

Douben, P.E.T.; Eduljee, G.H.; Dyke, P. (1995) A review of potential PCDD and PCDF emission sources in the UK. Organohalogen Compounds 24:131-136.

Doucet, L.G. (1995) Reassessment of dioxin emissions from MWIs. In: Comments submitted by the American Hospital Association to the U.S. Environmental Protection Agency on EPA's Reassessment Document for 2,3,7,8-TCDD and Related Compounds. January 13, 1995.

Duinker, J.C.; Hillebrand, M.T.J. (1983) Characterization of PCB components in Clophen formulations by capillary GC-MS and GC-ECD techniques. Environ. Sci. Technol. 17(8):449-456.

Duinker, J.C.; Schulz, D.E.; Petrick, G. (1988) Multidimensional gas chromatography with electron capture detection for the determination of toxic congeners of polychlorinated biphenyl mixtures. Analytical Chemistry 60:478-482.

Dumler-Gradl, R.; Thoma, H.; Vierle, O. (1995a) Research program on dioxin/furan concentration in chimney soot from house heating systems in the Bavarian area. Organohalogen Compounds 24:115-118.

Dumler-Gradl, R.; Tartler, D.; Thoma, H.; Vierle, O. (1995b) Detection of polybrominated diphenylethers (PBDE), dibenzofurans (PBDF) and dibenzodioxins (PBDD) in scrap of electronics and recycled products. Organohalogen Compounds 24:101-104.

Dung, M.; O'Keefe, P.W. (1992) Comparative rates of photolysis of polychlorinated dibenzofurans in organic solvents and in aqueous solutions. Organohalogen Compounds 8:233-236.

Dyke, P,; Coleman, P. (1995) Dioxins in ambient air, Bonfire Night 1994. Organohalogen Compounds 24:213-216.

Eduljee, G.H.; Dyke, P. (1996) An updated inventory of potential PCDD and PCDF emission sources in the UK. The Science of the Total Environment. 177:303-321.

EIA (Energy Information Administration) (1991) Estimates of U.S. biofuels consumption in 1990. Washington, DC: U.S. Department of Energy, Office of Coal, Nuclear, Electric and Alternate Fuels. DOE/EIA-0548(90).

EIA (Energy Information Administration) (1992) Fuel oil and kerosene sales 1991. Washington, DC: U.S. Department of Energy, Office of Oil and Gas. DOE/EIA-0535(91).

EIA (Energy Information Administration) (1993) Petroleum supply annual 1992, volume 1. Washington, DC: U.S. Deprtment of Energy, Office of Oil and Gas. DOE/EIA-0340(92)/1.

EIA (Energy Information Administration) (1994) Estimates of U.S. biomass energy consumption 1992. Washington, DC: U.S. Department of Energy, Office of Coal, Nuclear, Electric, and Alternative Fuels. DOE/EIA-0548(92).

EIA (Energy Information Administration) (1995a) Fuel oil and kerosene sales 1994. Washington, DC: U.S. Department of Energy, Office of Oil and Gas. DOE/EIA-0535(94).

EIA (Energy Information Administration) (1995b) Monthly energy review - October 1995. Washington, DC: U.S. Department of Energy, Office of Energy Markets and End Use. DOE/EIA-0035(95/10).

EIA (Energy Information Administration) (1995c) Annual energy review 1994. Washington, DC: U.S. Department of Energy, Office of Energy Markets and End Use. DOE/EIA-0884(94).

EIA (Energy Information Administration) (1997a) Fuel oil and kerosene sales 1996. Washington, DC: U.S. Department of Energy, Office of Oil and Gas. DOE/EIA-0535(96).

EIA (Energy Information Administration) (1997b) Annual energy review 1996. Washington, DC: U.S. Department of Energy, Office of Energy Markets and End Use. DOE/EIA-0384(96).

Environmental Risk Sciences, Inc. (1995) An analysis of the potential for dioxin emissions in the primary copper smelting industry. Prepared for the National Mining Association.

Envisage Environmental Inc. (1995) Test result summary for development of MACT standards. Testing location: Wabash Alloys. Richfield, OH: Envisage Environmental Inc.

EPRI (Electric Power Research Institute) (1994) Electric utility trace substances synthesis report. Palo Alto, CA: EPRI. EPRI TR-104614.

Erickson, M. (1986) Analytical chemistry of PCBs. Boston, MA, Butterworth Publishers.

Erickson, M.D.; Cole, C.J.; Flora, J.D.; Gorman, P.G.; Haile, C.L.; Hinshaw, G.D.; Hopkins, F.C.; Swanson, S.E. (1984) Thermal degradation products from dielectric fluids. Washington, D.C.: U.S. Environmental protection Agency, Office of Toxic Substances. EPA-560/5-84-009.

Esposito, M.P.; Tiernan, T.O.; Drydent, F.E. (1980). Dioxins. Prepared for the U.S. Environmental Protection Agency, Cincinnati, OH. November, 1980. EPA-600/2-80-197.

Federal Register (1979) Decision and emergency order suspending registrations for certain uses of 2,4,5-T and Silvex. F.R. (March 15) 44:15874-15920.

Federal Register (1982a) Polychlorinated biphenyls (PCBs) use in electrical equipment. F.R. (April 22) 47:17426.

Federal Register (1982b) Polychlorinated biphenyls (PCBs) manufacturing, processing, distribution in commerce and use prohibitions; use in electrical equipment. F.R. (August 25) 47:37342.

Federal Register (1985a) Regulation of fuels and fuel additives; Gasoline lead content: final rule and supplemental notice of proposed rulemaking. F.R. (March 7) 50:9386-9408.

Federal Register (1985b) Polychlorinated biphenyls in electrical transformers. F.R. (July 17) 50:29170.

Federal Register (1987a) Pentachlorophenol; amendment of notice of intent to cancel registrations. F.R. (January 2) 52:140-148.

Federal Register (1987b) Final determination and intent to cancel and deny applications for registrations of pesticide products containing pentachlorophenol (including but not limited to its salts and esters) for non-wood uses. F.R. (January 21) 52:2282-2293.

Federal Register (1987c) Polyhalogenated dibenzo-p-dioxins/dibenzofurans; testing and reporting requirements; final rule. F.R. (June 5) 52:21412-21452.

Federal Register (1987d) Appendix A to part 60 (Amended). F.R. (December 16) 52:47853-47856.

Federal Register (1990) National sewage sludge survey: availability of information and data, and anticipated impacts on proposed regulation. F.R. (November 9) 55:47210-47283.

Federal Register (1991a) Standards of performance for new stationary sources and final guidelines for municipal waste combustors. F.R. (February 11) 56:5488-5527.

Federal Register (1991b) Standards of performance for new stationary sources and guidelines for control of existing sources: municipal solid waste landfills: proposed rule and guideline. F.R. (May 30) 56:24468.

Federal Register (1991c) F.R. (February 21) 56:7134.

Federal Register (1993a) 2,3,5,6-Tetrachloro-2,5-cyclohexadiene-1,4-dione; proposed significant new use of a chemical substance. F.R. (May 12). 58:27980-27986.

Federal Register (1993b) Standards for the use or disposal of sewage sludge; final rules. F.R. (February 19) 58:9248-9404.

Federal Register (1993c) Chemicals; toxic chemical release reporting; community right-to-know; significant new use rule. F.R. (December 1) 58:63500-63518.

Federal Register (1993d) Standards of performance for new stationary sources and guidelines for control of existing sources: municipal solid waste landfills. F.R. (June 21) 58:33790-33792.

Federal Register (1995a) Proposed standards of performance for new stationary sources and emission guidelines for existing sources: medical waste incinerators. F.R. (February 27) 60:10654-010691.

Federal Register (1995b) Hazardous waste management system; identification and listing of hazardous waste: petroleum refining process wastes; land disposal restrictions for newly identified wastes; and CERCLA hazardous substance designation and reportable quantities. F.R. (November 20) 60:57747-57800.

Federal Register (1995c) National emission standards for hazardous air pollutants from secondary lead smelting: final rule. F.R. (June 23) 60:32587-32601.

Federal Register (1995d) National emission standards for hazardous air pollutants (NESHAP); secondary lead smelters; PVC in feedstock: proposed rule; amendments. F.R. (April 19) 60:19556.

Federal Register (1995e) Standards of performance for new stationary sources and emission guidelines for existing sources: municipal waste combustors, final rule. F.R. (December 19) 60:65387-65436.

Federal Register (1996a) Standards of performance for new stationary sources and guidelines for control of existing sources: municipal solid waste landfills: final rule and guideline. F.R. (March 12) 61:9905-9944.

Federal Register (1996b) Revised standards for hazardous waste combustors: proposed rule. F.R. (April 19) 61: 17357-17536.

Federal Register (1997a) Toxic chemicals; PCBs; submission of IRC No. 1000 to OMB; information collection activities. F.R. (January 21) 62:3035-3036.

Federal Register (1997b) F.R. (September 15) 62:48388-48394.

Fenton, M. (1996) Minerals yearbook - iron and steel. Washington, DC: U.S. Department of the Interior, U.S. Geological Survey.

Fiedler, H.; Hutzinger, O. (1992) Sources and sinks of dioxins: Germany. Chemosphere, 25:1487-1491.

Fiedler, H. (1993) Formation and sources of PCDD/PCDF. Organohalogen Compounds 11:221-228.

Fiedler, H.; Hutzinger, O.; Hosseinpour, J. (1993) Analyses and remedial actions following an accidental fire in a kindergarten. Organohalogen Compounds 14:19-22.

Firestone, D.; Ress, J.; Brown, N.L.; Barron, R.P.; Damico, J.N. (1972) Determination of polychlorodibenzo-p-dioxins and related compounds in commercial chlorophenols. J. Assoc. Off. Anal. Chem. 55(1):85-92.

Frame, G.M. (1995) A comprehensive, multicenter study of PCB elution on capillary GC columns. Pittcon '95. New Orleans, LA; March 8, 1995; Paper 717.

Friesen, J.K.; Muir, D.C.G.; Webster, G.R.B. (1990) Evidence of sensitized photolysis of polychlorinated dibenzo-p-dioxins in natural waters under sunlight conditions. Environ. Sci. Technol. 24(11):1739-1744.

Friesen, K.J.; Loewen, M.D.; Foga, M.M. (1993) Environmental aquatic photodegradation of chlorinated dibenzofurans and their photoproducts. Organohalogen Compounds 12:135-137.

Fuchs, R.; Towara, J.; Hutzinger, O. (1990) PCDD/F in the dry-cleaning process. Organohalogen Compounds 3:441-444.

Funcke, W.; Theisen, J.; Balfanz, E.; Konig, J. (1988) Polychlorierte Dibenzofurane (PCDF) und polychlorierte Dibenzo(p)dioxine (PCDD) in Ruckstanden und emissionen eines Brandes in Anwesenheit von PBC-haltigen materialien. Staub-Reinhaltung der Luft 48. 393-396.

Funk, S. (1996) Memorandum from S. Funk (EPA/OPP/HED) to Wm. Hazel (EPA/OPP/HED). Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs. May 28, 1996.

Galson Corporation (1995) Source test report: Source emission testing at Roth Brothers Smelting Corporation. East Syracuse, NY: Galson Corporation.

Gan, D.R.; Berthouex, P.M. (1994) Disappearance and crop uptake of PCBs from sludge-amended farmland. Water Environment Research 66(1):54-69.

Gertler, A.W.; Sagebiel, J.C.; Dippel, W.A.; Sheetz, L.H. (1996) A study to quantify on-road emissions of dioxins and furans from mobile sources: phase 2. Reno, NV: Desert Research Institute.

Gertler, A.; Sagebiel, J.; Dippel, W.; Faring, R. (1998) Measurement of dioxin and furan emissions factors from heavy duty diesel vehicles. J. of the Air and Waste Mgmt. Assoc. 48:276-278.

Gillespie, W.J. (1994) A summary of data reflective of U.S. pulp and paper industry progress in reducing the TCDD/TCDF content of effluents, pulps and wastewater treatment sludges. Organohalogen Compounds 20:255-260.

Gillespie, W.J. (1995) Progress in reducing the TCDD/TCDF content of effluents, pulps and wastewater treatment sludges from the manufacturing of bleached chemical pulp. Research Triangle Part, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

Gillespie, W.J. (1997) Letter to G. Schweer (Versar, Inc.) dated February 10, 1997. Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

Gilman, A.P.; Douglas, V.M.; Newhook, R.C.; Arbuckle, T.E. (1988) Chlorophenols and their impurities: a health hazard evaluation. Health and Welfare Canada. Document No. H46-2/88-110E.

Gobran, T.; Khurana, V.; MacPherson, K.; Waddell, D. (1995) PCDD/PCDF levels in raw sewage, final effluent, sludge, and ash samples from an Ontario wastewater treatment plant. Organohalogen Compounds 24:75-80.

Goldfarb, T.D.; Malloy, T.A.; Surico, M. (1992) PCDDs, PCDFs, PCBs, chlorophenols (CPs) and chlorobenzenes (CBzs) in samples from various types of composting facilities in the United States. Organohalogen Compounds 8:253-256.

Green, L.C.; Lester, R.L.; Armstrong, S.R. (1995) Comments on Estimating Exposures to Dioxin-Like Compounds: Review Draft. Cambridge, MA: Cambridge Environmental Inc. Dated January 12, 1995, and May 11, 1995.

Greenpeace (1993) Dioxin factories: a study of the creation and discharge of dioxins and other organochlorines from the production of PVC. Amsterdam, The Netherlands: Greenpeace International.

Greer, W.L.; Johnson, M.D.; Raught, E.C.; Steuch, H.E.; Trusty, C.B. (1992) Portland cement. In: Buonicore, A.J.; Davis, W.T.; eds. Air pollution engineering manual, Air and Waste Management Association. New York, NY: Van Nostrand Reinhold.

Gribble, G.W. (1994) The natural production of chlorinated compounds. Environ. Sci. Technol. 28(7):310A-319A.

Guerin, M.R.; Jenkins, R.A.; Tomkins, B.A. (1992) The chemistry of environmental tobacco smoke: composition and measurement. Chelsea, MI: Lewis Publishers.

Gullett, B.K.; Ryan, J.V. (1997) On-road sampling of diesel engine emissions of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran. Organohalogen Compounds 32:451-456.

Gutenmann, W.H.; Rutzke, M.; Kuntz, H.T.; Lisk, D.J. (1994) Elements and polychlorinated biphenyls in sewage sludges of large cities in the United States. Chemosphere 28(4):725-728.

Hagenmaier, H. (1986) Determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin in commercial chlorophenols and related products. Fresenius Z Anal Chem. 325:603-606.

Hagenmaier, H. (1987) Belastung der umwelt mit dioxinen. Institut für Organische Chemie der Universität Tübingen.

Hagenmaier, H.; Brunner, H. (1987) Isomer-specific analysis of pentachlorophenol and sodium pentachlorophenate for 2,3,7,8-substituted PCDD and PCDF at sub-ppb levels. Chemosphere 16:1759-1764.

Hagenmaier, H.; Dawidowsky, V.; Weber, U.B.; Hutzinger, O.; Schwind, K.H.; Thoma, H.; Essers, U.; Buhler, B.; Greiner, R. (1990) Emission of polyhalogenated dibenzodioxins and dibenzofurans from combustion-engines. Organohalogen Compounds 2:329-334.

Hagenmaier, H. (1994) Contributions of diesel-powered vehicles and wood burning to overall PCDD/PCDF emissions. Organohalogen Compounds 20:267-270.

Haglund, P.; Egeback, K.-E.; Jansson, B. (1988) Analysis of PBDD/F in vehicle exhaust. Presented at: Dioxin '88, 8th International Symposium on Chlorinated Dioxins and Related Compounds; Umea, Sweden; August 1988.

Hammerstrom, K.; Schweer, G.; Adkins, L.; Freed, J.; Chambers, T. (1985) Exposure assessment for polychlorinated biphenyls (PCBs): incidental production, recycling, and selected authorized uses. Washington, DC: U.S. Environmental Protection Agency, Office of Toxic Substances. EPA Contract No. 68-01-6271, Task No. 21.

Harnly, M.; Stephens, R.; McLaughlin, C.; Marcotte, J.; Petreas, M.; Goldman, L. (1995) Polychlorinated dibenzo-p-dioxin and dibenzofuran contamination at metal recovery facilities, open burn sites, and a railroad car incineration facility. Environ. Sci. Technol. 29(3):677-684.

Harrad, S.J.; Malloy, T.A.; Khan, M.A.; Goldfarb, T.D. (1991) Levels and sources of PCDDs, PCDFs, chlorophenols (CPs) and chlorobenzenes (CBzs) in composts from a municipal yard waste composting facility. Chemosphere 23(2):181-191.

Harrad, S.J.; Jones, K.C. (1992b) A source inventory and budget for chlorinated dioxins and furans in the United Kingdom environment. The Science of the Total Environment 126:89-107.

Heath (1995) Heath, Elizabeth of Research Triangle Institute, to Joseph Wood of Emission Standards Division, OAQPS, EPA, August 23, 1995. Memorandum "Assignment of Existing Cement Kilns to Model Kilns by Type of Process."

Heindl, A.; Hutzinger, O. (1987) Search for industrial sources of PCDD/PCDF. III. Short-chain chlorinated hydrocarbons. Chemosphere 16(8/9):1949-1957.

Helble, J.J. (1993) Analysis of dioxin emissions from the incineration of hazardous waste. Washington, DC: U.S. Environmental Protection Agency, Office of Solid Waste, Permits and State Programs Division.

Hengstmann, R.; Hamann, R.; Weber, H.; Kettrup, A. (1990) Impact of sewage sludge and sewer slimes by polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Organohalogen Compounds 4:407-412.

Hickey, W.J. (1995) Enhancing PCB biodegradatin in soil with chlorobenzoate-degrading inoculants. Organohalogen Compounds 24:29-32.

Himberg, K.; Sippola, E. (1990) Multidimensional gas chromatography - mass spectrometry as a method for the determination of coplanar PCB congeners. Organohalogen Compounds 4:183-186.

Ho, A.K.W.; Clement, R.E. (1990) Chlorinated dioxins/furans in sewage and sludge of municipal water pollution control plants. Chemosphere 20(10-12):1549-1552.

Holderman, T.S. (1995) Dioxin levels from D/F test rule data submittals. Memorandum from T.S. Holderman (EPA/OPPT/CMD) to A. Adenuga (Versar, Inc.). Dated Aug. 2, 1995.

Holderman, T.S.; Cramer, P.H. (1995) Updated results of polyhalogenated dibenzo-p-dioxin/dibenzofuran testing and reporting under the Toxic Substances Control Act (TSCA). Organohalogen Compounds 24:137-140.

Horstmann, M.; McLachlan, M.; Reissinger, M. (1992) Investigation of the origin of PCDD/CDF in municipal sewage. Organohalogen Compounds 9:97-100.

Horstmann, M.; McLachlan, M.; Reissinger, M. (1993a) Further investigations of the sources of PCDD/CDF in municipal sewage sludge. Organohalogen Compounds 11:293-296.

Horstmann, M.; McLachlan, M.; Reissinger, M.; Morgenroth, M. (1993b) An investigation of PCDD/CDF formation during textile production and finishing. Organohalogen Compounds 11:417-420.

Horstmann, M.; McLachlan, M.S. (1994a) Textiles as a source of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/CDF) in human skin and sewage sludge. Environ. Sci. & Pollut. Res. 1(1):15-20.

Horstmann, M.; McLachlan, M.S. (1994b) Polychlorinated dibenzo-p-dioxins and dibenzofurans in textiles and their transfer to human skin, sewage sludge and other matrices. Organohalogen Compounds 20:251-254.

Horstmann, M.; McLachlan, M.S. (1995) Concentrations of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in urban runoff and household wastewaters. Chemosphere 31(3):2887-2896.

Huang, C.W.; Miyata, H.; Lu, J.; Ohta, S.; Chang, T.; Kashimoto, T. (1992) Levels of PCBs, PCDDs and PCDFs in soil samples from incineration sites for metal reclamation in Taiwan. Chemosphere 24(11):1669-1676.

Huckins, J.N.; Stalling,D.L.; Petty, J.D. (1980) Carbon-foam chromatographic separation of non-*o*-*o*'-chlorine substituted PCBs from Aroclor mixtures. J. Assoc. Off. Anal. Chem. 63(4):750-755.

Hutzinger, O.; Fiedler, H. (1991a) Formation of dioxins and related compounds in industrial processes. In: Bretthauer, E.W.; Kraus, H.W.; di Domenico, A., eds. Dioxin perspectives. A pilot study on international information exchange on dioxins and related compounds. New York, NY: Plenum Press.

Hutzinger, O.; Fiedler, H. (1991b) Formation of dioxins and related compounds from combustion and incineration processes. In: Bretthauer, E.W.; Kraus, H.W.; di Domenico, A., eds. Dioxin perspectives. A pilot study on international information exchange on dioxins and related compounds. New York, NY: Plenum Press.

Hutzinger, O; Essers, U.; Hagenmaier, H. (1992) Untersuchungen zur emission halogenierter dibenzodioxine und dibenzofurane aus verbrennungsmortoren beim betrieb mit handelsüblichen betriebsstoffen. Universities of Bayreuth, Stuttgart and Tübingen, Germany. GSF-Forschungszentrum, Munich, Germany, ISSN 0937-9932.

Jager, J.; Wilken, M.; Zeschmar-Lahl, B. (1992) Dioxin und furan emissionen in Berlin eine hochrechnung. Staub-Reinhaltung der Luft. 52:99-106.

Jensen, S.; Sundström, G.; Frescati, L. (1974) Structures and levels of most chlorobiphenyls in two technical PCB products and in human adipose tissue. Ambio 3(2):70-76.

Kannan, N.; Tanabe, S.; Wakimoto, T.; Tatsukawa, R. (1987) Coplanar polychlorinated biphenyls in Aroclor and Kanechlor mixtures. J. Assoc. Off. Anal. Chem. 70(3):451-454.

Kieatiwong, S.; Nguyen, L.V.; Hebert, V.R.; Hackett, M.; Miller, G.C.; Miille, M.J.; Mitzel, R. (1990) Photolysis of chlorinated dioxins in organic solvents and on soils. Environ. Sci. Technol. 24(10):1575-1580.

Kirby, R. (1994) Petroleum refining industry - presence of dioxins and furans in wastewater generated by reforming operations. Washington, DC: U.S. Environmental Protection Agency, Office of Water, Engineering and Analysis Division. May 1994.

Klasmeier, J.; McLachlan, M.S. (1995) A screening method for detection of OCDD/F in textiles. Organohalogen Compounds 23:131-134.

KMG-Bermuth, Inc. (1997) Letter from Thomas H. Mitchell (KMG-Bermuth) to Matthew Lorber (U.S. EPA/ORD/NCEA). March 5, 1997. Houston, TX: KMG-Bermuth, Inc.

Knepper, W.A. (1981) Iron. In: Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. 13:735-753. New York, NY: John Wiley and Sons.

Koester, C.J.; Hites, R.A. (1992) Photodegradation of polychlorinated dioxins and dibenzofurans adsorbed to fly ash. Environ. Sci. Technol. 26(3):502-507.

Koning, J.; Sein, A.A.; Troost, L.M.; Bremmer, H.J. (1993) Sources of dioxin emissions in the Netherlands. Organohalogen Compounds 14:315-318.

Krauss, T.; Krauss, P.; Hagenmaier, H. (1994) Formation of PCDD/PCDF during composting? Chemosphere 28(1):155-158.

Kwok, E.S.C.; Atkinson, R.; Arey, J. (1995) Rate constants for the gas-phase reactions of the OH radical with dichlorobiphenyls, 1-chlorodibenzo-p-dioxin, 1,2-dimethoxybenzene, and diphenyl ether: estimation of OH radical reaction rate constants for PCBs, PCDDs, and PCDFs. Environ. Sci. Technol. 29(6):1591-1598.

Lahl, U.; Wilken, M.; Zeschmar-Lahl, B.; Jager, J. (1991) PCDD/PCDF balance of different municipal waste management methods. Chemosphere 23(8-10):1481-1489.

Lahl, U. (1993) Sintering plants of steel industry - the most important thermical PCDD/CDF source in industrialized regions. Organohalogen Compounds 11:311-314.

Lahl, U. (1994) Sintering plants of steel industry - PCDD/F emission status and perspectives. Chemosphere 29(9-11):1939-1945.

Lamparski, L.L.; Stehl, R.H.; Johnson, R.L. (1980) Photolysis of pentachlorophenol-treated wood. Chlorinated dibenzo-p-dioxin formation. Environ. Sci. Technol. 14(2):196-200.

Lamparski, L.L.; Nestrick, T.J.; Cutie, S.S. (1990) The impact on the environment of airborne particulate matter from the eruption of Mount Saint Helens in May 1980. In: Clement, R.; Kogel, R., eds, Emissions from combustion processes: origin, measurement, control. Chelsea, MI: Lewis Publishers.

Larsen, B.; Bøwadt, S.; Facchetti, S. (1992) Separation of toxic congeners from PCB mixtures on two series coupled narrow-bore columns (50 m SIL-8 and 25 m HT-5). International Journal of Environmental Analytical Chemistry (47):147-166.

Larsen, B.R. (1995) HRGC separation of PCB congeners. J. High Resol. Chromatogr. 18:141-151.

Larsson, P.; Lemkemeier, K. (1989) Microbial mineralization of chlorinated phenols and biphenyls in sediment-water systems from humic and clear-water lake. Water Research 23(9):1081-1085.

Larssen, S.; Brevick, E.M.; Oehme, M. (1990) Emission factors of PCDD and PCDF for road vehicles obtained by a tunnel experiment. Organohalogen Compounds 1:453-456.

Leifer, A.; Brink, R.H.; Thom, G.C.; Partymiller, K.G. (1983) Environmental transport and transformation of polychlorinated biphenyls. Washington, D.C.: U.S. Environmental Protection Agency, Office of Toxic Substances. EPA-560/5-83-025.

Lemieux, P.M. (1997) Evaluation of emissions from the open burning of household waste in barrels. Research Triangle Park, NC: U.S. Environmental Protection Agency, National Risk Management Research Laboratory.

Lepine, F.; Milot, S.; Vincent, N. (1992) Formation of toxic PCB congeners and PCB-solvent adducts in a sunlight irradiated cyclohexane solution of Aroclor 1254. Bull. Environ. Contam. Toxicol. 48:152-156.

Lew, G. (1993) Letter to John Schaum concerning CARB (1987) draft report on CDD/CDFs in vehicle exhausts. Sacramento, CA: California Air Resources Board, Monitoring and Laboratory Division. Available for inspection at: U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Washington, D.C.

Lew, G. (1996) Letter to G. Schweer (Versar, Inc.) dated January 11, 1996. Sacramento, CA: State of California Air Resources Board, Engineering and Laboratory Branch. Available for inspection at: U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Washington, D.C.

Lexen, K.; De Wit, C; Jansson, B.; Kjeller, L.O.; Kulp, S.E.; Ljung, K.; Söderstrom, G.; Rappe, C. (1993) Polychlorinated dibenzo-p-dioxin and dibenzofuran levels and patterns in samples from different Swedish industries analyzed within the Swedish dioxin survey. Chemosphere 27(1-3):163-170.

Löfroth, G.; Zebühr, Y. (1992) Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDFs) in mainstream and sidestream cigarette smoke. Bull. Environ. Contam. Toxicol. 48:789-794.

Lorang, P.A. (1996) Comments on the API document: A study to quantify on-road emissions of dioxins and furans from mobile sources: phase 2. Ann Arbor, MI: U.S. Environmental Protection Agency, National Vehicle and Fuel Emissions Laboratory. Memorandum dated December 1996.

Lorenz, W.; Wichmann, H.; Bahadir, M. (1996) Balancing of the release of polychlorinated dibenzo-p-dioxins and dibenzofurans in fire accidents--a contribution to the discussion. Reinhaltung der Luft. 56:49-53.

Luijk, R.; Govers, H.A.; Neilssen, L. (1992) Formation of polybrominated dibenzofurans during extrusion of high impact polystyrene/decabromodiphenyl ether/antimony (III) oxide. Environ. Sci. Technol. 26(11):2191-2198.

Lykins, B.W.; Clark, R.; Cleverly, D.H. (1987) Polychlorinated dioxin and furan discharge during carbon reactivation. Journal of Environmental Engineering 114(2): 330-316.

Malisch, R. (1994) Determination of PCDD/PCDF in PCB products and milk samples; correlation between PCB- and PCDD/PCDF-contamination of milk samples. Organohalogen Compounds. 20:209-214.

Malloy, T.A.; Goldfarb, T.D.; Surico, M.T.J. (1993) PCDDs, PCDFs, PCBs, chlorophenols (CPs) and chlorobenzenes (CBzs) in samples from various types of composting facilities in the United States. Chemosphere 27(1-3):325-334.

Maniff, K.; Lewis, M. (1988) MISA monitoring discovers dioxins and furans in wastewater stream of petroleum refinery. Ministry of the Environment Communique. December 5, 1988.

Marklund, S.; Rappe, C.; Tysklind, M.; Egeback, K.E. (1987) Identification of polychlorinated dibenzofurans and dioxins in exhausts from cars run on leaded gasoine. Chemosphere 16(1):29-36.

Marklund, S.; Andersson, R.; Tysklind, M.; Rappe, C. (1989) Emissions of PCDDs and PCDFs from a PVC-fire in Holmsund, Sweden. Chemosphere 18(1-6):1031-1038.

Marklund, S.; Andersson, R.; Tysklind, M.; Rappe, C.; Egeback, K.E.; Bjorkman, E.; Grigoriadis, V. (1990) Emissions of PCDDs and PCDFs in gasoline and diesel fueled cars. Chemosphere 20(5):553-561.

Matsueda, T.; Kurokawa, Y.; Nakamura, M.; Takada, S.; Fukamachi, K. (1994) Concentrations of PCDDs, PCDFs and coplanar PCBs in cigarettes from various countries. Organohalogen Compounds 20:331-334.

McCrady, J.K.; Maggard, S.P. (1993) Uptake and photodegradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin sorbed to grass foliage. Environ. Sci. Technol. 27:343-350.

Merk, M.; Schramm, K.W.; Lenoir, D.; Henkelmann, B.; Kettrup, A. (1995) Determination of the PCDD/F concentration in the fumes from a PVC fire. Organohalogen Compounds 23:491-494.

Metal Producing (1991) Sinter plant roundup. 33 Metal Producing. May 1991. p. 24.

Metal Producing (1996) Census of the North American steel industry. 33 Metal Producing. March 1996. pp. 39-52.

Micklewright, J.T. (1994) Wood preservation statistics, 1993. A report to the wood preserving industry in the United States.

Mill, T.; Rossi, M.; McMillen, D.; Coville, M.; Leung, D.; Spang, J. (1987) Photolysis of tetrachlorodioxin and PCBs under atmospheric conditions. Internal report prepared by SRI International for U.S. Environmental Protection Agency, Office of Health and Environmental Assessment, Washington, D.C.

Miller, A. (1993) Dioxin emissions from EDC/VCM plants. Environ. Sci. Technol. 27:1014-1015.

Miller, G.C.; Hebert, V.R.; Miille, M.J.; Mitzel, R.; Zepp, R.G. (1989) Photolysis of octachlorodibenzo-p-dioxin on soils: production of 2,3,7,8-TCDD. Chemosphere 18:1265-1274.

Morimoto, K.; Kenji, T. (1995) Effect of humic substances on the enzymatic formation of OCDD from PCP. Organohalogen Compounds 23:387-392.

Muto, H.; Takizawa, Y. (1989) Dioxins in cigarette smoke. Archives of Environmental Health 44(3):171-174.

Muto, H.; Takizawa, Y. (1992) Potential health risk via inhalation/ingestion exposure to polychlorinated dibenzo-p-dioxins and dibenzofurans. Bull. Environ. Contam. Toxicol. 49:701-707.

Näf, C.; Broman, D.; Ishaq, R.; Zebühr, Y. (1990) PCDDs and PCDFs in water, sludge and air samples from various levels in a waste water treatment plant with respect to composition changes and total flux. Chemosphere 20(10-12):1503-1510.

NATO (North Atlantic Treaty Organization) (1988) Pilot study on international information exchange on dioxins and related compounds: Emissions of dioxins and related compounds from combustion and incineration sources. North Atlantic Treaty Organization, Committee on the Challenges of Modern Society. Report #172. August 1988.

NCASI (National Council of the Paper Industry for Air and Stream Improvement) (1993) Summary of data reflective of pulp and paper industry progress in reducing the TCDD/TCDF content of effluents, pulps and wastewater treatment sludges. New York, NY. NCASI. June 1993.

NCASI (National Council of the Paper Industry for Air and Stream Improvement) (1995) NCASI summary of PCDD/F emission from wood residue and black liquor combustion. Attachment 2 to comments submitted on January 13, 1995, to EPA's Office of Health and Environmental Assessment concerning the draft document entitled "Estimating Exposure to Dioxin-Like Compounds."

Nestrick, T.J.; Lamparski, L.L. (1982) Isomer-specific determination of chlorinated dioxins for assessment of formation and potential environmental emission from wood combustion. Anal. Chem. 54(13):2292-2299.

Nestrick, T.J.; Lamparski, L.L. (1983) Assessment of chlorinated dibenzo-p-dioxin formation and potential emission to the environment from wood combustion. Chemosphere 12(4/5):617-626.

Nies, L.; Vogel, T.M. (1990) Effects of organic substrates on dechlorination of Aroclor 1242 in anaerobic sediments. Applied and Environmental Microbiology 56(9):2612-2617.

Oberg, L.G.; Glas, B.; Swanson, S.E.; Rappe, C.; Paul, K.G. (1990) Peroxidase-catalyzed oxidation of chlorophenols to polychlorinated dibenzo-p-dioxins and dibenzofurans. Arch. Environ. Contam. Toxicol. 19:930-938.

Oberg, L.G.; Rappe, C. (1992) Biochemical formation of PCDD/Fs from chlorophenols. Chemosphere 25(1-2):49-52.

Oberg, L.G.; Andersson, R.; Rappe, C. (1992) De novo formation of hepta- and octachlorodibenzo-p-dioxins from pentachlorophenol in municipal sewage sludge. Organohalogen Compounds 9:351-354.

Oberg, L.G.; Wagman, N,; Andersson, R.; Rappe, C. (1993) De novo formation of PCDD/Fs in compost and sewage sludge - a status report. Organohalogen Compounds 11:297-302.

Oberg, L.G., Wagman, N.; Koch, M.; Rappe, C. (1994) Polychlorinated dibenzo-p-dioxins, dibenzofurans and non-ortho PCBs in household organic-waste compost and mature garden waste compost. Organohalogen Compounds 20:245-250.

Oehme, M.; Mano, S.; Bjerke, B. (1989) Formation of polychlorinated dibenzofurans and dibenzo-p-dioxins by production processes for magnesium and refined nickel. Chemosphere 18(7-8):1379-1389.

Oehme, M.; Larssen,S.; Brevik, E.M. (1991) Emission factors of PCDD/CDF for road vehicles obtained by a tunnel experiment. Chemosphere 23:1699-1708.

Office of Nature Conservancy (1991) Organochlorine compounds from dishwashing detergents and bleach? Sweden Office of Nature Conservancy Report No. 4009.

O'Keefe, P.W.; Smith, R.M. (1989) PCB capacitor/transformer accidents. In: Kimbrough, R.D.; Jensen, A.A., eds. Halogenated biphenyls, terphenyls, napthalenes, dibenzodioxins and related products. New York, NY: Elsevier Science Publishers.

Opatick, R.E. (1995) Chlorobenzene Producers Association comments on EPA's external review draft of Estimating Exposure to Dioxin-Like Compounds. Chlorobenzene Producers Association. January 10, 1995.

Orazio, C.E.; Kapila, S.; Puri, R.K.; Yanders, A.F. (1992) Persistence of chlorinated dioxins and furans in the soil environment. Chemosphere 25(7-10):1469-1474.

O'Rourke, K. (1996) Memorandum to David Cleverly dated December 16, 1996, concerning MWI phone survey summary. Available for inspection at: U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Washington, D.C.

Palmer, F. H.; Sapudar, R.A.; Heath, J.A.; Richard, N.J.; Bowes, G.W. (1988) Chlorinated dibenzo-p-dioxin and dibenzofuran contamination in California from chlorophenol wood preservative use. California State Water Resources Control Board. Report No. 88-5WQ.

Pardue, J.H.; Delaune, R.D.; Patrick, W.H. (1988) Effect of sediment pH and oxidation-reduction potential on PCB mineralization. Water, Air and Soil Pollution 37:439-447.

Pentachlorophenol Task Force (1997) Letter from John Wilkinson (Pentachlorophenol Task Force) to Matthew Lorber (U.S. EPA/ORD/NCEA). February 7, 1997. Washington, DC: Pentachlorophenol Task Force.

Persson, P.E.; Bergström, J. (1991) Emission of chlorinated dioxins from landfill fires. Proceedings Sardinia 91: Third International Landfill Symposium. pp. 1635-1641.

Plimmer, J.R. (1980) Herbicides. In: Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. Vol. 12, pp. 297-351.

Quensen, J.F.; Tiedje, J.M.; Boyd, S.A. (1988) Reductive dechlorination of polychlorinated biphenyls by anaerobic microorganisms from sediment. Science 242:752-754.

Quensen, J.F.; Boyd, S.A.; Tiedje, J.M. (1990) Dechlorination of four commercial polychlorinated biphenyl mixtures (Aroclors) by anaerobic microorganisms from sediments. Appl. Environ. Microbiol. 56(1):2360-2369.

Randall, D. (1995) Memorandum dated April 8, 1995, from David Randall and Brian Hardee, Midwest Research Institute, Cary, North Carolina, to Richard Copland, Combustion Group, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. Subject: Emission factors for medical waste incinerators (MWIs), EPA Contract No. 68-01-0115; EPA Docket Number A-91-61; IV B 042.

Rappe, C. (1992a) Sources of PCDDs and PCDFs. Introduction. Reactions, levels, patterns, profiles and trends. Chemosphere 25(1-2):41-44.

Rappe, C. (1992b) Sources of exposure, environmental levels and exposure assessment of PCDDs and PCDFs. Organohalogen Compounds 9:5-8.

Rappe, C. (1993) Sources of exposure, environmental concentrations and exposure assessment of PCDDs and PCDFs. Chemosphere 27(1-3):211-225.

Rappe, C.; Marklund, S.; Buser, H.R.; Bosshardt, H.P. (1978a) Formation of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) by burning or heating chlorophenates. Chemosphere 3:269-281.

Rappe, C.; Gara, A.; Buser, H.R. (1978b) Identification of polychlorinated dibenzofurans (PCDFs) in commercial chlorophenol formulations. Chemosphere 12:981-991.

Rappe, C.; Kjeller, L.O.; Bruckmann, P.; Hackhle, K.H. (1988) Identification and quantification of PCDD/CDFs in urban air. Chemosphere 17(1):3-20.

Rappe, C.; Kjeller, L.O.; Andersson, R. (1989a) Analyses of PCDDs and PCDFs in sludge and water samples. Chemosphere 19(1-6):13-20.

Rappe, C.; Swanson, S.; Gals, B.; Kringstad, K.P.; de Sousa, P.; Zensaku, A. (1989b) Formation of PCDDs and PCDFs by the chlorination of water. Chemosphere 19(12):1875-1880.

Rappe, C.; Kjeller, L.O.; Kulp, S.E. (1990a) Sampling and analysis of PCDDs and PCDFs in surface water and drinking water at 0.001 ppq levels. Organohalogen Compounds 2:207-210.

Rappe, C.; Glas, B.; Kjeller, L.O.; Kulp, S.E. (1990b) Levels of PCDDs and PCDFs in products and effluent from the Swedish pulp and paper industry and chloralkali process. Chemosphere 20(10-12):1701-1706.

Rappe, C.; Andersson, R.; Lundström, K.; Wiberg, K. (1990c) Levels of polychlorinated dioxins and dibenzofurans in commercial detergents and related products. Chemosphere 21(1-2):43-50.

Rappe, C.; Kjeller, L.; Kulp, S.; deWit, C.; Hasselsten, I.; Palm, O. (1991) Levels, profile and pattern of PCDDs and PCDFs in samples related to the production and use of chlorine. Chemosphere 23(11-12):1629-1636.

Rappe, C.; Andersson, R.; Karlaganis, G.; Bonjour, R. (1994) PCDDs and PCDFs in samples of sewage sludge from various areas in Switzerland. Organohalogen Compounds 20:79-84.

Ree, K.C.; Evers, E.H.G.; Van Der Berg, M. (1988) Mechanism of formation of polychlorinated dibenzo(p)dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from potential industrial sources. Toxicological and Environmental Chemistry 17:171-195.

Remmers, J.; Dupuy, A.; McDaniel, D.; Harless, R.; Steele, D. (1992) Polychlorinated dibenzo-p-dioxin and dibenzofuran contamination in chloranil and carbazole violet. Chemosphere 25(7-10):1505-1508.

Rhee, G.Y.; Bush, B.; Brown, M.P.; Kne, M.; Shane, L. (1989) Anaerobic biodegradation of polychlorinated biphenyls in Hudson River sediments and dredged sediments in clay encapsulation. Water Research 23(8):957-964.

Rieger, R.; Ballschmiter, K. (1992) Search for sources of CLxDD/CLxDF in sewage sludge of mixed industrial/domestic origin. Organohalogen Compounds 9:203-206.

Riggs, K.B.; Brown, T.D.; Schrock, M.E. (1995) PCDD/PCDF emissions from coal-fired power plants. Organohalogen Compounds 24:51-54.

Risatti, J.B. (1992) Rates of microbial dechlorination of polychlorinated biphenyls (PCBs) in anaerobic sediments from Waukegan Harbor. Champaign, IL: The Illinois Hazardous Waste Research and Information Center. HWRIC RR-061.

Riss, A.; Aichinger, H. (1993) Reduction of dioxin emissions and regulatory measures in Austria. Organohalogen Compounds 14:341-344.

Rotard, W. (1993) Fires. In: Current views on the impact of dioxins and furans on human health and the environment. Washington, D.C.: Toxicology Forum, Inc.

Rubin, A.; White, C. (1992) Computer printout from National Sewage Sludge Survey Data Base. U.S. Environmental Protection Agency, Office of Science and Technology, Health and Ecological Criteria Division, Sludge Risk Assessment Branch. December 21, 1992.

Ruokojärvi, P.; Ettala, M.; Rahkonen, P.; Tarhanen, J.; Ruuskanen, J. (1995) Polychlorinated dibenzo-p-dioxins and -furans (PCDDs and PCDFs) in municipal waste landfill fires. Chemosphere 30(9):1697-1708.

Safe, S. (1994) Polychlorinated biphenyls (PCBs): environmental impact, biochemical and toxic responses, and implications for risk assessment. Crit. Rev. Toxicol. 21(1):51-88.

SAIC (1994) Identification of sources of dioxin in catalytic reformers and potential mitigation. Cincinnati, OH: U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory. EPA Contract No. 68-C0-0044.

Sakai, S.; Hiraoka, M.; Takeda, N.; Shiozaki, K. (1993a) Coplanar PCBs and PCDD/PCDFs in municipal waste incineration. Chemosphere 27(1-3):233-240.

Sakai, S.; Hiraoka, M.; Takeda, N.; Shiozaki, K. (1993b) On emission and formation of non-ortho CBs and mono-ortho CBs in municipal waste incineration. Organohalogen Compounds 11:245-248.

Sakai, S.; Hiraoka, M.; Takeda, N.; Shiozaki, K. (1994) Behavior of coplanar PCBs in oxidative condition of municipal waste incineration. Organohalogen Compounds 20:309-313.

Santl, H.; Gruber, L.; Stöhrer, E. (1994a) Mass balance of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) in a recycling paper mill. Chemosphere 28(9-11):1633-1639.

Santl, H.; Gruber, L.; Stöhrer, E. (1994b) Investigation on the input, formation and fate of polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) in the pulp and paper industry. Chemosphere 29(9-11):1987-1994.

Santl, H.; Gruber, L.; Stöhrer, E. (1994c) Some new sources of polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) in waste papers and recycled pulps. Chemosphere 29(9-11):1995-2003.

Schäfer, K.; McLachlan, M.S.; Reissinger, Ml; Hutzinger, O. (1993) An investigation of PCDD/F in a composting operation. Organohalogen Compounds 11:425-428.

Schatowitz, B.; Brandt, G.; Gafner, F.; Schlumpf, E.; Biihler, R.; Hasler, P.; Nussbaumer, T. (1993) Dioxin emissions from wood combustion. Organohalogen Compounds 11:307-310.

Schecter, A.; Papke, O.; Isaac, J.; Hrimat, N.D.; Neiroukk, F.; Safi, J.; El-Nahhal, Y. (1997) 2,3,7,8 Chlorine substituted dioxin and dibenzofuran congeners in 2,4-D, 2,4,5-T and pentachlorophenol. Organohalogen Compounds 32:51-55.

Schoonenboom, M.H.; Tromp, P.C.; Olie, K. (1993) The formation of coplanar PCBs, PCDDs and PCDFs in a fly-ash model system. Organohalogen Compounds 11:277-280.

Schreiner, M.; Reifenhäuser, W; Vierle, O. (1992) Measurements of the emission concentrations of PCDD/PCDF in a digester-torch of a municipal sewage plant. Organohalogen Compunds 9:255-257.

Schreiner, G.; Schimmel, H.; Ballschmiter, K. (1995) Influence of the substitution pattern on the microbial degradation of mono- to tetrachlorinated dibenzofurans and dibenzodioxins. Organohalogen Compounds 24:43-46.

Schulz, D.E.; Petrick, G.; Duinker, J.C. (1989) Complete characterization of polychlorinated biphenyl congeners in commerical Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. Environ. Sci. Technol. 23:852-859.

Schwartz, T.R.; Tillitt, D.E.; Feltz, K.P.; Peterman, P.H. (1993) Determination of mono- and non--*o-o'*-chlorine substituted polychlorinated biphenyls in Aroclors and environmental samples. Chemosphere 26(8):1443-1460.

Schwind, K-H.; Thoma, H.; Hutzinger, O.; Dawidowsky, N.; Weberuss, U.; Hagenmaier, H.; Buehler, U.; Greiner, R.; Essers, U.; Bessey, E. (1991) Emission halogenierter dibenzodioxine (PXDD) und dibenzofurane (PXDF) aus verbrennungsmotoren. UWSF-Z. Umweltchem. Oekotox. 3, 291-298. [English translation]

Schwind, K.H.; Hosseinpour, J.; Fiedler, H.; Lau, C.; Hutzinger, O. (1995) Human exposure to consumer products: analysis of chlorinated organic compounds in candles and their exhaust fumes. Organohalogen Compounds 26:113-116.

Secor International Inc. (1995a) Emission measurement results for furans and dioxins from the main stack at the Phelps Dodge-Hidalgo Smelter, Playos, New Mexico. Prepared for the Phelps Dodge Mining Company.

Secor International Inc. (1995b) Furans and dioxins emission measurement results for Cyprus Miami Mining Corporation. Prepared for the Cypress Amax Minerals Company.

Sedlak, D.L.; Andren, A.W. (1991) Aqueous-phase oxidation of polychlorinated biphenyls by hydroxyl radicals. Environ. Sci. Technol. 25(8):1419-1427.

Sewart, A.; Harrad, S.J.; McLachlan, M.S.; McGrath, S.P.; Jones, K.C. (1995) PCDD/Fs and non-o-PCBs in digested U.K. sewage sludges. Chemosphere 30(1):51-67.

Shane, B.S.; Henry, C.B.; Hotchkiss, J.H.; Klausner, K.A.; Gutenmann, W.H.; Lish, D.J. (1990) Organic toxicants and mutagens in ashes from eighteen municipal refuse incinerators. Arch. Environ. Contam. Toxicol. 19:665-673.

Sivils, L.D.; Kapila, S.; Yan, Q.; Elseewi, A.A. (1994) Studies on gas-phase phototransformation of polychlorinated dibenzo-p-dioxins. Organohalogen Compounds 19:349-353.

Sivils, L.D.; Kapila, S.; Yan, Q.; Zhang, X.; Elseewi, A.A. (1995) Studies on vapor phase phototransformation of polychlorinated dibenzo-p-dioxins (PCDDs): effect of environmental parameters. Organohalogen Compounds 24:167-172.

Solid Waste Technologies. (1994) A comprehensive status report on MSW waste-to-energy facilities, incinerators refuse-derived-fuel, and tire processing facilities throughout North America. Kansas City, MO: HCI Publications. 84 pp.

Someshwar, A.V.; Pinkerton, J.E. (1992) Wood processing industry. In: Buonicore, A.J., Davis, W.T., eds., Air pollution engineering manual. Air and Waste Management Association. New York, NY: Van Nostrand Reinhold. pp. 835-847.

Springer, J.M. (1997) Personal communication with A. Paintal, Versar, Inc. Cremation Association of North America. January 7, 1998.

Strandell, M.E.; Lexen, K.M.; deWit, C.A.; Järnberg, U.G.; Jansson, B.; Kjeller, L.O.; Kulp, E.; Ljung, K.; Söderström, G.; Rappe, C. (1994) The Swedish Dioxin Survey: Summary of results from PCDD/F and coplanar PCB analyses in source-related samples. Organohalogen Compounds 20:363-366.

Stringer, R.L.; Costner, P.; Johnston, P.A. (1995) PVC manufacture as a source of PCCD/Fs. Organohalogen Compounds 24:119-123.

Strong, B. (1996) Memorandum dated January 31, 1996, from Brian Strong and Brian Hardee, Midwest Research Institute, Cary, North Carolina, to Richard Copland, Combustion Group, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. Subject: Updated medical waste incinerator data base, EPA Contract No. 68-01-0115; EPA Docket Number A-91-61; IV B 022.

Stuart, B.; Carter, D.; Hoodless, R.A. (1993) Report on the examination of sewage sludges for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. London, England: Laboratory of the Government Chemist.

Svenson, A.; Kjeller, L.O.; Rappe, C. (1989) Enzyme-mediated formation of 2,3,7,8-tetrasubstituted chlorinated dibenzodioxins and dibenzofurans. Environ. Sci. Technol. 23(7):900-902.

Systems Application International (1995) MSWI database of all existing facilities in the U.S. Prepared in Sept. 1995 for U.S. Environmental Protection Agency, Office of Policy Analysis.

Takizawa, Y.; Asada, S.; Muto, H. (1994) Dioxins in dust fall and volcanic ash from the active volcanos Fugendake and Sakurajima. Organohalogen Compounds 20:359-362.

Tanabe, S,; Kannan, N.; Wakimoto, T.; Tatsukawa, R. (1987) Method for the determination of three toxic non-orthochlorine substituted coplanar PCBs in environmental samples at part-per-trillion levels. Intern. J. Environ. Anal. Chem. 29:199-213.

Tashiro, C.; Clement, R.E.; Stocks, B.J.; Radke, L.; Cofer, W.R.; Ward, P. (1990) Preliminary report: dioxins and furans in prescribed burns. Chemosphere 20:1533-1536.

Taylor, A. and Zannes, M. (1996) The 1996 IWSA municipal waste combustion directory of United States facilities. Integrated Waste Services Association. 16 pps.

The Aluminum Association (1997) U.S. aluminum industry plant directory, November 1997. Washington, DC: The Aluminum Association.

The Tobacco Institute (1995) Tobacco industry profile 1995. Washington, DC: The Tobacco Institute.

The Vinyl Institute (1996) Dioxin characterization program. Interim Phase I Report. Morristown, NJ: The Vinyl Institute. November 1, 1996.

Thiesen, J.; Funcke, W.; Balfanz, E.; König, J. (1989) Determination of PCDFs and PCDDs in fire accidents and laboratory combustion tests involving PVC-containing materials. Chemosphere 19(1-6):423-428.

Thoma, H.; Hutzinger, O. (1989) Content and formation of toxic products in flame retardants. Presented at: Workshop on Brominated Aromatic Flame Retardants. Slokloster, Sweden; October 24-26, 1989.

Thomas, V.M.; Spiro, T.G. (1995) An estimation of dioxin emissions in the United States. Toxicological and Environmental Chemistry 50:1-37.

Thomas, V.M.; Spiro, T.G. (1996) The U.S. dioxin inventory: are there missing sources. Environ. Sci. Technol. 30(2):82A-85A.

Thompson, T.S.; Clement, R.E.; Thornton, N.; Luty, J. (1990) Formation and emission of PCDDs/PCDFs in the petroleum refining industry. Chemosphere 20(10-12):1525-1532.

Thub, U.; Popp, P.; Ehrlich, C.; Kalkoff, W.D. (1995) Domestic lignite combustion as source of polychlorodibenzodioxins and furans (PCDD/F). Chemosphere 31(2):2591-2604.

Tiernan, T.O.; Wagel, D.J.; Garrett, J.H.; Van Ness, G.F.; Solch, J.G.; Ernes, D.A. (1995) Determination of PCDD/PCDF in polyvinyl chloride (PVC) and in related manufacturing process samples. Organohalogen Compounds 23:65-68.

Towara, J.; Hiller, B.; Hutzinger, O.; Kurz, J.; Klein, P. (1992) PCDD/F in distillation residues from dry cleaning machines. Chemosphere 25:1509.

Two Rivers Regional Council of Public Officials and Patrick Engineering, Inc. (1994) Emission characteristics of burn barrels. Prepared for U.S. Environmental Protection Agency, Region V.

Tysklind, M.; Söderström; Rappe, C.; Hägerstedt, L-E.; Burström, E. (1989) PCDD and PCDF emissions from scrap metal melting processes at a steel mill. Chemosphere 19(1-6):705-710.

Tysklind, M.; Rappe, C. (1991) Photolytic transformation of polychlorinated dioxins and dibenzofurans in fly ash. Chemosphere 23(8-10):1365-1375.

Tysklind, M.; Carey, A.E.; Rappe, C.; Miller, G.C. (1992) Photolysis of OCDF and OCDD on soil. Organohalogen Compounds 8:293-296.

Umlauf, G.; Horstmann, M.; Klein, P.; Kurz, J. (1993) Mass balance of PCDD/F in a dry cleaning machine. Organohalogen Compounds 11:413-416.

Umweltbundesamt (1996) Determination of requirements to limit emissions of dioxins and furans. Report from the Working Group of the Subcommittee Air/Technology of the Federal Government/Federal States Immission Control Committee. Berlin, Germany.

United Kingdom Department of the Environment (1995) United Kingdom comments on "Estimating Exposure to Dioxin-Like Compounds." Comments submitted to EPA's Office of Health and Environmental Assessment. January 10, 1995.

U.S. Department of Agriculture (1997) Tobacco leaf and products statistics and analysis. Washington, DC: U.S. Department of Agriculture, Economic Research Service.

U.S. Department of Commerce (1990a) 1987 Census of manufactures. Smelting and refining of nonferrous metals and alloys. Washington, DC: Bureau of the Census. Report No. 33C-18.

U.S. Department of Commerce (1990b) 1987 Census of manufacturers. Soap, cleaners, and toilet goods. Washington, DC: Bureau of the Census. Report No. MC-87-I-28D.

U.S. Department of Commerce (1990c) 1987 Census of manufactures. Industrial inorganic chemicals. Washington, DC: Bureau of the Census. Report No. MC87-I-28A.

U.S. Department of Commerce (1995a) Statistical abstract of the United States, 1995. 118th ed.

U.S. Department of Commerce (1995b) 1992 Census of transportation. Truck inventory and use survey. Washington, DC: Bureau of the Census. Report No. TC92-T-52.

U.S. Department of Commerce (1995c) 1992 Census of manufactures. Smelting and refining of nonferrous metals and alloys. Washington, DC: Bureau of the Census. Report No. MC92-I-33C.

U.S. Department of Commerce (1995d) 1992 Census of manufactures. Blast furnaces, steel works, and rolling and finishing mills. Washington, DC: Bureau of the Census. Report No. MC92-I-33A.

U.S. Department of Commerce (1996) 1992 Economic census report series - disc 1G. Washington, DC: Bureau of the Census. CD-EC92-1G.

U.S. Department of Commerce (1997) Statistical abstract of the United States, 1997. 117th edition. Washington, DC: Bureau of the Census.

U.S. Department of Health and Human Services (DHHS) (1989) Toxicology and carcinogenesis studies of two pentachlorophenol technical-grade mixtures in B6C3F1 mice (feed studies). Research Triangle Park, NC: U.S. Department of Health and Human Services, National Toxicology Program. NIH Publication No. 89-2804.

U.S. Environmental Protection Agency; Environment Canada (1991) The environmental characterization of RDF combustion technology. Mid-Connecticut facility, Hartford,CT. Test program and results, volume II., June 1991.

U.S. Environmental Protection Agency. (1979) Polychlorinated biphenyls (PCBs) in manufacturing, processing, distribution in commerce, and use prohibition: Final rule. Federal Register 44:31514-31568.

U.S. Environmental Protection Agency (1982a) Development document for effluent limitations guidelines and standards for the inorganic chemicals manufacturing point source category. Washington, DC: Office of Water Regulations and Standards. EPA 440/1-82/007.

U.S. Environmental Protection Agency (1982b) Development document for effluent limitations guidelines and standards for the iron and steel manufacturing point source category. Volume II. Washington, DC: Office of Water. EPA-440/1-82/024.

U.S. Environmental Protection Agency (1984) Thermal degradation products from dielectric fluids. Washington, DC: Office of Toxic Substances. EPA-560/5-84-009.

U.S. Environmental Protection Agency (1987a) National dioxin study Tier 4 - combustion sources. Engineering analysis report. Research Triangle Park, NC: Office of Air Quality Planning and Standards. EPA-450/4-84-014h.

U.S. Environmental Protection Agency (1987b) Municipal waste combustion study. Characterization of the municipal waste combustion industry. Washington, DC: Office of Air and Radiation. EPA/530-SW-87-021b.

U.S. Environmental Protection Agency (1987c) Locating and estimating air emissions from sources of polychlorinated biphenyls (PCB). Research Triangle Park, NC: Office of Air Quality Planning and Standards, EPA-450/4-84-007n.

U.S. Environmental Protection Agency (1987d) Hospital waste combustion study: Data gathering phase. Research Triangle Park, NC: Office of Air Quality Planning and Standards. EPA-450/3-88-017.

U.S. Environmental Protection Agency (1988a) U.S. EPA cooperative dioxin screening study. Washington, DC: Office of Water Regulations and Standards. EPA-440/1-88-025.

U.S. Environmental Protection Agency (1988b) Pesticide assessment guidelines, subdivision D - product chemistry. Series 61-4, addendum 1 on data reporting. Washington, DC: Office of Pesticide Programs. NTIS No. PB88-191705.

U.S. Environmental Protection Agency (1988c) Pesticide industry sales and usage: 1987 market estimates. Washington, DC: Office of Pesticide Programs.

U.S. Environmental Protection Agency (1989) Interim procedures for estimating risks associated with exposures to mixtures of chlorinated dibenzo-p-dioxins and -dibenzofurans (CDDs and CDFs) and 1989 update. Washington, DC: Risk Assessment Forum. EPA/625/3-89/016.

U.S. Environmental Protection Agency (1990a) Summary report on USEPA/Industry Cooperative Dioxin Study. "The 104 Mill Study." Washington, DC: Office of Water Regulations and Standards. July 1990.

U.S. Environmental Protection Agency (1990b) Medical waste incineration emission test report. AMI Central Carolina Hospital, Sanford, North Carolina. Volume I. Research Triangle Park, NC: Office of Air Quality Planning and Standards. EMB Report No. 90-MWI-5.

U.S. Environmental Protection Agency (1990c) Characterization of municipal waste combustion ash, ash extracts, and leachates. Washington, DC: Office of Solid Waste and Emergency Response. EPA 530-SW-90-029A.

U.S. Environmental Protection Agency (1990d) Operation and maintenance of hospital medical waste incinerators. Research Triangle Park, NC: Office of Air Quality Planning and Standards. EPA/625/6-89/024.

U.S. Environmental Protection Agency (1991a) Regulatory determination-landfills and surface impoundments receiving pulp and paper mill sludge. Washington, DC: Office of Solid Waste and Emergency Response. EPA/530-SW-91-077.

U.S. Environmental Protection Agency (1991b) Methodology for assessing environmental releases of and exposure to municipal solid waste combustor residuals. Washington, DC: Office of Research and Development. EPA/600/8-91/031.

U.S. Environmental Protection Agency (1991c) Medical waste incineration emission test report: Jordan Hospital, Plymouth, Massachusetts. Volume 1. Research Triangle Park, NC: Office of Air Quality Planning and Standards. EMB Report 90-MWI-6.

U.S. Environmental Protection Agency (1991d) Medical and institutional waste incineration: regulations, management, technology, emissions, and operations. Cincinnati, OH: Center for Environmental Research Information. EPA/625/4-91/030.

U.S. Environmental Protection Agency (1992a) Markets for scrap tires. Washington, DC: Office of Solid Waste and Emergency Response. EPA/530-SW-90-074A.

U.S. Environmental Protection Agency (1992b) Industry agrees to switch to low-dioxin chloranil from contaminated chloranil. Chemicals in Progress Bulletin 12(2):23.

U.S. Environmental Protection Agency (1992c) 1990 National census of pulp, paper, and paperboard manufacturing facilities. Response to 308 questionnaire. Part A: Technical Information. Washington, DC: Office of Water.

U.S. Environmental Protection Agency (1992d) Economic impact and preliminary regulatory impact analysis for proposed MACT-based emission standards and guidelines for municipal waste combustors. Research Triangle Park, NC: Office of Air Quality Planning and Standards. EPA-450/3-91-029.

U.S. Environmental Protection Agency (1992e) Secondary lead smelter emission test report, East Penn Manufacturing, Lyon Station, Pennsylvania. Research Triangle Park, NC: Office of Air Quality Planning and Standards, Emission Measurement Branch. EMB Report No. 92-SLS-3.

U.S. Environmental Protection Agency (1993a) 1992 Needs survey report to Congress. Washington, DC: Office of Water. EPA-832-R-93-002.

U.S. Environmental Protection Agency (1993b) States support efforts on forming voluntary agreement on pulp and paper mill sludge. Chemicals in Progress Bulletin 14(3):20.

U.S. Environmental Protection Agency (1993c) EPA publishes proposed rule for chloranil. Chemicals in Progress Bulletin 14(2):26.

U.S. Environmental Protection Agency (1993d) Development document for proposed effluent limitations guidelines and standards for the pulp, paper and paperboard point source category. Washington, DC: Office of Water. EPA-821-R-93-019.

U.S. Environmental Protection Agency (1993e) Economic analysis of impacts of integrated air/water regulations for the pulp and paper industry on disposal of wastewater sludge. Washington, DC: Office of Pollution Prevention and Toxics, Regulatory Impacts Branch.

U.S. Environmental Protection Agency (1993f) Press advisory: EPA terminates special review of non-wood pesticide uses of pentachlorophenol. Washington, DC: Office of Pesticide Programs. January 8, 1993.

U.S. Environmental Protection Agency (1993g) Report to Congress on cement kiln dust. Washington, DC: Office of Solid Waste. December 1993.

U.S. Environmental Protection Agency (1993h) 1991 Toxics release inventory - public data release. Washington, DC: Office of Pollution Prevention and Toxics. EPA-745-R-93-003.

U.S. Environmental Protection Agency (1994a) Secondary lead smelting industry: background information document for proposed standards. Final report. Research Triangle Park, NC: Office of Air Quality Planning and Standards. EPA-450/R-94-024.

U.S. Environmental Protection Agency (1994b) Pesticide industry sales and usage: 1992 and 1993 market estimates. Washington, DC: Office of Prevention, Pesticides and Toxic Substances. EPA 733-K-94-001.

U.S. Environmental Protection Agency (1994c) Medical waste incinerators background information for proposed standards and guidelines: Industry profile report for new and existing facilities. Research Triangle Park, NC: Office of Air Quality Planning and Standards. EPA-453/R-94-042a.

U.S. Environmental Protection Agency (1994d) Medical waste incinerators-background information for proposed standards and guidelines: Environmental impacts report for new and existing facilities. Research Triangle Park, NC: Office of Air Quality Planning and Standards. EPA-453/R-94-046a.

U.S. Environmental Protection Agency (1994e) Universe of hazardous waste combustion facilities. Washington, DC: Office of Solid Waste and Emergency Response. EPA-530-F-94-030.

U.S. Environmental Protection Agency (1994f) Combustion emissions technical resource document (CETRED). Washington, DC: Office of Solid Waste and Emergency Response. Draft Report. EPA/530-R-94-014.

U.S. Environmental Protection Agency (1995a) SRRD's dioxin/furan status report. Washington, DC: Office of Pesticide Programs, Special Review and Reregistration Division. September 12, 1995.

U.S. Environmental Protection Agency (1995b) Compilation of air pollutant emission factors. 5th edition. Research Triangle Park, NC: Office of Air Quality Planning and Standards.

U.S. Environmental Protection Agency (1995c) Locating and estimating air emissions from sources of dioxins and furans. Draft final report. Research Triangle Park, NC: Office of Air Quality Planning and Standards. Contract No. 68-D2-0160.

U.S. Environmental Protection Agency (1995d) Final emission test report, HAP emission testing on selected sources at a secondary lead smelter, Tejas Resources, Inc., Terrell, Texas. Research Triangle Park, NC: Office of Air Quality Planning and Standards, Emission Measurement Branch. EMB Report No. 93-SLS-1.

U.S. Environmental Protection Agency (1995e) Final emission test report, HAP emission testing on selected sources at a secondary lead smelter, Schuylkill Metals Corporation, Forest City, Missouri. Research Triangle Park, NC: Office of Air Quality Planning and Standards, Emission Measurement Branch. EMB Report No. 93-SLS-2.

U.S. Environmental Protection Agency (1995f) An SAB report: A second look at dioxin. Review of the Office of Research and Development's reassessment of dioxin and dioxin-like compounds by the Dioxin Reassessment Review Committee. Science Advisory Board (1400) September 1995. EPA-SAB-EC-95-021.

U.S. Environmental Protection Agency (1995g) 1993 Toxics release inventory - public data release. Washington, DC: Office of Pollution Prevention and Toxics. EPA-745-R-95-010.

U.S. Environmental Protection Agency (1995h) Secondary aluminum plant emission test report: Rochester Aluminum Smelting Corporation. Research Triangle Park, NC: Office of Air Quality Planning and Standards. EMC Report 95-SAL-01.

U.S. Environmental Protection Agency (1996a) Percentile estimates used to develop the list of pollutants for round two of the Part 503 Regulation. Washington, DC: Office of Science and Technology. EPA Contract No. 68-C4-0046.

U.S. Environmental Protection Agency (1996b) Municipal solid waste factbook, version 3.0. Washington, DC: Office of Solid Waste.

U.S. Environmental Protection Agency (1996c) EPA OSW hazardous waste combustion data base. Washington, DC: U.S. EPA, Office of Solid Waste.

U.S. Environmental Protection Agency (1996d) National dioxin emission estimates from municipal waste combustors. Research Triangle Park, NC: U.S. EPA, Office of Air Quality Planning and Standards. June 1996.

U.S. Environmental Protection Agency (1996e) National dioxin emissions from medical waste incinerators. Research Triangle Park, NC: Office of Air Quality Planning and Standards. Docket #A-91-61, Item IV-A-007.

U.S. Environmental Protection Agency (1996f) Emissions inventory of Section 112(c)(6) pollutants: polycyclic organic matter (POM), 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)/2,3,7,8-tetrachlorodibenzofuran (TCDF), polychlorinated biphenyl compounds (PCBs), hexachlorobenzene, mercury, and alkylated lead. Research Triangle Park, NC: Office of Air Quality Planning and Standards. September 1996.

U.S. Environmental Protection Agency (1996g) PCBs: Cancer dose-response assessment and application to environmental mixtures. Washington, D.C.: Office of Research and Development. EPA/600/P-96/001.

U.S. Environmental Protection Agency (1996h) Draft technical support document for hazardous waste combustor MACT standards. Volume I: Description of source categories. Washington, DC: Office of Solid Waste and Emergency Response. February 1996.

U.S. Environmental Protection Agency (1997a) Pesticide industry sales and usage: 1994 and 1995 market estimates. Washington, DC: Office of Prevention, Pesticides and Toxic Substances. EPA-733-R-97-002.

U.S. Environmental Protection Agency (1997b) Locating and estimating air emissions from sources of dioxins and furans. Research Triangle Park, NC: Office of Air Quality Planning and Standards. DCN No. 95-298-130-54-01.

U.S. Environmental Protection Agency (1997c) 1996 Clean Water Needs Survey Report to Congress. Washington, DC: Office of Water.

U.S. Environmental Protection Agency (1997d) Draft technical support document for hazardous waste combustors MACT standards (NODA). Volume I: MACT evaluations based on revised database. Washington, DC: Office of Solid Waste and Emergency Response. April 1997.

U.S. Geological Survey (1997a) Minerals yearbook: recycling - nonferrous metals chapter. Reston, VA: U.S Geological Survey, Geologic Division.

U.S. Geological Survey (1997b) Mineral commodity survey - iron and steel scrap. Washington, DC: U.S. Department of the Interior, U.S. Geological Survey.

U.S. International Trade Commission (1946 through 1994) Synthetic organic chemicals - United States production and sales. Washington, DC: U.S. International Trade Commission.

U.S. International Trade Commission (1984) Imports of benzenoid chemicals and products 1983; investigation no. 332-135. Washington, DC: U.S. International Trade Commission. USITC Publication No. 1548.

Van Dort, H.M.; Bedard, D.L. (1991) Reductive ortho and meta dechlorination of a polychlorinated biphenyl congener by anaerobic microorganisms. Appl. Environ. Microbiol. 57:1576-1578.

Van Oostdam, J.C.; Ward, J.E.H. (1995) Dioxins and furans in the British Columbia environment. Victoria, British Columbia: BC Environment, Environmental Protection Department.

Van Wijnen, J.H.; Liem, A.K.D.; Olie, K.; van Zorge, J.A. (1992) Soil contamination with PCDDs and PCDFs of small (illegal) scrap wire and scrap car incineration sites. Chemosphere 24(2):127-134.

Versar, Inc. (1976) PCBs in the United States: industrial use and environmental distribution. Washington, DC: U.S. Environmental Protection Agency, Office of Toxic Substances. EPA Contract No. 68-01-3259, Task I.

Versar Inc. (1985) List of chemicals contaminated or precursors to contamination with incidentally generated polychlorinated and polybrominated dibenzodioxins and dibenzofurans. EPA Contract No. 68-02-3968, Task No. 48.

Versar, Inc. (1988) PCB exposure assessment of scrap/salvage facilities. Washington, DC: U.S. Environmental Protection Agency, Office of Toxic Substances. EPA Contract No. 68-02-4254. Task No. 136.

Vikelsoe, J.; Madsen, H.; Hansen, K. (1993) Emission of dioxins from Danish wood-stoves. Organohalogen Compounds 11:405-408.

Vikelsoe, J.; Lassen, P.; Johansen, E.; Carlsen, L. (1994) Formation of PCDD/PCDFs via an enzymatically mediated chlorination of humic acids. Organohalogen Compounds 20:351-354.

Villanueva, E.C.; Jennings, R.W.; Burse, V.W.; Kimbrough, R.D. (1974) Evidence of chlorodibenzo-p-dioxin and chlorodibenzofuran in hexachlorobenzene. J. Agr. Food Chem. 22(5):916-917.

Vollmuth, S.; Zajc, A.; Niessner, R. (1994) Formation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans during the photolysis of pentachlorophenol-containing water. Environ. Sci. Technol. 28(6):1145-1149.

Waddell, D.S.; Boneck-Ociesa, H.; Gobran, T.; Ho, T.F.; Botton, J.R. (1995) PCDD/PCDF formation by UV photolysis of pentachlorophenol with and without the addition of hydrogen peroxide. Organohalogen Compounds 23:407-412.

Wagner, H.C.; Schramm, K.W.; Hutzinger, O. (1990) Biogenic polychlorinated dioxin and furan from trichlorophenol. Organohalogen Compounds 3:453-456.

Walsh, P.J.J.; Brimblecombe, P.; Creaser, C.S.; Olphert, R. (1994) Biomass burning and polychlorinated dibenzo-p-dioxins & furans in soil. Organohalogen Compounds (20):283-287.

Ward, D.E.; McMahon, C.K.; Johansen, R.W. (1976) An update on particulate emissions from forest fires. Presented at: 69th Annual Meeting of the Air Pollution Control Association. Portland, OR. June 27-July 1, 1976.

Ward, D.E.; Peterson, J.; Hao, W.M. (1993) An inventory of particulate matter and air toxic emissions from prescribed fires in the USA for 1989. Presented at: 86th Annual Meeting & Exhibition, Air & Waste Management Association; Denver, Colorado; June 1993.

Watanabe, I; Tatsukawa, R. (1987) Formation of brominated dibenzofurans from the photolysis of flame retardant decabromobiphenyl ether in hexane solution by UV and sun light. Bull. Environ. Contam. Toxicol. 39:953-959.

Water Pollution Control Federation (1990) Operation of municipal wastewater treatment plants. Manual of Practice No. 11. Alexandria, VA: Water Pollution Control Federation.

Weber, H.; Disse, G.; Hamann, R.; Haupt, H.J. (1995) Influence of the aerobic and anaerobic digestion on the levels of chlorinated dibenzofurans and dibenzodioxins in sewage sludge. Organohalogen Compounds 24:81-85.

Welsch-Pausch, K.; McLachlan, M.S. (1995) Photodegradation of PCDD/Fs on pasture grass. Organohalogen Compounds 24:509-512.

Welsch-Pausch, K.; McLachlan, M.S.; Umlauf, G. (1995) Determination of the principal pathways of polychlorinated dibenzo-p-dioxins and dibenzofurans to *Lolium multiflorum* (Welsh Ray Grass). Environ. Sci. Technol. 29:1090-1098.

Wevers, M.; De Fre, R.; Rymen, T. (1992) Dioxins and dibenzofurans in tunnel air. Volume 9 (Sources of Exposure) of Extended Abstracts. Organohalogen Compounds 9:321-324.

Wevers, M.; De Fre, R. (1995) Estimated evolution of dioxin emissions in Belgium from 1988 to 1995. Organohalogen Compounds 24:105-108.

WHO (World Health Organization) (1991) IARC monographs on the evaluation of carcinogenic risks to humans: occupational exposures in insecticide application, and some pesticides.

Wichmann, H.; Zelinski, V.; Scholz-Böttcher, B.; Lorenz, W.; Bahadir, M. (1993) Sampling strategy to investigate the distribution behavior of low volatile pollutants like "dioxins" during vehicle fires in traffic tunnels. Chemosphere 26(6):1159-1166.

Wichmann, H.; Lorenz, W.; Bahadir, M. (1995) Release of PCDD/F and PAH during vehicle fires in traffic tunnels. Chemosphere 31(2):2755-2766.

Wienecke, J.; Kruse, H.; Wassermann, O. (1992) Organic compounds in the flue gas from a power station with circulatory fluid bed combustion of coal. Chemosphere 25(12):1889-1895.

Williams, C.H.; Prescott, C.L.; Stewart, P.B.; Choudhary, G. (1985) Formation of polychlorinated dibenzofurans and other potentially toxic chlorinated pyrolysis products in PCB fires. In: Keith, L.H.; Rappe, C.; Choudhary, G., eds., Chlorinated dioxins and dibenzofurans in the total environment II. Boston, MA: Butterworth Publishers.

Williams, D.T.; LeBel, G.L.; Benoit, F.M. (1992) Polychlorodibenzodioxins and polychlorodibenzofurans in dioxazine dyes and pigments. Chemosphere 24(2):169-180.