

1.0. BACKGROUND AND SUMMARY

1.1. BACKGROUND

This reassessment is comprised of three reports:

Part 1. *Estimating Exposure to Dioxin-Like Compounds* (U.S. EPA, 2000b) (which expanded upon a 1988 draft exposure report titled, *Estimating Exposure to 2,3,7,8-TCDD* [U.S. EPA, 1988d]);

Part 2. *Health Assessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds* (U.S. EPA, 1994a; U.S. EPA, 2000c); and

Part 3. *Dioxin: Integrated Summary and Risk Characterization for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds* (U.S. EPA, 2000d).

Throughout the remainder of this document, these three parts as a whole will be abbreviated as the Reassessment Documents, and the individual parts will be referred to as the Exposure Reassessment Document, the Health Reassessment Document, and the Risk Characterization. The Exposure Reassessment Document has expanded to three volumes, as discussed below. Volumes 1 and 2 of the Exposure Reassessment Document are summarized in Section 4 of the Risk Characterization.

The process for developing the Reassessment Documents has been open and participatory. Each of the documents has been developed in collaboration with scientists from inside and outside the Federal Government. Each document has undergone extensive internal and external review, including review by EPA's Science Advisory Board (SAB). In September 1994, drafts of each document were made available for public review and comment. This included a 150-day comment period and 11 public meetings around the country to receive oral and written comments. These comments, along with those of the SAB (U.S. EPA, 1995a), have been considered in the drafting of this final document. The Dose-Response Chapter of the Health Document underwent peer review in 1997 (U.S. EPA, 1997a); an earlier version of the Integrated Summary and Risk Characterization underwent development and review in 1997 and 1998, and comments have been incorporated. In 1998, EPA released a workshop review version of the sources inventory (U.S. EPA, 1998a), one of the three volumes of the Exposure Reassessment Document. In

addition, as requested by the SAB, a chapter on Toxic Equivalency has been developed and underwent external peer review in parallel with the Integrated Summary and Risk Characterization in July 2000. The November 2000, review by the SAB of the Dose-Response Chapter, the Toxic Equivalency Chapter and the Integrated Summary and Risk Characterization was the final step in this open and participatory process of reassessment. The full set of background documents and the integrative summary and risk characterization replace the previous dioxin assessments as the scientific basis for EPA decision-making.

The final Exposure Reassessment Document reflects changes made as a result of both review comments and analyses of a variety of other types of information that has come available. These include relevant information obtained from published peer-reviewed literature, EPA program offices, and other Federal agencies. This version of the Exposure Reassessment Document is current in this regard through 2000.

The purpose of the Exposure Reassessment Document is threefold: 1) to inventory the known sources of release of dioxins into the environment, 2) to develop an understanding of dioxins in the environment, including fate and transport properties, environmental and exposure media concentrations, background as well as elevated exposures, and temporal trends in exposure, and 3) provide site-specific procedures for evaluating the incremental exposures due to specific sources of dioxin-like compounds. Following this structure, the Exposure Reassessment Document is presented in three volumes:

Volume 1 - Sources of Dioxin-Like Compounds in the United States

This volume presents a comprehensive review of known sources of environmental releases of dioxin-like compounds in the United States. It includes an inventory of known source activity in terms of estimates of annual releases of dioxin-like compounds into the U.S. environment (i.e., air, water and land). This inventory is specific for two reference years, 1987 and 1995. From these data, it is possible to compare and contrast releases of dioxin-like compounds among the sources and between the reference years.

Volume 2 - Properties, Environmental Levels, and Background Exposures

This volume presents and evaluates information on the physical-chemical properties, environmental fate, environmental and exposure media levels, background and elevated human exposures, and temporal trends of dioxin-like compounds in the U.S. environment during the 20th century.

Volume 3 - Site-Specific Assessment Procedures

This volume presents procedures for evaluating the incremental impact from sources of dioxin release into the environment. The sources covered include contaminated soils, stack emissions, and point discharges into surface water. This volume includes sections on: exposure parameters and exposure scenario development; stack emissions and atmospheric transport modeling; aquatic and terrestrial fate, and food chain modeling; demonstration of methodologies; and uncertainty evaluations including exercises on sensitivity analysis and model validation, review of Monte Carlo assessments conducted for dioxin-like compounds, and other discussions.

The primary technical resource supporting the development of the inventory of sources of dioxin-like compounds discussed in Volume I (above) is the Database of Sources of Environmental Releases of Dioxin-Like Compounds in the United States (EPA/600/C-01/012. March, 2001). This database includes congener-specific CDD and CDF emissions data extracted from original engineering test reports. It has been published independently from the Reassessment and is available on Compact Disk-Read only Memory (CD-ROM), without cost, from EPA's National Service Center for Environmental Publications (NSCEP) in Cincinnati, Ohio (telephone: 1-800-490-9198, or 513-489-8190; fax: 513-489-8695). Summary files from the database will be available for downloading from the Web page of the National Center for Environmental Assessment, www.epa.gov/ncea/dioxin.htm. Instructions on how to order and obtain the CD-ROM will also be available on the Web page.

1.2. DEFINITION OF DIOXIN-LIKE COMPOUNDS

This assessment addresses specific compounds in the following chemical classes: polychlorinated dibenzo-*p*-dioxins (PCDDs or CDDs), polychlorinated dibenzofurans (PCDFs

or CDFs), polybrominated dibenzo-*p*-dioxins (PBDDs or BDDs), polybrominated dibenzofurans (PBDFs or BDFs), and polychlorinated biphenyls (PCBs), and describes this subset of chemicals as “dioxin-like.” Dioxin-like refers to the fact that these compounds have similar chemical structure, similar physical-chemical properties, and invoke a common battery of toxic responses. Because of their hydrophobic nature and resistance towards metabolism, these chemicals persist and bioaccumulate in fatty tissues of animals and humans. The CDDs include 75 individual compounds; CDFs include 135 different compounds. These individual compounds are referred to technically 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 a minimum, 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. This suggests that 17 individual CDDs/CDFs, and an additional 17 BDDs/BDFs, exhibit dioxin-like toxicity. The database on many of the brominated compounds regarding dioxin-like activity has been less extensively evaluated, and these compounds have not been explicitly considered in this assessment.

There are 209 PCB congeners. Only 13 of the 209 congeners are thought to have dioxin-like toxicity; these are PCBs with 4 or more lateral chlorines with 1 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 (PBBs) are likely to have similar properties. However, the database on these compounds with regard to dioxin-like activity has been less extensively evaluated, and these compounds have not been explicitly considered in this assessment. Mixed chlorinated and brominated congeners of dioxins, furans, and biphenyls also exist, increasing the number of compounds potentially considered dioxin-like within the definitions of this assessment. 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. Again, these compounds have not been explicitly considered in this assessment. Generally speaking, this assessment focuses on the 17 CDDs/CDFs and a few of the coplanar PCBs that are frequently

encountered in source characterization or environmental samples. While recognizing that other “dioxin-like” compounds exist in the chemical classes discussed above (e.g., brominated or chlorinated/brominated congeners) or in other chemical classes (e.g., halogenated naphthalenes or benzenes, azo- or azoxybenzenes), the evaluation of less than two dozen chlorinated congeners is generally considered sufficient to characterize environmental “dioxin.”

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

1.3. TOXIC EQUIVALENCY FACTORS

CDDs, CDFs, and PCBs are commonly found as complex mixtures when detected in environmental media and biological tissues, or when measured as environmental releases from specific sources. Humans are likely to be exposed to variable distributions of CDDs, CDFs, and dioxin-like PCB congeners that vary by source and pathway of exposures. This complicates the human health risk assessment that may be associated with exposures to variable mixtures of dioxin-like compounds. In order to address this problem, the concept of toxic equivalency has been considered and discussed by the scientific community, and TEFs have been developed and introduced to facilitate risk assessment of exposure to these chemical mixtures.

On the most basic level, TEFs compare the potential toxicity of each dioxin-like compound comprising the mixture to the well-studied and understood toxicity of TCDD, the most toxic member of the group. The background and historical perspective regarding this procedure is described in detail in Part II, Chapter 9, Section 9.1, 9.2, and in Agency

documents (U.S. EPA, 1987e; 1989a,b; 1991i). This procedure involves assigning individual TEFs to the 2,3,7,8-substituted CDD/CDF congeners and “dioxin-like” PCBs. To accomplish this, scientists have reviewed the toxicological databases along with considerations of chemical structure, persistence, and resistance to metabolism, and have agreed to ascribe specific, “order of magnitude” TEFs for each dioxin-like congener relative to TCDD, which is assigned a TEF of 1.0. The other congeners have TEF values ranging from 1.0 to 0.00001. Thus, these TEFs are the result of scientific judgment of a panel of experts using all of the available data and are selected to account for uncertainties in the available data and to avoid underestimating risk. In this sense, they can be described as “public health conservative” values. To apply this TEF concept, the TEF of each congener present in a mixture is multiplied by the respective mass concentration and the products are summed to represent the 2,3,7,8-TCDD Toxic Equivalence (TEQ) of the mixture, as determined by Equation (1-1):

$$TEQ \cong \sum_{i=1}^n (\text{Congener}_i \times TEF_i) + \dots + (\text{Congener}_n \times TEF_n) \quad (1-1)$$

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

1. I-TEQ refers to the International TEF scheme adopted by EPA in 1989 (U.S. EPA, 1989a). See Table 1-1.
2. TEQ-WHO₉₄ refers to the 1994 WHO extension of the I-TEF scheme to include 13 dioxin-like PCBs (Ahlborg et al., 1994). See Table 1-2.
3. TEQ-WHO₉₈ refers to the 1998 WHO update to the previously established TEFs for dioxins, furans, and dioxin-like PCBs (van den Berg et al., 1998). See Table 1-3.

The nomenclature also uses subscripts to indicate which family of compounds is included in any specific TEQ calculation. Under this convention, the subscript D is used to designate dioxins, the subscript F to designate furans and the subscript P to designate PCBs. As an example, "TEQ_{DF}-WHO₉₈" would be used to describe a mixture for which only dioxin and furan congeners were determined and where the TEQ was calculated using the WHO₉₈ scheme. If PCBs had also been determined, the nomenclature would be "TEQ_{DFP}-WHO₉₈." Note that the designations TEQ_{DF}-WHO₉₄ and I-TEQ_{DF} are interchangeable, as the TEFs for dioxins and furans are the same in each scheme. Note also that in this document, I-TEQ sometimes appears without the D and F subscripts. This indicates that the TEQ calculation includes both dioxins and furans.

This reassessment recommends that the WHO₉₈ TEF scheme be used to assign toxic equivalency to complex environmental mixtures for assessment and regulatory purposes. Sections in the Health Reassessment Document, and summarized in the Risk Characterization, describe the mode(s) of action by which dioxin-like chemicals mediate biochemical and toxicological actions. These data provide the scientific basis for the TEF/TEQ methodology. In its 20-year history, the approach has evolved, and decision criteria supporting the scientific judgment and expert opinion used in assigning TEFs has become more transparent. Numerous states, countries, and several international organizations have evaluated and adopted this approach to evaluating complex mixtures of dioxin and related compounds. It has become the accepted methodology, although the need for research to explore alternative approaches is widely endorsed. Clearly, basing risk on TCDD alone or assuming all chemicals are equally potent to TCDD is inappropriate on the basis of available data. Although uncertainties in the use of the TEF methodology have been identified (which are described in detail in the Health Reassessment Document, Chapter 9, Section 9.5), one must examine the use of this method in the broader context of the need to evaluate the potential public health impact of complex mixtures of persistent, bioaccumulative chemicals. It can be generally concluded that the use of TEF methodology for evaluating complex mixtures of dioxin-like compounds decreases the overall uncertainties in the risk assessment process as compared to alternative approaches. Use of the latest consensus values for TEFs assures that the most recent scientific information informs this "useful, interim approach" (U.S. EPA, 1989a; Kutz et al., 1990) to dealing with complex environmental mixtures of dioxin-like compounds. As

stated by the U.S. EPA Science Advisory Board (U.S. EPA, 1995a), "The use of the TEFs as a basis for developing an overall index of public health risk is clearly justifiable, but its practical application depends on the reliability of the TEFs and the availability of representative and reliable exposure data." EPA will continue to work with the international scientific community to update these TEF values to assure that the most up-to-date and reliable data are used in their derivation and to evaluate their use on a periodic basis.

A chemical is assigned a TEF value based on all the available data comparing the chemical to either TCDD or PCB 126. In addition, there are weighting criteria that place more emphasis on chronic and subchronic studies examining toxic endpoints (van den Berg et al., 1998). There is a broad range in the quantity and quality of the data available for individual congeners. For example, the TEF for PCB 126 is based on over 60 in vivo endpoints examining responses as diverse as enzyme induction, developmental toxicity, immunotoxicity, hepatic toxicity, alterations in hormones and tumor promotion, while the TEF for 3,4,4',5-tetrachlorobiphenyl (PCB 81) is based on in vitro CYP1A induction and QSAR calculations. Fortunately, PCB 81 does not significantly contribute to human TEQ exposures. There are 5 congeners that contribute approximately 80% of the total TEQ in humans: 2,3,7,8-TCDD, 1,2,3,7,8-PCDD, 1,2,3,6,7,8-HxCDD, 2,3,4,7,8-PCDF, and PCB 126 (See Part I, Volume 2 and Section 4.4.3 of this document). With the exception of 1,2,3,6,7,8-HxCDD, the TEFs for these chemicals are based on a number of different endpoints from multiple studies performed in different laboratories. The TEF for 1,2,3,6,7,8-HxCDD is based on a two-year bioassay in which rats were exposed to a mixture of 1,2,3,6,7,8-HxCDD and 1,2,3,7,8,9-HxCDD. The TEFs for 2,3,4,7,8-PCDF and PCB 126 are similar to the mean REP value for all in vivo endpoints and are similar to their REPs for tumor promotion. The TEF for 1,2,3,7,8-PCDD is based largely on its REP for tumor promotion in rats. From these data, it is clear that the chemicals that contribute approximately 80% to the total human TEQ are well studied and the assigned TEFs provide reasonable estimates of the relative potency of these chemicals. In contrast, while there are some chemicals in the TEF methodology which have minimal data sets to reliably assess their relative potency, these chemicals do not contribute substantially to the human blood TEQ.

The ability of the TEF methodology to predict the biological effects of mixtures containing dioxin-like chemicals has been evaluated in a number of experimental systems. These studies generally demonstrate that the assumption of additivity provides a reasonable estimate of the dioxin-like potential of a mixture (described in the Health Reassessment Document, Chapter 9, Section 9.4). In addition, there are examples of non-additive interactions between dioxins and non-dioxins. Both greater than additive and less than additive interactions have been observed in these studies. In general the non-additive interactions between the dioxins and non-dioxins have been observed at doses that are considerably higher than present background human exposures.

There are a number of natural chemicals that bind and activate the aryl hydrocarbon receptor (AhR) and induce some dioxin-like effects. It has been proposed by some scientists that these chemicals contribute significantly to the total TEQ exposures and that these exposures far outweigh those from PCDDs, PCDFs and PCBs (Safe, 1995). While this hypothesis is intriguing, there are several limitations to these analyses. The in vivo data on the natural aromatic hydrocarbon receptor (AhR) ligands is limited to enzyme induction and a single developmental study. Few, if any, toxicology studies demonstrating clear dioxin-like toxicities have been published. The natural AhR ligands are rapidly metabolized and result in both transient tissue concentrations and transient effects. The natural ligands also have significant biological effects that are independent of the AhR and it is not clear as to the role of the AhR in the biological effects of these chemicals. Clearly this issue requires further research in order to better understand the relative potential health effect of dioxin and related chemicals as compared to natural AhR ligands.

One of the limitations of the use of the TEF methodology in risk assessment of complex environmental mixtures is that the risk from non-dioxin-like chemicals is not evaluated in concert with that of dioxin-like chemicals. Another limitation of the TEF methodology is their application to non-biological samples. The fate and distribution of PCDDs, PCDFs and PCBs are not necessarily related to their TEF. Thus, the use of the TEF for non-biological media must be done cautiously. Future approaches to the assessment of environmental mixtures should focus on the development of methods that will allow risks to be predicted when multiple mechanisms are present from a variety of contaminants.

1.4. OVERVIEW OF SOURCES AND EMISSIONS INVENTORY METHODOLOGY

In the United States, the major identified sources of environmental release have been grouped into five broad categories 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 or uncontrolled combustion sources (such as forest fires, building fires, and open burning of wastes).
- Metals Smelting, Refining 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 suggest 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 that 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, biota, water and some anthropogenic materials. Reservoirs become sources when they have releases to the circulating environment.

1.4.1. Overview and Organization of Source Analysis

Only sources judged to have a reasonable likelihood for releases to the "circulating environment" were addressed in this document. Examples of the circulating environment system boundary are as follows:

- CDD/CDFs and dioxin-like PCBs in air emissions and wastewater discharges were included; whereas, CDD/CDFs and dioxin-like PCBs in intermediate products or internal wastestreams were excluded. For example, the CDD/CDFs in a wastestream going to an on-site incinerator would not be addressed in this document, but any CDD/CDFs in the stack emissions from the incinerator would be included.

- CDD/CDFs and dioxin-like PCBs in wastestreams 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.

The sources addressed in this document (as defined above) can be divided into two subclasses: 1) contemporary formation sources (sources which have essentially simultaneous formation and release) and 2) reservoir sources (materials or places that contain previously formed CDD/CDFs or dioxin-like PCBs that are re-released to environment). The contemporary formation sources are discussed in Chapters 2 through 11 and the reservoir sources are discussed in Chapter 12. The presence of CDD/CDFs in ball clay is discussed in Chapter 13. Table 1-5 provides a comprehensive list of all known or suspected sources of CDDs/CDFs in the United States. The checkmarks indicate how each source was classified in terms of the following six categories:

- Contemporary formation sources with reasonably well quantified releases (referred to in this document as the Quantitative Inventory of Sources). These sources are listed in Table 1-5 and release estimates are shown in Tables 1-7 and 1-8.
- Contemporary formation sources with preliminary release estimates. These sources are listed in Table 1-5 and release estimates are shown in Tables 1-7 and 1-8.
- Contemporary formation sources without quantified release estimates. These sources are listed in Table 1-5.
- Reservoir sources with reasonably well quantified releases. These sources are listed in Table 1-5.
- Reservoir sources with preliminary release estimates. These sources are listed in Table 1-5 and release estimates are shown in Tables 1-7 and 1-8.
- Reservoir sources without quantified releases. These sources are listed in Table 1-5.

This document includes discussions on products which contain dioxin-like compounds. Some of these, such as 2,4-D, are considered to be sources since they are clearly used in ways that result in environmental releases. These products have been classified into one of the above six groups. Other products containing dioxin-like compounds, such as vinyl chloride products, do not appear to have environmental releases

and are not considered sources. For all CDD/CDF containing products, this document summarizes the available information about the contamination levels and, where possible, makes estimates of the total amount of CDD/CDF produced annually in these products. Estimates of the CDD/CDF TEQ amounts in products are summarized in Tables 1-11 and 1-12.

Throughout this document, environmental release estimates are presented in terms of TEQs. This is done for convenience in presenting summary information and to facilitate comparisons across sources. For purposes of environmental fate modeling, however, it is important to use the individual CDD/CDF and PCB congener values, rather than TEQs. This is because the physical/chemical properties of individual CDD/CDF congeners vary and, consequently, the congeners will behave differently in the environment. For example, the relative mix of congeners released from a stack cannot be assumed to remain constant during transport through the atmosphere and deposition to various media. The full congener-specific release rates for most sources are given in an electronic database which is available as a companion to this document (Database of Sources of Environmental Releases of Dioxin-Like Compounds in the United States, EPA/600/R-01/012). In Part I-Volume 3, site-specific procedures are provided for estimating the impact of emissions on local populations and emphasizes that congener-specific emission values should be used in modeling environmental fate. Finally, it is important to understand that this series of documents does not use source release estimates to generate background population intake/risk estimates (rather these estimates are derived in Volume 2 primarily from food levels and consumption rates).

1.4.2 Quantitative Inventory of Sources

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 this recommendation, EPA developed in this report emission estimates for two reference years: 1987 and 1995.

EPA selected 1987 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 when 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.

EPA selected 1995 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-1990s. So the emissions data and media/food data in these two volumes are presented on a roughly consistent basis. Since 1995, EPA has promulgated regulations limiting CDD/CDF emissions for a number of the source categories that contribute to the inventory including municipal waste combustors, medical waste incinerators, hazardous waste incinerators, cement kilns burning hazardous waste, and pulp and paper facilities using chlorine bleached processes. Consequently, the estimate of releases in the 1995 inventory should not be assumed to accurately represent post-1995 releases. EPA intends to periodically revise this inventory.

A key element of the inventory is the method of extrapolation from tested facilities to national estimates of environmental releases. Because not every U.S. facility in each of the source categories have been tested for CDD/CDF emissions and releases, an extrapolation procedure was developed 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 is then multiplied by a national value for the activity level basis

of the emission factor (e.g., total kilogram [kg] of material processed in the United States annually).

With the exception of certain releases from the bleached chemical wood pulp/paper industry, no source category has 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 that grouped facilities with common features and then to develop separate emission factors for each subcategory. Implicit in this procedure is the assumption that facilities with similar design and operating conditions should have similar CDD/CDF release potential. For most source categories, however, the specific combination of features that contributes 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 vary considerably. Consequently, it is important that emission estimates be accompanied by some indicator of the uncertainties associated with their development. For this reason, a qualitative 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 1-6, presents the qualitative criteria used to assign a high, medium, or low confidence rating to the emission factor and

activity level terms for those source categories for which emission estimates can be reliably quantified. The overall "confidence rating" assigned to an emission estimate was determined by the confidence ratings assigned to the corresponding "activity level" term and "emission factor" term. If the lowest rating assigned to either the activity level or emission factor terms is "high," then the category rating assigned to the emission estimate is high (also referred to as "A"). If the lowest rating assigned to either the activity level or emission factor terms is "medium," then the category rating assigned to the emission estimate is medium (also referred to as "B"). If the lowest rating assigned to either the activity level or emission factor terms is "low," then the category rating assigned to the emission estimate is low (also referred to as "C"). It is emphasized that this confidence rating scheme should be interpreted as subjective judgements of the relative uncertainty among sources, not statistical measures.

For many source categories, either emission factor information or activity level information were inadequate to support development of reliable quantitative release estimates for one or more media. For some of these source categories, sufficient information was available to make preliminary estimates of emissions of CDD/CDFs or dioxin-like PCBs; however, the confidence in the activity level estimates or emission factor estimates was so low that the estimates cannot be included in the sum of quantified emissions from sources with confidence ratings of A, B and C. These preliminary estimates were given an overall confidence class rating of D (see Tables 1-7 and 1-8). As preliminary estimates of source magnitude, they can be used, however, to help prioritize future research and data collection. The actual magnitude of emissions from these sources could be significantly lower or higher than these preliminary estimates. Although EPA has chosen not to include them in the more thoroughly characterized emissions of the national inventory, some of these poorly characterized sources have the potential of being major contributors of releases to the environment. As the uncertainty around these sources is reduced, they will be included in future inventory calculations. For other sources, some information exists which suggests that they may release dioxin-like compounds; however, the available data were judged to be insufficient for developing any quantitative emission estimate. These source categories were assigned a confidence category rating of "E" and also were not included in the national inventory (See listings in Table 1-5 under the "Not Quantifiable" column).

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 for any individual facility. Given the limited amount of data available for deriving emission factors, and the limitations of our understanding about facility-specific conditions that determine formation and control of dioxin-like compounds, the current state of knowledge cannot support the development of emission factors that can be used to accurately estimate emissions on an individual facility-specific basis.

1.5. GENERAL FINDINGS OF THE EMISSIONS INVENTORY

Nationwide emission estimates of I-TEQ_{DF} and TEQ_{DF}-WHO₉₈ for the United States inventory are presented in Tables 1-7 and 1-8, respectively, for those source categories for which emission estimates can be reliably quantified. Nationwide emission estimates for dioxin-like PCBs are presented in Chapter 11. Figures 1-2 and 1-3 are charts that visually display the range of I-TEQ_{DF} emission estimates to air that are reported in Table 1-7 with confidence ratings of A, B, or C. Figure 1-4 compares the I-TEQ_{DF} emission estimates to air for the two reference years (i.e., 1987 and 1995). Figures 1-5 and 1-6 are charts that visually display the range of TEQ_{DF}-WHO₉₈ emission estimates to air that are reported in Table 1-8 with confidence ratings of A, B, or C. Figure 1-7 compares the TEQ_{DF}-WHO₉₈ emission estimates to air for the two reference years.

Table 1-9 lists the I-TEQ_{DF} emission factors used to derive the emission estimates presented in Table 1-7 with confidence ratings of A, B, or C. Table 1-10 lists the TEQ_{DF}-WHO₉₈ emission factors used to derive the emission estimates presented in Table 1-8 with confidence ratings of A, B, or C. 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.

Tables 1-7 and 1-8 also present preliminary indications of the potential magnitude of I-TEQ_{DF} and TEQ_{DF}-WHO₉₈ emissions, respectively, from category D sources in reference year 1995. These estimates are based on very limited data whose representativeness is unknown. The estimates were developed primarily as a tool to direct future investigations and studies.

EPA's best estimates of releases of CDD/CDFs to air, water, and land from reasonably quantifiable sources were approximately 3,000 gram (g) I-TEQ_{DF} (3,300 g TEQ_{DF}-WHO₉₈) in 1995 and 12,800-g I-TEQ_{DF} (14,000 g TEQ_{DF}-WHO₉₈) in 1987.

The environmental releases of CDD/CDFs 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 indicates that quantifiable emissions from combustion sources are more than an order of magnitude greater than quantifiable emissions from all other categories combined. Approximately 71% of all quantifiable environmental releases were dominated by air emissions from just three source categories in 1995: municipal waste incinerators (representing 38% of total environmental releases); backyard burning of refuse in barrels (representing 19% of total releases); and medical waste incinerators (representing 14% of total releases).

The decrease in estimated emissions of CDD/CDFs between 1987 and 1995 (approximately 77 percent) was due primarily to reductions in air emissions from municipal and medical waste incinerators, and further reductions are anticipated. 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. EPA's regulatory programs estimate that full compliance with recently promulgated regulations should result in further reductions in emissions from the 1995 levels (i.e., a reduction of more than 1,800 grams I-TEQ_{DF} by the year 2005). Specifically, the Office of Air and Radiation estimates that full compliance with Maximum Achievable Control Technology (MACT) standards under the Clean Air Act (CAA) will result in annual emissions of 12 g I-TEQ_{DF} from municipal solid waste incinerators and 6 g I-TEQ_{DF} from medical waste incinerators by the year 2005. The Office of Solid Waste anticipates that full compliance with regulations promulgated under the combined authorities of the CAA and the Resource

Conservation and Recovery Act (RCRA) will result in annual emissions from hazardous waste incinerators and cement kilns burning hazardous waste of about 4 and 8 g I-TEQ_{DF}, respectively, by 2002. The Office of Water estimates that full compliance with effluent guidelines promulgated under the Clean Water Act for the pulp and paper industry will result in annual releases to water of 5 g I-TEQ_{DF}. However, no Federal regulations are in place or currently under development for limiting CDD/CDF emissions from backyard burning of refuse in barrels. A number of states have general restrictions on the practice of backyard trash burning.

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 I-TEQ_{DF} or TEQ_{DF}-WHO₉₈ for 1987 and 28 g I-TEQ_{DF} or TEQ_{DF}-WHO₉₈ for 1995) and manufacture of ethylene dichloride (EDC)/vinyl chloride monomer (VCM) (< 1 g I-TEQ_{DF} or TEQ_{DF}-WHO₉₈ in 1995). Other releases to water bodies that cannot be quantified on the basis of existing data include effluents from POTWs and most industrial/commercial sources.

Based on the available information, the quantitative inventory of sources includes only a limited set of activities that result in direct environmental releases to land. The only releases to land quantified in the national inventory are land application of sewage sludge or commercial sludge products (106.5 g I-TEQ_{DF} or 79 g TEQ_{DF}-WHO₉₈ in 1995), land application of pulp and paper mill wastewater sludges (2.0 g I-TEQ_{DF} or TEQ_{DF}-WHO₉₈ in 1995), use of 2,4-D pesticides (18.4 g I-TEQ_{DF} or 28.9 g TEQ_{DF}-WHO₉₈), and manufacturing wastes from EDC/VCM (< 1 g I-TEQ_{DF} or TEQ_{DF}-WHO₉₈). Not included in the Inventory's definition of an environmental release is the disposal of sludges and ashes into approved and regulated landfills.

Significant amounts of dioxin-like compounds produced annually are not considered environmental releases and, therefore, are not included in the national inventory. Examples include dioxin-like compounds generated internal to a process, but destroyed before release, waste streams which are disposed of in approved landfills and are therefore outside the definition of annual environmental releases, and products which contain dioxin-like compounds but for which environmental releases, if any, cannot be estimated.

The procedures and results of the U.S. inventory may have underestimated releases from contemporary sources. A number of investigators have suggested that national

inventories may underestimate emissions because of 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; Bruzy and Hites, 1995). The uncertainty, however, in both the emissions and deposition estimates for the United States prevents the use of this approach for reliably evaluating the issue (U.S. EPA, 1995a). As explained below, this document has instead evaluated this issue by making preliminary estimates of poorly characterized sources and listing other sources that have been reported to emit dioxin-like compounds but cannot be characterized on even a preliminary basis.

- A number of sources were not included in the inventory even though limited evidence exists indicating that these sources can emit CDD/CDFs. These sources include various components of the metals industries such as electric arc furnaces and foundries and uncontrolled or minimally controlled combustion practices (e.g., backyard trash burning and accidental fires at landfills). Tables 1-11 and 1-12 present preliminary estimates of U.S. national emissions using the emission factors reported in these other studies as though they were representative of emission factors for U.S. facilities.
- The possibility remains that truly unknown sources exist. Many of the sources that 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 not recognized as a source until the early 1990s.

1.6. GENERAL SOURCE OBSERVATIONS

For any given time period, releases from both contemporary formation sources and reservoir sources determine the overall amount of the dioxin-like compounds that are being released to the open and circulating environment. Because existing information is incomplete with regard to quantifying contributions from contemporary and reservoir sources, it is not currently possible to estimate total magnitude of release for dioxin-like compounds into the U.S. environment from all sources. For example, in terms of 1995 releases from reasonably quantifiable sources, this document estimates releases of 3,000 g T-TEQ_{DF} (3,300 g TEQ_{DF}-WHO₉₈) for contemporary formation sources and 2,900 g I-TEQ_{DF} or TEQ_{DF}-WHO₉₈ for reservoir sources. In addition, there remains a number of unquantifiable and poorly quantified sources. No quantitative release estimates can be made for agricultural burning or for most CDD/CDF reservoirs or for any dioxin-like PCB

reservoirs. The preliminary estimate of 1995 poorly characterized contemporary formation sources is 1,500 g I-TEQ_{DF} or TEQ_{DF}-WHO₉₈.

The contribution of dioxin-like compounds to waterways from nonpoint source reservoirs is likely to be greater than the contributions from point sources. Current data are only sufficient to support preliminary estimates of nonpoint source contributions of dioxin-like compounds to water (i.e., urban storm water runoff and rural soil erosion). These estimates suggest that, on a nationwide basis, total nonpoint releases are significantly larger than point source releases.

Current releases of CDD/CDFs to the U.S. environment result principally from anthropogenic activities. This finding applies to both sources of newly formed dioxin-like compounds and reservoir sources. Four lines of evidence support this finding:

- As discussed in Volume 2, the companion document to this report, 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 pollution abatement actions are likely to have resulted in decreased CDD/CDF emissions (i.e., elimination of much open burning of solid waste, installation of particulate controls on combustors, phase out of leaded gasoline, and bans or restrictions on PCBs, 2,4,5-T, and PCP).
- In at least one case, soil erosion to surface waters, reservoir sources are thought to be a significant contributor to the environment. However, the principal source of CDD/CDFs in surface soils is air deposition. As discussed in the first bullet, it appears that CDD/CDFs associated with air deposition are primarily of anthropogenic origin.
- 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. Recently CDD/CDFs have been discovered in ball clay deposits in western Mississippi,

Kentucky, and Tennessee. Although the origin of the CDD/CDFs in these clays may be natural, it has not been confirmed.

- As discussed in Volume 2, the companion document to this report, 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.

Although chlorine is an essential component for the formation of CDD/CDFs in combustion systems, the empirical evidence indicates that for commercial scale incinerators, chlorine levels in feed are not the dominant controlling factor for rates of CDD/CDF stack emissions. Important factors which can affect the rate of CDD/CDF formation include the overall combustion efficiency, post-combustion flue gas temperatures and residence times, and the availability of surface catalytic sites to support CDD/CDF synthesis. Data from bench, pilot and commercial scale combustors indicate that CDD/CDF formation can occur by a number of mechanisms. Some of these data, primarily from laboratory and pilot scale combustors, have shown direct correlation between chlorine content in fuels and rates of CDD/CDF formation. Other data, primarily from commercial scale combustors, show little relation between availability of chlorine in feeds and rates of CDD/CDF formation. These studies are summarized below:

- Evidence from laboratory studies - A number of laboratory studies indicate that changes in the chlorine content of feed materials may result in changes in the amount of CDD/CDFs formed in the post-combustion region of a bench scale combustion system (Kanters and Louw, 1994; Kanters et al., 1996; De Fre and Rymen 1989; Wagner and Green, 1993).
- Evidence from pilot-scale studies - Recent evidence from a pilot-scale combustion study suggests that the amount of CDD/CDFs formed is not strongly correlated with chlorine content of the feed material when the feed material contains less than one percent chlorine; when chlorine in the feed is above one percent, the chlorine feed content appears to be directly proportional to the amount of CDD/CDFs formed (Wikstrom et al., 1996). Other pilot-scale studies indicate a strong relationship between the amount of HCl formed (from organically-bound chlorine in feeds) and the amount of CDD/CDFs formed (Bruce et al., 1991; Wagner and Green, 1993). Wagner and Green (1993) concluded that a decrease in the levels of organically-bound chlorine in the feed leads to a decrease in chlorinated organic emissions.

- Evidence from studies of full-scale systems - Combustors having poor combustion characteristics and hot-sided particulate control devices show a positive correlation between chlorine in feeds/fuels and CDD/CDF stack emissions (Thomas and Spiro 1995; U.S. EPA, 1987a). Combustors with high combustion efficiency, cool-sided particulate control devices, and advanced dioxin-specific air pollution control systems, however, do not show a strong correlation between chlorine amounts in feeds/fuels and the amount of CDDs/CDFs emitted from the stack (Rigo et al., 1995). This conclusion has been questioned in a paper by Costner (1998) who claims that many of the facilities assessed by Rigo et al. (1996) show a positive (though small) correlation between chlorine in feed and CDD/CDF emissions. Conversely, Costner (1998) also found that about half the facilities showed a weak inverse relationship. The American Society of Mechanical Engineers (ASME) has concluded that, "Whatever effect chlorine has on PCDD/CDF emissions in commercial scale systems is masked by the effect of APCS (air pollution control systems), temperature, ash chemistry, combustion conditions, measurement imprecision, and localized flow stratification (ASME, 1995)."

The conclusion that chlorine in feed is not a strong determinant of CDD/CDF emissions applies to the overall population of commercial scale combustors. For any individual commercial scale combustor, circumstances may exist in which changes in chlorine content of feed could affect CDD/CDF emissions. For uncontrolled combustion, such as open burning of household waste, the chlorine content of the waste may play a more significant role in rates of CDD/CDF formation and release than is observed at commercial scale combustors.

Dioxins are present in some ball clays, but insufficient data are available to estimate whether environmental releases occur during the mining and use. Recent studies in the U.S. and Europe have measured dioxins (principally CDDs) in some ball clays and other related clays. As discussed in Chapter 13, it is likely that the CDDs present in ball clay are of a natural origin. Ball clay is principally used in the manufacture of ceramics which involves firing the clay in high temperature kilns. This activity may cause some portion of the CDDs contained in the clay to be released into the air, but emission tests have not yet been conducted which would allow characterizing these releases.

Data are available to estimate the amounts of CDD/CDFs 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 to be made of the amounts of dioxin-like compounds in bleached pulp (40 g I-TEQ_{DF} or TEQ_{DF}-WHO₉₈ in 1995), POTW sludge used in fertilizers (3.5 g I-TEQ_{DF} or 2.6 g

TEQ_{DF}-WHO₉₈ in 1995), pentachlorophenol-treated wood (8,400 g I-TEQ_{DF} or 4,800 g TEQ_{DF}-WHO₉₈ in 1995), dioxazine dyes and pigments (< 1 g I-TEQ_{DF} or TEQ_{DF}-WHO₉₈ in 1995) and 2,4-D (18.4 g I-TEQ_{DF} or 28.9 g TEQ_{DF}-WHO₉₈ in 1995).

No 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 it has been demonstrated that small quantities of dioxin-like PCBs can be produced during waste combustion, no strong evidence exists that the dioxin-like PCBs make a significant contribution to TEQ releases during combustion. The occurrences of dioxin-like PCBs in the U.S. environment most likely reflect past releases associated with PCB production, use, and disposal. Further support for this finding is based on observations of reductions since the 1980s in PCB concentrations in Great Lakes sediment and other areas.

It is unlikely that the emission rates of CDD/CDFs from known sources correlate proportionally with general population exposures. Although the 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 affecting CDD/CDF concentrations in food (see discussion in Section 2.6 of Volume 2) may not be those sources that represent the largest fractions of current 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 are produced are important to consider. That is, many of the agricultural areas that produce dietary animal fats are not located near or directly down wind of the major sources of dioxin-like compounds.

The contribution of reservoir sources to human exposure may be significant.

Several factors support this finding:

- Because the magnitude of releases from current sources of newly formed PCBs are most likely negligible, human exposure to the dioxin-like PCBs is thought to be derived almost completely from reservoir sources. Key pathways involve releases from both soils and sediments to both aquatic and terrestrial food chains. As discussed in Volume 2, one third of general population TEQ_{DFP} exposure is due to PCBs. Thus, at least one third of the overall risk from dioxin-like compounds comes from reservoir sources.
- CDD/CDF releases from soil via soil erosion and runoff to waterways may be significant. These releases appear to be greater than releases to water from the

primary sources included in the inventory. CDD/CDFs in waterways can bioaccumulate in fish leading to human exposure via consumption of fish. As discussed in Volume 2, fish consumption makes up about one third of the total general population CDD/CDF TEQ exposure. This suggests that a significant portion of the CDD/CDF TEQ exposure could be due to releases from the soil reservoir. It is not known, however, how much of the soil erosion and runoff represents recently deposited CDD/CDFs from primary sources or longer term accumulation. Much of the eroded soil comes from tilled agricultural lands which would include a mix of CDD/CDFs from various deposition times. The age of CDD/CDFs in urban runoff is less clear.

- Potentially, soil reservoirs could have vapor and particulate releases which deposit on plants and enter the terrestrial food chain. The magnitude of this contribution, however, is unknown. EPA plans future studies in agricultural areas which will compare modeled air concentrations from primary sources to measured levels as a way to get further insight to this issue.

1.7. CONGENER PROFILES OF CDD/CDF SOURCES

This section summarizes congener profiles of known sources of dioxin-like compounds in the United States (Cleverly et. al, 1998). Congener profiles are the fractional distribution of CDD/CDF congeners in an environmental release, in an environmental sample, or in a biological sample. Under some circumstances, 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. There are numerous procedures one could elect to use to derive a congener profile, and there is no single agreed-upon convention (Cleverly et al., 1998; Lorber et al., 1996; Hagenmaier et al., 1994). In this report, congener profiles were developed primarily by calculating the ratio of specific 2,3,7,8-substituted CDDs and CDFs in the emission or product to the total (Cl₄ - Cl₈) CDDs/CDFs. With respect to combustion sources, the profiles were derived by: (a) dividing the congener-specific emission factors by the total (Cl₄ - Cl₈) CDD/CDF emission factor for each tested facility; and (b) then averaging the congener profiles developed for all tested facilities within the combustor type. For chemical processes and commercial chemicals, CDD/CDF profiles were typically generated by dividing average congener concentrations (ppt) in the chemical by the total CDD/CDF present. Profiles for selected source categories are presented in Figure 1-8.

On the basis of inspection and comparisons of the average CDD/CDF congener profiles across combustion and non-combustion sources, the following observations are made (Cleverly et al., 1998): (These generalizations are derived from this data set, and their application beyond these data is uncertain).

- i. It appears that combustion sources emit all 2,3,7,8-substituted CDDs and CDFs, although in varying percentages of total CDD/CDF.
- ii. In combustion source emissions, 2,3,7,8-TCDD is usually 0.1 to 1.0 percent of total CDD/CDF. The exception to this are stack emissions from industrial oil-fired boilers where the available, but limited data, indicate that 2,3,7,8-TCDD constitutes an average of 7 percent of total CDD/CDF emissions.
- iii. It cannot be concluded that OCDD is the dominant congener for all combustion generated emissions of CDD/CDFs. OCDD dominates total emissions from: mass burn municipal solid waste incinerators (MSWI) that have dry scrubbers and fabric filters (DS/FF) for dioxin controls; industrial oil-fired boilers; industrial wood-fired boilers; unleaded gasoline combustion; diesel fuel combustion in trucks; and sewage sludge incinerators. The dominant congeners for other combustion sources are: 1,2,3,4,6,7,8-HpCDF in emissions from mass burn MSWIs equipped with hot-sided electrostatic precipitators (ESPs); OCDF in emissions from medical waste incineration; 1,2,3,4,6,7,8-HpCDF in hazardous waste incinerators; 2,3,4,7,8-PeCDF in cement kilns burning hazardous waste; 2,3,7,8-TCDF in cement kilns not burning hazardous waste; OCDF in industrial/utility coal-fired boilers; 1,2,3,4,6,7,8-HpCDF in secondary aluminum smelters; and 2,3,7,8-TCDF in secondary lead smelters.
- iv. The 1,2,3,4,6,7,8-HpCDF appears to be the dominant congener in the following sources: secondary aluminum smelters; MSWIs equipped with hot-sided ESPs; hazardous waste incinerators; and 2,4-D salts and esters.
- v. Evidence for a shift in the congener patterns potentially caused by the application of different air pollution control systems within a combustion source-type can be seen in the case of mass burn MSWIs. For mass burn MSWIs equipped with hot-sided ESPs, the most prevalent CDD/CDF congeners are: 1,2,3,4,6,7,8-HpCDF; OCDD; 1,2,3,4,6,7,8-HpCDD/1,2,3,4,7,8-HxCDF; 2,3,4,6,7,8-HxCDF/OCDF; 1,2,3,6,7,8-HxCDF. The most prevalent congeners emitted from MSWIs equipped with DS/FF are: OCDD; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,8-HpCDF; OCDF; 2,3,7,8-TCDF/1,2,3,4,7,8-HxCDD; 2,3,4,6,7,8-HxCDF.
- vi. There is evidence of marked differences in the distribution of CDD/CDF congeners between cement kilns burning and not burning hazardous waste. When not burning hazardous waste as supplemental fuel, the dominant congeners appear to be 2,3,7,8-TCDF; OCDD; 1,2,3,4,6,7,8-HpCDD, and OCDF. When burning hazardous waste, the dominant congeners are: 2,3,7,8-PeCDF; 2,3,7,8-TCDF; 1,2,3,4,7,8-

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

- vii. The congener profile of 2,4-D salts and esters seems to mimic a combustion source profile in the number of congeners represented, and in the minimal amount of 2,3,7,8-TCDD relative to all 2,3,7,8-substituted congeners. A major difference is the prevalence of 1,2,3,7,8-PeCDD in 2,4-D (i.e., 14 percent), which is not seen in any other combustion or non-combustion sources presented here.
- viii. There are similarities in the congener profiles of pentachlorophenol (PCP), diesel truck emissions, unleaded gasoline vehicle emissions, and industrial wood combustors. In these sources, OCDD dominates total emissions, but the relative ratio of 1,2,3,4,6,7,8-HpCDD to OCDD is also quite similar.
- ix. The congener profiles for diesel truck exhaust and air measurements from a tunnel study of diesel traffic are quite similar.

Table 1-1. The TEF Scheme for I-TEQ_{DF}

Dioxin (D) Congener	TEF	Furan (F) Congener	TEF
2,3,7,8-TCDD	1.0	2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDD	0.5	1,2,3,7,8-PeCDF	0.05
1,2,3,4,7,8-HxCDD	0.1	2,3,4,7,8-PeCDF	0.5
1,2,3,6,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8- HpCDD	0.01	1,2,3,7,8,9-HxCDF	0.1
OCDD	0.001	2,3,4,6,7,8-HxCDF	0.1
		1,2,3,4,6,7,8-HpCDF	0.01
		1,2,3,4,7,8,9-HpCDF	0.01
		OCDF	

Table 1-2. The TEF Scheme for Dioxin-Like PCBs, as Determined by the World Health Organization in 1994

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

Table 1-3. The TEF Scheme for TEQ_{DFF-WHO}₉₈

Dioxin Congeners	TEF	Furan Congeners	TEF
2,3,7,8-TCDD	1.0	2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDD	1.0	1,2,3,7,8-PeCDF	0.05
1,2,3,4,7,8-HxCDD	0.1	2,3,4,7,8-PeCDF	0.5
1,2,3,6,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDD	0.01	1,2,3,7,8,9-HxCDF	0.1
OCDD	0.0001	2,3,4,6,7,8-HxCDF	0.1
		1,2,3,4,6,7,8-HpCDF	0.01
		1,2,3,4,7,8,9-HpCDF	0.01
		OCDF	0.0001

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

Table 1-4. Nomenclature for Dioxin-Like Compounds

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., 22 isomers constitute the congener group of TCDDs).
Specific Isomer	Denoted by unique chemical notation (e.g., 2,4,8,9-tetrachlorodibenzofuran is referred to as 2,4,8,9-TCDF).
D	Symbol for congener class: dibenzo-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)

Table 1-5. List of Known and Suspected CDD/CDF Sources

Emission Source Category	Contemporary Formation Sources			Reservoir Sources		
	Quantifiable	Preliminary Estimate	Not Quantifiable	Quantifiable	Preliminary Estimate	Not Quantifiable
I. COMBUSTION SOURCES						
<i>Waste Incineration</i>						
Municipal waste incineration	✓					
Hazardous waste incineration	✓					
Boilers/industrial furnaces	✓					
Medical waste/pathological incineration	✓					
Crematoria	✓					
Sewage sludge incineration	✓					
Tire combustion	✓					
Pulp and paper mill sludge incinerators	✓					
BioGas combustion		✓				
<i>Power/Energy Generation</i>						
Vehicle fuel combustion						
- leaded ^p	✓					
- unleaded	✓					
- diesel	✓					
Wood combustion - residential	✓					
- industrial	✓					
Coal combustion - residential		✓				
- industrial/utility	✓					
Oil combustion - residential		✓				
- industrial/utility	✓					
<i>Other High Temperature Sources</i>						
Cement kilns (haz waste burning)	✓					
Cement kilns (non haz waste burning)	✓					
Asphalt mixing plants		✓				
Petro. refining catalyst regeneration	✓					
Cigarette combustion	✓					
Carbon reactivation furnaces	✓					
Kraft recovery boilers	✓					
Manufacture of ball clay products			✓			

Table 1-5. List of Known and Suspected CDD/CDF Sources (continued)

Emission Source Category	Contemporary Formation Sources			Reservoir Sources		
	Quantifiable	Preliminary Estimate	Not Quantifiable	Quantifiable	Preliminary Estimate	Not Quantifiable
Minimally Controlled or Uncontrolled Combustion						
Combustion of landfill gas in flares		✓				
Landfill fires		✓				
Accidental fires (structural)		✓				
Accidental fires (vehicles)		✓				
Forest, brush, and straw fires		✓				
Backyard barrel burning	✓					
Uncontrolled combustion of PCBs			✓			
II. METAL SMELTING/REFINING						
<i>Ferrous metal smelting/refining</i>						
- Sintering plants	✓					
- Coke production		✓				
- Electric arc furnaces		✓				
- Ferrous foundries		✓				
<i>Nonferrous metal smelting/refining</i>						
- Primary aluminum			✓			
- Primary copper	✓					
- Primary magnesium		✓				
- Primary nickel			✓			
- Secondary aluminum	✓					
- Secondary copper	✓					
- Secondary lead	✓					
Scrap electric wire recovery	✓					
Drum and barrel reclamation	✓					
III. CHEMICAL MANUFACTURING						
<i>(Releases to the Environment)</i>						
Bleached chemical wood pulp and paper mills	✓					
Mono- to tetrachlorophenols			✓			
Pentachlorophenol			✓			
Chlorobenzenes			✓			
Chlorobiphenyls (leaks/spills)			✓			

Table 1-5. List of Known and Suspected CDD/CDF Sources (continued)

Emission Source Category	Contemporary Formation Sources			Reservoir Sources		
	Quantifiable	Preliminary Estimate	Not Quantifiable	Quantifiable	Preliminary Estimate	Not Quantifiable
Ethylene dichloride/vinyl chloride	✓					
Dioxazine dyes and pigments			✓			
2,4-Dichlorophenoxy acetic acid			✓			
Municipal wastewater treatment		✓				
Tall oil-based liquid soaps			✓			
IV. BIOLOGICAL AND PHOTOCHEMICAL PROCESSES			✓			
V. RESERVOIR SOURCES						
<i>Natural</i>						
- Land					✓	
- Air						✓
- Water						✓
- Sediments						✓
<i>Anthropogenic Structures</i>						
- PCP Treated Wood						✓

Table 1-6. Confidence Rating Scheme for U.S. Emission Estimates

Confidence Rating	Activity Level Estimate	Emission Factor Estimate
<i>Categories/Media for Which Releases Can Be Reasonably Quantified</i>		
High	Derived from comprehensive survey	Derived from comprehensive survey
Medium	Based on estimates of average plant activity level and number of plants or limited survey	Derived from testing at a limited but reasonable number of facilities believed to be representative of source category
Low	Based on data judged possibly nonrepresentative	Derived from testing at only a few, possibly nonrepresentative facilities or from similar source categories
<i>Categories/Media for Which Releases Cannot Be Reasonably Quantified</i>		
Preliminary Estimate	Based on extremely limited data, judged to be clearly nonrepresentative	Based on extremely limited data, judged to be clearly nonrepresentative
Not Quantified	No data available	<ol style="list-style-type: none"> 1) Argument based on theory but no data, or 2) Data available indicating formation, but not in a form that allows developing an emission factor

Table 1-7. Inventory of Environmental Releases (grams/year) of I-TEQ_{DF}
From Known Sources in the United States for 1995 and 1987

Emission Source Category	Confidence Rating ^a Reference Year 1995				Confidence Rating ^a Reference Year 1987		
	A	B	C	D	A	B	C
Releases (g TEQ/yr) to Air							
WASTE INCINERATION							
Municipal waste incineration		1,100				7,915	
Hazardous waste incineration		5.7				5.0	
Boilers/industrial furnaces			0.38				0.77
Medical waste/pathological incineration			461				2,440
Crematoria			9.1				5.5
Sewage sludge incineration		14.7				6.0	
Tire combustion			0.11				0.11
Pulp and paper mill sludge incinerators ^e							
Biogas Combustion				> 1			
POWER/ENERGY GENERATION							
Vehicle fuel combustion - leaded ^b			1.7				31.9
- unleaded			5.6				3.3
- diesel			33.5				26.3
Wood combustion - residential			62.8				89.6
- industrial		26.2				25.1	
Coal combustion - utility boilers		60.9				51.4	
Coal Combustion - residential				30.0			
Coal Combustion - commercial/Industrial				40.0			
Oil combustion - industrial/utility			9.3				15.5
Oil combustion - residential				6.0			
OTHER HIGH TEMPERATURE SOURCES							
Cement kilns (hazardous waste burning)			145.3				109.6
Lightweight aggregate kilns burning hazardous waste			3.3				2.4
Cement kilns (non hazardous waste burning)			16.6				12.7
Asphalt mixing plants				7			
Petroleum Refining Catalyst Regeneration			2.11				2.14
Cigarette combustion			0.8				1.0
Carbon reactivation furnaces			0.08				0.06
Kraft recovery boilers		2.3				2.0	
MINIMALLY CONTROLLED OR UNCONTROLLED COMBUSTION^d							
Backyard barrel burning ^f			595				573
Combustion of Landfill Gas				7.0			
Landfill fires				1,000			
Accidental Fires (Structural)				> 20			
Accidental Fires (Vehicles)				30.0			
Forest and Brush Fires				200			
METALLURGICAL PROCESSES							
Ferrous metal smelting/refining							
- Sintering plants		25.1					29.3
- Coke production				7.0			
- Electric arc furnaces				40.0			
- Foundries				20.0			

Table 1-7. Inventory of Environmental Releases (grams/year) of I-TEQ_{DF}
From Known Sources in the United States for 1995 and 1987 (continued)

Emission Source Category	Confidence Rating ^a Reference Year 1995				Confidence Rating ^a Reference Year 1987		
	A	B	C	D	A	B	C
Nonferrous metal smelting/refining							
- Primary copper		< 0.5				< 0.5	
- Secondary aluminum			27.4				15.3
- Secondary copper			266				966
- Secondary lead		1.63				1.22	
- Primary Magnesium				15.0			
Drum and barrel reclamation			0.08				0.08
CHEMICAL MANUFAC./PROCESSING SOURCES							
Ethylene dichloride/vinyl chloride		11.2					
TOTAL RELEASES TO AIR^c			2,888				12,331
<i>Releases (g TEQ/yr) to Water</i>							
CHEMICAL MANUF./PROCESSING SOURCES							
Bleached chemical wood pulp and paper mills	28.0				356		
POTW (municipal) wastewater				10			
Ethylene dichloride/vinyl chloride		0.43					
RESERVOIR SOURCES							
Urban runoff to surface water				190			
Rural soil erosion to surface water				2,700			
TOTAL RELEASES TO WATER^c			28.43		356		
<i>Releases (g TEQ/yr) to Land</i>							
CHEMICAL MANUF./PROCESSING SOURCES							
Bleached chemical wood pulp and paper mill sludge	2.0				14.1		
Ethylene dichloride/vinyl chloride		0.73					
Municipal wastewater treatment sludge	103				103		
Commercially marketed sewage sludge	3.5				3.5		
2,4-Dichlorophenoxy acetic acid	18.4				21.3		
TOTAL RELEASES TO LAND^c			127.6		141.8		
OVERALL RELEASES (g/yr) TO THE OPEN and CIRCULATING ENVIRONMENT			3,044 (SUM OF COLUMNS A, B, C)		12,829 (SUM OF COLUMNS A, B, C)		

^{1/} The most reliable estimates of environmental releases are those sources within Categories A, B and C (see footnote 'a' for definitions).

- ^a A = Characterization of the Source Category judged to be **Adequate for Quantitative Estimation with High Confidence** in the **Emission Factor** and **High Confidence** in **Activity Level**.
- B = Characterization of the Source Category judged to be **Adequate for Quantitative Estimation with Medium Confidence** in the **Emission Factor** and at least **Medium Confidence** in **Activity Level**.
- C = Characterization of the Source Category judged to be **Adequate for Quantitative Estimation with Low Confidence** in either the **Emission Factor** and/or the **Activity Level**.
- D = **Preliminary Indication** of the Potential Magnitude of I-TEQ_{DF} Emissions from "Unquantified" (i.e., Category D) Sources in Reference Year 1995. **Based on extremely limited data, judged to be clearly nonrepresentative.**
- ^b Leaded fuel production and the manufacture of motor vehicle engines requiring leaded fuel for highway use have been prohibited in the United States. (See Section 4.1 for details.)
- ^c TOTAL reflects only the total of the estimates made in this report.
- ^d This refers to conventional pollutant control, not dioxin emissions control. Very few of the sources listed in this inventory control specifically for CDD/CDF emissions.
- ^e Included within estimate for Wood Combustion - industrial.
- ^f This term refers to the burning of residential waste in barrels.

Table 1-8. Inventory of Environmental Releases (grams/year) of TEQ_{DF}-WHO₉₈
From Known Sources in the United States for 1995 and 1987

Emission Source Category	Confidence Rating ^a Reference Year 1995				Confidence Rating ^a Reference Year 1987		
	A	B	C	D	A	B	C
Releases (g TEQ/yr) to Air							
WASTE INCINERATION							
Municipal waste incineration		1,250				8,877	
Hazardous waste incineration		5.8				5.0	
Boilers/industrial furnaces			0.39				0.78
Medical waste/pathological incineration			488				2,590
Crematoria			9.1 ^e				5.5 ^e
Sewage sludge incineration		14.8				6.1	
Tire combustion			0.11				0.11
Pulp and paper mill sludge incinerators ^f							
Biogas Combustion				< 1			
POWER/ENERGY GENERATION							
Vehicle fuel combustion - leaded ^b			2.0				37.5
- unleaded			5.6				3.6
- diesel			33.5				27.8
Wood combustion - residential			62.8 ^e				89.6 ^e
- industrial		27.6				26.4	
Coal combustion - utility boilers		60.1				50.8	
Coal Combustion - residential				30			
Coal Combustion - commercial/Industrial				40			
Oil combustion - industrial/utility			10.7				17.8
Oil combustion - residential				6			
OTHER HIGH TEMPERATURE SOURCES							
Cement kilns (hazardous waste burning)			156.1				117.8
Lightweight aggregate kilns burning hazardous waste			3.3 ^e				2.4 ^e
Cement kilns (non hazardous waste burning)			17.8				13.7
Asphalt mixing plants				7			
Petroleum Refining Catalyst Regeneration			2.21				2.24
Cigarette combustion			0.8				1.0
Carbon reactivation furnaces			0.08 ^e				0.06 ^e
Kraft recovery boilers		2.3				2.0	
MINIMALLY CONTROLLED OR UNCONTROLLED COMBUSTION^d							
Backyard barrel burning ^g			628				604
Combustion of Landfill Gas				7			
Landfill fires				1,000			
Accidental Fires (Structural)				> 20			
Accidental Fires (Vehicles)				30			
Forest and Brush Fires				200			
METALLURGICAL PROCESSES							
Ferrous metal smelting/refining							
- Sintering plants		28					32.7
- Coke production				7.0			
- Electric arc furnaces				40			
- Foundries				20			

Table 1-8. Inventory of Environmental Releases (grams/year) of TEQ_{DF}-WHO₉₈
From Known Sources in the United States for 1995 and 1987 (continued)

Emission Source Category	Confidence Rating ^a Reference Year 1995				Confidence Rating ^a Reference Year 1987		
	A	B	C	D	A	B	C
Nonferrous metal smelting/refining							
- Primary copper		< 0.5 ^e				< 0.5 ^e	
- Secondary aluminum			29.1				16.3
- Secondary copper			271				983
- Secondary lead		1.72				1.29	
- Primary Magnesium				15.0			
Drum and barrel reclamation			0.08				0.08
CHEMICAL MANUFAC./PROCESSING SOURCES							
Ethylene dichloride/vinyl chloride		11.2 ^e					
TOTAL RELEASES TO AIR^c			3,125				13,515
<i>Releases (g TEQ/yr) to Water</i>							
CHEMICAL MANUF./PROCESSING SOURCES							
Bleached chemical wood pulp and paper mills	19.5				356		
POTW (municipal) wastewater				10			
Ethylene dichloride/vinyl chloride		0.43 ^e					
RESERVOIR SOURCES							
Urban runoff to surface water				190			
Rural soil erosion to surface water				2,700			
TOTAL RELEASES TO WATER^c			19.93				356
<i>Releases (g TEQ/yr) to Land</i>							
CHEMICAL MANUF./PROCESSING SOURCES							
Bleached chemical wood pulp and paper mill sludge	1.4				14.1		
Ethylene dichloride/vinyl chloride		0.73 ^e					
Municipal wastewater treatment sludge	76.6				76.6		
Commercially marketed sewage sludge	2.6				2.6		
2,4-Dichlorophenoxy acetic acid	28.9				33.4		
TOTAL RELEASES TO LAND^c			110.23				126.7
OVERALL RELEASES (g/yr) TO THE OPEN and CIRCULATING ENVIRONMENT			3,255 (SUM OF COLUMNS A, B, C)				13,998 (SUM OF COLUMNS A, B, C)

^{1/} The most reliable estimates of environmental releases are those sources within Categories A, B and C (see footnote 'a' for definitions).

^a A = Characterization of the Source Category judged to be **Adequate for Quantitative Estimation** with **High Confidence** in the **Emission Factor** and **High Confidence** in **Activity Level**.

B = Characterization of the Source Category judged to be **Adequate for Quantitative Estimation** with **Medium Confidence** in the **Emission Factor** and at least **Medium Confidence** in **Activity Level**.

C = Characterization of the Source Category judged to be **Adequate for Quantitative Estimation** with **Low Confidence** in either the **Emission Factor** and/or the **Activity Level**.

D = **Preliminary Indication** of the Potential Magnitude of I-TEQ_{DF} Emissions from "Unquantified" (i.e., Category D) Sources in Reference Year 1995. **Based on extremely limited data, judged to be clearly nonrepresentative.**

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

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

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

^e Congener-specific emissions data were not available; the I-TEQ_{DF} emission estimate was used as a surrogate for the TEQ_{DF}-WHO₉₈ emission estimate.

^f Included within estimate for Wood Combustion - industrial.

^g This term refers to the burning of residential waste in barrels.

Table 1-9. I-TEQ_{DF} Emission Factors Used to Develop National Emission Inventory Estimates of Releases to Air

Emission Source	I-TEQ _{DF} Emission Factor		Emission Factor Units
	1995	1987	
Waste Incineration			
Municipal waste incineration	38.2 ^a	573 ^a	ng TEQ/kg waste combusted
Hazardous waste incineration	3.83	3.83	ng TEQ/kg waste combusted
Boilers/industrial furnaces	0.64	0.64	ng TEQ/kg waste combusted
Medical waste/pathological incineration	598 ^a	1,706 ^a	ng TEQ/kg waste combusted
Crematoria	17	17	μg TEQ/body
Sewage sludge incineration	6.94	6.94	ng TEQ/kg dry sludge combusted
Tire combustion	0.282	0.282	ng TEQ/kg tires combusted
Pulp and paper mill sludge incinerators	b	b	
Power/Energy Generation			
Vehicle fuel combustion - leaded ^b	45	45	pg TEQ/km driven
- unleaded	1.5	1.5	pg TEQ/km driven
- diesel	172	172	pg TEQ/km driven
Wood combustion - residential	2	2	ng TEQ/kg wood combusted
- industrial	0.56 to 13.2 ^c	0.56 to 13.2 ^c	ng TEQ/kg wood combusted
Coal combustion - utility	0.079	0.079	ng TEQ/kg coal combusted
Oil combustion - industrial/utility	0.20	0.20	ng TEQ/L oil combusted
Other High Temperature Sources			
Cement kilns burning hazardous waste	1.04 to 28.58 ^e	1.04 to 28.58 ^e	ng TEQ/kg clinker produced
Cement kilns not burning hazardous waste	0.27	0.27	ng TEQ/kg clinker produced
Petroleum refining catalyst regeneration	1.52	1.52	ng TEQ/barrel reformer feed
Cigarette combustion	0.00043 to 0.0029	0.00043 to 0.0029	ng TEQ/cigarette
Carbon reactivation furnaces	1.2	1.2	ng TEQ/kg of reactivated carbon
Kraft recovery boilers	0.029	0.029	ng TEQ/kg solids combusted
Minimally Controlled or Uncontrolled Combustion			
Backyard barrel burning	72.8	72.8	ng TEQ/kg waste combusted
Metallurgical Processes			
Ferrous metal smelting/refining			
- Sintering plants	0.55 to 4.14	0.55 to 4.14	ng TEQ/kg sinter
Nonferrous metal smelting/refining			
- Primary copper	< 0.31	< 0.31	ng TEQ/kg copper produced
- Secondary aluminum smelting	21.1	21.1	ng TEQ/kg scrap feed
- Secondary copper smelting	^d	^d	ng TEQ/kg scrap consumed
- Secondary lead smelters	0.05 to 8.31	0.05 to 8.31	ng TEQ/kg lead produced
Drum and barrel reclamation	16.5	16.5	ng TEQ/drum
Chemical Manuf./Processing Sources			
Ethylene dichloride/vinyl chloride	0.95 ^a		ng TEQ/kg EDC produced

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

b Included within total for Wood Combustion - Industrial.

c Emission factor of 0.56 ng I-TEQ_{DF}/kg used for non-salt-laden wood; emission factor of 13.2 ng I-TEQ_{DF}/kg used for salt-laden wood.

d Facility-specific emission factors were used ranging from 3.6 to 16,600 ng I-TEQ_{DF}/kg scrap consumed.

e Emission factor of 1.04 ng I-TEQ_{DF}/kg used for kilns with APCD inlet temperatures less than 450°F; emission factor of 28.58 ng I-TEQ_{DF}/kg used for kilns with APCD inlet temperatures greater than 450°F.

TEQ = Toxic equivalency factor.

ng = nanogram.

kg = kilogram.

pg = picogram.

Table 1-10. TEQ_{DF}-WHO₉₈ Emission Factors Used to Develop National Emission Inventory Estimates of Releases to Air

Emission Source	TEQ _{DF} -WHO ₉₈ Emission Factor		Emission Factor Units
	1995	1987	
Waste Incineration			
Municipal waste incineration	43.4 ^a	644 ^a	ng TEQ/kg waste combusted
Hazardous waste incineration	3.88	3.88	ng TEQ/kg waste combusted
Boilers/industrial furnaces	0.65	0.65	ng TEQ/kg waste combusted
Medical waste/pathological incineration	633 ^a	1,811 ^a	ng TEQ/kg waste combusted
Crematoria	17 ^f	17 ^f	μg TEQ/body
Sewage sludge incineration	7.04	7.04	ng TEQ/kg dry sludge combusted
Tire combustion	0.281	0.281	ng TEQ/kg tires combusted
Pulp and paper mill sludge incinerators	b	b	
Power/Energy Generation			
Vehicle fuel combustion - leaded ^b	53	53	pg TEQ/km driven
- unleaded	1.6	1.6	pg TEQ/km driven
- diesel	182	182	pg TEQ/km driven
Wood combustion - residential	2 ^f	2 ^f	ng TEQ/kg wood combusted
- industrial	0.60 to 13.2	0.60 to 13.2	ng TEQ/kg wood combusted
Coal combustion - utility	0.078	0.078	ng TEQ/kg coal combusted
Oil combustion - industrial/utility	0.23	0.23	ng TEQ/L oil combusted
Other High Temperature Sources			
Cement kilns burning hazardous waste	1.11 to 30.70 ^e	1.11 to 30.70 ^e	ng TEQ/kg clinker produced
Cement kilns not burning hazardous waste	0.29	0.29	ng TEQ/kg clinker produced
Petroleum refining catalyst regeneration	1.59	1.59	ng TEQ/barrel reformer feed
Cigarette combustion	0.00044 to 0.0030	0.00044 to 0.0030	ng TEQ/cigarette
Carbon reactivation furnaces	1.2 ^f	1.2 ^f	ng TEQ/kg of reactivated carbon
Kraft recovery boilers	0.028	0.028	ng TEQ/kg solids combusted
Minimally Controlled or Uncontrolled Combustion			
Backyard barrel burning	76.8 ^f	76.8 ^f	ng TEQ/kg waste combusted
Metallurgical Processes			
Ferrous metal smelting/refining			
- Sintering plants	0.62 to 4.61	0.62 to 4.61	ng TEQ/kg sinter
Nonferrous metal smelting/refining			
- Primary copper	< 0.31 ^f	< 0.31 ^f	ng TEQ/kg copper produced
- Secondary aluminum smelting	22.4	22.4	ng TEQ/kg scrap feed
- Secondary copper smelting	d	d	ng TEQ/kg scrap consumed
- Secondary lead smelters	0.05 to 8.81	0.05 to 8.81	ng TEQ/kg lead produced
Drum and barrel reclamation	17.5	17.5	ng TEQ/drum
Chemical Manuf./Processing Sources			
Ethylene dichloride/vinyl chloride	0.95 ^{a,f}		ng TEQ/kg EDC produced

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

b Included within total for Wood Combustion - Industrial.

c Emission factor of 0.60 ng TEQ_{DF}-WHO₉₈/kg used for non-salt-laden wood; emission factor of 13.2 ng I-TEQ_{DF}/kg used for salt-laden wood.

d Facility-specific emission factors were used ranging from 3.6 to 16,900 ng TEQ_{DF}-WHO₉₈/kg scrap consumed.

e Emission factor of 1.11 ng TEQ_{DF}-WHO₉₈/kg used for kilns with APCD inlet temperatures less than 450°F; emission factor of 30.70 ng TEQ_{DF}-WHO₉₈/kg used for kilns with APCD inlet temperatures greater than 450°F.

f Congener-specific data were not available; the I-TEQ_{DF} emission factor was used as a surrogate for the TEQ_{DF}-WHO₉₈ emission factor.

TEQ = Toxic equivalency factor.

ng = nanogram.

kg = kilogram.

pg = picogram.

Table 1-11. Identification of Products Containing CDD/CDF in 1995 and 1987
(g I-TEQ_{DF}/yr)

Product	1995	1987
Bleached chemical wood pulp	40	505
Ethylene dichloride/vinyl chloride	0.02	NA
Dioxazine dyes and pigments	0.36	64.0
Pentachlorophenol	8,400	36,000
<i>Total Amounts in Products</i>	8,440	36,569

NA = information not available

Table 1-12. Identification of Products Containing CDD/CDF in 1995 and 1987
(g TEQ_{DF}-WHO₉₈/yr)

Product	1995	1987
Bleached chemical wood pulp	40	505
Ethylene dichloride/vinyl chloride	0.02	NA
Dioxazine dyes and pigments	0.36	64.0
Pentachlorophenol	4,800	20,000
<i>Total Amounts in Products</i>	4,840	20,569

NA = information not available

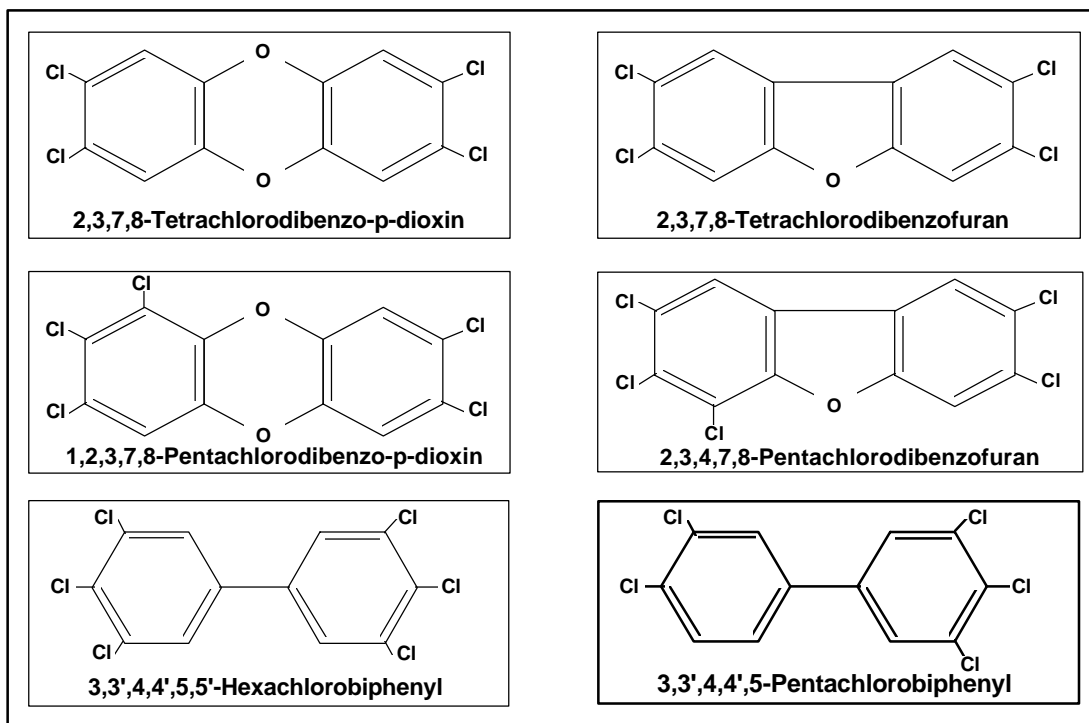
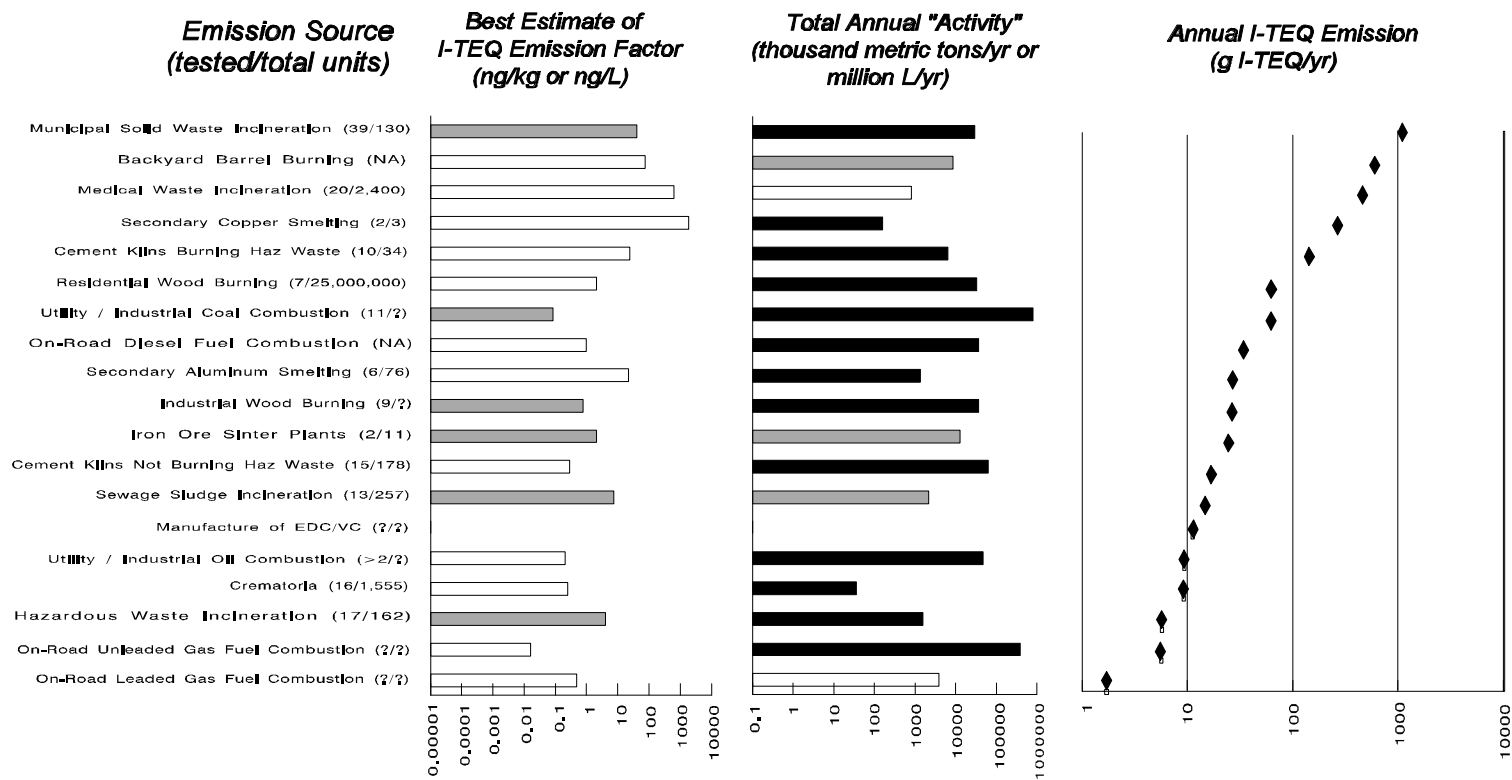
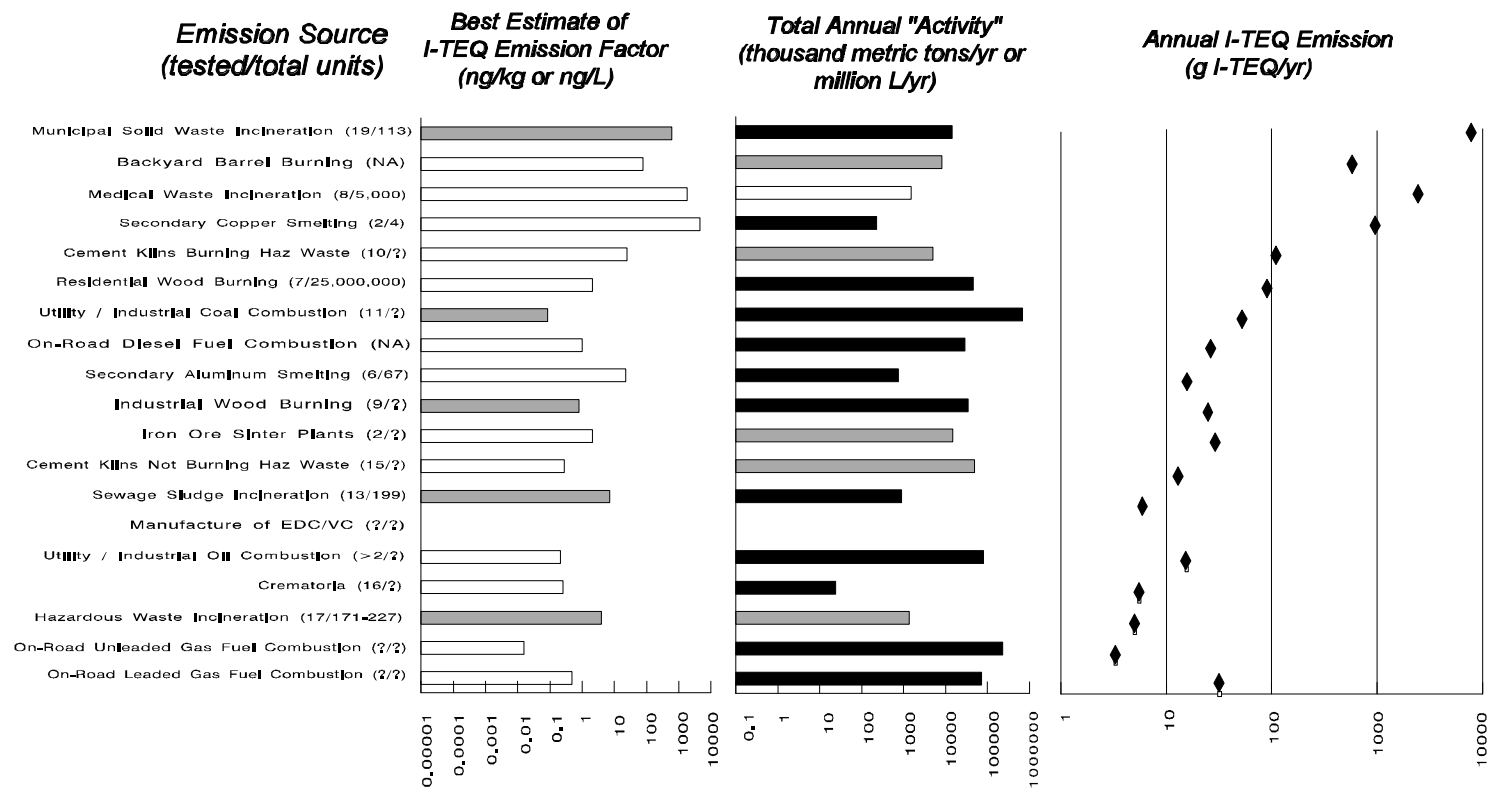


Figure 1-1. Chemical Structure of 2,3,7,8-TCDD and Related Compounds



The figures include sources with annual I-TEQ emission estimates greater than 5 g I-TEQ/yr in one or both of 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 1-2. Estimated CDD/CDF I-TEQ Emissions to Air from Combustion Sources in the United States (Reference Time Period: 1995)



The figures include sources with annual I-TEQ emission estimates greater than 5 g I-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.

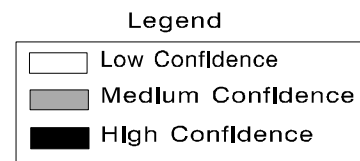


Figure 1-3. Estimated CDD/CDF I-TEQ Emissions to Air from Combustion Sources in the United States (Reference Time Period: 1987)

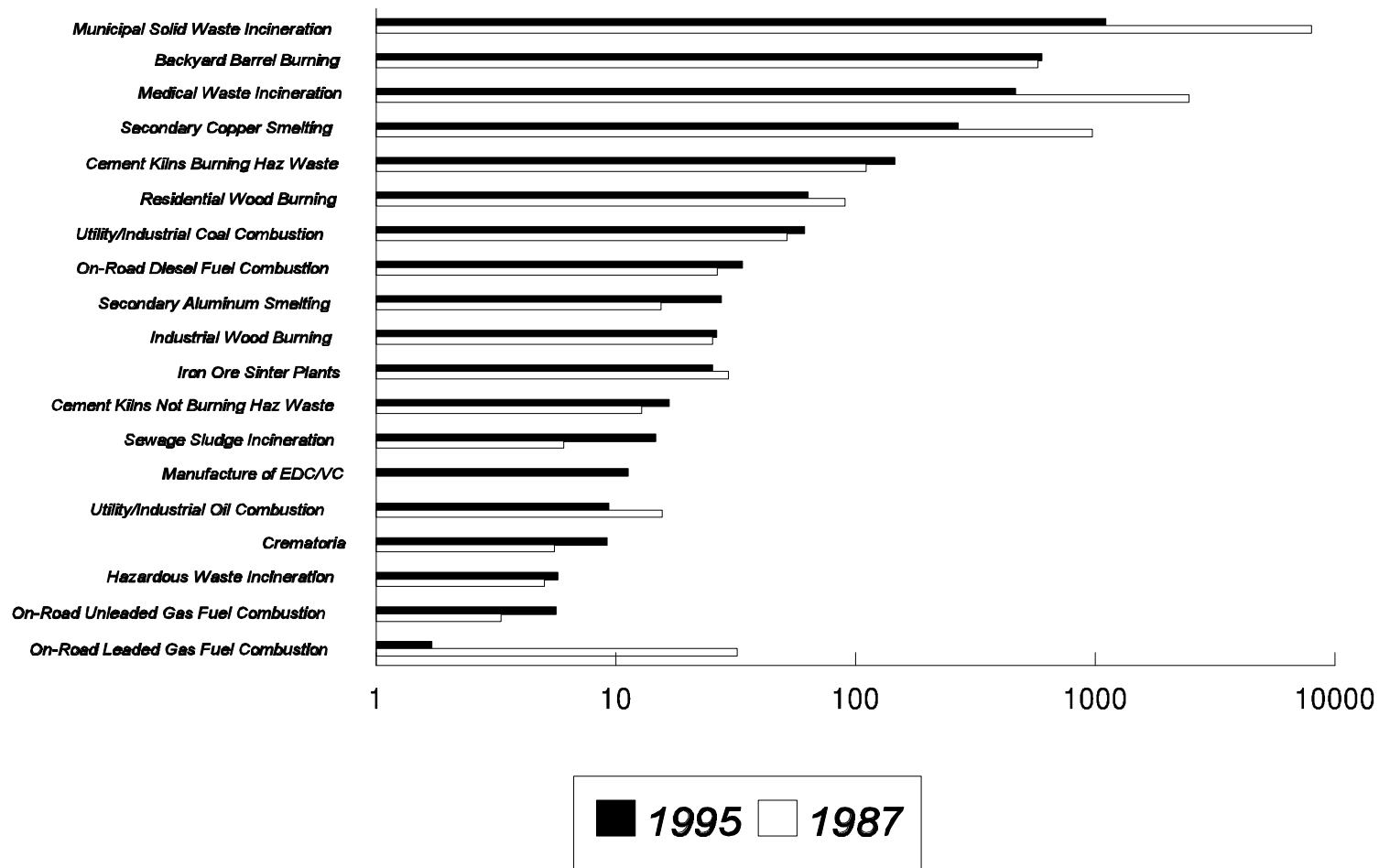
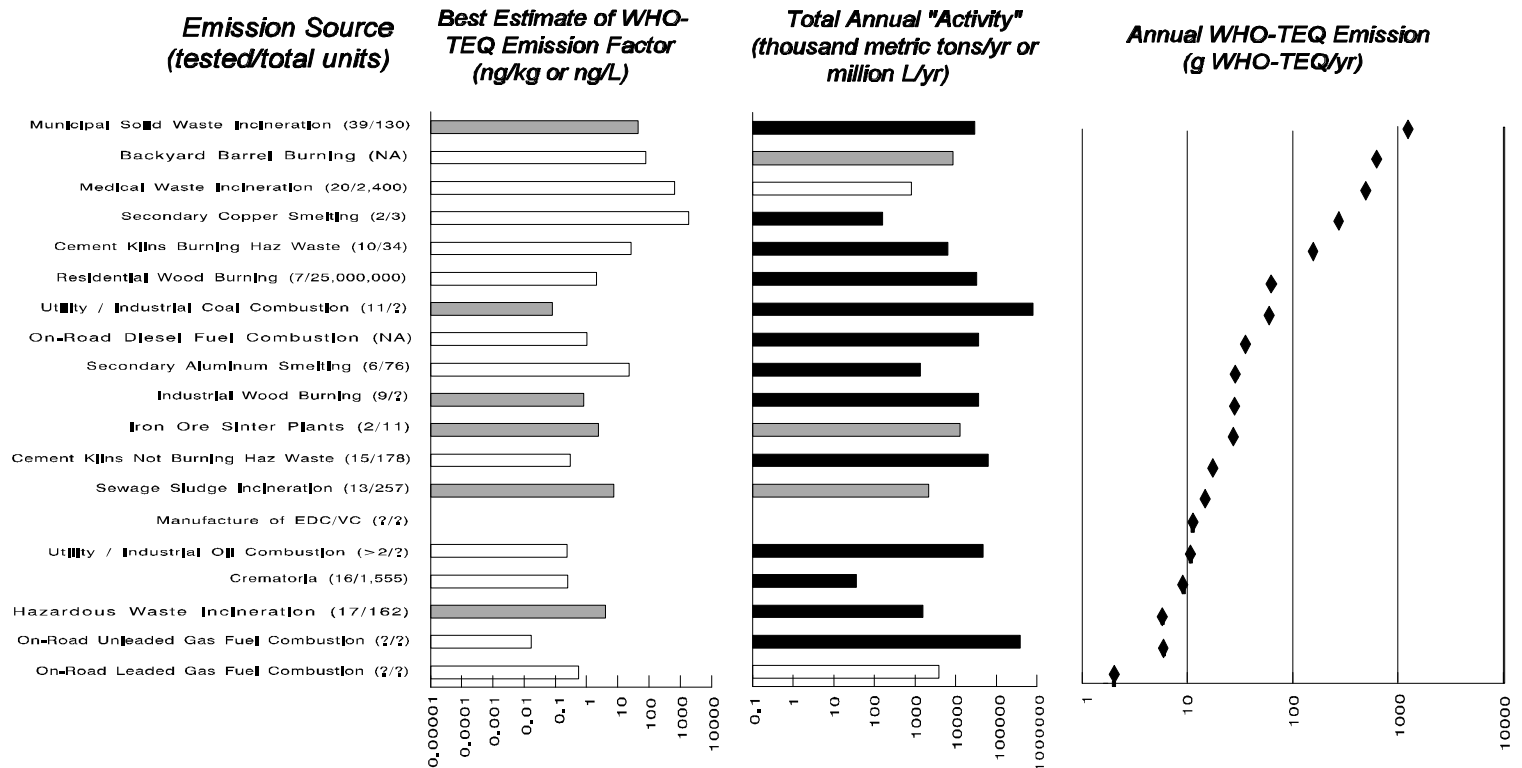


Figure 1-4. Comparison of Estimates of Annual I-TEQ Emissions to Air (grams I-TEQ/year) for Reference Years 1987 and 1995



The figures include sources with annual I-TEQ emission estimates greater than 5 g I-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.

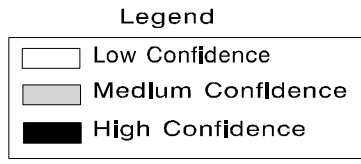
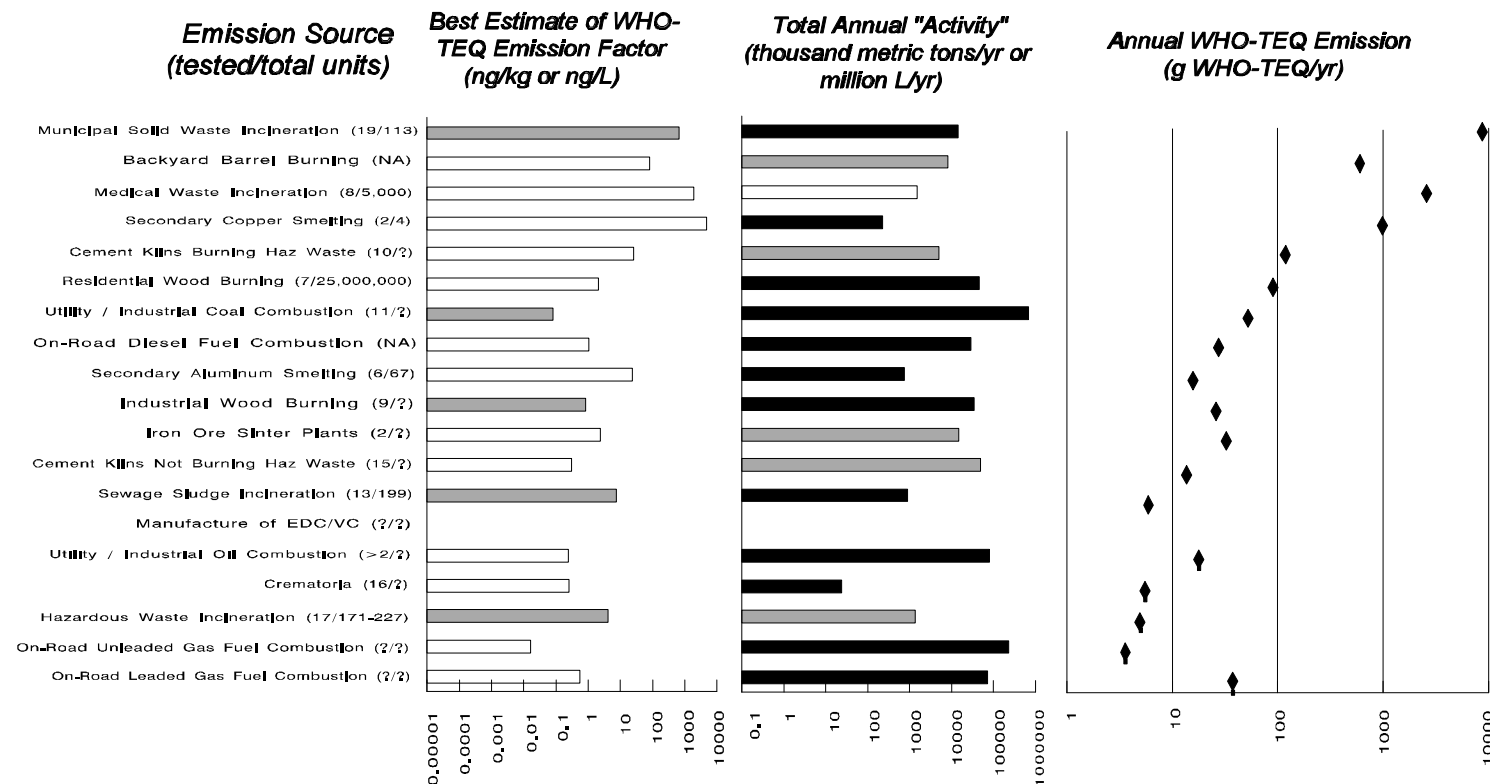


Figure 1-5. Estimated CDD/CDF WHO-TEQ Emissions to Air from Combustion Sources in the United States (Reference Time Period: 1995)



The figures include sources with annual I-TEQ emission estimates greater than 5 g I-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.

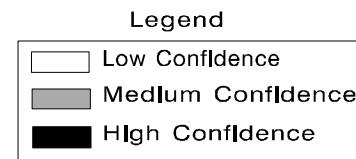


Figure 1-6. Estimated CDD/CDF WHO-TEQ Emissions to Air From Combustion Sources in the United States (Reference Time Period: 1987)

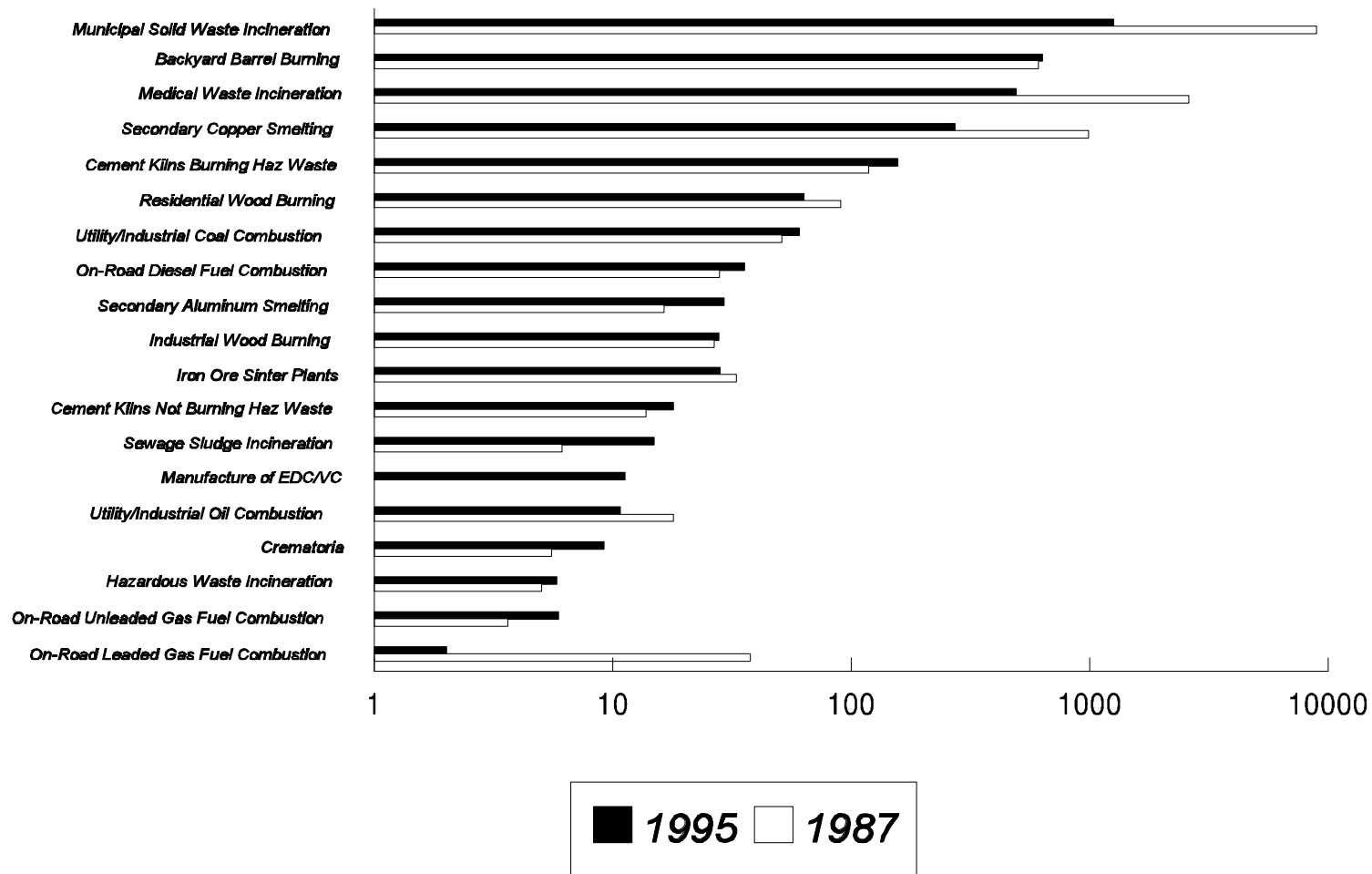


Figure 1-7. Comparison of Estimates of Annual WHO-TEQ Emissions to Air (grams WHO-TEQ/year) for Reference Years 1987 and 1995

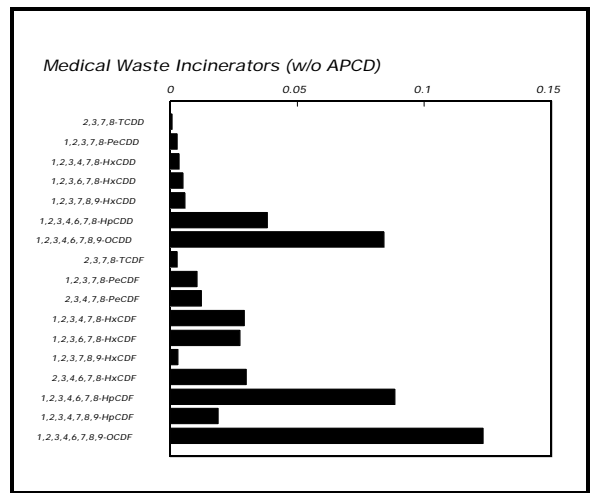
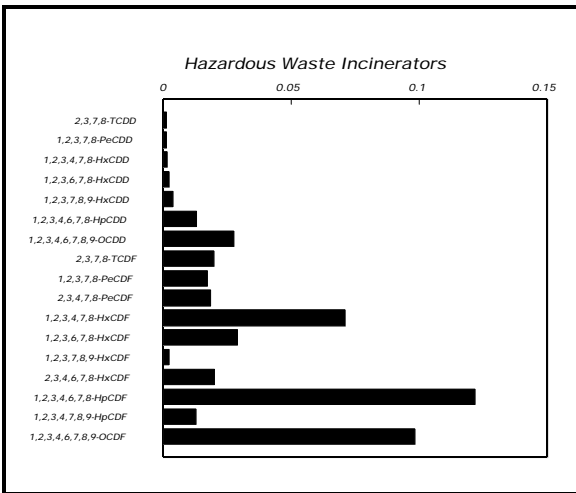
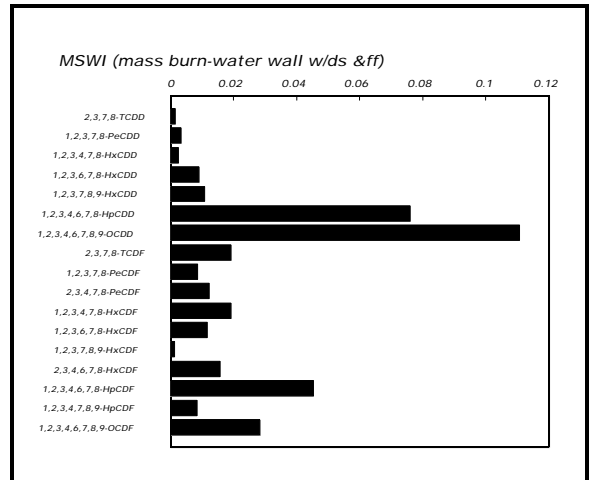
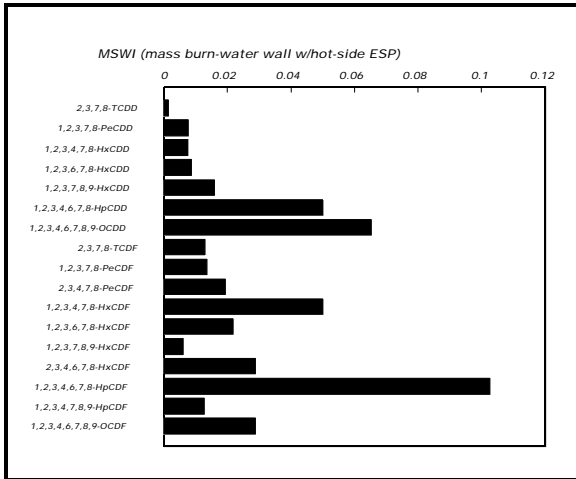


Figure 1-8. The Congener Profiles (as fractional distributions to total CDD/CDF) of Anthropogenic Sources of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans in the United States

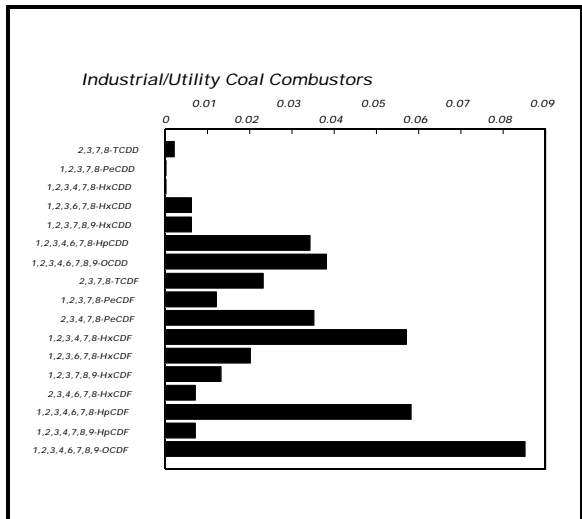
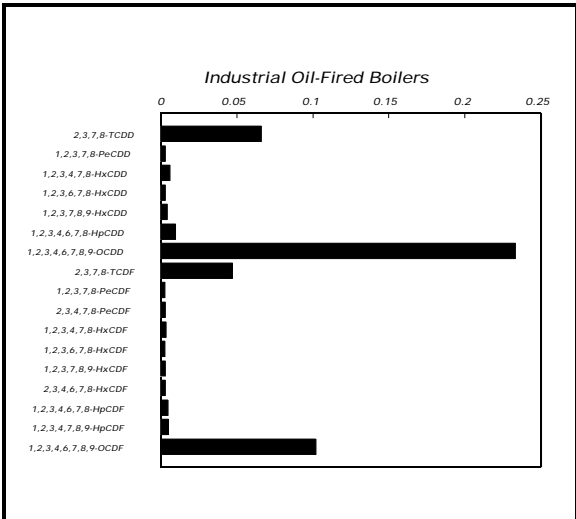
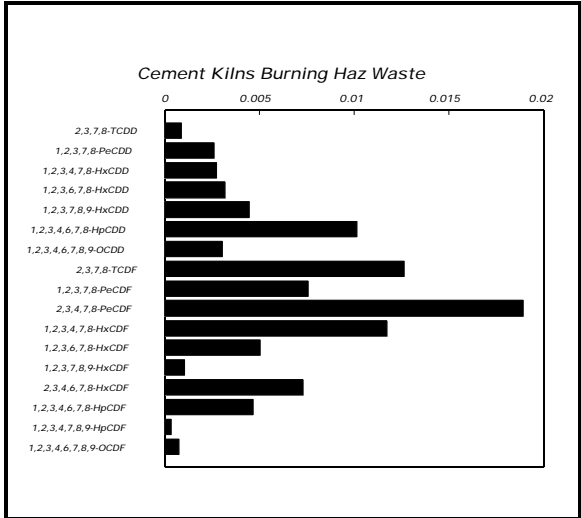
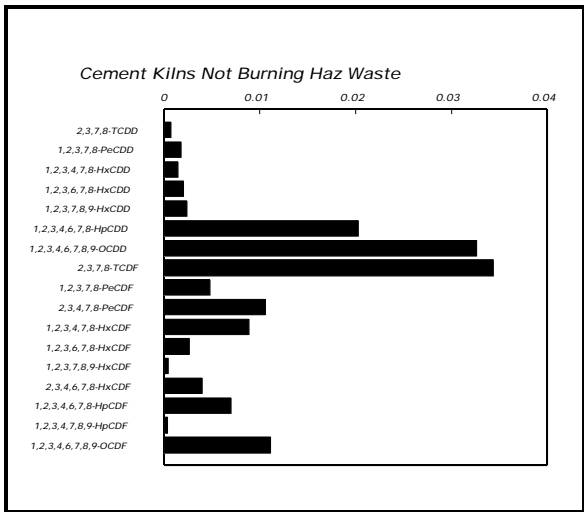


Figure 1-8. The Congener Profiles (as fractional distributions to total CDD/CDF) of Anthropogenic Sources of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans in the United States (continued)

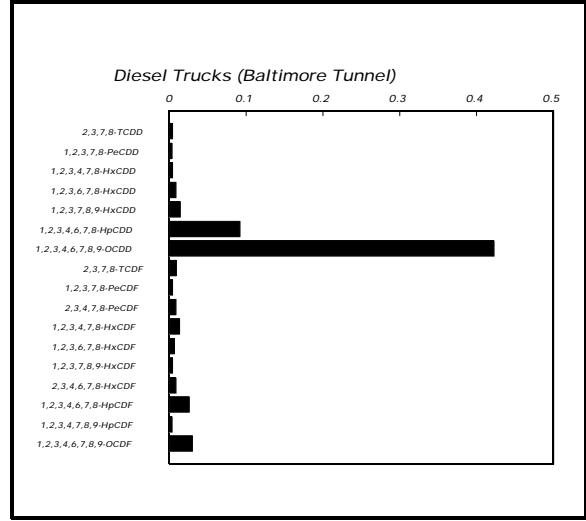
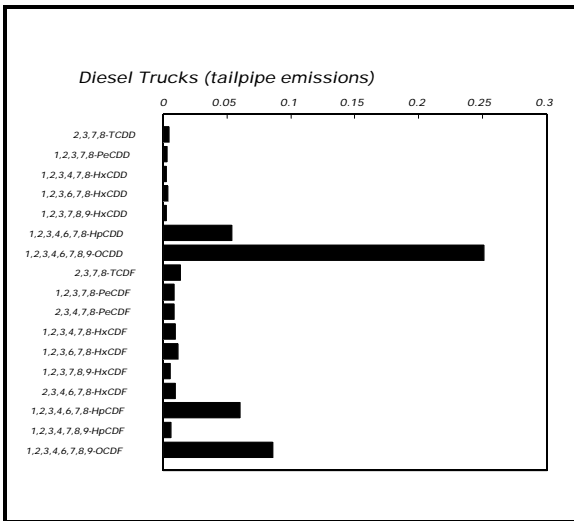
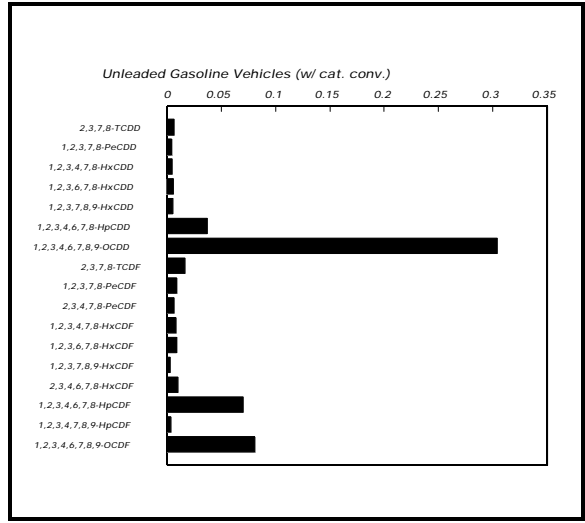
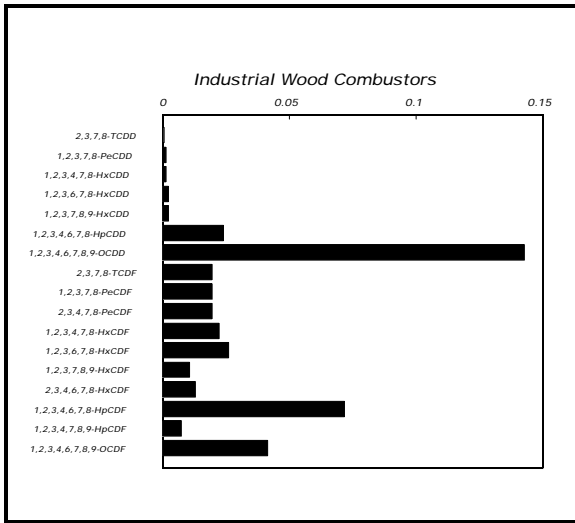


Figure 1-8. The Congener Profiles (as fractional distributions to total CDD/CDF) of Anthropogenic Sources of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans in the United States (continued)

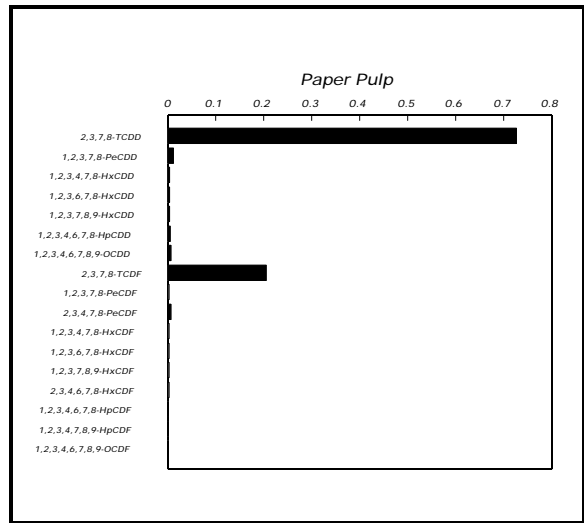
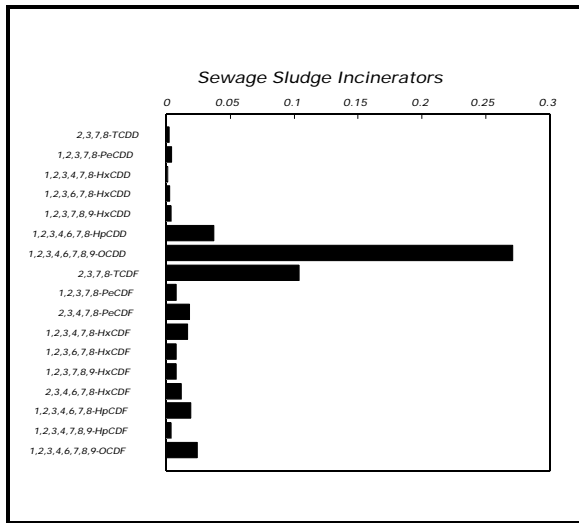
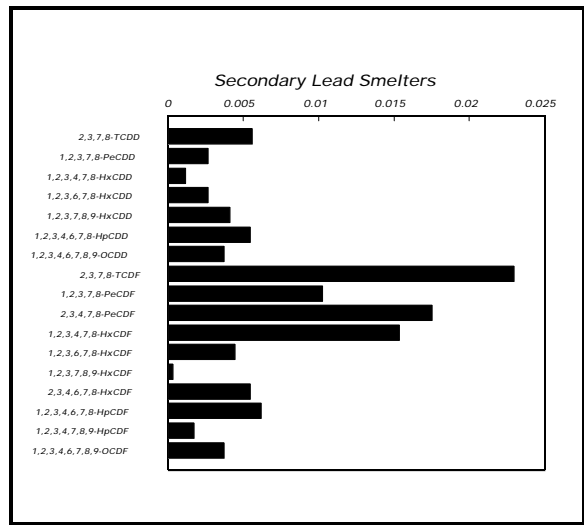
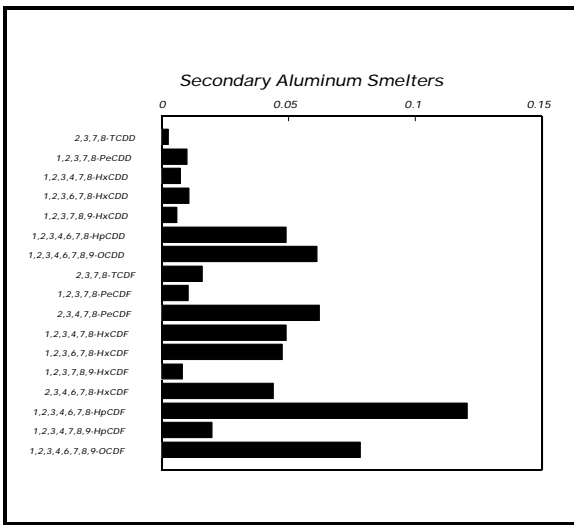


Figure 1-8. The Congener Profiles (as fractional distributions to total CDD/CDF) of Anthropogenic Sources of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans in the United States (continued)

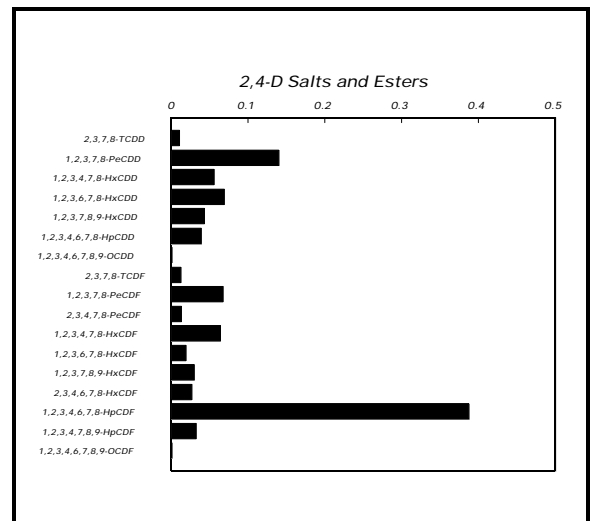
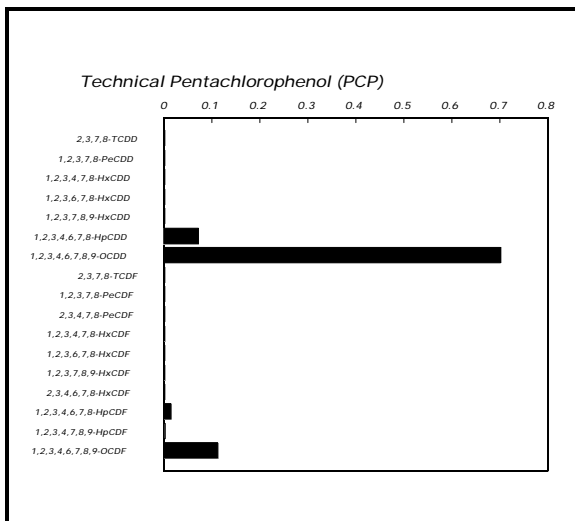


Figure 1-8. The Congener Profiles (as fractional distributions to total CDD/CDF) of Anthropogenic Sources of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans in the United States (continued)