## 8. CHEMICAL MANUFACTURING AND PROCESSING SOURCES

#### 8.1. BLEACHED CHEMICAL WOOD PULP AND PAPER MILLS

In March 1988, EPA and the U.S. pulp and paper industry jointly released the results from a screening study that provided the first comprehensive data on formation and discharge of CDDs and CDFs from pulp and paper mills (U.S. EPA, 1988d). This early screening study of five bleached kraft mills ("Five Mill Study") confirmed that the pulp bleaching process was primarily responsible for the formation of the CDDs and CDFs. The study results showed that 2,3,7,8-TCDD was present in seven of nine bleached pulps, five of five wastewater treatment sludges, and three of five treated wastewater effluents. The study results also indicated that 2,3,7,8-TCDD and 2,3,7,8-TCDF were the principal CDDs and CDFs formed.

To provide EPA with more complete data on the release of these compounds by the U.S. industry, EPA and the U.S. pulp and paper industry jointly conducted a survey during 1988 of 104 pulp and paper mills in the United States to measure levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF in effluent, sludge, and pulp. This study, commonly called the 104 Mill Study, was managed by the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI), with oversight by EPA, and included all U.S. mills where chemically produced wood pulps were bleached with chlorine or chlorine derivatives. The final study report was released in July 1990 (U.S. EPA, 1990a).

An initial phase of the 104 Mill Study involved the analysis of bleached pulp (10 samples), wastewater sludge (9 samples), and wastewater effluent (9 samples) from eight kraft mills and one sulfite mill for all 2,3,7,8-substituted CDDs and CDFs. These analyses were conducted to test the conclusion drawn in the Five Mill Study that 2,3,7,8-TCDD and 2,3,7,8-TCDF were the principal CDDs and CDFs found in pulp, wastewater sludge, and wastewater effluent on a toxic equivalents basis. Although at the time of this study there were no reference analytical methods for many of the 2,3,7,8-substituted CDDs/CDFs, the data obtained were considered valid by EPA for the purposes intended because of the identification and quantification criteria used, duplicate sample results, and limited matrix spike experiments. Table 8-1 presents a summary of the results obtained in terms of the median concentrations and the range of concentrations observed for each matrix (i.e., pulp, sludge, and effluent). Figures 8-1 through 8-3 present congener profiles

for each matrix (normalized to total CDD/CDF and to total I-TEQ<sub>DF</sub>) using the median reported concentrations. After examination of the raw, mill-specific data, EPA (1990a) concluded that the congener profiles were fairly consistent across matrices within mills and that 2,3,7,8-TCDD and 2,3,7,8-TCDF account for the majority of TEQ in the samples. Using the median concentrations and treating nondetected values as either zero or onehalf the detection limit, EPA concluded that 2,3,7,8-TCDF accounted for 95.8 to 99.0 percent of the total I-TEQ<sub>DF</sub> in pulp (95.4 to 99.5 percent of TEQ<sub>DF</sub>-WHO<sub>98</sub>), 94.1 to 95.8 percent of the I-TEQ<sub>DF</sub> in sludge (94.1 to 96.5 percent of TEQ<sub>DF</sub>-WHO<sub>98</sub>), and 81.1 to 91.7 of the I-TEQ<sub>DF</sub> in effluent (81.7 to 96.4 percent of TEQ<sub>DF</sub>-WHO<sub>98</sub>).

NCASI reported on a similar full-congener analysis study for samples collected from eight mills during the mid-1990s (Gillespie, 1997). The results of these analyses are presented in Table 8-2. The frequencies of detection of 2,3,7,8-TCDD and 2,3,7,8-TCDF were significantly lower than in the 1988 study. Therefore, deriving meaningful summary statistics concerning the relative importance of 2,3,7,8-TCDD and 2,3,7,8-TCDF to the total TEQ is difficult. With all nondetected values assumed to be zero, 2,3,7,8-TCDD and 2,3,7,8-TCDF account for 91 percent of the total effluent I-TEQ<sub>DF</sub> (97 percent of TEQ<sub>DF</sub><sup>-</sup> WHO<sub>98</sub>), 46 percent of the total sludge I-TEQ<sub>DF</sub> (53 percent of TEQ<sub>DF</sub>-WHO<sub>98</sub>), and 87 percent of the total pulp I-TEQ<sub>DF</sub> (87 percent of TEQ<sub>DF</sub>-WHO<sub>98</sub>). Because of the high frequency of nondetects, when all nondetected values are one-half the detection limits, 2,3,7,8-TCDD and 2,3,7,8-TCDF account for only 13 percent of the total effluent I-TEQ<sub>DF</sub>.

In 1992, the pulp and paper industry conducted its own NCASI-coordinated survey of 2,3,7,8-TCDD and 2,3,7,8-TCDF emissions (NCASI, 1993). Ninety-four mills participated in the NCASI study, and NCASI assumed that the remaining 10 (of 104) operated at the same levels as measured in the 1988 104 Mill Study. All nondetected values were counted as half the detection limit. If detection limits were not reported, they were assumed to be 10 pg/L for effluent and 1 ng/kg ppt for sludge or bleached pulp. The data used in the report were provided by individual pulp and paper companies that had been requested by NCASI to generate the data using the same protocols used in the 104 Mill Study.

As part of its efforts to develop revised effluent guidelines and standards for the pulp, paper, and paperboard industry, EPA in 1993 published the development document

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for the guidelines and standards being proposed for this industry (U.S. EPA, 1993d). The development document presents estimates of the 2,3,7,8-TCDD and 2,3,7,8-TCDF annual discharges in wastewater from the mills in this industry as of January 1, 1993. To estimate these discharges, EPA used the most recent information about each mill from four databases (104 Mill Study, EPA short-term monitoring studies at 13 mills, EPA long-term monitoring studies at 8 mills, and industry self-monitoring data submitted to EPA). The 104 Mill Study data were used for only those mills that did not report making any process changes subsequent to the 104 Mill Study and did not submit any more recent effluent monitoring data.

Gillespie (1994, 1995) reported the results of 1993 and 1994 updates, respectively, to the 1992 NCASI survey. As in the 1992 survey, companies were requested to follow the same protocols for generating data used in the 104 Mill Study. Gillespie (1994, 1995) reported that less than 10 percent of mills had 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in effluent above the nominal detection limits of 10 pg/L and 100 pg/L, respectively. EPA obtained similar results in its short- and long-term sampling for 18 mills; 2,3,7,8-TCDD was detected at four mills, and 2,3,7,8-TCDF was detected at nine mills (U.S. EPA, 1993d). Gillespie (1994) reported that wastewater sludges at most mills (i.e., 90 percent) contained less than 31 ng/kg of 2,3,7,8-TCDD and less than 100 ng/kg of 2,3,7,8-TCDF. Gillespie (1995) also reported that 90 percent of the mills reported 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in sludge of less than 17 ng/kg and 76 ng/kg, respectively, in 1994. U.S. EPA (1993d) reported similar results but found detectable levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF in sludges from 64 percent and 85 percent of the facilities sampled, respectively. Gillespie (1994) reported that nearly 90 percent of the bleached pulps contained less than 2 ng/kg of 2,3,7,8-TCDD and less than 160 ng/kg of 2,3,7,8-TCDF. Gillespie (1995) reported that 90 percent of the bleached pulps contained 1.5 ng/ng or less of 2,3,7,8-TCDD and 5.9 ng/kg or less of 2,3,7,8-TCDF. The final levels in white paper products would correspond to levels in bleached pulp, so bleached paper products would also be expected to contain less than 2 ng/kg of 2,3,7,8-TCDD.

On April 15, 1998, EPA promulgated effluent limitations guidelines and standards for certain segments of the pulp, paper and paperboard industry (Federal Register, 1998c). The industry segments covered by this rulemaking (i.e., the bleached papergrade kraft and

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soda subcategory and the papergrade sulfite subcategory) are those segments responsible for more than 90 percent of the bleached chemical pulp production in the United States. For this rule, EPA updated the estimates of baseline loadings made in 1993 for the proposed rule by using more recent data collected by EPA, NCASI (including the 1994 NCASI survey), and individual facilities (U.S. EPA, 1997f). These revised estimates are presented in the last column in Table 8-3. EPA projects that, after full compliance with these rules, annual TEQ discharges will be reduced to 5 grams in effluent and 7 grams in sludge.

Estimates of National Emissions in 1987 and 1995 - The U.S. annual discharges of 2,3,7,8-TCDD and 2,3,7,8-TCDF are summarized in Table 8-3 for each of the six surveys discussed above. The release estimates for 1995 from U.S. EPA (1997f) and for 1988 from U.S. EPA (1990a) are believed to best represent emissions in the reference years 1995 and 1987, respectively. During the period between EPA's 104 Mill Study and issuance of the development document (U.S. EPA, 1993d), the U.S. pulp and paper industry reduced releases of CDD/CDFs primarily by instituting numerous process changes to reduce the formation of CDD/CDFs during the production of chemically bleached wood pulp. Details on the process changes implemented are provided in U.S. EPA (1993d) and Gillespie (1995). Much of the reduction between 1988 and 1995 can be attributed to process changes for pollution prevention.

The confidence ratings for these release estimates were judged to be high because direct measurements were made at virtually all facilities, indicating a high level of confidence in both the production and emission factor estimates. The best estimates of annual emissions in 1995 (i.e., the 1995 estimates presented in Table 8-3) are 28 g TEQ/yr for effluent, 50 g TEQ/yr for sludge, and 40 g TEQ/yr for pulp (i.e., TEQs that will enter the environment in the form of paper products). The best estimates of annual emissions in 1987 (i.e., the 1988 estimates presented in Table 8-3) are 356 g TEQ/yr for effluent, 343 g TEQ/yr for sludge, and 505 g TEQ/yr for pulp.

In 1990, the majority of the wastewater sludge generated by these facilities was placed in landfills or in surface impoundments (75.5 percent), with the remainder incinerated (20.5 percent), applied to land directly or as compost (4.1 percent), or distributed as a commercial product (less than 1 percent) (U.S. EPA, 1993e). Data more recent than 1995 or earlier than 1988 are not available on disposition of wastewater

sludges. On the basis of these statistics, the best estimate of TEQ applied to land (i.e., not incinerated or landfilled) in 1995 is 2.0 g (i.e., 4.1 percent of 50 g). The estimate for 1987 is 14.1 g TEQ (i.e., 4.1 percent of 343 g).

# 8.2. MANUFACTURE OF CHLORINE, CHLORINE DERIVATIVES, AND METAL CHLORIDES

No testing of CDD/CDF emissions to air, land, or water from U.S. manufacturers of chlorine, chlorine derivatives, and metal chlorides has been reported on which to base estimates of national emissions. Sampling of graphite electrode sludges from European chlorine manufacturers indicates high levels of CDFs. Limited sampling of chlorine derivatives and metal chlorides in Europe indicates low-level contamination in some products.

## 8.2.1. Manufacture of Chlorine

Chlorine gas is produced by electrolysis of brine electrolytic cells. Until the late 1970s, the primary type of electrolytic process used in the chloralkali industry to produce chlorine consisted of mercury cells containing graphite electrodes. As shown in Table 8-4, high levels of CDFs have been found in several samples of graphite electrode sludge from facilities in Europe. The CDFs predominate in these sludges, and the 2,3,7,8-substituted congeners account for a large fraction of the respective congener totals (Rappe et al., 1990b; Rappe et al., 1991; Rappe, 1993; Strandell et al., 1994). During the 1980s, titanium metal anodes were developed to replace graphite electrodes (U.S. EPA, 1982a; Curlin and Bommaraju, 1991). Currently, no U.S. facility is believed to use graphite electrodes in the production of chlorine gas (telephone conversation between L. Phillips, Versar, Inc., and T. Fielding, U.S. EPA, Office of Water, February 1993).

Although the origin of the CDFs in graphite electrode sludge is uncertain, chlorination of the cyclic aromatic hydrocarbons (such as dibenzofuran) present in the coal tar used as a binding agent in the graphite electrodes has been proposed as the primary source (Strandell et al., 1994). For this reason, sludges produced using metal electrodes were not expected to contain CDFs. However, results of an analysis of metal electrode sludge from a facility in Sweden, analyzed as part of the Swedish Dioxin Survey, showed the sludge contained high levels of CDFs (similar to those of the graphite sludge) and

primarily nondetectable levels of CDDs (Strandell et al., 1994). The sludge showed the same type of CDF congener pattern reported by Rappe et al. (1991) and Rappe (1993). Strandell et al. (1994) suggested that chlorination of PAHs present in the rubber linings of the electrolytic cell may have formed the CDFs found in the one sample analyzed.

Although EPA does not regulate CDD/CDFs specifically, it issued restrictions under the Resource Conservation and Recovery Act (RCRA) on the land disposal of wastewater and sludges generated by chlorine manufacturers that use the mercury cell process and the diaphragm process (with graphite electrodes) (Waste Codes K071, K073, and K106) (40 CFR 268).

#### 8.2.2. Manufacture of Chlorine Derivatives and Metal Chlorides

The limited sampling of chlorine-derivative products indicates that these products contain very low, if any, concentrations of CDD/CDFs. Rappe et al. (1990c) analyzed a sample of chlorine bleach consisting of 4.4 percent sodium hypochlorite. Most of the 2,3,7,8-substituted CDD/CDF congeners were below the limits of detection (0.3 to 7 pg/L for all congeners, except OCDD and OCDF, which were 12 and 20 pg/L, respectively). No 2,3,7,8-substituted CDDs were detected. Tetra-, penta-, and hexa-CDFs were detected at levels of 13 pg/L or lower. The TEQ content of the sample was 4.9 pg I-TEQ<sub>DF</sub>/L. Hutzinger and Fiedler (1991a) reported finding no CDD/CDFs at a detection limit of 4  $\mu$ g/kg in chlorine gas or in samples of 10 percent sodium hypochlorite, 13 percent sodium hypochlorite, and 31–33 percent hydrochloric acid at a detection limit of 1  $\mu$ g/kg.

Hutzinger and Fiedler (1991a) reported the results of analyses of samples of FeCl<sub>2</sub>, AICl<sub>3</sub>, CuCl<sub>2</sub>, CuCl, SiCl<sub>4</sub>, and TiCl<sub>4</sub> for their content of HpCDF, OCDF, HpCDD, and OCDD. The sample of FeCl<sub>3</sub> contained HpCDF and OCDF in the low  $\mu$ g/kg range, but no HpCDD or OCDD were detected at a detection limit of 0.02  $\mu$ g/kg. One of the two samples of AICl<sub>3</sub> analyzed also contained a low  $\mu$ g/kg concentration of OCDF. The samples of CuCl<sub>2</sub> and CuCl contained concentrations of HpCDF, OCDF, and OCDD less that 1  $\mu$ g/kg. The results are presented in Table 8-5.

# 8.3. MANUFACTURE OF HALOGENATED ORGANIC CHEMICALS

Several chemical production processes generate CDDs and CDFs (Versar, 1985; Hutzinger and Fiedler, 1991a). CDDs and CDFs can be formed during the manufacture of

chlorophenols, chlorobenzenes, and chlorobiphenyls (Versar, 1985; Ree et al., 1988). Consequently, disposal of industrial wastes from manufacturing facilities producing these compounds may result in the release of CDDs and CDFs to the environment. Also, the products themselves may contain these compounds, and their use or consumption, may result in additional releases to the environment. CDD and CDF congener distribution patterns indicative of noncombustion sources have been observed in sediments in southwest Germany and The Netherlands. According to Ree et al (1988), the congener patterns found suggest that wastes from the production of chlorinated organic compounds may be important historical sources of CDD and CDF contamination in these regions. The production and use of many of the chlorophenols, chlorophenoxy herbicides, and PCB products are now banned or strictly regulated in most countries. However, these products may have been a source of the environmental contamination that occurred prior to the 1970s and may continue to be a source of environmental releases under certain limited use and disposal conditions (Rappe, 1992a).

## 8.3.1. Chlorophenols

Chlorophenols have been widely used for a variety of pesticidal applications. The higher chlorinated phenols (i.e., tetrachlorophenol and pentachlorophenol) and their sodium salts have been used primarily for wood preservation. The lower chlorinated phenols have been used primarily as chemical intermediates in the manufacture of other pesticides. For example, 2,4-dichlorophenol is used to produce the herbicides 2,4-Dichlorophenoxyacetic acid (2,4-D), 4-(2,4-Dichlorophenoxy)butanoic acid (2,4-DB), 2-(2,4-Dichlorophenoxy)-propanoic acid (2,4-DP), Nitrophen, Genite, and Zytron, and 2,4,5-trichlorophenol was used to produce hexachlorophene, 2,4,5-T, Silvex, Erbon, Ronnel, and Gardona (Gilman et al., 1988; Hutzinger and Fiedler, 1991a). [Note: Sections 8.3.7 and 8.3.8 contain information on EPA actions to control CDD/CDF contamination of pesticides (including pentachlorophenol and its salts) and to obtain additional data on CDD/CDF contamination of pesticides.]

The two major commercial methods used to produce chlorophenols are (1) electrophilic chlorination of molten phenol by chlorine gas in the presence of catalytic amounts of a metal chloride and organic chlorination promoters and stabilizers, and (2) alkaline hydrolysis of chlorobenzenes under heat and pressure using aqueous methanolic

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sodium hydroxide. Other manufacturing methods include conversion of diazonium salts of various chlorinated anilines, and chlorination of phenolsulfonic acids and benzenesulfonic acids, followed by the removal of the sulfonic acid group (Gilman et al., 1988; Hutzinger and Fiedler, 1991a).

Because of the manufacturing processes employed, commercial chlorophenol products can contain appreciable amounts of impurities (Gilman et al., 1988). During the direct chlorination of phenol, CDD/CDFs can form either by the condensation of tri-, tetra-, and pentachlorophenols or by the condensation of chlorophenols with hexachlorocyclohexadienone (which forms from excessive chlorination of phenol). During alkaline hydrolysis of chlorobenzenes, CDD/CDFs can form through chlorophenate condensation (Ree et al., 1988; Gilman et al., 1988; Hutzinger and Fiedler, 1991a).

The limited information on CDD/CDF concentrations in chlorophenols published in the 1970s and early 1980s was compiled by Versar (1985) and Hutzinger and Fiedler (1991a). The results of several major studies cited by these reviewers (Firestone et al., 1972; Rappe et al., 1978a, 1978b) are presented in Table 8-6. Typically, CDD/CDFs were not detected in monochlorophenols (MCP) and dichlorophenols (DCP) but were reported in trichlorophenols (TrCP) and tetrachlorophenols (TeCP). More recent results of testing of 2,4-dichlorophenol (2,4-DCP), performed in response to the Toxic Substances Control Act (TSCA) Dioxin/Furan Test Rule, showed no detectable concentrations of 2,3,7,8substituted tetra- through hepta-CDD/CDFs. Other than a study by Hagenmaier (1986) that reported finding 2,3,7,8-TCDD at a concentration of 0.3  $\mu$ g/kg in a sample of 2,3,4,5-tetrachlorophenol, no more recent data on concentrations of CDDs and CDFs could be found in the literature for the mono- through tetra-chlorophenols. Tables 8-7 and 8-8 present summaries of several studies that reported CDD/CDF concentrations in PCP and in PCP-Na products, respectively. Many of these studies do not report congenerspecific concentrations, and many are based on products obtained from non-U.S. sources.

**Regulatory Actions** - Section 8.3.8 of this report describes regulatory actions taken by EPA to control the manufacture and use of chlorophenol-based pesticides.

In the mid-1980s, EPA's Office of Solid Waste promulgated land disposal restrictions on wastes under RCRA (i.e., wastewaters and nonwastewaters) resulting from the manufacture of chlorophenols (40 CFR 268). Table 8-9 lists all wastes in which CDDs and CDFs are specifically regulated as hazardous constituents by EPA, including

chlorophenol wastes (waste codes F020 and F021). The regulations prohibit the land disposal of these wastes until they are treated to a level below the routinely achievable detection limits in the waste extract listed in Table 8-9 for each of the following congener groups: TCDDs, PeCDDs, HxCDDs, TCDFs, PeCDFs, and HxCDFs. Wastes from PCP-based wood-preserving operations (waste codes K001 and F032) are also regulated as hazardous wastes under RCRA (40 CFR 261).

EPA's Office of Water promulgated effluent limitations for facilities that manufacture chlorinated phenols and discharge treated wastewater (40 CFR 414.70). These effluent limitations do not specifically regulate CDDs and CDFs. The effluent limitations for the individually regulated chlorinated phenols are less than or equal to 39  $\mu$ g/L for facilities that use biological end-of-pipe treatment.

DCPs and TrCPs are subject to reporting under the Dioxin/Furan Test Rule, which is discussed in Section 8.3.7 of this report. Since the effective date of that rule (i.e., June 5, 1987), only the 2,4-DCP isomer has been commercially produced (or imported) in the United States, and as noted in Table 8-6, no CDD/CDFs were detected in the product. Testing is required for the other DCPs and TrCPs, if manufacture or importation resumes. Similarly, TeCPs were subject to reporting under the Dioxin/Furan Pesticide Data Call-In or DCI (discussed in Section 8.3.8 of this report). Since issuance of the DCI, the registrants of TeCP-containing pesticide products have elected to no longer support the registration of their products in the United States.

In January 1987, EPA entered into a Settlement Agreement with pentachlorophenol (PCP) manufacturers, which set limits on allowed uses of PCP and its salts and set maximum allowable concentrations of 2,3,7,8-TCDD and HxCDDs, effective in February 1989. Section 8.3.8 discusses the 1987 PCP Settlement Agreement and estimates current releases of CDD/CDFs associated with use of PCP in the United States. Section 12.3.1 provides an estimate of the amount of CDD/CDFs that may have entered the environment or that are contained within treated wood products as a result of prior use of PCP and PCP-Na.

Since the late 1980s, U.S. commercial production of chlorophenols has been limited to 2,4-dichlorophenol (2,4-DCP) and PCP. As noted above, disposal of wastes generated during the manufacture of chlorophenols is strictly regulated, and thus releases to the environment are expected to be negligible. With regards to releases associated

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with the use of 2,4-DCP, no CDD/CDFs have been detected in 2,4-DCP. Releases associated with the use of PCP are presented in Sections 8.3.8 and 12.3.1.

## 8.3.2. Chlorobenzenes

Chlorobenzenes have been produced in the United States since 1909. U.S. production operations were developed primarily to provide chemical raw materials for the production of phenol, aniline, and various pesticides based on the higher chlorinated benzenes. Because of [incremental] changes in the processes used to manufacture phenol and aniline and the phaseout of highly chlorinated pesticides such as DDT and hexachlorobenzene, by 1988 U.S. production of chlorobenzenes had decreased to 50 percent of the peak production level in 1969.

Chlorobenzenes can be produced via three methods: (1) electrophilic substitution of benzene (in liquid or vapor phase) with chlorine gas in the presence of a metal salt catalyst; (2) oxidative chlorination of benzene with HCl at 150–300°C in the presence of a metal salt catalyst; and (3) dehydrohalogenation of hexachlorocyclohexane wastes at 200–240°C with a carbon catalyst to produce trichlorobenzene, which can be further chlorinated to produce higher chlorinated benzenes (Ree et al., 1988; Hutzinger and Fiedler, 1991a; Bryant, 1993).

All chlorobenzenes currently manufactured in the United States are produced using the electrophilic substitution process using liquid-phase benzene (i.e., temperature is at or below 80°C). Ferric chloride is the most common catalyst employed. Although this method can be used to produce mono- through hexachlorobenzene, the extent of chlorination is controlled to yield primarily MCBz and DCBz. The finished product is a mixture of chlorobenzenes, and refined products must be obtained by distillation and crystallization (Bryant, 1993).

CDD/CDFs can be produced inadvertently during the manufacture of chlorobenzenes by nucleophilic substitution and pyrolysis mechanisms (Ree et al., 1988). The criteria required for production of CDD/CDFs via nucleophilic substitution are (1) oxygen as a nuclear substituent (i.e., presence of chlorophenols) and (2) production or purification of the substance under alkaline conditions. Formation via pyrolysis requires reaction temperatures above 150°C (Ree et al., 1988; Hutzinger and Fiedler, 1991a). The liquid-phase electrophilic substitution process currently used in the United States does not

meet either of these criteria. Although Ree et al. (1988) and Hutzinger and Fiedler (1991a) state that the criteria for formation of CDD/CDFs via nucleophilic substitution may be present in the catalyst neutralization and purification/distillation steps of the manufacturing process, Opatick (1995) states that the chlorobenzene reaction product in U.S. processes remains mildly acidic throughout these steps.

Table 8-10 summarizes the very limited published information on CDD/CDF contamination of chlorobenzene products. The presence of CDD/CDFs has been reported in TCBz, PeCBz, and HCBz. No CDD/CDFs have been reported in monochlorobenzene (MCBz) and DCBz. Conflicting data exist concerning the presence of CDD/CDFs in TCBz. One study (Villanueva et al., 1974) detected no CDD/CDFs in one sample of 1,2,4-TCBz at a detection limit of 0.1  $\mu$ g/kg. Hutzinger and Fiedler (1991a) reported unpublished results of Dr. Hans Hagenmaier showing CDD/CDF congener group concentrations ranging from 0.02 to 0.074  $\mu$ g/kg in a sample of mixed TCBz. Because the TCBz examined by Hagenmaier contained about 2 percent hexachlorocyclohexane, it is reasonable to assume that the TCBz was produced by dehydrohalogenation of hexachlorocyclohexane (a manufacturing process not currently used in the United States).

**Regulatory Actions** - EPA has determined, as part of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Pesticide Data Call-In (discussed in Section 8.3.8), that the 1,4-DCBz manufacturing processes used in the United States are not likely to form CDD/CDFs. MCBz, DCBz, and TCBz are listed as potential precursor chemicals under the TSCA Dioxin/Furan Test Rule and are subject to reporting. (See Section 8.3.7.) In addition, EPA issued a Significant New Use Rule (SNUR) under Section 5(a)(2) of TSCA on December 1, 1993 (effective January 14, 1994) for PeCBz and 1,2,4,5-TeCBz (Federal Register, 1993c). This rule requires persons to submit a notice to EPA at least 90 days before manufacturing, importing, or processing either of these compounds in amounts of 10,000 pounds or greater per year per facility for any use. All registrations of pesticide products containing HCBz were cancelled in the mid-1980s (Carpenter et al., 1986).

EPA's Office of Solid Waste promulgated land disposal restrictions on wastes (i.e., wastewaters and nonwastewaters) resulting from the manufacture of chlorobenzenes (40 CFR 268). Table 8-9 lists all solid wastes for which EPA specifically regulates CDDs and CDFs as hazardous constituents, including chlorobenzene wastes. The regulations prohibit the land disposal of these wastes until they are treated to a level below the routinely

achievable detection limits in the waste extract listed in Table 8-9 for each of the following congener groups: TCDDs, PeCDDs, HxCDDs, TCDFs, PeCDFs, and HxCDFs.

EPA's Office of Water promulgated effluent limitations for facilities that manufacture chlorinated benzenes and discharge treated wastewater (40 CFR 414.70). These effluent limitations do not specifically address CDDs and CDFs. The following chlorinated benzenes are regulated: chlorobenzene; 1,2-dichlorobenzene; 1,3dichlorobenzene; 1,4-dichlorobenzene; 1,2,4-trichlorobenzene; and hexachlorobenzene. The effluent limitations for the individual regulated chlorinated benzenes are less than or equal to 77  $\mu$ g/L for facilities that use biological end-of-pipe treatment and are less than or equal to 196  $\mu$ g/L for facilities that do not use biological end-of-pipe treatment.

Since at least 1993, U.S. commercial production of chlorobenzenes has been limited to MCBz, 1,2-dichlorobenzene (1,2-DCBz), 1,4-dichlorobenzene (1,4-DCBz), and, to a much lesser extent, 1,2,4-trichlorobenzene (1,2,4-TCBz). As noted above, CDD/CDF formation is not expected under the normal operating conditions of the processes currently used in the United States to produce these four chemicals. No tetra-, penta-, or hexachlorinated benzenes are now intentionally produced or used in the United States (Bryant, 1993). Thus, releases of CDD/CDFs from manufacture of chlorobenzenes in 1995 were estimated to be negligible. Because the information available on CDD/CDF content of MCBz to PeCBz is very limited and is based primarily on unpublished European data, and because information on the chlorobenzene manufacturing processes in place during 1987 is not readily available, no emission estimates can be made for 1987.

#### 8.3.3. Chlorobiphenyls

PCBs are manufactured by the direct batch chlorination of molten biphenyl in the presence of a catalyst, followed by separation and purification of the desired chlorinated biphenyl fractions. During the manufacture of PCBs, the inadvertent production of CDFs also occurrs. This section addresses potential releases of CDD/CDFs associated with leaks and spills of PCBs. CDFs have been shown to form when PCB-containing transformers and capacitors undergo malfunctions or are subjected to fires that result in accidental combustion of the dielectric fluid. This combustion source of PCB-associated CDFs is discussed in Section 6.6. Section 11.2 addresses releases of dioxin-like PCBs.

PCB production is believed to have occurred in 10 countries. The total amount of PCBs produced worldwide since 1929 (i.e., the first year of known production) is estimated to total 1.5 billion kg. Initially, PCBs were primarily used as dielectric fluids in transformers. After World War II, PCBs found steadily increasing use as dielectric fluids in capacitors, as heat-conducting fluids in heat exchangers, and as heat-resistant hydraulic fluids in mining equipment and vacuum pumps. PCBs also were used in a variety of "open" applications (i.e., uses from which PCBs cannot be re-collected) including in plasticizers, carbonless copy paper, lubricants, inks, laminating agents, impregnating agents, paints, adhesives, waxes, additives in cement and plaster, casting agents, dedusting agents, sealing liquids, fire retardants, immersion oils, and pesticides (DeVoogt and Brinkman, 1989).

PCBs were manufactured in the United States from 1929 until 1977. U.S. production peaked in 1970, with a volume of 85 million pounds. Monsanto Corporation, the major U.S. producer, voluntarily restricted the use of PCBs in 1971, and annual production fell to 40 million pounds in 1974. Monsanto ceased PCB manufacture in mid-1977 and shipped the last inventory in October 1977. Regulations issued by EPA beginning in 1977, principally under TSCA (40 CFR 761), strictly limited the production, import, use, and disposal of PCBs. (See Section 4.1 for details on TSCA regulations.) The estimated cumulative production and consumption volumes of PCBs in the United States from 1930 to 1975 were 1,400 million pounds produced; 3 million pounds imported (primarily from Japan, Italy, and France), 1,253 million pounds sold in the United States; and 150 million pounds exported (ATSDR, 1993; DeVoogt and Brinkman, 1989).

Monsanto Corporation marketed technical-grade mixtures of PCBs primarily under the trade name Aroclor. The Aroclors are identified by a four-digit numbering code in which the last two digits indicate the chlorine content by weight percent. The exception to this coding scheme is Aroclor 1016, which contains only mono- through hexachlorinated congeners with an average chlorine content of 41 percent. The following list shows the percentages of total Aroclor production, by Aroclor mixture, during 1957 to 1977, as reported by Brown (1994).

	1957–1977	
	U.S. Production	
<u>Aroclor</u>	(%)	
1221	0.96	
1016	12.88	
1232	0.24	
1242	51.76	
1248	6.76	
1254	15.73	
1260	10.61	
1262	0.83	
1268	0.33	

The trade names of the major commercial technical-grade mixtures of PCBs manufactured in other countries included *Clophen* (Germany), *Fenclor* and *Apirolio* (Italy), *Kanechlor* (Japan), *Phenoclor* and *Pyralene* (France), *Sovtel* (USSR), *Delor* and *Delorene* (Czechoslovakia), and *Orophene* (German Democratic Republic) (DeVoogt and Brinkman, 1989). Some of the mixtures marketed under these trade names were similar in terms of chlorine content (by weight percent and average number of chlorines per molecule) to various Aroclors, as shown below. Mixtures that are comparable in terms of chlorine content were marketed under several trade names, as shown below.

<u>Aroclor</u>	<u>Clophen</u>	<u>Pyralene</u>	<u>Phenoclor</u>	<u>Fenclor</u>	<u>Kanechlor</u>
1232		2000			200
1242	A-30	3000	DP-3	42	300
1248	A-40		DP-4		400
1254	A-50		DP-5	54	500
1260	A-60		DP-6	64	600

During the commercial production of PCBs, thermal oxidative cyclization under alkaline conditions resulted in the inadvertent production of CDFs in most of the commercial PCB mixtures (Brown et al., 1988; ATSDR, 1993). Bowes et al. (1975a) first reported detection of CDFs in Aroclor products; samples of unused Aroclors manufactured in 1969 and 1970 were found to have CDF (i.e., TCDF through HxCDF) concentrations ranging from 0.8 to 2.0 mg/kg. Bowes et al. (1975b) employed congener-specific analytical methodology and detected 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF at concentrations ranging from 0.11 to 0.33 mg/kg and 0.12 to 0.83 mg/kg, respectively, in unused samples of Aroclor 1254 and Aroclor 1260. The presence of CDDs in commercial PCB mixtures, although at much lower concentrations than those of the CDFs, was reported by Hagenmaier (1987) and Malisch (1994). Table 8-11 presents the CDF and CDD congener group concentrations reported by Bowes et al. (1975a) and those reported in subsequent years for unused PCBs by Erickson (1986), ATSDR (1993), Hagenmaier (1987), and Malisch (1994).

Several researchers reported concentrations of specific CDD/CDF congeners in commercial PCB mixtures (Bowes et al., 1975b; Brown et al., 1988; Hagenmaier, 1987; Malisch, 1994). Only the Hagenmaier (1987) and Malisch (1994) studies, however, reported the concentrations of all 2,3,7,8-substituted CDDs and CDFs. Table 8-12 presents the results of these four studies. It is evident from the table that major variations are found in the levels of 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF in the Clophen mixtures reported by Hagenmaier (1987) and Malisch (1994) and the corresponding levels in the Aroclor mixtures reported by Bowes et al. (1975b) and Brown et al. (1988).

Brown et al. (1988) compared the levels of 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, and 1,2,3,7,8,9-HxCDF in used samples (i.e., samples from previously used capacitors and transformers) and unused samples of Aroclors 1016, 1242, 1254, and 1260. The concentration ranges reported for the used and unused Aroclors were similar, leading Brown et al. (1988) to conclude that CDFs are not formed during the normal use of PCBs in electrical equipment.

Amounts of CDD/CDF TEQ that may have been released to the environment during 1987 and 1995 from spills and leaks of in-service PCBs cannot be accurately estimated because reliable data regarding leaked and spilled PCBs are not available. However, preliminary estimates can be made using the release data reported to EPA's Toxics Release Inventory (TRI) by those manufacturing facilities required to submit annual reports to TRI. Table 11-6 in Section 11 lists the amounts of PCBs reported to TRI to have been released to the environment during 1988 through 1996. These TRI data include emissions to the air, discharges to bodies of water, and releases to land. On the basis of these data, annual emissions of PCBs to air during 1988 and 1996 could have been as high as 2.7 kg and as low as 0 kg, respectively. If it is further assumed that the ratio of TEQ (I-TEQ<sub>DF</sub> and TEQ<sub>DF</sub>-WHO<sub>98</sub>) to total PCB in the air emissions was 0.17:1,000,000 (i.e., the average of the TEQ contents for Clophen A-30 and Clophen A-50, or 170  $\mu$ g/kg, as reported by Hagenmaier (1987) and presented in Table 8-12), then annual emissions of I-TEQ<sub>DF</sub> to air

in 1988 and 1995 could have been 0.5 and 0 mg, respectively. Similar assumptions for PCB releases to water of 4.5 kg in 1988 and 0 kg in 1995 yield estimated TEQ emissions during 1988 and 1995 of 0.8 and 0 mg, respectively. For land releases of 341 kg in 1988 and 0 kg in 1995, estimated TEQ emissions during 1988 and 1995 are 58 and 0 mg, respectively. All of these estimated releases are considered to be negligible.

## 8.3.4. Polyvinyl Chloride

Polyvinyl chloride (PVC) resins are produced when free radical initiators are used to induce the polymerization of vinyl chloride monomer (VCM). VCM is typically produced by the thermal dehydrochlorination (commonly known as cracking) of ethylene dichloride (EDC). One plant in the United States still uses the catalytic reaction of acetylene and HCl to manufacture VCM directly. The cracking of EDC requires elevated pressure (20 to 30 atmospheres) and temperature (450 to 650°C) and yields VCM and HCl at about a 1:1 molar ratio. EDC is produced by two different methods: (1) direct chlorination of ethylene with chlorine in the presence of a catalyst at a temperature of 50 to 60°C and pressure of 4 to 5 atmospheres; and (2) oxychlorination, which involves reaction of ethylene with HCl and oxygen in the presence of a catalyst at temperatures generally less than 325°C. The primary source of HCl for the oxychlorination process is the HCl produced from the cracking of EDC to form VCM; all VCM plants, with the exception of the one facility noted above, are integrated with EDC production facilities (The Vinyl Institute, 1998).

Although it has generally been recognized that CDD/CDFs are formed during the manufacture of EDC/VCM/PVC, manufacturers and environmental public interest groups have disagreed as to the quantity of CDD/CDFs that are formed and released to the environment in wastes and possibly in PVC products. Although EPA regulates emissions from EDC/VCM production facilities under the Clean Water Act (40 CFR 61), the Clean Air Act (40 CFR 414), and RCRA (40 CFR 268 - Waste Codes F024, K019, and K020), CDD/CDFs are not specifically regulated pollutants; as a consequence, monitoring data for CDD/CDFs in emissions are generally lacking.

In 1993, Greenpeace International issued a report on CDD/CDF emissions associated with the production of EDC/VCM (Greenpeace, 1993). Greenpeace estimated that 5 to 10 g I-TEQ<sub>DF</sub> are released to the environment (air, water, and ground combined) annually for every 100,000 metric tons of VCM produced. This emission factor was

based on data gathered by Greenpeace on four European plants. The Vinyl Institute responded with a critique of the Greenpeace report (ChemRisk, 1993). Miller (1993) summarized the differing views of the two parties. According to Miller (1993), European PVC manufacturers claim the emission factor is 0.01 to 0.5 g I-TEQ<sub>DF</sub>/100,000 metric tons of VCM. Although Greenpeace (1993) and ChemRisk (1993) used basically the same monitoring information to develop their emission factors, Greenpeace adjusted the emission factor to account for unquantified fugitive emissions and waste products that contain unspecified amounts of CDD/CDFs.

In 1995, Greenpeace issued another report reiterating the organization's concern that the generation and emission of CDD/CDFs may be significant and urging that further work be initiated to quantify and prevent emissions (Stringer et al., 1995). Stringer et al. (1995) presented the results of analyses of three samples of chlorinated wastes obtained from U.S. EDC/VCM manufacturing facilities. The three wastes were characterized according to EPA hazardous waste classification numbers as follows: (1) an F024 waste (i.e., waste from the production of short chain aliphatics by free radical catalyzed processes), (2) a K019 waste (i.e., heavy ends from the distillation of ethylene from EDC production), and a probable K020 waste (i.e., heavy ends from distillation of VC in VCM manufacture). Table 8-13 presents the analytical results reported by Stringer et al. (1995). This study acknowledged that because EDC/VCM production technologies and waste treatment and disposal practices are very site-specific, the limited information available on CDD/CDF generation and emissions made it difficult to quantify amounts of CDD/CDFs generated and emitted.

In response to the lack of definitive studies and at the recommendation of EPA, U.S. PVC manufacturers initiated an extensive monitoring program, the Dioxin Characterization Program, to evaluate the extent of any CDD/CDF releases to air, water, and land, as well as any product contamination. Manufacturers performed emission and product testing at various facilities that were representative of various manufacturing and process control technologies. The Vinyl Institute has completed studies of CDD/CDF releases in wastewater, wastewater treatment plant solids, and stack gases, as well as studies of CDD/CDF content of products (i.e., PVC resins and "sales" EDC). The following subsections discuss the results for each of these media (The Vinyl Institute, 1998). The Vinyl Institute created an External Advisory Group to advise the institute on the conduct of the Dioxin Characterization Program and to provide an independent review of the Program results. In their final evaluation report, the Advisory Group judged the industry's coverage, in terms of the number of facilities and waste streams sampled, to be fairly comprehensive. The number of samples of PVC product, stack emissions, wastewaters, and wastewater sludges obtained from the different types of manufacturing facilities was deemed by the Advisory Group to provide a sufficient database to evaluate industrywide annual releases. The Advisory Group concluded that the process established by The Vinyl Institute to ensure that data collected as part of its Dioxin Characterization Program are representative of normal process operations was a good one. After auditing The Vinyl Institute's estimates of annual releases, the Advisory Group concluded that the data were properly validated and the results were extrapolated to annual industrywide release estimates in a creditable, scientific manner.

EPA has reviewed The Vinyl Institute (1998) study and concurs with the conclusions of the External Advisory Group. EPA assigns a high confidence rating to the activity level estimates and a medium confidence rating to the emission factor estimates developed by The Vinyl Institute (1998).

**Wastewater** - The Vinyl Institute (1998) presented results for treated wastewater samples collected during April and May of 1995 at six sites that manufactured only PVC, at three sites that manufactured EDC and VCM, and at one site that manufactured EDC, VCM, and PVC. In terms of production, the six PVC-only sites represent approximately 15 percent of the total estimated 1995 U.S. and Canadian PVC production. The three EDC/VCM sites and the one EDC/VCM/PVC site together represent 27 percent of the total estimated 1995 U.S. EDC production. Samples taken from PVC-only sites were taken from sites that manufactured suspension PVC resin as well as sites that manufactured dispersion PVC resin. Samples for the other four sites were taken from sites that used direct and oxychlorination processes, fixed and fluidized beds, and low- and hightemperature direct chlorination. The wastewater samples from one of the EDC/VCM sites, one of the PVC-only sites, and the EDC/VCM/PVC site were taken from effluents derived from process areas not limited to EDC/VCM, EDC/VCM/PVC, or PVC manufacturing.

The results of the sampling are presented in Table 8-14. The method detection limits (MDLs) for all congeners except OCDD and OCDF in all samples were 10 pg/L or

less. The MDLs for OCDD and OCDF were 50 pg/L or less. CDD/CDFs were detected in two of the six samples from PVC-only sites (0.52 and 2.0 pg I-TEQ<sub>DF</sub>/L, assuming ND = 0). The overall mean TEQ concentrations were 0.88 pg I-TEQ<sub>DF</sub>/L (ND = 0) and 4.7 pg I-TEQ<sub>DF</sub>/L (ND = 1/2 MDL). CDD/CDFs were detected in all four of the samples from EDC/VCM/PVC sites. The overall mean TEQ concentrations were 0.42 pg I-TEQ<sub>DF</sub>/L (ND = 0) and 4.4 pg I-TEQ<sub>DF</sub>/L (ND = 1/2 MDL).

Based on these sample results, The Vinyl Institute developed I-TEQ<sub>DF</sub> emission factors for PVC-only and EDC/VCM/PVC manufacturing facilities. First, individual site release rates were estimated using the treated wastewater effluent flow rate recorded by the site during sampling and assuming that the site continuously releases CDD/CDFs at its calculated total I-TEQ<sub>DF</sub>, 24 hours per day, 360 days per year, at the recorded water effluent rate. The total releases from each site-type category (i.e., PVC-only or EDC/VCM/PVC facilities) were then estimated by averaging the individual release rates on a per-1,000-metric-ton-of-PVC basis or per-1,000-metric-ton-of-EDC basis using the estimated 1995 PVC and EDC production statistics for the sampled sites. These values were then "scaled up" to estimate total U.S. releases in treated wastewater from the sitetype categories. It is not possible using the data presented in the Vinyl Institute (1998) to calculate emission factors for TEQ<sub>DF</sub>-WHO<sub>98</sub>. However, because 1,2,3,7,8-PeCDD was not detected in any wastewater sample, the TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factors would be lower than the I-TEQ<sub>DF</sub> emission factors.

The mean emission factors derived from the sample results for the PVC-only facilities are 2.3  $\mu$ g I-TEQ<sub>DF</sub>/1,000 metric tons of PVC (ND = 0) and 29  $\mu$ g I-TEQ<sub>DF</sub>/1,000 metric tons of PVC (ND = 1/2 MDL). The mean emission factors for the EDC/VCM/PVC facilities are 2.9  $\mu$ g I-TEQ<sub>DF</sub>/1,000 metric tons (ND = 0) and 15  $\mu$ g I-TEQ<sub>DF</sub>/1,000 metric tons of EDC (ND = 1/2 MDL).

The Vinyl Institute (1998) combined these emission factors with 1995 industry production statistics (i.e., 5,212 thousand metric tons of PVC and 11,115 thousand metric tons of EDC), to yield release estimates of 0.011 grams I-TEQ<sub>DF</sub> (ND = 0) and 0.15 g I-TEQ<sub>DF</sub> (ND = 1/2 DL) from PVC-only manufacturing sites and 0.032 g I-TEQ<sub>DF</sub> (ND = 0) and 0.17 g I-TEQ<sub>DF</sub> (ND = 1/2 DL) from EDC/VCM and EDC/VCM/PVC facilities for a total I-TEQ<sub>DF</sub> release in 1995 of 0.043 g (ND = 0) and 0.32 g (ND = 1/2 DL).

Wastewater Treatment Plant Solids - The Vinyl Institute (1998) presented results for 14 samples collected in 1996 from 9 EDC/VCM/PVC manufacturing sites. Samples were collected from 4 of the 5 U.S. sites that manufactured EDC, VCM, and PVC; 3 of the 7 U.S. sites that manufactured EDC and VCM, but not PVC; and 2 of the 21 sites that manufacture PVC, but not EDC or VCM. On the basis of 1995 production data, the two PVC-only sites manufactured approximately 4.7 percent of the total estimated U.S. and Canadian PVC resin production. The sampled EDC/VCM and EDC/VCM/PVC sites manufactured 56 percent of the total estimated 1995 U.S. EDC production. Samples from the PVC-only sites were taken from sites that manufactured suspension PVC resin as well as sites that manufactured dispersion PVC resin. Samples taken from the EDC/VCM and EDC/VCM/PVC sites were taken from sites that used direct and oxychlorination processes; fixed and fluidized EDC reactor beds; low- and high-temperature direct chlorination; and air, oxygen, and mixed air/oxygen feeds.

Using the sample results and their determination that the results for facilities using different EDC reactor bed technologies (i.e., fluidized bed vs. fixed bed) appear to differ significantly, The Vinyl Institute developed annual I-TEQ<sub>DF</sub> emission estimates for three categories: PVC-only, EDC/VCM/PVC fixed bed, and EDC/VCM/PVC fluidized bed facilities. Nine U.S. sites use fixed bed technology and six use fluidized bed technology. Four of each type of facility were sampled by The Vinyl Institute. It is not possible using the data presented in The Vinyl Institute (1998) to calculate emission factors for TEQ<sub>DF</sub>-WHO<sub>98</sub>. Because 1,2,3,7,8-PeCDD was detected in only 3 of 10 samples, but OCDD and OCDF were detected in all samples, it is likely that the TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factors would not be significantly different from the I-TEQ<sub>DF</sub> emission factors.

Results of the sampling are presented in Table 8-14. The MDLs for all congeners were less than 150 ng/kg, and usually were less than 10 ng/kg. CDD/CDFs were detected in all samples. The ranges of TEQ concentrations (dry weight basis) for the two PVC-only facilities were 1.1 to 2.6 ng I-TEQ<sub>DF</sub>/kg (ND = 0) and 2.8 to 4.4 ng I-TEQ<sub>DF</sub>/kg (ND = 1/2 MDL). On an emission factor basis, the ranges were 1.7 to 46  $\mu$ g I-TEQ<sub>DF</sub>/1,000 metric tons of PVC produced (ND = 0) and 4.3 to 78  $\mu$ g I-TEQ<sub>DF</sub>/1,000 metric ton of PVC produced (ND = 1/2 DL). The range of TEQ concentrations for the samples from the EDC/VCM or EDC/VCM/PVC sites were 88 to 6,850 ng I-TEQ<sub>DF</sub>/kg (ND = 0) and 93 to 6,850 ng I-TEQ<sub>DF</sub>/kg (ND = 1/2 DL). On an emission factor basis, the

ranges were 28 to 4,000  $\mu$ g I-TEQ<sub>DF</sub>/1,000 metric tons of EDC (ND = 0) and 29 to 4,000  $\mu$ g I-TEQ<sub>DF</sub>/1,000 metric tons of EDC (ND = 1/2 DL).

The annual amounts of I-TEQ<sub>DF</sub> generated in 1995 in each of the three facility categories were estimated by The Vinyl Institute as follows. First, total annual contributions at each sampled site were estimated by multiplying the I-TEQ<sub>DF</sub> from the sample by the annual production of wastewater solids at that site. These annual site contributions of I-TEQ<sub>DF</sub> were then summed for each of the three facility types and multiplied by the ratio of each category's total annual production of PVC or EDC to the sum of the annual production of the sampled sites in that category.

The Vinyl Institute (1998) combined these emission factors with 1995 industry production statistics (i.e., 5,212 thousand metric tons of PVC and 11,115 thousand metric tons of EDC) to yield estimated amounts of I-TEQ<sub>DF</sub> in wastewater treatment plant solids. For PVC-only facilities, estimated amounts are 0.069 g I-TEQ<sub>DF</sub> per year (ND = 0) and 0.12 g I-TEQ<sub>DF</sub> per year (ND = 1/2 DL), assuming an annual PVC production of 5,212 thousand metric tons. For EDC/VCM/PVC fixed bed facilities, the estimated amounts of TEQ are 1.0 g I-TEQ<sub>DF</sub> per year (ND = 0 or ND = 1/2 DL), assuming an EDC annual production volume of 5,400 thousand metric tons. For EDC/VCM/PVC fluidized bed facilities, the estimated amount of TEQ is 11 g I-TEQ<sub>DF</sub> per year (ND = 0 or ND = 1/2 DL), assuming EDC annual production volume of 5,600 thousand metric tons. Thus, total amounts of TEQ in wastewater treatment plant solids are estimated to have been 12.1 g I-TEQ<sub>DF</sub> in 1995 (ND = 0 or ND = 1/2 DL).

Based on The Vinyl Institute survey data, Institute member companies dispose of wastewater solids by three methods: (1) RCRA hazardous waste landfilling (approximately 1 percent of industry total solids), (2) landfarming (approximately 6 percent), and (3) "secure" on-site landfilling (93 percent of industry total solids). Solids disposed of by methods 1 and 3 are assumed to be well controlled to prevent release into the general environment, whereas solids disposed of by landfarming are not as well controlled and could be released to the environment. Therefore, an estimated 0.73 g I-TEQ<sub>DF</sub> (i.e., 6 percent of 12.1 g I-TEQ<sub>DF</sub>) can be considered as potentially released to the environment.

**Stack Gas Emissions** - By grouping similarities of design and service, The Vinyl Institute (1998) subcategorized thermal destruction units at EDC/VCM and/or PVC manufacturing units into three categories: (a) type A-vent gas incinerators at PVC-only resin plants; (b) type B—vent gas thermal oxidizers at EDC/VCM plants; and (c) type C—liquid only and liquid/vent gas thermal oxidizers at EDC/VCM plants. Using an industrywide survey, The Vinyl Institute (1998) identified 22 type A units at 11 facilities, 23 type B units at 10 facilities, and 17 type C units at 10 facilities. The Vinyl Institute gathered test data from 5 of the 22 type A units (from three facilities representing 7 percent of total U.S. and Canadian EDC/VCM/PVC production in 1995), 14 of the 23 type B units (from 8 facilities), and 13 of the 17 type C units (from 7 facilities). The sampled types B and C units represent 70 percent of total U.S. and Canadian EDC/VCM/PVC production in 1995.

Annual I-TEQ<sub>DF</sub> emission estimates were generated by The Vinyl Institute by combining estimated emissions from tested units (i.e., based on measured stack gas results and plant-specific activity data) with an estimate of emissions from untested units. The emissions from the untested units were estimated by multiplying the average emission factor for the tested units in the category (i.e., called the "most likely" estimate by The Vinyl Institute) or by multiplying the average emission factor of the three highest tested units in each class (i.e., the "upper bound" estimate) by the activity level for the untested units. It is not possible using the data presented in The Vinyl Institute (1998) to calculate emission factors for TEQ<sub>DF</sub>-WHO<sub>98</sub>.

The Vinyl Institute (1998) estimates of "most likely" and "upper-bound" emissions during 1995 for these three categories are as follows:

Category	"Most Likely" Emission Estimate (g I-TEQ <sub>DF</sub> /yr)	"Upper Bound" Emission Estimate (g I- TEQ <sub>DF</sub> /yr)
PVC-only incinerators	0.0014	0.0019
EDC/VCM liquid and liquid/vents	3.7	7.2
EDC/VCM vents for VCM only	6.9	21.6

The Vinyl Institute (1998) also estimated emissions that may result from incineration of EDC/VCM/PVC wastes processed by off-site third-party processing. Using the emission factors for liquid and liquid/vents developed in their study, The Vinyl Institute estimated that potential emissions to air from this source category would be 0.65 g l-

 $TEQ_{DF}/yr$  (most likely estimate) and 2.3 g I- $TEQ_{DF}/yr$  (upper-bound estimate). Including these third-party release estimates with those developed above yields a most likely estimate of 11.2 g I- $TEQ_{DF}/yr$  and an upper-bound estimate of 31 g I- $TEQ_{DF}/yr$ .

**Products** - The Vinyl Institute (1998) presented results for 22 samples from 14 of the 24 U.S. and Canadian facilities manufacturing suspension and mass PVC resins (i.e., 13 pipe resins, 3 bottle resins, and 6 packaging resins). The results are summarized in Table 8-15. The 14 sampled sites represent approximately 74 percent of estimated 1995 U.S. and Canadian suspension and mass PVC resin production. CDD/CDFs were detected in only one sample (0.043 ng I-TEQ<sub>DF</sub>/kg, assuming ND = 0). The overall mean TEQ concentrations were 0.002 ng I-TEQ<sub>DF</sub>/kg (ND = 0) and 0.7 ng I-TEQ<sub>DF</sub>/kg (ND = 1/2 MDL). The MDLs were 2 ng/kg or less for all congeners in all samples except for OCDD and OCDF, which had MDLs of 6 ng/kg or less.

The Vinyl Institute (1998) also presented results for six samples from four of the seven U.S. facilities manufacturing dispersion PVC resins. CDD/CDFs were detected in five of the samples. The results are summarized in Table 8-15. In terms of production, the four sampled sites represent approximately 61 percent of estimated 1995 U.S. dispersion PVC resin production. The results ranged from not detected to 0.008 ng I-TEQ<sub>DF</sub>/kg (overall mean = 0.001 ng I-TEQ<sub>DF</sub>/kg assuming ND = 0, and 0.4 ng I-TEQ<sub>DF</sub>/kg, assuming ND = 1/2 MDL). The MDLs were 2 ng/kg or less for all congeners in all samples except OCDD and OCDF, which had MDLs of 4 ng/kg or less.

The Vinyl Institute (1998) also presented results for 5 samples from 5 of the 15 U.S. facilities manufacturing EDC. The results are summarized in Table 8-15. In terms of production, the five sampled sites represent approximately 71 percent of total U.S. estimated 1995 "sales" EDC production. CDD/CDFs were detected in only one sample (0.03 ng I-TEQ<sub>DF</sub>/kg). The overall mean TEQ concentrations were 0.006 ng I-TEQ<sub>DF</sub>/kg (ND = 0) and 0.21 ng I-TEQ<sub>DF</sub>/kg (ND = 1/2 MDL). The MDLs for all congeners were 1 ng/kg or less.

Using 1995 U.S. production data (i.e., 4.846 million metric tons of suspension and mass PVC, 0.367 million metric tons of dispersion PVC resins, and 1.362 million metric tons of "sales" EDC) and the average TEQ observed for the samples analyzed, The Vinyl Institute estimated the total I-TEQ<sub>DF</sub> contents of suspension/mass PVC resins, dispersion PVC resins, and "sales" EDC in 1995 to be 0.01 g, 0.004 g, and 0.008 g, respectively

(ND = 0) and 3.39 g, 0.15 g, and 0.29 g, respectively (ND = 1/2 MDL). Therefore, total I-TEQ<sub>DF</sub> present in PVC in 1995 was estimated at between 0.02 g (ND = 0) and 3.83 g (ND = 1/2 MDL). It is not possible using the data presented in The Vinyl Institute (1998) to calculate emission factors for TEQ<sub>DF</sub>-WHO<sub>98</sub>. However, because neither 1,2,3,7,8-PeCDD nor OCDD were detected in any sample, the TEQ<sub>DF</sub>-WHO<sub>98</sub> emission factors would be very similar to the I-TEQ<sub>DF</sub> emission factors.

#### 8.3.5. Other Aliphatic Chlorine Compounds

Aliphatic chlorine compounds are used as monomers in the production of plastics, as solvents and cleaning agents, and as precursors for chemical synthesis (Hutzinger and Fiedler, 1991a). These compounds are produced in large quantities. In 1992, 14.6 million metric tons of halogenated hydrocarbons were produced (U.S. International Trade Commission, 1946–1994). The production of 1,2-dichloroethane and vinyl chloride accounted for 82 percent of this total production. Highly chlorinated CDDs and CDFs (i.e., hexa- to octachlorinated congeners) have been found in nanograde-guality samples of 1,2-dichloroethane (55 ng/kg of OCDF in one of five samples), tetrachloroethene (47 ng/kg of OCDD in one of four samples), epichlorohydrin (88 ng/kg of CDDs and 33 ng/kg of CDFs in one of three samples), and hexachlorobutadiene (360 to 425 ng/kg of OCDF in two samples) obtained in Germany from the company Promochem (Hutzinger and Fiedler, 1991a; Heindl and Hutzinger, 1987). No CDD/CDFs were detected in two samples of allyl chloride, three samples of 1,1,1-trichloroethane, and four samples of trichloroethylene (detection limit ranged from 5 to 20 ng/kg) (Heindl and Hutzinger, 1987). Because no more recent or additional data could be found in the literature to confirm these values for products manufactured or used in the United States, no national estimates of CDD/CDF emissions are made for the inventory.

EPA's Office of Water promulgated effluent limitations for facilities that manufacture chlorinated aliphatic chlorine compounds and discharge treated wastewater (40 CFR 414.70). These effluent limitations do not specifically address CDDs and CDFs. The following chlorinated aliphatic compounds are regulated: 68  $\mu$ g/L for 1,2dichloroethane and 22  $\mu$ g/L for tetrachloroethylene. Similarly, EPA's Office of Solid Waste promulgated restrictions on land disposal of wastes generated during manufacture of many chlorinated aliphatics (40 CFR 268); however, these restrictions do not specifically regulate CDD/CDFs.

#### 8.3.6. Dyes, Pigments, and Printing Inks

Several researchers analyzed various dyes, pigments, and printing inks obtained in Canada and Germany for the presence of CDDs and CDFs (Williams et al., 1992; Hutzinger and Fiedler, 1991a; Santl et al., 1994c). The following paragraphs discuss the findings of those studies.

**Dioxazine Dyes and Pigments** - Williams et al. (1992) analyzed the CDD/CDF content in dioxazine dyes and pigments available in Canada. As shown in Table 8-16, OCDD and OCDF concentrations in the ng/kg range, and HpCDD, HxCDD, and PeCDD concentrations in the  $\mu$ g/kg range were found in Direct Blue 106 dye (3 samples), Direct Blue 108 dye (1 sample), and Violet 23 pigments (6 samples) (Williams et al., 1992). These dioxazine pigments are derived from chloranil, which has been found to contain high levels of CDD/CDFs and has been suggested as the source of contamination among these dyes (Christmann et al., 1989a; Williams et al., 1992; U.S. EPA, 1992b). In May 1990, EPA received test results showing that chloranil was heavily contaminated with dioxins; levels as high as 3,065  $\mu$ g I-TEQ<sub>DF</sub>/kg (2,903  $\mu$ g TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg) were measured in samples from four importers (mean value of 1,754  $\mu$ g I-TEQ<sub>DF</sub>/kg or 1,388  $\mu$ g TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg) (U.S. EPA, 1992b; Remmers et al., 1992). (See Section 8.3.7 for analytical results.)

In the early 1990s, EPA learned that I-TEQ<sub>DF</sub> levels in chloranil could be reduced by more than two orders of magnitude (to less than 20  $\mu$ g/kg) through manufacturing feedstock and process changes. EPA's Office of Pollution Prevention and Toxics (OPPT) subsequently began efforts to complete an industrywide switch from the use of contaminated chloranil to low-dioxin chloranil. Although chloranil is not manufactured in the United States, significant quantities are imported. As of May 1992, EPA had negotiated agreements with all chloranil importers and domestic dye/pigment manufacturers known to EPA that use chloranil in their products to switch to low-dioxin chloranil. In May 1993, when U.S. stocks of chloranil with high levels of CDD/CDFs had been depleted, EPA proposed a significant new use rule (SNUR) under Section 5 of TSCA that requires industry to notify EPA at least 90 days prior to the manufacture, import, or

processing, for any use, of chloranil containing CDD/CDFs at a concentration greater than 20  $\mu$ g I-TEQ<sub>DF</sub>/kg (Federal Register, 1993a; U.S. EPA, 1993c).

In 1983, approximately 36,500 kg of chloranil were imported (U.S. ITC, 1984). The U.S. International Trade Commission (ITC) has not published quantitative import data for chloranil since 1984. If it is assumed that this import volume reflects actual usage of chloranil in the United States during 1987, and the CDD/CDF contamination level was 1,754  $\mu$ g I-TEQ<sub>DF</sub>/kg (1,388  $\mu$ g TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg), then the maximum release into the environment via processing wastes and finished products was 64.0 g I-TEQ<sub>DF</sub>. If it is assumed that the import volume in 1995 was also 36,500 kg, but that the imported chloranil contained 10  $\mu$ g I-TEQ<sub>DF</sub>/kg on average, then the total potential annual TEQ release associated with chloranil in 1995 was 0.36 g I-TEQ<sub>DF</sub> (50.6 g TEQ<sub>DF</sub>-WHO<sub>98</sub>).

**Phthalocyanine Dyes and Printing Inks** - Hutzinger and Fiedler (1991a) found CDD/CDFs (tetra-, penta-, and hexachlorinated congeners) in the  $\mu$ g/kg range in a sample of a Ni-phthalocyanine dye. No CDD/CDFs were detected (detection limit of 0.1 to 0.5  $\mu$ g/kg) in two samples of Cu-phthalocyanine dyes and in one Co-phthalocyanine dye (Hutzinger and Fiedler, 1991a).

Santl et al. (1994) reported the results of analyses of four printing inks obtained from a supplier in Germany. Two of the inks are used for rotogravure printing, and two are used for offset printing. The results of the analyses are presented in Table 8-17. The I-TEQ<sub>DF</sub> content of the inks ranged from 15.0 to 88.6 ng/kg (17.7 to 87.2 ng/kg on a TEQ<sub>DF</sub>-WHO<sub>98</sub> basis). Primarily non-2,3,7,8-substituted congeners were found. The identities of the dyes and pigments in these inks were not reported.

## 8.3.7. TSCA Dioxin/Furan Test Rule

Citing evidence that halogenated dioxins and furans may be formed as by-products during chemical manufacturing processes (Versar, 1985), EPA issued a rule under Section 4 of TSCA that requires chemical manufacturers and importers to test for the presence of chlorinated and brominated dioxins and furans in certain commercial organic chemicals (Federal Register, 1987c). The rule listed 12 manufactured or imported chemicals that required testing and 20 chemicals not currently manufactured or imported that would require testing if manufacture or importation resumed. These chemicals are listed in Table 8-18. The specific dioxin and furan congeners that require quantitation and the target limits of quantitation (LOQ) that are specified in the rule are listed in Table 8-19. Under Section 8(a) of TSCA, the final rule also required that chemical manufacturers submit data on manufacturing processes and reaction conditions for chemicals produced using any of the 29 precursor chemicals listed in Table 8-20. The rule stated that subsequent to this data-gathering effort, testing may be proposed for additional chemicals if any of the manufacturing conditions used favored the production of dioxins and furans.

Sixteen sampling and analytical protocols and test data for 10 of the 12 chemicals that required testing were submitted to EPA (Holderman and Cramer, 1995). Data from 15 submissions were accepted; one submission is under review. Manufacture or import of two substances (tetrabromobisphenol-A-bis-2,3-dibromopropylether and tetrabromobisphenol-A-diacrylate) have stopped since the test rule was promulgated. [Note: All data and reports in the EPA TSCA docket are available for public review and inspection at EPA Headquarters in Washington, DC.]

Table 8-21 presents the results of analytical testing for CDDs and CDFs for the chemicals that have data available in the TSCA docket. Five of these 10 chemicals contained CDD/CDFs. Positive results were obtained for 2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione (chloranil), pentabromodiphenyloxide, octabromodiphenyloxide, decabromodiphenyloxide, and 1,2-Bis(tribromophenoxy)-ethane. Table 8-22 presents the quantitative analytical results for the four submitted chloranil samples, as well as the results of an EPA analysis of a sample of carbazole violet, which is manufactured from chloranil.

Although testing conducted under this test rule for 2,4,6-tribromophenol indicated no halogenated dioxins or furans above the LOQs, Thoma and Hutzinger (1989) reported detecting BDDs and BDFs in a technical-grade sample of this substance. Total TBDD, TBDF, and PeBDF were found at 84  $\mu$ g/kg, 12  $\mu$ g/kg, and 1  $\mu$ g/kg, respectively. No hexa-, hepta-, or octa-BDFs were detected. Thoma and Hutzinger (1989) also analyzed analytical-grade samples of two other brominated flame retardants, pentabromophenol and tetrabromophthalic anhydride; no BDDs or BDFs were detected (detection limits not reported).

#### 8.3.8. Halogenated Pesticides and FIFRA Pesticides Data Call-In

In the late 1970s and early 1980s, attention began to focus on pesticides as potential sources of CDDs and CDFs in the environment. Up to that time, CDD and CDF levels were not regulated in end-use pesticide products. Certain pesticide active ingredients, particularly chlorinated phenols and their derivatives, were known or suspected, however, to be contaminated with CDDs and CDFs. During the 1980s and 1990s, EPA took several actions to investigate and control CDD/CDF contamination of pesticides.

Actions to Regulate 2,4,5-T and Silvex: In 1983, EPA cancelled the sale of Silvex and 2,4,5-T for all uses (Federal Register, 1983). Earlier, in 1979, EPA had ordered emergency suspension of the forestry, rights-of-way, and pasture uses of 2,4,5-T. Emergency suspensions of the forestry, rights-of-way, pasture, home and garden, commercial/ornamental turf, and aquatic weed control/ditch bank uses of Silvex were also ordered (Federal Register, 1979; Plimmer, 1980). The home and garden, commercial/ornamental turf, and aquatic weed control/ditch bank uses of 2,4,5-T had been suspended in 1970.

Actions to Regulate pentachlorophenol (PCP): In 1984, EPA issued a notice of intent to cancel registrations of pesticide products containing PCP (including its salts) for all wood preservative uses (Federal Register, 1984). This notice specified modifications to the terms and conditions of product registrations that were required in order to avoid cancellation of the products. In response to this notice, several trade associations and registrants requested administrative hearings to challenge EPA's determinations. After carefully considering the comments and alternatives suggested during the prehearing stage of the administrative proceedings, EPA concluded that certain changes to the 1984 notice were appropriate. These were finalized in 1986 (Federal Register, 1986) and included the following: (i) all wood preservative uses of PCP and its salts were classified as "restricted use" only by certified applicators; (ii) specific worker protection measures were required; (iii) limits were placed on the HxCDD content of PCP; and (iv) label restrictions for home and farm uses of PCP prohibiting its application indoors and to wood intended for interior use (with a few exceptions), as well as prohibiting application of these products in a manner that may result in direct exposure of domestic animals or livestock, or in the contamination of food, feed, or drinking and irrigation water.

EPA subsequently amended the wood preservative uses Notice to establish reliable and enforceable methods for implementing certified limits for HxCDD and 2,3,7,8-TCDD in registered wood-preservative pesticide products (Federal Register, 1987a). Levels of 2,3,7,8-TCDD were not allowed to exceed 1.0 ppb in any product, and after February 2, 1989, any manufacturing-use PCP released for shipment could not contain HxCDD levels that exceeded an average of 2 ppm over a monthly release or a batch level of 4 ppm (a gradually phased in requirement). On January 21, 1987, EPA prohibited the registration of PCP and its salts for most nonwood uses (Federal Register, 1987b). EPA deferred action on several uses (i.e., uses in pulp/paper mills, oil wells, and cooling towers) pending receipt of additional exposure, use, and ecological effects data. On January 8, 1993, EPA issued a press advisory stating that the EPA special review of these deferred nonwood uses was being terminated, because all of these uses either had been voluntarily cancelled by the registrants or had been cancelled by EPA for failure of the registrants to pay the required annual maintenance fees (U.S. EPA, 1993f).

Pentachlorophenol (PCP) was one of the most widely used biocides in the United States prior to the regulatory actions to cancel and restrict certain wood and nonwood preservative uses of PCP. PCP was registered for use as a herbicide, defoliant, mossicide, and as a mushroom house biocide. It also found use as a biocide in pulp-paper mills, oil wells, and cooling towers. These latter three uses were terminated on or before 1993 (U.S. EPA, 1993f). However, the major use (greater than 80 percent of consumption) of PCP was and continues to be wood preservation.

The production of PCP for wood preserving began on an experimental basis in the 1930s. In 1947, nearly 3,200 metric tons of PCP were reported to have been used in the United States by the commercial wood preserving industry. Use in this industry steadily increased through the mid-1970s (American Wood Preservers Institute, 1977). Although domestic consumption volumes are not available for all years, based on historical production/export data for PCP reported in Mannsville (1983), it is estimated that 90 to 95 percent of production volume have typically been consumed domestically rather than exported. A reasonable estimate of average annual domestic PCP consumption during the period 1970 to 1995 is about 400,000 metric tons. This estimate assumes an average annual consumption rate of 20,000 metric tons/yr during the 1970s, 15,000 metric tons/yr during the 1980s, and 10,000 metric tons/yr during the 1990s.

Table 8-7 presents a compilation of published data on the CDD/CDF content of technical grade PCP. The only samples that have been analyzed for all dioxin-like CDD/CDFs were manufactured in the mid to late 1980s. Figure 8-4 presents these data in graphical form. It is evident from the figures that the predominant congener groups are OCDD, OCDF, HpCDF, and HpCDD, and the dominant 2,3,7,8-substituted congeners are OCDD, 1,2,3,4,6,7,8-HpCDD, and OCDF. Waddell et al. (1995) tested analytical grade PCP (from Aldrich Chemical Co.) for CDD/CDF content and found the same congener profile; however, the CDD/CDF levels were three to four orders of magnitude lower. Table 8-8 presents a similar compilation of published data on the CDD/CDF content of PCP-Na. The table shows the same patterns of dominant congeners and congener groups reported for PCP.

Samples of technical PCP manufactured during the mid to late 1980s contained about 3 mg I-TEQ/kg, (1.7 mg TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg) based on the data presented in Table 8-7. No published reports could be located that present the results of any congener-specific analyses of PCP manufactured since the late 1980s. However, monthly measurements of CDD/CDF congener group concentrations in technical PCP manufactured for use in the United States have been reported to EPA from 1987 to the present (KMG-Bernuth, 1997; Pentachlorophenol Task Force, 1997; U.S. EPA, 1999a). The average congener group concentrations reported to EPA for the years 1988 (i.e., 1 year after EPA regulations were imposed limiting HxCDD and 2,3,7,8-TCDD concentrations in PCP) to 1999 are presented in Table 8-7. In general, the average congener group concentrations during the period 1988-1999 are lower by factors of 2 to 4 than observed in the mid to late 1980s full congener analysis samples. If it is assumed that the toxic CDD/CDF congeners have also been reduced by similar factors, then the TEQ content of PCP manufactured since 1988 is about 1 mg I-TEQ/kg (0.6 mg TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg).

An estimated 8,400 metric tons of PCP were used for wood preservation in the United States in 1994 (American Wood Preservers Institute, 1995); for purposes of this report, it is assumed that an identical amount was used in 1995. An estimated 12,000 metric tons were used in 1987 (WHO, 1991). Combining these activity level estimates with the TEQ concentration estimates presented above indicates that 8,400 g I-TEQ<sub>DF</sub> (4,800 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) and 36,000 g I-TEQ<sub>DF</sub> (20,000 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) were incorporated into PCP-treated wood products in 1995 and 1987, respectively. This estimate for 1987

is assigned a high confidence rating, indicating high confidence in both the activity level and TEQ concentration in PCP estimates. The estimate for 1995 is assigned a medium confidence estimate because of uncertainties about the actual TEQ content of PCP manufactured in 1995.

Although the estimates of the mass of TEQ in treated wood are fairly certain, no studies are available that provide measured CDD/CDF release rate data from which a reliable estimate can be made of the amount of CDD/CDFs that have or will volatilize or leach from treated wood. Several recent field studies, discussed in the following paragraphs demonstrate that CDD/CDFs do apparently leach into soil from PCP-treated wood, but the studies do not provide release rate data. No studies were located that provide any measured CDD/CDF volatilization rates from PCP-treated wood. Although CDD/CDFs have very low vapor pressures, they are not bound nor react with the wood in any way that would preclude volatilization. Several studies, discussed below, have attempted to estimate potential CDD/CDF volatilization releases using conservative assumptions or modeling approaches, but these estimates span many orders of magnitude.

Gurprasad et al. (1995) analyzed three PCP-treated utility poles and their surrounding surface soils for penta- through octa-CDD content. All three poles showed significant levels of HxCDD (0.29 to 0.47 mg/kg), HpCDD (4.69 to 6.63 mg/kg), and OCDD (27.9 to 42.1 mg/kg), but no PeCDD. Surface soils collected 2 cm from the poles also had detectable levels of HxCDD, HpCDD, and OCDD; however, no consistent pattern was found between the CDD concentrations in the poles and in the adjacent soils. The soil concentrations did, however, show the same relative congener group pattern observed in the wood. CDD concentrations in soils obtained 20 cm from the poles were an order of magnitude less than the soil concentrations measured at 2 cm. Soils 26 meters from the poles showed nondetected values or values close to the detection limit of 0.01 to 0.02 mg/kg.

In a study of the leaching of PCP from 31 utility poles, the Electric Power Research Institute (EPRI) (1995) found similar patterns of PCP distribution in soils surrounding poles as those found by Gurprasad et al. (1995) for CDDs. PCP concentrations decreased by as much as two orders of magnitude between 7.5 cm from the poles and 20 cm from the poles, with an average decrease of slightly more than one order of magnitude over this distance. EPRI (1995) also found no obvious trend between PCP concentration in the wood (eight poles analyzed) and the age of the poles (4 to 11 years) or the PCP concentration in the surface soil. Based on their results and those of EPRI (1995), Gurprasad et al. (1995) concluded that CDDs probably leach from PCP-treated utility poles with the PCP/oil carrier and travel in the soil in a similar manner.

Wan (1995) and Wan and Van Oostdam (1995) measured CDD/CDF concentrations in waters and sediments from ditches surrounding utility poles and railroad ties and demonstrated that chlorophenol-treated wood could serve as a source of CDD/CDFs to the aquatic environment. Ten samples were collected at each of six utility pole sites and five railroad tie sites 1 to 2 days after major rainfall events and then were composited into one sample per site prior to analyses. Total CDDs (mean value of 76.7 mg/kg) and total CDFs (mean value of 18.7 mg/kg) detected in chlorophenol/creosote-treated utility poles were about 6 to 8 times greater, respectively, than the CDD and CDF concentrations detected in chlorophenol/creosote-treated railroad ties. Total CDDs found in water from railway ditches without utility poles (i.e., only treated railroad ties were present) were approximately 20 times higher than the background level found in farm ditch water. Total CDDs in railway ditches with utility poles were 4,300 times higher than the background levels. Water from railway ditches without utility poles contained total CDF levels 13 times higher than background, whereas water in ditches adjacent to poles were 8,500 times higher than background. Total CDDs in ditches adjacent to, and 4 m downstream of, utility poles were about 5,900 and 2,200 times, respectively, higher than background; total CDFs for the same sites were about 8,100 and 1,700 times, respectively, higher than background. Total CDDs found in ditch sediments of railway and ditch sediments adjacent to utility poles were about 5 and 700 times, respectively, higher than background; while total CDFs were about 9 and 1,800 times, respectively, higher than background. Both CDDs and CDFs were found in utility ditch sediments 4 m downstream of treated power poles, but at levels of 200 and 400 times, respectively, lower than those found adjacent to poles, indicating that they were transported from point sources of contamination. The corresponding values for CDFs were 5,400 and 8,000 times, respectively, higher in concentration.

Bremmer et al. (1994) estimated an annual release of 15 to 125 g of I-TEQ<sub>DF</sub> from PCP-treated wood in The Netherlands. The lower estimate was based on three basic

assumptions: (1) the half-life of PCP in treated wood is 15 years (according to industry sources); (2) the half-life of CDD/CDFs in treated wood is 10 times that of PCP (i.e., 150 years) because of the lower vapor pressures of CDD/CDFs relative to PCP; and (3) the typical CDD/CDF concentration in PCP has been 3,000  $\mu$ g/kg. The higher estimate was based on an assumed half-life of PCP in wood of 15 years and the results of an indoor air study by Papke et al. (1989) conducted at several kindergartens where PCP-treated wood had been used. Although Papke et al. (1989) found no clear correlation between indoor air concentrations of CDD/CDF and PCP across the range of CDD/CDF concentrations observed in the 20-plus samples (2.6 to 427 pg CDD/CDF/m<sup>3</sup>), there did appear to be a positive correlation at the sites with more elevated CDD/CDF concentrations. Bremmer et al. (1994) reported that the average ratio of PCP to I-TEQ <sub>DF</sub> air concentration of I-TEQ <sub>DF</sub> in technical PCP). The results of the Papke et al. (1989) study imply that CDD/CDFs may be released from PCP-treated wood at the same rate as PCP, rather than at a rate 10 times slower.

Rappe (1995) used the emission factor approach developed by Bremmer et al. (1994) and an assumed U.S. usage volume of PCP over the past 50 years (0.5 million metric tons) to estimate that as much as 10.5 kg of I-TEQ<sub>DF</sub> could volatilize from PCP-treated wood in the United States annually. Eitzer and Hites (1987) derived a dramatically different estimate of CDD/CDF volatilization from PCP-treated wood in the United States, 3 kg of total CDD/CDF per year (or 66 g of I-TEQ<sub>DF</sub> per year assuming an I-TEQ<sub>DF</sub> content in PCP of 3 mg/kg). Eitzer and Hites (1987) based their estimate on: (1) an assumption that 0.1 percent of the PCP produced annually enters the atmosphere, and (2) that the CDD/CDF contaminants present in the PCP (assumed to be 130 mg/kg) are released to the atmosphere at the same rate as the PCP (i.e., 0.1 percent). The basis for the first assumption of Eitzer and Hites (1987) is not clear because U.S. EPA (1980), which was cited as the source of the 0.1 percent emission factor, does not appear to address volatilization of PCP from in-service treated wood. The report does, however, estimate that most PCP in treated wood leaches relatively rapidly from the wood, presumably to land, within a period of 12 years.

Eduljee and Dyke (1996) and Douben et al. (1995) estimate that 0.8 g of I-TEQ<sub>DF</sub> is released to the air annually from PCP-treated wood in the U.K. This estimate is based on

the assumed emission of 0.1 percent of the CDD/CDF present in PCP-treated wood during the first year of the service life of the wood that was assumed by Eitzer and Hites (1987). No emission is assumed for subsequent years of use of the treated wood.

The California Air Resources Board (Chinkin et al., 1987) generated estimates of CDD/CDF volatilization releases at wood treatment facilities from bundles of treated wood that remain on-site for 1 month prior to shipment. An "adapted" version of a model developed by McCord (1981) was used for estimating volatile releases from a constantly filling lagoon. The model is primarily driven by chemical-specific vapor pressures and air diffusivity coefficients. Chinkin et al. (1987) do not provide all model input parameter values used to generate the emission estimates. However, running the model with typical dimensions for treated poles yields an I-TEQ<sub>DF</sub> emission rate on the order of 6E-12 g/yr-pole, an extremely low number (i.e., 170 billion poles would together emit 1 g TEQ/yr).

Actions to Identify Other Pesticides Containing CDD/CDFs: In addition to cancelling some pesticide registrations and establishing product standards, EPA's Office of Pesticide Programs (OPP) issued two Data Call-Ins (DCIs) in 1987. Pesticide manufacturers are required to register their products with EPA in order to market them commercially in the United States. Through the registration process, mandated by FIFRA, EPA can require that the manufacturer of each active ingredient generate a wide variety of scientific data through several mechanisms. The most common process is the five-phase reregistration process with which the manufacturers (i.e., registrants) of older pesticide products must comply. In most registration activities, registrants must generate data under a series of strict testing guidelines, 40 CFR 158--Pesticide Assessment Guidelines (U.S.EPA, 1988b). EPA can also require additional data from registrants, when necessary, through various mechanisms, including the DCI process.

The purpose of the first DCI, dated June and October 1987, "Data Call-In Notice for Product Chemistry Relating to Potential Formation of Halogenated Dibenzo-p-dioxin or Dibenzofuran Contaminants in Certain Active Ingredients," was to identify, using an analysis of raw materials and process chemistry, those pesticides that may contain halogenated dibenzo-p-dioxin and dibenzofuran contaminants. The 93 pesticides (76 pesticide active ingredients) to which the DCI applied, along with their corresponding Shaughnessey and Chemical Abstract code numbers, are presented in Table 8-23. [Note: The Shaughnessey code is an internal EPA tracking system--it is of interest because

chemicals with similar code numbers are similar in chemical nature (e.g., salts, esters, and acid forms of 2,4-D).] All registrants supporting registrations for these chemicals were subject to the requirements of the DCI, unless their product qualified for a Generic Data Exemption (i.e., a registrant exclusively used a FIFRA-registered pesticide product(s) as the source(s) of the active ingredient(s) identified in Table 8-23 in formulating their product(s)). Registrants whose products did not meet the Generic Data Exemption were required to submit the types of data listed below to enable EPA to assess the potential for formation of tetra- through hepta-halogenated dibenzo-p-dioxin or dibenzofuran contaminants during manufacture. Registrants, however, had the option to voluntarily cancel their product or "reformulate to remove an active ingredient," to avoid having to comply with the DCI.

- <u>Product Identity and Disclosure of Ingredients</u>: EPA required submittal of a Confidential Statement of Formula (CSF), based on the requirements specified in 40 CFR 158.108 and 40 CFR 158.120 - Subdivision D: Product Chemistry. Registrants who had previously submitted still-current CSFs were not required to resubmit this information.
- <u>Description of Beginning Materials and Manufacturing Process</u>: Under the requirements mandated by 40 CFR 158.120 Subdivision D, EPA required submittal of a manufacturing process description for each step of the manufacturing process, including specification of the range of acceptable conditions of temperature, pressure, or pH at each step.
- <u>Discussion of the Formation of Impurities</u>: Under the requirements mandated by 40 CFR 158.120 - Subdivision D, EPA required submittal of a detailed discussion and assessment of the possible formation of halogenated dibenzo-p-dioxins and dibenzofurans.

The second DCI, dated June and October 1987, "Data Call-In for Analytical Chemistry Data on Polyhalogenated Dibenzo-p-Dioxins/Dibenzofurans (HDDs and HDFs)," was issued for 68 pesticides (16 pesticide active ingredients) suspected to be contaminated by CDD/CDFs. (See Table 8-24.) All registrants supporting registrations for these pesticides were subject to the requirements of this DCI, unless the product qualified

for various exemptions or waivers. Pesticides covered by the second DCI were strongly suspected by EPA to contain detectable levels of CDD/CDFs.

Under the second DCI, registrants whose products did not qualify for an exemption or waiver were required to generate and submit the following types of data in addition to the data requirements of the first DCI:

- <u>Quantitative Method for Measuring CDDs or CDFs</u>: Registrants were required to develop an analytical method for measuring the HDD/HDF content of their products. The DCI established a regimen for defining the precision of the analytical method. Target limits of quantitation were established in the DCI for specific CDD and CDF congeners. (See Table 8-25.)
- <u>Certification of Limits of CDDs or CDFs</u>: Registrants were required to submit a "Certification of Limits" in accordance with 40 CFR 158.110 and 40 CFR 158.120 - Subdivision D. Analytical results were required that met the guidelines described above.

Registrants could select one of two options to comply with the second DCI. The first option was to submit relevant existing data, develop new data, or share the cost to develop new data with other registrants. The second option was to alleviate the DCI requirements through several exemption processes, including a Generic Data Exemption, voluntary cancellation, reformulation to remove the active ingredient of concern, an assertion that the data requirements do not apply, or the application or award of a low-volume, minor-use waiver.

The data contained in CSFs, as well as any other data generated under 40 CFR 158.120 - Subdivision D, are typically considered Confidential Business Information (CBI) under the guidelines prescribed in FIFRA, because they usually contain information regarding proprietary manufacturing processes. In general, all analytical results submitted to EPA in response to both DCIs are considered CBI and cannot be released by EPA into the public domain. Summaries based on the trends identified in that data, as well as data made public by EPA, are summarized below.

The two DCIs included 161 pesticides. Of these, 92 are no longer supported by registrants. Following evaluation of the process chemistry submissions required under the
DCIs, OPP determined that formation of CDD/CDFs was not likely during the manufacture of 43 of the remaining 69 pesticides; thus, analysis of samples of these 43 pesticides was not required by OPP. Evaluation of process chemistry data is ongoing at OPP for an additional seven pesticides. Tables 8-23 and 8-24 indicate which pesticides are no longer supported, those for which OPP determined that CDD/CDF formation is unlikely, and those for which process chemistry data or analytical testing results are under review in OPP (U.S. EPA, 1995f).

OPP required that analysis of production samples be performed on the remaining 19 pesticides. (See Table 8-26.) The status of the analytical data generation/evaluation to date is summarized as follows: (1) no detection of CDD/CDFs above the LOQs in registrant submissions for 13 active ingredients, (2) detection of CDD/CDFs above the LOQs for 2,4-D acid (two submissions) and 2,4-D 2-ethyl hexyl acetate (one submission), and (3) ongoing data generation or evaluation for four pesticides.

Table 8-25 presents a summary of results obtained by EPA for CDDs and CDFs in eight technical 2,4-D herbicides; these data were extracted from program files in OPP. Because some of these files contained CBI, the data in this table were reviewed by OPP staff to ensure that no CBI was being disclosed (Funk, 1996). Figure 8-5 presents a congener profile for 2,4-D based on the average congener concentrations reported in Table 8-25.

Schecter et al. (1997) reported the results of analyses of samples of 2,4-D manufactured in Europe, Russia, and the United States. (See Table 8-27.) The total TEO concentrations measured in the European and Russian samples are similar to those measured in the EPA DCI samples; however, the levels reported by Schecter et al. (1997) for U.S. samples are significantly lower.

As discussed in Section 12.2.1, an estimated 26,300 metric tons of 2,4-D were used in the United States in 1995, making it one of the top 10 pesticides in terms of quantity used (U.S. EPA, 1997e). An estimated 30,400 metric tons were used during 1987 (U.S. EPA, 1988c). On the basis of the average CDD/CDF congener concentrations in 2,4-D presented in Table 8-25 (not including OCDD and OCDF), the corresponding I-TEQ<sub>DF</sub> concentration is 0.70  $\mu$ g/kg (1.10  $\mu$ g TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg). Combining this TEQ concentration with the activity level estimates for 1995 and 1987 indicates that 18.4 g I-TEQ<sub>DF</sub> (28.9 g TEQ<sub>DF</sub>-WHO<sub>98</sub>) may have entered the environment in 1995 and 21.3 g I-

 $TEQ_{DF}$  (33.4 g  $TEQ_{DF}$ -WHO<sub>98</sub>) may have entered the environment in 1987. These release estimates are assigned a high confidence rating, indicating high confidence in both the production and emission factor estimates.

### 8.4. OTHER CHEMICAL MANUFACTURING AND PROCESSING SOURCES

### 8.4.1. Municipal Wastewater Treatment Plants

*Sources* - CDD/CDFs have been measured in nearly all sewage sludges tested, although the concentrations and, to some extent, the congener profiles and patterns differ widely. Potential sources of the CDD/CDFs include microbial formation (discussed in Chapter 9), runoff to sewers from lands or urban surfaces contaminated by product uses or deposition of previous emissions to air (discussed in Section 12.2.1), household wastewater, industrial wastewater, chlorination operations within the wastewater treatment facility, or a combination of all the above (Rappe, 1992a; Rappe et al., 1994; Horstmann et al., 1992; Sewart et al., 1995; Cramer et al., 1995; Horstmann and McLachlan, 1995).

The major source(s) for a given Publicly Owned Treatment Works (POTW) is likely to be site-specific, particularly in industrialized areas. For example, Rieger and Ballschmiter (1992) traced the origin of CDDs and CDFs found in municipal sewage sludge in Ulm, Germany, to metal manufacturing and urban sources. The characteristics of both sources were similar and suggested generation via thermal processing. However, in a series of recent studies, Horstmann et al. (1992, 1993a, 1993b) and Horstmann and McLachlan (1994a, 1994b, 1995) demonstrated that wastewater generated by laundering and bathing could be the major source at many, if not all, POTWs that serve primarily residential populations. Although runoff from streets during precipitation events, particularly from streets with high traffic density, was reported by these researchers as contributing measurably, the total contribution of TEQ from household wastewater was eight times greater than that from surface runoff at the study city.

Horstmann et al. (1992) provided initial evidence that household wastewater could be a significant source. Horstmann et al. (1993a) measured CDD/CDF levels in the effluent from four different loads of laundry from two different domestic washing machines. The concentrations of total CDD/CDF in the four samples ranged from 3,900 to 7,100 pg/L and were very similar in congener profile, with OCDD being the dominant

congener followed by the hepta- and hexa-CDDs. Because of the similar concentrations and congener profiles found, Horstmann et al. (1993a) concluded that the presence of CDD/CDF in washing machine wastewater is widespread. A simple mass balance performed using the results showed that the CDD/CDFs found in the four washing machine wastewater samples could account for 27 to 94 percent of the total CDD/CDF measured in the sludge of the local wastewater treatment plant (Horstmann and McLachlan, 1994a).

Horstmann et al. (1993a) also performed additional experiments that showed that detergents, commonly used bleaching agents, and the washing cycle process itself were not responsible for the observed CDD/CDFs. To determine if the textile fabric or fabric finishing processes could account for the observed CDD/CDFs, Horstmann et al. (1993b), Horstmann and McLachlan (1994a, 1994b), and Klasmeier and McLachlan (1995) analyzed the CDD/CDF content of eight different raw (unfinished) cotton cloths containing fiber from different countries and five different white synthetic materials (acetate, viscose, bleached polyester, polyamide, and polyacrylic), as well as more than 100 new textile finished products. Low concentrations were found in most products (i.e., less than 50 ng/kg of total CDD/CDF), but a small percentage contained high concentrations up to 290  $\mu$ g/kg of total CDD/CDF. On the basis of the concentrations and patterns found, the authors concluded that neither unfinished new fabrics nor common cotton finishing processes can explain the CDD/CDF levels found in wastewater. Rather, the use of CDD/CDF-containing textile dyes and pigments and the use in some developing countries of pentachlorophenol to treat unfinished cotton appear to be the sources of the detected CDDs/CDFs.

Horstmann and McLachlan (1994a, 1994b, 1995) reported the results of additional experiments that demonstrated that the small percentage of clothing items with high CDD/CDF levels could be responsible for the quantity of CDD/CDFs observed in household wastewater and sewage sludge. They demonstrated that the CDD/CDFs can be gradually removed from the fabric during washing, can be transferred to the skin, subsequently transferred back to other textiles, and then washed out, or can be transferred to other textiles during washing and then removed during subsequent washings.

**Releases to Water** - The presence of CDD/CDFs in sewage sludge suggests that CDD/CDFs may also be present in the wastewater effluent discharges of POTWs;

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however, few studies reporting the results of effluent analyses for CDD/CDFs have been published.

Rappe et al. (1989a) tested the effluent from two Swedish POTWs for all 2,3,7,8substituted CDD/CDF congeners. OCDD was detected in the effluents from both facilities at concentrations ranging from 14 to 39 pg/L. Rappe et al. detected 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF in the effluent of one facility at concentrations of 2.8 and 2.0 pg/L, respectively. No 2,3,7,8-substituted tetra-, penta-, and hexa-CDDs and CDFs were detected (detection limits of 0.2 to 20 pg/L).

Ho and Clement (1990) reported the results of sampling during the late 1980s of 37 POTWs in Ontario, Canada, for each of the five CDD/CDF congener groups with four to eight chlorines. The sampled facilities included 27 secondary treatment facilities, 7 primary treatment facilities, 1 tertiary plant, and 2 lagoons. The facilities accounted for about 73 percent of the sewage discharged by POTWs in Ontario. No CDDs/CDFs were detected (detection limit in low ng/L range) in the effluents from the lagoons and the tertiary treatment facilities (two and one effluent samples, respectively). HpCDD, OCDD, TCDF, and OCDF were detected in the effluents from the secondary treatment facilities (detected in four or fewer samples at levels ranging from 0.1 to 11 ng/L).

Gobran et al. (1995) analyzed the raw sewage and final effluent of an Ontario, Canada, wastewater treatment plant for CDD/CDF congeners over a 5-day period. Although HpCDD, OCDD, HpCDF, and OCDF were detected in the raw sewage (12 to 2,300 pg/L), no CDD/CDFs were detected in the final effluent at congener-specific detection limits ranging from 3 to 20 pg/L.

The California Regional Water Quality Control Board (CRWQCB, 1996) reported the results of effluent testing at nine POTWs in the San Francisco area. A total of 30 samples were collected during 1992-1995; 1 to 6 samples were analyzed for each POTW. Table 8-28 summarizes the sampling results. With the exception of OCDD, most 2,3,7,8-substituted CDD/CDF congeners were seldom detected.

The CRWQCB (1996) data were collected to provide representative effluent concentrations for the San Francisco area; these data cannot be considered to be representative of CDD/CDF effluent concentrations at the 16,000-plus POTWs nationwide. Therefore, the data can only be used to generate a preliminary estimate of the potential mass of CDD/CDF TEQ that may be released annually by U.S. POTWs. Approximately 122 billion liters of wastewater are treated daily by POTWs in the United States (U.S. EPA, 1997c). Multiplying this value by 365 days/year and by the "overall mean" TEQ concentrations listed in Table 8-28 (i.e., 0.29 pg I-TEQ<sub>DF</sub>/L and 0.27 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L) yields annual TEQ release estimates of 13 g of I-TEQ<sub>DF</sub> or 12 g of TEQ<sub>DF</sub>-WHO<sub>98</sub>.

*Sewage Sludge Land Disposal* - EPA conducted the National Sewage Sludge Survey in 1988 and 1989 to obtain national data on sewage sludge quality and management. As part of this survey, EPA analyzed sludges from 174 POTWs that employed at least secondary wastewater treatment for more than 400 analytes, including CDD/CDFs. Although sludges from only 16 percent of the POTWs had detectable levels of 2,3,7,8-TCDD, all sludges had detectable levels of at least one CDD/CDF congener (U.S. EPA, 1996a). I-TEQ<sub>DF</sub> concentrations as high as 1,820 ng/kg dry weight were measured. The congener-specific results of the survey are presented in Table 8-29. If all nondetected values found in the study are assumed to be zero, then the mean and median I-TEQ<sub>DF</sub> concentrations of the sludges from the 174 POTWs are 50 and 11.2 ng/kg (dry weight basis), respectively. If the nondetected values are set equal to the detection limit, then the mean and median I-TEQ<sub>DF</sub> concentrations are 86 and 50.4 ng/kg, respectively (U.S. EPA, 1996a; Rubin and White, 1992).

Green et al. (1995) and Cramer et al. (1995) reported the results of analyses of 99 samples of sewage sludge collected from wastewater treatment plants across the United States during the summer of 1994. These data are summarized in Table 8-30. To calculate average results in units of TEQ, Green et al. (1995) averaged results from all samples collected from the same facility to ensure that results were not biased toward the concentrations found at facilities from which more than one sample were collected. Also, eight samples were excluded from the calculation of the overall TEQ averages because it was unclear as to whether they were duplicate samples from other POTWs. POTW average TEQ concentrations were calculated for 74 POTWs. If all nondetected values are assumed to be zero, then the overall study mean and median I-TEQ<sub>DF</sub> concentrations were 47.7 and 33.4 ng I-TEQ<sub>DF</sub>/kg (dry weight basis), respectively (standard deviation of 44.7 ng I-TEQ<sub>DF</sub>/kg). The corresponding mean and median TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg). The mean and median results reported by Green et al. (1995) and Cramer et

al. (1995) are very similar in terms of total TEQ to those reported by EPA for samples collected 5 years earlier (U.S. EPA, 1996a; Rubin and White, 1992). The predominant congeners in both data sets are the octa- and hepta-CDDs and -CDFs. Although not present at high concentrations, 2,3,7,8-TCDF was commonly detected.

The CDD/CDF concentrations and congener group patterns observed in these two U.S. surveys are similar to the results reported for sewage sludges in several other Western countries. Stuart et al. (1993) reported mean CDD/CDF concentrations of 23.3 ng I-TEQ<sub>DF</sub>/kg (dry weight) for three sludges from rural areas, 42.3 ng I-TEQ<sub>DF</sub>/kg for six sludges from light industry/domestic areas, and 52.8 ng I-TEQ<sub>DF</sub>/kg for six sludges from industrial/domestic areas collected during 1991-1992 in England and Wales. Näf et al. (1990) reported concentrations ranging from 31 to 40 ng I-TEQ<sub>DF</sub>/kg (dry weight) in primary and digested sludges collected from the POTW in Stockholm, Sweden, during 1989. Gobran et al. (1995) reported an average concentration of 15.7 ng I-TEQ<sub>DF</sub>/kg in anaerobically digested sludges from an industrial/domestic POTW in Ontario, Canada. In all three studies, the congener group concentrations increased with increasing degrees of chlorination, with OCDD the dominant congener. Figure 8-6 presents congener profiles, using the mean concentrations reported by Green et al. (1995).

Approximately 5.4 million dry metric tons of sewage sludge are estimated by EPA to be generated annually in the United States according to the results of the 1988/1989 EPA National Sewage Sludge Survey (Federal Register, 1993b). Table 8-31 lists the volume, by use and disposal practices, of sludge disposed of annually. More recent comprehensive survey data are not available to characterize sludge generation and disposal practices during 1995. For this reason, and because the mean I-TEQ<sub>DF</sub> concentration values reported in the 1988/1989 survey (U.S. EPA, 1996a) and the 1995 survey (Green et al., 1995; Cramer et al., 1995) were very similar, the estimated amounts of TEQs that may have been present in sewage sludge and been released to the environment in 1987 and 1995 were assumed to be the same. These values, presented in Table 8-31, were estimated using the average (i.e., 49 ng I-TEQ<sub>DF</sub>/kg) of the mean I-TEQ<sub>DF</sub> concentration values (nondetected values set at detection limits) reported by EPA (1996a) (i.e., 50 ng I-TEQ<sub>DF</sub>/kg) and by Green et al. (1995) and Cramer et al. (1995) (i.e., 47.7 ng I-TEQ<sub>DF</sub>/kg). Multiplying this mean total TEQ concentration by the sludge volumes generated yields an annual potential total release of 204 g I-TEQ<sub>DF</sub> or 151 g TEQ<sub>DF</sub>-WHO<sub>98</sub>

for nonincinerated sludges. Of this 204 g I-TEQ<sub>DF</sub>, 3.5 g enter commerce as a product for distribution and marketing. The remainder is applied to land (103 g) or is landfilled (97 g). In units of  $TEQ_{DF}$ -WHO<sub>98</sub>, the comparable estimates are 2.6 g to commerce, 76.6 g applied to land, and 71.7 g landfilled.

These release estimates are assigned a high confidence rating for both the production and emission factor estimates. The high rating was based on the judgment that the 174 facilities tested by EPA (U.S. EPA, 1996a) and the 74 facilities tested by Green et al. (1995) and Cramer et al. (1995) were reasonably representative of the variability in POTW technologies and sewage characteristics nationwide.

#### 8.4.2. Drinking Water Treatment Plants

There is no strong evidence that chlorination of water for drinking purposes results in the formation of CDD/CDFs. Few surveys of CDD/CDF content in finished drinking water have been conducted. The few that have been published only rarely report the presence of any CDD/CDF even at low pg/L detection limits, and in those cases, the CDD/CDFs were also present in the untreated water.

Rappe et al. (1989b) reported the formation of CDFs (tetra- through octachlorinated CDFs) when tap water and double-distilled water were chlorinated using chlorine gas. The CDF levels found in the single samples of tap water and double-distilled water were 35 and 7 pg I-TEQ<sub>DF</sub>/L, respectively. No CDDs were detected at detection limits ranging from 1 to 5 pg/L. However, the water samples were chlorinated at a dosage rate of 300 mg of chlorine per liter of water, which is considerably higher (by a factor of one to two orders of magnitude) than the range of dosage rates typically used to disinfect drinking water. Rappe et al. (1989b) hypothesized that the CDFs or their precursors are present in chlorine gas. Rappe et al. (1990a) analyzed a 1,500-liter sample of drinking water from a municipal drinking water treatment plant in Sweden. Although the untreated water was not analyzed, a sludge sample from the same facility was. The large sample volume enabled detection limits on the order of 0.001 pg/L. The TEQ content of the water and sludge was 0.0029 pg  $I-TEQ_{DF}/L$  and 1.4 ng/kg, respectively. The congener patterns of the drinking water and sludge sample were very similar, suggesting that the CDD/CDFs detected in the finished water were present in the untreated water.

#### 8.4.3. Soaps and Detergents

As discussed in Section 8.4.1, CDD/CDFs were detected in nearly all sewage sludges tested, whether obtained from industrialized areas or rural areas. Because of the ubiquitous presence of CDD/CDFs in sewage sludge, several studies have been conducted to determine the source(s). A logical category of products to test, because of their widespread use are detergents, particularly those that contain or release chlorine during use (i.e., hypochlorite-containing and dichloroisocyanuric acid-containing detergents). The results of studies conducted to date, which are summarized below, indicate that CDD/CDFs are not formed during use of chlorine-free detergents, chlorine-containing or chlorine-releasing detergents, and chlorine bleach during household bleaching operations.

Sweden's Office of Nature Conservancy (1991) reported that the results of a preliminary study conducted at one household indicated that CDD/CDFs may be formed during use of dichloroisocyanurate-containing dishwasher detergents. A more extensive main study was then conducted using standardized food, dishes, cutlery, etc., and multiple runs. Testing of laundry washing and fabric bleaching, and actual testing of the CDD/CDF content of detergents, was also performed. The study examined (1) hypochlorite- and dichloroisocyanurate-containing dish-washing machine detergents; (2) sodium hypochlorite-based bleach (4.4 percent NaOCI) in various combinations with and without laundry detergent; and (3) sodium hypochlorite-based bleach, used at a high enough concentration to effect bleaching of a pair of imported blue jeans. CDD/CDFs were not detected in either the chlorine-free detergent or the detergent with hypochlorite; 0.6 pg TEQ/g was detected in the detergent containing dichloroisocyanurate. The results of all dish and laundry washing machine tests showed very low levels of CDD/CDFs, often nondetected values. There was no significant difference between the controls and test samples. In fact, the control samples contained higher TEQ content than some of the experimental samples. The drain water from the dish washing-machine tests contained < 1.0 to < 3.0 pg I-TEQ<sub>DF</sub>/L (the water-only control sample contained < 2.8 pg I-TEQ<sub>DF</sub>/L). The CDD/CDF content of the laundry drain water samples ranged from <1.1 to <4.6 pg I-TEQ<sub>DF</sub>/L (the water-only control sample contained <4.4 pg I-TEQ<sub>DF</sub>/L).

Thus, under the test conditions examined by Sweden's Office of Nature Conservancy (1991), CDD/CDFs are not formed during dish washing and laundry washing nor during bleaching with hypochlorite-containing bleach. No definitive reason could be

found to explain the difference in results between the preliminary study and the main study for dish washing with dichloroisocyanurate-containing detergents. The authors of the study suggested that differences in the foods used and the prewashing procedures employed in the two studies were the likely causes of the variation in the results.

Rappe et al. (1990c) analyzed a sample of a Swedish commercial soft soap, as well as a sample of tall oil and a sample of tall resin, for CDD/CDF content. Tall oil and tall resin, by-products of the pulping industry, are the starting materials for the production of soft, liquid soap. Crude tall oil, collected after the Kraft pulping process, is distilled under reduced pressure at temperatures of up to 280-290°C, yielding tall oil and tall resin. The measured TEQ content of the liquid soap was 0.447 ng I-TEQ<sub>DF</sub>/L (0.647 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/L). PeCDDs were the dominant congener group followed by HpCDDs, HxCDDs, PeCDFs, and OCDD with some tetra-CDFs and -CDDs also present. The TEQ content of the tall oil (9.4 ng I-TEQ<sub>DF</sub>/kg, or 12.0 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg) and tall resin (200 ng I-TEF<sub>DF</sub>/kg, 196 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg) was significantly higher than the level found in the liquid soap. The tall oil contained primarily tetra- and penta-CDDs and -CDFs, while the tall resin contained primarily HpCDDs, HxCDDs, and OCDD. Rappe et al. (1990c) compared the congener patterns of the three samples and noted that although the absolute values for the tetra- and penta-CDDs and -CDFs differed between the tall oil, tall resin and liquid soap samples, the same congeners were present in the samples. The congener patterns for the more chlorinated congeners were very similar. Table 8-32 presents the results reported by Rappe et al. (1990c).

In 1987, 118 million liters of liquid household soaps were shipped in the United States (U.S. DOC, 1990b); shipment quantity data are not available for liquid household soap in the 1992 U.S. Economic Census (U.S. DOC, 1996). Because only one sample of liquid soap has been analyzed for CDD/CDF content (Rappe et al., 1990c), only a very preliminary estimate of the annual release of CDD/CDF TEQ from liquid soap can be made. If it is assumed that an average 118 million liters of liquid soap contain 0.447 ng I-TEQ<sub>DF</sub>/L (0.647 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/L), then the resulting estimate is 0.05 g I-TEQ<sub>DF</sub>/yr (0.08 g TEQ<sub>DF</sub>-WHO<sub>98</sub>/yr).

#### 8.4.4. Textile Manufacturing and Dry Cleaning

As discussed in Section 8.4.1, CDD/CDFs have been detected in nearly all sewage sludges tested, whether obtained from industrialized areas or rural areas. To determine if the textile fabric or fabric finishing processes could account for the observed CDD/CDFs, several studies were conducted in Germany. These studies, summarized in the following paragraphs, indicate that some finished textile products do contain detectable levels of CDD/CDFs and that these CDD/CDFs can be released from the textile during laundering or dry cleaning; however, textile finishing processes are typically not sources of CDD/CDF formation. Rather, the use of CDD/CDF-containing dyes and pigments and the use in some countries of pentachlorophenol to treat unfinished cotton appear to be the sources of the detected CDD/CDFs.

Horstmann et al. (1993b) analyzed the CDD/CDF content of eight different raw (unfinished) cotton cloths containing fiber from different countries and five different white synthetic materials (acetate, viscose, bleached polyester, polyamide, and polyacrylic). The maximum concentrations found in the textile fabrics were 30 ng/kg in the cotton products and 45 ng/kg in the synthetic materials. Also, a cotton finishing scheme was developed that subjected one of the cotton materials to a series of 16 typical cotton finishing processes; one sample was analyzed following each step. The fabric finishing processes showing the greatest effect on CDD/CDF concentration were the application of an indanthrene dye and the "wash and wear" finishing process, which together resulted in a CDD/CDF concentration of about 100 ng/kg. On the basis of the concentrations found, the authors concluded that neither unfinished new fabrics nor common cotton finishing processes can explain the CDD/CDF levels found in laundry wastewater.

Fuchs et al. (1990) reported that dry-cleaning solvent redistillation residues that were collected from 12 commercial and industrial dry-cleaning operations contained considerable amounts of CDD/CDFs. The reported I-TEQ<sub>DF</sub> content ranged from 131 to 2,834 ng/kg, with the dominant congeners always OCDD and the HpCDDs. Towara et al. (1992) demonstrated that neither the use of chlorine-free solvents nor variation of the dry-cleaning process parameters lowered the CDD/CDF content of the residues.

Umlauf et al. (1993) conducted a study to characterize the mass balance of CDD/CDFs in the dry-cleaning process. The soiled clothes (containing 16 pg total CDD/CDF per kg) accounted for 99.996 percent of the CDD/CDF input. Input of CDD/CDF

from indoor air containing 0.194 pg/m<sup>3</sup> accounted for the remainder (i.e., 0.004 percent). The dry-cleaning process removed 82.435 percent of the CDD/CDF in the soiled clothing. Most of the input CDD/CDF (82.264 percent) was found in the solvent distillation residues. Air emissions (at 0.041 pg/m<sup>3</sup>) accounted for 0.0008 percent of the total input, which was less than the input from indoor air. The fluff (at a concentration of 36 ng/kg) accounted for 0.1697 percent, and water effluent (at a concentration of 0.07 pg/L) accounted for 0.0000054 percent.

Horstmann and McLachlan (1994a, 1994b, 1995) analyzed 35 new textile samples (primarily cotton products) obtained in Germany for CDD/CDFs. Low levels were found in most cases (total CDD/CDF less than 50 ng/kg). The dominant congeners found were OCDD and the HpCDDs. However, several colored T-shirts from a number of clothing producers had extremely high levels, with concentrations up to 290,000 ng/kg. Because the concentrations in identical T-shirts purchased at the same store varied by up to a factor of 20, the authors concluded that the source of CDD/CDFs is not a textile finishing process, because a process source would have resulted in a more consistent level of contamination. Klasmeier and McLachlan (1995) subsequently analyzed 68 new textile products obtained in Germany for OCDD and OCDF. Most samples had nondetectable levels (42 samples <60 ng/kg). Only four samples had levels exceeding 500 ng/kg.

Horstmann and McLachlan (1994a, 1994b) reported finding two different congener group patterns in the more contaminated of the 35 textile products. One pattern agreed with the congener pattern for PCP reported by Hagenmaier and Brunner (1987), while the other pattern was similar to that reported by Remmers et al. (1992) for chloranil-based dyes. The authors hypothesize that the use of PCP to preserve cotton, particularly when it is randomly strewn on bales of cotton as a preservative during sea transport, is the likely source of the high levels occasionally observed. Although the use of PCP for nonwood uses was prohibited in the United States in 1987 (see Section 8.3.8), PCP is still used in developing countries, especially to preserve cotton during sea transport (Horstmann and McLachlan, 1994a).

Horstmann and McLachlan (1994a, 1994b) conducted additional experiments that demonstrated that the small percentage of clothing items with high CDD/CDF levels could be responsible for the quantity of CDD/CDFs observed in household wastewater. They demonstrated that the CDD/CDFs can be gradually removed from the fabric during

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washing, can be transferred to the skin and subsequently transferred back to other textiles and then washed out, or can be transferred to other textiles during washing and then removed during subsequent washings.

		Bleached Pulp			Wastewater Sludge		Ī	Wastewater Effluent	
Congener/Congener Group	Median (ng/kg)	Range (ng/kg)	No. of Detects (10 samples)	Median (ng/kg)	Range (ng/kg)	No. of Detects (9 samples)	Median (pg/L)	Range (pg/L)	No. of Detects (9 samples)
2.3.7.8-TCDD	6.4	0.4 to 124	10	63	ND (6.3) to 180	α	42	ND (11) to 98	α
1,2,3,7,8-PeCDD	ND (0.3)	ND (0.1) to 1.4	2 2	ND (2.5)	ND (1.4) to 28	) —	ND (9.6)	ND (2.8) to ND (25)	0 0
1,2,3,4,7,8-HxCDD	ND (0.4)	ND (0.2) to 0.4	1	ND (3.1)	ND (1.5) to 40	1	ND (12)	ND (6.6) to ND (12)	0
1,2,3,6,7,8-HxCDD	ND (0.5)	ND (0.2) to 1.6	2	ND (3.2)	ND (1.7) to 95	1	ND (12)	ND (6.6) to ND (24)	0
1,2,3,7,8,9-HxCDD	ND (0.5)	ND (0.2) to 0.5	1	ND (3.9)	ND (1.7) to 80	1	ND (12)	ND (6.6) to ND (23)	0
1,2,3,4,6,7,8-HpCDD	З.З	2.3 to 8.4	10	37	18 to 490	o	170	77 to 270	o -
OCDD	46	28 to 81	10	698	263 to 1,780	9	3,000	1,000 to 4,600	6
2,3,7,8-TCDF	18	1.4 to 716	10	233	13 to 1,150	თ	120	12 to 840	ი
1,2,3,7,8-PeCDF	ND (0.7)	ND (0.1) to 3.9	4	6.2	ND (1.2) to 22	9	ND (7.2)	ND (2.2) to 36	2
2,3,4,7,8-PeCDF	ND (0.2)	ND (0.1) to 4.7	ю	4.7	ND (0.9) to 38	9	ND (6.3)	ND (2.2) to 33	2
1,2,3,4,7,8-HxCDF	ND (0.3)	ND (0.2) to ND (0.6)	0	ND (2.5)	ND (0.9) to 31	2	ND (8.4)	ND (4.8) to ND (15)	0
1,2,3,6,7,8-HxCDF	ND (0.3)	ND (0.1) to ND (0.4)	0	ND (1.4)	ND (0.9) to 33	1	ND (7.1)	ND (4.8) to ND (15)	0
1,2,3,7,8,9-HxCDF	ND (0.3)	ND (0.1) to ND (0.4)	0	ND (1.7)	ND (0.9) to ND (4.0)	0	ND (6.2)	ND (2.5) to ND (15)	0
2,3,4,6,7,8-HxCDF	ND (0.3)	ND (0.2) to ND (0.4)	0	ND (1.7)	ND (0.9) to 34	1	ND (8.2)	ND (4.8) to ND (15)	0
1,2,3,4,6,7,8-HpCDF	ND (0.6)	ND (0.1) to 0.8	ю	6.6	ND (3.6) to 70	7	ND (23)	ND (13) to 44	ю
1,2,3,4,7,8,9-HpCDF	ND (0.6)	ND (0.1) to ND (2.1)	0	ND (1.6)	ND (1.2) to 10	1	ND (22)	ND (6.4) to ND (41)	0
OCDF	2.2	ND(2.8) to 4.3	8	22	ND (54) to 168	8	190	ND (180) to 230	8
Total 2,3,7,8-CDD <sup>a,b</sup>	55.7			798			3,212		
Total 2,3,7,8-CDF <sup>a,b</sup>	18			272.5			310		
Total I-TEQ <sub>DF</sub> (ND = zero) <sup>b</sup>	8.28			90.12			58.89		
Total I-TEQ <sub>DF</sub> (ND = $\frac{1}{2}$ DL) <sup>b</sup>	8.56			91.72			66.57		
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (ND = zero) <sup>b</sup> Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (ND = $\frac{1}{2}$ DL) <sup>b</sup>	8.24 8.59		89.47 91.7				56.02 66.09		
Total CDD/CDF <sup>b</sup>	120			1,695			4,013		

Table 8-1. CDD/CDF Concentrations in Pulp and Paper Mill Bleached Pulp, Wastewater Sludge, and Effluent (circa 1988)

ND = Not detected; value in parentheses is the detection limit. ng/kg = nanograms per kilogram pg/L = picograms per liter

 $^{\rm a}$  Calculated assuming nondetected values are zero.  $^{\rm b}$  Sum of median values.

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

		Ble	ached Pulp			Wast	ewater Sludge			Wast	ewater Effluent	
Congener/Congener Group	Mean ND = 0 (ng/kg)	Median (ng/kg)	Range (ng/kg)	No. of Detects/ No. of Samples	Mean ND = 0 (ng/kg)	Median (ng/kg)	Range (ng/kg)	No. of Detects/ No. of Samples	Mean ND = 0 (pg/L)	Median (ng/kg)	Range (pg/L)	No. of Detects/ No. of Samples
2,3,7,8-TCDD 1 2 3 7 8-PeCDD	0.3	ND(1) ND(5)	ND(1) to 5 ND(3) to ND(7)	1/18 0/18	0.8	ND(1) ND(5)	ND(1) to 4 ND(4) to ND(52)	4/12 0/12	1.2	ND(11) ND(53)	ND(10) to 21 ND(50) to ND(55)	1/18 0/18
1,2,3,4,7,8-HxCDD	00	ND(5)	ND(3) to ND(7)	0/18	0.5	ND(5)	ND(4) to 7	1/13	00	ND(53)	ND(50) to ND(55)	0/18
1,2,3,6,7,8-H×CDD	0	ND(5)	ND(3) to ND(7)	0/18	2.3	ND(5)	ND(4) to 18	2/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,7,8,9-HxCDD 1,2,3,4,6,7,8-HpCDD	00	ND(5) ND(5)	ND(3) to ND(7) ND(3) to ND(7)	0/18 0/18	1.6 41.4	ND(5) 7	ND(4) to 14 ND(4) to 330	2/13 9/13	3.2 3.2	ND(53) ND(53)	ND(50) to ND(55) ND(50) to 58	0/18 1/18
JCDD JCDD	2.4	ND(10)	ND(10) to 15	3/16	445	150	21 to 2,900	10/10	99.0	ND(110)	ND(100) to 370	6/14
2,3,7,8-TCDF	10.3	ND(1)	ND(1) to 170	7/18	6.2	ю	ND(1) to 31	9/12	2.3	ND(11)	ND(10) to 23	2/18
1,2,3,7,8-PeCDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13	0	ND(53)	ND(50) to ND(55)	0/18
2,3,4,7,8-PeCDF	0.4	ND(5)	ND(3) to 7	1/18	0.5	ND(5)	ND(4) to 7	1/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,4,7,8-H×CDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,6,7,8-HxCDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,7,8,9-HxCDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13	0	ND(53)	ND(50) to ND(55)	0/18
2,3,4,6,7,8-HxCDF	0	ND(5)	ND(3) to ND(7)	0/18	0.5	ND(5)	ND(4) to 6	1/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,4,6,7,8-HpCDF	0	ND(5)	ND(3) to ND(7)	0/18	1.2	ND(5)	ND(4) to 10	2/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,4,7,8,9-HpCDF JCDF	00	ND(5) ND(10)	ND(3) to ND(7) ND(6) to ND(14)	0/18 0/18	00	ND(5) ND(10)	ND(4) to ND(52) ND(9) to ND(100)	0/13 0/13	00	ND(53) ND(106)	ND(50) to ND(55) ND(104) to ND(110)	0/18 0/18
Total 2 3 7 8-CDD <sup>a</sup>	7.6				492				1.03			
Total 2,3,7,8-CDF <sup>a</sup>	10.7				8.4				2.3			
Total I-TEQ <sub>DF</sub> (ND = zero) <sup>a</sup>	1.53				3.0				1.5			
Total I-TEQ <sub>DF</sub> (ND = $\frac{1}{2}$ DL) <sup>a</sup>	6.4				12.9				53.6			
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> (ND = zero) <sup>a</sup>	1.5				2.6				1.4			
$Total TEQ_{DF}-WHO_{98} (ND = \frac{1}{2} DL)^{a}$	7.6				15.2				66.5			

Table 8-2. CDD/CDF Concentrations in Pulp and Paper Mill Bleached Pulp, Wastewater Sludge, and Effluent (circa 1996)

ND = Not detected; value in parentheses is the detection limit. ng/kg = nanograms per kilogram pg/L = picograms per liter

<sup>a</sup> Sum of mean values.

Source: Gillespie (1997).

Table 8-3.	Summary of Bleached Chemical Pulp and Paper Mill Discharges	
	of 2,3,7,8-TCDD and 2,3,7,8-TCDF	

Matrix	Congener	EPA 1988 Discharge <sup>a</sup> (g/year)	NCASI 1992 Discharge <sup>b</sup> (g/year)	EPA 1993 Discharge <sup>c</sup> (g/year)	NCASI 1993 Discharge <sup>b</sup> (g/year)	NCASI 1994 Discharge <sup>b</sup> (g/year)	EPA 1995 Discharge <sup>e</sup> (g/year)
Effluent	2,3,7,8-TCDD	201	22	71	19	14.6	16
	2,3,7,8-TCDF	1,550	99	341	76	49.0	120
	TEQ	356	32	105	27	19.5	28
Sludge <sup>d</sup>	2,3,7,8-TCDD	210	33	NR	24	18.9	NR
	2,3,7,8-TCDF	1,320	118	NR	114	95.2	NR
	TEQ	343	45	177	35	28.4	50
Pulp	2,3,7,8-TCDD	262	24	NR	22	16.2	NR
	2,3,7,8-TCDF	2,430	124	NR	106	78.8	NR
	TEQ	505	36	149	33	24.1	40

NR = Not reported.

g/year = grams per year

- <sup>a</sup> The total discharge rate of congener or TEQ (based only on 2,3,7,8-TCDD and 2,3,7,8-TCDF concentration) was summed across all 104 mills. 104-Mill Study (U.S. EPA, 1990a).
- <sup>b</sup> The total discharge rate of congener or TEQ (based only on 2,3,7,8-TCDD and 2,3,7,8-TCDF concentration) was summed across all 104 mills. The daily discharge rates reported in NCASI (1993), Gillespie (1994), and Gillespie (1995) were multiplied by a factor of 350 days/yr to obtain estimates of annual discharge rates. NCASI 1992 Survey (NCASI, 1993), 1993 Update (Gillespie, 1994), and 1994 Update (Gillespie, 1995).
- <sup>c</sup> The discharges in effluent and sludge were estimated in U.S. EPA (1993d; 1997f) for January 1, 1993. The TEQ discharge in pulp was estimated by multiplying the 1988 discharge estimate by the ratio of the 1993 and 1988 effluent discharge estimates (i.e., the estimate of the reduction in 1988 discharges achieved by pollution prevention measures taken by the industry between 1988 and 1993).
- <sup>d</sup> Approximately 20.5 percent of the sludge generated in 1990 were incinerated. The remaining 79.5 percent were predominantly landfilled (56.5 percent) or placed in surface impoundments (18.1 percent); 4.1 percent were land-applied directly or as compost, and 0.3 percent were distributed/marketed (U.S. EPA, 1993e).
- <sup>e</sup> The discharges in effluent and sludge were estimated in U.S. EPA (1997f) for mid-1995. The TEQ discharge in pulp was estimated by multiplying the 1988 discharge estimate by the ratio of the 1995 and 1988 effluent discharge estimates (i.e., the estimate of the reduction in 1988 discharges achieved by pollution prevention measures taken by industry between 1988 and 1995).

Congener/Congener Group	Sludge 1 (µg/kg)	Sludge 2 (µg/kg)	Sludge 3 (µg/kg)	Sludge 4 (µg/kg)
2,3,7,8-TCDD 1,2,3,7,8-PeCDD 1,2,3,4,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD 1,2,3,4,6,7,8-HpCDD OCDD 2,3,7,8-TCDF 1,2,3,4,7,8-PeCDF 1,2,3,4,7,8-PeCDF 1,2,3,4,7,8-HxCDF 1,2,3,4,6,7,8-HxCDF 1,2,3,4,6,7,8-HxCDF 1,2,3,4,6,7,8-HxCDF 1,2,3,4,6,7,8-HpCDF 1,2,3,4,7,8,9-HpCDF	ND (0.006) ND (0.007) ND (0.018) ND (0.012) ND (0.016) 0.095 0.92 26 25 12 32 7 1.3 0.87 9.1 8.1 21	ND (0.009) ND (0.009) ND (0.026) ND (0.016) ND (0.022) 0.21 2.0 56 55 25 71 16 2.8 1.9 19 19 19 76	ND (0.009) ND (0.009) ND (0.029) ND (0.025) 0.25 2.2 57 56 24 73 15 2.6 2.0 19 20 71	ND ND (0.033) ND (0.49) ND (0.053) ND (1.2) 0.055 0.65 52 55 27 44 12 1.7 44 12 1.7 1.3 15 14 81
Total 2,3,7,8-CDD* Total 2,3,7,8-CDF* Total I-TEQ <sub>DF</sub> * Total TEQ <sub>DF</sub> -WHO <sub>98</sub> *	1.02 152.37 14.2 14.1	2.21 341.7 30.5 30.4	2.45 339.6 30.2 30.2	0.70 303.0 27.7 27.6
Total TCDD Total PeCDD Total HxCDD Total HpCDD Total OCDD Total TCDF Total PeCDF Total HxCDF Total HpCDF Total OCDF	ND (0.006) ND (0.070) ND (0.046) 0.22 0.92 64 75 68 24 31	ND (0.009) ND (0.009) ND (0.064) 0.48 2 150 240 140 53 76	ND (0.009) ND (0.009) ND (0.074) 0.56 2.2 140 240 140 54 71	NR NR NR 0.65 NR NR NR NR 81
Total CDD/CDF*	263.14	661.48	647.76	NR

## Table 8-4. CDD/CDF Concentrations in Graphite Electrode Sludge from Chlorine Production

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

NR = Not reported.

 $\mu$ g/kg = micrograms per kilogram

\* Calculated assuming not detected values were zero.

Sources: Rappe et al. (1991), Rappe (1993).

	FeCI <sub>3</sub>	AICI <sub>3</sub>	AICI <sub>3</sub>	CuCl <sub>2</sub>	CuCl	TiCl₄	SiCl₄
Congener Group	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)
Total TCDD	NR	NR	NR	NR	NR	NR	NR
Total PeCDD	NR	NR	NR	NR	NR	NR	NR
Total HxCDD	NR	NR	NR	NR	NR	NR	NR
Total HpCDD	QN	ND	ND	0.03	DN	DN	DN
Total OCDD	QN	ND	0.1	0.6	0.03	QN	DN
Total TCDF	NR	NR	NR	NR	NR	NR	NR
Total PeCDF	NR	NR	NR	NR	NR	NR	NR
Total HxCDF	NR	NR	NR	NR	NR	NR	NR
Total HpCDF	12	ND	ND	0.1	0.08	DN	DN
Total OCDF	42	QN	34	0.5	0.2	ΠN	ND

Table 8-5. CDD/CDF Concentrations in Metal Chlorides

NR = Not reported. ND = Not detected; detection limit of 0.02  $\mu g/kg$ .

= micrograms per kilogram *µ*g/kg Source: Hutzinger and Fiedler (1991a).

Table 8-6. CDD/CDF Concentrations in Mono- through Tetra-Chlorophenols

2,3,4,6-TeCP (Na salt) (Ref. B & C) (mg/kg)	0.7	5.2	9.5	5.6	0.7	0.5	10	70	70	10	:
2,3,4,6-TeCP (Ref. A) (mg/kg)	ND (0.02)	ND (0.02)	ND (0.02) - 15	ND (0.02) - 5.1	ND (0.02) - 0.17	+	+	+	+	+	:
2,4,6-TrCP (Na salt) (Ref. B & C) (mg/kg)	< 0.02	< 0.03	< 0.03	< 0.1	< 0.1	1.5	17.5	36	4.8		:
2,4,6-TrCP (Ref. A) (mg/kg)	ND (0.02) - 49	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	+	+	+	ND	ND	1
2,4,5-TrCP (Ref. A) (mg/kg)	ND (0.02) - 6.5	ND (0.02) - 1.5	ND (0.02)	ND (0.02)	ND (0.02)	DN	QN	QN	QN	ND	:
2,4,5-TrCP (Na salt) (Ref. A) (mg/kg)	ND (0.02) - 14	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	QN	QN	QN	QN	DN	:
2,6-DCP (Ref. A) (mg/kg)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ΠN	QN	ΠN	ΟN	DN	:
2,4-DCP (Ref. A) (mg/kg)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND	QN	ND	ΠN	ND	1
2-CP (Ref. A) (mg/kg)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	+	QN	QN	QN	DN	;
Congener/ Congener Group	Total TCDD	Total PeCDD	Total HxCDD	Total HpCDD	Total OCDD	Total TCDF	Total PeCDF	Total HxCDF	Total HpCDF	Total OCDF	Total CDD/CDF

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

= Detected but not quantified. Q +

-- = Not reported. mg/kg = milligrams per kilogram

Ref. A: Firestone et al. (1972); because of poor recoveries, authors stated that actual CDD/CDF levels may be considerably higher than those reported. Ref. B: Rappe et al. (1978a); common Scandinavian commercial chlorophenols. Ref. C: Rappe et al. (1978b); common Scandinavian commercial chlorophenols.

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PCP (Ref. K) (unknown) (µg/kg)	ND (10) ND (10) ND (10) 860 20 36,400 296,810	ND (10) ND (10) ND (10) 200 ND (20) ND (20) ND (20) 2,000 1,40	334,090 22,280 810 525		ł
PCP (Ref. J) (1988-99) (µg/kg)	ND (0.5)			ND 3 1,490 48,430 191,700 48 520 13,650 76,090 76,090	468,240
PCP (Ref. H) (1988-99) (µg/kg)				ND (1) ND (10) 1,440 55,560 55,560 ND (10) 3,070 3,6730 36,530	1
PCP (Ref. G) (1991) (µg/kg)	UN UN 	ND ND ND ND ND ND ND ND ND ND ND ND ND N	 ≥1,270 >127	ND (10) ND (10) 8,900 130,000 1,100,000 1,100,000 11,000 14,000 36,000 170,000	1,459,000
PCP (Ref. 1) (1985-88) (µg/kg)	ND (0.05) ND (1) 8 600 13 89,000	ND (0.5) ND (1) ND (1) ND (1) 67 2 ND (1) ND (1) 22,000 3,400 3,400	2,812,621 262,469 4,173 1,509	ND ND 912 117,000 2,723,000 ND 200 1,486 99,000 237,000	3,178,598
PCP (Ref. F) (1987) (µg/kg)	ND (0.05) 2 ND (1) 1,480 53 99,900	ND (0.1) 0.2 0.2 0.3 163 163 146 ND (1) 19,940 980 980	891,435 158,230 2,321 1,488	0.4 15.2 3.300 198,000 799,000 799,000 799,000 793,303 13,900 127,000 137,000	1,270,000
PCP (Ref. E) (1987) (//g/kg)	ND (0.03) 1 ND (1) 831 28 78,000	ND (0.1) 0.5 1.5 1.5 125 ND (1) 32 ND (1) 11,280 637 637	811,860 130,076 1,853 1,088	1.9 6.5 1,700 154,000 733,000 0.8 0.8 141 4,300 74,000 118,000	1,085,000
PCB (Ref. I) (1986) (µg/kg)	ND (0.05) ND (1) 8 1,532 28 106,000 930,000	ND (0.5) ND (1) ND (1) 34 4 ND (1) 29,000 6,200	1,037,568 268,238 2,736 1,689	ND ND 2,925 134,000 930,000 ND 3 3 1,407 1407 233,000	1,447,335
PCP (Ref. I) (1985) (//g/kg)	ND (0.05) ND (1) 6 2,565 244 210,000	ND (1.5) ND (1) ND (1) 49 5 5 34,000 4,100 222,000	1,687,615 260,159 4,445 2,918	ND ND 4,694 283,000 1,475,000 6 1 1,982 125,000 2222,000	2,111,692
PCP (Ref. D) (1984) (μg/kg)	ND (10) ND (10)  2,200 100,000 610,000	ND (10) 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	712,300  1,970 1,304	ND (10) ND (10) 4,500 135,000 610,000 ND (10) ND (10) 130,000	941,500
РСР (Ref. A) (1979) (µg/kg)					1,834,400
PCP (Ref. C) (1978) ( <i>µ</i> g/kg)		130,000			1,280,000
PCP (Ref. B) (1973) (µg/kg)				ND(20) ND(30) 5,500 98,000 220,000 40 250 22,000 150,000 160,000	655,800
Congener/ Congener/	2,3,7,8-TCDD 1,2,3,7,8-PeCDD 1,2,3,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,4,6,7,8-HxCDD 1,2,3,4,6,7,8-HxCDD 1,2,3,4,6,7,8-HxCDD 0,20D	2,3,7,8-TCDF 2,3,7,8-PECDF 2,3,4,7,8-PECDF 1,2,3,4,7,8-PECDF 1,2,3,6,7,8-PHCDF 1,2,3,4,6,7,8-HKCDF 1,2,3,4,6,7,8-HKCDF 1,2,3,4,6,7,8-HPCDF 1,2,3,4,7,8,9-HPCDF 0,00F	Total 2,3,7,8-CDD* Total 2,3,7,8-CDF* Total I-TEQ <sub>0F</sub> * Total TEQ <sub>0F</sub> -WHO <sub>98</sub> *	Total TCDD Total PeCDD Total HeCDD Total HpCDD Total ApCDD Total AcDF Total HeCDF Total HpCDF Total ApCDF	Total CDD/CDF*

Table 8-7. CDD/CDF Concentrations in Historical and Current Technical Pentachlorophenol Products

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

 - = Not reported.

 μg/kg
 = micrograms per kilogram

\* Calculated assuming not detected values are zero.

Table 8-7. CDD/CDF Concentrations in Historical and Current Technical Pentachlorophenol Products (continued)

Sources

- U.S. Department of Health and Human Services (1989); composite of technical-grade materials produced in 1979 by Monsanto Industrial Chemical Co. (St. Louis, MO), Buser and Bosshardt (1976); mean of 10 samples of "high" CDD/CDF content PCP received from Swiss commercial sources in 1973. Reichhold Chemicals, Inc. (White Plains, NY), and Vulcan Materials Co. (Birmingham, AL) Ref. A: ä Ref.
  - Rappe et al. (1978b); sample of U.S. origin, "presumably prepared by alkaline hydrolysis of hexachlorobenzene.
- Cull et al. (1984); mean of four "recent" production batches from each of two manufacturers of technical PCP using three different analytical methods; ANOVA showed no statistically significant difference in CDD/CDF concentrations between the eight samples (samples obtained in the United Kingdom) Ref. C: Ref. D:
  - Hagenmaier and Brunner (1987); sample of Witophen P (Dynamit Nobel Lot no. 7777) (obtained in Germany). ய் Ref.
    - Hagenmaier and Brunner (1987); sample of PCP produced by Rhone Poulenc (obtained in Germany). ц. Ref.
- Harrad et al. (1991); PCP-based herbicide formulation from NY State Dept. Environmental Conservation. Ref. G:
- Pentachlorophenol Task Force (1997); average of monthly batch samples for the period Jan. 1987 to Aug. 1996. Ϊ Ref.
  - Pentachlorophenol Task Force (1997); samples of "penta" manufactured in 1985, 1986, and 1988. Ref. I:
- Ref. J:
- KMG-Bermuth, Inc. (1997); average of monthly batch samples for the period Feb. 1987 to Dec. 1996 (excluding the following months, for which data were not available: Feb. 993, Jan. 1992, Dec. 1991, Sept. 1991, Dec. 1988, and Sept. 1988).
  - Schecter et al. (1997); sample found stored in a barn in Vermont.  $\stackrel{\cdots}{\simeq}$ Ref.

Table 8-8.	Historical CDD/CDF	Concentrations in	Pentachlorophenol-Na
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	PCP-Na	PCP-Na	PCP-Na	PCP-Na	PCP-Na	PCP-Na	PCP-Na
	(Ref. A)	(Ref. B)	(Ref. C)	(Ref. D)	(Ref. E)	(Ref. F)	(Ref. G)
Congener/Congener Group	(1969)	(1973)	(1973)	(1987)	(1987)	(1992)	(1980s)
	( <i>µ</i> g/kg)	$(\mu g/kg)$	(µg/kg)	( <i>µ</i> g/kg)	( <i>µ</i> g/kg)	(µg/kg)	(µg/kg)
2,3,7,8-TCDD				0.23	0.51	0.076	ND (1.4)
1,2,3,7,8-PeCDD				18.2	3.2	18.7	28.3
1,2,3,4,7,8-HxCDD				28.3	13.3	96	ND (6.1)
1,2,3,6,7,8-HxCDD				2,034	53.0	4,410	4,050
1,2,3,7,8,9-HxCDD				282	19.0	328	ND (1.4)
1,2,3,4,6,7,8-HpCDD				9,100	3,800	175,400	33,800
OCDD	3,600			41,600	32,400	879,000	81,000
2 2 7 8 TODE				1 0	0.70		140
				1.0	0.79	ND (1.0)	210
				0.2	1.9	ND (4.0)	224
				10.0	1.1	ND (4.0)	324 ND (2.9)
				40	4.0	27.0	ND (2.0)
				09 ND (1)	1.3	21.9	225
					1.3	9.0	
				600	4.0	103	ND (385)
				639	197	9,050	0,190
1,2,3,4,7,8,9-HPCDF				27 200	30	2,080	154
OCDF				37,200	4,250	114,000	30,000
Total 2,3,7,8-CDD*				53,063	35,289	1,059,253	118,878
Total 2,3,7,8-CDF*				38,795	4,499	126,492	43,841
Total I-TEQ <sub>DE</sub> *				452	79.5	3,374	1,201
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> *				406	58.5	2,566	1,096
T		4.45					4.5
		140	50	2/	52	3.6	1.9
Total PeCDD		40	ND (30)	213	31	142.7	140
	17,000	140	3,400	3,900	230	9,694	14,000
	9,600	1,600	38,000	18,500	5,800	260,200	100,000
I otal OCDD	3,600	4,000	110,000	41,600	32,400	879,000	81,000
I otal TCDF		ND (20)	ND (20)	82	12	10.1	1200
I otal PeCDF		60	40	137	27	88.4	6400
Total HxCDF		1,400	11,000	3,000	90	9,082.3	49,000
I otal HpCDF		4,300	47,000	13,200	860	75,930	91,000
Total OCDF		4,300	26,500	37,200	4,250	114,600	36,000
Total CDD/CDF*		15,980	235,990	117,859	43,752	1,348,751	378,742

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

-- = Not reported.

 $\mu$ g/kg = micrograms per kilogram

Sources:

Ref. A: Firestone et al. (1972); mean of two samples of PCP-Na obtained in the United States between 1967 and 1969.

Ref. B: Buser and Bosshardt (1976); mean of five samples of "low" CDD/CDF content PCP-Na received from Swiss commercial sources.

Ref. C: Buser and Bosshardt (1976); sample of "high" CDD/CDF content PCP-Na received from a Swiss commercial source.

Ref. D: Hagenmaier and Brunner (1987); sample of Dowicide-G purchased from Fluka; sample obtained in Germany.

Ref. E: Hagenmaier and Brunner (1987); sample of Preventol PN (Bayer AG); sample obtained in Germany.

Ref. F: Santl et al. (1994c); 1992 sample of PCP-Na from Prolabo, France.

Ref. G: Palmer et al. (1988); sample of a PCP-Na formulation collected from a closed sawmill in California in the late 1980s.

<sup>\*</sup> Calculated assuming not-detected values are zero.

		Land Disposal	Regulated	Treatment 9	Standard <sup>a</sup> (ppb)
EPA Hazardous Waste Number	Waste Description	Restriction Effective Date	waste Constituent	Wastewaters (µg/L)	Nonwastewaters (µg/kg)
F020	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri- or tetrachlorophenol, or of intermediates used to produce their pesticide derivatives. (This listing does not include wastes from the production of hexachlorophene from highly purified 2,4,5-trichlorophenol.)	November 8, 1988	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HXCDFs	0.063 0.063 0.063 0.063 0.035 0.035	
F021	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of pentachlorophenol, or of intermediates used to produce its derivatives.	November 8, 1988	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HXCDFs	0.063 0.063 0.063 0.063 0.063 0.035	
F022	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzenes under alkaline conditions.	November 8, 1988	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs	0.063 0.063 0.063 0.063 0.035 0.063	
F023	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials on equipment previously used for the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri- and tetrachlorophenols. (This listing does not include wastes from equipment used only for the production or use of hexachlorophene from highly purified 2,4,5-trichlorophenol.)	November 8, 1988	TCDDS PeCDDS HxCDDS TCDFs PeCDFs HxCDFs	0.063 0.063 0.063 0.063 0.063 0.063	
F026	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials on equipment previously used for the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzene under alkaline conditions.	November 8, 1988	TCDDS PeCDDS HxCDDS TCDFs PeCDFs HxCDFs	0.063 0.063 0.063 0.063 0.063 0.063	
F027	Discarded unused formulations containing tri-, tetra-, or pentachlorophenol or discarded unused formulations containing compounds derived from these chlorophenols. (This listing does not include formulations containing hexachlorophene synthesized from prepurified 2,4,5-trichlorophenol as the sole component.)	November 8, 1988	TCDDS PeCDDS HxCDDS TCDFs PeCDFs HxCDFs	0.063 0.063 0.063 0.063 0.063 0.063	

Table 8-9. Summary of Specific Dioxin-Containing Wastes That Must Comply with Land Disposal Retrictions

Standard <sup>a</sup> (ppb)	Nonwastewaters (µg/kg)				
Treatment	Wastewaters (µg/L)	0.063 0.063 0.063 0.063 0.035 0.035	0.063 0.063 0.063 0.063 0.063 0.035	0.063 0.063 0.063 0.063 0.063 0.063	0.063 0.063 0.063 0.063 0.063 0.063
Regulated	Waste Constituent	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs	TCDDs PeCDDs HxCDDs TCDFs PeCDFs HxCDFs
Land Disposal	Restriction Effective Date	November 8, 1988	August 8, 1990 (wastewater) May 8, 1992 (non-wastewater)	June 8, 1989	August 8, 1988
	Waste Description	Residues resulting from the incineration or thermal treatment of soil contaminated with EPA Hazardous Waste Nos. F020-F023, F026, and F027	Leachate (liquids that have percolated through land disposed wastes) resulting from the disposal of more than one restricted waste classified as hazardous under subpart D of 40 CFR 268. (Leachate resulting from the disposal of one or more of the following EPA Hazardous Wastes and no other Hazardous Wastes retains its EPA Hazardous Waste Number(s): F020, F021, F022, F027, and/or F028.)	2,6-dichlorophenol waste from the production of 2,4-D.	Untreated wastewater from the production of 2,4-D.
	EPA Hazardous Waste Number	F028	F039	K043	660X

Table 8-9. Summary of Specific Dioxin-Containing Wastes That Must Comply with Land Disposal Retrictions (continued)

<sup>a</sup> Treatment standards (i.e., maximum allowable concentration in waste extract) are based on incineration to 99.9999 percent destruction and removal efficiency.

 $\mu$ g/L = micrograms per liter  $\mu$ g/kg = micrograms per kilogram

Source: 40 CFR 268

HCBz (Ref. B) (µg/kg)	1 1	  50 - 212,000		: :	350 - 58,300	1
HCBz (97%) (Ref. A) (µg/kg)	ND (20) ND (20)	470 8,700 8,700	ND (20) ND (20)	ND (20) 455	2,830	:
PeCBz (98%) (Ref. A) (µg/kg)	ND (0.02) ND (0.02)	0.02 0.05 0.05	0.02 ND (0.02)	ND (0.02) 0.1	0.1	ł
1,2,4,5-TeCBz (99%) (Ref. A) (µg/kg)	ND (0.02) 0.2	c.0 8.0 4.0	0.03 0.2	0.8 1.5	2.1	ł
Mixed TrCBz (47%) (Ref. A) (µg/kg)	0.027 0.140	0.253 0.253 0.081	0.736 0.272	0.091 0.030	0.016	1.904
1 , 2 , 4-TrCBz ("pure") (Ref. B) (µg/kg)	ND (0.1) ND (0.1)	ND (0.1) ND (0.1) ND (0.1)	ND (0.1) ND (0.1)	ND (0.1) ND (0.1)	ND (0.1)	1
1,2-DCBz (for synthesis) (Ref. A) (µg/kg)	0.3 ND (0.02)	ND (0.02) ND (0.02) ND (0.02)	ND (0.02) 0.5	ND (0.02) ND (0.02)	ND (0.02)	:
MCBz (Ref. A) (µg/kg)	ND (0.02) ND (0.02)	ND (0.02) ND (0.02) ND (0.02)	ND (0.02) ND (0.02)	ND (0.02) ND (0.02)	ND (0.02)	-
Congener/ Congener Group	Total TCDD Total PeCDD	Total HXCUU Total HpCDD Total OCDD	Total TCDF Total PeCDF	Total HxCDF Total HpCDF	Total OCDF	Total CDD/CDF

Table 8-10. CDD/CDF Concentrations in Chlorobenzenes

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

ł

Q

Not reported.micrograms per kilogram µg/kg

Ref. A: Hutzinger and Fiedler (1991a); unpublished results of tests performed at the Univ. of Bayreuth, Germany, and by Dr. H. Hagenmaier. Ref. B: Villanueva et al. (1974); range of three samples of commercially available HCBz.

Table 8-11. Concentrations of CDD/CDF Congener Groups in Unused Commercial PCB Mixtures

							1		-					-								-		r
Referenc	e Number	A	B, C	B, C	в	шС			B, C	٨	٩	B, C	ш	Δ	B, C	٩	B, C	۷	ш	۵	٩	A	В	B
(g)	Total CDD			1	1	0:039	-	0.042	1		1	1	:	0.038		:	1	1	0.022	0.046	1	1		
ons (mg/k	осрр	-	-	1		0.031		0.030	1	-			-	0.027	-	-			0.015	0.032	1	-	-	1
oncentrati	НрСDD	-		1	1	0.006		0.012	1		:	-	1	0.011		1	:	:	0.003	0.014	1	1	-	
r Group C	Н×СDD	-	-	1	1	0.001 UN		ND	1	-	1	1	:	ND	-	1	1	1	0.002	ND	1			1
) Congene	PeCDD	1	1	1	1	ON ON		ND	1	1	1	1	1	ND	1	1	ł	1	0.002	DN	1	1	1	ł
CDI	TCDD	-		ł	ł	0.0007		DN	1		ł	ł	1	ND		1	I	1	0.0004	ND	ł	1	-	
	Total CDF	ND	0.15	4.5	1.9	9.708 0.855	2.0	2.235	20.0	1.7	1.5	0.8	0.2	10.318	3.8	1.0	2.2	0.8	34.052	48.681	8.6	13.6	5.4	2.0
s (mg/kg)	OCDF	-	1	1	1	0.016 UN		0.011	1	-	1	1	I	0.069	1	I	1	ł	0.639	1.024	1	-	-	ł
ncentration	HpCDF		-	ł	ł	0.108		0.020	ł	-	ł	ł	I	0.479	1.35	I	ł	ł	1.517	2.522	1	1	0.82	1
ner Group Co	H×CDF	ND	0.003	ND	0.81	0.805	0.3	0.144	1	1.4	0.9	0.6	0.02	2.214	1.10	0.5	0.5	0.3	4.456	7.630	2.2	2.9	2.45	0.07
CDF Conger	PeCDF	ND	0.03	2.2	0.7	2.402	1.2	0.771	1	0.2	0.4	0.2	0.1	2.154	1.0	0.4	0.9	0.3	11.655	21.164	5.0	10.0	1.73	0.35
	TCDF	ND	0.07	2.3	0.25	6.377	0.5	1.289	ł	0.1	0.2	0.02	0.05	5.402	0.3	0.1	0.8	0.2	15.786	16.340	1.4	0.7	0.3	1.08
Year of	Manufacture	1972		1	1	: :	1969		-	1969	1970	1	1		1	1969	1	1	1	1	1	-	:	
	PCB Mixture	Aroclor 1016	Aroclor 1242	Aroclor 1242	Aroclor 1242	Clophen A-30 Clophen A-30	Araclar 1248	Clophen A-40	Kanechlor 400	Aroclor 1254	Aroclor 1254	Aroclor 1254	Aroclor 1254	Clophen A-50	Aroclor 1260	Aroclor 1260	Aroclor 1260	Aroclor 1260	Clophen A-60	Clophen A-60	Clophen A-60	Phenoclor DP-6	Clophen T-64	Prodelec 3010

Not detected.
 Not reported.
 milligram per kilogram

QN :

mg/kg

Ref. A: Bowes et al. (1975a). Ref. B: Erickson (1986). Ref. C: ATSDR (1993).

2,3,7,8-Substituted Congener Concentrations in Unused PCB Mixtures Table 8-12.

		Congener	Concentra	tions in Clop	hens ( <i>u</i> g/kg					ongener C	oncentratic	ons in Aroc	lors (µg/kg)			
Congener	A-30 (Ref. A)	A-30 (Ref. B)	A-40 (Ref. B)	A-50 (Ref. B)	A-60 (Ref. A)	A-60 (Ref. B)	1016 (Ref. C)	1242 (Ref. C)	1248 (Ref. D)	1254 (Ref. C)	1254 (Ref. C)	1254 (Ref. C)	1254 (Ref. D)	1260 (Ref. C)	1260 (Ref. C)	1260 (Ref. C)
2,3,7,8-TCDD	ND	QN	DN	ND	ND	QN	I	I	I	I	I	1	1	1	1	1
1,2,3,7,8-PeCDD	ND	ND	ND	ND	0.1	ND	I	I	ł	ł	I	I	I	1	I	1
1,2,3,4,7,8-HxCDD	ND	ND	ND	ND	0.2	ND	1	:	1	1	:	:	:	-	:	1
1,2,3,6,7,8-HxCDD	0.8	ND	DN	ND	ΔN	ND	1	1	1	1	1	1	1	1	1	1
1,2,3,7,8,9-HxCDD	ND	ND	DN	ND	ND	ND	I	1	1	1	I	1	I	:		-
1,2,3,4,6,7,8-HpCDD	5.6	2.4	4.4	5.3	2.5	6.8	1	1	1	1	1	:	1	1	-	-
OCDD	31.1	24.7	30.3	26.9	14.9	32.3	1	:	1	1	1	:	:	:	:	-
2,3,7,8-TCDF	1032.6	36.9	250.2	1005.7	2287.7	3077.2	0.10	40.1	330	28.0	20.9	55.8	110	63.5	6.88	29.0
1,2,3,7,8-PeCDF	135.8	14.9	52.7	155.2	465.2	1750.8	1	ł	ł	ł	I	I	ł	-	-	-
2,3,4,7,8-PeCDF	509.2	13.1	171.3	407.5	1921.9	2917.0	1.75	40.8	830	110	179	105	120	135	58.2	112
1,2,3,4,7,8-HxCDF	301.4	1.9	48.4	647.5	1604.2	2324.1	1	ł	ł	ł	I	I	I	1	ł	1
1,2,3,6,7,8-HxCDF	65.3	0.8	19.6	227.5	157.6	351.3	1	1	1	1	1	1	1	1	1	1
1,2,3,7,8,9-HxCDF	ND	ND	0.7	8.3	42.8	19.0	0.08	0.26	1	28.8	28.7	19.4	1	5.1	9.7	10.7
2,3,4,6,7,8-HxCDF	50.6	0.1	6.8	62.5	369.5	408.3	1	1	1	1	I	1	1		-	1
1,2,3,4,6,7,8-HpCDF	43.7	0.6	7.0	205.5	480.6	1126.1	1	1	ł	ł	I	1	1	-	1	1
1,2,3,4,7,8,9-HpCDF	22.5	ND	2.8	72.2	321.7	304.0	1	ł	ł	ł	ł	I	ł	-	-	1
OCDF	15.7	ND	11.4	69.2	639.2	1024.3	1	1	-	-	-	-			-	
	r 0				Ċ	Q										
					5 0		I	I	l	l	I	I	I	1	1	1
	ND,		בי צו	בי צו	2.U		I	I	I	I	I	I	1	•	1	
I otal HxCDD	1.2	ND	CN N	ND	1.8	ND	I	1	1	1	1	1	1	-	-	1
Total HpCDD	5.6	5.4	11.6	11.0	3.0	13.5	1	1	1	1	ł	1	1	-	-	1
Total OCDD	31.1	24.7	30.3	26.9	14.9	32.3	:	1	1	:	1	1	1	1	:	:
Total TCDF	6376.6	713	1289.4	5402.3	15785.7	16340	1	1	1	1	1	:	1	:	:	1
Total PeCDF	2402.4	136.5	770.8	2153.7	11654.6	21164	1	I	1	1	I	I	I	1	1	-
Total HxCDF	804.8	5.1	143.6	2213.8	4455.8	7630.2	1	I	1	1	I	I	1	1	1	-
Total HpCDF	108.3	0.8	19.5	478.8	1517.0	2522.3	1	ł	ł	ł	I	1	1	-	-	:
Total OCDF	15.7	ND	11.4	69.2	639.2	1024.3	1	1	1	1	1	1	1	1	1	1
	0746 4	885 F	2276 6	10366 7	31074 4	18776 E	1	-			1	1		1		
		0.000	1010		C CCK F	02101	1					1				
	407.2	5.11 5.11	0.121	409.6	1439.2	21/9	I	I	1	1	I	1	1	1	1	1
	401.2	0.11	121.0	403.5	1409	21/0	-	-	:	:	:	:	-	-	ł	1

QN

Ref. A: Malisch (1994). Ref. B: Hagenmaier (1987). Ref. C: Brown et al. (1988). Ref. D: Bowes (1975b).

D = Not detected.
 = Not reported.
 //kg = micrograms per kilogram.
 Calculated assuming not-detected values are zero. --µg/kg \* Calc

Congener/Congener Group	F024 Waste (µg/kg)	K019 Waste (µg/kg)	K020 Waste (µg/kg)
2,3,7,8-TCDD 1,2,3,7,8-PeCDD	0.37 0.14	260 890	0.06 0.05
1,2,3,4,7,8-HxCDD	.30	260	0.08
1,2,3,6,7,8-HxCDD	0.14	330	0.06
1,2,3,7,8,9-HxCDD	0.11	620	0.07
	4.20	920	0.89
	15.00	1,000	3.00
2,3,7,8-TCDF	0.91	680	0.44
1,2,3,7,8-PeCDF	9.5	975	1.80
2,3,4,7,8-PeCDF	1.6	1,050	0.58
1,2,3,4,7,8-HxCDF	110	10,100	11.0
	24.0	9,760	2.4
2 3 4 6 7 8-HyCDF	9.0	21,800	0.89
1 2 3 4 6 7 8-HpCDF	250	13 400	38.0
1,2,3,4,7,8,9-HpCDF	51.0	1,340	6.0
OCDF	390	43,500	650
	20.3	4 340	4 21
Total 2,3,7,8 CDE	849.6	103.535	712.4
	20.0	5,928	3.2
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	19.7	6,333	2.6
Total TCDD	3.1	1.230	1.9
Total PeCDD	3.6	3,540	1.7
Total HxCDD	1.3	3,950	NR
Total HpCDD	5.0	1,270	1.7
Total OCDD	15.0	1,060	3.0
Total TCDF	15.0	20,600	6.0
Total PeCDF	65.0	45,300	11.0
Total HxCDF	300	63,700	27.0
	450	16,600	58.0
	390	43,500	650
Total CDD/CDF	1,248	200,750	760.3

NR = Congener group concentration reported in source is not consistent with reported congener concentrations.

 $\mu$ g/kg = micrograms per kilogram

Source: Stringer et al. (1995).

Congener and	Treated <sup>1</sup> PVC-onl <sup>5</sup>	Wastewa y Facilitie	ter	Treated EDC/VCM	Wastewa /PVC Faci	ter lities	Wast EDC/VC	ewater S M/PVC F	olids acilities	Wastev PVC-or	vater Soli Ny Faciliti	ds es
Congener Groups	No. Detects/	Concen	itration	No. Detects/	Concer	ntration	No. Detects/	Con	centration	No. Detects/	Conce	ntration
	No. Samples	Ran (ng	ge <sup>a</sup> /L)	No. Samples	Ran (ng	Ige <sup>a</sup> /L)	No. Samples	E C	ange <sup>b,c</sup> ng/kg)	No. Samples	Ran (ng	ge <sup>b,c</sup> /kg)
		Min.	Max.		Min.	Max.		Min.	Max.		Min.	Max.
2,3,7,8-TCDD	9/0	ND	DN	0/4	ND	ND	4/8	ND	109	1/2	ND	2.0
1,2,3,7,8-PeCDD	0/6	QN	QN	0/4	DN	QN	3/8	QN	320	0/2	ND	DN
1,2,3,4,7,8-HxCDD	0/6	DN	QN	0/4	DN	QN	4/8	QN	455	1/2	ND	3.2
1,2,3,6,7,8-HxCDD	0/6	QN	QN	0/4	QN	QN	7/8	QN	520	1/2	ND	2.3
1,2,3,7,8,9-HxCDD	0/6	QN	QN	0/4	QN	Q	6/8	QN	645	1/2	ND	2.4
1,2,3,4,6,7,8-HpCDD	2/6	QN	26	1/4	QN	14	8/8	74	3,230	2/2	28	35
OCDD	1/6	DN	260	1/4	DN	130	8/8	390	9,700	2/2	200	640
2,3,7,8-TCDF	0/6	ND	QN	0/4	DN	QN	8/8	18	460	0/2	ND	DN
1,2,3,7,8-PeCDF	0/6	QN	QN	0/4	QN	QN	8/8	36	1,500	0/2	ND	ΩN
2,3,4,7,8-PeCDF	0/6	QN	QN	0/4	QN	Q	8/8	50	1,750	0/2	DN	ŊŊ
1,2,3,4,7,8-HxCDF	1/6	QN	5.8	0/4	QN	Q	8/8	180	7,550	1/2	ND	3.6
1,2,3,6,7,8-HxCDF	1/6	QN	3.8	0/4	QN	Q	8/8	74	3,650	1/2	ND	2.4
1,2,3,7,8,9-HxCDF	0/6	QN	QN	0/4	QN	QN	8/8	78	2,800	1/2	ND	3.8
2,3,4,6,7,8-HxCDF	1/6	QN	6.1	1/4	QN	6.5	7/8	QN	425	0/2	DN	ŊŊ
1,2,3,4,6,7,8-HpCDF	1/6	QN	26	3/4	QN	78	8/8	570	20,600	1/2	9.7	12
1,2,3,4,7,8,9-HpCDF	1/6	QN	6.2	2/4	QN	20	7/8	QN	12,000	1/2	ND	2.0
OCDF	2/6	ND	33	4/4	DN	006	8/8	1,800	4,200,000	2/2	39	43
Mean I-TEQ <sub>DF</sub> (ND = zero)		0.42			0.88			1,680			1.90	
Mean I-TEQ <sub>DF</sub> (ND = $1/2$ DL)			4.4			4.7			1,680			3.6
Total TCDD	0/6	ND	QN	0/4	DN	QN	6/8	ND	730	1/2	ND	6.3
Total PeCDD	0/6	QN	QN	0/4	QN	QN	5/8	QN	1,630	1/2	ND	3.3
Total HxCDD	0/6	QN	QN	0/4	QN	Q	7/8	QN	3,915	1/2	ND	14
Total HpCDD	2/6	QN	48	1/4	DN	22	8/8	74	5,300	2/2	58	64
Total OCDD	1/6	QN	260	1/4	DN	130	8/8	390	9,700	2/2	200	640
Total TCDF	0/6	QN	QN	0/4	QN	Q	8/8	210	9,800	1/2	DN	4.8
Total PeCDF	0/6	Q	Q	0/4	QN	Q	8/8	380	18,000	1/2	DN	4.0
Total HxCDF	1/6	QN	30	1/4	QN	14	8/8	750	31,000	2/2	1.5	11
Total HpCDF	1/6	QN	49	3/4	QN	140	8/8	880	39,400	2/2	11	18
Total OCDF	2/6	QN	33	4/4	QN	006	8/8	1,800	4,200,000	2/2	39	43

Table 8-14. CDD/CDF Measurements in Treated Wastewater and Wastewater Solids from U.S. EDC/VCM/PVC Manufacturers

g

Not detected.

Method detection limits (MDLs) for individual samples were less than 10 pg/L for all congeners and congener groups except OCDD and OCDF, which had MDLs less than 50 pg/L. Dry weight basis. MDLs for all congeners were less than 150 ng/kg, and usually were less than 10 ng/kg. σ പറ

Table 8-15. CDD/CDF Measurements in Products from U.S. EDC/VCM/PVC Manufacturers

loride	le of rations <sup>e</sup> kg)	Max.		ри ри 1.40 01-1 01-1 01-1	0.21	nd nd nd 2.02 11
ylene Dichl EDC) <sup>d</sup>	Concent (ng/	Min.	p p p c c c c c c c c c c c c c c c c c	22222222222222222222222222222222222222	0.0006	22222222222222222222222222222222222222
"Sales" Eth	No. Detects/ No. Samples		0/5 0/5 0/5 0/5 0/5 0/5	, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1,		00/9 00/9 1/9 2/9 2/9 2/9 2/9 2/9 2/9 2/9 2/9 2/9 2
ins	je of trations <sup>c</sup> 'kg)	Max.	br br br br br br	nd bn bn bn bn bn bn 0.38	0.4	0.24 0.32 0.97 0.32 0.32 0.32 0.32 0.38
n PVC Res	Ranç Conceni (ng/	Min.	рри рри рри	20000000000000000000000000000000000000	0.001	
Dispersio	No. Detects/ No. Samples		9/6 0/6 0/6 0/6 0/6 0/6	00000000000000000000000000000000000000		2/6 2/6 2/6 2/6 2/6
C Resins	je of trations <sup>a</sup> /kg)	Max.	nd nd nd 0.64 nd	nd nd nd NG Nd Nd Nd Nd Nd	0.7	nd nd 0.64 nd 0.37 nd 7 nd
d Mass PV	Ranç Concen (ng,	Min.		20000000000000000000000000000000000000	0.002	22222222222222222222222222222222222222
Suspension and	No. Detects/ No. Samples <sup>b</sup>		0/22 0/222 0/222 0/222 0/222 0/222	0000-000000000000000000000000000000000		00/22 00/222222222222222222222222222222
	Congener and Congener Groups		2,3,7,8-TCDD 1,2,3,7,8-PeCDD 1,2,3,4,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,4,6,7,8-HpCDD 1,2,3,4,6,7,8-HpCDD 0CDD	2,3,7,8-TCDF 1,2,3,7,8-PeCDF 1,2,3,4,7,8-HeCDF 1,2,3,6,7,8-HeCDF 1,2,3,6,7,8-HeCDF 1,2,3,6,7,8-HeCDF 1,2,3,4,6,7,8-HeCDF 1,2,3,4,6,7,8-HPCDF 1,2,3,4,6,7,8-HPCDF 0CDF	Mean I-TEQ <sub>DF</sub> (ND = zero) Mean I-TEQ <sub>DF</sub> (ND = $1/2$ DL)	Total TCDD Total PeCDD Total HxCDD Total OCDDD Total OCDD Total TCDF Total HxCDF Total HxCDF Total OCDF

nd = Not detected.

Source: The Vinyl Institute (1998)

ng/kg = nanograms per kilogram a Method detection limits (MDLs) for individual samples were less than 2 ng/kg for all congeners and congener groups except OCDD and OCDF, which had MDLs less than 6 ng/kg.

b Two of these 22 samples were duplicate samples from two sites. The results were averaged and treated as one sample for each site.

c MDLs for individual samples were less than 2 ng/kg for all congeners and congener groups except OCDD and OCDF, which had MDLs less than 4 ng/kg.

<sup>&</sup>quot;Sales" EDC is defined as EDC sold commercially for non-VCM uses or exported from the United States. σ

MDLs were less than 1 ng/kg for all congeners in all samples. e

Table 8-16. CDD/CDF Concentrations in Dioxazine Dyes and Pigments (Canada)

Congener/Congener Group		Blue 106 ( <i>µ</i> g/kg)		Blue 108 (µg/kg)			Viole ( <i>µ</i> g	∋t 23 /kg)		
2,3,7,8-TCDD 1 2 3 7 8-PeCDD	ND (0.3)	ND (0.3)	ND (0.3) ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3) ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,4,7,8-HxCDD				-						
1,2,3,6,7,8-HxCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,7,8,9-HxCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,4,6,7,8-HpCDD	31	9	6	ND (0.3)	6	-	16	10	2	4
OCDD	41,953	28,523	18,066	23	7,180	806	11,022	7,929	1,627	1,420
2,3,7,8-TCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,7,8-PeCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	0.5	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
2,3,4,7,8-PeCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,4,7,8-HxCDF	12	2	2	ND (0.3)	76	4	39	31	ი	7
1,2,3,6,7,8-HxCDF	*	*	*	*	*	*	*	*	*	*
1,2,3,7,8,9-HxCDF	1	1	1	1	1	I	1	1	I	I
2,3,4,6,7,8-HxCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,4,6,7,8-HpCDF	50	10	14	6	13	10	11	4	1	12
1,2,3,4,7,8,9-HpCDF	1	1	1	1	1	1	1	1	1	1
OCDF	12,463	1,447	1,006	11	941	125	3,749	1,556	147	425
Total 2,3,7,8-CDD	41,984	28,529	18,075	23	7,189	807	11,038	7,939	1,629	1,424
Total 2,3,7,8-CDF	12,525	1,459	1,022	20	1,031	139	3,799	1,591	157	444
Total I-TEQ <sub>DF</sub> **	56.4	30.3	19.5	0.1	16.0	1.4	18.9	12.7	2.7	2.7
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> **	7.45	3.4	2.3	0.1	8.7	0.6	5.6	4.2	1.1	1.0
Total TCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
Total PeCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
Total HxCDD	ND (0.3)	ND (0.3)	ND (0.3)	1	21	2	7	ND (0.3)	ND (0.3)	1
Total HpCDD	34	ω	12	ND (0.3)	30	5	36	11	2	9
Total OCDD	41,953	28,523	18,066	23	7,180	806	11,022	7,929	1,627	1,420
Total TCDF	ND (0.3)	0.3	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	0.4	ND (0.3)
Total PeCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	0.5	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
Total HxCDF	12	2	2	ND (0.3)	76	Ð	39	31	6	7
Total HpCDF	71	32	26	12	26	14	29	13	2	21
Total OCDF	12,463	1,447	1,006	11	941	125	3,749	1,556	147	425
Total CDD/CDF**	54,533	30,012	19,112	47	8,275	957	14,882	9,540	1,787	1,880

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

-- = Not reported.
 µg/kg = micrograms per kilogram
 \* = Results listed for 1,2,3,4,7,8-HxCDF include concentrations for 1,2,3,6,7,8-HxCDF.
 \* \* = Calculations assume nondetected values are equal to zero.

Congener/Congener Group	Rotogravure	Rotogravure	Offset	Offset
	(2-color)	(4-color)	(4-color)	(4-color)
	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	ND (1)	ND (1.5)	ND (2)	ND (2)
1,2,3,7,8-PeCDD	8	ND (4)	15	6
1,2,3,4,7,8-HxCDD	19	ND (5)	16	11
1,2,3,6,7,8-HxCDD	325	310	82	21
1,2,3,7,8,9-HxCDD	155	105	42	14
1,2,3,4,6,7,8-HpCDD	2,770	1,630	540	240
OCDD	5,810	2,350	890	230
2,3,7,8-TCDF 1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF 1,2,3,4,7,8-HxCDF 1,2,3,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF 2,3,4,6,7,8-HxCDF 1,2,3,4,6,7,8-HpCDF 1,2,3,4,7,8,9-HpCDF 0CDF	2.5 ND (2) ND (2) 4 ND (3) ND (3) ND (3) 40 ND (4) 129	14 ND (4) ND (4) 7 ND (5) ND (5) ND (5) 14 ND (7) ND (10)	7 ND (4) ND (4) 27 ND (5) ND (5) 315 11 960	7 ND (3) ND (3) 35 ND (5) ND (5) 42 ND (6) 165
Total 2,3,7,8-CDD	9,087	4,395	1,585	522
Total 2,3,7,8-CDF	175.5	35	1320	249
Total I-TEQ <sub>DF</sub> *	88.6	62.4	35.4	15.0
Total TEQ <sub>DF</sub> -WHO <sub>98</sub>	87.2	60.3	41.2	17.7
Total TCDD	4	ND (2)	77	38
Total PeCDD	58	145	35	25
Total HxCDD	2,679	2,485	660	246
Total HpCDD	5,630	3,460	1,100	445
Total OCDD	5,810	2,350	890	230
Total TCDF	5.5	28	90	35
Total PeCDF	13	ND (4)	340	110
Total HxCDF	29	45	95	94
Total HpCDF	64	14	566	63
Total OCDF	129	ND (10)	960	165
Total CDD/CDF	14,422	8,527	4,813	1,451

Table 8-17.	CDD/CDF	Concentrations	in Printing	Inks (Germany	1)
	000,001	00110011010110	m i i i i i i i i i i i i i i i i i i i	niko (Gonnany	,

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

-- = Not reported.

ng/kg = nanograms per kilogram.

\* Calculations assume not-detected values are zero.

Source: Santl et al. (1994c).

	Currently Manufactured or Imported as of June 5, 1987 <sup>a</sup>
CAS No.	Chemical Name
79-94-7	Tetrabromobisphenol-A
118-75-2	2,3,5,6-Tetrachloro-2,5-cvclohexadiene-1,4-dione
118-79-6	2,4,6-Tribromophenol
120-83-2	2,4-Dichlorophenol
1163-19-5	Decabromodiphenyloxide
4162-45-2	Tetrabromobisphenol-A-bisethoxylate
21850-44-2	Tetrabromobisphenol-A-bis-2,3-dibromopropylether <sup>a</sup>
25327-89-3	Allyl ether of tetrabromobisphenol-A
32534-81-9	Pentabromodiphenyloxide
32536-52-0	Octabromodiphenyloxide
37853-59-1	1,2-Bis(tribromophenoxy)-ethane
55205-38-4	Tetrabromobisphenol-A-diacrylate <sup>a</sup>
	Not Currently Manufactured or Imported as of June 5, 1987 <sup>b</sup>
CAS No.	Chemical Name
79-95-8	Tetrachlorobisphenol-A
87-10-5	3,4',5-Tribromosalicylanide
87-65-0	2,6-Dichlorophenol
95-77-2	3,4-Dichlorophenol
95-95-4	2,4,5-Trichlorophenol
99-28-5	2,6-Dibromo-4-nitrophenol
120-36-5	2[2,4-(Dichlorophenoxy)]-propanoic acid
320-72-9	3,5-Dichlorosalicyclic acid
488-47-1	Tetrabromocatechol
576-24-9	2,3-Dichlorophenol
583-78-8	2,5-Dichlorophenol
608-71-9	Pentabromophenol
615-58-7	2,4-Dibromophenol
933-75-5	2,3,6-Trichlorophenol
1940-42-7	4-Bromo-2,5-dichlorophenol
2577-72-2	3,5-Dibromosalicylanide
3772-94-9	Pentachlorophenyl laurate
37853-61-5	Bismethylether of tetrabromobisphenol-A
-	Alkylamine tetrachlorophenate
-	l etrabromobisphenol-B

<sup>a</sup> Tetrabromobisphenol-A-bis-2,3-dibromopropylether and tetrabromobisphenol-A-diacrylate are no longer manufactured in or imported into the United States (Cash, 1993).

<sup>b</sup> As of August 5, 1995, neither manufacture nor importation of any of these chemicals had resumed in the United States (Holderman, 1995).

Chlorinated Dioxins and Furans	Brominated Dioxins and Furans	LOQ (µg/kg)
2,3,7,8-TCDD	2,3,7,8-TBDD	0.1
1,2,3,7,8-PeCDD	1,2,3,7,8-PeBDD	0.5
1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-HxBDD	2.5
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxBDD	2.5
1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-HxBDD	2.5
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpBDD	100
2,3,7,8-TCDF	2,3,7,8-TBDF	1
1,2,3,7,8-PeCDF	1,2,3,7,8-PeBDF	5
2,3,4,7,8-PeCDF	2,3,4,7,8-PeBDF	5
1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxBDF	25
1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-HxBDF	25
1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-HxBDF	25
2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-HxBDF	25
1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpBDF	1,000
1,2,3,4,7,8,9-HpCDF	1,2,3,4,7,8,9-HpBDF	1,000

 $\mu$ g/kg = microgram per kilogram

CAS No.	Chemical Name
85-22-3	Pentabromoethylbenzene
87-61-6	1,2,3-Trichlorobenzene
87-84-3	1,2,3,4,5-Pentabromo-6-chlorocyclohexane
89-61-2	1,4-Dichloro-2-nitrobenzene
89-64-5	4-Chloro-2-nitrophenol
89-69-0	2,4,5-Trichloronitrobenzene
92-04-6	2-Chloro-4-phenylphenol
97-74-6	4-Chloro-o-toloxy acetic acid
94-81-5	4-(2-Methyl-4-chlorophenoxy) butyric acid
95-50-1	o-Dichlorobenzene
95-56-7	o-Bromophenol
95-57-8	o-Chlorophenol
95-88-5	4-Chlororesorcinol
95-94-3	1,2,4,5-Tetrachlorobenzene
95-50-7	5-Chloro-2,4-dimethoxyaniline
99-30-9	2,6-Dichloro-4-nitroaniline
99-54-7	1,2-Dichloro-4-nitrobenzene
106-37-6	Dibromobenzene
106-46-7	p-Dichlorobenzene
108-70-3	1,3,5-Trichlorobenzene
108-86-1	Bromobenzene
108-90-7	Chlorobenzene
117-18-0	1,2,4,5-Tetrachloro-3-nitrobenzene
120-82-1	1,2,4-Trichlorobenzene
348-51-6	o-Chlorofluorobenzene
350-30-1	3-Chloro-4-fluoronitrobenzene
615-67-8	Chlorohydroquinone
626-39-1	1,3,5-Tribromobenzene
827-94-1	2,6-Dibromo-4-nitroaniline

CAS Number	Chemical Name	No. of Chemical Companies That Submitted Data	No. of Positive Studies	Congeners Detected (detection range: μg/kg)
79-94-7	Tetrabromobisphenol-A	3	0	NDª
118-75-2	2,3,5,6-Tetrachloro-2,5- cyclohexadiene- 1,4-dione (chloranil)	4	4	See Table 8-22
118-79-6	2,4,6-Tribromophenol	1	0	NDª
120-83-2	2,4-Dichlorophenol	1	0	ND <sup>a</sup>
1163-19-5	Decabromodiphenyl oxide	3	3	2,3,7,8-PeBDD (ND-0.1) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD (ND-0.5) 1,2,3,7,8,9-HxBDD (ND-0.76) 1,2,3,7,8-PeBDF (ND-0.7) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (ND-0.8) 1,2,3,4,6,7,8-HpBDF (17-186)
25327-89-3	Allyl ether of tetrabromobisphenol-A	1	0	ND <sup>a</sup>
32536-52-0	Octabromodiphenyl oxide	3	3	2,3,7,8-TBDD (ND-0.71) 1,2,3,7,8-PeBDD (ND-0.1) 2,3,7,8-TBDF (ND-12.6) 1,2,3,7,8-PeBDF (ND-6.3) 2,3,4,7,8-PeBDF (ND-83.1) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (ND-67.8) 1,2,3,7,8,9-HxBDF (ND-56.0) 1,2,3,4,6,7,8-HpBDF (ND-330)
378-53-59-1	1,2-Bis(tribromo-phenoxy)- ethane	1	1	2,3,7,8-TBDF (ND-0.04) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (ND-0.03) 1,2,3,4,6,7,8-HpBDF (ND-0.33)
32534-81-9	Pentabromodiphenyl oxide	2	2	1,2,3,7,8-PeBDD (ND-5.9) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD (ND-6.8) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD (ND-6.8) 1,2,3,7,8,9-HxBDD (ND-0.02) 2,3,7,8-TBDF(ND-3.1) 1,2,3,7,8-PeBDF (0.7-10.2) 2,3,4,7,8-PeBDF (0.1-2.9) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (15.6-61.2) 1,2,3,4,6,7,8-HpBDF (0.7-3.0)
4162-45-2	Tetrabromobisphenol-A- bisethoxylate	1	0	ND <sup>a</sup>

# Table 8-21. Results of Analytical Testing for Dioxins and Furans in the ChemicalsTested to Date under Section 4 of the Dioxin/Furan Test Rule

 $\mu$ g/kg = micrograms per kilogram

<sup>a</sup> No 2,3,7,8-substituted dioxins and furans detected above the Test Rule target limits of quantitation (LOQ). (See Table 8-18.)

Source: Holderman and Cramer (1995).

# Table 8-22.CDDs and CDFs in Chloranil and Carbazole VioletSamples Analyzed Pursuant to the EPA Dioxin/Furan Test Rule

Concentration (µg/kg) in Chloranil					Concentration
Congener	Importer 1	Importer 2	Importer 3	Importer 4	- (μg/kg) in Carbazole Violet
2,3,7,8-TCDD	nd (1)	nd (1)	nd (2)	nd (2)	nd (0.8)
1,2,3,7,8-PeCDD	nd (2)	nd (2)	nd (5)	nd (6)	nd (0.5)
1,2,3,4,7,8-HxCDD	nd (3)	nd (10)	nd (5)	nd (3)	nd (1.2)
1,2,3,6,7,8-HxCDD	nd (3)	75	nd (5)	6	nd (1.2)
1,2,3,7,8,9-HxCDD	nd (1)	48	nd (5)	9	nd (1.2)
1,2,3,4,6,7,8-HpCDD	110	8,200	390	2,300	28
OCDD	240,000	180,000	760,000 71,000		1,600
2,3,7,8-TCDF	nd (1)	nd (2)	nd (1)	nd (2)	nd (1.6)
1,2,3,7,8-PeCDF	nd (1)	nd (1)	nd (3)	nd (5)	nd (0.9)
2,3,4,7,8-PeCDF	nd (1)	nd (1)	nd (3)	nd (5)	nd (0.9)
1,2,3,4,7,8-HxCDF	35	nd (860)	nd (4)	5,600	nd (20)
1,2,3,6,7,8-HxCDF	nd (5)	nd (860)	nd (4)	nd (600)	nd (20)
1,2,3,7,8,9-HxCDF	6	nd (680)	nd (4)	nd (600)	nd (20)
2,3,4,6,7,8-HxCDF	nd (5)	nd (680)	nd (4)	nd (600)	nd (20)
1,2,3,4,6,7,8-HpCDF	33	240,000	36	230,000	15,000
1,2,3,4,7,8,9-HpCDF	nd (15)	nd (100)	nd (15)	nd (400)	nd (20)
OCDF	18,000	200,000	50,000	110,000	59,000
TOTAL I-TEQ <sub>DF</sub> *	263	2,874	814	3,065	211
TOTAL TEQ <sub>DF</sub> -WHO <sub>98</sub> *	31	2,532	85	2,903	156

nd = Not detected; minimum limit of detection shown in parentheses.  $\mu$ g/kg = micrograms per kilogram.

\* Calculated assuming not-detected values are zero.

Source: Remmers et al. (1992).
Table 8-23. Status of First Pesticide Data Call-In: Pesticides Suspected of Having the Potential to Become Contaminated with Dioxins if Synthesized under Conditions Favoring Dioxin Formation

Shaughnessey Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
000014	Dichlorodifluoromethane	75-71-8	Yes	:
008706	0-(4-Bromo-2,5-dichlorophenyl) 0,0-dimethyl phosphorothioate	2104-96-3	Yes	-
009105	Dimethylamine 2,3,5-triiodobenzoate	17601-49-9	Yes	-
012001	Neburon	555-37-3	Yes	-
012101	Crufomate	299-86-5	Yes	-
019201	MCPB, 4-butyric acid [4-(2-Methyl-4-chlorophenoxy)butyric acid]	94-81-5	No	Yes
019202	MCPB, Na salt [Sodium 4-(2-methyl-4-chlorophenoxy)butyrate]	6062-26-6	No	No
019401	4-Chlorophenoxyacetic acid	122-88-3	No	Yes
025501	Chloroxuron	1982-47-4	Yes	-
027401	Dichlobenil	1194-65-6	No	Yes
028201	Propanil [3',4'-Dichloropropionanilide]	709-98-8	No	No
028601	Dichlofenthion [O-(2,4-Dichlorophenyl) O,O-diethyl phosphorothioate)]	97-17-6	Yes	1
029201	DDT [Dichloro diphenyl trichloroethane]	50-29-3	Yes	:
029601	Dichlone [2,3-dichloro-1,4-naphthoquinone]	117-80-6	Yes	-
029902	Ammonium chloramben [3-amino-2,5-dichlorobenzoic acid]	1076-46-6	Yes	-
029906	Sodium chloramben [3-amino-2,5-dichlorobenzoic acid]	1954-81-0	Yes	1
030602	Sodium 2-(2,4-dichlorophenoxy)ethyl sulfate	136-78-7	Yes	:
031301	DCNA [2,6-Dichloro-4-nitroaniline]	99-30-9	No	Yes
031503	Potassium 2-(2-methyl-4-chlorophenoxy)propionate	1929-86-8	Yes	1
031516	MCCP, DEA Salt [Diethanolamine 2-(2-methyl-4-chlorophenoxy)propionate]	1432-14-0	Yes	1
031563	MCPP, IOE [Isooctyl 2-(2-methyl-4-chlorophenoxy)propionate]	28473-03-2	No	No
034502	Dicapthon [O-(2-chloro-4-nitrophenyl) O,O-dimethyl phosphorothioate]	2463-84-5	Yes	1
035502	Monuron trichloroacetate [3-(4-chlorophenyl)-1,1-dimethylurea trichloroacetate]	140-41-0	Yes	:
035505	Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea]	330-54-1	No	No

Become Contaminated with Dioxins if Synthesized under Conditions Favoring Dioxin Formation (continued) Status of First Pesticide Data Call-In: Pesticides Suspected of Having the Potential to Table 8-23.

Shaughnessey Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
035506	Linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea]	330-55-2	No	No
035901	Metobromuron [3-(p-bromophenyl)-1-methoxy-1-methylurea]	3060-89-7	Yes	ł
053501	Methyl parathion [O,O-Dimethyl O-p-nitrophenyl phosphorothioate]	298-00-0	No	No
055001	Dichlorophene [Sodium 2,2'-methylenebis(4-chlorophenate)]	97-23-4	Yes	ł
055005	Dichlorophene, sodium salt [Sodium 2,2'-methylenebis(4-chlorophenate)]	10254-48-5	Yes	1
055201	1,2,4,5-Tetrachloro-3-nitrobenzene	117-18-0	Yes	1
057501	Ethyl parathion [O,O-diethyl O-p-nitrophenyl phosphorothioate]	56-38-2	No	No
058102	Carbophenothion [S-(((p-chlorophenyl)thio)methyl) 0,0-diethyl phosphorodithioate]	786-19-6	Yes	1
058301	Ronnel [O,O-dimethyl O-(2,4,5-trichlorophenyl) phosphorothioate]	229-84-3	Yes	ł
058802	Mitin FF [Sodium 5-chloro-2-(4-chloro-2-(3-(3,4-dichlorophenyl)ureido)phenoxy) benzenesulfonate]	3567-25-7	No	No
059401	Orthodichlorobenzene	95-50-1	Yes	1
061501	Paradichlorobenzene	106-46-7	No	No
062201	Chlorophene [2-Benzyl-4-chlorophenol]	120-32-1	No	No
062202	Potassium 2-benzyl-4-chlorophenate	35471-49-9	No	In review
062203	Sodium 2-benzyl-4-chlorophenate	3184-65-4	No	In review
062204	2-Chlorophenol	95-57-8	Yes	-
062206	2-Chloro-4-phenylphenol	92-04-6	Yes	-
062207	Potassium 2-chloro-4-phenylphenate	18128-16-0	Yes	:
062208	4-Chloro-2-phenylphenol	not available	Yes	:
062209	4-Chloro-2-phenylphenol, potassium salt	53404-21-0	Yes	ł
062210	6-Chloro-2-phenylphenol	85-97-2	Yes	1
062211	6-Chloro-2-phenylphenol, potassium salt	18128-17-1	Yes	:
062212	4-Chloro-2-phenylphenol, sodium salt	10605-10-4	Yes	:
062213	6-Chloro-2-phenylphenol, sodium salt	10605-11-5	Yes	ł

Become Contaminated with Dioxins if Synthesized under Conditions Favoring Dioxin Formation (continued) Table 8-23. Status of First Pesticide Data Call-In: Pesticides Suspected of Having the Potential to

Shaughnessey Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
062214	4 and 6-Chloro-2-phenylphenol, diethanolamine salt	53537-63-6	Yes	:
062215	2-Chloro-4-phenylphenol, sodium salt	31366-97-9	Yes	:
064202	4-Chloro-2-cyclopentylphenol	13347-42-7	Yes	:
064208	Fentichlor [2,2'-Thiobis(4-chloro-6-methylphenol)]	4418-66-0	Yes	
064209	Fentichlor [2,2'-Thiobis(4-chlorophenol)]	97-24-5	Yes	:
064214	4-Chloro-2-cyclopentylphenol, potassium salt of	35471-38-6	Yes	:
064218	4-Chloro-2-cyclopentylphenol, sodium salt	53404-20-9	Yes	ı
067707	Chlorophacinone	3691-35-8	No	No
069105	ADBAC [AlkyI* dimethyl benzyl ammonium chloride *(50% C14, 40% C12, 10% C16)]	68424-85-1	No	No
069144	ADBAC [AlkyI* dimethyl 3,4-dichlorobenzyl ammonium chloride *(61% C12, 23% C14, 11% C16, 5% C18)]	not available	No	No
077401	Niclosamide [2-Aminoethanol salt of 2',5-dichloro-4'-nitrosalicylanilide]	1420-04-8	No	No
077406	5-Chlorosalicylanilide	4638-48-6	Yes	:
078780	2-Methyl-4-isothiazolin-3-one	Not available	Yes	:
079202	Tetradifon [4-chlorophenyl 2,4,5-trichlorophenyl sulfone]	116-29-0	Yes	1
079301	Chloranil [tetrachloro-p-benzoquinone]	118-75-2	Yes	:
080403	6-Chlorothymol	89-68-9	Yes	:
080811	Anilazine [2,4-Dichloro-6-(o-chloroanilino)-s-triazine]	101-05-3	Yes	:
081901	Chlorothalonil [tetrachloroisophthalonitrile]	1897-45-6	No	Yes
082602	Sodium 2,3,6-Trichlorophenylacetate	2439-00-1	Yes	:
084101	Chlorfenvinphos	470-90-6	Yes	:

Become Contaminated with Dioxins if Synthesized under Conditions Favoring Dioxin Formation (continued) Table 8-23. Status of First Pesticide Data Call-In: Pesticides Suspected of Having the Potential to

Shaughnessey Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
100601	Fenamiphos	Not available	No	No
101001	p-Chlorophenyl diiodomethyl sulfone	20018-12-6	Yes	:
101101	Metribuzin	21087-64-9	No	No
104301	Bifenox [methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate]	42576-02-3	Yes	1
106001	Methazole [2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione]	20354-26-1	Yes	1
108201	Diflubenzuron [N-(((4-chlorophenyl)amino)carbonyl)-2,6-difluorobenzamide]	35367-38-5	No	Yes
109001	Oxadiazon [2-tert-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)- delta 2 -1,3,4- oxadiazoline-5-one]	19666-30-9	No	Yes
109301	Fenvalerate	51630-58-1	No	In review
109302	Fluvalinate [N-2-Chloro-4-trifluoromethyl)phenyl-DL-valine (+-)-cyano(3-phenoxy- phenyl)methyl ester]	69409-94-5	No	No
109801	Iprodione [3-(3,5-Dichlorophenyl)-N-(1-methylethyl)-2,4-dioxo-1- imidazolidinecarboxamide (9CA)]	36734-19-7	No	No
109901	Triadimefon [1-(4-Chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone]	43121-43-3	No	No
110902	Diclofop - methyl [methyl 2-(4-(2,4-dichlorophenoxy)phenoxy)propanoate]	51338-27-3	No	Yes
111401	Profenofos [O-(4-Bromo-2-chlorophenyl)-O-ethyl S-propyl phosphorothioate]	41198-08-7	No	In review
111601	Oxyfluorfen [2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene]	42874-03-3	No	In review
111901	Imazalil [1-(2-(2,4-Dichlorophenyl)-2-(2-propenyloxy)ethyl)-1H-imidazole]	35554-44-0	No	No
112802	Bromothalin [N-Methyl-2,4-dinitro-n-(2,4,6-tribromophenyl)-6- (trifuloromethyl)benzenamine]	63333-35-7	No	No
113201	Vinclozolin [3-(3,5-Dichlorophenyl)-5-ethenyl-5-methyl-2,4-oxazolidinedione (9CA)]	50471-44-8	No	No
119001	Fenridazon [Potassium 1-(p-chlorophenyl)-1,4-dihydro-6-methyl-4-oxo- pyridazine- 3-carboxylate]	83588-43-6	No	In review
123901	Tridiphane [2-(3,5-Dichlorophenyl)-2-(2,2,2-trichloroethyl) oxirane]	58138-08-2	No	No
125601	Paclobutrazol	76738-62-0	No	No
128838	Linalool	78-70-6	No	In review
206600	Fenarimol [a-(2-chlorophenyl)-a-(4-chlorophenyl)-5-pyrimidinemethanol]	60168-88-9	No	No

Status of Second Pesticide Data Call-In: Pesticides Suspected of Being Contaminated with Dioxins Table 8-24.

Shaughnessey			Support	Testing
Code	Pesticide (Active Ingredient)	CAS Number	Withdrawn	Required
029801	Dicamba [3,6-dichloro-o-anisic acid]	1918-00-9	No	Yes
029802	Dicamba dimethylamine [3,6-dichloro-o-anisic acid]	2300-66-5	No	Yes
029803	Diethanolamine dicamba [3,6-dichloro-2-anisic acid]	25059-78-3	Yes	
030001	2,4-Dichlorophenoxyacetic acid	94-75-7	No	Yes
030002	Lithium 2,4-dichlorophenoxyacetate	3766-27-6	No	No
030003	Potassium 2,4-dichlorophenoxyacetate	14214-89-2	Yes	-
030004	Sodium 2,4-dichlorophenoxyacetate	2702-72-9	No	No
030005	Ammonium 2,4-dichlorophenoxyacetate	2307-55-3	Yes	-
030010	Alkanol* amine 2,4-dichlorophenoxyacetate *(salts of the ethanol and ispropanol series)	Not available	Yes	
030011	Alkyl* amine 2,4-dichlorophenoxyacetate *(100% C12)	2212-54-6	Yes	
030013	Alkyl* amine 2,4-dichlorophenoxyacetate *(100% C14)	28685-18-9	Yes	-
030014	Alkyl* amine 2,4-dichlorophenoxyacetate *(as in fatty acids of tall oil)	Not available	Yes	1
030016	Diethanolamine 2,4-dichlorophenoxyacetate	5742-19-8	No	No
030017	Diethylamine 2,4-dichlorophenoxyacetate	20940-37-8	Yes	-
030019	Dimethylamine 2,4-dichlorophenoxyacetate	2008-39-1	No	No
030020	N,N-Dimethyloleylamine 2,4-dichlorophenoxyacetate	53535-36-7	Yes	
030021	Ethanolamine 2,4-dichlorophenoxyacetate	3599-58-4	Yes	-
030023	Heptylamine 2,4-dichlorophenoxyacetate	37102-63-9	Yes	
030024	Isopropanolamine 2,4-dichlorophenoxyacetate	6365-72-6	Yes	-
030025	Isopropylamine 2,4-dichlorophenoxyacetate	5742-17-6	No	No
030028	Morpholine 2,4-dichlorophenoxyacetate	6365-73-7	Yes	-
030029	N-Oleyl-1,3-propylenediamine 2,4-dichlorophenoxyacetate	2212-59-1	Yes	ł
030030	Octylamine 2,4-dichlorophenoxyacetate	2212-53-5	Yes	:
030033	Triethanolamine 2,4-dichlorophenoxyacetate	2569-01-9	Yes	-
030034	Triethylamine 2,4-dichlorophenoxyacetate	2646-78-8	No	No

Status of Second Pesticide Data Call-In: Pesticides Suspected of Being Contaminated with Dioxins (continued) Table 8-24.

Shaughnessey	Pesticide [∆ctive Indredient]	CAS Number	Support Withdrawn	Testing Bequired
030035	Triisopropanolamine 2.4-dichlorophenoxvacetate	32341-80-3	No	No
030039	N,N-Dimethyl oleyl-linoleyl amine 2,4-dichlorophenoxyacetate	55256-32-1	Yes	:
030052	Butoxyethoxypropyl 2,4-dichlorophenoxyacetate	1928-57-0	Yes	
030053	Butoxyethyl 2,4-dichlorophenoxyacetate	1929-73-3	No	No
030055	Butoxypropyl 2,4-dichlorophenoxyacetate	1928-45-6	Yes	:
030056	Butyl 2,4-dichlorophenoxyacetate	94-80-4	Yes	:
030062	Isobutyl 2,4-dichlorophenoxyacetate	1713-15-1	Yes	:
030063	Isooctyl(2-ethylhexyl) 2,4-dichlorophenoxyacetate	1928-43-4	No	Yes
030064	Isooctyl(2-ethyl-4-methylpentyl) 2,4-dichlorophenoxyacetate	25168-26-7	Yes	1
030065	Isooctyl(2-octyl) 2,4-dichlorophenoxyacetate	1917-97-1	Yes	:
030066	Isopropyl 2,4-dichlorophenoxyacetate	94-11-1	No	No
030072	Propylene glycol butyl ether 2,4-dichlorophenoxyacetate	1320-18-9	Yes	:
030801	4-(2,4-Dichlorophenoxy)butyric acid	94-82-6	No	Yes
030804	Sodium 4-(2,4-dichlorophenoxy)butyrate	10433-59-7	No	No
030819	Dimethylamine 4-(2,4-dichlorophenoxy)butyrate	2758-42-1	No	No
030853	Butoxyethanol 4-(2,4-dichlorophenoxy)butyrate	32357-46-3	Yes	:
030856	Butyl 4-(2,4-dichlorophenoxy)butyrate	6753-24-8	Yes	:
030863	Isooctyl 4-(2,4-dichlorophenoxy)butyrate	1320-15-6	Yes	:
031401	2-(2,4-Dichlorophenoxy)propionic acid	120-36-5	No	Yes
031419	Dimethylamine 2-(2,4-dichlorophenoxy)propionate	53404-32-3	No	No
031453	Butoxyethyl 2-(2,4-dichlorophenoxy)propionate	53404-31-2	No	No
031463	Isooctyl 2-(2,4-dichlorophenoxy)propionate	28631-35-8	No	No

Status of Second Pesticide Data Call-In: Pesticides Suspected of Being Contaminated with Dioxins (continued) Table 8-24.

Shaughnessey Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
031519	MCPP, DMA [Dimethylamine 2-(2-methyl-4-chlorophenoxy)propionate]	32351-70-5	No	No
035301	Bromoxynil [3,5-dibromo-4-hydroxybenzonitrile]	1689-84-5	No	Yes
044901	Hexachlorophene [2,2'-Methylenebis(3,4,6-trichlorophenol)]	70-30-4	Yes	:
044902	Hexachlorophene, Na salt [Monosodium 2,2'-methylenebis(3,4,6-trichlorophenate)]	5736-15-2	Yes	:
044904	Hexachlorophene, K salt [Potassium 2,2'-methylenebis(3,4,6-trichlorophenate)]	67923-62-0	Yes	:
054901	Irgasan [5-Chloro-2-(2,4-dichlorophenoxy)phenol]	3380-34-5	No	Yes
063004	Tetrachlorophenols	25167-83-3	Yes	:
063005	Tetrachlorophenols, sodium salt	25567-55-9	Yes	:
063006	Tetrachlorophenols, alky1* amine salt*(as in fatty acids of coconut oil)	not available	Yes	:
063007	Tetrachlorophenols, potassium salt	53535-27-6	Yes	:
064203	Bithionolate sodium [Disodium 2,2'-thiobis(4,6-dichlorophenate)]	6385-58-6	Yes	:
064212	Phenachlor [2,4,6-Trichlorophenol]	88-06-2	Yes	:
064219	Potassium 2,4,6-trichlorophenate	2591-21-1	Yes	:
064220	2,4,6-Trichlorophenol, sodium salt	3784-03-0	Yes	:
064501	Phenothiazine	92-84-2	Yes	:
078701	Dacthal-DCPA [Dimethy] tetrachloroterephthalate]	1861-32-1	No	Yes
079401	Endosulfan [hexachlorohexahydromethano-2,4,3-benzodioxathiepin-3-oxide]	115-29-7	No	No
082501	Silvex [2-(2,4,5-trichlorophenoxy)propionic acid]	93-72-1	Yes	1
083701	Tetrachlorvinphos [2-Chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate]	961-11-5	No	Yes
104101	Edolan [Sodium 1,4',5'-trichloro-2'-(2,4,5-trichlorophenoxy) methanesulfonanilide]	69462-14-2	Yes	1

Congener	EPA LOQª (µg/kg)	Total Number of Technicals	Number of Technicals Greater Than LOQ	Observed Maximum Concentration (µg/kg)	Average Concentration <sup>b</sup> (µg/kg)
2,3,7,8-TCDD	0.1	8	2	0.13	0.06
1,2,3,7,8-PeCDD	0.5	8	3	2.6	0.78
1,2,3,4,7,8-HxCDD	2.5	8	0	0.81	0.31
1,2,3,6,7,8-HxCDD	2.5	8	0	0.77	0.39
1,2,3,7,8,9-HxCDD	2.5	8	0	0.68	0.24
1,2,3,4,6,7,8-HpCDD	100	8	0	1.5	0.21
OCDD					
2,3,7,8-TCDF	1	8	0	0.27	0.07
1,2,3,7,8-PeCDF	5	8	0	0.62	0.38
2,3,4,7,8-PeCDF	5	7	0	0.73	0.07
1,2,3,4,7,8-HxCDF	25	8	0	1.6	0.36
1,2,3,6,7,8-HxCDF	25	8	0	1.2	0.11
1,2,3,7,8,9-HxCDF	25	8	0	1.4	0.16
2,3,4,6,7,8-HxCDF	25	8	0	1.1	0.14
1,2,3,4,6,7,8-HpCDF	1000	8	0	8.3	2.17
1,2,3,4,7,8,9-HpCDF	1000	8	0	1.2	0.18
OCDF					
				TOTAL <sup>c</sup> I-TEQ <sub>DF</sub> TEQ <sub>DF</sub> -WHO <sub>98</sub>	5.60 0.70 1.10

<sup>a</sup> Limit of quantitation required by EPA in the Data Call-In.

<sup>b</sup> Average of the mean results for multiple analyses of four technical 2,4-D and/or 2,4-D ester products for which detectable CDD/CDF congener concentrations less than the LOQs were quantified; not-detected values were assumed to be zero.

<sup>c</sup> Total equals the sum of the individual congener averages.

 $\mu$ g/kg = micrograms per kilogram

-- = Analyses not performed.

Source: U.S. EPA Office of Pesticide Program file.

	Pesticide	Number of Positive
nmon Name	Chemical Name	Submissions <sup>a</sup> to Date
4-butyric acid	4-(2-methyl-4-chlorophenoxy)butyric acid	0
	4-Chlorophenoxyacetic acid	0
obenil	2,6-Dichlorobenzonitrile	0
nba	3,6-Dichloro-o-anisic acid	0
nba, dimethylamine	3,6-Dichloro-o-anisic acid, dimethylamine salt	0
D	2,4-Dichlorophenoxy acetic acid	2
D, 2EH	Isooctyl(2-ethylhexyl)2,4-dichlorophenoxyacetate	-
DB	4-(2,4-Dichlorophenoxy)butyric acid	0
٨A	2,6-Dichloro-4-nitroaniline	Pending
-DP	2-(2,4-Dichlorophenoxy)propionic acid	0
coprop (MCPP)	2-(2-methyl-4-chlorophenoxy)propionic acid	0
moxynil	3,5-Dibromo-4-hydroxybenzonitrile	0
asan	5-Chloro-2-(2,4-dichlorophenoxy)phenol	0
sthal (DCPA)	Dimethyl tetrachloroterephthalate	Pending
orothalonil	Tetrachloroisophthalonitrile	Pending
achlorvinphos.	2-Chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate	0
lbenzuron	N-(((4-chlorophenyl)amino)carbonyl)-2,6-difluorobenzamide	0
diazon	2-Tert-butyl-4(2,4-dichloro-5-isopropoxyphenyl)-delta2-1,3,4-oxadiazoline-5-one	Pending
lofop-methyl	Methyl-2-(4-(2,4-dichlorophenoxy)phenoxy) propanoate	0

Table 8-26. Summary of Analytical Data Submitted to EPA in Response to Pesticide Data Call-Ins

December 2003

<sup>a</sup> "Positive" is defined as the detection of any congener at a concentration equal to or exceeding the LOQs listed in Table 8-24.

Sources: U.S. EPA (1995a); personal communication with S. Funk (EPA/OPP/HED) on March 27, 1996.

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Congener/Congener Group	Acbar Super (Gaza City*) (µg/kg)	Amco Super (Gaza City*) (µg/kg)	(Bethlehem)* (µg/kg)	Chimprom (Russia) (µg/kg)	Dragon Lawn Weed Killer (µg/kg)	KGRO (U.S.) (µg/kg)	Pro Care Premium (U.S.) (µg/kg)	Ortho Weed-B-Gone (U.S.) (µg/kg)	Sigma Co. (U.S.) ( <i>µ</i> g/kg)	American Brand Chemical Co. (U.S.) (µg/kg)
2,3,7,8-TCDD 1,2,3,7,8-PeCDD 1,2,3,4,7,8-H×CDD 1,2,3,6,7,8-H×CDD 1,2,3,4,6,7,8-H×CDD 1,2,3,4,6,7,8-HPCDD 1,2,3,4,6,7,8-HPCDD 0CDD	ND (0.1) 0.1 ND (0.1) ND (0.1) ND (0.1) 0.1 0.1	ND (0.1) ND (0.1) ND (0.1) 0.2 ND (0.1) 1.2 2.6	ND (0.1) 1.2 ND (0.1) 0.6 0.3 0.3	ND (0.02) 0.03 0.02 0.05 ND (0.02) 0.23 0.85	ND (0.001) 0.0014 ND (0.001) 0.0024 0.0010 0.0017 0.0063					
2,3,7,8-TCDF 1,2,3,7,8-7,2,3,4,8-PeCDF 2,3,4,7,8-PeCDF 1,2,3,4,7,8-PeCDF 1,2,3,4,7,8-NCDF 1,2,3,6,7,8-HxCDF 1,2,3,6,7,8-HxCDF 1,2,3,4,6,7,8-HpCDF 1,2,3,4,6,7,8-HpCDF 1,2,3,4,7,8,9-HpCDF 0CDF	0.3 ND (0.1) ND (0.1) ND (0.1) ND (0.1) ND (0.1) 0.1 0.1 0.2	ND (0.1) 0.2 0.1 0.1 0.1 ND (0.1) ND (0.1) ND (0.1) 0.8 3.8 3.8	ND (0.1) 0.7 0.1 0.1 0.1 ND (0.1) 0.1 ND (0.1) 0.4	ND (0.1) 1.2 0.06 0.08 0.11 ND (0.02) 0.05 0.02 0.02 0.02	0.0036 0.0010 0.0011 0.0013 ND (0.001) ND (0.001) 0.0016 ND (0.001) 0.0039					
Total 2,3,7,8-CDD (ND = 0) Total 2,3,7,8-CDF (ND = 0) Total 1-TEQ <sub>DF</sub> (ND = 0) ** Total TEQ <sub>DF</sub> (ND = 0) ** 0) * *	0.3 0.6 0.082 0.134	4 4.9 0.066 0.061	2.6 1.9 0.850 1.449	1.18 2.22 0.142 0.156	0.0128 0.0136 0.0023 0.0030	0.0144 0.1628 0.0009	0.0143 0.4253 0.0012	0.0091 0.1095 0.0014	0.127 3.0507 0.0013	0.0278 0.0822 0.0019
Total TCDD Total PeCDD Total HxCDD Total HxCDD Total HpCDD Total OCDD Total OCDF Total HxCDF Total HxCDF Total OCDF										

-- = Not reported.
 µg/kg = micrograms per kilogram
 \* 2,4-D manufactured in Europe and packaged in Palestine.
 \* Calculated assuming not-detected values are zero.

		Range of Detection	Range of Concen (POTW m	Detected trations ean_basis)	Overa	ll Means*
Congener/Congener Group	No. Detections/ No. Samples	Limits (pg/L)	Minimum Detected Conc. (pg/L)	Maximum Detected Conc. (pg/L)	Mean Conc. (ND = 0) (pg/L)	Mean Conc. (ND = 1/2DL) (pg/L)
2,3,7,8-TCDD 1,2,3,7,8-PeCDD 1,2,3,4,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD 1,2,3,4,6,7,8-HpCDD OCDD	0/30 0/30 0/30 0/30 0/30 3/30 13/30	0.31 - 8.8 0.45 - 15 0.43 - 9.8 0.81 - 10 0.42 - 9.7 0.75 - 18 6.2 - 57	nd nd nd nd nd nd	nd nd nd nd 5.0 99.75	0.00 0.00 0.00 0.00 1.06 29.51	0.98 1.32 1.38 1.42 1.31 3.61 37.95
2,3,7,8-TCDF 1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF 1,2,3,4,7,8-HxCDF 1,2,3,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF 2,3,4,6,7,8-HxCDF 1,2,3,4,6,7,8-HpCDF 1,2,3,4,7,8,9-HpCDF 0CDF	1/27 1/30 1/30 1/30 1/30 1/30 1/30 2/30 0/30 1/30	0.74 - 4.4 0.64 - 9.4 0.61 - 14 0.25 - 6.8 0.23 - 6.8 0.57 - 10 0.25 - 7.9 0.36 - 6.9 0.19 - 11 0.86 - 28	nd nd nd nd nd nd nd nd nd	1.3 2.0 2.8 2.4 1.5 2.0 nd 4.6 nd 3.2	0.14 0.22 0.31 0.27 0.17 0.22 0.00 0.68 0.00 0.36	0.98 1.58 1.68 1.22 0.97 1.72 0.93 1.83 1.18 3.40
Total 2,3,7,8-CDD Total 2,3,7,8-CDF Total I-TEQ <sub>DF</sub> Total TEQ <sub>DF</sub> -WHO <sub>98</sub>			nd nd nd nd	99.75 16.6 2.42 2.33	30.57 2.37 0.29 0.27	47.98 15.49 3.66 4.28
Total TCDD Total PeCDD Total HxCDD Total HpCDD Total OCDD Total TCDF Total PeCDF Total HxCDF Total HpCDF Total OCDF	4/27 0/27 1/30 3/30 13/30 2/30 1/30 2/30 1/30	$\begin{array}{c} 1.2 - 8.8 \\ 0.62 - 200 \\ 0.84 - 11 \\ 0.75 - 18 \\ 6.2 - 57 \\ 0.39 - 6.8 \\ 0.64 - 25 \\ 0.93 - 17 \\ 0.36 - 19 \\ 0.86 - 28 \end{array}$	nd nd nd nd nd nd nd nd nd nd	9.7 nd 1.7 8.4 99.75 25.0 20.0 13.0 4.6 3.2	$\begin{array}{c} 1.23\\ 0.00\\ 0.19\\ 1.83\\ 29.51\\ 6.61\\ 2.22\\ 1.44\\ 0.68\\ 0.36\end{array}$	2.61 6.27 1.93 4.77 37.95 7.70 4.72 3.43 2.41 3.40
Total CDD/CDF			nd	99.75	42.00	71.96

nd = Not detected.

pg/L = picograms per liter.

\* The "overall means" are the means of the individual POTW mean concentrations rather than the means of the individual sample concentrations.

Source: California Regional Water Quality Control Board (1996).

Congener         Percent         Detected         Nondetects         Nondetects           2,3,7,8-TCDD         16         109/kg)         Set to         Set to         Set to           2,3,7,8-TCDD         16         116         6.86         0         Set to         Set to           1,2,3,7,8-PeCDD         18         736         9.84         0         Set to         Set to           1,2,3,7,8-PeCDD         18         737         22.5         0         Zero         Set to           1,2,3,7,8-PeCDD         18         737         22.5         0         3         2         3         2         3         0         3         0 <th></th> <th></th> <th>Maximum Concentration</th> <th>Median Concer</th> <th>ntration (ng/kg)</th> <th>Mean Conce</th> <th>entration (ng/kg)</th>			Maximum Concentration	Median Concer	ntration (ng/kg)	Mean Conce	entration (ng/kg)
2,3,7,8-TCDD       16       116       6.86       0         1,2,3,7,8-PeCDD       18       736       9.84       0         1,2,3,7,8-PeCDD       18       736       9.84       0         1,2,3,7,8-PeCDD       25       737       22.5       0         1,2,3,7,8-PeCDD       29       737       22.5       0         1,2,3,4,7,8-HxCDD       39       737       28.0       0         1,2,3,4,6,7,8-HpCDD       98       52,500       3,320       3,320         1,2,3,4,6,7,8-HpCDD       98       52,500       3,320       3,320         0,23,7,8-FeCDF       100       905,000       3,320       3,320         2,3,7,8-FeCDF       17.0       3,320       3,320       3,320         2,3,7,8-FeCDF       65       337       17.0       3,90       0         2,3,4,7,8-FeCDF       26       736       10.4       0       0         1,2,3,4,7,8-FeCDF       28       736       10.4       0       0         1,2,3,4,7,8-FeCDF       28       736       10.4       0       0         1,2,3,4,7,8-FeCDF       26       736       10.4       0       0         1,2,3,4,7,8-FeCDF	Congener	Percent Detected	Detected (ng/kg)	Nondetects Set to Det. Limit	Nondetects Set to Zero	Nondetects Set to Det. Limit	Nondetects Set to Zero
1,2,3,7,8-FecUD         18         730         9.84         0           1,2,3,4,7,8-HxCDD         25         737         22.5         0           1,2,3,4,7,8-HxCDD         39         737         22.5         0           1,2,3,4,7,8-HxCDD         39         737         22.5         0           1,2,3,4,6,7,8-HxCDD         39         737         22.5         0           1,2,3,4,6,7,8-HpCDD         98         52,500         335         335           1,2,3,4,6,7,8-HpCDD         98         52,500         335         335           0CDD         100         905,000         3,320         3,320           2,3,7,8-FeCDF         65         337         17.0         3,90           2,3,4,7,8-HxCDF         26         736         10.4         0           1,2,3,4,7,8-HxCDF         26         736         10.4         0           1,2,3,4,6,7,8-HxCDF         35         736         10.4         0           1,2,3,4,6,7,8-HxCDF         26         736         10.4         0           1,2,3,4,6,7,8-HxCDF         35         736         10.4         0           1,2,3,4,6,7,8-HxCDF         35         736         10.4         0	3,7,8-TCDD	16	116	6.86	0	R N	A N
1,2,3,6,7,8+HxCDD         49         737         27.3         0           1,2,3,7,8,9+HxCDD         39         737         28.0         0           1,2,3,7,8,9+HxCDD         38         52,500         335         335           1,2,3,4,6,7,8-HpCDD         98         52,500         335         335           0CDD         100         905,000         3,320         3,320           2,3,7,8-FeCDF         65         337         17.0         3,90           1,2,3,7,8-FeCDF         65         337         17.0         3,90           2,3,4,7,8-HxCDF         65         337         17.0         3,90           2,3,4,7,8-HxCDF         26         736         9.60         0           1,2,3,4,6,7,8-HxCDF         26         736         10.4         0           1,2,3,4,6,7,8-HxCDF         35         737         18.0         0           1,2,3,4,6,7,8-HxCDF         35         737         18.0         0           1,2,3,4,6,7,8-HxCDF         35         737         18.0         0           1,2,3,4,6,7,8-HxCDF         27         737         18.0         0           1,2,3,4,6,7,8-HxCDF         27         737         18.0         0 </td <td>2,3,7,8-PeCUU 2,3,4,7,8-HxCDD</td> <td>18 25</td> <td>737</td> <td>9.84 22.5</td> <td>00</td> <td>Х Х Х Х Х</td> <td>х X X Z</td>	2,3,7,8-PeCUU 2,3,4,7,8-HxCDD	18 25	737	9.84 22.5	00	Х Х Х Х Х	х X X Z
1,2,3,7,8,9-HXCUU         39         7,37         28.0         0           1,2,3,4,6,7,8-HpCDD         98         52,500         335         335         335           0CDD         12,3,4,6,7,8-HpCDD         98         52,500         3,320         3,320         3,320           2,3,7,8-TCDF         65         337         17.0         3,320         3,320         3,320           2,3,7,8-PeCDF         22         736         9.60         0         0         0           1,2,3,7,8-PeCDF         26         736         17.0         3.90         0         0           2,3,4,7,8-HXCDF         26         736         1,600         28.0         0         0         0           1,2,3,4,6,7,8-HXCDF         35         737         18.0         0         0         0           1,2,3,7,8,9-HXCDF         16         1,260         18.0         0         0         0           1,2,3,4,6,7,8-HXCDF         26         737         18.0         0         0         0           1,2,3,4,6,7,8-HXCDF         27         737         18.0         0         0         0           1,2,3,4,6,7,8-HXCDF         26         842         23.0         0	2,3,6,7,8-HxCDD	49	737	27.3	0 0	RN 2	AN A
OCDD         100         905,000         3,320         3,320           2,3,7,8-TCDF         65         337         17.0         3.90           1,2,3,7,8-PECDF         22         736         9.60         0           2,3,4,7,8-PECDF         22         736         9.60         0           1,2,3,4,7,8-PECDF         26         736         10.4         0           1,2,3,4,7,8-HxCDF         35         736         10.4         0           1,2,3,4,7,8-HxCDF         35         737         18.0         0           1,2,3,6,7,8-HxCDF         35         737         18.0         0           1,2,3,4,6,7,8-HxCDF         16         1,260         18.0         0           1,2,3,4,6,7,8-HxCDF         35         737         18.0         0           2,3,4,6,7,8-HxCDF         27         737         18.0         0           1,2,3,4,6,7,8-HxCDF         27         737         18.0         0           1,2,3,4,6,7,8-HxCDF         26         842         23.0         0         0           1,2,3,4,6,7,8-HxCDF         26         730         57.0         36.0         0	2,3,4,6,7,8-HXCUU	5 8 5 6	737 52,500	28.U 335	0 335	r RN	r RZ
2,3,7,8-TCDF     65     337     17.0     3.90       1,2,3,7,8-PeCDF     22     736     9.60     0       2,3,4,7,8-PeCDF     22     736     10.4     0       1,2,3,4,7,8-PeCDF     26     736     10.4     0       1,2,3,4,7,8-PeCDF     26     736     10.4     0       1,2,3,4,7,8-HxCDF     35     1,500     28.0     0       1,2,3,6,7,8-HxCDF     35     737     18.0     0       1,2,3,4,6,7,8-HxCDF     16     1,260     18.0     0       2,3,4,6,7,8-HxCDF     27     737     18.0     0       1,2,3,4,6,7,8-HxCDF     71     7,100     57.0     36.0       1,2,3,4,6,7,8-HxCDF     71     7,100     57.0     0	CDD COL	100	905,000	3,320	3,320	NR	NR
1,2,3,7,8-PeCDF         22         736         9.60         0           2,3,4,7,8-PeCDF         26         736         10.4         0           1,2,3,4,7,8-HxCDF         26         736         10.4         0           1,2,3,4,7,8-HxCDF         43         1,500         28.0         0           1,2,3,6,7,8-HxCDF         35         737         18.0         0           1,2,3,6,7,8-HxCDF         35         737         18.0         0           1,2,3,7,8,9-HxCDF         16         1,260         18.0         0           2,3,4,6,7,8-HxCDF         27         737         18.0         0           2,3,4,6,7,8-HxCDF         27         737         18.0         0           1,2,3,4,6,7,8-HxCDF         71         7,100         57.0         36.0           1,2,3,4,6,7,8-HxCDF         26         842         23.0         0	3,7,8-TCDF	65	337	17.0	3.90	NR	NR
2,3,4,7,8-PeCDF     26     736     10.4     0       1,2,3,4,7,8-HxCDF     43     1,500     28.0     0       1,2,3,6,7,8-HxCDF     35     737     18.0     0       1,2,3,7,8,9-HxCDF     35     737     18.0     0       1,2,3,7,8,9-HxCDF     16     1,260     18.0     0       2,3,4,6,7,8-HxCDF     16     1,260     18.0     0       1,2,3,4,6,7,8-HxCDF     27     737     18.0     0       1,2,3,4,6,7,8-HpCDF     71     7,100     57.0     36.0       1,2,3,4,6,7,8-9-HbCDF     26     842     23.0     0	2,3,7,8-PeCDF	22	736	9.60	0	NR	NR
1,2,3,4,7,8-HxCDF     43     1,500     28.0     0       1,2,3,6,7,8-HxCDF     35     737     18.0     0       1,2,3,7,8,9-HxCDF     16     1,260     18.0     0       2,3,4,6,7,8-HxCDF     27     737     18.0     0       2,3,4,6,7,8-HxCDF     27     737     18.0     0       1,2,3,7,8,9-HxCDF     27     737     18.0     0       1,2,3,4,6,7,8-HxCDF     27     737     18.0     0       1,2,3,4,6,7,8-HpCDF     71     7,100     57.0     36.0       1,2,3,4,7,8,9-HpCDF     26     842     23.0     0	3,4,7,8-PeCDF	26	736	10.4	0	NR	NR
1,2,3,6,7,8-HxCDF         35         737         18.0         0           1,2,3,7,8,9-HxCDF         16         1,260         18.0         0           2,3,4,6,7,8-HxCDF         27         737         18.0         0           2,3,4,6,7,8-HxCDF         27         737         18.0         0           1,2,3,4,6,7,8-HxCDF         27         737         18.0         0           1,2,3,4,6,7,8-HxCDF         27         7,100         57.0         36.0           1,2,3,4,6,7,8-HpCDF         26         842         23.0         0	2,3,4,7,8-HxCDF	43	1,500	28.0	0	NR	NR
1,2,3,7,8,9-HxCDF         16         1,260         18.0         0           2,3,4,6,7,8-HxCDF         27         737         18.0         0           1,2,3,4,6,7,8-HpCDF         71         7,100         57.0         36.0           1,2,3,4,6,7,8-HpCDF         26         842         23.0         0	2,3,6,7,8-HxCDF	35	737	18.0	0	NR	NR
2,3,4,6,7,8-HxCDF         27         737         18.0         0           1,2,3,4,6,7,8-HpCDF         71         7,100         57.0         36.0           1,2,3,4,6,7,8-9-HpCDF         26         842         23.0         0	2,3,7,8,9-HxCDF	16	1,260	18.0	0	NR	NR
1,2,3,4,6,7,8-HpCDF 71 7,100 57.0 36.0 1.2.3,4,7,8,9-HpCDF 26 842 23.0 0	3,4,6,7,8-HxCDF	27	737	18.0	0	NR	NR
1.2.3.4.7.8.9-HnCDF 26 842 23.0 0	2,3,4,6,7,8-HpCDF	71	7,100	57.0	36.0	NR	NR
	2,3,4,7,8,9-HpCDF	26	842	23.0	0	NR	NR
0CDF 80 69,500 110 80.0	CDF	80	69,500	110	80.0	NR	NR
Total I-TEQ <sub>DF</sub> 1,820         50.4         11.2	tal I-TEO <sub>DF</sub>		1,820	50.4	11.2	86*	50 *
Total 2,3,7,8-CDD/CDF NR NR NR NR	tal 2,3,7,8-CDD/CDF		NR	NR	NR	NR	NR

Table 8-29. CDD/CDF Concentrations Measured in EPA's National Sewage Sludge Survey

NR = Not reported.

ng/kg = nanograms per kilogram.

\* Values presented by Rubin and White (1992) for 175 rather than 174 POTWs.

Source: U.S. EPA (1996a); for POTWs with multiple samples, the pollutant concentrations were averaged before the summary statistics presented in the table were calculated. All concentrations are in units of ng/kg dry weight.

		Maximum				
		Concentration	Median Concer	itration (ng/kg)	Mean Conce	ntration (ng/kg)
	Percent	Detected	Nondetects	Nondetects	Nondetects	Nondetects
Congener	Detected	(ng/kg)	Set to	Set to	Set to	Set to
			Det. Limit	Zero	Det. Limit <sup>a</sup>	Zero <sup>a</sup>
2,3,7,8-TCDD	40	12.3	1.95	0	2.72 (2.40)	1.71 (2.86)
1,2,3,7,8-PeCDD	23	37.5	8.23	0	10.9 (7.80)	3.34 (7.43)
1,2,3,4,7,8-HxCDD	34	45.6	5.25	0	11.1 (8.13)	6.03 (10.2)
1,2,3,6,7,8-HxCDD	87	130	25.6	24.7	33.8 (27.6)	32.2 (28.8)
1,2,3,7,8,9-HxCDD	64	88.8	12.3	9.48	20.2 (17.7)	17.0 (19.8)
1,2,3,4,6,7,8-HpCDD	98	5,380	642	642	981 (977)	981 (977)
OCDD	99	65,500	6,630	6,630	11,890 (12,540)	11,890 (12,540)
2,3,7,8-TCDF	76	156	7.53	6.28	12.8 (19.6)	11.1 (20.2)
1,2,3,7,8-PeCDF	21	60.3	7.91	0	10.7 (11.3)	3.53 (9.36)
2,3,4,7,8-PeCDF	42	155	9.70	0	15.7 (19.8)	10.5 (21.6)
1,2,3,4,7,8-HxCDF	48	170	11.5	0	20.4 (25.3)	14.0 (25.9)
1,2,3,6,7,8-HxCDF	17	200	14.0	0	30.4 (53.6)	5.13 (21.9)
1,2,3,7,8,9-HxCDF	4	115	7.53	0	11.1 (13.6)	1.56 (11.7)
2,3,4,6,7,8-HxCDF	35	356	9.85	0	21.8 (40.4)	13.6 (41.0)
1,2,3,4,6,7,8-HpCDF	64	1,460	91.7	31.8	223 (271)	97.5 (207)
1,2,3,4,7,8,9-HpCDF	31	213	11.7	0	27.1 (34.8)	15.0 (33.4)
OCDF	93	11,200	286	281	786 (1,503)	775 (1,506)
Average I-TEQ <sub>DF</sub> (facility basis) <sup>b</sup>		246	49.6	33.4	64.5 (50.1)	47.7 (44.7)
Total 2,3,7,8-CDD/CDF		73,520	7,916	7,881	14,110 (14,390)	13,880 (14,200)
Average TEO <sub>DF</sub> -WHO <sub>98</sub> (facility basis) <sup>b</sup>			44.6	25.5	57.2 (44.4)	36.3 (38.6)

Table 8-30. CDD/CDF Concentrations Measured in 99 Sludges Collected from U.S. POTWs During 1994

<sup>a</sup> Values in parentheses are standard deviations.

presented in the table. A total of 74 POTW average concentrations were used in the calculations. In addition, the following sample ID numbers were not included in the averaging because, according to Green et al. (1995), it was not possible to determine if they were duplicate or multiple samples from other POTWs: 87, 88, 89, 90, 91, 97, 98, and 106. For POTWs with multiple samples, the sample TEQ concentrations were averaged to POTW averages before calculation of the total TEQ mean and median values ٩

Source: Green et al. (1995); Cramer et al. (1995).

## Table 8-31. Quantity of Sewage Sludge Disposed of Annually by Primary, Secondary, or Advanced Treatment POTWs and Potential Dioxin TEQ Releases

Use/Disposal Practice	Volume Disposed (thousands of dry	Percent of Total	Potential Dioxin Release° (g of TEQ/yr)	
	metric tons/year)	Volume	I-TEQ <sub>DF</sub>	TEQ <sub>DF</sub> -WHO <sub>98</sub>
Land Application	1,714	32.0 <sup>e</sup>	84.0	62.2
Distribution and Marketing	71	1.3	3.5	2.6
Surface Disposal Site/Other	396	7.4	19.4	14.4
Sewage Sludge Landfill	157	2.9	7.7	5.7
Co-disposal Landfills <sup>a</sup>	1,819	33.9	89.1	66.0
Sludge Incinerators and Co-incinerators <sup>b</sup>	865	16.1	(f)	(f)
Ocean Disposal	(336) <sup>d</sup>	(6.3) <sup>d</sup>	(O) <sup>d</sup>	(O) <sup>d</sup>
TOTAL	5,357	100.0	204.0	151.0

<sup>a</sup> Landfills used for disposal of sewage sludge and solid waste residuals.

<sup>b</sup> Co-incinerators treat sewage sludge in combination with other combustible waste materials.

<sup>c</sup> Potential dioxin TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (i.e., column 2) by the average of the mean I-TEQ<sub>DF</sub> concentrations in sludge reported by Rubin and White (1992) (i.e., 50 ng/kg dry weight) and Green et al. (1995) and Cramer et al. (1995) (i.e., 47.7 ng/kg). The calculations of TEQ<sub>DF</sub>-WHO<sub>98</sub> used the mean concentration of 36.3 ng TEQ<sub>DF</sub>-WHO<sub>98</sub>/kg for the results reported by Green et al. (1995) and Cramer et al. (1995).

<sup>d</sup> The Ocean Dumping Ban Act of 1988 generally prohibited the dumping of sewage sludge into the ocean after December 31, 1991. Ocean dumping of sewage sludge ended in June 1992 (Federal Register, 1993b). The current method of disposal of the 336,000 metric tons of sewage sludge that were disposed of in the oceans in 1988 has not been determined.

Includes 21.9 percent applied to agricultural land, 2.8 percent applied as compost, 0.6 percent applied to forestry land, 3.1 percent applied to "public contact" land, 1.2 percent applied to reclamation sites, and 2.4 percent applied in undefined settings.

<sup>f</sup> See Section 3.6.5 for estimates of CDD/CDF releases to air from sewage sludge incinerators.

Congener/Congener Group	Liquid Soap	Tall Oil	Tall Resin
	(ng/L)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	ND (0.009)	3.6	ND (1)
1,2,3,7,8-PeCDD	0.400	5.3	3.1
1,2,3,4,7,8-HxCDD	ND (0.020)	ND (2)	ND (4)
1,2,3,6,7,8-HxCDD	0.320	ND (2)	810
1,2,3,7,8,9-HxCDD	0.180	ND (2)	500
1,2,3,4,6,7,8-HpCDD	1.900	ND (1)	5,900
OCDD	1.000	5.3	6,000
2,3,7,8-TCDF 1,2,3,4,8-/1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF 1,2,3,4,7,8/9-HxCDF 1,2,3,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF 2,3,4,6,7,8-HxCDF 1,2,3,4,6,7,8-HpCDF 1,2,3,4,7,8,9-HpCDF 0CDF	0.620 0.290 0.200 0.013 ND (0.004) ND (0.004) ND (0.004) ND (0.005) ND (0.010) NA	17 4.2 1.9 1.4 0.7 ND (0.7) ND (0.5) ND (0.8) ND (0.8) ND (2) NA	ND (2) ND (0.4) ND (0.5) 24  ND (1) ND (0.7) 10 9.0 NA
Total 2,3,7,8-CDD*	3.8	14.2	13213.1
Total 2,3,7,8-CDF*	1.123	25.2	43
Total I-TEQ <sub>DF</sub> *	0.447	9.4	200
Total TEQ <sub>DF</sub> WHO <sub>98</sub> *	0.647	12.0	196
Total TCDD	0.120	31	ND (1)
Total PeCDD	15.000	380	25
Total HxCDD	3.400	3.3	6,800
Total HpCDD	3.600	ND (1)	11,000
Total OCDD	1.000	5.3	6,000
Total TCDF	1.000	26	ND (2)
Total PeCDF	1.300	41	ND (0.5)
Total HxCDF	0.150	4.9	56
Total HpCDF	ND (0.010)	ND (2)	19
Total OCDF	NA	NA	NA
Total CDD/CDF*	25.57	491.5	23,900

\* Calculations assume not-detected values are zero.

ng/kg = nanograms per kilogram.

Ng/L = nanograms per liter.

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

NA = Not analyzed.

-- = Not reported.

Source: Rappe et al. (1990c).







Figure 8-1. 104 Mill Study Full Congener Analysis Results for Pulp



Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.



Figure 8-2. 104 Mill Study Full Congener Analysis Results for Sludge





Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.







Source: Based on data reported in Table 8-7; nondetects set equal to zero.

Figure 8-4. Congener and Congener Group Profiles for Technical PCP



Source: Based on mean concentrations reported in Table 8-24; nondetects set equal to zero.

Figure 8-5. Congener Profile for 2,4-D (salts and esters)







Source: Green et al. (1995); nondetects set equal to 1/2 detection limit.

Figure 8-6. Congener Profiles for Sewage Sludge