

12.0 RESERVOIR SOURCES OF CDD/CDF AND DIOXIN-LIKE PCBs

National CDD/CDF source inventories have been conducted in several nations, including the United Kingdom, The Netherlands, Germany, Austria, and Sweden to characterize emissions from various source categories and estimate annual CDD/CDF emissions to air (and sometimes other media). These inventories focused primarily on emissions from primary sources (i.e., emissions from the site or process where the CDD/CDF are formed). The authors of these inventories (Rappe, 1991; Harrad and Jones, 1992b; Bremmer et al., 1994; Thomas and Spiro, 1995 and 1996; Eduljee and Dyke, 1996; Jones and Alcock, 1996; Duarte-Davidson et al., 1997) indicated that the annual estimates of releases to air provided in these inventories may be underestimates of actual emissions for several reasons. First, from an empirical basis, estimates of the amounts of CDD/CDFs deposited annually from the atmosphere were greater than the estimates of annual CDD/CDF emissions to the atmosphere. Second, the investigators indicated that because of limited emission test data the inventories may underestimate releases from known sources or may not identify all primary sources. Third, the investigators acknowledged the existence of potential reservoir (or secondary) sources but were not able to reliably quantify emissions from these sources. Potential reservoir sources identified by these investigators included volatilization of CDD/CDFs from PCP-treated wood, volatilization from soil, and resuspension of soil particles. Relatively little research of either a monitoring or theoretical nature has been performed to identify reservoir sources and to quantify the magnitude of current or potential future releases from these sources.

This chapter presents background information on reservoir sources of CDD/CDF/PCBs. Section 12.1 presents a working definition for reservoir sources. Section 12.2 describes major environmental reservoirs (i.e., soil, water, sediment, and biota) and presents information on: (1) the potential magnitude (mass) of CDD/CDF/PCBs in each reservoir; (2) the chemical/physical mechanisms responsible for releases of these compounds; and (3) estimates of potential annual releases from each reservoir, if such estimates are feasible, given the available state of knowledge. Section 12.3 presents a summary of the information presented in this chapter.

12.1. POTENTIAL RESERVOIRS

Chapters 2 through 11 have discussed both known and suspected sources of newly formed dioxin-like compounds to the environment in the United States. Once released into the open environment, CDDs, CDFs, PCBs partition to air, soils, water, sediments and biota according to both the nature of the release, and the contaminant's chemical and physical properties (see Volume 2, Chapter 2). The definitions adopted for this analysis of reservoirs and reservoir sources are as follows:

Reservoirs are materials or places that contain previously formed CDD/CDFs or dioxin-like PCBs and have the potential for redistribution and circulation of these compounds into the environment. Potential reservoirs include soils, sediments, biota, water and some anthropogenic materials. Reservoirs become sources when they have releases of dioxin-like compounds to the circulating environment over a defined time and space. Like other sources they would not include purely intermediate products or materials properly disposed in a secure landfill.

Reservoir sources are not included in the quantitative inventory of contemporary sources because they do not involve original releases, but rather the recirculation of past releases. They can, however, contribute to human exposure and, therefore, are important to consider. Figure 12-1 presents a conceptual diagram of flux and exchange of dioxin-like compounds to multiple environmental compartments including the principal environmental reservoirs: soil, water, air, sediment, and biota. This dynamic system consists of fluxes in and out of the atmosphere, as well as other exchanges between reservoirs and the atmosphere. Movement between media can be induced by volatilization, wet and dry atmospheric particle and vapor deposition, adsorption, erosion and runoff, resuspension of soils into air, and resuspension of sediments into water. The rate of movement from one environmental medium to another is termed 'flux,' and refers to the direction and magnitude of flow and exchange over a reference time period and space.

12.2. CHARACTERIZATION OF RESERVOIR SOURCES

This section is organized according to reservoir type (soil, water, sediment, and biota) with each subsection providing information in three parts: (1) the potential magnitude (mass) of dioxin-like compounds in the reservoir; (2) the chemical/physical mechanisms responsible for releases of these compounds; and (3) estimates of potential annual releases from the reservoir, if such estimates are feasible, given the available state of knowledge. Although, anthropogenic structures are potential reservoir sources, they are not discussed here because they were covered earlier in Chapter 8 (the most detailed discussion is on PCP, Section 8.3.8.).

12.2.1. Soil

Potential Mass of Dioxin-Like Compounds Present

The companion document to this report, Volume 2 (Fate, Environmental Levels, and Exposure), presents a compilation of CDD/CDF/PCB concentrations in surface soils reported in various published studies. Based on this compilation of studies, the mean TEQ values for background urban and rural soils are estimated to be 13.4 and 4.1 ng I-TEQ_{DF}/kg of soil, respectively (or 11.9 and 3.6 ng TEQ_{DF}-WHO₉₈/kg, respectively). It should be noted that no comprehensive survey of CDD/CDF concentrations in U.S. soils has yet been performed. The surface area of the United States (excluding Alaska) is approximately 7.85 million square kilometers (sq km). Land use statistics for 1992 indicate that 0.37 million sq km are classified as "developed" and can be considered to be principally urban areas. The remaining 7.48 million sq km are considered rural. Of this rural area, 1.55 million sq km are cropland (U.S. DOC, 1997). Further breakdown of the rural land area into pasture land, range land, and forest land is available, but the available monitoring data are considered to be inadequate for deriving background CDD/CDF concentrations for these land use types.

In estimating burdens for the United Kingdom, Harrad and Jones (1992) and Duarte-Davidson et al. (1997) assumed that the majority of CDD/CDFs in soil is present in the top 5 centimeters (except possibly in cropland, which may involve a deeper depth due to plowing) and that the soil density is 1,000 kg/m³. Coupling these assumptions regarding depth of contamination and average soil density with the rural and urban U.S. surface areas and TEQ concentrations yields soil burden estimates of 1,530 kg I-TEQ_{DF} (1,350 kg

TEQ_{DF}-WHO₉₈) in rural soils and 250 kg I-TEQ_{DF} (220 kg TEQ_{DF}-WHO₉₈) in urban soils in the United States.

Higher concentrations of CDD/CDFs than those presented above for background urban and rural soils may be present in soils underlain by municipal and industrial waste and in soils at contaminated industrial sites. The lack of comprehensive data on CDD/CDF concentrations in these soils, as well as the lack of data on the mass of these soils nationwide, precludes estimating total national soil burdens for these soils at present. Higher concentrations of CDD/CDFs may also be present in the soils of areas that have been treated with pesticides contaminated with CDD/CDFs. For the same reasons presented above for industrially contaminated soil, it is not possible to estimate current soil burdens of CDD/CDF associated with past pesticide use. However, estimates can be made of the total mass of CDD/CDF TEQs that have been applied to soil from past use of the pesticides 2,4-D and 2,4,5-T.

2,4-Dichlorophenoxy acetic acid (2,4-D) and its salts and esters are widely used in agricultural and nonagricultural settings in the United States as post-emergence herbicides for control of broadleaf weeds and brush. In terms of volumes of pesticides used annually, 2,4-D ranks among the top 10 pesticides in the United States (U.S. EPA, 1994b, 1997e) and has been in large-scale, large-volume commercial use for many years (U.S. EPA, 1975). Commercial production of 2,4-D in the United States started in 1944 (Esposito et al., 1980). Table 12-1 presents a compilation of historical domestic production, sales, and usage volumes for 2,4-D and its salts and esters.

As described in Section 8.3.8, CDD/CDFs were detected in several formulations of 2,4-D and its derivatives during analyses performed to comply with EPA's 1987 Data Call-In (DCI) for CDD/CDFs. Although the analytical results of these tests indicated that CDD/CDFs were seldom above the regulatory limits of quantification (LOQ) established by EPA for the DCI, several registrants detected and quantified CDD/CDFs at lower LOQs. The results of these tests are summarized in Table 8-25. The average TEQ in these tests was 0.70 μg I-TEQ_{DF}/kg (1.10 μg TEQ_{DF}-WHO₉₈/kg). Schechter et al. (1997) recently reported similar concentrations in 2,4-D samples manufactured in Europe and Russia; lower levels were observed in U.S. products. The results of Schechter et al. (1997) are presented in Table 8-27.

If it is assumed that the EPA DCI results (i.e., average TEQ level of $0.70 \mu\text{g I-TEQ}_{\text{DF}}/\text{kg}$ or $1.10 \mu\text{g TEQ}_{\text{DF-WHO}_{98}}/\text{kg}$) are typical of CDD/CDF levels in 2,4-D pesticides over the past 20 years and that the average annual use of these pesticides in the United States has been approximately 25,000 metric tons, then the estimated CDD/CDF TEQ released to the environment from 2,4-D use during the period 1975 to 1995 was $350 \text{ g I-TEQ}_{\text{DF}}$ ($550 \text{ g TEQ}_{\text{DF-WHO}_{98}}$).

2,4,5-Trichlorophenoxy acetic acid (2,4,5-T) was used in the United States for a variety of herbicidal uses until the late 1970s to early 1980s. The major use of 2,4,5-T (about 41 percent of annual usage) was for control of woody and herbaceous weed pests on rights-of-way. The other major herbicidal uses were forestry (28 percent of usage), rangeland (20 percent of usage), and pasture (5 percent of usage). As discussed in Section 3.4.2.8, uses of 2,4,5-T for home or recreation areas and for lakes, ponds, and ditches were suspended by EPA in 1970. Rights-of-way, forestry, and pasture uses were suspended by EPA in 1979, and all uses were canceled in 1983.

Table 12-2 presents a compilation of historical domestic production, sales, and usage volumes for 2,4,5-T and its salts and esters. As shown in Table 12-2, production and use of 2,4,5-T generally increased each year following its introduction in the 1940s until the late 1960s. Production, sales, and usage information for the 1970s are generally not available but are reported to have steadily declined during that period (Federal Register, 1979; Esposito et al., 1980).

Some information is available on the 2,3,7,8-TCDD content of 2,4,5-T, but little information is available on the concentrations of the other 2,3,7,8-substituted CDD/CDFs that may have been present.

- Plimmer (1980) reported that 2,3,7,8-TCDD concentrations as high as $70,000 \mu\text{g/kg}$ were detected in 2,4,5-T during the late 1950s.
- In a study of 42 samples of 2,4,5-T manufactured before 1970, Woolson et al. (1972) found 500 to $10,000 \mu\text{g/kg}$ of TCDDs in 7 samples, and another 13 samples contained 10,000 to $100,000 \mu\text{g/kg}$ of TCDDs. HxCDDs were found in four samples at levels between 500 and $10,000 \mu\text{g/kg}$ and in one sample at a concentration exceeding $10,000 \mu\text{g/kg}$, but less than $100,000 \mu\text{g/kg}$. The detection limit in the study was $500 \mu\text{g/kg}$.
- The average 2,3,7,8-TCDD concentration in 200 samples of Agent Orange, a defoliant containing about a 50/50 mixture of the butyl esters of 2,4,5-T and

2,4-D that was used by the U.S. Air Force in Vietnam, was 1,910 $\mu\text{g/kg}$ (Kearney et al., 1973). Of the 200 samples, 64 (or 32 percent) contained more than 500 $\mu\text{g/kg}$ of 2,3,7,8-TCDD, with the highest concentration reported to be 47,000 $\mu\text{g/kg}$.

- Storherr et al. (1971) reported detecting 2,3,7,8-TCDD at concentrations ranging from 100 to 55,000 $\mu\text{g/kg}$ in five samples of 2,4,5-T.
- Kearney et al. (1973) reported that production samples of 2,4,5-T obtained from the three principal 2,4,5-T manufacturers in 1971 contained 2,3,7,8-TCDD at levels of < 100 $\mu\text{g/kg}$, 100 $\mu\text{g/kg}$, and 2,300 $\mu\text{g/kg}$.
- A 1975 survey of 10 lots of a commercial formulation containing 2,4,5-T showed 2,3,7,8-TCDD concentrations ranging from 10 to 40 $\mu\text{g/kg}$ (Dow Chemical Co., undated).
- Analyses by EPA of 16 technical grade 2,4,5-T samples from five different manufacturers revealed 2,3,7,8-TCDD contents ranging from < 10 to 25 $\mu\text{g/kg}$ (Federal Register, 1979).
- Schecter et al. (1997) recently reported the analytical results of one sample of 2,4,5-T purchased from Sigma Chemical Co. (product number T-5785, lot number 16H3625). The results, presented in Table 12-3, indicate a total I-TEQ_{DF} concentration of 2.88 $\mu\text{g/kg}$ (3.26 $\mu\text{g TEQ}_{\text{DF}}\text{-WHO}_{98}/\text{kg}$).

Because of the wide variability (i.e., three orders of magnitude) in the available limited information on the 2,3,7,8-TCDD content of 2,4,5-T (particularly the 2,4,5-T used in the 1950s) and incomplete information on domestic usage, it is difficult to reliably estimate the amount of 2,3,7,8-TCDD that was released to the U.S. environment as a result of 2,4,5-T use. A very uncertain estimate can be made using the following assumptions: (1) the average annual consumptions during the 1950s, 1960s, and 1970s were 2,000 metric tons/yr, 4,000 metric tons/yr, and 1,500 metric tons/yr, respectively; and (2) the average 2,3,7,8-TCDD concentrations in 2,4,5-T used over these three decades were 10,000 $\mu\text{g/kg}$ in the 1950s, 4,000 $\mu\text{g/kg}$ in the 1960s, and 100 $\mu\text{g/kg}$ in the 1970s. Based on these assumptions, the very uncertain estimate of 2,3,7,8-TCDD input from 2,4,5-T use over the period 1950-1979 is 36,000 g.

Another source contributing to the soil reservoir is CDD/CDF in sewage sludge applied to land (i.e., surface disposal or land farming) is estimated to have been 103 g I-TEQ_{DF} in 1995 (75 g TEQ_{DF}-WHO₉₈) [Note: See Section 8.4.1 for details]. If this same amount of TEQ had been applied each year during the period 1975 to 1995, the total amount applied would have been 2,000 g I-TEQ_{DF} (1,500 g TEQ_{DF}-WHO₉₈).

Mechanisms Responsible for Releases from Surface Soils

Atmospheric deposition is believed to be the current primary means of supply of dioxin-like compounds to surface soil. CDD/CDFs/PCBs are highly lipid soluble, low volatility compounds, and tend to partition to soil instead of into air or water. Once present in or on soils, physical/chemical and biological mechanisms (i.e., photolysis and biodegradation) can slowly alter the composition and amount of CDD/CDFs/PCBs present. Studies indicate that the dioxin-like compounds (particularly the more highly chlorinated CDD/CDFs) exhibit little downward mobility once deposited in or on soil (Puri et al. 1989; Freeman and Schroy, 1985; Orazio et al., 1992; and Paustenbach et al., 1992). However, remobilization of the compounds to the atmosphere is possible through volatilization and resuspension of soil particles.

For example, Young (1983) conducted field studies on the persistence and movement of 2,3,7,8-TCDD during 1973-1979 on a military test area that had been aerially sprayed with 73,000 kg of 2,4,5-T during 1962-1970. TCDD levels of 10 to 1,500 ng/kg could be found in the top 15 cm of soil 14 years after the last application of herbicide at the site. Although actual data were not available on the amount of 2,3,7,8-TCDD originally applied as a contaminant of the 2,4,5-T, best estimates indicated that less than 1 percent of the applied 2,3,7,8-TCDD remained in the soil after 14 years. Photodegradation at the time of and immediately after aerial application was believed by Young (1983) to be responsible for most of the disappearance. However, once incorporated into the soil, the data indicated a half-life of 10 to 12 years (Young, 1983). Similarly, Paustenbach et al. (1992), concluded that half-lives of 2,3,7,8-TCDD in soils at the surface might be 9 to 15 years and half-lives below the surface could be 25 to 100 years.

Ayris and Harrad (1997) studied the mechanisms affecting volatilization fluxes of several PCB congeners (PCB numbers 28, 52, 101, 138, and 180) from soil and found positive correlations between flux and soil temperature, soil moisture content, and soil PCB concentration. For PCBs, secondary releases from soils (primarily via volatilization) are believed to currently exceed primary emissions in the United Kingdom (Harner et al., 1995; Jones and Alcock, 1996). Lee et al. (1998) recently quantified PCBs in air samples taken every 6 hours over a 7-day period in the summer at a rural site in England and found a strong correlation between air temperature and PCB congener concentrations. The

concentrations followed a clear diurnal cycle, thus providing some evidence that rapid, temperature controlled soil to air exchange of PCBs influences air concentrations and enables regional/global scale cycling of these compounds.

CDD/CDFs and PCBs sorbed to soil and urban dust particles can also be moved from the terrestrial environment to the aquatic environment via stormwater runoff/erosion. Results of recent research indicate that, for at least some waterbodies, erosion/stormwater runoff is currently the dominant mechanism for CDD/CDF input. For example, Smith et al. (1995) analyzed CDD/CDF concentrations in sediment cores, air, precipitation, soil, and stormwater runoff in an effort to determine the contributing sources of these compounds to the lower Hudson River. The mass balance estimates developed from these data for 1990-1993 are: stormwater runoff entering tributaries (76 percent of total CDD/CDF input), anthropogenic wastes (19 percent), atmospheric deposition (4 percent), and shoreline erosion (less than 1 percent). Smith et al. (1995) also projected the percent contribution of these same sources for 1970 as: anthropogenic wastes (70 percent), stormwater runoff into tributaries (15 percent), atmospheric deposition (15 percent), and shoreline erosion (0.1 percent).

Lebeuf et al. (1996) analyzed sediment cores from different locations in the lower St. Lawrence River Estuary and the Gulf of St. Lawrence. The congener group profiles found in the samples indicate that the input of CDD/CDFs is primarily from the atmosphere. Comparison of the CDD/CDF concentrations in sediments collected from areas where sediment accumulation is due primarily to fluvial transport with sediments from areas where sediment accumulation is due primarily to direct atmospheric deposition onto the water indicates that the contribution of CDD/CDF from direct atmospheric deposition represents less than 35 percent of the sediment burden. Thus, the primary source of CDD/CDFs is emissions to the atmosphere upwind of the Estuary that are deposited within the watershed and subsequently transported downstream by fluvial waters.

Paustenbach et al. (1996) and Mathur et al. (1997) reported that stormwater runoff from 15 sites in the San Francisco area contained CDD/CDF TEQ at levels ranging from 0.01 to 65 pg I-TEQ_{DF}/L; most samples contained less than 15 pg I-TEQ_{DF}/L. The sites differed widely in land use; the highest levels measured were obtained from an urban, but nonindustrialized area. A distinct variability was noted in the results obtained at the same sampling location during different rain events. The profiles of CDD/CDFs in the urban

stormwater samples were similar particularly in samples collected at the onset of rain events. Stowe (1996) reported similar findings from analyses of sediments from three stormwater basins collecting runoff from a military base, city street, and parking lots.

Fisher et al. (1998) reported that urban runoff samples from eight sites (15 samples) in the Santa Monica Bay watershed contained CDD/CDF TEQ at levels ranging from 0.7 to 53 pg I-TEQ_{DF}/L (all but one sample were in the range of 0.7 to 10 pg I-TEQ_{DF}/L). The samples were collected in 1988/1989 from continuously flowing storm drains during both dry and storm periods. The mean concentration measured during storm events, 18 pg I-TEQ_{DF}/L, was higher than concentration observed during dry periods, 1 pg I-TEQ_{DF}/L.

Estimated Annual Releases from Soil to Water

Nonpoint sources of CDD/CDFs to waterways include stormwater runoff from urban areas and soil erosion in rural areas during storms. Approaches to estimate national loadings to water for both of these sources are described below. The estimate derived below for the potential annual national loading of CDD/CDFs in urban runoff to waterways is uncertain, but suggests that the loading may be comparable to the contribution from known industrial point sources (at least 20 g I-TEQ_{DF} in 1995). Similarly, the estimate derived below for the potential annual national loading of CDD/CDFs in rural eroded soils to waterways is uncertain, but has a stronger analytical base than the urban run off estimate. This loading estimate, however, is significantly higher than the contribution from known industrial point sources.

Urban Runoff - Few data on CDD/CDF concentrations in urban runoff have been reported. The most recent and largest data sets were reported in studies conducted in the San Francisco Bay and Santa Monica Bay regions (Mathur et al, 1997; Fisher et al., 1998). These studies found a wide range of CDD/CDF levels in samples of stormwater runoff from 23 sites, varying from 0.01 to 83 pg I-TEQ_{DF}/L. The wide variability and limited geographic coverage of these data preclude derivation of a national emission estimate at this time. However, by making a number of assumptions, a preliminary estimate of the potential CDD/CDF magnitude from this source can be made. In order to estimate the amount of rainfall in urbanized areas of the conterminous United States, a Geographic Information Systems (GIS) analysis was performed to: determine the total area of every U.S. Census

urbanized area; to determine the 30-year annual average rainfall for each of those areas; and to calculate the product of the total areas of urbanized areas with the annual average rainfall (Lockeed Martin, 1998). This approach yields an estimate of 1.9×10^{14} L/year. If it is assumed that urban runoff in the United States averages 1 pg I-TEQ_{DF}/L (or 1 pg TEQ_{DF}-WHO₉₈/L) (i.e., approximately the midpoint of the range reported by Mathew et al. (1997) and Fisher et al. (1998)), this source could contribute a total of 190 g I-TEQ_{DF} or TEQ_{DF}-WHO₉₈ per year to U.S. waterways. No data were available to make similar estimates for PCBs.

Rural Soil Erosion - The total annual sheet and rill erosion in the United States during 1992 has been estimated as 1.6 billion metric tons from rangeland and 1.1 billion metric tons from cropland (USDA, 1995). The total amount of eroded soil entering waterways is greater than this value, because this value does not include soil erosion from construction areas, forests, and other non-crop and non-rangelands. The data summarized in the companion document to this report (Volume 2) suggest that typical concentrations of CDD/CDFs in soils in rural areas is about 4.1 ng I-TEQ_{DF}/kg (or 3.6 ng TEQ_{DF}-WHO₉₈/kg). It is not known how well this estimate represents eroded soil from cropland and rangeland. If these soils contain an average of 1 ng TEQ/kg (i.e., slightly lower than the background value for all types of rural soil), they would contribute 2,700 g TEQ/yr (I-TEQ_{DF} and TEQ_{DF}-WHO₉₈) to the Nation's waterways. As with urban runoff, no data were available to make similar estimates for PCBs.

Estimated Annual Releases from Soil to Air

No quantitative estimates of the mass of dioxin-like compounds that may be released to the atmosphere annually from U.S. soils have been published in the literature and none are developed in this report. As noted above, the vapor flux of these compounds from soil to air is dependent on the soil and air concentrations of dioxin-like compounds, and the temperature, moisture content, and organic carbon content of the soil. Most of these parameters are not adequately characterized for the United States as a whole to enable a reliable estimate to be made at present. Particle flux is dependent on many factors including wind speed, vegetative cover, activity level, particle size, soil type/conditions, moisture content and particle density. Through use of models and various assumptions, Kao and Venkataraman (1995) estimated the fraction of ambient air

CDD/CDF concentrations in the upper Midwest United States that may be the result of atmospheric reentrainment of soil particles. Similarly, through use of models and various assumptions, Jones and Alcock (1996) and Harner et al. (1995) reached tentative conclusions about the relative importance of volatilization of dioxin-like compounds from soils in the United Kingdom.

Modeling re-entrainment of soil to the atmosphere was conducted by Kao and Venkataraman (1995). The soil re-entrainment model incorporated information on particle sizes, deposition velocities, and concentrations of CDD/CDFs in soils. Smaller particulates, with median diameters ranging from about 0.01 μm to 0.3 μm , are primarily formed from combustion sources when hot vapors condense and through accumulation of secondary reaction products on smaller nuclei. Particles at the upper end of this size range will deposit to the ground in several days. Large or coarse particles, having median diameters of about 8 μm , are generated from wind-blown dust, sea spray, and mechanically-generated particles. CDD/CDFs absorbed onto re-entrained soil would be included in this larger particle size. These larger particles have a lifetime in the atmosphere from a few to many hours (Kao and Venkataraman, 1995).

The fraction of ambient air concentration of CDD/CDF that results from soil re-entrainment was established based on the contribution of crustal sources to the ambient aerosol. Data on typical crustal soil concentrations in air (15 to 50 $\mu\text{g}/\text{m}^3$ for rural areas and 5 to 25 $\mu\text{g}/\text{m}^3$ for urban areas) were combined with data on the average concentrations of CDD/CDFs in soils (73 ng/kg for rural, 2,075 ng/kg for urban, and 8,314 ng/kg for industrial soils) published by Birmingham (1990) for Ontario, Canada, and several Midwest States. This analysis estimated the concentrations of CDD/CDFs in the ambient aerosol that originate from soils to be 1×10^{-3} to 4×10^{-3} pg/m^3 in rural areas and 0.01 to 0.05 pg/m^3 in urban areas. These particulate dioxin concentrations were compared to average total particulate dioxin levels of 1.36 pg/m^3 by Eitzer and Hites (1989) to arrive at the conclusion that soil re-entrainment could only account for 1 to 4 percent of the particulate dioxins in the atmosphere in urban areas and 0.1 to 0.3 percent for rural regions (Kao and Venkataraman, 1995).

This information on the size distribution of ambient aerosols and relative CDD/CDF concentrations in different particle size fractions was integrated with particle size-deposition velocities to estimate the relative contribution to the total mass deposition flux

for small and large particle sizes. Even though re-entrained soil may constitute only a small fraction of the atmospheric levels of CDD/CDFs, the contribution of dioxins in re-entrained surface soil to the total deposition flux could be significant, because coarse particles dominate dry deposition. Soil re-entrainment could possibly account for as much as 70 to 90 percent of the total dry deposition of CDD/CDFs in urban areas and 20 to 40 percent in rural regions (Kao and Venkataraman, 1995).

Two approaches were used by Jones and Alcock (1996) to assess the potential significance of CDD/CDF volatilization from soils: (1) the fugacity quotient concept and (2) a simple equilibrium partitioning model. The fugacity quotient model compares fugacities of individual CDD/CDF compounds in different environmental media to determine the tendency for these compounds to accumulate in particular environmental compartments (McLachlan, 1996). Fugacities for individual compounds, by media, were estimated by Jones and Alcock (1996) based on physical/chemical properties of the compounds, as well as the concentrations in the media. In this instance, fugacity quotients were calculated for air and soil by dividing each compound's fugacity for air by that of soil. Quotients near 1 indicate equilibrium conditions between media; values greater than 1 represent a tendency for flux (volatilization) from soil to air, while values less than 1 indicate a net flux to the soil from the air. The equilibrium partitioning model used by Jones and Alcock (1996) predicts the maximum (possible 'worst case') flux of CDD/CDFs from soil to the atmosphere. Air phase to soil partition coefficients were calculated using the ratios of soil and air fugacity capacities. Equilibrium air concentrations were then calculated using typical U.K. soil concentrations for both urban and rural settings.

From the fugacity quotient model, Jones and Alcock (1996) concluded that the lower-chlorinated CDD/CDFs may be close to soil-air equilibrium in the United Kingdom while for other congeners, soil is a sink rather than a source to the atmosphere. Jones and Alcock (1996) reported that the equilibrium partitioning model predicted that 0.15 kg I-TEQ volatilizes annually from soil in the United Kingdom. However, the authors discounted this estimate and concluded that soil volatilization is unlikely to be a significant contributor to emissions. The likelihood that these estimates were high was attributed to the fact that: (1) assumptions were made that the concentrations of CDD/CDFs in air were zero and (2) the model does not consider the resistance of CDD/CDFs to volatilize from soil.

Harner et al. (1995) developed a model to predict the long-term fate of PCBs in soils, with emphasis on soil to air exchanges. Using data on levels of PCBs in air, soil, and vegetation in the U.K., Harner et al. (1995) developed a mass balance model to simulate the fate of PCBs in U.K. soils from 1935 to 1994. Specifically, monitoring data and physical/chemical property data were compiled to calculate fugacities for PCB congeners 28, 52, 138, and 153. The model was designed to provide an order-of-magnitude-level of accuracy, due in part to the inherent variability in the input data. The mass balance equations in the model included a bell-shaped function for rates of emissions of PCBs, with the maximum emission rate occurring in 1967. From these emissions rates, fluxes between air and soil over several decades were estimated. Table 12-4 summarizes the calculated fluxes. During the 1960s and 1970s, levels of total PCBs in U.K. soils reached average levels of approximately 300 $\mu\text{g/kg}$ as a result of atmospheric deposition. Because of restrictions on PCB use during the last two decades, air concentrations have fallen, and the primary source to the atmosphere is now believed to be volatilization from soils. The mass balance model estimated a net flux of 700 kg/yr of total PCBs from soils to the atmosphere in 1994. However, this estimate is presented with the caveat that the model tends to underestimate the rate of reduction of PCB concentrations in recent years, which could be attributed to other mechanisms such as biodegradation, photolysis, and other degradation processes.

12.2.2. Water

Potential Mass of Dioxin-Like Compounds Present

The surface area of inland waters (including the Great Lakes) in the United States is about 359,000 sq km (U.S. DOC, 1995a). Assuming that the mean depth of inland water is 10 meters (Duarte-Davidson et al., 1997), the total inland water volume is approximately 3,600 billion m^3 . No compilation of CDD/CDF measurements in inland surface waters is made for this report. However, if it is assumed that the "typical" value used by Duarte-Davidson et al. (1997) for rivers in the United Kingdom, 38 pg I-TEQ_{DF}/ m^3 , is representative of U.S. waters, then the burden is calculated to be 137 g I-TEQ_{DF}.

Mechanisms Responsible for Supply to and Releases from Water

As discussed previously in Section 12.2.1, dioxin-like compounds enter surface water from atmospheric deposition, stormwater runoff erosion, and discharges of anthropogenic wastes. Volatilization is the primary mechanism for release of dioxin-like compounds from the water column to the atmosphere. Several studies have addressed the water-air exchange of dioxin-like PCBs through volatilization in the Great Lakes (Achman et al., 1993; Hornbuckle et al., 1993; Swackhamer and Armstrong, 1986; Baker and Eisenreich, 1990). No similar body of literature has been developed to address volatilization of CDD/CDFs from water.

Most studies that have addressed PCB water/air exchange have used the two-film model developed by Whitman (1927) and made popular by Liss and Slater (1974). When assessing gas exchange between air and water, the interface between the two phases can be considered as a two-layer (film) system consisting of well-mixed gas and liquid films adjacent to the interface; the rate of transfer is controlled by molecular diffusion through the stagnant boundary layer (Achman et al., 1993). Liss and Slater (1974) applied the model to assess the flux of various gases, specifically in the air-sea systems, and indicated the possibility of its use at any air-water interface in the environment, if the necessary data are available. Hornbuckle et al. (1993) concluded that the two-film model is the best available tool for estimating regional and local flux of PCBs from natural waters. The following paragraph, from Achman et al. (1993), succinctly summarizes the model. The basic equation used to describe the rate of transfer across the interface is

$$F = K_{ol}(C_w - C^*) \quad (\text{Eqn. 12-1})$$

where F is the flux ($\text{mol/m}^2\text{-day}$), C_w (mol/m^3) is the dissolved PCB concentration in the bulk water, and C^* (P/H , mol/m^3) is the air concentration expressed as a water concentration in equilibrium with the air. The variable P is the vapor-phase air concentration measured (mol/m^3) and converted to units of pressure using the ideal gas law. H is Henry's Law constant ($\text{atm}\cdot\text{m}^3/\text{mol}$). The overall mass-transfer coefficient, K_{ol} , has units of velocity (m/day). The concentration gradient determines the direction of flux and drives the mass transfer; whereas, K_{ol} is a kinetic parameter that quantifies the rate of transfer. The value of K_{ol} is dependent on the physical and chemical properties of the

compound as well as environmental conditions. The reciprocal of K_{ol} is the total resistance to transfer expressed on a gas- (RT/Hk_a) and liquid- ($1/k_w$) phase basis:

$$1/K_{ol} = 1/k_w + RT/Hk_a \quad (\text{Eqn. 12-2})$$

where k_w is the water-side mass-transfer coefficient (m/day) and k_a is the air-side mass-transfer coefficient (m/day). H is Henry's Law constant, R is the universal gas constant ($8.2057 \times 10^{-5} \text{ atm} \cdot \text{m}^3/\text{mol K}$), and T is the absolute temperature, K.

Achman et al. (1993) and Hornbuckle et al. (1993) calculated the volatilization rates of PCBs from Green Bay on Lake Michigan, based on air and water samples simultaneously collected over a 14-day period above and below the air-water interphase and analyzed for 85 PCB congeners. Air samples collected over nearby land were also analyzed for the 85 PCB congeners. The direction and magnitude of flux for each congener were then calculated using Henry's Law and meteorological and hydrological parameters in the "two-film" model. (See Eqn. 12-1.)

The net total PCB transfer rate (i.e., sum of all congener transfer rates) was found to be from water to air (i.e., volatilization). However, during cool water temperature periods (i.e., October), the direction of transfer reversed for many congeners. Calculated transfer rates to air ranged from 15 to 300 ng/m² per day at low wind speeds (1-3 m/sec) to 50 to 1,300 ng/m² per day at higher wind speeds (4-6 m/sec). On a congener basis, the lower chlorinated congeners dominated total fluxes. The summary of flux calculations is presented in Table 12-5. The most important factors influencing the magnitude of volatilization were the water concentration of PCBs, wind speed, and water temperature. In addition, Achman et al. (1993) and Hornbuckle et al. (1993) found that (1) atmospheric PCB concentrations are higher over contaminated water than over nearby land, (2) atmospheric PCBs over water tend to increase with increasing dissolved PCB concentrations, and (3) the congener distribution in the atmosphere correlates linearly with the congener distributions in the adjacent water.

Achman et al. (1993) also summarized the PCB volatilization rates reported by other researchers (Baker and Eisenreich, 1990; Swackhamer and Armstrong, 1986; Strachan and Eisenreich, 1988; and Swackhamer et al., 1988) for Great Lakes water bodies. The results of these other studies, presented below, also show net flux of PCBs from water to air.

Water Body	Total PCB Volatilization Rate (ng/m ² -day)	Reference
Lake Superior	141	Baker and Eisenreich (1990)
Lake Michigan	240	Strachan and Eisenreich (1988)
Lake Superior	63	Strachan and Eisenreich (1988)
Siskiwit Lake	23	Swackhamer et al. (1988)
Lake Michigan	15	Swackhamer and Armstrong (1986)

12.2.3. Sediment

Potential Mass of Dioxin-Like Compounds Present

EPA conducted congener-specific measurements of CDD/CDFS in the sediments from 11 U.S. lakes located in areas relatively unimpacted by nearby industrial activity. The mean TEQ concentration in the uppermost sediment layers from these 11 lakes is 5.3 ng I-TEQ_{DF}/kg (dry weight) (or 5.3 ng TEQ_{DF}-WHO₉₈/kg). For most of the lakes, the uppermost layer represents about 10 years worth of sedimentation. CDD/CDF concentrations in lakes impacted by industrial activity may have higher concentrations. For example, Duarte-Davidson et al. (1997) report a TEQ concentration of 54 ng I-TEQ_{DF}/kg for urban sediments in the United Kingdom.

The surface area of inland waters in the United States is approximately 359,000 sq km (U.S. DOC, 1995a). In their calculations of sediment burdens in the United Kingdom, Duarte-Davidson et al. (1997) assumed that (1) the sediment surface area equals the water surface area, (2) the majority of CDD/CDF are located in the top 5 cm of sediment, and (3) that sediment density is 0.13 g dry weight/cm³. Applying these assumptions to the water surface area and background TEQ concentration for U.S. sediments yields a burden of at least 120 kg I-TEQ_{DF} (or 120 kg TEQ_{DF}-WHO₉₈).

Mechanisms Responsible for Supply to and Releases from Sediment

Because sediment is closely connected to the water column above it, evaluating the potential for sediment to act as a reservoir of dioxin-like compounds is complex and likely to be more difficult than studying dioxin-like compounds in a single medium such as water or soil. Volatilization and sedimentation are two mechanisms whereby persistent chemicals such as CDD/CDF/PCBs are lost from water bodies/columns. Numerous authors

have noted that sediments are a likely sink for persistent hydrophobic organic compounds, because these compounds are likely to be strongly bound to organic particles in the sediment (Swackhamer and Armstrong, 1986; Muir et al., 1985; Ling et al., 1993).

For example, Muir et al. (1985) radiolabeled 2,3,7,8-TCDD and studied its dissipation from sediments (collected from a farm pond and a lake) to the water column in laboratory studies under static aerobic conditions at 10°C. After 675 days, more than 80 percent of the labeled TCDD were still present in the pond sediment, and 87 percent were still present in the lake sediment. Aeration had little effect on the dissipation rates.

The concept of fugacity is a useful way to estimate the behavior of dioxin-like compounds in sediments. Fugacity (tendency of a chemical to escape from a phase) is expressed in units of pressure (pascals or Pa) and is the partial pressure exerted by the chemical in each medium. Fugacity models estimate equilibrium concentrations in specific media at given chemical concentrations in the environment. Clark et al. (1988) suggested evaluating contaminant concentrations in multiple environmental media by comparing fugacity of adjoining media (e.g., comparing sediment fugacity with water column fugacity to determine the chemical's tendency to move from one to the other). The authors evaluated fugacities of certain organochlorine compounds, including PCBs, in air, water, sediment, fish, fish-eating birds, and their eggs. The authors presented PCBs fugacities developed from data collected in a study of the Lake Ontario region. The fugacities of PCBs in various media can be ranked as birds > fish > water > bottom sediment, indicating that PCBs and other similar chemicals are likely to remain in bottom sediment and are less likely to re-enter the water column (Clark et al., 1988).

Estimated Annual Releases from Sediment to Water

Ling et al. (1993) evaluated the fate of various chemicals, including PCBs, in Hamilton Harbour, located in Ontario, Canada, using a modified version of the Quantitative Water Air Sediment Interaction (QWASI) fugacity model. Among the processes evaluated were diffusion between air and water, and sediment and water; sediment deposition, resuspension, and burial; and sediment transformation. Three primary compartments were studied: air, water, and bottom sediments. The sediment was treated as a simple, well-mixed surface layer of active sediment and the buried sediment underneath. Chemicals in the active sediment were assumed to be able to exchange with the overlying

water; chemicals in the buried sediment were assumed to be isolated from the sediment-water exchange. Sediment is assumed to be homogenous instead of heterogenous. The epi- and hypolimnetic compartments of the water column were defined based on a thermocline, and the atmosphere was defined as a semi-infinite medium of constant, defined composition.

Ling et al. (1993) estimated rates of PCB movement based on 1987 loadings using two models: a model with and a model without a thermocline. The results for the water-sediment transfer using the model with a thermocline were: ~32 kg/yr enter the hypolimnion from the epilimnion; ~27 kg/yr enter the surface sediment from the hypolimnion; and ~18 kg/yr (> 50%) go to burial. For sediment to water transfer, ~7 kg/yr and 12.5 kg/yr transfer to the hypolimnion and then to the epilimnion, respectively. Similar numbers were found in the single water column model (i.e., model without a thermocline). Both models predicted volatilization from the water to the atmosphere: 1.6 and 1.8 kg/yr for thermocline and the single water column models, respectively. However, the actual contribution of PCBs from sediment to air was not determined. A comparison of estimated concentrations with observed values are presented in Table 12-6. For PCBs, 68 percent were buried in the sediment, 20 percent exported to Lake Ontario, 5.4 percent degraded in the water and sediment, and 6 percent volatilize. The authors note that these percentages are uncertain. At the sediment water exchange, more than 90 percent of each chemical are contained in the sediment because of particle deposition and the high affinity of the chemical for sediment. There was no indication that contaminants buried in the bottom sediments are transferred through diffusion mechanisms back to the surface sediments. However, episodic release of these chemicals from surface sediments can occur through mechanisms such as resuspension during flooding or lake inversions and uptake/ingestion by benthic biota.

12.2.4. Biota

Potential Mass of Dioxin-Like Compounds Present

The mass of CDD/CDFs in biota in the United States was not estimated as part of this reassessment. However, to place perspective on the potential magnitude of this reservoir, 82 g I-TEQ_{DF} have been estimated to be present in biota in the United Kingdom (50 g in humans and 32 g in vegetation), which is about three orders of magnitude less

than that estimated to be present in U.K. surface soils (Duarte-Davidson et al., 1997; Eduljee and Dyke, 1996). Applying this ratio to the estimates of CDD/CDF TEQ soil burden in the United States that were presented in Section 12.2.1 (i.e., 1,780 kg I-TEQ_{DF}) yields a biota burden in the United States of about 2 kg I-TEQ_{DF}.

Mechanisms Responsible for Supply to and Releases from Biota

Apparently, very little of the dioxin-like compounds contained in contaminated soil, unlike certain other compounds and heavy metals, is ultimately taken up by the vegetation growing in the soil. For example, Kjeller et al. (1991) analyzed concentrations of CDD/CDFs in archived soil and grass samples collected at an English experimental station from mid-1840s to the present and found that only 0.006 to 0.02 percent of the soil burden of CDD/CDFs was taken up by the grass. In addition, scientists generally agree that, once taken up by plant tissue, CDD/CDFs are not translocated to other parts of the plant (e.g., fruits, shoots, etc.) (Bacci and Gaggi, 1985; Hülster and Marschner, 1993, 1994; Nakamura et al., 1994).

Researchers have found that the concentration of dioxin-like compounds in the plant should reach equilibrium with the vapor phase concentrations of dioxin-like compounds in the surrounding air (Bacci et al., 1990a, 1990b; Frank and Frank, 1989; Horstman and McLachlan, 1992; McCrady and Maggard, 1993; McLachlan et al., 1995; Paterson et al., 1991; Simonich and Hites, 1994; Tolls and McLachlan, 1994; Welsch-Pausch et al., 1995). Horstman and McLachlan (1992) stated that the leaf-air transfer of volatile compounds is a reversible process governed by concentration gradients. If CDD/CDF concentrations are higher in the surrounding air than they are in the air spaces within plant tissue, CDD/CDF should diffuse into the plant. Once equilibrium is reached and CDD/CDF concentrations in the plant equal that of surrounding air, no more CDD/CDF should be taken into the plant. When CDD/CDF concentrations in surrounding air begin to decrease, CDD/CDFs should diffuse (probably at a slow rate) out of the plant tissue. Apparently, CDD/CDFs are not bioconcentrated to a significant extent in the lipid portion of the leaf cuticle (Gaggi et al., 1985). The CDD/CDFs present in the leaf tissue are predominantly released from the plant through leaf fall onto soil. As a result, vegetation is not likely to be a long-term reservoir of dioxin-like compounds.

Research suggests that dioxin-like compounds within animal tissue, unlike in vegetation, seldom, if ever, reach equilibrium with vapor phase concentrations in the surrounding atmosphere (or water column concentrations in the case of aquatic life). Rather, animals exposed to dioxin-like compounds are known to bioaccumulate these compounds, primarily in body fat (U.S. EPA, 1993a; 1993j). Nonetheless, animals, unlike plants, can metabolize certain chlorinated hydrocarbons after they enter the body (Carlberg et al., 1983). Dioxin-like compounds can be released from an animal's body (at congener-specific rates) through metabolic processes or through weight loss, breast-feeding, or sweating. McLachlan (1996) reported the half-life for the clearance of 2,3,7,8-TCDD from humans to be 7 years. As a result, animal life has a greater potential than does vegetation for being a long-term reservoir source of CDD/CDFs. The majority of the dioxin-like compounds released by animals in the form of waste materials will be released to water or soil. Similarly, upon death, the dioxin-like compounds remaining in the body will be deposited onto soil or aquatic sediments or will be ingested by other animals.

Approaches to Measure and Estimate Releases from Biota - Researchers have investigated the uptake and release of CDD/CDFs by vegetation through measurement of actual concentrations of CDD/CDFs during uptake and release by vegetation grown in closed systems (greenhouses). Bacci et al. (1992) conducted uptake and release studies of 1,2,3,4-TCDD by plant foliage in a closed system (specially constructed greenhouse). Concentrations of TCDD vapor in the greenhouse air were maintained during the 370-hour uptake phase at a mean concentration of 0.0062 ng/L (air concentration varied slightly from 0.0050 to 0.0075 ng/L). To begin the release phase, the TCDD vapor source (amended sand), as well as the greenhouse walls were removed, and release of CDD/CDFs from the leaves was measured for 500 hours. Bacci et al. (1992) concluded that during uptake, TCDD concentration in the leaves varied as a function of time and was dependent on the concentration of vapor-phase TCDD in the surrounding air. These researchers estimated the release of TCDD from the vegetation to be relatively slow with a half-life of TCDD of 3,300 hours.

McCrady and Maggard (1993) conducted a mass balance study of uptake and release of dioxin in grass foliage. The results indicated a half-life of dioxin in grass of 128 hours (McCrady and Maggard, 1993). These researchers also noted that photodegradation

of dioxins on the foliage appeared to be a significant removal mechanism in addition to volatilization. They calculated the photodegradation half-life to be 44 hours (McCrary and Maggard, 1993).

Interpretation of uptake and release data over variable exposure times and contaminant concentrations has led to the development of models describing air-to-vegetation equilibrium and kinetics controlling the behavior of dioxin in vegetation. Some earlier fugacity modeling attempts described the leaf of a plant as behaving as a single compartment. One-compartment models were described by Bacci et al. (1990a; 1990b), Trapp et al. (1990), and Schramm et al. (1987) (as cited in Tolls and McLachlan, 1994). Researchers presenting most of the recently developed models claim that the available data better support the concept of a leaf behaving as two-compartments (Riederer, 1990; Paterson et al., 1991; Horstman and McLachlan, 1992; McCrary and Maggard, 1993; Tolls and McLachlan, 1994; McLachlan et al., 1995). Input parameters considered by most models include critical chemical characteristics of the contaminant, characteristics of the plant, exposure times, and contaminant concentrations measured within the plant.

Riederer (1990) suggested treating a leaf as multiple compartments, having different accessibility to the atmosphere and different diffusion resistances. Input parameters for the two-compartment model are octanol/water coefficients, cuticle/water partition coefficients, aqueous solubility, and saturation vapor pressure of the chemical of concern. Outputs of the model are prediction of equilibrium concentration in different leaf tissues, estimates of air-to-vegetation bioconcentration equilibria, and identification of leaf compartments in which compounds are likely to accumulate. Riederer (1990) also presents an approach for using the model to semiquantitatively assess the potential for revolatilization of dioxins from vegetation.

One advantage of the model presented by Riederer (1990) is that it considers critical plant characteristics in the release of dioxins. A plant is an active organism, responding to changes in its environment, and acting accordingly to ensure its survival. Certain plant characteristics, such as the action of stomata (specialized cells usually on the lower leaf surface that open and close to control passage of vapors into and out of the leaf interior) and total leaf volume, are important factors that effect the release rates of vapor phase contaminants from vegetation.

Paterson et al. (1991) also presented a two-compartment model for release of dioxin-like compounds from vegetation. This model describes a plant as being made up of compartments in terms of their volume fractions of air, water, and nonpolar (lipid-soluble, or octanol-equivalent) organic matter. Paterson et al. (1991) attempted to show that leaf-air equilibrium and kinetics can be correlated with chemical properties of the contaminant and properties of the leaf. Paterson et al. (1991) suggest that the clearance rate constant (k_2) can be correlated with the bioconcentration factor (BCF). This model does not consider critical plant characteristics, such as action of the stomata, and for this reason may be less reliable than models that do consider plant characteristics, such as the model presented by Riederer (1990).

Horstman and McLachlan (1992) developed a fugacity model to describe release of semivolatile organic compounds from the surface of a solid (spruce needles). Their approach was slightly different in that their goal was instrument/method development, but their data supported the behavior of a leaf as a two-compartment system.

McCrary and Maggard (1993) also collected data supporting the importance of viewing a leaf as a two-compartment system. They used a two-compartment model similar to the one described by Paterson et al. (1991), which also does not consider critical plant characteristics, and may be less reliable than models that do (e.g., Reiderer, 1990).

Tolls and McLachlan (1994) exposed grass cultures for up to 240 hours to several semivolatile organic compounds and then measured the release of contaminants from the grass. They developed a two-compartment partitioning model based on the data they collected. The model consisted of a small surface compartment (the leaf cuticle) and large interior reservoir (air spaces within the leaf). Their model assumes the flux of a chemical is the product of the fugacity difference (surface fugacity minus reservoir fugacity) and the conductance between the leaf compartments.

In an attempt to validate this model, McLachlan et al. (1995) compared concentrations of semivolatile organic compounds measured in grass grown under field conditions with concentrations predicted by their previous laboratory work with a fugacity meter. The concentrations measured in the grass cultures agreed with results predicted by the mathematical model described by Tolls and McLachlan (1994).

12.3. SUMMARY AND CONCLUSIONS

As depicted in Figure 12-1 a set of complex relationships exist among reservoirs and between reservoirs and contemporary formation sources. The significance of reservoirs for human exposure is more dependent on their ability to affect the concentration of dioxin-like compounds in other media than on their size or net release rate. This Section, first summarizes and draws conclusions from the limited information available regarding the character and magnitude of reservoir sources. Second, it uses this information to discuss the implications of reservoir sources to human exposure.

12.3.1. Reservoir Sources

Noted below are some summary statements about soil reservoir sources

- Soil is likely to be the reservoir source with the greatest potential for release of CDD/CDFs to other environmental media, particularly to water. This is due in part to its relatively large mass of stored CDD/CDF, but more importantly, it is due to the existence of demonstrated transport mechanisms for intermedia exchange, i.e. soil erosion to surface waters and particle resuspension to air.
- The preliminary estimates of CDD/CDF runoff from urban areas to waterways is comparable to known industrial point source releases and runoff from agricultural areas to surface waters is over 100 times greater. It is unclear how much of the soil erosion and runoff represents recently deposited CDD/CDFs from primary sources or longer term accumulation. Much of the eroded soil comes from tilled agricultural lands which would include a mix of CDD/CDFs from various deposition times. The age of CDD/CDFs in urban runoff is less clear.
- Based on the limited information currently available (i.e., primarily fugacity modeling), volatilization of CDD/CDFs from soils is not believed to significantly alter ambient air concentrations. However, volatilization of PCBs from soil may be a significant process.
- Based on the limited information currently available, resuspension of soil may account for a small fraction (~4 percent) of CDD/CDF concentrations in air. This resuspended soil may, however, constitute a more significant portion of dry deposition.

Noted below are some summary statements about water reservoir sources:

- It is unclear if volatilization of CDD/CDFs from water can significantly alter air concentrations. For PCBs, however, the water-air exchange appears to

be significant and for some water bodies results in a net transfer from water to air.

- Water is the major media contributing CDD/CDF/PCBs to sediment. Note that most of the CDD/CDF in sediments originally came from soils. For specific water bodies, however, the CDD/CDFs/PCBs in sediments may have been dominated by local industrial discharges to water.

Noted below are some summary statements about sediment reservoir sources:

- It is important to distinguish between surface and deep sediments. Surface sediments are commonly resuspended and introduced back into the water and deep sediments generally do not interact with the water column. Surface sediments can contribute significantly to the CDD/CDF/PCB concentration in water; whereas deep sediments do not.
- There is little, if any, movement of dioxin-like compounds once they are buried in the bottom sediments. Bottom sediments may be considered as sinks.

Noted below are some summary statements about biota reservoir sources:

- The mass of CDD/CDF in vegetation at any given time is likely to be small compared to the mass in soil. Vegetation does play an important role in transferring CDD/CDF from the air to the soil via the decay of plant biomass.
- Release by volatilization from vegetation has been studied and modeled using the fugacity approach, and half-lives have been estimated. Based on these results, volatilization is not believed to be a significant mechanism for release of CDD/CDFs or PCBs except possibly during forest/brush fires.
- The mass of CDD/CDF in animals at any given time is likely to be small compared to the mass in soil. Similarly releases are small and occur primarily by excretion and decomposition of dead biomass.

12.3.2. Implications for Human Exposure

Although, the ability to make quantitative estimates of releases from reservoir sources is limited at present, it is reasonable to conclude that the contribution of reservoir sources to human exposure may be significant. As explained in Volume 2, the diet accounts for over 95% of human exposure. Although the size of the biota reservoir is small compared to the soil and sediment reservoirs, it is clearly the key contributor to human exposure. The potential contribution of the other reservoirs to human exposure is discussed below.

PCB Reservoir Releases: Since current sources of newly formed PCBs are most likely negligible, human exposure to the dioxin-like PCBs is thought to be derived almost completely from current releases of old PCBs stored in reservoir sources. Key pathways involve releases from both soils and sediments to both aquatic and terrestrial food chains. As discussed in Volume 2, one third of general population TEQ_{DFP} exposure is due to PCBs. Thus, at least one third of the overall risk to the general population from dioxin-like compounds comes from reservoir sources.

CDD/CDF Releases from Soil and Sediments to Water and Exposure via the Aquatic Pathway: The earlier discussion has shown that soils can have significant inputs to waterways via soil erosion and runoff. Similarly the sediment reservoir contributes significantly to CDD/CDF concentration in water. These releases appear to be greater than those from the primary sources included in the inventory. Dioxins in waterways bioaccumulate in fish and fish consumption causes human exposure. Fish consumption makes up about one third of the total general population CDD/CDF TEQ exposure. This suggests that a significant portion of the CDD/CDF TEQ exposure could be due to releases from the soil and sediment reservoir.

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

Table 12-1. Historical Production, Sales, and Usage Quantities for 2,4-D^a

Year	2,4-D, acid			2,4-D, esters and salts (as reported)		
	Production Volume (metric tons)	Sales Volume (metric tons)	Domestic Usage/ Disappearance (metric tons)	Production Volume (metric tons)	Sales Volume (metric tons)	Domestic Usage/ Disappearance (metric tons)
1994/95	--	--	21,800-26,300 ⁱ			
1993	--	--	16,800-20,400 ^c	--	--	
1992	--	--	16,800-20,400 ^c	--	--	
1991	--	--	18,100-29,500 ^d	--	--	
1990	--	--	18,100-29,500 ^d	--	--	
1989	--	--	18,100-29,500 ^e	--	--	
1988	--	--	23,600-30,400 ^f	--	--	
1987	--	--	23,600-30,400 ^g	--	--	
1986	--	--		8,618	12,150	
1985	--	--		--	0	
1984	--	--		--	0	
1983	--	--		7,702	8,234	
1982	--	--		8,762	8,400	
1981	5,859	3,275		8,987	8,002	
1980	6,164	3,137		11,313	11,147	
1979	5,763	6,187		11,874	13,453	
1978	--	--		8,958	9,256	
1977	--	--		12,552	10,196	
1976	--	--	17,418 ^b	10,913	7,813	
1975	--	--		16,134	13,414	
1974	--	--		6,558	5,991	
1973	--	--		13,400	13,698	
1972	24,948 ^b	--	21,772 ^b	10,192	10,899	
1971	--	5,619	15,700 ^b	--	18,654	
1970	19,766	7,159		--	19,920	
1969	21,354	8,521		25,854	20,891	
1968	35,953	10,352		42,690	30,164	
1967	34,990	15,432		37,988	29,300	
1966	30,927	12,710	28,985 ^h	32,895	25,075	
1965	28,721	11,816	22,906 ^h	28,740	21,454	
1964	24,364	11,343	19,958 ^h	24,660	18,263	

Table 12-1. Historical Production, Sales, and Usage Quantities for 2,4-D^a (Continued)

Year	2,4-D, acid			2,4-D, esters and salts (as reported)		
	Production Volume (metric tons)	Sales Volume (metric tons)	Domestic Usage/ Disappearance (metric tons)	Production Volume (metric tons)	Sales Volume (metric tons)	Domestic Usage/ Disappearance (metric tons)
1963	21,007	9,446	15,059 ^h	20,178	16,333	
1962	19,503	7,716	16,284 ^h	16,831	13,075	
1961	19,682	7,591	14,107 ^h	16,683	12,533	
1960	16,413	--	14,107 ^h	15,436	13,661	
1959	13,282	7,240	15,468 ^h	12,438	7,070	
1958	14,036	6,234	9,662 ^h	11,295	5,649	
1957	15,536	6,871		12,392	7,125	
1956	13,079	6,465		9,635	7,294	
1955	15,656	5,924		13,390	8,121	
1954	--	4,838		10,268	6,886	
1953	11,761	--		10,733	8,855	
1952	13,933	--		11,358	9,637	
1951	--	--		--	--	
1950	6,421	4,301		5,274	3,219	
1949	6,852	2,991		5,829	3,211	
1948	9,929	4,152		2,458	1,598	
1947	2,553	2,320		1,468	1,108	
1946	2,479	2,330		515	81	
1945	416	286		--	--	

"--" = Not reported to avoid disclosure of proprietary data.

^a All values from the U.S. International Trade Commission's (USITC) annual report series entitled Synthetic Organic Chemicals - United States Production and Sales unless footnoted otherwise (USITC, 1946-1994).

^b U.S. EPA (1975).

^c U.S. EPA (1994b).

^d U.S. EPA (1992f).

^e U.S. EPA (1991h).

^f U.S. EPA (1990e).

^g U.S. EPA (1988c).

^h USDA (1970).

ⁱ U.S. EPA (1997e).

Table 12-2. Historical Production, Sales, and Usage Quantities 2,4,5-T^a

Year	2,4,5-T, acid			2,4,5-T, esters and salts (as reported)		
	Production Volume (metric tons)	Sales Volume (metric tons)	Domestic Usage/ Disappearance (metric tons)	Production Volume (metric tons)	Sales Volume (metric tons)	Domestic Usage/ Disappearance (metric tons)
1993	--	--		--	--	
1992	--	--		--	--	
1991	--	--		--	--	
1990	--	--		--	--	
1989	--	--		--	--	
1988	--	--		--	--	
1987	--	--		--	--	
1986	--	--		--	--	
1985	--	--		--	--	
1984	--	--		--	--	
1983	--	--		--	--	
1982	--	--		--	--	
1981	--	--		--	--	
1980	--	--	900 ^f	--	--	
1979	3,200-4,100 ^b	--		--	--	
1978	--	--	3,200 ^h	--	--	
1977	--	--	4,100 ^b	--	--	
1976	--	--		--	--	
1975	--	--	3,200 ^h	--	--	
1974	--	--	900 ^c	--	--	
1973	--	--		--	--	
1972	--	--		--	--	
1971	--	--	694 ^d	--	1,675	
1970	--	--	3,200 ^h	5,595	3,272	
1969	2,268	--		5,273	2,576	
1968	7,951	1,329	~ 7,000 ^{e,g}	19,297	15,021	
1967	6,601	757	~ 7,000 ^{e,g}	12,333	11,657	
1966	7,026	2,312	7,756 ^e	8,191	4,553	
1965	5,262	--	3,266 ^e	6,131	5,977	
1964	5,186	1,691	4,037 ^e	5,880	3,128	
1963	4,123	1,928	3,266 ^e	4,543	2,585	

Table 12-2. Historical Production, Sales, and Usage Quantities 2,4,5-T^a (continued)

Year	2,4,5-T, acid			2,4,5-T, esters and salts (as reported)		
	Production Volume (metric tons)	Sales Volume (metric tons)	Domestic Usage/ Disappearance (metric tons)	Production Volume (metric tons)	Sales Volume (metric tons)	Domestic Usage/ Disappearance (metric tons)
1962	3,796	1,021	3,674 ^e	4,765	2,543	
1961	3,134	1,196	2,449 ^e	3,536	2,372	
1960	2,874	--	2,676 ^e	3,594	1,891	
1959	2,516	1,039	2,495 ^e	3,644	1,843	
1958	1,668	692	1,724 ^e	2,372	1,151	
1957	2,419	--		3,098	1,337	
1956	2,345	816		3,196	1,473	
1955	1,327	662	1,300 ^h	1,720	1,077	
1954	1,223	639		1,761	615	
1953	2,395	--		2,443	1,817	
1952	1,583	--		1,423	569	
1951	--	--	1,100 ^h	--	--	
1950	852	297		--	--	
1949	--	--		--	--	
1948	--	--		--	--	
1947	--	--		--	--	
1946	--	--		--	--	
1945	--	--		--	--	

"--" = Not reported to avoid disclosure of proprietary data.

^a All values from the U.S. International Trade Commission's annual report series entitled Synthetic Organic Chemicals - United States Production and Sales (U.S. ITC, 1946-1994) unless footnoted otherwise.

^b Federal Register (1979).

^c U.S. EPA (1977).

^d USDA (1971); reflects farm usage only.

^e USDA (1970); values include military shipments abroad.

^f Esposito et al. (1980).

^g Kearney et al. (1973) reports slightly lower domestic consumption for the years 1967 and 1968 than for 1966.

^h Thomas and Spiro (1995).

Table 12-3. CDD/CDF Concentrations in Recent Sample of 2,4,5-T

Congener/Congener Group	2,4,5-T Sample ($\mu\text{g/kg}$)
2,3,7,8-TCDD	1.69
1,2,3,7,8-PeCDD	0.412
1,2,3,4,7,8-HxCDD	0.465
1,2,3,6,7,8-HxCDD	2.28
1,2,3,7,8,9-HxCDD	1.35
1,2,3,4,6,7,8-HpCDD	18.1
OCDD	33.9
2,3,7,8-TCDF	0.087
1,2,3,7,8-PeCDF	0.102
2,3,4,7,8-PeCDF	0.183
1,2,3,4,7,8-HxCDF	1.72
1,2,3,6,7,8-HxCDF	0.356
1,2,3,7,8,9-HxCDF	ND (0.012)
2,3,4,6,7,8-HxCDF	0.126
1,2,3,4,6,7,8-HpCDF	2.90
1,2,3,4,7,8,9-HpCDF	0.103
OCDF	3.01
Total 2,3,7,8-CDD*	58.2
Total 2,3,7,8-CDF*	8.59
Total I-TEQ _{DF} *	2.88
Total TEQ _{DF} -WHO ₉₈ *	3.26
Total TCDD	NR
Total PeCDD	NR
Total HxCDD	NR
Total HpCDD	NR
Total OCDD	NR
Total TCDF	NR
Total PeCDF	NR
Total HxCDF	NR
Total HpCDF	NR
Total OCDF	NR
Total CDD/CDF	NR

ND = Nondetected; value in parenthesis is the detection limit.

NR = Not reported.

* = Calculation assuming not detected values are zero.

$\mu\text{g/kg}$ = micrograms per kilogram

Source: Schechter et al. (1997)

Table 12-4. PCB 138 Fluxes Predicted by Harner et al. (1995)

Year	Concentration in Air (pg/m ³)	Fugacity in Air (Pascals x 10 ⁻⁹)	Fugacity in Soil (Pascals x 10 ⁻⁹)	Concentration in Soil (ng/g)	Net Flux/Direction
1950	48	0.24	1.1	--	air → soil (444 kg/yr)
1965	280	1.5	12	--	air → soil (1,000 kg/yr)
1975	--	--	16	--	
1980	49	--	--	--	soil → air (820 kg/yr)
1994	6	--	8.3	--	soil → air (700 kg/yr)

-- = Not reported.

pg/m³ = picograms per cubic meter
ng/g = nanograms per gram
kg/yr = kilograms per year

Source: Harner et al. (1995).

Table 12-5. Summary of Flux Calculations for Total PCBs in Green Bay, 1989

Date	Site	Flux ^{a,b,c} (ng/m ² -day)
6-4	18	40
6-5	18	40
6-6	10	95
6-7	10	155
6-10	4	325
6-11	10	13
7-28	18	330
7-29	21	70
7-30	14	225
7-31	10	90
8-1	4	800
10-21	14	555
10-22	10	1,300
10-23	4	30

^a Numbers indicate water to air transfer of total PCBs.

^b Represents the sum of individual PCB congener fluxes.

^c Described as "daily" fluxes because they correspond to air samples collected over 5-10 hours and water samples collected over ~ 1 hour.

mg/m²-day = nanograms per square meter per day

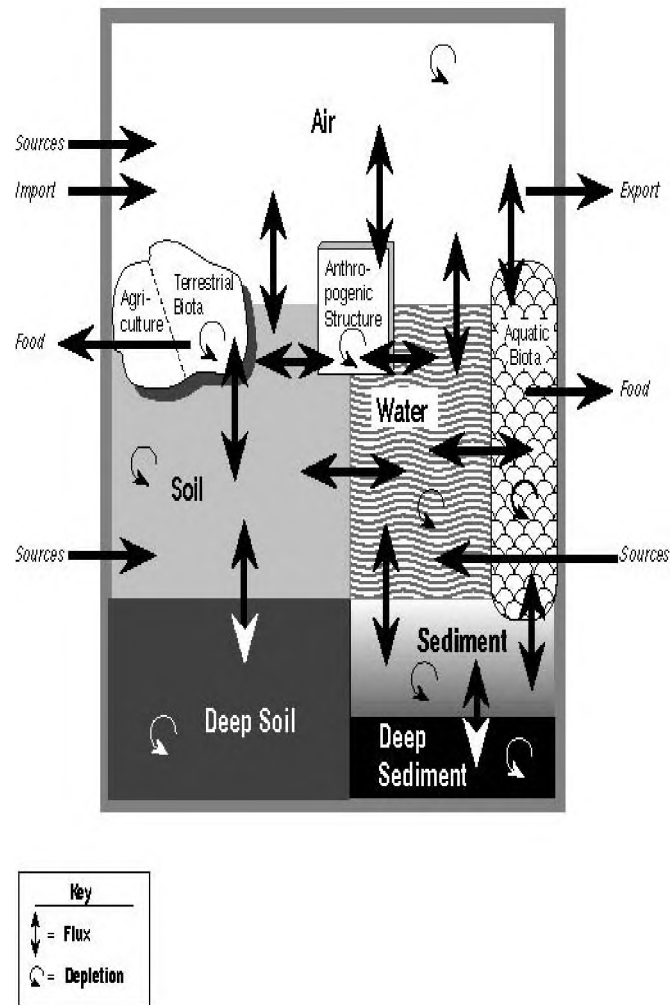
Source: Achman et al. (1993).

Table 12-6. Comparison of Estimated PCB Concentrations with Observed Values

Variable	Units	PCBs
Observed Concentration [C]		
Sediment	$\mu\text{g/g}$	0.23-1.04
Water	$\mu\text{g/m}^3$	< 20
Estimated [C] from Model Without Thermocline		
Sediment	$\mu\text{g/g}$	0.518
Water	$\mu\text{g/m}^3$	8.33
Amount in Sediment	kg	74.9
Amount in Water	kg	2.33
Total Mass	kg	77.2
Estimated [C] from Model with Thermocline		
Sediment	$\mu\text{g/g}$	0.527
Hypolimnion	$\mu\text{g/m}^3$	8.48
Epilimnion	$\mu\text{g/m}^3$	7.93
Amount in Sediment	kg	76.3
Amount in Hypo	kg	1.28
Amount in EPI	kg	1.02
Total Mass	kg	78.6

$\mu\text{g/g}$ = micrograms per gram
 $\mu\text{g/m}^3$ = micrograms per cubic meter
 kg = kilograms

Source: Ling et al. (1993).



Fluxes Among Dioxin Reservoirs

Figure 12-1. Fluxes Among Reservoirs