

## 12. RESERVOIR SOURCES OF CDDs/CDFs AND DIOXIN-LIKE PCBs

National CDD/CDF source inventories have been conducted in several nations, including the United Kingdom (U.K.), the Netherlands, Germany, Austria, and Sweden, to characterize emissions from various source categories and estimate annual CDD/CDF emissions to air (and sometimes other media). These inventories focused mainly on emissions from primary sources (i.e., emissions from the site or process where the CDDs/CDFs are formed).

The authors of these inventories (Rappe, 1991; Harrad and Jones, 1992b; Bremmer et al., 1994; Thomas and Spiro, 1995, 1996; Eduljee and Dyke, 1996; Jones and Alcock, 1996; Duarte-Davidson et al., 1997) indicated that the annual estimates of releases to air provided in these inventories may be underestimates of actual emissions for several reasons. First, on an empirical basis, estimates of the amounts of CDDs/CDFs deposited annually from the atmosphere were greater than the estimates of annual CDD/CDF emissions to the atmosphere. Second, because the emission test data were limited, the inventories may underestimate releases from known sources or may not identify all primary sources. Third, the investigators were not able to reliably quantify emissions from potential reservoir (secondary) sources, including volatilization of CDDs/CDFs from PCP-treated wood, volatilization from soil, and resuspension of soil particles. Relatively little research of either a monitoring or a theoretical nature has been performed to identify reservoir sources and to quantify the magnitude of current or potential future releases from these sources.

This chapter presents background information on the major reservoir sources of CDDs/CDFs and PCBs, including the potential magnitude (mass) of CDDs/CDFs and PCBs in each reservoir, the chemical/physical mechanisms responsible for releases of these compounds, and estimates of potential annual releases from each reservoir, if such estimates are feasible. Annual releases from reservoir sources are not counted in the quantitative inventory of dioxin sources because such releases are considered as recirculation of “old” and previously formed dioxin.

### 12.1. POTENTIAL RESERVOIRS

Chapters 2 through 11 discuss both known and suspected sources of newly formed dioxin-like compound releases to the environment in the United States. Once released into the open environment, CDDs, CDFs, and PCBs partition to air, soils, water, sediments, and biota

1 according to both the nature of the release and the contaminant’s chemical and physical  
2 properties.

3 For this analysis, reservoirs are defined as materials or places that contain previously  
4 formed CDDs/CDFs or dioxin-like PCBs and have the potential for redistribution and circulation  
5 of these compounds into the environment. Potential reservoirs include soils, sediments, biota,  
6 water, and some anthropogenic materials. Reservoirs become sources when they release dioxin-  
7 like compounds to the circulating environment over a defined time and space. Like other  
8 sources, they would not include purely intermediate products or materials properly disposed in a  
9 secure landfill. Reservoir sources are not included in the quantitative inventory of contemporary  
10 sources because they do not involve original releases but rather the recirculation of past releases.  
11 They can, however, contribute to human exposure and, therefore, are important to consider.

12 The rate of movement from one environmental medium to another is termed “flux,” and  
13 it refers to the direction and magnitude of flow and exchange over a reference time period and  
14 space. Figure 12-1 presents a conceptual diagram of flux and exchange of dioxin-like  
15 compounds to multiple environmental compartments, including the principal environmental  
16 reservoirs—soil, water, air, sediment, and biota. This dynamic system consists of fluxes in and  
17 out of the atmosphere as well as other exchanges between reservoirs and the atmosphere.  
18 Movement between media can be induced by volatilization, wet and dry atmospheric particle  
19 and vapor deposition, adsorption, erosion and runoff, resuspension of soils into air, and  
20 resuspension of sediments into water.

## 21 **12.2. CHARACTERIZATION OF RESERVOIR SOURCES**

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

1 **12.2.1. Soil**

2 **12.2.1.1. Potential Mass of Dioxin-Like Compounds Present**

3 In estimating burdens for the U.K., Harrad and Jones (1992b) and Duarte-Davidson et al.  
4 (1997) assumed that the majority of CDDs/CDFs in soil is present in the top 5 cm (except  
5 possibly in cropland, where they may be present at greater depths due to plowing) and that the  
6 soil density is 1,000 kg/m<sup>3</sup>. Coupling these assumptions with the rural and urban U.S. surface  
7 areas and TEQ concentrations yields soil burden estimates of 1,350 kg TEQ<sub>DF</sub>-WHO<sub>98</sub> (1,530 kg  
8 I-TEQ<sub>DF</sub>) in rural soils and 220 kg TEQ<sub>DF</sub>-WHO<sub>98</sub> (250 kg I-TEQ<sub>DF</sub>) in urban soils in the United  
9 States.

10 Higher concentrations of CDDs/CDFs than those presented above for background urban  
11 and rural soils may be present in soils underlain by municipal and industrial waste and in soils at  
12 contaminated industrial sites. The lack of comprehensive data on CDD/CDF concentrations in  
13 these soils, as well as the lack of data on the mass of these soils nationwide, precludes estimating  
14 total national soil burdens for these soils at present. Higher concentrations may also be present  
15 in the soils of areas that have been treated with pesticides contaminated with CDDs/CDFs.  
16 Because of the lack of data, it is not possible to estimate current soil burdens of CDDs/CDFs  
17 associated with past pesticide use; however, estimates can be made of the total mass of  
18 CDD/CDF TEQs that have been applied to soil from past use of the pesticides 2,4-  
19 dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T).

20 2,4-D and its salts and esters are widely used in agricultural and nonagricultural settings  
21 in the United States as post-emergence herbicides for control of broadleaf weeds and brush.  
22 Commercial production in the United States started in 1944 (Esposito et al., 1980) and 2,4-D has  
23 been in large-scale, large-volume commercial use for many years (U.S. EPA, 1975). In terms of  
24 annual volume, 2,4-D ranks among the top 10 pesticides used in the United States (U.S. EPA,  
25 1994b, 1997e). Table 12-1 presents a compilation of domestic production, sales, and usage  
26 volumes for 2,4-D and its salts and esters.

27 As described in Section 8.3.8, CDDs/CDFs were detected in several formulations of 2,4-  
28 D and its derivatives during analyses performed to comply with EPA's 1987 Data Call-In (DCI)  
29 for CDDs/CDFs. Although the analytical results of these tests indicated that CDDs/CDFs were  
30 seldom above the regulatory limits of quantification (LOQ) established by EPA for the DCI,  
31 several registrants detected and quantified CDDs/CDFs at lower LOQs. The results of these  
32 tests are summarized in Table 8-25. The average TEQ in these tests was 1.1 µg TEQ<sub>DF</sub>-

1 WHO<sub>98</sub>/kg (0.7 µg I-TEQ<sub>DF</sub>/kg). Schechter et al. (1997) reported similar concentrations in 2,4-D  
2 samples manufactured in Europe and Russia; lower levels were observed in U.S. products. The  
3 results of Schechter et al. (1997) are presented in Table 8-27.

4 If it is assumed that the EPA DCI results are typical of CDD/CDF levels in 2,4-D  
5 pesticides over the past 20 yr and that the average annual use of these pesticides in the United  
6 States has been approximately 25,000 metric tons, then the estimated CDD/CDF TEQ released  
7 to the environment from 2,4-D use during the period 1975 to 1995 was 550 g TEQ<sub>DF</sub>-WHO<sub>98</sub>  
8 (350 g I-TEQ<sub>DF</sub>).

9 2,4,5-T was used in the United States for a variety of herbicidal applications until the late  
10 1970s to early 1980s. The major use of 2,4,5-T (about 41% of annual usage) was for control of  
11 woody and herbaceous weed pests on rights-of-way. The other major herbicidal uses were  
12 forestry (28% of usage), rangeland (20% of usage), and pasture (5% of usage). Uses of 2,4,5-T  
13 for home or recreation areas and for lakes, ponds, and ditches were suspended by EPA in 1970;  
14 rights-of-way, forestry, and pasture uses were suspended by EPA in 1979; and all uses were  
15 canceled in 1983.

16 Table 12-2 presents a compilation of domestic production, sales, and usage volumes for  
17 2,4,5-T and its salts and esters. As shown in Table 12-2, production and use of 2,4,5-T generally  
18 increased each year following its introduction in the 1940s until the late 1960s. Production,  
19 sales, and usage information for the 1970s are generally not available but are reported to have  
20 steadily declined during that decade (Federal Register, 1979; Esposito et al., 1980).

21 Some information is available on the 2,3,7,8-TCDD content of 2,4,5-T, but little  
22 information is available on the concentrations of the other 2,3,7,8-substituted CDD/CDFs that  
23 may have been present. Plimmer (1980) reported that 2,3,7,8-TCDD concentrations as high as  
24 70,000 µg/kg were detected in 2,4,5-T during the late 1950s. In a study of 42 samples of 2,4,5-T  
25 manufactured before 1970, Woolson et al. (1972) found 500 to 10,000 µg/kg of TCDDs in 7  
26 samples, and another 13 samples contained 10,000 to 100,000 µg/kg of TCDDs. HxCDDs were  
27 found in 4 samples at levels between 500 and 10,000 µg/kg and in 1 sample at a concentration  
28 exceeding 10,000 µg/kg but less than 100,000 µg/kg. The detection limit in the study was 500  
29 µg/kg.

30 The average 2,3,7,8-TCDD concentration in 200 samples of Agent Orange, a defoliant  
31 containing about a 50/50 mixture of the butyl esters of 2,4,5-T and 2,4-D that was used by the  
32 U.S. Air Force in Vietnam, was 1,910 µg/kg (Kearney et al., 1973). Of the 200 samples, 64

1 (32%) contained more than 500 µg/kg of 2,3,7,8-TCDD, with the highest concentration reported  
2 to be 47,000 µg/kg. Storherr et al. (1971) reported detecting 2,3,7,8-TCDD at concentrations  
3 ranging from 100 to 55,000 µg/kg in five samples of 2,4,5-T. Kearney et al. (1973) reported that  
4 production samples of 2,4,5-T obtained from the three principal 2,4,5-T manufacturers in 1971  
5 contained 2,3,7,8-TCDD at levels of <100 µg/kg, 100 µg/kg, and 2,300 µg/kg.

6 A 1975 survey of 10 lots of a commercial formulation containing 2,4,5-T showed 2,3,7,8-  
7 TCDD concentrations ranging from 10 to 40 µg/kg (Dow Chemical Co., undated). Analyses by  
8 EPA of 16 technical-grade 2,4,5-T samples from five different manufacturers revealed 2,3,7,8-  
9 TCDD contents ranging from <10 to 25 µg/kg (Federal Register, 1979). Schecter et al. (1997)  
10 reported the analytical results of one sample of 2,4,5-T purchased from Sigma Chemical Co.  
11 (product number T-5785, lot number 16H3625). The results, presented in Table 12-3, indicate a  
12 total TEQ<sub>DF</sub>-WHO<sub>98</sub> concentration of 3.26 µg/kg (2.88 µg I-TEQ<sub>DF</sub>/kg).

13 Because of the wide variability (three orders of magnitude) in the limited available  
14 information on the 2,3,7,8-TCDD content of 2,4,5-T (particularly the 2,4,5-T used in the 1950s)  
15 and incomplete information on domestic usage, it is difficult to reliably estimate the amount of  
16 2,3,7,8-TCDD that was released to the U.S. environment as a result of 2,4,5-T use. A very  
17 uncertain estimate can be made using the following assumptions: (1) the average annual  
18 consumptions during the 1950s, 1960s, and 1970s were 2,000, 4,000, and 1,500 metric tons/yr,  
19 respectively; and (2) the average 2,3,7,8-TCDD concentrations in 2,4,5-T used over these three  
20 decades were 10,000 µg/kg in the 1950s, 4,000 µg/kg in the 1960s, and 100 µg/kg in the 1970s.  
21 Based on these assumptions, the very uncertain estimate of 2,3,7,8-TCDD input from 2,4,5-T use  
22 over the period 1950 to 1979 is 36,000 g.

23 Another contributing source to the soil reservoir is CDD/CDF in sewage sludge applied  
24 to land (i.e., surface disposal or land farming), estimated to have been 75 g TEQ<sub>DF</sub>-WHO<sub>98</sub> (103  
25 g I-TEQ<sub>DF</sub>) in 1995 (see Section 8.4.1 for details). If this same amount of TEQ had been applied  
26 each year during the period 1975 to 1995, the total amount applied would have been 1,500 g  
27 TEQ<sub>DF</sub>-WHO<sub>98</sub> (2,000 g I-TEQ<sub>DF</sub>).

#### 28 29 **12.2.1.2. Mechanisms Responsible for Releases from Surface Soils**

30 Atmospheric deposition is believed to be the current primary source of dioxin-like  
31 compounds in surface soil. CDDs/CDFs and PCBs are highly lipid soluble and have low  
32 volatility, and they tend to partition to soil rather than into air or water. Once present in or on

1 soils, physical/chemical and biological mechanisms (photolysis and biodegradation) can slowly  
2 alter the composition and amount of compound present. Studies indicate that the dioxin-like  
3 compounds (particularly the more highly chlorinated CDDs/CDFs) exhibit little downward  
4 mobility after they are deposited in or on soil (Puri et al. 1989; Freeman and Schroy, 1985;  
5 Orazio et al., 1992; Paustenbach et al., 1992). However, remobilization of the compounds to the  
6 atmosphere is possible through volatilization and resuspension of soil particles.

7 Young (1983) conducted field studies on the persistence and movement of 2,3,7,8-TCDD  
8 during 1973 to 1979 on a military test area that had been aerially sprayed with 73,000 kg of  
9 2,4,5-T during 1962 to 1970. TCDD levels of 10 to 1,500 ng/kg were found in the top 15 cm of  
10 soil 14 yr after the last application of herbicide at the site. Although actual data were not  
11 available on the amount of 2,3,7,8-TCDD originally applied as a contaminant of the 2,4,5-T, best  
12 estimates indicated that less than 1% of the applied 2,3,7,8-TCDD remained in the soil after  
13 14 yr. Young suggested that photodegradation at the time of and immediately after aerial  
14 application was responsible for most of the disappearance; however, once incorporated into the  
15 soil, the data indicated a half-life of 10 to 12 yr. Similarly, Paustenbach et al. (1992) concluded  
16 that the half-life of 2,3,7,8-TCDD in soils at the surface might be 9 to 15 yr and the half-life  
17 below the surface could be 25 to 100 yr.

18 Ayris and Harrad (1997) studied the mechanisms affecting volatilization fluxes of several  
19 PCB congeners (PCB numbers 28, 52, 101, 138, and 180) from soil and found positive  
20 correlations between flux and soil temperature, soil moisture content, and soil PCB  
21 concentration. For PCBs, secondary releases from soils (primarily via volatilization) are  
22 believed to currently exceed primary emissions in the U.K. (Harner et al., 1995; Jones and  
23 Alcock, 1996). Lee et al. (1998) quantified PCBs in air samples taken every 6 hr over a 7-day  
24 period in the summer at a rural site in England and found a strong correlation between air  
25 temperature and PCB congener concentrations. The concentrations followed a clear diurnal  
26 cycle, thus providing some evidence that rapid, temperature-controlled soil-to-air exchange of  
27 PCBs influences air concentrations and enables regional/global scale cycling of these  
28 compounds.

29 CDDs/CDFs and PCBs sorbed to soil and urban dust particles can also be moved from  
30 the terrestrial environment to the aquatic environment via stormwater runoff/erosion. Results of  
31 recent research indicate that, for at least some water bodies, erosion/stormwater runoff is  
32 currently the dominant mechanism for CDD/CDF input. Smith et al. (1995) analyzed CDD/CDF

1 concentrations in sediment cores, air, precipitation, soil, and stormwater runoff in an effort to  
2 determine the contributing sources of these compounds to the lower Hudson River. The mass  
3 balance estimates developed from these data for 1990 to 1993 are stormwater runoff entering  
4 tributaries (76% of total CDD/CDF input), anthropogenic wastes (19%), atmospheric deposition  
5 (4%), and shoreline erosion (less than 1%). The authors projected the percent contribution of  
6 these same sources for 1970 as anthropogenic wastes (70%), stormwater runoff into tributaries  
7 (15%), atmospheric deposition (15%), and shoreline erosion (0.1%).

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

18 Paustenbach et al. (1996) and Mathur et al. (1997) reported that stormwater runoff from  
19 15 sites in the San Francisco area contained CDD/CDF TEQ at levels ranging from 0.01 to 65 pg  
20 I-TEQ<sub>DF</sub>/L; most samples contained less than 15 pg I-TEQ<sub>DF</sub>/L. The sites differed widely in land  
21 use; the highest levels measured were obtained from an urban but nonindustrialized area. A  
22 distinct variability was noted in the results obtained at the same sampling location during  
23 different rain events. The profiles of CDDs/CDFs in the urban stormwater samples were similar,  
24 particularly in samples collected at the onset of rain events. Stowe (1996) reported similar  
25 findings from analyses of sediments from three stormwater basins collecting runoff from a  
26 military base, a city street, and parking lots.

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

1 **12.2.1.3. Estimated Annual Releases from Soil to Water**

2 Nonpoint sources of CDDs/CDFs to waterways include stormwater runoff from urban  
3 areas and soil erosion in rural areas during storms. Approaches for estimating national loadings  
4 to water for both of these sources are described below. The estimate derived below for the  
5 potential annual national loading of CDDs/CDFs in urban runoff to waterways is uncertain, but it  
6 suggests that the loading may be comparable to the contribution from known industrial point  
7 sources (at least 20 g I-TEQ<sub>DF</sub> in 1995). Similarly, the estimate derived below for the potential  
8 annual national loading of CDDs/CDFs in rural eroded soils to waterways is uncertain, but it has  
9 a stronger analytical base than does the urban runoff estimate. This loading estimate, however,  
10 is significantly higher than the contribution from known industrial point sources.

11 **Urban Runoff.** Few data on CDD/CDF concentrations in urban runoff have been  
12 reported. The most recent and largest data sets were reported in studies conducted in the San  
13 Francisco Bay and Santa Monica Bay regions (Mathur et al., 1997; Fisher et al., 1998). These  
14 studies found a wide range of CDD/CDF levels in samples of stormwater runoff from 23 sites,  
15 varying from 0.01 to 83 pg I-TEQ<sub>DF</sub>/L. The wide variability and limited geographic coverage of  
16 these data preclude derivation of a national emission estimate at this time. However, by making  
17 a number of assumptions, a preliminary estimate of the potential CDD/CDF magnitude from this  
18 source can be made.

19 In order to estimate the amount of rainfall in urbanized areas of the conterminous United  
20 States, a Geographic Information System (GIS) analysis was performed to determine the total  
21 area of every U.S. Census urbanized area and the 30-yr annual average rainfall for each of those  
22 areas and to calculate the product of the total areas of urbanized areas with the annual average  
23 rainfall (Lockheed Martin Corp., 1998). This approach yields an estimate of  $1.9 \times 10^{14}$  L/yr. If  
24 it is assumed that urban runoff in the United States averages 1 pg TEQ<sub>DF</sub>-WHO<sub>98</sub>/L (1 pg I-  
25 TEQ<sub>DF</sub>/L) (i.e., approximately the midpoint of the range reported by Mathur et al., 1997, and  
26 Fisher et al., 1998), this source could contribute a total of 190 g TEQ<sub>DF</sub>-WHO<sub>98</sub> or I-TEQ<sub>DF</sub>/yr to  
27 U.S. waterways. No data were available to make similar estimates for PCBs.

28 A similar analysis was conducted using historical precipitation data from the National  
29 Oceanic and Atmospheric Administration (NOAA, 2004) and metropolitan/urban area statistics  
30 from the 1990 and 2000 census. The 30-year annual average rainfall for each state was  
31 calculated for 1987, 1995, and 2000. An approximation of the urban area for each state was  
32 estimated by summing the acreage for each metropolitan area identified in the 1990 census.

1 Assuming that the amount of land classified as urban did not change significantly from 1987 to  
2 1990, the urban areas for each state in 1990 were assumed to be equal to those in 1987.  
3 Similarly, an approximation for urban area for each state was estimated by summing the urban  
4 area acreage available from the 2000 census. An approximation of the 1995 urban area for each  
5 State was estimated by taking the average of the 1990 and 2000 estimates. Multiplying the 30-  
6 year average rainfall by the urban area for each state and summing the results provides an  
7 estimated amount of urban runoff for the conterminous United States. The urban runoff was  
8  $1.24 \times 10^{14}$ ,  $1.33 \times 10^{14}$ , and  $1.42 \times 10^{14}$  L/year for 1987, 1995, and 2000, respectively.  
9 Applying the emission factors generated above, urban runoff contributed 124, 133, and 142 g I-  
10  $\text{TEQ}_{\text{DF}}$  or  $\text{TEQ}_{\text{DF}}\text{-WHO}_{98}$  to U.S. waterways in 1987, 1995, and 2000, respectively. These  
11 numbers are in agreement with the estimate developed using Lockheed Martin (1998) data.

12 **Rural Soil Erosion.** Using acreage and erosion factors for cropland provided in the  
13 2001 Annual National Resources Inventory (USDA, 2003), 1.36, 1.07, 0.96, and 0.91 billion  
14 metric tons of soil and rill erosion were generated in 1987, 1992, 1997, and 2001, respectively.  
15 Likewise, using acreage data for rangeland from USDA (2003) and a soil and rill erosion factor  
16 of 4.2 tons/acre/year (USDA, 1995), approximately 1.55 billion metric tons of soil and rill  
17 erosion were generated in 1987, 1992, 1997, and 2001. For purposes of estimating values for the  
18 reference years 1995 and 2000, it is assumed that the 1995 erosion estimate will be the average  
19 of soil and rill erosion estimates developed for 1992 and 1997, and that the 2001 numbers will  
20 approximate those generated in 2000. The total amount of eroded soil entering waterways is  
21 greater than this value, because this value does not include soil erosion from construction areas,  
22 forests, and other non-crop and non-rangelands. The data summarized in the U.S. EPA, 2000b  
23 report suggest that typical concentrations of CDDs/CDFs in soils in rural areas is about 2.8 ng  
24  $\text{TEQ}_{\text{DF}}\text{-WHO}_{98}/\text{kg}$ . It is not known how well this estimate represents eroded soil from cropland  
25 and rangeland. If these soils contain an average of 1 ng  $\text{TEQ}_{\text{DF}}/\text{kg}$  (i.e., a lower value than the  
26 background value for all types of rural soil), they would contribute 2,900, 2,600, and 2,500 g  
27  $\text{TEQ}_{\text{DF}}\text{-WHO}_{98}$  to the Nation's waterways in 1987, 1995, and 2000, respectively. Given the  
28 uncertainties in both the amount of eroded soil and dioxin levels, these estimates are considered  
29 preliminary (i.e., category D). As with urban runoff, no data were available to make similar  
30 estimates for PCBs.

1 **12.2.1.4. *Estimated Annual Releases from Soil to Air***

2 No quantitative estimates of the mass of dioxin-like compounds that may be released to  
3 the atmosphere annually from U.S. soils have been published in the literature and none are  
4 developed in this report. As noted above, the vapor flux of these compounds from soil to air is  
5 dependent on the soil and air concentrations of dioxin-like compounds and the temperature,  
6 moisture content, and organic carbon content of the soil. Most of these parameters are not  
7 characterized well enough for the United States as a whole to enable a reliable estimate to be  
8 made at present. Particle flux is dependent on many factors, including wind speed, vegetative  
9 cover, activity level, particle size, soil type/conditions, moisture content, and particle density.  
10 Through use of models and various assumptions, Kao and Venkataraman (1995) estimated the  
11 fraction of ambient air CDD/CDF concentrations in the upper midwestern section of the United  
12 States that may be the result of atmospheric re-entrainment of soil particles. Similarly, through  
13 use of models and various assumptions, Jones and Alcock (1996) and Harner et al. (1995)  
14 reached tentative conclusions about the relative importance of volatilization of dioxin-like  
15 compounds from soils in the U.K.

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

26 The fraction of ambient air concentration of CDDs/CDFs that results from soil  
27 re-entrainment was established on the basis of the contribution of crustal sources to the ambient  
28 aerosol. Data on typical crustal soil concentrations in air (15 to 50  $\mu\text{g}/\text{m}^3$  for rural areas and 5 to  
29 25  $\mu\text{g}/\text{m}^3$  for urban areas) were combined with data on the average concentrations of  
30 CDDs/CDFs in soils (73 ng/kg for rural, 2,075 ng/kg for urban, and 8,314 ng/kg for industrial  
31 soils) published by Birmingham (1990) for Ontario, Canada, and several U.S. midwestern states.  
32 This analysis estimated the concentrations of CDDs/CDFs in the ambient aerosol that originate

1 from soils to be  $1 \times 10^{-3}$  to  $4 \times 10^{-3}$  pg/m<sup>3</sup> in rural areas and 0.01 to 0.05 pg/m<sup>3</sup> in urban areas.  
2 These particulate dioxin concentrations were compared to average total particulate dioxin levels  
3 of 1.36 pg/m<sup>3</sup> in Eitzer and Hites (1989) to arrive at the conclusion that soil re-entrainment could  
4 account for only 1 to 4% of the particulate dioxins in the atmosphere in urban areas and 0.1 to  
5 0.3% of those in rural regions (Kao and Venkataraman, 1995).

6 This information on the size distribution of ambient aerosols and relative CDD/CDF  
7 concentrations in different particle size fractions was integrated with particle size deposition  
8 velocities to estimate the relative contribution to the total mass deposition flux for small and  
9 large particle sizes. Even though re-entrained soil may constitute only a small fraction of the  
10 atmospheric levels of CDDs/CDFs, the contribution of dioxins in re-entrained surface soil to the  
11 total deposition flux could be significant because coarse particles dominate in dry deposition.  
12 Soil re-entrainment could possibly account for as much as 70 to 90% of the total dry deposition  
13 of CDDs/CDFs in urban areas and 20 to 40% in rural regions (Kao and Venkataraman, 1995).

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

29 From the fugacity quotient model, Jones and Alcock (1996) concluded that the less-  
30 chlorinated CDDs/CDFs may be close to soil-air equilibrium in the U.K., whereas for other  
31 congeners, soil is a sink rather than a source to the atmosphere. The authors reported that the  
32 equilibrium partitioning model predicted that 0.15 kg I-TEQ volatilizes annually from soil in the

1 U.K. However, they discounted this estimate and concluded that soil volatilization is unlikely to  
2 be a significant contributor to emissions. The likelihood that these estimates were high was  
3 attributed to the fact that assumptions were made that the concentrations of CDDs/CDFs in air  
4 were zero and the model does not consider the resistance of CDDs/CDFs to volatilize from soil.

5 Harner et al. (1995) developed a model to predict the long-term fate of PCBs in soils,  
6 with emphasis on soil-to-air exchanges. Using data on levels of PCBs in air, soil, and vegetation  
7 in the U.K., the investigators developed a mass balance model to simulate the fate of PCBs in  
8 U.K. soils from 1935 to 1994. Specifically, monitoring data and physical/chemical property data  
9 were compiled to calculate fugacities for PCB congeners 28, 52, 138, and 153. The model was  
10 designed to provide an order-of-magnitude level of accuracy, due in part to the inherent  
11 variability in the input data. The mass balance equations in the model included a bell-shaped  
12 function for rates of emissions of PCBs, with the maximum emission rate occurring in 1967.  
13 From these emissions rates, fluxes between air and soil over several decades were estimated.  
14 Table 12-4 summarizes the calculated fluxes.

15 During the 1960s and 1970s, levels of total PCBs in U.K. soils reached average levels of  
16 approximately 300  $\mu\text{g}/\text{kg}$  as a result of atmospheric deposition. Because of restrictions on PCB  
17 use during the last two decades, air concentrations have fallen, and the primary source to the  
18 atmosphere is now believed to be volatilization from soils. The mass balance model estimated a  
19 net flux of 700  $\text{kg}/\text{yr}$  of total PCBs from soils to the atmosphere in 1994. However, this estimate  
20 is presented with the caveat that the model tends to underestimate the rate of reduction of PCB  
21 concentrations in recent years, which could be attributed to other mechanisms such as  
22 biodegradation, photolysis, and other degradation processes.

## 23 24 **12.2.2. Water**

### 25 **12.2.2.1. *Potential Mass of Dioxin-Like Compounds Present***

26 The surface area of inland waters (including the Great Lakes) in the United States is  
27 about 359,000  $\text{km}^2$  (U.S. DOC, 1995a). Assuming that the mean depth of inland water is 10 m  
28 (Duarte-Davidson et al., 1997), the total inland water volume is approximately 3,600 billion  $\text{m}^3$ .  
29 No compilation of CDD/CDF measurements in inland surface waters is made for this report;  
30 however, if it is assumed that the “typical” value used by Duarte-Davidson et al. (1997) for  
31 rivers in the U.K., 38  $\text{pg I-TEQ}_{\text{DF}}/\text{m}^3$ , is representative of U.S. waters, then the burden is  
32 calculated to be 137  $\text{g I-TEQ}_{\text{DF}}$ .

#### 12.2.2.2. Mechanisms Responsible for Supply to and Releases from Water

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

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

The basic equation used to describe the rate of transfer across the interface is

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

where  $F$  is the flux ( $\text{mol}/\text{m}^2\text{-day}$ ),  $C_w$  ( $\text{mol}/\text{m}^3$ ) is the dissolved PCB concentration in the bulk water, and  $C^*$  ( $P/H$ ,  $\text{mol}/\text{m}^3$ ) is the air concentration expressed as a water concentration in equilibrium with the air. The variable  $P$  is the vapor-phase air concentration measured ( $\text{mol}/\text{m}^3$ ) 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 ( $\text{m}/\text{day}$ ). 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

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

$$1/K_{oi} = 1/k_w + RT/Hk_a \quad (12-2)$$

4  
5  
6  
7 where  $k_w$  is the water-side mass transfer coefficient (m/day) and  $k_a$  is the air-side mass transfer  
8 coefficient (m/day).  $H$  is Henry's Law constant,  $R$  is the universal gas constant ( $8.2057 \times 10^{-5}$   
9 atm-m<sup>3</sup>/mol K), and  $T$  is the absolute temperature, K.

10 Achman et al. (1993) and Hornbuckle et al. (1993) calculated the volatilization rates of  
11 PCBs from Green Bay on Lake Michigan on the basis of air and water samples simultaneously  
12 collected over a 14-day period above and below the air-water interphase and analyzed for 85  
13 PCB congeners. Air samples collected over nearby land were also analyzed for the 85 PCB  
14 congeners. The direction and magnitude of flux for each congener were then calculated using  
15 Henry's Law and meteorological and hydrological parameters in the "two-film" model (see eq  
16 12-1).

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

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

	<u>Water Body</u>	Total PCB volatilization rate (ng/m <sup>2</sup> -day)	<u>Reference</u>
1	Lake Superior	141	Baker and Eisenreich (1990)
2	Lake Michigan	240	Strachan and Eisenreich (1988)
3	Lake Superior	63	Strachan and Eisenreich (1988)
4	Siskiwit Lake	23	Swackhamer et al. (1988)
5	Lake Michigan	15	Swackhamer and Armstrong (1986)
6			
7			
8			

9 **12.2.3. Sediment**

10 **12.2.3.1. Potential Mass of Dioxin-Like Compounds Present**

11 EPA conducted congener-specific measurements of CDDs/CDFs in the sediments from  
 12 11 U.S. lakes located in areas relatively unimpacted by nearby industrial activity. The mean  
 13 TEQ concentration in the uppermost sediment layers from these 11 lakes is 5.3 ng TEQ<sub>DF</sub>-  
 14 WHO<sub>98</sub>/kg (5.3 ng I-TEQ<sub>DF</sub>/kg) dry weight. For most of the lakes, the uppermost layer  
 15 represents about 10 yr worth of sedimentation. CDD/CDF concentrations in lakes impacted by  
 16 industrial activity may have higher concentrations. For example, Duarte-Davidson et al. (1997)  
 17 reported a TEQ concentration of 54 ng I-TEQ<sub>DF</sub>/kg for urban sediments in the U.K.

18 As noted above, the surface area of inland waters in the United States is approximately  
 19 359,000 km<sup>2</sup> (U.S. DOC, 1995a). In their calculations of sediment burdens in the U.K., Duarte-  
 20 Davidson et al. (1997) assumed that (1) the sediment surface area equals the water surface area,  
 21 (2) the majority of CDDs/CDFs are located in the top 5 cm of sediment, and (3) that sediment  
 22 density is 0.13 g dry weight/cm<sup>3</sup>. Applying these assumptions to the water surface area and  
 23 background TEQ concentration for U.S. sediments yields a burden of at least 120 kg TEQ<sub>DF</sub>-  
 24 WHO<sub>98</sub> (120 kg I-TEQ<sub>DF</sub>).

26 **12.2.3.2. Mechanisms Responsible for Supply to and Releases from Sediment**

27 Because sediment is closely connected to the water column above it, evaluating the  
 28 potential for sediment to act as a reservoir of dioxin-like compounds is complex and likely to be  
 29 more difficult than studying dioxin-like compounds in a single medium, such as water or soil.  
 30 Volatilization and sedimentation are two mechanisms whereby persistent chemicals such as  
 31 CDDs/CDFs and PCBs are lost from water bodies/columns. Numerous authors (Swackhamer  
 32 and Armstrong, 1986; Muir et al., 1985; Ling et al., 1993) have noted that sediments are a likely

1 sink for persistent hydrophobic organic compounds, because these compounds are likely to be  
2 strongly bound to organic particles in the sediment.

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

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

### 21 22 **12.2.3.3. Releases from Sediment to Water**

23 Given the lack of data, no quantitative estimates of annual releases can be made. Ling et  
24 al. (1993) evaluated the fate of various chemicals, including PCBs, in Hamilton Harbour, located  
25 in Ontario, Canada, using a modified version of the Quantitative Water Air Sediment Interaction  
26 (QWASI) fugacity model. Among the processes evaluated were diffusion between air and water  
27 and sediment and water; sediment deposition, resuspension, and burial; and sediment  
28 transformation. Three primary compartments were studied: air, water, and bottom sediments.  
29 The sediment was treated as a simple, well-mixed surface layer of active sediment and the buried  
30 sediment underneath. Chemicals in the active sediment were assumed to be able to exchange  
31 with the overlying water; chemicals in the buried sediment were assumed to be isolated from the  
32 sediment-water exchange. Sediment was assumed to be homogenous rather than heterogenous.

1 The epi- and hypolimnetic compartments of the water column were defined on the basis of a  
2 thermocline, and the atmosphere was defined as a semi-infinite medium of constant, defined  
3 composition.

4 Ling et al. estimated rates of PCB movement on the basis of 1987 loadings using two  
5 models: one with and one without a thermocline. The results for the water-sediment transfer  
6 using the model with a thermocline were ~32 kg/yr entering the hypolimnion from the  
7 epilimnion, ~27 kg/yr entering the surface sediment from the hypolimnion, and ~18 kg/yr  
8 (>50%) going to burial. For sediment-to-water transfer, ~7 kg/yr transferred to the hypolimnion  
9 and then 12.5 kg/yr transferred to the epilimnion. Similar numbers were found in the single  
10 water column model (the model without a thermocline).

11 Both the model with a thermocline and the model without a thermocline predicted  
12 volatilization from the water to the atmosphere—1.6 kg/yr and 1.8 kg/yr, respectively.  
13 However, the actual contribution of PCBs from sediment to air was not determined. A  
14 comparison of estimated concentrations with observed values are presented in Table 12-6. For  
15 PCBs, 68% were buried in the sediment, 20% were exported to Lake Ontario, 5.4% degraded in  
16 the water and sediment, and 6% volatilized. The authors noted that these percentages are  
17 uncertain. At the sediment-water exchange, more than 90% of each chemical was contained in  
18 the sediment because of particle deposition and the high affinity of the chemical for sediment.  
19 There was no indication that contaminants buried in the bottom sediments are transferred  
20 through diffusion mechanisms back to the surface sediments; however, episodic release of these  
21 chemicals from surface sediments can occur through mechanisms such as resuspension during  
22 flooding or lake inversions and uptake/ingestion by benthic biota.

#### 23 24 **12.2.4. Biota**

##### 25 **12.2.4.1. *Potential Mass of Dioxin-Like Compounds Present***

26 The mass of CDDs/CDFs in biota in the United States was not estimated as part of this  
27 report. However, to place perspective on the potential magnitude of this reservoir, 82 g I-TEQ<sub>DF</sub>  
28 have been estimated to be present in biota in the U.K. (50 g in humans and 32 g in vegetation),  
29 which is about three orders of magnitude less than the mass estimated to be present in U.K.  
30 surface soils (Duarte-Davidson et al., 1997; Eduljee and Dyke, 1996). No data are available to  
31 estimate the biota burden in the United States.

1 **12.2.4.2. Mechanisms Responsible for Supply to and Releases from Biota**

2       Apparently, very little of the dioxin-like compounds contained in contaminated soil is  
3 ultimately taken up by the vegetation growing in the soil. Kjeller et al. (1991) analyzed  
4 concentrations of CDDs/CDFs in archived soil and grass samples collected from the mid-1840s  
5 to 1989 at an English experimental station and found that only 0.006 to 0.02% of the soil burden  
6 of CDDs/CDFs was taken up by the grass. In addition, scientists generally agree that, once taken  
7 up by plant tissue, CDDs/CDFs are not translocated to other parts of the plant (e.g., fruits or  
8 shoots) (Bacci and Gaggi, 1985; Hülster and Marschner, 1993, 1994; Nakamura et al., 1994).

9       Researchers have found that the concentration of dioxin-like compounds in a plant should  
10 reach equilibrium with the vapor phase concentrations of dioxin-like compounds in the  
11 surrounding air (Bacci et al., 1990a, b; Frank and Frank, 1989; Horstman and McLachlan, 1992;  
12 McCrady and Maggard, 1993; McLachlan et al., 1995; Paterson et al., 1991; Simonich and Hites,  
13 1994; Tolls and McLachlan, 1994; Welsch-Pausch et al., 1995). Horstman and McLachlan  
14 (1992) stated that the leaf-air transfer of volatile compounds is a reversible process governed by  
15 concentration gradients. If CDD/CDF concentrations are higher in the surrounding air than they  
16 are in the air spaces within plant tissue, CDDs/CDFs should diffuse into the plant. Once  
17 equilibrium is reached and CDD/CDF concentrations in the plant equal that of surrounding air,  
18 no more CDDs/CDFs should be taken into the plant. When CDD/CDF concentrations in  
19 surrounding air begin to decrease, CDDs/CDFs should diffuse (probably at a slow rate) out of  
20 the plant tissue. Apparently, CDDs/CDFs are not bioconcentrated to a significant extent in the  
21 lipid portion of the leaf cuticle (Gaggi et al., 1985). The CDDs/CDFs present in the leaf tissue  
22 are predominantly released from the plant through leaf fall onto soil. Therefore, vegetation is  
23 not likely to be a long-term reservoir of dioxin-like compounds.

24       Research suggests that dioxin-like compounds in animal tissue, unlike in vegetation,  
25 seldom, if ever, reach equilibrium with vapor phase concentrations in the surrounding  
26 atmosphere (or water column concentrations in the case of aquatic life). Rather, animals  
27 exposed to dioxin-like compounds are known to bioaccumulate these compounds, primarily in  
28 body fat (U.S. EPA, 1993a, j). Nonetheless, animals, unlike plants, can metabolize certain  
29 chlorinated hydrocarbons after they enter the body (Carlberg et al., 1983). Dioxin-like  
30 compounds can be released from an animal's body (at congener-specific rates) through  
31 metabolic processes or through weight loss, breast-feeding, or sweating. McLachlan (1996)  
32 reported the half-life for the clearance of 2,3,7,8-TCDD from humans to be 7 yr. As a result,

1 animal life has a greater potential than does vegetation for being a long-term reservoir source of  
2 CDDs/CDFs. The majority of the dioxin-like compounds released by animals in the form of  
3 waste materials will be released to water or soil. Similarly, upon death, the dioxin-like  
4 compounds remaining in the body will be deposited onto soil or aquatic sediments or will be  
5 ingested by other animals.

#### 7 **12.2.4.3. Approaches for Measuring and Estimating Releases from Biota**

8 Researchers have investigated the uptake and release of CDDs/CDFs by vegetation  
9 through measurement of actual concentrations during uptake and release by vegetation grown in  
10 closed systems (greenhouses). Bacci et al. (1992) conducted uptake and release studies of  
11 1,2,3,4-TCDD by plant foliage in a closed system (specially constructed greenhouse).  
12 Concentrations of TCDD vapor in the greenhouse air were maintained during the 370-hr uptake  
13 phase at a mean concentration of 0.0062 ng/L (air concentration varied slightly from 0.005 to  
14 0.0075 ng/L). To begin the release phase, the TCDD vapor source (amended sand) as well as the  
15 greenhouse walls were removed, and release of CDDs/CDFs from the leaves was measured for  
16 500 hr. The authors concluded that, during uptake, TCDD concentration in the leaves varied as a  
17 function of time and was dependent on the concentration of vapor-phase TCDD in the  
18 surrounding air. They estimated the release of TCDD from the vegetation to be relatively slow,  
19 with a half-life of TCDD of 3,300 hr.

20 McCrady and Maggard (1993) conducted a mass balance study of uptake and release of  
21 dioxin in grass foliage. The results indicated a half-life of dioxin in grass of 128 hr. These  
22 researchers also noted that photodegradation of dioxins on the foliage appeared to be a  
23 significant removal mechanism, in addition to volatilization. They calculated the  
24 photodegradation half-life to be 44 hr.

25 Interpretation of uptake and release data over variable exposure times and contaminant  
26 concentrations has led to the development of models describing air-to-vegetation equilibrium  
27 and kinetics controlling the behavior of dioxin in vegetation. Some earlier fugacity modeling  
28 attempts described the leaf of a plant as behaving as a single compartment. One-compartment  
29 models were described by Bacci et al. (1990a, b), Trapp et al. (1990), and Schramm et al. (1987)  
30 (as cited in Tolls and McLachlan, 1994). Researchers presenting most of the recently developed  
31 models claim that the available data better support the concept of a leaf behaving as two  
32 compartments (Riederer, 1990; Paterson et al., 1991; Horstman and McLachlan, 1992; McCrady

1 and Maggard, 1993; Tolls and McLachlan, 1994; McLachlan et al., 1995). Input parameters  
2 considered by most models include critical chemical characteristics of the contaminant,  
3 characteristics of the plant, exposure times, and contaminant concentrations measured within the  
4 plant. Riederer (1990) suggested treating a leaf as multiple compartments having different  
5 accessibility to the atmosphere and different diffusion resistances.

6 Input parameters for the two-compartment model are octanol/water coefficients,  
7 cuticle/water partition coefficients, aqueous solubility, and saturation vapor pressure of the  
8 chemical of concern. Outputs of the model are prediction of equilibrium concentration in  
9 different leaf tissues, estimates of air-to-vegetation bioconcentration equilibria, and  
10 identification of leaf compartments in which compounds are likely to accumulate. Riederer  
11 (1990) also presented an approach for using the model to semiquantitatively assess the potential  
12 for revolatilization of dioxins from vegetation.

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

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

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

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

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

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

### 18 **12.3. SUMMARY AND CONCLUSIONS**

19 As depicted in Figure 12-1 a set of complex relationships exists among reservoirs and  
20 between reservoirs and contemporary formation sources. The significance of reservoirs for  
21 human exposure is more dependent on their ability to affect the concentration of dioxin-like  
22 compounds in other media than on their size or net release rate. This section first summarizes  
23 and draws conclusions from the limited information available regarding the character and  
24 magnitude of reservoir sources. This information is then used to discuss the implications of  
25 reservoir sources to human exposure.

#### 27 **12.3.1. Reservoir Sources**

28 Summary statements about soil reservoir sources:

- 29
- 30 • Soil is likely to be the reservoir source with the greatest potential for release of  
31 CDDs/CDFs to other environmental media, particularly to water. This is due in part  
32 to its relatively large mass of stored CDDs/CDFs, but more importantly, it is due to

1 the existence of demonstrated transport mechanisms for intermedia exchange, for  
2 example, soil erosion to surface waters and particle resuspension to air.

- 3
- 4 • The preliminary estimates of CDD/CDF runoff from urban areas to waterways is  
5 comparable to known industrial point source releases, and runoff from agricultural  
6 areas to surface waters is more than 100 times greater. It is unclear how much of the  
7 soil erosion and runoff represents recently deposited CDDs/CDFs from primary  
8 sources or longer-term accumulation. Much of the eroded soil comes from tilled  
9 agricultural lands, which would include a mix of CDDs/CDFs from various  
10 deposition times. The age of CDDs/CDFs in urban runoff is less clear.
- 11
- 12 • Based on the limited information currently available (i.e., primarily fugacity  
13 modeling), volatilization of CDDs/CDFs from soils is not believed to significantly  
14 alter ambient air concentrations. However, volatilization of PCBs from soil may be a  
15 significant process.
- 16
- 17 • Based on the limited information currently available, resuspension of soil may  
18 account for a small fraction (~4%) of CDD/CDF concentrations in air. This  
19 resuspended soil may, however, constitute a more significant portion of dry  
20 deposition.

21

22 Summary statements about water reservoir sources:

- 23
- 24 • It is unclear whether volatilization of CDDs/CDFs from water can significantly alter  
25 air concentrations. For PCBs, however, the water-air exchange appears to be  
26 significant and for some water bodies results in a net transfer from water to air.
- 27
- 28 • Water is the major media contributing CDDs/CDFs and PCBs to sediment. Note that  
29 most of the CDDs/CDFs in sediments originally came from soils. For specific water  
30 bodies, however, the CDDs/CDFs and PCBs in sediments may have been dominated  
31 by local industrial discharges to water.

32

33 Summary statements about sediment reservoir sources:

- 34
- 35 • It is important to distinguish between surface and deep sediments. Surface sediments  
36 are commonly resuspended and introduced back into the water; deep sediments  
37 generally do not interact with the water column. Surface sediments can contribute  
38 significantly to the CDD/CDF and PCB concentrations in water, whereas deep  
39 sediments do not.
- 40
- 41 • There is little, if any, movement of dioxin-like compounds once they are buried in the  
42 bottom sediments. Bottom sediments may be considered as sinks.

1 Summary statements about biota reservoir sources:

- 2
- 3 • The mass of CDDs/CDFs in vegetation at any given time is likely to be small  
4 compared to the mass in soil. Vegetation does play an important role in transferring  
5 CDDs/CDFs from the air to the soil via the decay of plant biomass.  
6
- 7 • Release by volatilization from vegetation has been studied and modeled using the  
8 fugacity approach, and half-lives have been estimated. Based on these results,  
9 volatilization is not believed to be a significant mechanism for release of  
10 CDDs/CDFs and PCBs except possibly during forest/brush fires.  
11
- 12 • The mass of CDDs/CDFs in animals at any given time is likely to be small compared  
13 to the mass in soil. Similarly, releases are small and occur primarily by excretion and  
14 decomposition of dead biomass.  
15

### 16 **12.3.2. Implications for Human Exposure**

17 Although, the ability to make quantitative estimates of releases from reservoir sources is  
18 limited at present, it is reasonable to conclude that the contribution of reservoir sources to human  
19 exposure may be significant. Diet accounts for more than 95% of human exposure. Although  
20 the size of the biota reservoir is small compared to the soil and sediment reservoirs, it is clearly  
21 the key contributor to human exposure. The potential contribution of the other reservoirs to  
22 human exposure is discussed below.

23 **PCB reservoir releases.** Because current sources of newly formed PCBs are most likely  
24 negligible, human exposure to the dioxin-like PCBs is thought to be derived almost completely  
25 from current releases of old PCBs stored in reservoir sources. Key pathways involve releases  
26 from both soils and sediments to both aquatic and terrestrial food chains. One-third of general  
27 population TEQ<sub>DFP</sub> exposure is due to PCBs. Thus, at least one-third of the overall risk to the  
28 general population from dioxin-like compounds comes from reservoir sources.

29 **CDD/CDF releases from soil and sediments to water and exposure via the aquatic**  
30 **pathway.** The earlier discussion has shown that soils can have significant inputs to waterways  
31 via soil erosion and runoff. Similarly, the sediment reservoir contributes significantly to  
32 CDD/CDF concentrations in water. These releases appear to be greater than those from the  
33 primary sources included in the inventory. Dioxins in waterways bioaccumulate in fish, and fish  
34 consumption causes human exposure. Fish consumption makes up about one-third of the total

1 general population CDD/CDF TEQ exposure. This suggests that a significant portion of the  
2 CDD/CDF TEQ exposure could be due to releases from the soil and sediment reservoir.

3 **CDD/CDF releases from soil to air and exposure via the terrestrial pathway.**

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

**Table 12-1. Historical production, sales, and usage of 2,4-dichlorophenoxyacetic acid (2,4-D) (metric tons)<sup>a</sup>**

Year	2,4-D, acid			2,4-D, esters and salts (as reported) <sup>b</sup>	
	Production volume (metric tons)	Sales volume (metric tons)	Domestic usage/ disappearance (metric tons)	Production volume (metric tons)	Sales volume (metric tons)
2000	—	—	23,600–28,100 <sup>c</sup>	—	—
1998/99	—	—	23,600–28,100 <sup>d</sup>	—	—
1996/97	—	—	23,600–27,200 <sup>e</sup>	—	—
1994/95	—	—	21,800–26,300 <sup>f</sup>	—	—
1993	—	—	16,800–20,400 <sup>g</sup>	—	—
1992	—	—	16,800–20,400 <sup>g</sup>	—	—
1991	—	—	18,100–29,500 <sup>h</sup>	—	—
1990	—	—	18,100–29,500 <sup>h</sup>	—	—
1989	—	—	18,100–29,500 <sup>i</sup>	—	—
1988	—	—	23,600–30,400 <sup>j</sup>	—	—
1987	—	—	23,600–30,400 <sup>k</sup>	—	—
1986	—	—	--	8,618	12,150
1985	—	—	--	—	0
1984	—	—	--	—	0
1983	—	—	--	7,702	8,234
1982	—	—	--	8,762	8,400
1981	5,859	3,275	--	8,987	8,002
1980	6,164	3,137	--	11,313	11,147
1979	5,763	6,187	--	11,874	13,453
1978	—	—	--	8,958	9,256
1977	—	—	--	12,552	10,196
1976	—	—	17,418 <sup>l</sup>	10,913	7,813
1975	—	—	--	16,134	13,414
1974	—	—	--	6,558	5,991
1973	—	—	--	13,400	13,698
1972	24,948 <sup>b</sup>	—	21,772 <sup>l</sup>	10,192	10,899
1971	—	5,619	15,700 <sup>l</sup>	—	18,654
1970	19,766	7,159	--	—	19,920
1969	21,354	8,521	--	25,854	20,891

**Table 12-1. Historical production, sales, and usage of 2,4-dichlorophenoxyacetic acid (2,4-D) (metric tons)<sup>a</sup> (continued)**

Year	2,4-D, acid			2,4-D, esters and salts (as reported) <sup>b</sup>	
	Production volume (metric tons)	Sales volume (metric tons)	Domestic usage/ disappearance (metric tons)	Production volume (metric tons)	Sales volume (metric tons)
1968	35,953	10,352	--	42,690	30,164
1967	34,990	15,432	--	37,988	29,300
1966	30,927	12,710	28,985 <sup>m</sup>	32,895	25,075
1965	28,721	11,816	22,906 <sup>m</sup>	28,740	21,454
1964	24,364	11,343	19,958 <sup>m</sup>	24,660	18,263
1963	21,007	9,446	15,059 <sup>m</sup>	20,178	16,333
1962	19,503	7,716	16,284 <sup>m</sup>	16,831	13,075
1961	19,682	7,591	14,107 <sup>m</sup>	16,683	12,533
1960	16,413	—	14,107 <sup>m</sup>	15,436	13,661
1959	13,282	7,240	15,468 <sup>m</sup>	12,438	7,070
1958	14,036	6,234	9,662 <sup>m</sup>	11,295	5,649
1957	15,536	6,871	--	12,392	7,125
1956	13,079	6,465	--	9,635	7,294
1955	15,656	5,924	--	13,390	8,121
1954	—	4,838	--	10,268	6,886
1953	11,761	—	--	10,733	8,855
1952	13,933	—	--	11,358	9,637
1951	—	—	--	—	—
1950	6,421	4,301	--	5,274	3,219
1949	6,852	2,991	--	5,829	3,211
1948	9,929	4,152	--	2,458	1,598
1947	2,553	2,320	--	1,468	1,108
1946	2,479	2,330	--	515	81
1945	416	286	--	—	—

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

<sup>b</sup>No data were reported for domestic usage/disappearance of 2,4-D esters and salts.

<sup>c</sup>Source: U.S. EPA (1991i).

<sup>d</sup>Source: U.S. EPA (2000e).

<sup>e</sup>Source: U.S. EPA proprietary data.

<sup>f</sup>Source: U.S. EPA (1997e).

<sup>g</sup>Source: U.S. EPA (1994b).

<sup>h</sup>Source: U.S. EPA (1992f).

**Table 12-1. Historical production, sales, and usage of 2,4-dichlorophenoxyacetic acid (2,4-D) (metric tons)<sup>a</sup> (continued)**

<sup>i</sup>Source: U.S. EPA (1991h).

<sup>j</sup>Source: U.S. EPA (1990e).

<sup>k</sup>Source: U.S. EPA (1988c).

<sup>l</sup>Source: U.S. EPA (1975).

<sup>m</sup>Source: USDA (1970).

— = Not reported to avoid disclosure of proprietary data

-- = No information given

**Table 12-2. Historical production, sales, and usage of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) (metric tons)<sup>a</sup>**

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

**Table 12-2. Historical production, sales, and usage of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) (metric tons)<sup>a</sup> (continued)**

Year	2,4,5-T			2,4,5-T, esters and salts (as reported) <sup>b</sup>	
	Production volume (metric tons)	Sales volume (metric tons)	Domestic usage/ disappearance (metric tons)	Production volume (metric tons)	Sales volume (metric tons)
1963	4,123	1,928	3,266 <sup>h</sup>	4,543	2,585
1962	3,796	1,021	3,674 <sup>h</sup>	4,765	2,543
1961	3,134	1,196	2,449 <sup>h</sup>	3,536	2,372
1960	2,874	—	2,676 <sup>h</sup>	3,594	1,891
1959	2,516	1,039	2,495 <sup>h</sup>	3,644	1,843
1958	1,668	692	1,724 <sup>h</sup>	2,372	1,151
1957	2,419	—	--	3,098	1,337
1956	2,345	816	--	3,196	1,473
1955	1,327	662	1,300 <sup>e</sup>	1,720	1,077
1954	1,223	639	--	1,761	615
1953	2,395	—	--	2,443	1,817
1952	1,583	—	--	1,423	569
1951	—	—	1,100 <sup>e</sup>	—	—
1950	852	297	--	—	—
1949	—	—	--	—	—
1948	—	—	--	—	—
1947	—	—	--	—	—
1946	—	—	--	—	—
1945	—	—	--	—	—

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

<sup>b</sup>No data were reported for domestic usage/disappearance of 2,4-D esters and salts.

<sup>c</sup>Source: Esposito et al. (1980).

<sup>d</sup>Source: Federal Register (1979).

<sup>e</sup>Source: Thomas and Spiro (1995).

<sup>f</sup>Source: U.S. EPA (1977).

<sup>g</sup>Source: USDA (1971); reflects farm usage only.

<sup>h</sup>Source: USDA (1970); values include military shipments abroad.

<sup>i</sup>Source: Kearney et al. (1973) reports slightly lower domestic consumption for the years 1967 and 1968 than for 1966.

— = Not reported to avoid disclosure of proprietary data

-- = No information given

**Table 12-3. CDD/CDF concentrations in recent sample of 2,4,5-trichloro-phenoxyacetic acid (2,4,5-T)**

Congener/congener group	2,4,5-T sample (µg/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	2.9
1,2,3,4,7,8,9-HpCDF	0.103
OCDF	3.01
Total 2,3,7,8-CDD <sup>a</sup>	58.2
Total 2,3,7,8-CDF <sup>a</sup>	8.59
Total I-TEQ <sub>DF</sub> <sup>a</sup>	2.88
Total TEQ <sub>DF</sub> -WHO <sub>98</sub> <sup>a</sup>	3.26
Total TCDD	--
Total PeCDD	--
Total HxCDD	--
Total HpCDD	--
Total OCDD	--
Total TCDF	--
Total PeCDF	--
Total HxCDF	--
Total HpCDF	--
Total OCDF	--
Total CDD/CDF	--

<sup>a</sup> Calculated assuming nondetect values are zero.

ND = Not detected (value in parenthesis is the detection limit)

-- = No information given

Source: Schecter et al. (1997).

**Table 12-4. PCB 138 fluxes predicted by Harner et al. (1995)**

<b>Year</b>	<b>Concentration in air (pg/m<sup>3</sup>)</b>	<b>Fugacity in air (Pascals × 10<sup>-9</sup>)</b>	<b>Fugacity in soil (Pascals × 10<sup>-9</sup>)</b>	<b>Concentration in soil (ng/g)</b>	<b>Net flux/direction</b>
1950	4	0.24	1.1	--	air → soil (444 kg/yr)
1965	280	1.5	12	--	air → soil (1000 kg/yr)
1975	--	--	16	--	
1980	49	--	--	--	soil → air (820 kg/yr)
1994	6	--	8.3	--	soil → air (700 kg/yr)

-- = No information given

**Table 12-5. Summary of flux calculations for total PCBs in Green Bay, 1989**

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

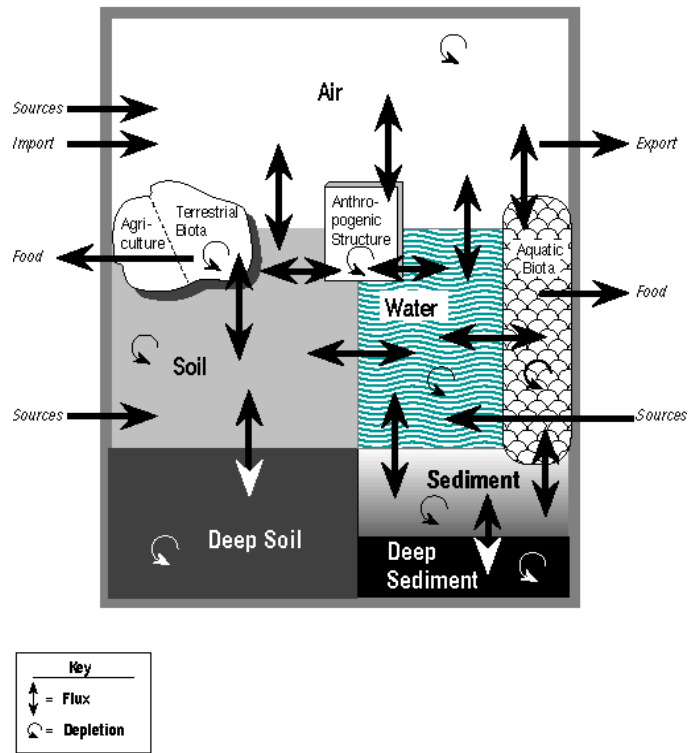
<sup>a</sup>Numbers indicate water-to-air transfer of total PCBs. They represent the sum of individual PCB congener fluxes and are described as “daily” fluxes because they correspond to air samples collected over 5–10 hr and water samples collected over ~1 hr.

Source: Achman et al. (1993).

**Table 12-6. Comparison of estimated PCB concentrations with observed values**

Variable	PCBs
Observed concentration Sediment Water	0.23–1.04 µg/g <20 µg/m <sup>3</sup>
Estimated concentration from model without thermocline Sediment Water Amount in sediment Amount in water Total mass	0.518 µg/g 8.33 µg/m <sup>3</sup> 74.9 kg 2.33 kg 77.2 kg
Estimated concentration from model with thermocline Sediment Hypolimnion Epilimnion Amount in sediment Amount in hypolimnion Amount in epilimnion Total mass	0.527 µg/g 8.48 µg/m <sup>3</sup> 7.93 µg/m <sup>3</sup> 76.3 kg 1.28 kg 1.02 kg 78.6 kg

Source: Ling et al. (1993).



**Figure 12-1. Fluxes among reservoirs.**