2. PHYSICAL AND CHEMICAL PROPERTIES AND FATE

2.1. INTRODUCTION

This chapter summarizes available information regarding the physical and chemical properties and fate of the dioxin-like CDDs, CDFs, BDDs, BDFs, and PCBs. Physical/ chemical properties addressed in this chapter include melting point, water solubility, vapor pressure, Henry's Law constant, octanol/water partition coefficient, organic carbon partition coefficient, and photochemical quantum yield. Fate and transport processes addressed include photolysis, oxidation, hydrolysis, biodegradation, volatilization, and sorption. Biologically-mediated transport properties (i.e., bioconcentration, plant uptake, etc.) are also addressed in this volume, but are also addressed in the companion volume to this report, Volume 3: Site-Specific Assessment Procedures.

Knowledge of physical and chemical properties is essential to understanding and modeling the environmental transport and transformation of organic compounds such as the dioxin-like compounds. The properties most important for understanding the environmental behavior of the dioxin and dioxin-like compounds appear to be water solubility (WS), vapor pressure (VP), octanol/water partition coefficient (K_{ow}), organic carbon partition coefficient (K_{oc}), and photochemical quantum yield. The ratio of VP to WS (VP/WS) can be used to calculate the Henry's Law constant (H_c) for dilute solutions of organic compounds when the VP and WS are measured at the same temperature and for the same physical state. Henry's Law constant is an index of partitioning for a compound between the atmospheric and the aqueous phase (Mackay et al., 1982).

To maximize and optimize the identification of information on the physical/chemical properties of these compounds, a thorough search of the recent literature was conducted. A computer literature search was conducted using the on-line Chemical Abstracts (CA) data base maintained by the Scientific Technical Network (STN). Printed abstracts were obtained and screened, and selected literature were retrieved and critically evaluated. The most definitive value for each physical/ chemical property for each congener was selected. The evaluation method used to select the most definitive physical/chemical property values is detailed in Section 2.3. The property values obtained from the scientific literature are summarized in Appendix A. Sections 2.4 and 2.5 present the property values for the dioxin-like compounds that are considered to be the most definitive. These values are utilized in the modeling equations in the companion volume to this report, Volume 3 Site-Specific Assessment Procedures. Appendix A lists reported chemical property values for the CDDs, CDFs, and dioxin-like PCBs. Where technically feasible and appropriate, estimation procedures have been used to provide values where measured data are not available. For those compounds for which data could not be found and estimates are not appropriate, the field is left blank, and a congener group average is presented as the property value for that congener group. The congener group average was calculated by averaging the selected (i.e., most definitive) property values listed for the congeners in that group.

The values suggested in this document as most definitive are, in the authors' opinion, the best values derivable from current data. Because the document has undergone extensive review inside the Agency, by scientific community outside the Agency, and by the Science Advisory Board, the values can be interpreted as generally representative of the Agency and scientific community. The authors recommend that document users consider the values as defaults in the sense that users are encouraged to accept them as a starting point but should feel free to modify them as new data become available.

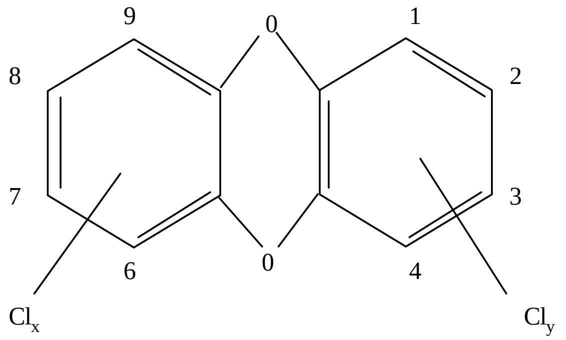
Brief summaries of the recent and relevant scientific literature on the environmental fate of the polychlorinated and polybrominated dibenzodioxins, dibenzofurans, and biphenyls are provided in Sections 2.6 and 2.7.

2.2. GENERAL INFORMATION

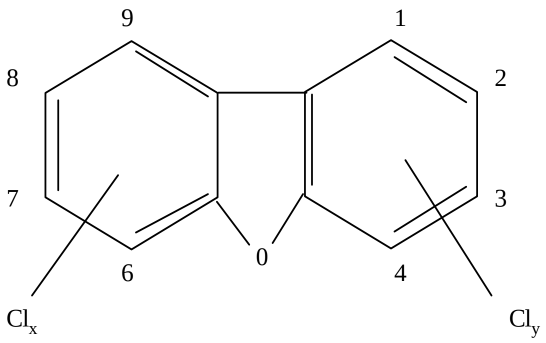
Polychlorinated dibenzo-p-dioxins (CDDs), polychlorinated dibenzofurans (CDFs), and polychlorinated biphenyls (PCBs) are chemically classified as halogenated aromatic hydrocarbons. CDDs and CDFs can be formed as unintentional by-products through a variety of chemical reactions and combustion processes. Both compound classes have a triple-ring structure that consists of two benzene rings connected by a third oxygenated ring. For CDDs, the benzene rings are connected by a pair of oxygen atoms. CDFs are connected via a single oxygen atom. (See structures below.) PCBs are a class of compounds formed by the chlorination of a biphenyl molecule.

There are 75 possible different positional congeners of CDDs and 135 different congeners of CDFs. Likewise, there are 75 possible different positional congeners of

BDDs and 135 different congeners of BDFs. (See Table 2-1.) The basic structure and numbering of each chemical class is shown below.



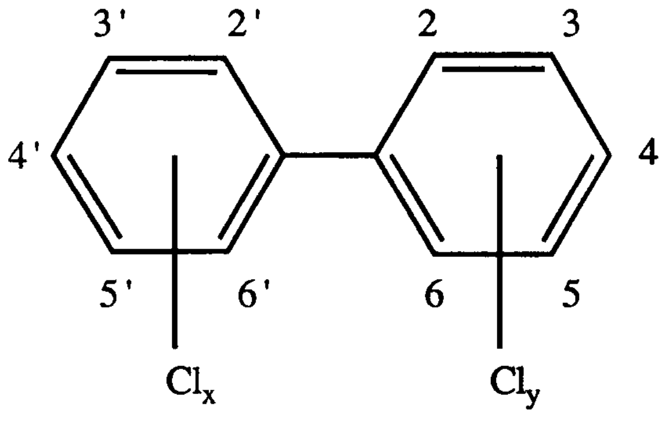
PCDDs



PCDFs

$X = 0$ to 4, $Y = 0$ to 4, $X + Y \geq 1$

There are 209 possible PCB congeners. (See Table 2-1.) The physical/ chemical properties of each congener vary according to the degree and position of chlorine substitution. The list of dioxin-like PCBs can be found in Table 1-2. The PCBs assume a dioxin-like structure when the substituent chlorines occupy: (a) usually no more than one of the ortho positions; (b) both para positions; and (c) at least two meta positions; and (d) the structure is not hindered from assuming the preferred planar configuration. The basic structure and numbering scheme for PCBs is shown below.



$X = 1$ to 5, $Y = 1$ to 5, $X + Y \geq 1$

2.3. PHYSICAL/CHEMICAL PROPERTY EVALUATION METHODOLOGY

As discussed above, a thorough search of the recent published scientific literature was conducted to maximize and optimize the identification of measured physical/chemical properties. For the purpose of identifying the most definitive of two or more physical/chemical property values reported in the literature for a given dioxin-like compound, a ranking methodology was developed to evaluate the degree of confidence in the reported values. A property value with a ranking of 1 is considered to have the highest level of confidence; a property value with a ranking of 5 is considered to have the lowest level of confidence. The ranking scheme assumes that measured values are more definitive than estimated values. The ranking scheme is based on five ranking criteria or factors. These factors are described below:

Factor 1: *Confirmation.* Value, measured or derived, confirmed by at least one other laboratory, or different experimental technique. Confirmation was assumed if the reported values were within 50 percent of the highest value (within 5 percent for values reported in logarithmic units).

Factor 2: *Measurement Technique.* Direct measurement technique used. No measurements reported less than 10 times the method detection limit.

Factor 3: *GLP Followed.* Good Laboratory Practice was followed in the experimental work. This includes the use of traceable, pure standards; sensitive, selective detection technique was employed; repeatability of measurements demonstrated; all experimental details sufficiently documented so others could reproduce experiments; and sources of determinate error considered - error analysis conducted.

Factor 4: *Derived Value.* Value derived from other directly measured physical/chemical properties by use of known physical/chemical relationships developed for structurally similar chemicals (e.g., other dioxin, furan, and PCB congeners, multiple-ring halogenated compounds). The input value (i.e., the independent variable) used to derive the property value of interest from the equation (i.e., the physical/chemical relationship) is a directly measured value.

Factor 5: *Estimated Value.* Value estimated using a physical/chemical relationship that was developed using estimated values or a combination of estimated and measured values; this includes QSAR (Quantitative Structure Activity Relationship) methods. Also includes values derived from other directly measured physical/chemical properties by use of known physical/chemical relationships developed, in large part, for structurally dissimilar compounds.

Although this ranking scheme is subjective in nature, it is a reasonable method for identifying the most definitive physical/chemical property value. The ranking scheme has several advantages. First, it identifies where more work is needed to obtain a more definitive p-chem property value. Second, it allows for later adjustments in these values when more definitive studies are conducted. A low ranking for a study does not mean that a particular reported value is incorrect - only that insufficient evidence exists to determine its accuracy. The ranking scheme is as follows:

Rank 1: Confirmed Measured Values. The reported value has met Factors 1, 2, and 3. (See Table 2-2.) This value is considered definitive.

Rank 2: Unconfirmed Measured Values. The reported value has met Factors 2 and 3. The value is considered accurate; it could be definitive subject to confirmation.

Rank 3: Confirmed Derived Values. The reported value has met Factors 1, 3, and 4. The value is considered to be a close approximation.

Rank 4: Unconfirmed Derived Value. The reported value has met Factors 3 and 4. The value is considered to be an approximation.

Rank 5: Estimated Value. The reported value has met Factor 5 only. The value is considered to be an "order-of-magnitude" estimate.

If two or more values have the same ranking, then the value that has been selected as most definitive by Mackay et al. (1992a, 1992b), by other EPA offices, other government agencies, or scientific data bases (e.g., the Syracuse Research Corporation (SRC) Chemfate Data Base) was deemed to be the most definitive value for this document. If two or more values with the same ranking have not been peer reviewed as above, typically the most current value was chosen as the most definitive value. This decision was made on the assumption that the most current value would have been developed by the latest scientific method; however, an evaluation of the techniques used to derive the values was also considered in choosing the more definitive value. The ranking of the literature can be found in Table A-2 in Appendix A. Table 2-3 lists the property values for the dioxin-like compounds that are considered to be most definitive.

2.4. PHYSICAL/CHEMICAL PROPERTIES - CHLORINATED COMPOUNDS

Limited research has been conducted to determine physical and chemical properties of CDFs, CDDs, and the dioxin-like PCBs. The CDD/CDF congeners having 2,3,7,8-chlorination have received the most research attention, with 2,3,7,8,-TCDD being the most intensely studied compound. All 2,3,7,8-substituted CDD/CDF congeners are now available commercially, but many of these congeners have not been prepared in pure form. Another factor that is likely to have limited research on these compounds is the high toxicity of these compounds, which necessitates extreme precautions to prevent potential adverse effects.

2.4.1. Water Solubility

Although water solubility data are not directly used in the exposure scenario equations in Volume 3, water solubility data can be used to estimate Henry's Law constants (using the VP/WS ratio technique) that are used in the equations in Volume 2. Very few measured water solubility values are available in the literature. Marple et al. (1986a) reported the water solubility of 2,3,7,8-TCDD as 19.3 ± 3.7 parts per trillion (nanograms per liter, ng/L) at 22°C. Marple et al. (1986a) used a procedure of equilibrating thin films of resublimed 2,3,7,8-TCDD with a small volume of water followed by gas chromatography (GC) analysis with 63Ni electron capture detection. Other water solubility values for 2,3,7,8-TCDD have been reported in the literature and are summarized in U.S. EPA (1990) and Mackay et al. (1992a). Values ranging from 7.9 ng/L to 483 ng/L are reported in U.S. EPA (1990) and Mackay et al. (1992a) with 19.3 ng/L selected as the recommended value. The value of 19.3 ng/L was confirmed by Marple et al. (1987) using both radio-labeled and unlabeled 2,3,7,8-TCDD. Marple et al. (1987) reported values of 10.6 ng/L and 10.4 ng/L for the labeled and unlabeled compounds respectively. Because the value of 19.3 ng/L was confirmed by other techniques and was recommended by U.S. EPA (1990), it was chosen as the most definitive value.

Friesen et al. (1985) and Shiu et al. (1988) used high-performance liquid chromatography (HPLC) generator column techniques to measure the water solubilities of a series of chlorinated dioxins including the following dioxin-like congeners: 1,2,3,4,7,8-HxCDD; 1,2,3,4,6,7,8-HpCDD; and OCDD. Reported water solubilities ranged from 4.42 ng/L to 0.074 ng/L for the 1,2,3,4,7,8-HxCDD and OCDD congeners, respectively. Friesen et al. (1990b) used a gas chromatography/mass spectrometry detection (GC/MSD) generator column technique to measure the water solubilities of a series of 2,3,7,8-substituted CDFs (2,3,7,8-TCDF; 2,3,4,7,8-PeCDF; 1,2,3,6,7,8- and 1,2,3,4,7,8-HxCDF; and 1,2,3,4,6,7,8-HpCDF) and reported a decrease in water solubility with an increase in the number of chlorine substituents. The reported water solubility values ranged from 419 ng/L for 2,3,7,8-TCDF to 1.35 ng/L for 1,2,3,4,6,7,8-HpCDF.

Few measured data have been reported for the dioxin-like PCB compounds. The selected water solubility values for the dioxin-like PCB compounds are typically one to two orders of magnitude greater than the similarly chlorinated CDD and CDF congeners. For example, the selected value for 3,3',4,4'-TCB is 1 μg/l whereas the selected water solubility values averages for 2,3,7,8-TCDD and 2,3,7,8-TCDF are 0.019 and 0.42 μg/l, respectively.

For those compounds without reported measured water solubility values, estimations were calculated by the congener group-average method. For example, for the tetra-chlorinated dioxins, values reported in the literature were averaged to yield an estimated water solubility value for the tetra-chlorinated dioxin congener group. A similar procedure was used to develop the average value for each of the other CDD and CDF congener groups. The most definitive value for each isomer was used to derive the congener group average.

2.4.2. Vapor Pressure

Vapor pressure data are not directly used in the exposure scenario equations in Volume 3. However, vapor pressure data can be used to estimate Henry's Law constant using the VP/WS ratio technique. Very few measured vapor pressure values are available in the literature for the CDDs and CDFs, but the majority of the measured vapor pressures are for the 2,3,7,8-substituted congeners.

Mackay et al. (1992a) reviewed the published vapor pressure data for 2,3,7,8-TCDD and selected a recommended value of 1.50 x 10^{-9} mm Hg at 25°C. This value had been measured by Rordorf (1987, 1989) using a gas-flow method in a saturation oven. SRC (1991) reported this same value by extrapolating the vapor pressures measured by Schroy et al. (1985) at four higher temperatures, 30°, 55°, 62°, and 71°C. Rordorf (1987, 1989) also reported experimental vapor pressure values for OCDD (8.25 x 10^{-13}mm Hg) and OCDF (3.75 x 10^{-12} mm Hg). These values were chosen as the most definitive because they were the most current directly measured values and also because they were selected by Mackay et al. (1992a) as the most definitive values.

Eitzer and Hites (1988) reported experimental vapor pressure values for several dioxin-like compounds utilizing GC capillary column retention time data. The values were reported as subcooled liquids and then converted to solid-phase vapor pressures. The solid-phase vapor pressures ranged from 2.16 x 10^{-12} mm Hg to 9.48 x 10^{-10} mm Hg for the CDDs and from 1.07 x 10^{-10} mm Hg to 8.96 x 10^{-9} for the CDFs. Rordorf (1987, 1989) used a vapor pressure correlation method to predict the vapor pressures of 15 CDDs and 55 CDFs (including most of the 2,3,7,8-substituted CDDs and CDFs) based on the measured vapor pressures for 10 CDDs, 4 CDFs, and the deduced boiling point and enthalpy data for the larger series of CDDs and CDFs. Measured boiling point and enthalpy data are in good agreement with the deduced data used in the correlation method. The values from Rordorf (1987, 1989) were considered the more definitive based on the review of the data from these two studies by Mackay et al. (1992a).

The ranges of selected values reported within various congener groups are as follows:

Congener Group	Vapor Pressure Range (mm Hg)		
TCDD	1.5×10^{-9}	to	4.80×10^{-8}
PeCDD	4.4×10^{-10}	to	6.6×10^{-10}
HxCDD	3.6×10^{-11}	to	5.1×10^{-11}
HpCDD	5.6×10^{-12}		
OCDD	8.2×10^{-13}		
TCDF	1.5×10^{-8}	to	4.0×10^{-8}
PeCDF	1.5×10^{-9}	to	4.3×10^{-9}
HxCDF	1.80×10^{-10}	to	5.70×10^{-10}
HpCDF	3.53×10^{-11}	to	5.8×10^{-11}
OCDF	3.75×10^{-12}		

The selected vapor pressure values reported for the dioxin-like PCBs are typically one to two orders of magnitude greater than the similarly chlorinated CDD and CDF congeners. (See Table 2-3.) The directly measured values of Murphy et al. (1987) and the derived values of Foreman and Bidleman (1985) were considered the most definitive. As with the CDDs and CDFs, the vapor pressures of the PCBs decrease with an increase in the number of chlorine substituents. The highest selected value for the dioxin-like PCBs is 1.09×10^{-6} mm Hg for 2,3,3',4,4'-PeCB, and the lowest value selected is 1.46×10^{-8} mm Hg for 2,3,3',4,4',5,5'-HpCB.

Estimated vapor pressure values for those CDDs and CDFs for which measured values were not found in the literature were calculated by the congener group-average method using the literature-reported values within a congener group. For example, the literature values for the TCDDs were averaged to obtain an estimated vapor pressure assumed to apply to the TCDD congeners that did not have literature values. A similar procedure was used to develop a congener-average for each of the other congener groups. The most definitive value for each isomer was used to derive the congener group average. Compounds with vapor pressures in the ranges reported for these compounds are considered to have very low vapor pressures.

2.4.3. Henry's Law Constant

Henry's Law constants are used in Volume 3 to estimate the volatilization of the dioxin-like compounds from soil. They are also utilized in estimating the vapor-phase bioconcentration factor from air to plant leaves. Directly measured Henry's Law constants have been reported for only three compounds. Measured values have been reported for 1,2,3,4-TCDD, 1.99 x 10^{-5} atm-m^3/mol (Santl et al., 1994); 1,3,6,8-TCDD, 6.81 x 10^{-5} atm-m^3/mol (Webster et al., 1985); and for 3,3',4,4'-PCB, 9.4 x 10^{-5} atm-m^3/mol (Dunnivant and Elzerman, 1988). These three values were considered the most definitive. Other values reported in the literature for CDDs, CDFs, and PCBs were calculated by the vapor pressure/water solubility (VP/WS) ratio technique or by structure-activity relationship techniques. A derived VP/WS ratio value, Rank 4, was determined to be more definitive than an estimated value, Rank 5.

Congener group-average Henry's Law constants were estimated for each congener group based on the selected congener values within that group. The Henry's Law constant values for the PCBs are similar to those for the CDDs and CDFs.

Lyman et al. (1982) offers guidelines, though not specific to these compounds, for comparing the degree to which organic compounds volatilize from water. These guidelines suggest that volatilization of polycyclic aromatic hydrocarbons and halogenated aromatics (which includes all the dioxin-like compounds) from water represents a significant transfer mechanism from the aqueous to the atmospheric phase.

2.4.4. Octanol/Water Partition Coefficient

The octanol/water partition coefficient (K_{ow}) is used in several exposure estimation procedures in Volume 3. The log K_{ow} is used to estimate log K_{oc} when measured data are not available, and it is utilized in estimating the root concentration factor (RCF). RCF is used to estimate the uptake of contaminants by plant roots. Log K_{ow} is also used to estimate the vapor-phase bioconcentration factor from air to plant leaves.

Marple et al. (1986b) reported the octanol/water partition coefficient of 2,3,7,8-TCDD as 4.24 (± 2.73) x 10^6 at 22 ± 1°C, yielding a log K_{ow} of 6.64 (Table A-1). Two similar experimental techniques were used, but the more reliable method involved equilibration of water-saturated octanol, containing the 2,3,7,8-TCDD, with octanol-saturated water, over 6 to 31 days. U.S. EPA (1990) reported that the available low K_{ow} data ranged from 6.15 to approximately 8.5. The 6.64 value reported by Marple et al. (1986b) was the value recommended in U.S. EPA (1990). More recently, Mackay et al. (1992a) evaluated all published measured and estimated log K_{ow} values for 2,3,7,8-TCDD and recommended a value of 6.80.

Burkhard and Kuehl (1986) used reverse-phase High Pressure Liquid Chromatography (HPLC) and Liquid Chromatography/Mass Spectrometry (LCMS) detection to determine octanol/water partition coefficients for 2,3,7,8-TCDD and a series of seven other tetrachlorinated planar molecules, including three other TCDD isomers (1,2,3,4-TCDD; 1,3,7,9-TCDD; 1,3,6,8-TCDD), 2,3,7,8-TCDF, and 3,3',4,4'-tetrachlorobiphenyl. The log K_{ow} values for the four TCDD isomers ranged from 7.02 to 7.20. The log K_{ow} for 2,3,7,8-TCDF was 5.82, and the log K_{ow} for 3,3',4,4'-TCB was 5.81.

Burkhard and Kuehl (1986) also re-evaluated data on 13 CDDs and CDFs previously reported by Sarna et al. (1984) under similar experimental techniques. In the re-evaluation, Burkhard and Kuehl (1986) used experimental rather than estimated log K_{ow} values in correlations with gas chromatographic retention times. This approach yielded log octanol-water partition coefficients ranging from about 4.0 for the nonchlorinated parent molecules to about 8.78 for the octa-chlorinated compounds, much lower than the values originally reported by Sarna et al. (1984).

Sijm et al. (1989) used a slow stirring method to obtain log K_{ow} values for 73 CDD and CDF congeners; values ranged from 6.10 to 7.92. Mackay et al. (1992a) reviewed all published measured and estimated log K_{ow} values for eight tetra- through octa-substituted CDDs and seven tetra- through octa-substituted CDFs; recommended values were selected by Mackay et al. (1992a) for the eight CDDs and for five of the CDFs. The most definitive values chosen were either those selected by Mackay et al. (1992a), a directly measured value, or the most current derived value. Selected values reported for congeners within the various congener groups ranged as follows:

Congener Group	Log K_{ow}
TCDD	6.1 to 7.1
PeCDD	6.2 to 7.4
HxCDD	6.85 to 7.8
HpCDD	8.0
OCDD	8.2
TCDF	5.6 to 6.79
PeCDF	6.19 to 6.92
HxCDF	7.0
HpCDF	7.4
OCDF	8.0

The selected log K_{ow} values for the PCBs are similar to those reported for the CDDs and CDFs. The values range from 6.5 (measured) for 3,3',4,4'-TeCB to 7.71 (literature-estimate) for 2,3,3',4,4',5,5'-HpCB. The log K_{ow} values increase with an increase in the number of chlorine substituents.

Partition coefficient values were calculated for those compounds for which no measured data were reported in the literature by averaging the literature values within congener groups, as were done for vapor pressure and water solubility. Partition coefficients in the ranges of these reported values indicate that the substances tend to adsorb strongly to organic components in the soil and may bioconcentrate in those organisms exposed to the compounds.

2.4.5. Organic Carbon Partition Coefficient

The organic carbon partition coefficient (K_{oc}) is used in several exposure estimations in Volume 3. K_{oc} is used in the estimation of the adsorption partition coefficient, which describes the partitioning of contaminants between suspended sediment and the water column. K_{oc} is also used in estimating the concentration of contaminants in below ground vegetables grown in contaminated soil.

Log K_{oc} values for 2,3,7,8-TCDD have been measured in several studies. Lodge and Cook (1989) used contaminated sediments from Lake Ontario and distilled water in glass cylinders to measure the log K_{oc} of 2,3,7,8-TCDD. Log K_{oc} values ranged from 7.25 to 7.59. Jackson et al. (1986) used 10 contaminated soil samples in a batch extraction procedure to measure log K_{oc}. The average log K_{oc} of the 10 soils was reported as 7.39. Marple et al. (1987) used two uncontaminated soils spiked by two different methods with 2,3,7,8-TCDD to obtain the log K_{oc} value. The soil was stirred with water in 2-liter flasks. The log K_{oc} values ranged from 5.96 to 6.54 for both soils, with an average value of 6.40 for the red clay soil and 6.02 for the alluvial soil.

Puri et al., (1989) studied log K_{oc} of 2,3,7,8-TCDD with several other co-contaminants such as crankcase oils and surfactants. An average log K_{oc} value of 5.68 was reported for 2,3,7,8-TCDD in the presence of 0.01 percent surfactant. Walters and Guiseppi-Elie (1988) used several soils and water/methanol mixtures in a batch shake testing procedure to determine the log K_{oc} of 2,3,7,8-TCDD. The study resulted in a log K_{oc} value of 6.6.

Five studies for log K_{oc} of 2,3,7,8-TCDD were ranked number 1. The studies by Jackson et al. (1986) and Lodge and Cook (1989) had confirming values of 7.39 and 7.42, respectively. The studies by Walters and Guiseppi-Elie (1988), Walters et al. (1989), and Marple et al. (1987) had confirming values of 6.6, 6.66, and 6.4, respectively. The 6.6 value reported by Walters and Guiseppi-Elie (1988) was chosen by Syracuse Research Corporation (SRC) in the CHEMFATE Database (SRC, 1991) as the most definitive. This value was determined in a mixed solvent system, water and methanol; therefore, it is not considered as appropriate as a pure water equilibration system determined value. The values reported by Marple et al. (1987) and Walters et al. (1989) were determined in uncontaminated soil and with pure water; therefore, these values are selected as the most definitive for this document.

Definitive values were not selected for other congeners because of few measured data points and, oftentimes, considerable differences in the reported values for those congeners with reported values. The ranges of reported values are presented in Table A-1 in Appendix A.

2.4.6. Photo Quantum Yields

Photo quantum yields, good semi-quantitative measures of phototransformation efficiency (Yan et al., 1995), have been reported for several CDD/CDF congeners. No values were located for the dioxin-like PCBs.

Congener	Photo Quantum Yield (mole/einstein)	Reference
1,2,3,7-TCDD	5.42×10^{-4}	(Choudhry and Webster, 1989)
1,3,6,8-TCDD	2.17×10^{-3}	(Choudhry and Webster, 1989)
2,3,7,8-TCDD	2.2×10^{-3}	(Dulin et al., 1986)
2,3,7,8-TCDD	3.3×10^{-2}	(Rapaport and Eisenreich, 1984)
2,3,7,8-TCDD	1.62×10^{-2}	(Yan et al., 1995)
1,2,3,4,7-PeCDD	9.78×10^{-5}	(Choudhry and Webster, 1987)
1,2,3,4,7,8-HxCDD	1.10×10^{-4}	(Choudhry and Webster, 1987)
1,2,3,4,7,8-HxCDD	1.58×10^{-3}	(Yan et al., 1995)
1,2,3,4,6,7,8-HpCDD	1.53×10^{-5}	(Choudhry and Webster, 1987)
OCDD	2.26×10^{-5}	(Choudhry and Webster, 1987)
OCDD	1.25×10^{-3}	(Yan et al., 1995)
1,2,4,7,8-PeCDF	1.29×10^{-2}	(Choudhry et al., 1990)
1,2,3,4,7,8-HxCDF	6.96×10^{-4}	(Choudhry et al., 1990)

All quantum yields were measured in a water-acetonitrile solution at 313 nm, except those reported by Rapaport and Eisenreich (1984) which were measured in the vapor phase and those reported by Yan et al. (1995) which were carried out in a butanol/decane mixture. Yan et al. (1995) also examined the effect of co-contaminants (pentachlorophenol, naphthalene, phenanthrene, and anthracene) on the photoquantum yield of OCDD and 2,3,7,8-TCDD. The presence of the co-contaminants decreased the photoquantum yield at a degree dependent upon both the concentration and extinction coefficient of the co-contaminants.

Congener group averages were not calculated because photo quantum yields are very sensitive to chlorine position and also to the physical medium (e.g., vapor or dilute solution) and conditions (e.g., the solvent system) used in the experiments (Yan et al, 1995).

2.5. PHYSICAL CHEMICAL PROPERTIES - BROMINATED COMPOUNDS

Information on the physical and chemical properties of the polybrominated dioxins and furans is very limited and has not been compiled for this report.

2.6. ENVIRONMENTAL FATE - CHLORINATED COMPOUNDS

CDD/CDFs and dioxin-like PCBs have been found throughout the world in practically all media including air, soil, water, sediment, and biota. The widespread occurrence observed is not unexpected considering the numerous sources that have emitted these compounds into the atmosphere and the overall resistance of these chemicals to abiotic and biotic transformation. Consequently, CDD/CDFs and PCBs emitted to the atmosphere can be transported long distances in the atmosphere before they are deposited onto vegetation, soil, and water via dry and wet deposition.

As depicted in Figure 2-1, deposition onto vegetation and subsequent ingestion of that plant material by animals is hypothesized to be the primary mechanism by which CDD/CDFs enter the terrestrial/agricultural food chain. Deposition onto soil with subsequent erosion and runoff into water bodies with subsequent bioaccumulation by aquatic biota is believed to be the major pathway by which CDD/CDFs enter the aquatic food chain in most freshwater bodies. These two pathways are also expected to be major pathways for entry of dioxin-like PCBs into the terrestrial and aquatic food chains.

However, because PCBs are more mobile in the environment (i.e., greater vapor pressures and water solubilities) than CDD/CDFs, there will be greater inter-media transport of PCBs (e.g., greater volatilization from soil and water to air). In addition, because of the previous widespread use and disposal of PCBs, localized sources of contamination may dominate aquatic food chain sources in more water bodies than is the case for CDD/CDFs.

The growing body of literature from laboratory, field, and monitoring studies examining the environmental transport, transformation, and distribution of CDD/CDFs and dioxin-like PCBs has increased the understanding of the fate of these environmentally ubiquitous compounds. The purpose of this section is to summarize the key findings from the growing body of literature dealing with the environmental fate of CDD/CDFs and PCBs.

Figure 2-2 presents a conceptual diagram of the intermedia movement of CDD/CDFs and PCBs among the five major environmental media: air, soil, water, sediment, and biota. As will be discussed in this section, the primary mechanism currently believed to be responsible for the widespread occurrence of CDD/CDFs and PCBs is long range atmospheric transport and deposition onto vegetation and soil.

2.6.1. Environmental Fate of CDDs and CDFs

2.6.1.1. Summary

Because of their high lipophilicity and low water solubility, CDD/CDFs are primarily associated with particulate and organic matter in soil, sediment, and the water column. Current understanding of CDD/CDF behavior on atmospheric particulate matter is that there is a partitioning between the particles and the gas phase. The two key parameters controlling the phase in which a particular congener is predominantly found are the congener's vapor pressure and the atmospheric temperature. Congeners with higher vapor pressures (i.e., the less chlorinated congeners) are found to a greater extent in the gas phase. CDD/CDFs sorbed to soil exhibit little potential for significant leaching or volatilization once sorbed to particulate matter.

The available evidence indicates that CDDs and CDFs, particularly the tetra- and higher chlorinated congeners, are extremely stable compounds under most environmental conditions. The only environmentally significant transformation processes for these congeners are believed to be atmospheric photooxidation and photolysis of nonsorbed species in the gaseous phase or at the soil or water-air interface. Several studies have, however, indicated that certain ligninolytic fungi can degrade these higher-chlorinated congeners and that anaerobic degradation in sediment may occur at a slow rate. To a large extent, these degradation processes involve dechlorination to less-chlorinated (and possibly more toxic) congeners.

Burial in-place or erosion of soil to water bodies appears to be the predominant fate of CDD/CDFs sorbed to soil. CDD/CDFs entering the water column primarily undergo sedimentation and burial with some uptake by aquatic biota. The ultimate environmental sink of CDD/CDFs is believed to be aquatic sediments. CDD/CDFs entering the atmosphere are removed either by photodegradation or by dry or wet deposition.

Vapor-phase dry deposition of CDD/CDFs onto vegetation is hypothesized to be the primary route of entry of CDD/CDFs into the terrestrial/agricultural food chain. Atmospheric deposition of CDD/CDFs onto land followed by runoff/erosion to water bodies is hypothesized to be the major route of entry of CDD/CDFs into the aquatic food chain of most freshwater bodies.

2.6.1.2. Transport Mechanisms in Air

Once released into the atmosphere, CDDs and CDFs can become widely dispersed throughout the environment by atmospheric transport and deposition. In an assessment of the atmospheric transport and deposition of CDDs and CDFs for EPA, Hites and Harless (1991) generated data and analyses that support the contention that background environmental levels and congener profiles of CDDs and CDFs in soils and sediment (i.e., higher rather than lower chlorinated congener patterns predominate) can be attributed, in large part, to the atmospheric transport and transformation of CDDs and CDFs released from combustion sources. More recently, Tysklind et al. (1993) reported the results of measurements of CDD/CDFs in the ambient air from a rural site in Sweden collected during 1989 and 1990. The highest concentrations of total CDD/CDFs were measured during sampling events with air masses coming with westerly to southerly winds, thus indicating long range transport. The congener profiles were found to vary depending on wind trajectories implicating source influences from industrialized and urbanized areas of Europe.

Deposition is a broad term defining a number of atmospheric phenomena, including the wet and dry deposition of CDD/CDF-contaminated airborne particulate matter onto soils and vegetation, and the wet and dry deposition of vapor-phase CDD/CDFs onto soils and vegetation. Mass-balance studies have been conducted in several countries in an effort to establish the mechanisms associated with the generation, transport, and environmental fate of CDD/CDFs. A wide range of estimated deposition rates have been developed in these studies. The variation in estimates may be attributed, in part, to the likely differences in precision and accuracy of the various sampling methods used, as well as the inherent difficulty in comparing results from differing collection devices. Table 2-4 presents a summary of some of the deposition rates generated by investigators in Sweden, the United Kingdom, Belgium, Germany and the United States. As noted in Table 2-4, deposition fluxes appear to be greater in urban areas than in rural areas.

A variety of methods have been developed by researchers in several countries for measuring dry and wet deposition of CDD/CDFs. However, because of the complexity of deposition as it occurs in the natural environment, all of these methods, with the possible exception of wet deposition monitoring techniques, have major drawbacks which limit their utility for generating data that provide a reliable and accurate measure of deposition as it naturally occurs. Methods have also been developed for measurement of total CDD/CDF concentrations in air; modifications to these methods have been developed that can enable consistent and reproducible measurements of particulate and vapor-phase ambient air concentrations. Mathematical models have also been developed to estimate dry and wet deposition rates. [Volume 3 provides a detailed discussion of these modeling techniques]. Because the current state of knowledge concerning deposition mechanisms/rates and methods to accurately measure deposition is not well-developed, the most effective program that could be deployed today to better understand deposition would consist of ambient air measurements coupled with specific deposition studies designed to improve the accuracy of deposition modeling.

Because of the importance of atmospheric deposition as a pathway for contamination of the terrestrial/agricultural food chain, the remainder of this section (i.e., Section 2.6.1.2) presents an overview discussion of three areas: (1) vapor/particle partitioning; (2) dry deposition processes relevant for CDD/CDF; and (3) wet deposition processes relevant for CDD/CDF.

2.6.1.2.1. Vapor/Particle (V/P) Partitioning. The relative importance of the various deposition processes (and associated phases) is related to congener-specific vapor/particle partitioning. Hites and Harless (1991), Hippelein et al. (1996), and others have demonstrated that partitioning of CDD/CDFs between the vapor and particle-associated phases occurs in the atmosphere. The key parameters controlling the phase in which a particular congener is found are the congener's vapor pressure, the atmospheric temperature, and the particulate matter concentration in the atmosphere. Congeners with higher vapor pressures (i.e., the less-chlorinated compounds) are found to a greater extent in the vapor phase. For a given congener, the fraction in the vapor phase increases with increasing ambient temperature and decreases with increasing particle concentration. A portion of the particle-associated compound appears to be freely exchangeable between the particulate and vapor phases. A second portion may be irreversibly sorbed or occluded by the particles and not in equilibrium with the gas phase.

A comprehensive review of the published literature addressing vapor/particle (V/P) partitioning of CDD/CDFs in stack gases and ambient air is provided in Volume 3. The Volume 3 review includes an evaluation of the results of stack testing data, ambient air sampling data, and theory rooted in basic physical chemistry that either imply, directly deduce, or theoretically calculate V/P partitioning. Table 2-5 presents a summary of the Volume 3 review of the ambient air monitoring studies. The most comprehensive set of partitioning data were collected by Hippelein et al. (1996); data were collected continuously over the course of 48 weeks at six urban sites on the outskirts of Augsburg, Germany, during 1992 and 1993.

A theoretical approach developed by Bidleman (1988) for predicting V/P partitioning of CDD/CDFs is described in detail in the Volume 3 review. Table 2-6 presents, for each of the 2,3,7,8-substituted CDD/CDFs, the percentage of mass predicted in Volume 3 using this theoretical approach to be in the particle phase under four airshed conditions: "clean continental," "average background," "background plus local sources," and "urban." From the review in Volume 3, the following conclusions were made:

- The stack test methods in use today to monitor and measure the concentration of CDD/CDFs emitted to the air from combustion sources have given inconclusive and contradictory V/P partitioning results and thus do not provide a credible basis, at present, for determining V/P partitioning at the point of release. There is no consistent pattern to the interpretation of V/P based on where the CDD/CDF segregate in the instrument (e.g., the glass fiber filter or the XAD resin). Factors that may contribute to this inconsistent pattern are: the relatively long residence time spent traversing the stack interior; the location of the probe to the instrument in a relatively hostile environment of the hot combustion gas; the static temperature of the particulate filter caused by heating the particulate filter housing; and the fact that located between the particulate trap and the vapor trap is a condensing section consisting of glass tubing surrounded by an ice bath.

- The use of a high-volume ambient air sampler consisting of a glass fiber particulate filter (GFF) and polyurethane foam adsorbent trap (PUF) is a reliable method for the collection and retention of CDD/CDFs in ambient air. Because the sampler is not artificially heated or cooled, but is allowed to operate at ambient air temperatures, the method can be used to imply the V/P partitioning of CDD/CDFs in ambient air. This is accomplished by separately extracting and analyzing the GFF and PUF. However, the method may only give an approximate indication of the V/P ratio since mass transfer of CDD/CDF from the particulate matter on the GFF to the PUF cannot be ruled out. For example, it is possible that a portion of the CDD/CDFs that are sorbed to particulate matter captured by the filter may be volatilized and carried with the air flow to the PUF sorbent trap (blow-off effect). If this were to occur, the observed V/P ratio would be overestimated. Also, the GFF will collect particles $\geq$0.1 microns in diameter and, therefore, it is possible that smaller particles will pass through the GFF and be trapped in the PUF. If this does occur, the observed V/P ratio will be overestimated.

  There are currently no empirical data that demonstrate the magnitude of these effects or that these effects actually occur. However, the potential impact of particle breakthrough may be ascertainable, if it is assumed that the CDD/CDF congener group pattern is the same on all particle size fractions. This assumption is supported by the findings of Kaupp et al. (1994) who demonstrated that CDD/CDF congener group profiles were nearly identical in four particle size ranges (1.35 to 4.05 um; 0.45 to 1.35 um; 0.15 to 0.45 um; and <0.15 um) collected in a rural area of Germany during the summer of 1992. Thus, if OCDD is, as is typical, the dominant congener in the collected material on the GFF, then the mass of any other CDD/CDF on the PUF that may be due to particle breakthrough can be estimated by multiplying: (1) the ratio of that congener's mass on the GFF to the mass of OCDD on the GFF by (2) the mass of OCDD in the PUF.

- Neither the currently available monitoring techniques nor the available models necessarily give the "correct" V/P partitions. Until the state of knowledge of CDD/CDF partitioning in air is improved through development of improved monitoring devices and laboratory investigations of the kinetics and thermodynamics of CDD/CDF sorption, the theoretical construct described in Chapter 3 of Volume 2 is the recommended approach for estimating V/P partitioning of CDD/CDFs at this time. Key advantages to the theoretical approach are that it relies on current adsorption theory, considers the molecular weight and the degree of halogenation of the congeners, uses the boiling points and vapor pressures of the congeners, and uses the availability of surface area for adsorption of atmospheric particles that correspond to a variety of ambient air shed classifications having variable particulate matter densities.

2.6.1.2.2. Dry Deposition. Dry deposition can involve two phases, dry particulate deposition and vapor phase deposition, the relative importance of which for a given congener is dependent primarily on the V/P partitioning. First, dioxin-like compounds associated with particulate matter can deposit by gravitational settling or turbulent diffusion. Secondly, dioxin-like compounds can be deposited by vapor-phase diffusion into the soil, vegetation, and the surface layer of water bodies. The rate at which atmospheric chemicals are deposited is termed the "deposition flux". The deposition flux is derived as the product of the concentration of the chemical in the vapor phase or on/in the particulate and the deposition velocity of the contaminated particles. The downward motion represented by deposition velocity is controlled by the gravitational settling velocity, atmospheric resistance, surface resistance and the atmospheric surface friction layer. The factors that most influence deposition flux can be divided into two types: (1) meteorological influences and (2) the properties of the chemical influencing it's V/P partitioning. A detailed list of the many factors that can affect dry deposition is shown in Table 2-7.

Dry Particulate Deposition. Dry particulate deposition is the best characterized of the dry deposition processes. As noted in Table 2-5, the vast majority of the atmospheric burden of hepta- and octa-chlorinated CDD/CDF (and, to a lesser extent, the burden of hexa- and penta-chlorinated congeners) is associated with particulate matter. As such, dry particulate deposition is a major mechanism for removal of these congeners from the atmosphere. The major factors controlling the transfer of particulate from some height above the surface through the surface layer down to the immediate vicinity of the receptor surface are the forces of gravity and turbulent diffusion. As a general rule, very large particles (i.e., greater than 20 μm) will be removed from the atmosphere fairly rapidly by the force of gravity (Kaupp et al., 1994). Particles less than 20 μm will be removed at a slower rate primarily by atmospheric turbulence and Brownian diffusion through the laminar sub-layer which often has a thickness of 10^{-1} to 10^{-2} cm. The deposition flux for these smaller particles is influenced by many factors, including: the distribution of particles by diameter and density; the atmospheric turbulence; and the friction and morphology of the impacted ground and vegetative surfaces.

Few studies have been published that have attempted to measure only dry particulate deposition of CDD/CDFs. Koester and Hites (1992a) used inverted frisbees and flat glass plates to collect dry particulate deposition. The collectors were coated with mineral oil and then deployed uncovered (except during precipitation events) for exposure periods of several weeks. The mineral oil is removed from the frisbees/plates after the exposure period and analyzed for CDD/CDF content. The extent to which these devices may also be acting as vapor phase collectors is not thought to be significant but has not been tested. Similarly, the extent of photodegradation of collected CDD/CDFs is not thought to be significant but has not been tested. Hall and Upton (1988) had previously conducted wind tunnel studies of the particle collection efficiency of inverted frisbees and had found an overall collection efficiency of approximately 50 percent with efficiencies decreasing as wind speed increased and particle diameter decreased.

The deposition velocity of particulate matter containing CDD/CDFs onto various surfaces has not been well characterized and is a major source of uncertainty in modeling particulate deposition. Bidleman (1988) estimated that particulates with diameters ranging from 0.08 to 2 μm have deposition velocities that vary from 0.003 to 0.036 cm/sec. Coarser particulates (i.e., >2 μm) were estimated to have much higher deposition velocities, 0.5 to 2.5 cm/sec (Bidleman, 1988). From the results of their study with inverted frisbees and glass plates, Koester and Hites (1992a) calculated an average deposition velocity for particulate-associated CDD/CDFs of 0.2 cm/sec; calculated deposition velocities for the tetra- through octa-chlorinated congener groups ranged from 0.086 to 0.6 cm/sec. Trapp and Matthies (1995) estimated that the fine particulates (i.e., diameters of 0.1 to 1.0 μm) that are responsible for the long range transport of atmospheric particle bound pollutants have deposition velocities of about 0.01 cm/sec.

Dry Vapor-Phase Deposition. Although not as well characterized, several studies have concluded that the transfer of all non-hepta- and non-octa-chlorinated dioxin-like compounds to leafy vegetation is dominated by vapor phase deposition which involves the movement of vapor-phase dioxin from ambient air into leafy vegetation (Bacci, et. al., 1990; Gaggi and Bacci, 1985; McLachlan, et. al., 1995; Rippen and Wesp, 1993; Simonich and Hites, 1995). Dry particulate and wet deposition are believed to be the dominant mechanisms by which vegetation and soil are exposed to hepta- and octa-chlorinated congeners. Vapor phase deposition directly onto soil is not believed to be a dominant process in most settings because soil is usually covered by vegetation or detritus which are likely to serve as more important exchange sites.

Major factors governing vapor-phase deposition include the ambient air concentration of CDD/CDFs, the exposed surface area of vegetation, the plant morphology/canopy density, and the air side resistance (i.e., a function of air turbulence which is dependent on wind speed and canopy structure). The latter two factors control, to a large extent, the vapor phase deposition velocity. Bidleman (1988) reported that vapor phase deposition velocities calculated from the results of field studies with Aroclors, p,p'-DDT, and chlordane ranged from 0.01 to 1.0 cm/sec. The limited studies that have modeled deposition of CDD/CDFs onto vegetation have employed deposition velocities of 0.5 cm/sec or higher. Trapp and Matthies (1995) used a default vapor phase deposition velocity of 0.5 cm/sec for modeling vapor phase deposition of CDD onto meadow vegetation. Smith et al. (1995) used a deposition velocity of 0.78 cm/sec for deposition of 2,3,7,8-TCDD onto tall grass. A deposition velocity of 0.5 cm/sec (calculated from the data of a ryegrass experiment) was used by McLachlan et al. (1995) to predict gaseous uptake of semivolatile organic compounds (such as CDD/CDFs and PCBs) by grass.

There are two principal applications for vegetation monitoring of gas phase deposition of CDD/CDFs: (1) monitoring short-term trends (i.e., week, month or season), and (2) long-term temporal trends (i.e., over the course of a year). To date, three methods have been employed for each of these two principal applications. Each method has its own advantages and disadvantages and each measures different components of total deposition.

Short-term monitoring methods include collection of pasture grass, grass from grass cultures, and passive collectors (e.g., McLachlan et al., 1995; McLachlan, 1995). These three types of methods differ in their ability to serve as measures of "true" deposition onto natural vegetation. However, the methods can be appropriate monitoring tools depending upon the objective(s) of the monitoring task at hand. Collection of pasture grass is easy and inexpensive and represents "true" deposition onto native pasture grass. However, it cannot be standardized and is a function of uncontrollable factors (i.e., weather, species present, and growth rate). Collection of grass from a grass culture can be semi-standardized but it may not accurately represent "true" deposition on native vegetation. Grass cultures can be elaborate and relatively costly, and it may be difficult to replicate rate of growth across sites and times. Passive collectors are easy to deploy, inexpensive, and easily standardized. However, there are no accepted, standardized passive methods available at present and the results obtained are not likely to be representative of "true" deposition on native vegetation.

The long-term methods include collection of conifer needles, canopy fall, and leaf fall. Collection of conifer needles is easy, inexpensive, and can integrate an entire year's deposition. Although the use of pine needles as CDD/CDF passive biomonitors has been extensively reported in Europe, few studies have been reported to date in the United States (Safe et al., 1992; Fiedler et al., 1995). Disadvantages of this method include potential loss of some CDD/CDFs because of wax erosion from needles over the year. Also, the method may not be an appropriate technique for a multi-year monitoring program because the canopy structure of a conifer forest will change over the course of many years. That is, the aerodynamic properties of a conifer forest, and consequently the extent and nature of deposition, will differ significantly over a 10 or 20 year period.

Collection of canopy fall using vessels to collect leaf fall, dry deposition, and wet deposition integrates the total deposition under the canopy for the entire exposure period. It is maintenance intensive and the canopy structure may change over the course of many years. The method captures most gas phase deposition, but not direct gaseous deposition to the forest floor; deposition onto the forest floor is likely to be much smaller than the deposition to the canopy. Collection of leaf fall in deciduous is easy, inexpensive, and can be easily standardized. In conifer forests, because only a small fraction of total annual deposition is reflected in fallen needles, the collection vessels must catch the eroded needle waxes as well as fallen needles. Leaf fall collection will also include measurement of some wet and dry particulate deposition that is retained on the leaves (personal communication with Dr. Michael McLachlan, University of Bayreuth, July 1996).

Investigations into the role of conifer forests in removing CDD/CDFs from the atmosphere and the consequences for accumulation in soil have recently been reported (Horstmann et al., 1995; Horstmann and McLachlan, 1996). These researchers measured bulk CDD/CDF deposition in a nature spruce forest and in an adjacent clearing over a 1-year period. Litter fall samples were also collected in the forest. The annual deposition flux of hepta- and octa-chlorinated CDD/CDFs was approximately equal in the clearing and in the spruce forest. However, the deposition flux of the lower chlorinated congeners was up to five times higher in the forest. During the warmest month of the year, the bulk deposition flux of some congener groups in the forest was up to 16 times higher than in the clearing. However, litter fall accounted for only 16 percent (OCDF) to 48 percent (TCDD) of total deposition in the forest, and canopy throughfall of wet or dry particulate deposition was demonstrated not to be responsible for the large forest deposition rates observed. The researchers hypothesize that the high deposition rates are due to dry gaseous deposition onto conifer needles followed by shedding or erosion of needle waxes, which may be enhanced during hot weather.

2.6.1.2.3. Wet Deposition. In the case of wet deposition, dioxin-like compounds can enter the soil and water and impact on the vegetation in one of two phases: either dissolved in the precipitation or associated with particulate material scavenged by the precipitation. Over the long term, wet deposition processes are believed to dominate dry deposition in terms of total mass deposition of CDD/CDFs. Wet deposition is the primary mechanism responsible for removal of small particulates from the atmosphere. For removal of particulate-associated chemicals, wet deposition flux is the product of the particulate scavenging ratio and the chemical concentration on/in various particulate size fractions. The scavenging ratio is calculated as the product of the scavenging coefficient and precipitation rate. The scavenging coefficient depends on the size distribution of the particulates and the intensity and form of precipitation (i.e., liquid or frozen). Scavenging coefficients have been developed for varying types and intensities of precipitation relative to different particle diameters based on measurements of scavenging of aerosol particles during precipitation events.

CDDs and CDFs are removed physically from the atmosphere by wet deposition (i.e., scavenged by precipitation), particle dry deposition (i.e., gravitational settling of particles), and gas-phase dry deposition (i.e., sorption of CDD/CDFs in the vapor phase onto plant surfaces) (Marklund et al., 1990; Rippen and Wesp, 1993; Welsch-Pausch et al., 1993). Precipitation can be very effective in removing CDDs and CDFs from the atmosphere. Listed in Table 2-8 are the average precipitation scavenging ratios for congener groups reported by Hites and Harless (1991) and Koester and Hites (1992a) for

Bloomington, Indiana, and Indianapolis, Indiana, respectively. The scavenging ratio is the ratio of the concentration of a chemical in precipitation (rain in these studies) to the concentration in the atmosphere and is a measure of the effectiveness of rain in removing the chemical. Also listed in Table 2-8 are the percentages of congener groups scavenged as particles in rain rather than as dissolved solutes in rain. Total rain scavenging ratios ranged from 10,000 to 150,000; hepta- and octa- CDDs (i.e., the congeners most strongly associated with particulates) were scavenged most efficiently.

Wet deposition samplers have been used to collect both rainfall and snow samples. Several types are available, including those which are equipped with photovoltaic cells or moisture sensors, which selectively open and close the sampler in response to weather changes. Precipitation samplers not equipped with moisture sensors are uncovered at all times and thus are subject to bias (i.e., due to collection of dryfall particles as well as wet particulate deposition). Wet deposition collectors have been designed to measure total wet deposition (i.e., dissolved and particulate-associated deposition combined) and dissolved deposition and particulate deposition separately.

The Bergerhoff method is a standard method specified in the German Clean Air Act for monitoring CDD/CDF deposition. The method consists of deploying open-mouth jars for a one month exposure period. Ten Bergerhoff jars have a combined sample collection area of about 0.1 m^2. The Bergerhoff method was designed to collect wet and dry particulate deposition. The samplers have the potential for evaporative loss of CDD/CDFs both in the collected wet and dry deposition. The addition of a water/solvent solution to the jar is reported to minimize this potential problem. The samplers are not thought to be collecting gas phase CDD/CDFs but no confirmatory testing has been reported.

2.6.1.2.4. Mechanisms for Entry of CDD/CDFs into the Terrestrial Food Chain

Air to Plant to Animal Hypothesis. Based on information currently available, the primary mechanism by which CDD/CDFs appear to enter the terrestrial food chain is by vapor phase atmospheric deposition (and to a lesser extent, dry particulate deposition) onto plant surfaces which are subsequently ingested by animals (e.g., cattle). This hypothesis was originally advanced by McLachlan and Hutzinger (1990). Deposits onto the soil can enter the food chain via direct ingestion (e.g., soil ingestion by earthworms, fur preening by burrowing animals, incidental ingestion by grazing animals, etc).

CDD/CDFs in soil can also become available to plants and thus enter the food chain by volatilization and vapor sorption or particle resuspension and adherence to plant surfaces. Although CDD/CDFs in soil can adsorb directly to underground portions of plants, uptake from soil via the roots into above ground portions of plants is thought to be insignificant (McCrady et al., 1990).

Support for this air-to-food hypothesis is provided by Hites and Harless (1991) who concluded that "background environmental levels of PCD/F are caused by PCD/F entering the environment through the atmospheric pathway." Their conclusion was based on demonstrations that the congener profiles in lake sediments could be linked to congener profiles of combustion sources. Further argument supporting this hypothesis is offered below:

- Numerous studies have shown that CDD/CDFs are emitted into the air from a wide variety of sources and that CDD/CDFs can be commonly detected in air at low concentrations. (See Chapter 3 and Volume 1.)
- Studies have shown that CDD/CDFs can be measured in wet and dry deposition in most locations including remote areas (Koester and Hites, 1992a; Rappe, 1991).
- Numerous studies have shown that CDD/CDFs are commonly found in soils throughout the world. (See Chapter 3.) Atmospheric transport and deposition is the most plausible mechanism that could lead to this widespread distribution.
- Models of the air-to-plant-to-animal food chain have been constructed. Exercises with these models show that measured deposition rates and air concentrations can be used to predict food levels that are similar to levels actually measured in food (Travis and Hattemer-Frey, 1991; also Volume 3).
- Alternative mechanisms of uptake into food appear less plausible:
    - Uptake in food crops and livestock from water is minimal due to the hydrophobic nature of these compounds. Travis and Hattemer-Frey (1987, 1991) estimate water intake accounts for less than 0.01 percent of the total daily intake of 2,3,7,8-TCDD in cattle. Experiments by McCrady et al. (1990) show very little uptake in plants from aqueous solutions.
    - Relatively little impact on the general food supply is expected from soil residues that originate from site-specific sources such as sewage sludge and other waste disposal operations. Sewage sludge application onto agricultural fields is not currently a widespread practice in the United States. Waste disposal operations can be the dominant source of CDD/CDFs in soils

at isolated locations such as Times Beach, but are not sufficiently widespread to explain the ubiquitous nature of these compounds.

- The release of CDD/CDFs to the environment from the use of pesticides contaminated with CDD/CDFs is believed to have declined in recent years; however, the past and current impact of pesticide use on CDD/CDF levels in the food supply is uncertain. CDD/CDFs have been associated with certain phenoxy herbicides most of which are no longer produced or have restricted uses. EPA has issued data call-ins requiring certain pesticide manufacturers to test their products for CDD/CDF content. The responses, so far, indicate that current levels in these products are below or near the limit of quantitation. (See Volume 1.)

- Current CDD/CDF levels in food resulting from the use of bleached paper products containing CDD/CDFs appears to be minimal. In the early 1980s, testing showed that CDD/CDFs could migrate from paper containers into food. Current CDD/CDF levels in paper products are now much lower than in the early 1980s. Also, testing of products such as milk and beef prior to packaging has shown detectable levels which cannot be attributed to the packaging. (See Chapter 3.)

A related issue is whether the CDD/CDFs in food result more from current or past emissions. Sediment core sampling indicates that CDD/CDF levels in the environment began increasing around the turn of the century, but also that CDF levels have been declining since about 1980 (Smith et al., 1992). Thus, CDD/CDFs have been accumulating for many years and may have created reservoirs that continue to impact the food chain. Researchers in several countries have attempted to compare known emissions with deposition rates. All of these studies suggest that annual atmospheric depositions exceed annual emissions by a factor of 2 to 10. One possible explanation for this discrepancy between source emissions and deposition may be that volatilization or particle resuspension from these reservoir sources followed by atmospheric scavenging is responsible. These mass balance studies are highly uncertain, and it remains unknown how much of the food chain impact is due to current vs past emissions.

Plant Accumulation Models. McLachlan (1995) presents a simple “scavenging” approach for predicting grass concentrations from air concentrations. He suggests that grass scavenges the equivalent of 9 m^3 or air per gram of grass, and that corn scavenges 4.5 m^3 of air per gram of corn. These scavenging ratios were empirically derived from a set of monitoring data including air, pasture, and corn samples. CDD/CDF concentrations in grass can be estimated by multiplying the air concentration by this scavenging coefficient of 9. McLachlan (1995) suggests that this simple scavenging coefficient would work with all CDD/CDF congeners since the deposition velocities of vapor and particle bound CDD/CDF appear to be similar.

EPA has developed an air-to-leaf transfer approach to estimate the concentration of CDD/CDFs in vegetation resulting from dry and wet deposition. The EPA approach, fully described in Volume 3, was developed from field test data. The approach is summarized below followed by a brief description of an alternative approach (the deposition velocity approach) recently applied to CDD/CDFs by Smith et al. (1995) and Trapp and Mattheis (1995).

EPA Empirical Air-to-Leaf Approach. Two processes, air-borne vapor phase absorption and air-borne particle deposition, are assumed to contribute to above ground vegetation concentrations:

$$C_{abv} = C_{vpa} + C_{ppa} \qquad \text{(Eqn. 2-1)}$$

where:

C_{abv} = concentration in above-ground vegetation, expressed on a dry weight basis (pg/g)
C_{vpa} = contribution of concentration due to vapor-phase absorption or airborne contaminants (pg/g)
C_{ppa} = contribution of concentration due to wet plus dry deposition of contaminated particulates onto plant matter (pg/g)

The algorithm estimating plant concentrations as a function of vapor-phase air concentrations, C_{vpa}, is:

$$C_{vpa} = \frac{B_{vpa} \quad C_{va} \quad VG_{ag}}{d_a} \qquad \text{(Eqn. 2-2)}$$

where:

C_{vpa} = contribution concentration due to vapor-phase absorption or airborne contaminants (pg/g)

B_{vpa} = mass-based air-to-leaf biotransfer factor, [(pg contaminant/g plant dry)/(pg contaminant/g air)]
C_{va} = vapor-phase concentration of contaminant in air (pg/m^3)
VG_{ag} = empirical correction factor which reduces vegetative concentrations considering that B_{vpa} was developed for transfer of air-borne contaminants into leaves rather than into bulky above ground vegetation
d_a = density of air (1,190 g/m^3)

The steady state solution for plant concentrations attributed to wet plus dry particle deposition, C_{ppa}, is:

$$C_{ppa} = \frac{F_p}{k_v\ Y_j} \qquad \text{(Eqn. 2-3)}$$

where:

C_{ppa} = vegetative concentration due to settling of contaminated particulates onto plant matter (pg/g)
F_p = unit contaminant wet plus dry deposition rate onto plant surfaces (pg/m^2-yr)
k_v = first-order dissipation constant (1/yr)
Y_j = dry matter yield of crop j (g/m^2)

The non-steady state solution has an additional term in the numerator of Equation 2-3, 1-e$^{(-kw\ t)}$, where t is the time to harvest or removal by grazing. Given that the k_v is relatively large (i.e., a relatively short half-life on the order of weeks), and the growing period for vegetation of concern can be weeks to months, this additional term reaches unity quickly, so a steady state solution is justified. The total deposition rate onto plants, F_p , is given as:

$$F_p = C_{pa}\ (V_d\ I_j + RN\ R_w\ W_p\ I_j) \qquad \text{(Eqn. 2-4)}$$

where:

F_p = unit contaminant wet plus dry deposition rate onto plant surfaces (pg/m^2-yr)
C_{pa} = air-borne particulate phase contaminant concentration (pg/m^3)

V_d = deposition velocity (m/yr)
I_j = fraction of particulates intercepted by crop j during deposition
RN = annual rainfall (m/yr)
R_w = fraction of particles retained on vegetation after rainfall
W_p = scavenging coefficient (unitless)

The major uncertainties of this modeling approach are:

- Vapor/particle partitioning: The V/P partitioning modeling approach (i.e., Junge-Pankow model) yields different partitioning ratios than suggested by the results of some monitoring studies (i.e., monitoring suggests a greater percentage in the vapor phase). The model could be inaccurate or the monitoring data could be biased to vapor (i.e., blow-off potential).

- Vapor transfers to vegetation: The basis for the vapor-phase biotransfer factors (B_{vpa}) is the research performed Welsch-Pausch et al. (1995). There is some uncertainty that the Welsch-Pausch experiments may not be representative of field situations (e.g., pots were raised off the ground, and the grass was a dense monoculture) and that more typical field situations (e.g., at ground level with varied vegetation of lesser density) may lead to lower vapor-phase transfer factors. However, because the vapor phase transfer factor is also a function of the length of exposure, grass that is several months old may have higher levels than the grass used by Welsch-Pausch et al. (1995).

- Particle deposition: There is uncertainty surrounding the following factors: R_w (fraction retained on vegetation from wet deposition), the weathering half-life on vegetation, absorption of particulate-associated dioxin by vegetation, and the particle deposition velocity.

Deposition Velocity Approach for Vapor Phase CDD/CDFs. This alternative approach is based on a transfer velocity (or conductance) term, a plant dissipation term, and a plant yield term as shown in Equation 2-5. The approach is exactly analogous to the EPA approach for modeling particle phase deposition. This approach has been described and parameterized for vapor phase 2,3,7,8-TCDD impacts to grassy plants in two articles, Trapp and Matthies (1995) and Smith et al. (1995). The steady state solution for the transfer velocity approach is given as:

$$C_{vpa} = \frac{F_v}{k_v\ Y_j} \qquad \text{(Eqn. 2-5)}$$

where:

C_{vpa} = plant concentration due to vapor-phase transfer (pg/g dry weight)
F_v = deposition of vapor-phase congener (pg/m^2-day)
k_v = first-order dissipation constant (day^{-1})
Y_j = yield of crop j (g/m^2)

Like the solution for particle phase deposition to plants, the non-steady state solution for Equation (2-5) has an additional term in the numerator, $1\text{-}e^{(-kv\ t)}$, where t is the time to harvest or removal by grazing. Both authors who applied this approach assumed a half-life for vapor phase dioxins on plants on the order of days to weeks. Because the "time to harvest" for grasses is also on the order of days to weeks, the additional term reaches unity quickly and again a steady state solution is justified.

The two articles evaluated do diverge at this point. The Trapp and Matthies (1995) approach is actually a comprehensive approach involving particle phase impacts and soil to plant impacts. Their analysis suggests vapor phase impacts to foliar vegetation dominate for 2,3,7,8-TCDD. They also present their solution in a more generalized fashion by having a volume term in the denominator of Equation 2-5 instead of a plant yield term; the volume term is easily converted to a mass (or yield) term with a plant density factor. Their solution for F_v is:

$$F_v = A\ g\ C_{va}\ 86400 \qquad \text{(Eqn. 2-6)}$$

where:

F_v = deposition of vapor-phase congener (pg/m^2-day)
A = leaf area index (m^2 leaf area/m^2 ground area)
g = conductance (m/sec)
C_{va} = vapor phase air concentration (pg/m^3)
86400 = conversion factor (sec to days)

Trapp and Matthies (1995) used a default value of 0.1 cm/sec for the conductance term, g, when modeling the deposition of 2,3,7,8-TCDD onto meadow grass. The appropriate value to use for conductance for a given chemical depends upon the plant species, the environmental conditions, and the lipophilicity of the vapor phase chemical. The possible range reported by Trapp and Matthies (1995) is 0.01 to 0.5 cm/sec with the appropriate value increasing as lipophilicity increases. Trapp and Matthies (1995) used a value of 5 for the leaf area index, A, in their TCDD modeling exercise. The product of the A term and the g term (i.e., 0.5 cm/sec) is analogous to a deposition velocity.

Smith et al. (1995) estimate the F_v as a multiplication of the vapor phase air concentration, C_{va} (pg/m^3), the transfer velocity, V_t, (cm/sec), and the plant interception fraction (unitless). They state that the transfer velocity is represented as the inverse of the sum of the resistances to transfer to the plant surface as:

$$V_t = \frac{1}{R_a + R_b + R_c} \qquad \text{(Eqn. 2-7)}$$

where:

V_t = transfer velocity (cm/sec)
R_a = atmospheric resistance (sec/cm) a function of vertical turbulent transport
R_b = surface boundary layer resistance (sec/cm) a function of molecular diffusivity
R_c = plant canopy/leaf resistance (sec/cm) a function of vegetative density, stomatal uptake, surface effects, and humidity

Smith et al. (1995) assumed the following reasonably conservative resistance values for deposition of 2,3,7,8-TCDD onto a flat open area with tall grass under neutral atmospheric stability conditions: $R_a = 0.4$ sec/cm; $R_b = 0.38$ sec/cm; and $R_c = 0.5$ sec/cm. The resulting transfer velocity is 0.78 cm/sec.

The deposition velocity approach is not uniform among researchers, and has the two key uncertain quantities: the velocity itself (termed V_t by Smith et al. (1995) and estimated as gA by Trapp and Matthies (1995)) and the plant degradation term - assigned values ranging by a factor of three by the two research efforts. The companion document to this report (i.e., Volume 3) provides a detailed comparison of the empirical EPA model, the Trapp and Matthies (1995) model, and the Smith et al. (1995) model.

2.6.1.3. Transport Mechanisms in Soil

Upon deposition of CDD/CDFs onto soil or plant surfaces, there can be an initial loss due to photodegradation and/or volatilization. The extent of initial loss due to volatilization and/or photodegradation is difficult to predict and is controlled by climatic factors, soil characteristics, and the concentration and physical form of the deposited CDD/CDFs (i.e., particulate-bound, dissolved in solvent, etc.) (Freeman and Schroy, 1989; Paustenbach et al., 1992; Nicholson et al., 1993). For example, observations from the Seveso incident indicated that the levels of 2,3,7,8-TCDD aerially deposited on the soil surface decreased substantially in the first six months (diDomenico et al., 1982) but that rate of disappearance then slowed by over two orders of magnitude (diDomenico et al., 1990). Nash and Beall (1980) reported that 12 percent of the 2,3,7,8-TCDD applied to bluegrass turf as a component (7.5 ppm concentration) of an emulsifiable Silvex concentrate volatilized over a period of 9 months. Schwarz and McLachlan (1993) observed no significant changes in CDD/CDF concentrations in sewage sludge amended soil that was exposed to natural sunlight for six weeks in the late summer/early fall in Germany. Similarly, Cousins et al. (1996) detected no volatilization from sludge-amended soils through which air was pumped for 30 days.

Although few studies have evaluated quantitatively the transport of soil-bound CDD/CDFs, the very low water solubilities, high K_{oc}s, and persistent nature of these chemicals indicate that erosion of soil to water bodies may be the dominant surface transport mechanism for CDD/CDFs sorbed to soil in settings where erosion is possible (Paustenbach et al., 1992; Nicholson et al., 1993). Because of their very low water solubilities and vapor pressures, CDD/CDFs below the soil surface (i.e., below the top few millimeters) are strongly adsorbed and show little upward or downward vertical migration, particularly in soils with a high organic carbon content (Yanders et al., 1989). Freeman et al. (1987) found no statistically meaningful changes in the concentration profile of 1,2,7,8-TCDD in the top 1 cm of Time Beach Soil over a 16-month period, with the exception of the top 3 mm of soil exposed to water and sunlight in which 50 percent reduction in 2,3,7,8-TCDD concentration was observed. In addition, the more chlorinated congeners do not show any significant degree of degradation below the soil surface.

Although for several years it was believed that near-surface (i.e., the top 1cm) CDD/CDFs could volatilize slowly to the surface (Freeman and Schroy, 1985), recent research has indicated that CDD/CDFs, particularly the tetra and higher chlorinated congeners, show little or no movement upward or downward in the subsurface unless surfactants or a carrier such as waste oil or diesel fuel is present to act as a solvent (Kapila et al., 1989; Puri et al., 1989; Puri et al., 1990; Yanders et al., 1989; Schramm et al., 1995). For example, Palausky et al. (1986) injected 2,3,7,8-TCDD dissolved in various organic solvents into soil columns to determine the extent of vapor phase diffusion; little movement due to volatilization was observed unless the soil was incubated at 40°C. However, laboratory studies have shown that 2,3,7,8-TCDD moves readily through soil with waste oil components and that mobility can also be enhanced by the presence of surfactants such as sodium lauryl sulfate (Yanders et al., 1989; Puri et al., 1989; Schramm et al., 1995). Overcash et al. (1991) developed a model that considers diffusive transport of 2,3,7,8-TCDD in solvents and takes into account the rate of adsorption and desorption of 2,3,7,8-TCDD from the soil particles.

Paustenbach et al. (1992) reviewed many major published studies on dioxin persistence in soil and concluded that 2,3,7,8-TCDD probably has a half-life of 25 to 100 years in subsurface soil and 9 to 15 years at the soil surface (i.e., the top 0.1 cm). Several major studies reviewed by Paustenbach et al. (1992) and additional recent studies are summarized below. Some of these recent studies have concluded that the binding of dioxin-like compounds to soil approaches irreversibility over time due to the encapsulation of the compounds in soil organic and mineral matter (Puri et al., 1989; Puri et al., 1992; Adriaens and Grbic-Galic, 1992).

McLachlan et al. (1996) presented data on CDD/CDF persistence in a sludge-amended soil sampled from a long-term field experiment started in 1968. Over 50 percent of the CDD/CDFs present in the soil in 1972 were still present in 1990. The concentrations of all congeners were observed to decrease gradually and in the same manner over this time, indicating that either physical loss of material from the experimental plot had occurred or all congeners had undergone a uniform reduction in extractability over time. Half-lives for the disappearance of CDD/CDFs from the sludge-amended soil after 1972 were on the order of 20 years. These half-lives were believed by McLachlan et al. (1996) to principally reflect physical removal rather than degradation.

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 the period 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 one 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.

Orazio et al. (1992) studied the persistence of di- to octa-chlorinated CDDs and CDFs in sandy loam soil held in laboratory columns under water-saturated soil conditions for a period of 15 months. Measurable upward movement was reported only for the dichlorofurans and dichlorodioxins. Downward movement was only noticeable for the dichloro- and trichloro-congeners. The mobility of the CDDs and CDFs was not significantly affected by co-contaminants (i.e., pentachlorophenol and creosote components) present at concentrations as high as 6,000 mg/kg. As much as 35 percent loss of the di- and trichloro-congeners due to degradation was observed; no significant degradation of the tetra- through octa-chlorinated congeners was reported (Orazio et al., 1992).

Hagenmaier et al. (1992) collected soil samples around two industrial plants in Germany in 1981, 1987, and 1989 at the same site and from the same depth, using the same sampling method. There was no indication (within the limits of analytical accuracy (+/- 20 percent)) of appreciable loss of CDDs and CDFs by vertical migration, volatilization, or degradation over the 8-year period. Also, there were no significant changes in the congener distribution pattern (i.e., tetra- through octa-) over this time period.

Yanders et al. (1989) reported that 12 years after oil containing 2,3,7,8-TCDD was sprayed on unpaved roads at Times Beach, Missouri, no dioxin was discovered deeper than 20 cm. However, these roads were paved about 1 year after the spraying episode, thus preventing volatilization to the atmosphere. Yanders et al. (1989) excavated this soil and placed the soil in bins located outdoors, subject to the natural conditions of sunlight and precipitation. They reported no appreciable loss nor vertical movement of 2,3,7,8-TCDD from the soil, even in the uppermost sections, during a 4-year study period. Puri et al. (1992) reported no migration or loss of 1,2,3,4-TCDD, 1,2,3,7,8-PeCDD, OCDD, and OCDF from samples of this soil which were examined for 2 years in controlled laboratory column experiments.

Hallett and Kornelson (1992) reported finding 2,3,7,8-TCDD at levels as high as 20 pg/g in the upper 2 inches of soil obtained from areas of cleared forest in New Brunswick, Canada, where the pesticides 2,4-D and 2,4,5-T had been applied in one or more applications 24 to 33 years earlier.

Pereira et al. (1985) reported contamination by CDDs of the sand and gravel aquifer underlying unlined surface impoundments at a wood-treatment facility that had utilized creosote and pentachlorophenol. CDDs migrated both vertically and horizontally in the subsurface. Puri et al. (1992), using soil column experiments in the laboratory, demonstrated that pentachlorophenol and naphthalene and methylnaphthalene (components of creosote) readily transported CDD/CDFs through soil. Puri et al. (1989) and Kapila et al. (1989) demonstrated that application of waste oil and anionic surfactant solutions to field and laboratory columns of Times Beach soil can move 2,3,7,8-TCDD through soil. Walters and Guiseppe-Elie (1988) showed that methanol/water solutions (1g/L or higher) substantially increase the mobility of 2,3,7,8-TCDD in soils.

2.6.1.4. Transport Mechanisms in Water

The dominant transport mechanism for removal of CDD/CDFs from the water column is believed to be sedimentation and, ultimately, burial in sediments. Sediment resuspension and remobilization of CDD/CDFs will vary on a site-by-site basis depending on the nature and extent of physical processes (e.g., winds/waves/currents) and biological processes (disturbance by benthic organisms) (Fletcher and McKay, 1992).

Even though CDD/CDFs have very low vapor pressures, they can volatilize from water. However, volatilization is not expected to be a significant loss mechanism for the tetra- and higher chlorinated CDD/CDFs from the water column under most non-spill scenarios. Podoll et al. (1986) calculated volatilization half-lives of 15 days and 32 days for 2,3,7,8-TCDD in rivers and ponds/lakes, respectively. Broman et al. (1992) used measured concentrations of CDD/CDFs in ambient air (gaseous phase) and in Baltic Sea water (truly dissolved concentrations) to calculate the fugacity gradient over the air-water interface. The fugacity ratios obtained indicated a net transport from air to water (ratios between 0.4 and 0.004).

Aquatic organisms can bioaccumulate significant levels of CDD/CDFs. Although the mass of CDD/CDFs in the biota in a given water body will account for only a small fraction of the total mass of CDD/CDFs in that water body (Mackay et al., 1992a), these bioaccumulated CDD/CDFs have entered the aquatic food chain and can lead to potentially significant human and wildlife exposures and cause sensitive fish species to be at increased risk (U.S. EPA, 1993).

2.6.1.4.1. Sorption to Particulates and Sedimentation

Most CDD/CDFs entering the aquatic environment are associated with particulate matter (i.e., dry and wet deposition of atmospheric particles, eroded soil/stormwater runoff solids, and solids in municipal and industrial discharges) and are likely to remain sorbed to the particulate matter once in the aquatic environment. Recent studies have demonstrated that dissolved CDD/CDFs entering the aquatic environment will, like other lipophilic, low water solubility organic compounds, partition to suspended solids or dissolved organic matter such as humic substances.

Muir et al. (1992) and Servos et al. (1992) recently reported that 48 hours after the addition of 2,3,7,8-TCDF, 1,3,6,8-TCDD, and OCDD in a sediment slurry to natural lake water/sediment limnocorrals, between 70 and 90 percent had partitioned to suspended particulates. The proportion freely dissolved in water ranged from <2 percent for 2,3,7,8-TCDF and OCDD to 10 to 15 percent for 1,3,6,8-TCDD. The remainder was associated with dissolved organic substances.

Broman et al. (1992) analyzed water collected from nine sampling points in the Baltic Sea selected to be representative of background levels. The concentration of particle-associated (>0.45mm) total CDD/CDFs varied between 0.170 and 0.390 pg/L with an average concentration of 0.230 pg/L (or 66 percent of total CDD/CDFs). The total CDD/CDF concentration of the "apparently" dissolved fraction varied between 0.036 and 0.260 pg/L with an average concentration of 0.120 pg/L (or 34 percent of the total). Subsequent calculations estimated that, on average, only 0.070 pg/L of the "apparently" dissolved CDD/CDFs were truly dissolved.

Servos et al. (1992) reported that the 1,3,6,8-TCDD and OCDD added as a sediment slurry to lake limnocorrals rapidly partitioned/settled to surficial sediments where they persisted over the 2 years of the study. The half-lives of 1,3,6,8-TCDD and OCDD in the water column were reported as 2.6 and 4.0 days, respectively. Based on sediment trap and mixed surface layer studies of the Baltic Sea, Broman et al. (1992) report that the mass of CDD/CDFs in the mixed surface layer at any moment represents about 1 percent of the total flux of CDD/CDFs to the sediment annually; this implies little recirculation of these compounds within the water column of the Baltic Sea. Broman et al. (1992) also reported that the concentration of CDD/CDFs in settling solids (i.e., sediment trap collected material) is approximately one order of magnitude greater than the concentration in suspended particulates. They attributed this elevated concentration to the capacity of settling solids to scavenge the dissolved fraction as the solids settle through the water column. Similar findings have been reported elsewhere (e.g., Baker et al., 1991) for PCBs and PAHs in the Great Lakes.

2.6.1.4.2. Bioaccumulation

Fish and invertebrates can strongly bioaccumulate 2,3,7,8-substituted CDD/CDFs, although the benthic and pelagic pathways by which the accumulation occurs are not well understood. Organisms have been shown to accumulate CDD/CDFs when exposed to contaminated sediments and also to bioconcentrate CDD/CDFs dissolved in water. However, because most CDD/CDFs in the water column and sediment are associated with particulate matter and dissolved organic matter, the accumulation observed in the environment may be primarily food chain-based starting with uptake by benthic organisms (e.g., mussels, chironomids) directly from sediment pore waters and/or by ingestion or filtering of contaminated particles. Those organisms consuming benthic organisms (e.g., crayfish, suckers) would then pass the contaminants up the food chain (Muir et al., 1992; Fletcher and McKay, 1992; U.S. EPA, 1993).

A thorough review of the concepts and available information on the bioaccumulation of 2,3,7,8-substituted CDD/CDFs is presented in U.S. EPA (1993) and U.S. EPA (1995). A brief overview of the material presented in these reports is provided in the remainder of this section.

Bioconcentration. For aquatic organisms, bioconcentration refers to the net accumulation (i.e., intake less elimination and metabolic transformation) of a chemical resulting from direct uptake from the water by gill membranes or other external body surfaces. A bioconcentration factor (BCF) is the ratio (in L/kg) of a chemical's concentration in the tissue of an aquatic organism to its concentration in the ambient water (U.S. EPA, 1993; 1995):

$$BCF = \frac{C_a}{C_w} \qquad \text{(Eqn. 2-8)}$$

where:

C_a = concentration of the chemical in the aquatic biota

C_w = concentration of the chemical in the ambient water

BCFs are measured in laboratory experiments. To be of most use in predicting bioaccumulation in natural settings, BCFs should be determined under steady-state conditions (i.e., conditions under which the concentrations in the biota and other ambient water are stable over a period of time). For highly hydrophobic chemicals like CDD/CDFs, steady-state takes a long time to reach and often may not be reached in laboratory experiments particularly with larger organisms which tend to have slower uptake rates and longer half-lives for elimination. Also, for highly hydrophobic compounds, a significant fraction of the chemical concentration in the water can be associated with suspended particles and dissolved organic matter and be less available for uptake by the organism.

In general, BCFs for a given species (particularly BCFs calculated using dissolved chemical concentrations rather than total water concentrations) are expected to be largely independent of site water characteristics (U.S. EPA, 1993). For hydrophobic compounds, the lipid component of an organism is believed to dominate partitioning of the chemical between the organism and water. Therefore, it is often useful to express BCFs on the basis of organism lipid content in order to reduce variability among whole weight BCFs reported for species differing in lipid content.

The expected equilibrium values for steady-state BCFs (lipid content basis) for 2,3,7,8-substituted CDD/CDFs are the corresponding K_{ow} values. However, because most reported BCFs for CDD/CDFs are calculated on the basis of total water concentrations, the reported BCFs are significantly less than these values. U.S. EPA (1993) presents a compilation of measured steady-state BCFs for 2,3,7,8-TCDD. The log BCFs vary by more than an order of magnitude (4.91 to 6.63 on a lipid content basis; 3.97 to 5.20 on a whole body basis). This variability is likely due to incomplete characterization of exposure concentrations or experimental shortcomings, including partitioning onto organic matter in test systems, oversaturation of the chemical in water, and time-varying concentrations in static systems (U.S. EPA, 1993). Table 2-9 presents log BCF values reported by various researchers for CDD/CDFs.

Bioaccumulation. For aquatic organisms, bioaccumulation refers to the net accumulation of a chemical from exposure via food and sediments as well as water. A bioaccumulation factor (BAF) is the ratio (in L/kg) of a chemical's concentration in the tissue of an aquatic organism to its concentration in the ambient water, in situations where both the organism and its food are exposed and the ratio does not change substantially over time (U.S. EPA, 1993; 1995).

$$BAF = \frac{C_a}{C_w} \qquad \text{(Eqn. 2-9)}$$

where:

C_a = concentration of the chemical in the aquatic biota
C_w = concentration of the chemical in the ambient water

The difference between BAFs and BCFs is primarily in the routes of exposure involved and the levels of accumulation attained because of these exposure routes. BCFs are measured in laboratory experiments designed to measure the chemical uptake by the organism only from water. BAFs are usually determined from measurements of chemical concentration in water and organism tissue samples that are obtained in the field from aquatic systems at presumed steady-state exposure conditions. Thus, BAFs include both direct uptake from the water as well as uptake from intake of food and sediments. The previous discussion under "Bioconcentration" concerning the form of the chemical in the water (i.e., dissolved or total) and the value of lipid normalization also applies to BAFs.

Because reliable measurements of trace levels of CDD/CDFs in ambient water are generally not available, it is not practical to develop measured BAFs for these compounds.

However, detectable concentrations of CDD/CDFs are generally measurable in sediments. The relationship between chemical concentrations in organisms and sediments is defined as the biota-sediment accumulation factor (BSAF). BSAFs can be used to measure and predict bioaccumulation directly from measured concentrations of chemicals in surface sediments and biota. They may also be used to estimate BAFs. Because BSAFs are based on field measurements and incorporate uptake from water and food, and the effects of metabolism and growth, BAFs estimated from BSAFs will incorporate the net affect of all these factors (U.S. EPA, 1993; 1995).

BSAFs are measured by relating lipid-normalized concentrations of a chemical in an organism to the organic carbon-normalized concentration of the chemical in surface sediment samples associated with the average exposure of the organism (U.S. EPA, 1995). The BSAF equation is:

$$\mathrm{BSAF} = \frac{C_l}{C_s} \qquad \text{(Eqn. 2-10)}$$

where:

C_l = lipid-normalized concentration of the chemical in aquatic biota

C_s = organic carbon-normalized concentration of the chemical in surface sediment

The ratios of BSAFs of CDD/CDFs to a BSAF for 2,3,7,8-TCDD yield bioaccumulation equivalency factors (BEFs) which can be used to estimate the combined toxic potential of CDD/CDFs as a toxic equivalence concentration. Table 2-10 presents BSAFs and BEFs derived for CDD/CDFs from Lake Ontario lake trout and sediment. A compilation of additional BSAFs is presented in the companion document to this report (i.e., Volume 3). Chapter 3 of this report summarizes concentrations of CDD/CDFs in aquatic organisms that have been reported in the literature.

2.6.1.4.3. Mechanisms for Entry of CDD/CDFs Into the Aquatic Food Chain

Air to Land to Water to Animal Hypothesis. Based on information currently available, the primary mechanism by which CDD/CDFs enter the aquatic food chain in most freshwater bodies is by atmospheric deposition onto land followed by transport of the deposited material in stormwater runoff/erosion into water bodies. Once in the water body, entry into the food chain starts with uptake by benthic organisms as described in Section 2.6.1.4.2.

CDD/CDFs can also enter aquatic systems directly from industrial and POTW effluent discharges, from deposition of CDD/CDFs in the atmosphere directly onto water bodies (of importance for the Great Lakes), and in erosion/stormwater runoff from areas where dioxin-containing material is present (e.g., a contaminated industrial or waste disposal site). Thus, for any given water body, the dominant transport mechanism will depend on site-specific conditions. For example, Pearson and Swackhammer (1997) report that atmospheric deposition is the dominant source of CDD/CDFs to Lake Superior, but not to Lake Michigan or Lake Ontario. However, for most freshwater bodies today, erosion/ stormwater runoff is the probable dominant mechanism for CDD/CDF input and the CDD/CDFs present in that runoff can be attributed to atmospheric deposition. Several studies support this hypothesis.

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 are, for the period 1990-1993: 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 the year 1970 to be: 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 was determined to be 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 I-TEQ$_{DF}$ at levels ranging from 0.01 to 65 pg/L; most samples contained less than 15 pg/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. However, the profiles of CDD/CDFs in the urban stormwater samples were similar at all sites, 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.

Further argument supporting this hypothesis is offered below:

- Much less data have been published on CDD/CDF discharges in wastewater than have been published on emissions to air. Nonetheless, the general scientific consensus is that because of their extremely low water solubilities and the restrictions on suspended particulate discharges in wastewater discharges, CDD/CDF emissions via wastewater are negligible compared to atmospheric emissions and land-disposed waste material. This is the conclusion drawn in the U.S. Inventory (see Volume 1), the European Dioxin Inventory (Quab and Fermann, 1997), and the recent United Nations compilation of national and regional CDD/CDF emissions inventories (UNEP, 1999).
- Studies have measured CDD/CDFs in wet and dry deposition in most locations, including remote areas (see Table 2-4).
- Studies have measured CDD/CDFs in soils in most locations, including remote areas (see Chapter 3). Volume 1 of this Reassessment presents preliminary rough estimates of the potential magnitude of soil erosion via rural runoff sources to be 2,700 grams of I-TEQ$_{DF}$ annually.
- The Paustenbach et al. (1996) and Mather et al. (1997) studies cited above detected CDD/CDFs in all stormwater samples collected in the San Francisco area. However, CDD/CDFs were only rarely detected in discharges collected

from nine POTWs in the San Francisco area during the same approximate time period (California Regional Water Quality Control Board, 1996).

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

2.6.1.5. Transformation Processes

2.6.1.5.1. Photolysis. Photolysis appears to be one of the most environmentally significant degradation mechanisms for CDD/CDFs in water and soil, and possibly in the atmosphere. CDD/CDFs absorb electromagnetic radiation at wavelengths greater than 290 nm (i.e., the lower bound of the Sun's radiation reaching the Earth's surface) and, therefore, can be expected to be subject to photolysis by sunlight. Numerous studies have demonstrated that CDD/CDFs undergo relatively rapid photolysis in a variety of organic solvents and at much slower rates in water, typically following first order kinetics. Because of the difficulties inherent in controlling experimental variables for nonvolatile and highly lipophilic compounds like CDD/CDFs, few photolysis studies have been performed with natural waters, with CDD/CDFs sorbed to soil or particulate matrices, and with gas phase CDD/CDFs. The photochemistry of CDD/CDFs has been reviewed by Miller and Zepp (1987), Choudry and Webster (1987), Atkinson (1991; 1996), and others.

The major products from photolysis are complex and, in most studies, good mass balances have not been obtained. Although, the photolytic pathway(s) for CDD/CDFs has not been fully identified, a major photolysis pathway appears to be photodechlorination resulting in formation of lower chlorinated CDD/CDFs. Several researchers have reported that carbon-oxygen cleavage and other mechanisms may be similarly or more important pathways for CDD/CDFs containing four or fewer chlorines (Choudry and Webster, 1989; Dulin et al., 1986; Miller et al., 1989; Kieatiwong et al., 1990). Studies performed to date suggest that the photolytic degradation products from irradiation of CDD/CDFs in organic solvents may be significantly different than those observed when surface-sorbed and gas-phase CDD/CDFs are irradiated. A preferential loss of chlorines from the lateral positions (i.e., chlorines at the 2, 3, 7, and 8 positions) rather than from the peri positions (i.e., chlorines at the 1, 4, 6, and 9 positions) has been reported for solution studies (Crosby et al., 1973; Dobbs and Grant, 1979; Tysklind and Rappe, 1991); the opposite trend is observed for some congener groups when irradiated as dry films, sorbed to soil, and as gas-phase CDD/CDFs (Choudry and Webster, 1989; Kieatiwong et al., 1990; Sivils et al., 1994; Sivils et al., 1995).

Most studies performed until recently have been conducted using artificial light, pure congeners, and reaction media consisting of homogenous solutions in aqueous-organic solvent mixtures, silica gel, or clean solid surfaces. Thus, although photolysis of CDD/CDFs at environmentally significant rates has been observed in laboratory studies, the results of these studies may not be representative of photolysis rates that occur under actual environmental conditions. The following subsections summarize the key findings of recent environmentally significant studies for the water, soil, and air media.

Photolysis in Solution. Numerous studies have demonstrated that CDD/CDFs will undergo photodechlorination following first order kinetics in solution with preferential loss of chlorine from the lateral positions. Photolysis is slow in pure water but increases dramatically when solvents serving as hydrogen donors are present such as hexane, benzene, methanol, acetonitrile, hexadecane, ethyl oleate, dioxane, and isooctane (Buser, 1976; Buser, 1988; Choudry and Webster, 1987; Choudry et al., 1990; Crosby et al., 1971; Crosby, 1978; Crosby, 1981; Dobbs and Grant, 1979; Dougherty et al., 1991; Dulin et al., 1986; Friesen et al., 1990a; Hutzinger, 1973; Koester and Hites, 1992b; Koshioka et al., 1990; Wagenaar et al., 1995; and others).

The photolytic behavior of CDD/CDFs in organic solvents or in pure water, however, is not expected to accurately reflect the photolytic behavior of these compounds in natural waters. Natural waters have differing quantities and types of suspended particulates and dissolved organic material that could either retard or enhance the photolysis of CDD/CDFs. However, only a few studies have been performed that have examined the photolysis of CDD/CDFs using natural waters and sunlight. Several other published studies have used a mixture of water and acetonitrile to enhance the solubility of CDD/CDFs. The following paragraphs summarize the results of these studies. Table 2-11 presents selected results from these studies.

Dulin et al. (1986) studied the photolysis of 2,3,7,8-TCDD in a water:acetonitrile solution (1:1, v/v) under sunlight and artificial light (i.e., a mercury lamp). The quantum yield for photodegradation of 2,3,7,8-TCDD in water was three times greater under artificial light at 313 nm than under sunlight which suggests that the medium-pressure mercury lamp used was a more efficient light source than the sun (Koester and Hites, 1992b). Podoll et al. (1986) used the Dulin et al. (1986) reaction rate data from the artificial light experiment to calculate seasonal half-life values for 2,3,7,8-TCDD at 40 degrees north latitude in clear near-surface water. The calculated seasonal values for half-lives ranged from 0.9 days in summer to 4.9 days in winter. Using the Dulin et al. (1986) reaction rate data from the sunlight experiment yields calculated seasonal values for half-lives ranging from 2.7 days in summer to 16 days in winter.

Choudry and Webster (1989) studied the photolytic behavior of a series of CDDs in a water:acetonitrile solution (2:3, v/v) using a low-pressure mercury lamp. Choudry et al. (1990) investigated the photolytic behavior of two CDFs (1,2,4,7,8-PeCDF and 1,2,3,4,7,8-HxCDF) using a similar experimental setup but with a 1:1 water:acetonitrile solution. Assuming that the quantum yields observed in these studies are the same as would be observed in natural waters, Choudry and Webster (1989) and Choudry et al. (1990) estimated the mid-summer half-life values at 40 degrees north latitude in clear near-surface water to be as follows: 1,2,3,7-TCDD (1.8 days); 1,3,6,8-TCDD (0.3 days); 1,2,3,4,7-PeCDD (15 days); 1,2,3,4,7,8-HxCDD (6.3 days); 1,2,3,4,6,7,8-HpCDD (47 days); OCDD (18 days); 1,2,4,7,8-PeCDF (0.2 hours); and 1,2,3,4,7,8-HxCDF (6 hours). However, Choudry and Webster (1989) also experimentally determined the sunlight photolysis half-life of 1,3,6,8-TCDD in pond water to be 3.5 days (i.e., more than 10 times greater than the half-life predicted by laboratory experiments). The authors attributed this significant difference in photolysis rates to the light screening/quenching effects of dissolved organic matter.

Friesen et al. (1990a) examined the photolytic behavior of 1,2,3,4,7-PeCDD and 1,2,3,4,6,7,8-HpCDD in water:acetonitrile (2:3, v/v) and in pond water under sunlight at 50 degrees north latitude. The observed half-lives of these two compounds in the water:acetonitrile solution were 12 and 37 days, respectively, which are very similar to the results observed by Choudry and Webster (1989) for these two congeners using artificial light. However, in contrast to the results observed by Choudry and Webster (1989) for 1,3,6,8-TCDD, Friesen et al. (1990a) found that the half-lives of 1,2,3,4,7-PeCDD and 1,2,3,4,6,7,8-HpCDD were much shorter in pond water (0.94 and 2.5 days, respectively) than in the water:acetonitrile solution. Similarly, Friesen et al. (1993) studied the photodegradation of 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF by sunlight using water:acetonitrile (2:3, v/v) and lake water. The observed half-lives of the 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF in the water:acetonitrile solution were 6.5 and 46 days, respectively, and 1.2 and 0.19 days in lake water, respectively. Friesen et al. (1990a) and Friesen et al (1993) attributed the significant differences between the natural water and water:acetonitrile solution results to indirect or sensitized photolysis due to the presence of naturally occurring components in the lake and pond water.

Dung and O'Keefe (1992), in their investigation of aqueous photolysis of 2,3,7,8-TCDF and 1,2,7,8-TCDF, reported findings similar to those of Friesen et al. (1993). Dung and O'Keefe prepared aqueous solutions by pumping water through "generator columns" containing particles coated with a thin film of the respective TCDF congener. Solutions in high purity HPLC water, distilled water, Hudson River water, and Saratoga Lake water were exposed to sunlight during September at approximately 42.5 degrees north latitude. The photolysis rates of the two TCDF congeners observed in the river and lake water (half-lives of about 4 to 6 hours) were double the rates observed in pure water (half-lives of about 8 to 11 hours). Dung and O'Keefe (1992) attribute the difference in rates to the presence of natural organics in the river and lake water that may be acting as sensitizers.

Kim and O’Keefe (1998) confirmed the results observed in Dung and O’Keefe (1992) by photolyzing 1,2,7,8-TCDD; 2,3,7,8-TCDF; OCDD; and OCDF in natural water from seven different locations. The values reported in Table 2-11 are the average values for the seven natural waters. The half-lives of TCDD and TCDF were at least two times shorter in all the natural waters than in pure water. However, the natural water half-lives of OCDD and OCDF showed greater variability with some half-lives greater than pure water and some less than pure water. Because there was no apparent relationship between the dissolved organic content of the water and the observed half-lives, it was hypothesized that certain waters may contain organic molecules which either act as photosensitizers or as photodesensitizers.

Photolysis on Soil. Photolysis of CDD/CDFs on soil has been reported but the factors affecting the rate and extent of photolysis have not been well characterized. Based on the data generated to date, photolysis is an operative degradation process only in the near-surface soil where UV light penetrates (i.e., the top few millimeters or less of soil) and dechlorination of peri-substituted chlorines appears to occur preferentially. Even within this near surface area, the rate of photolysis is substantially slower than the rate of photolysis that would be observed in a solution of same depth presumably as a result of the light-attenuating effects of soils. Below this near-surface level, photolysis is not a significant process, and CDD/CDFs present in soil at any greater depth are likely to persist (Miller et al., 1989; Puri et al., 1989; Yanders et al., 1989; Kieatiwong et al., 1990). The substantial research performed on the environmental persistence of 2,3,7,8-TCDD in the area around the ICMESA chemical plant in Seveso, Italy, demonstrates that photolysis in soils is a near-surface process. The Seveso area was contaminated when a trichlorophenol reaction vessel overheated in 1976, blowing out the safety devices and spraying 2,3,7,8-TCDD-contaminated material into the environment. The levels of dioxin in the soil decreased substantially during the first 6 months following the accident before reaching a relatively steady state of 1/5 to 1/11 of the initial levels (DiDomenico et al., 1982).

Kieatiwong et al. (1990) investigated the photolysis of 2,3,7,8-TCDD added to two agricultural soils (350 ug/kg) of approximately 0.3 mm depth and irradiated for 15 days with a mercury lamp. A loss of approximately 15 percent of 2,3,7,8-TCDD was observed on the soil of higher organic carbon and clay content. A loss of approximately 45 percent of 2,3,7,8-TCDD was observed on the soil of lower organic carbon and clay content. There was no significant loss on either soil after the first 5 days.

Miller et al. (1989) studied the CDD degradation products resulting from irradiation of ^{13}C-labeled OCDD on two soil types using sunlamps. Approximately 38 to 42 percent of the OCDD were degraded by day five of the experiment; no significant further loss of OCDD was observed over the following 10 days. Although determined not to be the dominant photolysis pathway, photodechlorination was observed in both soils; approximately 10 to 30 percent of the lower chlorinated congeners were produced from the immediate higher chlorinated congeners. The HpCDD and HxCDD congeners observed as degradation products were present in approximately similar proportions to the number of congeners in each congener group. However, Miller et al. (1989) found that, unlike the results reported for photolysis of OCDD in solution by Choudry and Webster (1989) and Dobbs and Grant (1979), 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were observed in greater yields than would be expected on the basis of the number of potential TCDD and PeCDD congeners. One-fifth to one-third of the total yield of PeCDDs was 1,2,3,7,8-PeCDD, and one-half of the total yield of TCDDs was 2,3,7,8-TCDD.

Kieatiwong et al. (1990) performed similar experiments to those of Miller et al. (1989) using natural sunlight rather than sunlamps for irradiation of ^{13}C-labeled OCDD on soils. Photodechlorination was estimated to account for approximately 10 percent of the loss of OCDD. One-third to one-half of the total yield of PeCDDs was 1,2,3,7,8-PeCDD, and one-half of the total yield of TCDDs was 2,3,7,8-TCDD. The findings of Miller et al. (1989) and Kieatiwong et al. (1990) indicate that the 2,3,7,8-substituted TCDD and PeCDD congeners were either preferentially formed or were photochemically less reactive than the other congeners that were formed.

Tysklind et al. (1992) also studied the sunlight photolysis of OCDD on soil and reported results in good agreement with those of Miller et al. (1989) and Kieatiwong et al. (1990). Photodechlorination was observed with production of HpCDDs, HxCDDs, PeCDDs, and TCDDs over the 16-day irradiation period. Photodechlorination at the peri-substituted positions was the preferred photodechlorination mechanism; the proportions of 2,3,7,8-substituted congeners present in the soils after 16 days for each congener group were as follows: HxCDD - 65 percent; PeCDD - 40 percent; and TCDD - 75 percent.

The sunlight photolysis of OCDF on soil was also studied by Tysklind et al. (1992). Photodechlorination was observed. However, unlike the case with OCDD, photodechlorination of the lateral-substituted positions was found to be the dominant photodechlorination mechanism resulting in a relative decreasing proportion of 2,3,7,8-substituted congeners during the irradiation period. 2,3,7,8-TCDF was not observed in any of the irradiated samples.

Schwarz and McLachlan (1993) studied the photolysis of CDD/CDFs in an experiment designed to simulate the application of sewage sludge to an agricultural field. No significant changes in CDD/CDF concentrations were observed during the 43-day exposure period to late summer/early fall natural sunlight. Although the OCDD concentration in the sludge had been increased by a factor of 1,000 through spiking, no increase in HpCDD concentrations were observed. The absence of any changes indicates that neither photodegradation nor volatilization are important mechanisms in the fate of CDD/CDF in sewage sludge following agricultural applications.

The addition of solvents to soil can increase the rate and extent of photolysis. Botre et al. (1978) reported the destruction of 8 μg/mL of 2,3,7,8-TCDD in 0.02 M hexadecylpyridinium chloride (an aqueous surfactant) applied to soil in 4 hours. Kieatiwong et al. (1990) reported that addition of hexadecane to soil containing 2,3,7,8-TCDD resulted both in an increased rate of photolysis and continued photochemical loss of 2,3,7,8-TCDD beyond the point at which soil containing no hexadecane showed photochemical loss.

Although only minimally related to soil environmental conditions, Buser (1988) studied the photolytic decomposition rates of 2,3,7,8-TCDF, 1,2,3,4-TCDF, and 1,2,7,8-TCDF dried as thin films on quartz vials. When exposed to sunlight, the substances slowly degraded with reported half-lives of 5 days, 4 days, and 1.5 days, respectively. Similarly, Koester and Hites (1992b) studied the photodegradation of a series of tetra- through octa-chlorinated CDDs and CDFs on silica gel. In general, the CDFs degraded much more rapidly than the CDDs, and half-lives increased with increasing level of chlorination (1,2,7,8-TCDF excluded). The half-lives for CDDs ranged from 3.7 days for 1,2,3,4-TCDD to 11.2 days for OCDD. The half-lives for CDFs ranged from 0.1 day for 1,2,3,8,9-PeCDF to 0.4 days for OCDF.

Photolysis on Vegetation. Photolysis of CDD/CDFs sorbed on the surface of vegetation has not been well characterized and the findings to date are somewhat contradictory. McCrady and Maggard (1993) reported that 2,3,7,8-TCDD sorbed on the surface of reed canary grass (*Phalaris arundinacea L.*) undergoes photolytic degradation with a half-life of 44 hours in natural sunlight. In contrast, Welsch-Pausch et al. (1995) found little difference in the CDD/CDF congener patterns between grass (*Lolium multiflorum*) grown on an outdoor plot and grass grown in a greenhouse (i.e., UV-light transmission blocked). In an attempt to clarify this contradiction, Welsch-Pausch and McLachlan (1995) studied the photodegradation of CDD/CDFs on pasture grass (*Arrhenatherion elatioris*) during two growing cycles (summer and autumn) using two greenhouses. One greenhouse was constructed of glass which blocks UV transmission and the other was constructed of plexiglass (4 mm) with an UV-light transmission of greater than 50 percent in the 280-320 mm range. In both the summer and autumn exposure periods, the concentrations of CDD/CDFs (on a congener group basis) were similar in the grass exposed to UV-light and the grass that was not exposed. Welsch-Pausch and McLachlan (1995) concluded that if photodegradation is occurring, it is a relatively insignificant factor in the accumulation of CDD/CDF in pasture grass.

Photolysis in Air. Photolysis of CDD/CDFs in the atmosphere has not been well-characterized. Based on the data generated to date, however, photolysis appears to be a significant mechanism for degradation (i.e., principally dechlorination of the peri-substituted chlorines) of those CDD/CDFs present in the atmosphere in the gas phase. For airborne CDD/CDFs sorbed to particulates, photolysis appears to proceed very slowly and may be influenced by the organic content of the particle. Because of the low volatility of CDD/CDFs, few studies have been attempted to measure actual rates of photodegradation of gaseous-phase CDD/CDF, and only recently have studies been undertaken to examine the relative importance of photolysis for particulate-bound CDD/CDFs.

Gas-Phase Photolysis - Podoll et al. (1986) estimated the photolysis rate of 2,3,7,8-TCDD vapors in the atmosphere based on the quantum yield for photolysis in hexane. The half-life in summer sunlight at 40 degrees north latitude was estimated to be 1 hour as an upper limit.

Mill et al. (1987) reported that photolysis of vapor phase 2,3,7,8-TCDD at 145°C in a flow system using a pulsed 308 nm laser light gave a photolysis quantum yield ranging from 0.013 to 0.03, equivalent to an atmospheric half-life of a few hours. However, the true gas phase quantum yield at 25°C is uncertain, and, therefore, the atmospheric lifetime in sunlight is uncertain.

Orth et al. (1989) conducted photolysis experiments with vapor-phase 2,3,7,8-TCDD under illumination with a Hg-Xe light source and filters to achieve radiation in the UV region from 250 nm to 340 nm. The temperature in the photolysis cell was approximately 150°C. Carrier gases included air and helium. No significant difference in the rate constants was observed in helium and air, 5.4×10^{-3} sec^{-1} and 5.9×10^{-3} sec^{-1}, respectively, which correspond to half-lives of a few minutes. The average quantum yield in air over the absorption band was found to be 0.033 ± 0.046. As with the results of Mill et al. (1987), the true gas phase quantum yield at 25°C is uncertain, and, therefore, the atmospheric lifetime in sunlight is uncertain.

Sivils et al. (1994; 1995) studied the gas phase photolysis of several CDDs (2,3,7-TrCDD; 2,3,7,8-TCDD; 1,2,3,4-TCDD; 1,2,3,7,8-PeCDD, and 1,2,4,7,8-PeCDD) by irradiating the effluent from a gas chromatograph with broadband radiation in the UV/visible region for periods of time up to 20 minutes. The irradiated sample was then introduced into a second gas chromatograph to measure the extent of dechlorination. The results showed that degradation followed first order kinetics and that there was an inverse relationship between the degree of chlorination and the rate of disappearance. Although the lack of photoproducts prevented an independent confirmation of the preferential loss mechanism, the results indicated that laterally-substituted congeners (i.e., chlorines at the 2, 3, 7, and 8 positions) degrade at a slower rate than the peri-substituted congeners (i.e., chlorines at the 1, 4, 6, and 9 positions). Although the rate constants were not presented in Sivils et al. (1994), the degradation rate for 2,3,7,8-TCDD (30 percent loss in 20 minutes) was reported to be slower than the rates for all other tested CDDs. Also, 1,2,4,7,8-PeCDD (with 2 peri-chlorines) degraded significantly faster than 1,2,3,7,8-PeCDD (with only 1 peri-chlorine).

Particulate Phase Photolysis - The photolysis of 2,3,7,8-TCDD sorbed onto small diameter fly ash particulates suspended in air was measured by Mill et al. (1987). The results indicated that fly ash appears to confer photostability on 2,3,7,8-TCDD. Little (8 percent) to no loss was observed on the two fly ash samples after 40 hours of illumination.

Koester and Hites (1992b) studied the photodegradation of CDD/CDFs naturally adsorbed to five fly ashes collected from electrostatic precipitators (one from a hospital incinerator, two from municipal incinerators, and two from coal-fired power plants) using a rotary reactor and a medium-pressure mercury lamp. Although they found that CDD/CDFs underwent photolysis in solution and when spiked onto silica gel, no significant degradation was observed in 11 photodegradation experiments performed on the ashes for periods ranging from 2 to 6 days. Three additional experiments were performed to determine what factors may have been inhibiting photolysis. From the results of these additional experiments, Koester and Hites (1992b) concluded that: (1) the absence of photodegradation was not due to the absence of a hydrogen-donor organic substance; (2) other molecules or the ash, as determined by a photolysis experiment with an ash extract, inhibit photodegradation either by absorbing light and dissipating energy or by quenching the excited states of the CDD/CDFs; and (3) the surface of the ash itself may hinder photolysis by shielding the CDD/CDFs from light.

Pennise and Kamens (1996) injected the emissions from the combustion of wood chips treated with PCP, plastic PVC pipe shavings, and solid 2,4,6-trichlorophenol into 25-m^3 outdoor Teflon film chambers. The behavior of the eight congener groups was monitored for approximately one day. Experiments were performed during January, June, and October of 1994 in North Carolina. Experiments with combustion temperatures ranging from 350 to 380°C were categorized as low-temperature experiments, and those ranging from 760 to 800°C were categorized as high temperature experiments. Little or no reactivity was observed for CDD/CDFs sorbed to particles resulting from the high temperature experiments. Greater photochemical reactivity was observed for CDD/CDFs sorbed to particles resulting from the low combustion experiments, where photolysis appeared to compete with a CDD/CDF production mechanism believed to be associated with non-combusted PCP. Photolysis rates appeared to decrease with increasing levels of chlorination. On low temperature combustion particles, estimated TCDD half-lives (excluding the impact of the observed formation from PCP) increased from 0.4 hours under summer conditions to 17 hours under winter conditions. On high-temperature particles, estimated TCDD half-lives ranged from 6.8 to 62 hours. Estimated OCDD half-lives ranged from 5 to 38 hours in low combustion temperature experiments to 36 to 257 hours in high temperature combustion experiments.

2.6.1.5.2. Photooxidation. Until recently, the reaction rates of hydroxyl (OH) radicals, ozone (O_3), and nitrate (NO_3) radicals with CDDs and CDFs had not been measured because, in large part, the low vapor pressures of these compounds make direct measurements very difficult with currently available techniques. In the absence of experimental data, Podoll et al. (1986) and Atkinson (1987) estimated the half-life of 2,3,7,8-TCDD vapor via OH oxidation in the atmosphere to be 8.3 days and 3 days, respectively. In a subsequent study, Atkinson (1991) used published reaction rate data for other organic compounds to estimate the OH radical reaction rate constants for vapor-phase dibenzofuran and dibenzo-p-dioxin, and from these estimates, Atkinson (1991) estimated the OH radical reaction rate constants for the CDDs and CDFs. Based on these empirical estimates, Atkinson (1991) concluded that the OH radical reaction is likely to be the dominant gas-phase transformation process for vapor phase CDDs and CDFs. The tropospheric lifetimes calculated by Atkinson (1991) from the rate constant estimates increased with increasing levels of chlorination from 2.0 days for 2,3,7,8-TCDD and 4.4 days for 2,3,7,8-TCDF to 9.6 days for OCDD and 39 days for OCDF.

Kwok et al. (1994) expanded the work of Atkinson (1991) by experimentally determining the room temperature gas-phase reaction rate constants of dibenzofuran and dibenzo-p-dioxin with hydroxyl radical to be 3.9E-12 cm^3 $molecule^{-1}$ s^{-1} and 1.48E-11 cm^3 $molecule^{-1}$ s^{-1}, respectively. These measured rate constants for dibenzo-p-dioxin and dibenzofuran are lower than those estimated by Atkinson (1991) by factors of 2.5 and 8. Assuming a 12-hour average daytime OH radical concentration of 8×10^5 $molecule/cm^3$, Kwok et al. (1994) estimated the atmospheric lifetimes for gas phase reactions of dibenzofuran and dibenzo-p-dioxin with OH radicals to be 3.7 days and 1.0 day, respectively. Also, based on experimental data, Kwok et al. (1994) calculated lifetimes for the gas phase reaction of dibenzofurans with NO_3 and O_3 to be greater than 7 years and greater than 205 days, respectively; the calculated lifetimes for the gas phase reaction of dibenzo-p-dioxin with NO_3 and O_3 were 4.9 days and greater than 330 days, respectively. The latter results indicate that reaction with the OH radical is the dominant photooxidation mechanism.

Kwok et al. (1995) extended the work of Kwok et al. (1994) by measuring the OH radical reaction rate constants for 1-chlorodibenzo-p-dioxin, diphenyl ether, and 1,2-dimethoxybenzene. These new reaction rate data when taken together with the measurements of Kwok et al. (1994) and the estimation method described in Atkinson (1991) were used to generate more reliable estimates of the reaction rate constants for the 2,3,7,8-substituted CDDs and CDFs (Atkinson, 1996). Table 2-12 presents these recalculated rate constants and tropospheric lifetimes and half-lives. As can be seen from Table 2-12, the persistence of CDD/CDFs increases with increasing degree of chlorination.

Recently, Brubaker and Hites (1997) measured the OH radical reaction rate constants for dibenzo-p-dioxin, dibenzofuran, 2,7-dichlorodibenzo-p-dioxin (2,7-D), 2,8-dichlorodibenzofuran (2,8-F), and 1,2,3,4-dibenzo-p-dioxin (1,2,3,4-D) over temperatures ranging from 72 to 159°C. From these results, OH reaction rate constants were estimated for each compound at 25°C. When these estimated values were compared to the previously measured rate constants reported by Kwok et al. (1994; 1995) and the values predicted by Atkinson (1995; 1996), Brubaker and Hites (1997) concluded that Atkinson's structure activity method is reliable.

2.6.1.5.3. Hydrolysis. There is no available evidence indicating that hydrolysis would be an operative environmental process for degradation of CDDs or CDFs. The attachment of chlorines directly to the aromatic ring in CDDs and CDFs confers hydrolytic stability. Specifically, S_N^1 and S_N^2 reactions do not take place readily at sp2 hybridized carbons (Leifer et al., 1983; Miller and Zepp, 1987).

2.6.1.5.4. Biotransformation and Biodegradation. Most investigations examining the biodegradability of CDDs and CDFs have, until recently, focused on the microbial degradation of 2,3,7,8-TCDD. Arthur and Frea (1989) provided a comprehensive review of studies conducted during the 1970s and 1980s and concluded that 2,3,7,8-TCDD is recalcitrant to microbial degradation. Several major studies conducted during that time period as well as more recent studies are discussed below.

Matsumura and Benezet (1973) tested approximately 100 strains of micro-organisms that were shown previously to degrade persistent pesticides; only five strains showed any ability to metabolize 2,3,7,8-TCDD, based on autoradiographs of thin-layer chromatograms. Hutter and Philippi (1982) concluded that although it is possible that the less chlorinated dioxins are more susceptible to biodegradation, microbial action on 2,3,7,8-TCDD is very slow under optimum conditions; the long-term incubations of radiolabeled 2,3,7,8-TCDD yielded no radioactivity in carbon dioxide traps after 1 year, and analyses of the cultures showed that, at most, 1 to 2 percent of the initial 2,3,7,8-TCDD were recovered as a potential metabolite (assumed to be a hydroxylated derivative of 2,3,7,8-TCDD). Camoni et al. (1982) added organic compost to contaminated soil from the Seveso area to enrich the soil and enhance the 2,3,7,8-TCDD biodegradation rate; however, the soil amendment had no clear effect on degradation. Quensen and Matsumura (1983) reported that low concentrations (5 ppb) of radiolabeled 2,3,7,8-TCDD were metabolized by pure cultures of *Nocardiopsis* spp. and *Bacillus megaterium* that had been isolated from farm soil. The extent of metabolism after 1-week incubation was strongly dependent on the carrier solvent used to dissolve and introduce the 2,3,7,8-TCDD to the culture medium. The solvent ethyl acetate gave the best results; 52 percent of ^{14}C were recovered as 2,3,7,8-TCDD out of a total of 77 percent ^{14}C recovered. However, incubation of 2,3,7,8-TCDD in farm soil, garden soil, and forest soil resulted in little, if any, metabolism of 2,3,7,8-TCDD.

Bumpus et al. (1985) tested the white rot fungus, *Phanerochaete chrysosporium*, which secretes a unique H_20_2-dependent extracellular lignin-degrading enzyme system capable of generating carbon-centered free radicals (Tien and Kirk, 1983; Tien and Kirk, 1984). Lignin is resistant to attack by all microorganisms except some species of fungi and a relatively small number of bacteria species. Radiolabeled 2,3,7,8-TCDD was oxidized to labeled $C0_2$ by nitrogen-deficient, ligninolytic cultures of *P. chrysosporium;* because the label was restricted to the ring, it was concluded that the strain was able to degrade halogenated aromatic rings. In 10 mL cultures containing 1,250 pmol of substrate, 27.9 pmol of 2,3,7,8-TCDD were converted to labeled-CO_2 during the 30-day incubation period; thus, only about 2 percent of the starting material were converted.

Hofmann et al. (1992) demonstrated that the fungi, *Fusarium redolens*, could degrade 3-chlorodibenzofuran and, to a lesser degree, mono- and di-CDDs. Hoffman et al. (1992) also identified 14 other strains of fungi that demonstrated the capability to degrade dibenzofuran (nonchlorinated). The strains are members of the following genera: *Mucor, Chaetomium, Phoma, Fusarium, Paecilomyces, Papulaspora, Inonotus, Lentinus, Phanerochaete, Polyporus, Pycnoporus, Schizophyllum*, and *Trametes*.

Takada et al. (1994; 1996) reported significant degradation of 2,3,7,8-substituted CDDs and CDFs by low-nitrogen medium cultures of the white rot fungus, *Phanerochaete sordida YK-624 strain*. Tetra- through octa- CDDs and CDFs were incubated for 14 days in glucose-amended cultures at 30°C. For both CDDs and CDFs, the 1,2,3,6,7,8-congeners showed the highest degradation values, 75 percent and 70 percent, respectively. The lowest degradation values were for 2,3,7,8-TCDD (40 percent), 1,2,3,7,8-TCDF (45 percent), and 1,2,3,7,8-PeCDF. Similar results were obtained under the same conditions for *P. chrysoporium IFO 31249 strain*.

Several recent reports indicate that CDDs and CDFs, like PCBs, may undergo microbial dechlorination in anaerobic sediments. Adriaens and Grbic-Galic (1992; 1993) and Adriaens et al. (1995) have reported the results of a series of microcosm studies utilizing Hudson River sediment (contaminated with Aroclor 1242) and aquifer material (contaminated with CDDs) from Pensacola, Florida. Both types of substrates were spiked with several CDDs (1,2,3,4,6,7,8-HpCDD; 1,2,3,4,7,8-HxCDD; and 1,2,4,6,8,9-/1,2,4,6,7,9-HxCDD) and CDFs (1,2,3,4,6,7,8-HpCDF and 1,2,4,6,8-PeCDF) and monitored over a period of 16 months at an incubation temperature of 30°C. The Hudson River sediment was spiked with 144 μg/kg of each congener and the Pensacola aquifer material was spiked with 63 μg/kg of each congener. Recoveries of the CDD/CDF congeners from the control samples decreased with increasing incubation time indicating that these congeners are strongly sorbed to the substrates. For example, after 50 days of incubation, the fraction of CDD/CDF that could be recovered by manual extraction had already decreased to 20-40 percent.

All of the congeners, with the exception of HpCDF, showed a slow decrease in concentration over time attributed to biologically mediated reductive dechlorination with net disappearance rates ranging from 0.0031 wk^{-1} to 0.0175 wk^{-1} (i.e., half-lives of approximately 1 to 4 years). However, Adriaens et al. (1995) conclude that the actual half-lives may be orders of magnitude higher. If it is assumed that transformation/ degradation occurs only for CDD/CDF in the aqueous phase, then the CDD/CDF that sorb to the sediments may never be biologically available because of the apparent very slow rates of desorption. The experiment with 1,2,3,4,6,7,8-HpCDD yielded formation of two HxCDD (1,2,3,4,7,8- and 1,2,3,6,7,8-). Thus, removal of the peri-substituted (1,4,6,9) chlorines was favored with enrichment of 2,3,7,8-substituted congeners. No lesser chlorinated congeners were identified from incubations with the other tested congeners. 1,2,4,6,8-PeCDF was also examined in dichlorophenol-enriched cultures. After 6 months incubation, several TCDFs were identified which also indicated that peri-dechlorination was the preferred route of reduction.

Barkovskii et al. (1994) expanded the testing of Adriaens and Grbic-Galic (1992; 1993) by spiking the sediments with higher doses to determine if faster rates could be achieved. Passaic River sediments (contaminated with CDD/CDFs) were spiked with 4,500 μg/kg of OCDD and incubated under anaerobic conditions for 6 months. Although no significant degradation of OCDD was observed, significant reductions in the concentrations of the hepta-, hexa-, penta-, and tetra-CDDs were observed.

Barkovskii and Adriaens (1995; 1996) reported that 2,3,7,8-TCDD (extracted from Passaic River sediments) was susceptible to reductive dechlorination when incubated at 30°C under methanogenic conditions in a mixture of aliphatic and organic acids inoculated with microorganisms obtained from Passaic River sediments. The initial concentration of 2,3,7,8-TCDD (20 ± 4 μg/L) decreased by 30 percent to 14 ± 2 μg/L over a period of 7 months with the consecutive appearance and disappearance of tri-, di-, and mono-CDDs. Experiments were also conducted by spiking the sediment with HxCDDs, HpCDDs, and OCDD. Up to 10 percent of the spiked OCDD was converted to hepta-, hexa-, penta-, tetra-, tri-, di-, and monochlorinated isomers, but the reaction stoichiometry was not determined. Two distinct pathways of dechlorination were observed: the *peri*-dechlorination pathway of 2,3,7,8-substituted hepta- to penta-CDDs, resulting in the production of 2,3,7,8-TCDD, and the *peri*-lateral dechlorination pathway of non-2,3,7,8-substituted congeners. Direct evidence of further lateral dechlorination of 2,3,7,8-TCDD was obtained from the historically contaminated incubations. Pasteurized cells exhibited no *peri*-dechlorination pathway, and triCDDs were the least-chlorinated congeners produced in these treatments. These results demonstrate that: (I) both freshly spiked and aged CDDs are available to microbial reductive dechlorination; (ii) the *peri* and triCDD dechlorinations are attributed to activities of nonmethanogenic, non-spore-forming microbial subpopulations; and (iii) the 2,3,7,8-residue patterns in historically contaminated sediments are likely affected by microbial activity.

2.6.2. Environmental Fate of Dioxin-Like PCBs

2.6.2.1. Summary

Little specific information exists on the environmental transport and fate of the dioxin-like PCBs. However, the available information on the physical/chemical properties of dioxin-like PCBs coupled with the body of information available on the widespread occurrence and persistence of PCBs in the environment indicates that these dioxin-like PCBs are likely to be associated primarily with soils and sediments, and to be thermally and chemically stable. Soil erosion and sediment transport in waterbodies and volatilization from the surfaces of soils/water bodies with subsequent atmospheric transport and deposition are believed to be the dominant current transport mechanisms responsible for the widespread environmental occurrence of PCBs. Photodegradation and biologically-mediated reductive dechlorination to less chlorinated congeners followed by slow anaerobic and/or aerobic biodegradation in soils/sediments are believed to be the principal paths for destruction of PCBs. Of note, however, is that the available photolysis studies to date indicate that the more toxic coplanar PCBs are more resistant to photolysis and are formed as products during the photolysis of more chlorinated less toxic congeners.

2.6.2.2. Transport Mechanisms

Based on their low vapor pressures, low water solubilities, and high K_{oc} values, dioxin-like PCBs are expected primarily to be associated with soils, sediments, and particulates. PCBs move from land to aquatic environments primarily associated with runoff sediments (Gan and Berthouex, 1994). However, due to the stability and persistence of dioxin-like PCBs via other transformation and transport pathways, volatilization is likely to be a significant transport mechanism from a global perspective. It should be noted that although dioxin-like PCBs have low vapor pressures and water solubilities, the Henry's Law constants for the similarly substituted CDDs and CDFs are expected to be one to two orders of magnitude lower. Therefore, it can be expected that volatilization of PCBs from soil and water into air is likely to be a more significant transport mechanism for PCBs than for CDDs and CDFs. For example, Cousins et al. (1996) recently demonstrated that PCBs with fewer than eight chlorines will volatilize but 2,3,7,8-substituted CDD/CDFs do not volatilize from sewage sludge amended soil. The rate of volatilization will be affected by soil characteristics (e.g., temperature, moisture content, and organic carbon content) and the concentration and physical form of the PCBs present (Ayris and Harrad, 1997).

Recent studies have shown that PCBs are cycling between the atmosphere and the terrestrial and aquatic environments. For example, Murray and Andren (1992) studied the precipitation scavenging of PCBs in the Great Lakes region. They reported that atmospheric PCBs are largely in the gas phase (typically >90 percent) rather than bound to particulate material. The results of their study support the hypothesis that precipitation provides episodic inputs of PCBs to the Great Lakes. However, several published studies indicate that, on an annual basis (and particularly during the summer and autumn), the Great Lakes are net sources of PCBs to the atmosphere through the process of volatilization. Shallow, warm, and impacted aquatic systems such as Green Bay, Lake Michigan and Chesapeake Bay exhibit the highest net volatilization fluxes due partially to intimate contact with contaminated sediments (Baker and Eisenreich, 1990; Eisenreich, 1997). Gregor et al. (1992) reported similar findings in a study of PCB deposition in the Arctic during the winter of 1990/1991. The results of the study indicated that snowfall and ice crystal deposition were scavenging the full range of PCB congeners from the atmosphere. The daily deposition rate during winter was about 2 ng/m^2/day. Also, a comparison of the PCB content of snow/ice samples from collectors and end of season samples from the snowpack suggested that volatilization of the PCBs, particularly of the lower chlorinated congeners, was occurring.

Like CDD/CDFs, the dioxin-like PCBs have a high potential for bioaccumulation in aquatic organisms thereby leading to elevated exposures to humans and wildlife from ingestion of contaminated fish. Table 2-13 presents BAFs, BCFs, and BSAFs reported in the literature for dioxin-like PCBs. A compilation of additional reported BSAFs is provided in the companion document to this report (i.e., Volume 3). Chapter 3 of this report summarizes concentrations of dioxin-like PCBs in fish that have been reported in the literature.

2.6.2.3. Transformation Processes

2.6.2.3.1. Photolysis. Based on the data available in 1983, Leifer et al. (1983) concluded that all PCBs, especially the more highly chlorinated congeners and those that contain two or more chlorines in the ortho position, photodechlorinate. In general, as the chlorine content increases, the photolysis rate increases. The products of photolysis are predominantly lower chlorinated PCBs.

More recently, Lepine et al. (1992) exposed dilute solutions (4 ppm) of Aroclor 1254 in cyclohexane to sunlight for 55 days in December and January. Isomer-specific analysis indicated that the amounts of many higher chlorinated congeners decreased while those of some lower chlorinated congeners increased. These results are consistent with the studies reviewed in Leifer et al. (1983) that indicated photodegradation of PCBs proceeds through successive dechlorination of the biphenyl molecule. The results for the dioxin-like PCBs indicated a 43.5 percent decrease in the amount of 2,3,4,4',5-PeCB; a 73.5 percent decrease in the amount of 2,3,3',4,4',5-HxCB; and a 24.4 percent decrease in the amount of 2,3,3',4,4',5'-HxCB. However, the more toxic 3,3',4,4'-TeCB (PCB77) and 3,3',4,4',5-PeCB (PCB126), which were not detected in unirradiated Aroclor 1254, represented 2.5 percent and 0.43 percent, respectively, of the irradiated mixture. The authors postulated that formation of these two congeners probably occurred, at least in part, from dechlorination at the ortho position of their mono-ortho-substituted precursors, considering the greater reactivity of PCB ortho chlorines toward photodechlorination. Dechlorination was reported to proceed by the loss of chlorine in the order of ortho>para>meta.

Brown et al. (1995) examined the changes in congener levels that occurred after exposing hexane solutions of various Aroclors and specific congeners in quartz tubes to direct summer sunlight (43°N). The reported disappearance rates and estimated half-lives for several of the dioxin-like PCBs are as follows:

PCB Congener	Substitution Pattern	Disappearance Rate (day^{-1})	Half-life (days)
105	234-34	0.11	6.3
156	2345-34	0.3	2.3
167	245-345	0.08	8.7
170	2345-234	0.006	115
180	2345-245	0.004	173
189	2345-345	0.08	8.7

Barr et al. (1997) irradiated several PCB congeners in solution on silica gel for up to 30 minutes. The results indicated that dechlorination in the ortho position is favored but also that steric congestion and structural symmetry are major factors in determining the relative reactivity of chlorines in the meta and para positions. The following conclusions were made:

- In all cases, the ring with the greatest degree of chlorination is the primary ring where the dechlorination occurs.

- Ortho-chlorine substituents and para-chlorine substituents that have two adjacent chlorines were preferentially lost in coplanar (non-ortho-substituted) PCBs.

- Chlorine substituents having neighboring chlorines are replaced more easily than isolated chlorines.

- Para-chlorine substituents were lost preferentially from coplanar hexa-, penta- or tetrachlorobiphenyls, while meta-chlorine was lost preferentially from trichlorobiphenyls.

- More symmetrical isomers tend to be formed more easily, and are more stable.

2.6.2.3.2. Oxidation. Reaction of PCBs with common environmental oxidants such as hydroperoxy radicals (HO_2) and ozone (O_3) has not been reported and is probably not very important because only very strong oxidant species can react with PCBs (Sedlak and Andren, 1991). However, reaction of gas-phase PCBs in the atmosphere and dissolved PCBs in certain surface waters with hydroxyl radicals (OH) (one of the strongest environmental oxidants known) may be an important degradation mechanism.

Oxidation in Air. Atkinson (1987) and Leifer, et al. (1983), using assumed steady-state atmospheric OH concentrations and measured oxidation rate constants for biphenyl and monochlorobiphenyl, estimated atmospheric decay rates and half-lives for gaseous-phase PCBs. Atmospheric transformation was estimated to proceed most rapidly for those PCB congeners containing either a small number of chlorines or those containing all or most of the chlorines on one ring. The predicted half-lives for the congener groups containing the 13 dioxin-like PCBs were as follows:

Congener Group	Half-Life in Air (days)
TeCBs	11 to 20
PeCBs	12 to 31
HxCBs	32 to 62
HpCBs	94+

Kwok et al. (1995) extended the work of Atkinson (1987) by measuring the OH radical reaction rate constants for 2,2'-, 3,3'-, and 3,5-dichlorobiphenyl. These reaction rate constants when taken together with the measurements of Atkinson (1987) for biphenyl and monochlorobiphenyl and the estimation method described in Atkinson (1991; 1995; 1996) have been used to generate more reliable estimates of the gas-phase OH radical reaction rate constants for the dioxin-like PCBs. Table 2-14 presents these estimated rate constants and the corresponding tropospheric lifetimes and half-lives. As can be seen from Table 2-14, the persistence of the PCB congeners increases with increasing degree of chlorination.

Oxidation in Water. Sedlak and Andren (1991) demonstrated in laboratory studies that OH radicals, generated with Fenton's reagent, rapidly oxidized PCBs (i.e., 2-mono-PCB and the DiCBs through PeCBs present in Aroclor 1242) in aqueous solutions. The results indicated that the reaction occurs via addition of a hydroxyl group to one nonhalogenated site; reaction rates are inversely related to the degree of chlorination of the biphenyl. The results also indicated that meta and para sites are more reactive than ortho sites due to stearic hindrance effects. Based upon their kinetic measurements and reported steady-state aqueous system OH concentrations or estimates of OH radical production rates, Sedlak and Andren (1991) estimated environmental half-lives for dissolved PCBs (mono-through octa-PCB) in several water systems as listed below.

Water System	Half-Life in Water (days)
Fresh surface water	4 to 11
Marine surface water	1,000 to 10,000
Cloud water	0.1 to 10

Estimates for dissolved PCBs in marine surface water are in excess of 1,000 days due to the very low concentration of OH radicals in these waters (10^{-18}M or about two orders of magnitude lower than in freshwater systems). The results of studies to date indicate that OH oxidation of PCBs dissolved in cloud water may be an important, although not very fast, degradation mechanism for PCBs from a global perspective.

2.6.2.3.3. Hydrolysis. PCBs are unlikely to be affected by hydrolysis under environmental conditions because the attachment of chlorines directly to the aromatic ring in PCBs confers hydrolytic stability. Specifically, S_N1 and S_N2 reactions do not take place readily at sp2 hybridized carbons (U.S. EPA, 1988; Leifer et al., 1983).

2.6.2.3.4. Biotransformation and Biodegradation. Leifer et al. (1983), Brown and Wagner (1990), and Abramowicz (1990) summarized the available information on the degradation of PCBs by microorganisms. Laboratory studies (e.g., Bedard et al., 1986; Pardue et al., 1988; Larsson and Lemkemeier, 1989; Hickey, 1995; Schreiner et al., 1995; and Fukuda et al., 1997) have revealed that more than two dozen strains of aerobic bacteria and fungi are widely distributed in the environment that are capable of degrading most PCB congeners with five or fewer chlorines. Many of these organisms are members of the genus *Pseudomonas* or the genus *Alcaligenes*. Only a few strains have been demonstrated to have the ability to degrade higher chlorinated congeners. The major metabolic pathway involves addition of O_2 at the 2,3-position by a dioxygenase enzyme with subsequent dehydrogenation to the catechol followed by ring cleavage. Several bacterial strains have been shown to possess a dioxygenase enzyme that attacks the 3,4-position.

In general, the rate of aerobic biodegradation decreases with increasing chlorination. Growth on biphenyl as the sole carbon source is required for optimal PCB degradative activity. Degradation in soil systems where numerous carbon sources are present is more than 50-fold slower compared to biphenyl assays. The half-lives for biodegradation of tetra-PCBs in fresh surface water and soil are 7 to 60+ days and 12 to 30 days, respectively. For penta-PCBs and higher chlorinated PCBs, the half-lives in fresh surface water and soil are likely to exceed 1 year. PCBs with all or most chlorines on one ring and PCBs with fewer than two chlorines in the ortho position tend to degrade more rapidly. For example, Gan and Berthouex (1994) monitored over a 5-year period the disappearance of PCB congeners applied to soil with sewage sludge. Three of the tetra- and penta-chlorinated dioxin-like PCBs (IUPAC Nos. 77, 105, and 118) followed a first-order disappearance model with half-lives ranging from 43 to 69 months. A hexa-substituted congener (IUPAC No. 167) and a hepta-substituted congener (IUPAC No. 180) showed no significant loss over the 5-year period.

Until recent years, little investigation focused on anaerobic microbial dechlorination or degradation of PCBs even though most PCBs eventually accumulate in anaerobic sediments (Abramowicz, 1990; Risatti, 1992). Environmental dechlorination of PCBs via losses of meta and para chlorines has been reported in field studies for freshwater, estuarine, and marine anaerobic sediments including those from the Acushnet Estuary, the Hudson River, the Sheboygan River, New Bedford Harbor, Escambia Bay, Waukegan Harbor, and the Housatonic River (Brown et al., 1987; Rhee et al., 1989; Van Dort and Bedard, 1991; Abramowicz, 1990; Bedard et al., 1995). The altered PCB congener distribution patterns found in these sediments (i.e., different patterns with increasing depth or distance from known sources of PCBs) have been interpreted as evidence that bacteria may dechlorinate PCBs in anaerobic sediment.

Results of laboratory studies have been reported recently that confirm anaerobic degradation of PCBs. Chen et al. (1988) found that "PCB-degrading" bacteria from the Hudson River could significantly degrade the mono-, di-, and tri-PCB components of a 20 ppm Aroclor 1221 solution within 105 days. These congeners make up 95 percent of Aroclor 1221. No degradation of higher chlorinated congeners (present at 30 ppb or less) was observed, and a separate 40-day experiment with tetra-PCB also showed no degradation.

Rhee et al. (1989) reported degradation of mono- to penta-substituted PCBs in contaminated Hudson River sediments held under anaerobic conditions in the laboratory (N_2 atmosphere) for 6 months at 25°C. Amendment of the test samples with biphenyl resulted in greater loss of PCB. No significant decreases in the concentrations of the more highly chlorinated (i.e., more than five chlorines) were observed. No evidence of degradation was observed in samples incubated in CO_2/H_2 atmospheres. Abramowicz (1990) hypothesized that this result could be an indication that, in the absence of CO_2, a selection is imposed favoring organisms capable of degrading PCBs to obtain CO_2 and/or low molecular weight metabolites as electron receptors.

VanDort and Bedard (1991) reported the first experimental demonstration of biologically-mediated ortho dechlorination of a PCB and stoichiometric conversion of that PCB congener (2,3,5,6-TeCB) to less-chlorinated forms. In that study, 2,3,5,6-TeCB was incubated under anaerobic conditions with unacclimated methanogenic pond sediment for 37 weeks with reported dechlorination to 2,5-DCB (21%); 2,6-DCB (63%); and 2,3,6-TrCB (16%).

Risatti (1992) examined the degradation of PCBs at varying concentrations (10,000 ppm, 1,500 ppm, and 500 ppm) in the laboratory with "PCB-degrading" bacteria from Waukegan Harbor. After 9 months of incubation at 22°C, the 500 ppm and 1,500 ppm samples showed no change in PCB congener distributions or concentrations, thus indicating a lack of degradation. Significant degradation was observed in the 10,000 ppm sediment with at least 20 congeners ranging from TrCBs to PeCBs showing decreases.

Quensen et al. (1988) also demonstrated that microorganisms from PCB-contaminated sediments (Hudson River) dechlorinated most PCBs in Aroclor 1242 under anaerobic laboratory conditions. Aroclor 1242 contains predominantly tri- and tetra-PCBs. Three concentrations of the Aroclor corresponding to 14, 140, and 700 ppm on a sediment dry-weight basis were used. Dechlorination was most extensive at the 700 ppm test concentration; 53 percent of the total chlorine were removed in 16 weeks, and the proportion of TeCBs through HxCBs decreased from 42 to 4 percent. Much less degradation was observed in the 140 ppm sediment, and no observable degradation was found in the 14 ppm sediment. These results and those of Risatti (1992) suggest that the organism(s) responsible for this dechlorination may require relatively high levels of PCB as a terminal electron acceptor to maintain a growing population.

Quensen et al. (1990) reported that dechlorination of Aroclor 1242, 1254, and 1260 by microorganisms from PCB-contaminated sediments in the Hudson River and Silver Lake occurred primarily at the meta and para positions; ortho-substituted mono- and di-PCBs increased in concentration.

Nies and Vogel (1990) reported similar results with Hudson River sediments incubated anaerobically with acetone, methanol, or glucose. Approximately 300 μg/g of Aroclor 1242 was added to the sediments to increase the concentrations of higher chlorinated congeners in the sediments prior to incubation for 22 weeks under an N_2 atmosphere. Significant dechlorination over time was observed with dechlorination occurring primarily at the meta- and para-positions on the highly chlorinated congeners resulting in the accumulation of less-chlorinated, primarily ortho-substituted congeners. No significant dechlorination was observed in the control samples (i.e., samples containing no added organic chemical substrate and samples which had been autoclaved).

Bedard et al. (1995) demonstrated that it is possible to stimulate substantial microbial dechlorination of the highly chlorinated PCB mixture Aroclor 1260 *in situ* with a single addition of 2,6-dibromobiphenyl. Bedard et al. (1995) added 365 g of 2,6-dibromobiphenyl to 6-foot diameter submerged caissons containing 400 kg sediment (dry weight) and monitored the change in PCB congener concentrations for a period of 1 year. At the end of the observation period, the hexa- through mono-chlorinated PCBs had decreased by 74 percent in the top of the sediment and 69 percent in the bottom. The average number of chlorines per molecule dropped by 21 percent from 5.83 to 4.61 with the largest reduction observed in meta-chlorines (54 percent reduction) followed by para-chlorines (6 percent). The dechlorination stimulated by 2,6-dibromobiphenyl selectively removed meta-chlorines positioned next to other chlorines.

The findings of these latter studies are significant because removal of meta and para chlorines from the dioxin-like PCBs should reduce their toxicity and bioaccumulative potential and also form less chlorinated congeners that are more amenable to aerobic biodegradation. In support of the findings of these studies, Mousa et al. (1997)

demonstrated that the PCBs present in extracts from PCB-contaminated sediments (i.e., Aroclor 1242 and 1254) that had been incubated for nine months under anaerobic conditions had either reduced biological activities or did not manifest any significant change, depending upon the toxicological endpoint used.

2.7. ENVIRONMENTAL FATE - BROMINATED COMPOUNDS

2.7.1. Summary

Although there are few published studies documenting measured fate rate constants, relatively few studies with measured physical/chemical property data, and few relevant environmental monitoring studies, it is possible to estimate the environmental transport and transformation processes for the brominated dioxin-like compounds using the available published information and using structure activity and property estimation methods. Mill (1989) performed such an assessment, and much of the limited information published since 1989 supports the conclusions of Mill (1989).

Mill (1989) concluded that the estimated physical/chemical properties of these compounds indicate they will behave in a similar fashion to their chlorinated analogues. In general, these chemicals are expected to be stable under normal environmental conditions, relatively immobile in the environment, and primarily associated with particulate and organic materials. The only environmentally significant path for destruction is photodegradation. If discharged to the atmosphere, any vapor-phase compounds will probably be rapidly photolyzed. The higher brominated congeners, like their chlorinated counterparts, may be present primarily in a particle-bound rather than gaseous phase. If so, they likely will be more resistant to photolysis and become more widely dispersed in the environment.

Upon deposition onto surfaces, there can be an initial loss due to photodegradation and/or volatilization. Once sorbed onto soils or sediments, however, they are expected to be strongly sorbed with erosion and aquatic transport of sediment the dominant physical transport mechanism. If discharged to water, they are expected to preferentially sorb to solids. Volatilization may also be a significant transport mechanism for nonsorbed chemicals even though they have negligible estimate vapor pressures.

2.7.2. Transport Mechanisms

Little information exists on the environmental transport of brominated dioxin-like compounds. For example, Jacobs et al. (1978) reported that less than 0.2 percent of 2,2',4,4',5,5'-hexa-PBB (14µg PBB/g of soil) and 2,2',3,4,4',5,5'-hepta-PBB (7µg PBB/g of soil) volatilized from soil incubated for 1 year at 28°C. However, the available information on the physical/chemical properties of these compounds and their chlorinated analogs coupled with the body of information available on the widespread occurrence and persistence of the chlorinated analogs in the environment indicate that these compounds are likely to be strongly sorbed by soils, sediments, and other particulate material, and to be resistant to leaching and volatilization.

2.7.3. Transformation Processes

2.7.3.1. Photolysis. Photolysis appears to be a major potential pathway for loss of brominated dioxin-like compounds in water, air, and soil. The available data indicate that BDDs and BDFs undergo photolytic degradation more readily than their chlorinated analogs. Also, BCDDs and BCDFs appear to undergo debromination more readily than dechlorination. However, no photolysis studies have been published that used natural waters as the reaction medium or that measured gas-phase photolysis rates. Most studies have been conducted using reaction media consisting of homogenous solutions in organic solvent mixtures or clean solid surfaces. Thus, although photolysis of brominated dioxin-like compounds at environmentally significant rates has been observed in laboratory studies, the results of these studies may not be representative of photolysis rates that occur under actual environmental conditions. The following subsections summarize the key findings of recent environmentally significant studies for the water, soil, and air media.

Photolysis in Organic Solvents. Buser (1988) studied the photolytic decomposition rates of the following compounds in dilute isooctane solutions in quartz vials and as solid phases on quartz surfaces under sunlight (47 degrees north latitude): 1,2,3,4-TBDD; 2,3,7,8-TBDD; 2,3,7,8-TBDF; and mono- and dibrominated 2,3,7,8-TCDD and 2,3,7,8-TCDF. Estimated half-lives were very short, on the order of minutes for solution photolysis. Solid-phase photolysis was significantly slower with half-lives in the range of 7 to 35 hours. The major photolytic pathway was reductive dehalogenation with the formation of lower halogenated or unsubstituted dibenzo-p-dioxins and dibenzofurans. The bromo-chlorodibenzofurans degraded faster than either the brominated or chlorinated congeners. The major pathway of photolysis was debromination to form a chlorinated dibenzofuran.

Lenoir et al. (1991) studied the photolysis in hexane and methanol of a series of mono-through octa-substituted BDD. Several BDFs (di-, tetra-, and hepta-BDF) were also studied as were a series of CDDs for comparison purposes. The results reported by Lenoir et al. (1991) were similar to those reported by Buser (1988) with half-lives on the order of minutes. Bromines at the lateral positions (i.e., 2, 3, 7, and 8 positions) reacted faster than bromines at the peri-positions (i.e., 1, 4, 6, and 9 positions). The bromine compounds reacted nearly an order of magnitude faster than the chlorine analogs. Photolysis in methanol was found to be nearly six times faster than in hexane.

Chatkittikunwong and Creaser (1994) studied the fate of a mixture of mono-through penta-substituted BDDs and BCDDs dissolved in dodecane in borosilicate glass vials exposed to sunlight through a laboratory window. The results indicated that for both the BDDs and the BCDDs the major mechanism of degradation was consecutive debromination from higher congeners to lower congeners. The half-lives calculated by Chatkittikunwong and Creaser (1994) for various congener groups (listed below) are much greater than those reported by Buser (1988). Chatkittikunwong and Creaser (1994) attribute the difference to the fact that borosilicate glass is more effective than quartz at absorbing those wavelengths most likely to cause degradation of these compounds.

Congener Group	Estimated Average Half-Life in Dodecane (hrs)
PeBDD	150
TBDD	480
Br_2Cl_2DD	580
Br_3Cl_1DD	650
Br_1Cl_4DD	480
Br_2Cl_3DD	995
Br_3Cl_2DD	300
Br_4Cl_1DD	520
Br_1Cl_5DD	520

Watanabe et al. (1994) extracted BDFs and BCDFs from the soil at a metal reclamation facility using hexane and exposed the hexane solution to natural sunlight. The half-lives calculated by Watanabe et al. (1994) for various congener groups are listed below. The half-lives decrease with increasing number of bromines.

Congener Group	Estimated Average Half-Life in Hexane (min)
Br_1Cl_3DF	43
Br_2Cl_2DF	11
Br_3Cl_1DF	6.5
TBDF	4.0
Br_1Cl_4DF	18
Br_2Cl_3DF	4.9
Br_3Cl_2DF	5.4
Br_4Cl_1DF	3.1
PeBDF	2.7
Br_1Cl_5DF	9.8
Br_2Cl_4DF	5.7
Br_1Cl_6DF	12

Photolysis in Water. No published studies were located that measured the photolysis rates of brominated dioxin-like compounds in water. Mill (1989) used the results obtained by Buser (1988) together with assumptions to overcome the lack of quantum yield data from Buser (1988) to estimate the photolysis half-lives of the three brominated-only compounds tested by Buser (1988). Mill (1989) estimated the following half-lives in water (top 1 meter) for clear-sky conditions in mid-summer at 40 degrees north latitude:

Congener	Estimated Half-Life in Water (hrs)
1,2,3,4-TBDD	7
2,3,7,8-TBDD	2
2,3,7,8-TBDF	1.7

Photolysis in Soil. Chatkittikunwong and Creaser (1994) studied the fate of a mixture of mono- through penta-substituted BDDs and BCDDs spiked onto soil (5 mm depth) exposed to full sun outdoors for a 3-month period. The pattern of degradation was similar to that observed in solution (i.e., debromination of higher congeners with formation of lower congeners) although the rate of degradation was much slower (by a factor of about 4) than observed in solution. For example, the calculated average half-lives for PeBDDs and TBDDs were 600 hours and 2,330 hours, respectively.

Photolysis in Air. No published studies were located that measured the photolysis rates of brominated dioxin-like compounds in the gas phase in air. Mill (1989) used the results obtained by Buser (1988) together with assumptions to overcome the lack of quantum yield data from Buser (1988) to estimate the photolysis half-lives of the three brominated-only compounds tested by Buser (1988). Mill (1989) estimated the following gas-phase half-lives (first kilometer above surface) for clear-sky conditions in mid-summer at 40 degrees north latitude:

Congener	Estimated Half-Life in Air (min)
1,2,3,4-TBDD	<1
2,3,7,8-TBDD	0.3
2,3,7,8-TBDF	0.2

Lutes et al. (1992a, 1992b) studied the short-term photochemistry of tetra- and penta-BDDs and BDFs sorbed onto airborne soot particles in 25 m^3 outdoor Teflon film chambers. The emissions from high temperature (640 to 760°C) controlled burning of polyurethane foam containing polybrominated diphenyl ether flame retardants served as the source of the particulate-bound BDDs and BDFs. Initial experiments demonstrated that more than 95 percent of the BDDs/BDFs were associated with airborne particulate material; less than 5 percent were in the vapor phase. Particulate phase concentrations of tetra- and penta-CDD/CDFs were monitored for 3 to 6 hours after introduction of the emissions from the foam burn to the chamber under winter and spring temperatures and sunlight regimes in Pittsboro, North Carolina. No significant reduction in concentration was observed. The authors concluded that if photolytic degradation was occurring, then the half-lives are much greater than 3 to 6 hours.

Birla and Kamens (1994) expanded the research of Lutes et al. (1992a; 1992b) by examining the effect of combustion temperature on the atmospheric stability of BDDs and BDFs generated using the same polyurethane combustion apparatus. Both "high temperature" (745 to 780°C) and "low temperature" (400 to 470°C) combustion temperatures were studied. The results obtained from the high temperature experiments were similar to those obtained by Lutes et al. (1992a; 1992b) in that there was little evidence of any decay in particulate-bound BDDs and BDFs. In the low temperature experiments, production of TBDFs and PeBDFs and decay of TBDDs were observed. Birla and Kamens (1994) attributed the increase in particulate-bound TBDF and PeBDF levels to photolysis of unburned polybrominated diphenyl ether flame retardants. The decay of TBDD was attributed to differences in physical and chemical properties of the particles generated from the high and low temperature experiments.

Watanabe et al. (1994) collected air dust on glass filters for a period of 24 hours in Osaka, Japan, and then exposed the glass filters to 24 hours of sunlight. More than 10 congener groups of BCDFs as well as TBDFs and PeBDFs were measured in the collected dust prior to irradiation. Although there was a reduction in the concentration of every congener group over the exposure period with the largest decrease observed for the lower halogenated congeners, Watanabe et al. (1994) concluded that most of the decrease was probably due to volatilization rather than photolysis.

2.7.3.2. Oxidation

No reaction rate data for OH radicals with gas-phase brominated dioxin-like compounds could be located. The low vapor pressures of these compounds make direct measurements very difficult with the current techniques. However, Mill (1989), using a structure activity relationship developed by Atkinson (1987), has estimated the half-lives of OH oxidation for the tetra- through octa- BDDs and BDFs. The estimated half-lives listed below indicate that OH oxidation is probably too slow to compete with photolysis.

Number of Bromines	BDD Half-Life in Air (hrs)	BDF Half-Life in Air (hrs)
4	50	420
5	50	430
6	100	960
7	200	1900
8	770	3800

2.7.3.3. Hydrolysis

No evidence is available indicating that hydrolysis would be a significant degradation process for these compounds.

2.7.3.4. Biotransformation and Biodegradation

Although no data are available concerning the biodegradability of the brominated dioxin-like compounds, it is expected that these brominated compounds, especially the more halogenated congeners, will be recalcitrant to biodegradation. The limited data available on PBBs (discussed below) indicate recalcitrance.

Jacobs et al. (1976) examined the distribution and fate of PBBs in the environment following the accidental contamination of livestock feed in Michigan in 1973 with the brominated flame retardant, FireMaster BPG. FireMaster BPG (a.k.a., PBB) was found by Jacobs et al. (1976) to be comprised of 2,2',4,4',5,5'-hexabromobiphenyl as the major component, two isomers of pentabromobiphenyl, three additional isomers of hexabromobiphenyl, and two isomers of heptabromobiphenyl. Jacobs et al. (1976) reported that PBBs are extremely persistent based on the results of aerobic and anaerobic soil incubation studies for 24 weeks with the flame retardant, PBB. Only one major PBB component, a pentabromobiphenyl isomer, showed any significant disappearance; however, Jacobs et al. (1976) were not certain whether the disappearance was due to microbial degradation, to poor soil extraction efficiency, or to sorption onto glassware. Jacobs et al. (1976) also detected components of PBB in soils from a field that had received manure from a PBB-contaminated dairy herd 10 months earlier (quantitative changes in PBB were not possible because no earlier soil samples had been obtained). Additional soil studies by Jacobs et al. (1978) found no degradation of 2,2',4,4',5,5'-hexa-PBB (14μg/25g soil) or 2,2',3,4,4',5,5'-hepta-PBB (7μg/25g soil) after incubation at 28°C for 1 year.

REFERENCES

Abramowicz, D. (1990) Aerobic and anaerobic biodegradation of PCBs: A review. Critical Reviews in Biotechnology. 10(3):241-251.

Abramowitz, R.; Yalkowsky, S.H. (1990) Estimation of aqueous solubility and melting point for PCB congeners. Chemosphere. 21(10-11): 1221-1229.

Adams, W.J.; Blaine, K.M. (1986) A water solubility determination of 2,3,7,8-TCDD. Chemosphere 15(9-12):1397-1400.

Adriaens, P.; Grbic-Galic, D. (1992) Effect of cocontaminants and concentration on the anaerobic biotransformation of PCDD/F in methanogenic river sediments. Organohalogen Compounds 8:209-212.

Adriaens, P.; Grbic-Galic, D. (1993) Reductive dechlorination of PCDD/F by anaerobic cultures and sediments. Organohalogen Compounds 12:107-110.

Adriaens, P.; Fu, Q.; Grbic-Galic, D. (1995) Bioavailability and transformation of highly chlorinated dibenzo-p-dioxins and dibenzofurans in anaerobic soils and sediments. Environ. Sci. Technol. 29(9):2252-2260.

Andersson, P.; Marklund, S.; Rappe, C. (1992) Levels and profiles of PCDDs and PCDFs in environmental samples as determined in snow deposited in northern Sweden. Organohalogan Compounds 8:307-310.

Arthur, M.F.; Frea, J.I. (1989) 2,3,7,8-Tetrachlorodibenzo-p-dioxin: aspects of its important properties and its potential biodegradation in soils. J. Environ. Qual. 18:1-11.

Atkinson, R. (1987) Estimation of OH radical reaction rate constants and atmospheric lifetimes for polychlorobiphenyls, dibenzo-p-dioxins, and dibenzofurans. Environ. Sci. Technol. 21:305-307.

Atkinson, R. (1991) Atmospheric lifetimes of dibenzo-p-dioxins and dibenzofurans. The Science of the Total Environment. 104:17-33.

Atkinson, R. (1995) Personal communication with Greg Schweer (Versar, Inc.): estimated congener-specific gas-phase reaction rate constants of OH radical with PCBs, PCDDs, PCDFs.

Atkinson, R. (1996) Atmospheric chemistry of PCBs, PCDDs and PCDFs. Issues in Environmental Science and Technology. 6:53-72.

Ayris, S.; Harrad, S. (1997) Factors affecting the volatilization of PCBs from soil. Organohalogen Compounds 33:250-254.

Baker, J.E.; Eisenreich, S.J. (1990) Concentrations and fluxes of polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air-water interface of Lake Superior. Environ. Sci. Technol. 24(3):342-352.

Baker, J.E.; Eisenreich, S.J.; Eadie, B.J. (1991) Sediment trap fluxes and benthic recycling of organic carbon, polycyclic aromatic hydrocarbons, and polychlorobiphenyl congeners in Lake Superior. Environ. Sci. Technol. 25(3):500-509.

Bacci, E.; Cerejeira, M.J.; Gaggi, C.; Chemello, G.; Calamari, D.; Vighi, M. (1990) Bioconcentration of organic chemical vapours in plant leaves: the azalea model. Chemosphere 21(4-5):525-535.

Barkovskii, A.; Adriaens, P. (1996) Microbial dechlorination of historically present and freshly spiked chlorinated dioxins and diversity of dioxin-dechlorinating populations. Applied and Environmental Microbiology 62(12):4556-4562.

Barkovskii, A.; Fu, Q.; Adriaens, P. (1994) Biological and abiotic dechlorination of highly chlorinated PCDD/PCDF: Issues of bioavailability and pathways. Organohalogen Compounds 21:469-473.

Barkovskii, A.L.; Adriaens, P. (1995) Reductive dechlorination of tetrachloro-dibenzo-p-dioxin partitioned from Passaic River sediments in an autochthonous microbial community. Organohalogen Compounds 24:17-21.

Barr, J.R.; Oida, T.; Kimata, K.; McClure, P.C.; Lapeza, C.R.; Maggio, V.L.; Hosoya, K.; Tanaka, N.; Patterson, D.G. (1997) Photolysis of environmentally important PCBs. Organohalogen Compounds 33:199-204.

Bedard, D.L.; Unterman, R.; Bopp, L.H.; Brennan, M.J.; Haberl, M.L.; Johnson, C. (1986) Rapid assay for screening and characterizing microorganisms for the ability to degrade polychlorinated biphenyls. Applied and Environmental Microbiology 51(4):761-768.

Bedard, D.L.; Smullen, L.A.; DeWeerd, K.A.; Dietrich, D.K.; Frame, G.M.; May, R.J.; Principe, J.M.; Rouse, T.O.; Fessler, W.A.; Nicholson, J.S. (1995) Chemical activation of microbially-mediated PCB dechlorination: a field study. Organohalogen Compounds 24:23-28.

Bidleman, T.F. (1988) Atmospheric processes. Wet and dry deposition of organic compounds are controlled by their vapor-particle partitioning. Environ. Sci. Technol. 22(4):361-367.

Birla, P.; Kamens, R.M. (1994) Effect of combustion temperature on the atmospheric stability of polybrominated dibenzo-p-dioxins and dibenzofurans. Environ. Sci. Technol. 28:1437-1443.

Bobet, E.; Berard, M.F.; Dann, T. (1990) The measurement of PCDD and PCDF in ambient air in southwestern Ontario. Chemosphere 20(10-12):1439-1445.

Bolgar, M.; Cunningham, J.; Cooper, R.; Kozloski, R.; Hubball, J.; Miller, D.P.; Crone, T.; Kimball, H.; Janooby, A.; Miller, B.; Fairless, B. (1995) Physical, spectral and chromatographic properties of all 209 individual PCB congeners. Chemosphere 31(2):2687-2705.

Botre, C.; Memoli, A.; Al-Haique, F. (1978) TCDD solubilization and photodecomposition in aqueous solutions. Environ. Sci. Technol. 12:335-336.

Broman, D.; Naf, C.; Zebühr, Y. (1992) Occurrence and dynamics of polychlorinated dibenzo-p-dioxins and dibenzofurans and other combustion related organic pollutants in the aquatic environment of the Baltic. Chemosphere 25(1-2):125-128.

Brown, J.F.; Bedard, D.L.; Brennan, M.J.; Carnahan, J.C.; Feng, H.; Wagner, R.E. (1987) Polychlorinated biphenyl dechlorination in aquatic sediments. Science 236:709-712.

Brown, J.F.; Wagner, R.E. (1990) PCB movement, dechlorination, and detoxication in the Acushnet Estuary. Environ. Toxicol. Chem. 9:1215-1233.

Brown, J.F.; Frame, G.M.; Olson, D.R.; Webb, J.L. (1995) The sources of PCBs. Organohalogen Compounds 26:427-430.

Brubaker, W.W.; Hites, R.A. (1997) Gas-phase hydroxyl radical reactions and related atmospheric removal of polychlorinated dibenzo-p-dioxins and dibenzofurans. Organohalogen Compounds 33:235-239.

Brzuzy, L.P.; Hites, R.A. (1995) Estimating the atmospheric deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans from soil. Environ. Sci. Technol. 29:2090-2098.

Bumpus, J.A.; Tien, M.; Wright, D.; Aust, S.D. (1985) Oxidation of persistent environmental pollutants by a white rot fungus. Science 228:1434-1436.

Burkhard, L.P.; Kuehl, D.W. (1986) N-octanol/water partition coefficients by reverse phase liquid chromatography/mass spectrometry for eight tetrachlorinated planar molecules. Chemosphere 15(2): 163-167.

Buser, H.R. (1976) Preparation of qualitative standard mixtures of polychlorinated dibenzo-p-dioxins and dibenzofurans by ultraviolet and gamma irradiation of the octachlorocompounds. J. Chromatogr. 192:303-307.

Buser, H.R. (1988) Rapid photolytic decomposition of brominated and brominated/chlorinated dibenzodioxins and dibenzofurans. Chemosphere 17:889-903.

California Regional Water Quality Control Board (CRWQCB) (1996) Memorandum to David Cleverly (U.S. Environmental Protection Agency) from Lila Tang (California Regional Water Quality Control Board).

Camoni, I.; Dimuccio, A.; Pontecorvo, D.; Taggi, F.; Vergori, I. (1982) Laboratory investigation for the microbial degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin in soil by addition of organic compost. Pergammon Ser. Environ. Sci. 5:95-103.

Chatkittikunwong, W.; Creaser, C.S. (1994) Stability of bromo- and bromochloro-dibenzo-p-dioxins under laboratory and environmental conditions. Chemosphere 29(3):547-557.

Chen, M.; Hong, C.S.; Bush, B.; Rhee, G.Y. (1988) Anaerobic biodegradation of polychlorinated biphenyls by bacteria from Hudson River sediments. Ecotoxicol. and Environ. Safety 16:95-105.

Choudhry, G.G.; Webster, G.R.B. (1987) Environmental photochemistry of polychlorinated dibenzofurans (PCDFs) and dibenzo-p-dioxins (PCDDs): A review. Toxicol. Environ. Chem. 14:43-61.

Choudhry, G.G.; Webster, G.R.B. (1989) Environmental photochemistry of PCDDs. 2. Quantum yields of direct phototransformation of 1,2,3,7-tetra-, 1,3,6,8-tetra-, 1,2,3,4,6,7,8-hepta-, and 1,2,3,4,6,7,8,9-octachlorodibenzo-p-dioxin in aqueous acetonitrile and their sunlight half-lives. J. Agric. Food Chem. 37:254-261.

Choudhry, G.G.; Foga, M.; Webster, G.R.B.; Muir, D.C.G.; Friesen, K. (1990) Quantum yields of the direct phototransformation of 1,2,4,7,8-penta- and 1,2,3,4,7,8-hexa chlorodibenzofuran in aqueous acetonitrile and their sunlight half-lives. Toxicological and Environmental Chemistry 26:181-195.

Cousins, I.T.; Hartlieb, N.; Teichmann, C.; Jones, K.C. (1996) Volatilization of polychlorinated biphenyls from sludge-amended soils. Organohalogen Compounds 28:58-63.

Crosby, D.G.; Wong, A.S.; Plimmer, J.R.; Woolson, E.A. (1971) Photodecomposition of chlorinated dibenzo-p-dioxins. Science 173:748.

Crosby, D.G.; Moilanen, K.W.; Wong, A.S. (1973) Environmental generation and degradation of dibenzodioxins and dibenzofurans. Environ. Health Perspect., Exp. Issue. 5:259-266.

Crosby, D.G. (1978) Conquering the monster - the photochemical destruction of chlorodioxins. In: Disposal and decontamination of pesticides. M.V.Kennedy, Ed. ACS Symposium Series 73:1-12.

Crosby, D.G. (1981) Methods of photochemical degradation of halogenated dioxins in view of environmental reclamation. Paper presented on "Human health aspects of accidental exposure to dioxins. Strategy for environmental reclamation and community protection" Bethesda, MD, October 5-7, 1982.

De Fre, R.; Van Cleuvenbergen, R.; Schoeters, J. (1994) Measurement of deposition of dioxins in Flanders, Belgium. Organohalogen Compounds 20:9-14.

Dickhut, R.M.; Andren, A.W.; Armstrong, D.E. (1986) Aqueous solubilities of six polychlorinated biphenyl congeners at four temperatures. Environ. Sci. Technol. 20(8): 807-810.

diDomenico, A.; Viviano, G.; Zapponi, G. (1982) Environmental persistence of 2,3,7,8-TCDD at Seveso. In: Chlorinated dioxins and related compounds, impact on the environment. O. Hutzinger et al., Eds. Elmsford, NY: Pergamon Press, pp. 105-113.

diDomenico, A.; Cerlesi, S.; Ratti, S. (1990) A two-exponential model to describe the vanishing trend of 2,3,7,8-tetrachlorodibenzodioxin (TCDD) in the soil at Seveso, Northern Italy. Chemosphere 20(10-12):1559-1566.

Dobbs, A.J.; Grant, C. (1979) Photolysis of highly chlorinated dibenzo-p-dioxins by sunlight. Nature 278(8):163-165.

Doucette, N.J.; Andren, A.W. (1988a) Estimation of octanol/water partition coefficients: Evaluation of six methods for highly hydrophobic aromatic hydrocarbons. Chemosphere 17(2):345-359.

Doucette, W.J.; Andren, A.W. (1988b) Aqueous solubility of selected biphenyl, furan, and dioxin congeners. Chemosphere 17(2):243-252.

Dougherty, E.J.; McPeters, A.L.; Overcash, M.R. (1991) Kinetics of photodegradation of 2,3,7,8-tetrachlorodibenzo-p-dioxins: theoretical maximum rate of soil decontamination. Chemosphere 23(5):589-600.

Dulin, D.; Drossman, H.; Mill, T. (1986) Products and quantum yields for photolysis of chloroaromatics in water. Environ. Sci. Technol. 20:72-77.

Dung, M.; O'Keefe, P.W. (1992) Comparative rates of photolysis of polychlorinated dibenzofurans in organic solvents and in aqueous solutions. Organohalogen Compounds 8:233-236.

Dunnivant, F.M.; Elzerman, A.W. (1988) Aqueous solubility and Henry's Law Constant data for PCB congeners for evaluation of quantitative structure-property relationships (QSPRs). Chemosphere 17(3): 525-541.

Dunnivant, F.M.; Coates, J.T.; Elzerman, A.W. (1988) Experimentally determined Henry's Law Constants for 17 polychlorobiphenyl congeners. Environ. Sci. Technol. 22(4):448-453.

Dunnivant, F.M.; Eizerman, A.W.; Jurs, P.C.; Hasan, M.N. (1992) Quantitative structure-property relationships for aqueous solubilities and Henry's Law Constants of polychlorinated biphenyls. Environ. Sci. Technol. 26(8):1567-1573.

Eisenreich, S.J. (1997) The role of air-water exchange of PCBs in whole-lake cycling. Organohalogen Compounds 33:255-258.

Eitzer, B.D.; Hites, R.A. (1988) Vapor pressures of chlorinated dioxins and dibenzofurans. Environ. Sci. Technol. 22(1):1362-1364.

Eitzer, B.D.; Hites, R.A. (1989) Polychlorinated dibenzo-p-dioxins and dibenzofurans in the ambient atmosphere of Bloomington, Indiana. Environ. Sci. Technol. 23:1389-1395.

EPRI (Electric Power Research Institute). (1990) Release and attenuation of PCB congeners: measurement of desorption kinetics and equilibrium sorption partition coefficients. Chicago, IL: Electric Power Research Institute; EPRI GS-6875, Project 1263-22.

Fernandez (1992) The analysis of toxic organic micro pollutants in ambient air and deposition. Chemosphere 26(7-10):1311-1316.

Fiedler, H.; Lau, C.; Cooper, K.; Andersson, R.; Kulp, S.E.; Rappe, C.; Howell, F.; Bonner, M. (1995) PCDD/PCDF in soil and pine needle samples in a rural area in the United States of America. Organohalogen Compounds 24:285-292.

Fisher, T.S.; Hayward, D.G.; Stephens, R.D.; Stenstrom, M.K. (1998) Polychlorinated di-benzo-dioxins and di-benzo-furans in Los Angeles urban runoff. Submitted for publication.

Fletcher, C.L.; McKay, W.A. (1992) Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in the aquatic environment - a literature review. AEA Environment and Energy. Report No. AEA-EE-0241.

Foreman, W.T.; Bidleman, T.F. (1985) Vapor pressure estimates of individual polychlorinated biphenyls and commercial fluids using gas chromatographic retention data. J. Chromatog. 330: 203-216.

Freeman, R.A.; Schroy, J.M. (1985) Environmental mobility of TCDD. Chemosphere 14:873-876.

Freeman, R.A.; Hileman, F.D.; Noble, R.W.; Schroy, J.M. (1987) Experiments on the mobility of 2,3,7,8-tetrachlorodibenzo-p-dioxin at Times Beach, Missouri. In: Exner, J.H. ed., Solving Hazardous Waste Problems, ACS Symposium Series Number 338.

Freeman, R.A.; Schroy, J.M. (1989) Comparison of the rate of TCDD transport at Times Beach and at Elgin AFB. Chemosphere 18(1-6):1305-1312.

Friesen, K.J.; Sarna, L.P.; Webster, G.R.B. (1985) Aqueous solubility of polychlorinated dibenzo-p-dioxins determined by high pressure liquid chromatography. Chemosphere 14(9): 1267-1274.

Friesen, J.K.; Muir, D.C.G.; Webster, G.R.B. (1990a) Evidence of sensitized photolysis of polychlorinated dibenzo-p-dioxins in natural waters under sunlight conditions. Environ. Sci. Technol. 24(11):1739-1744.

Friesen, K.J.; Vilk, J.; Muir, D.C.G. (1990b) Aqueous solubilities of selected 2,3,7,8-substituted polychlorinated dibenzofurans (PCDFs). Chemosphere 20(1-2): 27-32.

Friesen, K.J.; Loewen, M.D.; Foga, M.M. (1993) Environmental aquatic photodegradation of chlorinated dibenzofurans and their photoproducts. Organohalogen Compounds 12:135-137.

Fukuda, M.; Seto, M.; Hauschild, J.E.; Kimbara, K.; Masai, E. (1997) Concentration effect on the multiple transformation systems for polychlorinated biphenyls in a strong PCB degrader, *Rhodococcus* sp. Strain RHA1. Organohalogen Compounds. 31:425-428.

Gaggi, C.; Bacci, E. (1985) Accumulation of chlorinated hydrocarbon vapours in pine needles. Chemosphere 14(5):451-456.

Gan, D.R.; Berthouex, P.M. (1994) Disappearance and crop uptake of PCBs from sludge-amended farmland. Water Environment Research 66(1):54-69.

Govers, H.A.J.; Krop, H.B. (1996) Partition constants of chlorinated dibenzofurans and dibenzo-p-dioxins. Organohalogen Compounds 28:5-10.

Gregor, D.; Teixeira, C.; Rowsell, R. (1992) Deposition of atmospherically transported polychlorinated biphenyls in the Canadian Arctic. Organohalogen Compounds 8:341-344.

Hagenmaier, H.; She, J.; Linidig, C. (1992) Persistence of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in contaminated soil at Maulach and Rastatt in Southwest Germany. Chemosphere 25(7-10):1449-1456.

Hall, D.J.; Upton, S.L. (1988) A wind tunnel study of the particle collection efficiency of an inverted frisbee used as a dust deposition gauge. Atmospheric Environment 22(7):1383-1394.

Hallet, D.J.; Kornelson, P.J. (1992) Persistence of 2,4-dichlorophenol, 2,4,5-trichlorophenol, 2,3,7,8-tetrachlorodibenzo-p-dioxin, and 2,3,7,8-tetrachlorodibenzofuran in soils of a forest ecosystem treated with 2,4-D/2,4,5-T herbicide in Eastern Canada. Presented at: Dioxin '92, 12th International Symposium on Chlorinated Dioxins and Related Compounds; Tampere, Finland; August 1992.

Harless, R.L.; Lewis, R.G. (1992) Evaluation of a sampling and analysis method for determination of polyhalogenated dibenzo-p-dioxins and dibenzofurans in ambient air. Chemosphere 25(7-10):1317-1322.

Hawker, D.W.; Connell, D.W. (1988) Octanol-water partition coefficients of polychlorinated biphenyl congeners. Environ. Sci. Technol. 22(4): 382-387.

Hickey, W.J. (1995) Enhancing PCB biodegradation in soil with chlorobenzoate-degrading inoculants. Organohalogen Compounds 24:29-32.

Hiester, E.; Böhm, R.; Eynck, P.; Gerlock, A.; Mülder, W.; Restow, H. (1993) Longterm monitoring of PCDD, PCDF and PCB in bulk deposition samples. Organohalogen Compounds 12:147-150.

Hippelein, M.; Kaupp, H.; Dörr, G.; McLachlan, M.; Hutzinger, O. (1996) Baseline contamination assessment for a new resource recovery facility in Germany. Part II: Atmospheric concentrations of PCDD/F. Chemosphere 32(8):1605-1616.

Hites, R.A.; Harless, R.L. (1991) Atmospheric transport and deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Research and Development. EPA/600/3-91/002.

Hofmann, K.H.; Polnisch, E.; Kreisel, H.; Mach, H.; Schubert, M. (1992) Degradation of dibenzofuran and dibenzodioxins by fungi. Presented at: Dioxin '92, 12th International Symposium on Chlorinated Dioxins and Related Compounds; Tampere, Finland; August 1992.

Horstmann, M.; McLachlan, M.S. (1996) Evidence of a novel mechanism of semivolatile organic compound deposition in coniferous forests. Environ. Sci. Tech. 30(5):1794-1796.

Horstmann, M.; Bopp, U.; McLachlan, M.S. (1995) Comparison of bulk deposition of PCDD/Fs in a forest and an adjacent clearing. Organohalogen Compounds 24:505-508.

Hunt, G.T.; Maisel, B.E. (1992) Atmospheric concentrations of PCDD and PCDFs in southern California. J. Air Waste Manag. Assoc. 42:672-680.

Hutter, R.; Philippi, M. (1982) Studies in microbial metabolism of TCDD under laboratory conditions. In: Chlorinated dioxins and related compounds, impact on the environment. O. Hutzinger et al. eds. Elmsford, NY: Pergammon Press. pp. 87-93.

Hutzinger, O. (1973) Photochemical degradation of di and octachlorodibenzofuran. Environ. Health. Perspect. Exp. Issue. 5:253-256.

Jackson, D.R.; Roulier, M.H.; Grotta, H.M.; Rust, S.W.; Warner, J.S. (1986) Solubility of 2,3,7,8-TCDD in contaminated soils. In: Chlorinated dioxins and dibenzofurans in perspective. Rappe, C.; Choudhary, G.; Keith, L.H., Eds. Michigan: Lewis Publishers, Inc., pp. 185-200.

Jacobs, L.W.; Chou, S.F.; Tiedje, J.M. (1976) Fate of brominated biphenyls (PBBs) in soils. Persistence and plant uptake. J. Agric. Food Chem. 24(6):1198-1201.

Jacobs, L.W.; Chou, S.F.; Tiedje, J.M.(1978) Field concentrations and persistence of polybrominated biphenyls in soils and solubility of PBB in natural waters. Environ. Health Perspect. 23:1-8.

Kapila, S.; Yanders, A.F.; Orazio, C.E.; Meadows, J.E.; Cerlesi, S.; Clevenger, T.E. (1989) Field and laboratory studies on the movement and fate of tetrachlorodibenzo-p-dioxin in soil. Chemosphere 18:1297-1304.

Kaupp, H.; Towara, J.; McLachlan, M.S. (1994) Distribution of polychlorinated dibenzo-p-dioxins and dibenzofurans in atmospheric particulate matter with respect to particle size. Atmospheric Environment 28(4):585-593.

Kieatiwong, S.; Nguyen, L.V.; Hebert, V.R.; Hackett, M.; Miller, G.C.; Miille, M.J.; Mitzel, R. (1990) Photolysis of chlorinated dioxins in organic solvents and on soils. Environ. Sci. Technol. 24(10):1575-1580.

Kim, M.; O'Keefe, P. (1998) The role of natural organic compounds in photosensitized degradation of polychlorinated dibenzo-p-dioxins and dibenzofurans. Organohalogen Compounds. 36:377-380.

Koester, C.J.; Hites, R.A. (1992a) Wet and dry deposition of chlorinated dioxins and furans. Environ. Sci. Technol. 26(7):1375-1382.

Koester, C.J.; Hites, R.A. (1992b) Photodegradation of polychlorinated dioxins and dibenzofurans adsorbed to fly ash. Environ. Sci. Technol. 26(3):502-507.

Koshioka, M.; Ishizoka, M.; Yamada, T.; Kanazawa, J.; Murai, T. (1990) Quantum yields of the photodegradation of 1,2,3,4-, 1,3,6,8-, and 2,3,7,8-tetrachlorodibenzo-p-dioxins and their half-life periods. J. Pesticide Sci. 15:39-45.

Kwok, E.S.C.; Arey, J.; Atkinson, R. (1994) Gas-phase atmospheric chemistry of dibenzo-p-dioxin and dibenzofuran. Environ. Sci. Technol. 28(3):528-533.

Kwok, E.S.C.; Atkinson, R.; Arey, J. (1995) Rate constants for the gas-phase reactions of the OH radical with dichlorobiphenyls, 1-chlorodibenzo-p-dioxin, 1,2-dimethoxybenzene, and diphenyl ether: estimation of OH radical reaction rate constants for PCBs, PCDDs, and PCDFs. Environ. Sci. Technol. 29(6):1591-1598.

Larsson, P.; Lemkemeier, K. (1989) Microbial mineralization of chlorinated phenols and biphenyls in sediment-water systems from humic and clear-water lake. Water Research 23(9):1081-1085.

Lebeuf, M.; Gobeil, C.; Brochu, C.; Moore, S. (1996) Direct atmospheric deposition versus fluvial inputs of PCDD/Fs to the sediments of the Lower St. Lawrence Estuary. Organohalogen Compounds. 28:20-24.

Leifer, A.; Brink, R.H.; Thom, G.C.; Partymiller, K.G. (1983) Environmental transport and transformation of polychlorinated biphenyls. Washington, D.C.: U.S. Environmental Protection Agency, Office of Toxic Substances. EPA-560/5-83-025.

Lenoir, D.; Schramm, K.W.; Hutzinger, O.; Schedel, G. (1991) Photochemical degradation of brominated dibenzo-p-dioxins and -furans in organic solvents. Chemosphere 22(9-10):821-834.

Lepine, F.; Milot, S.; Vincent, N. (1992) Formation of toxic PCB congeners and PCB-solvent adducts in a sunlight irradiated cyclohexane solution of Aroclor 1254. Bull. Environ. Contam. Toxicol. 48:152-156.

Lieble, K.; Büchen, M.; Ott, W.; Fricke, W. (1993) Polychlorinated dibenzo(p)dioxins and dibenzofurans in ambient air; concentrations and deposition measurements in Hessen, Germany. Organohalogen Compounds 12:85-88.

Lodge, K.B. (1989) Solubility studies using a generator column for 2,3,7,8-tetrachlorodibenzo-p-dioxin. Chemosphere 18(1-6):933-940.

Lodge, K.B.; Cook, P.M. (1989) Partitioning studies of dioxin between sediment and water: the measurement of K_{oc} for Lake Ontario sediment. Chemosphere 19(1-6):439-444.

Lutes, C.C.; Charles, M.J.; Kamens, R.M. (1992a) The atmospheric stability of polybrominated dibenzo-p-dioxins and dibenzofurans. Chemosphere 25(1-2):99-102.

Lutes, C.C.; Charles, M.J.; Odum, J.R.; Kamens, R.M. (1992b) Chamber aging studies on the atmospheric stability of polybrominated dibenzo-p-dioxins and dibenzofurans. Environ. Sci. Technol. 26:991-998.

Lyman, W.J.; Reehl, W.F.; Rosenblatt, D.H. (1982) Handbook of chemical property estimation methods. New York, NY: McGraw-Hill.

Mackay, D.; Mascarenhas, R.; Shiu, W.Y.; Valvani, S.C.; Yalkowsky, S.H. (1980) Aqueous solubility of polychlorinated biphenyls. Chemosphere 9:257-264.

Mackay, D.; Bobra, A.; Chan, D.W.; Shiu, W.Y. (1982) Vapor pressure correlations for low-volatility environmental chemicals. Environ. Sci. Technol. 16(10): 645-649.

Mackay, D.; Shiu, W.Y.; Ma, K.C. (1992a) Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals: polynuclear aromatic hydrocarbons, polychlorinated dioxins, and dibenzofurans. Chelsea, MI: Lewis Publishers.

Mackay, D.; Shiu, W.Y.; Ma, K.C. (1992b) Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals: mono aromatic hydrocarbons, chlorobenzenes, and PCBs. Chelsea, MI: Lewis Publishers.

Marklund, S.; Tysklind, M.; Andersson, R.; Ljung, K.; Rappe, C. (1990) Environmental deposition of PCDDs and PCDFs as determined by the analyses of snow samples from the north part of Sweden. Organohalogen Compounds 1:437-440.

Marple, L.; Brunck, R.; Throop, L. (1986a) Water solubility of 2,3,7,8-tetrachlorodibenzo-p-dioxin. Environ. Sci. Technol. 20(2): 180-182.

Marple, L.; Berridge, B.; Throop, L. (1986b) Measurement of the water-octanol partition coefficient of 2,3,7,8-tetrachlorodibenzo-p-dioxin. Environ. Sci. Technol. 20(4):397-399.

Marple, L.; Brunck, R.; Berridge, B.; Throop, L. (1987) Experimental and calculated physical constants for 2,3,7,8-tetrachlorodibenzo-p-dioxin. In: Solving hazardous waste problems. Exner, J.H., Eds. ACS Symposium Series 338. Developed from a symposium sponsored by the Division of Environmental Chemistry at the 191st meeting of the American Chemical Society, New York, New York, April 13-18, 1986. pp. 105-113.

Mathur, D.B.; Stephenson, M.J.; Wenning, R.J.; Paustenbach, D.J.; Folwarkow, S.; Lursemburg, W.J. (1997) PCDD/PCDFs in storm water outfalls adjacent to urban areas and petroleum refineries in San Francisco Bay, California, USA. Organohalogen Compounds. 32:1-5.

Matsumura, F.; Benezet, J.H. (1973) Studies on the bioaccumulation and microbial degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin. Environ. Health Perspect. 5:253-258.

McCrady, J.K.; Maggard, S.P. (1993) Uptake and photodegradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin sorbed to grass foliage. Environ. Sci. Technol. 27:343-350.

McCrady, J.K.; McFarlane, C.; Gander, L.K. (1990) The transport and fate of 2,3,7,8-TCDD is soybean and corn. Chemosphere. 21(3):359-376.

McLachlan, M.S. (1995) Accumulation of PCDD/F in an agricultural food chain. Organohalogen Compounds 26:105-108.

McLachlan, M.S.; Hutzinger, O. (1990) Accumulation of organochlorine compounds in agricultural food chains. Organohalogen Compounds 1:479-484.

McLachlan, M.S.; Welsch-Pausch, K.; Tolls, J. (1995) Field validation of a model of the uptake of gaseous SOC in *Lolium multiflorum* (rye grass). Environ. Sci. Technol. 29(8):1988-2004.

McLachlan, M.S.; Sewart, A.P.; Bacon, I.R.; Jones, K.C. (1996) Persistence of PCDD/Fs in a sludge-amended soil. Environ. Sci. Technol. 30(8):2567-2571.

Mill, T.; Rossi, M.; McMillen, D.; Coville, M.; Leung, D.; Spang, J. (1987) Photolysis of tetrachlorodioxin and PCBs under atmospheric conditions. Internal report prepared by SRI International for USEPA, Office of Health and Environmental Assessment, Washington, D.C.

Mill, T. (1989) Environmental fate of polybrominated dibenzodioxins and dibenzofurans. Washington, D.C.: U.S. Environmental Protection Agency, Office of Toxic Substances.

Miller, G.C.; Zepp, R.G. (1987). 2,3,7,8-Tetrachlorodibenzo-p-dioxin: environmental chemistry. In: Exner, J.H. ed., Solving hazardous waste problems -- learning from dioxins. Washington, D.C.: American Chemical Society.

Miller, G.C.; Hebert, V.R.; Miille, M.J.; Mitzel, R.; Zepp, R.G. (1989) Photolysis of octachlorodibenzo-p-dioxin on soils: production of 2,3,7,8-TCDD. Chemosphere 18:1265-1274.

Mousa, M.; Ganey, P.E.; Quensen, J.F.; Madhukar, B.V.; Chou, K.; Giesy, J.P.; Fischer, L.J.; Boyd, S.A. (1997) Altered biological activity of commercial PCB mixtures due to microbial reductive dechlorination. Organohalogen Compounds. 34:1-5.

Muir, C.G.; Yarechewski, A.L.; Corbet, R.L.; Webster, G.R.B.; Smith, A.E. (1985) Laboratory and field studies on the fate of 1,3,6,8 - tetrachlorodibenzo-p-dioxin in soil and sediments. J. Agric. Food Chem. 33:518-523.

Muir, D.C.G.; Lawrence, S.; Holoka, M; Fairchild, W.L.; Segstro, M.D.; Webster, G.R.B.; Servos, M.R. (1992) Partitioning of polychlorinated dioxins and furans between water, sediments and biota in lake mesocosms. Chemosphere 25(1-2):199-124.

Murphy, T.J.; Pokojowczyk, J.C.; Mullin, M.D. (1983) Vapor exchange of PCBs with Lake Michigan: the atmosphere as a sink for PCBs. In: Physical Behavior of PCBs in the Great Lakes; Mackay, D.; Paterson, S.; Eisenreich, S.J.; Simmons, M.S.; eds. Ann Arbor Science: Ann Arbor, MI; pp. 49-58.

Murphy, T.J.; Mullin, M.D.; Meyer, J.A. (1987) Equilibration of polychlorinated biphenyls and toxaphene with air and water. Environ. Sci. Technol. 21(2):155-162.

Murray, M.W.; Andren, A.W. (1992) Precipitation scavenging of polychlorinated biphenyl congeners in the Great Lakes Region. Atmosp. Environ. 26A(5):883-897.

Nash, R.G.; Beall, M.L. (1980) Distribution of Silvex, 2,4-D, and TCDD applied to turf in chambers and field plots. J. Agric. Food Chem. 28(3):614-623.

Nicholson, K.W.; Rose, C.L.; Lee, D.S.; Pomeroy, I.R. (1993) Behaviour of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in the terrestrial environment: a review. AEA Environment and Energy. Report No. AEA-EE-0519.

Nies, L.; Vogel, T.M. (1990) Effects of organic substrates on dechlorination of Aroclor 1242 in anaerobic sediments. Applied and Environmental Microbiology 56(9):2612-2617.

Nirmalakhandan, N.N.; Speece, R.E. (1989) Prediction of aqueous solubility of organic chemicals based on molecular structure. 2. Application to PNAs, PCBs, PCDDs, etc. Environ. Sci. Technol. 23(6):708-713.

Oliver, B.C.; Niimi, A.J. (1988) Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem. Environ. Sci. Technol. 22:288-397.

Opperhuizen, A.; Gobas, F.A.P.C.; Van der Steen, J.M.D. (1988) Aqueous solubility of polychlorinated biphenyls related to molecular structure. Environ. Sci. Technol. 22(6):638-646.

Orazio, C.E.; Kapila, S.; Puri, R.K.; Yanders, A.F. (1992) Persistence of chlorinated dioxins and furans in the soil environment. Chemosphere 25(7-10):1469-1474.

Orth, R.G.; Ritchie, C.; Hileman, F. (1989) Measurement of the photoinduced loss of vapor phase TCDD. Chemosphere 18:1275-1282.

Overcash, M.R.; McPeters, A.L.; Dougherty, E.J.; Carbonell, R.G. (1991) Diffusion of 2,3,7,8-tetrachlorodibenzo-p-dioxin in soil containing organic solvents. Environ. Sci. Technol. 25(8):1479-1485.

Palausky, J.; Kapila, S.; Manahan, S.E.; Yanders, A.F.; Malhotra, R.K.; Clevenger, T.E. (1986) Studies on vapor phase transport and role of dispersing medium on mobility of 2,3,7,8-TCDD in soil. Chemosphere 15:1387-1396.

Pardue, J.H.; Delaune, R.D.; Patrick, W.H. (1988) Effect of sediment pH and oxidation-reduction potential on PCB mineralization. Water, Air and Soil Pollution 37:439-447.

Patil, G.S. (1991) Correlation of aqueous solubility and octanol-water partition coefficient based on molecular structure. Chemosphere 22(8):723-738.

Paustenbach, D.J.; Wenning, R.J.; Lau, V.; Harrington, N.W.; Rennix, D.K.; Parsons, A.H. (1992) Recent developments on the hazards posed by 2,3,7,8-tetrachlorobenzo-p-dioxin in soil: implications for setting risk-based cleanup levels at residential and industrial sites. J. Toxicol. and Environ. Health 36:103-149.

Paustenbach, D.J.; Wenning, R.J.; Mathur, D.; Kuksemburg, W. (1996) PCDD/PCDFs in urban stormwater discharged to San Francisco Bay, California, USA. Organohalogen Compounds. 28:111-116.

Pearson, R.F.; Swackhammer, D.L. (1997) Assessing the importance of atmospheric deposition of PCDD/Fs to the Great Lakes: compositional comparison of PCDD/F sedimentary accumulations. Organohalogen Compounds. 33:76-81.

Pennise, D.M.; Kamens, R.M. (1996) Atmospheric behavior of polychlorinated dibenzo-p-dioxins and dibenzofurans and the effect of combustion temperature. Environ. Sci. Technol. 30(9):2832-2842.

Pereira, W.E.; Rostad, C.E.; Sisak, M.E. (1985) Geochemical investigations of polychlorinated dibenzo-p-dioxins in the subsurface environment at an abandoned wood-treatment facility. Environ. Toxicol. and Chem. 4:629-639.

Podoll, R.T.; Jaber, H.M.; Mill, T. (1986) Tetrachlorodibenzodioxin: Rates of volatilization and photolysis in the environment. Environ. Sci. Technol. 20:490-492.

Prinn, R.G.; Weiss, R.E.; Miller, B.R.; Huang, J.; Alyea, F.N.; Cunnold, D.M.; Fraser, P.J.; Hartley, D.E.; Simmonds, P.G. (1995) 269:187.

Puri, R.K.; Clevenger, T.E.; Kapila, S.; Yanders, A.F.; Malhotra, R.K. (1989) Studies of parameters affecting translocation of tetrachlorodibenzo-p-dioxin in soil. Chemosphere 18:1291-1296.

Puri, R.K.; Kapila, S.; Lo, Y.H.; Orazio, C.; Clevenger, T.E.; Yanders, A.F. (1990) Effect of co-contaminants on the disposition of polychlorinated dibenzofurans in saturated soils. Chemosphere 20(10-12):1589-1596.

Puri, R.K.; Quiping, Y.; Orazio, C.E.; Yanders, A.F.; Kapila, S.; Cerlesi, S.; Facchetti, S. (1992) Transport and persistence of chlorinated organics in varied soil environments. Presented at: Dioxin'92, 12th International Symposium on Chlorinated Dioxins and Related Compounds; Tampere, Finland; August 1992.

Quab, U.; Fermann, M. (1997) Identification of relevant industrial sources of dioxins and furans in Europe. North Rhine-Westphalia State Environment Agency. Report No. 43.

Quensen, J.F.; Matsumura, F. (1983) Oxidative degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin by microorganisms. Environmental Toxicology and Chemistry. 2:261-268.

Quensen, J.F.; Tiedje, J.M.; Boyd, S.A. (1988) Reductive dechlorination of polychlorinated biphenyls by anaerobic microorganisms from sediment. Science 242:752-754.

Quensen, J.F.; Boyd, S.A.; Tiedje, J.M. (1990) Dechlorination of four commercial polychlorinated biphenyl mixtures (Aroclors) by anaerobic microorganisms from sediments. Appl. Environ. Microbiol. 56(1):2360-2369.

Rapaport, R.A.; Eisenreich, S.J. (1984) Chromatographic determination of octanol-water partition coefficients (K_{ow}s) for 58 polychlorinated biphenyl congeners. Environ. Sci. Technol. 18(3):163-170.

Rappe, C. (1991) Sources of human exposure to PCDDs and PCDFs. In: Gallo, M.; Scheuplein, R.; Van der Heijden, K. eds. Biological basis for risk assessment of dioxins and related compounds. Banbury Report #35. Plainview, NY: Cold Spring Harbor Laboratory Press.

Rhee, G.Y.; Bush, B.; Brown, M.P.; Kne, M.; Shane, L. (1989) Anaerobic biodegradation of polychlorinated biphenyls in Hudson River sediments and dredged sediments in clay encapsulation. Water Research 23(8):957-964.

Rippen, G.; Wesp, H. (1993) Kale update of PCDD/PCDF, PCB and PAH under field conditions: importance of gaseous dry deposition. Organohalogen Compounds 12:111-114.

Risatti, J.B. (1992) Rates of microbial dechlorination of polychlorinated biphenyls (PCBs) in anaerobic sediments from Waukegan Harbor. Champaign, IL: The Illinois Hazardous Waste Research and Information Center. HWRIC RR-061.

Risby, T.H.; Hsu, T.B.; Sehnert, S.S.; Bhan, P. (1990) Physiochemical parameters of individual hexachlorobiphenyl congeners. Environ. Sci. Technol. 24(11): 1680-1687.

Rordorf, B.F. (1985) Thermodynamic and thermal properties of polychlorinated compounds: the vapor pressures and flow tube kinetics of ten dibenzo-para-dioxins. Chemosphere 14(6-7):885-892.

Rordorf, B.F. (1987) Prediction of vapor pressures, boiling points, and enthalpies of fusion for twenty-nine halogenated dibenzo-p-dioxins. Thermochimica Acta 112:117-122.

Rordorf, B.F. (1989) Prediction of vapor pressures, boiling points and enthalpies of fusion for twenty-nine halogenated dibenzo-p-dioxins and fifty-five dibenzofurans by a vapor pressure correlation method. Chemosphere 18(1-6): 783-788.

Rordorf, B.F.; Sarna, L.P.; Webster, G.R.B.; Safe, S.H.; Safe, L.M.; Lenoir, D.; Schwind, K.H.; Hutzinger, O. (1990) Vapor pressure measurements on halogenated dibenzo-p-dioxins and dibenzofurans. An extended data set for a correlation method. Chemosphere 20(10-12):1603-1609.

Sabljić, A.; Güsten, H. (1989) Predicting Henry's Law Constants for polychlorinated biphenyls. Chemosphere 19(10/11): 1503-1511.

Sacan, M.T.; Inel, Y. (1995) Application of the characteristic root index model to the estimation of n-octanol/water partition coefficients. polychlorinated biphenyls. Chemosphere 30(1):39-50.

Safe, S.; Brown, K.W.; Donnelly, K.C.; Anderson, C.S.; Markiewicz, K.V. (1992) Polychlorinated dibenzo-p-dioxins and dibenzofurans associated with wood-preserving chemical sites: biomonitoring with pine needles. Environ. Sci. Technol. 26(2):394-396.

Santl, H.; Brandsch, R.; Gruber, L. (1994) Experimental determination of Henry's Law Constant (HLC) for some lower chlorinated dibenzodioxins. Chemosphere 29(9-11):2209-2214.

Sarna, L.P.; Hodge, P.E.; Webster, G.R.B. (1984) Octanol-water partition coefficients of chlorinated dioxins and dibenzofurans by reversed-phase HPLC using several C_{18} columns. Chemosphere 13(9): 975-983.

Schramm, K.W.; Wu, W.Z.; Henkelmann, B.; Merk, M.; Xu, Y.; Zhang, Y.Y.; Kettrup, A. (1995) Influence of linear alkybenzene sulfonate (LAS) as organic cosolvent on leaching behavior of PCDD/Fs from fly ash and soil. Organohalogen Compounds 24:513-516.

Schreiner, G.; Schimmel, H.; Ballschmiter, K. (1995) Influence of the substitution pattern on the microbial degradation of mono- to tetrachlorinated dibenzofurans and dibenzodioxins. Organohalogen Compounds 24:43-46.

Schroy, J.M.; Hileman, F.D.; Cheng, S.C. (1985) Physical/chemical properties of 2,3,7,8-TCDD. Chemosphere 14(6/7): 877-880.

Schwarz, K.; McLachlan, M.S. (1993) The fate of PCDD/F in sewage sludge applied to an agricultural field. Organohalogen Compounds 12:155-158.

Sedlak, D.L.; Andren, A.W. (1991) Aqueous-phase oxidation of polychlorinated biphenyls by hydroxyl radicals. Environ. Sci. Technol. 25(8):1419-1427.

Sehmel, G.A. (1980). Particle and gas dry deposition: A review. Atmospheric Environ. 14, pp 983-1011.

Servos, M.R.; Muir, D.C.G.; Webster, G.R.B. (1992) Environmental fate of polychlorinated dibenzo-p-dioxins in lake enclosures. Can. J. Fish. Aquat. Sci. 49:722-734.

Shiu, W.Y.; Doucette, W.; Gobas, F.A.P.C.; Andren, A.; Mackay, D. (1988) Physical-chemical properties of chlorinated dibenzo-p-dioxins. Environ. Sci. Technol. 22(6): 651-658.

Sijm, D.T.H.M.; Wever, H.; de Vries, P.J.; Opperhuizen, A. (1989) Octan-1-ol/water partition coefficients of polychlorinated dibenzo-p-dioxins and dibenzofurans: experimental values determined with a stirring method. Chemosphere 19(1-6): 263-266.

Simonich, S.L.; Hites, R.A. (1995) Global distribution of persistent organochlorine compounds. Science 269:1851-1854.

Sivils, L.D.; Kapila, S.; Yan, Q.; Elseewi, A.A. (1994) Studies on gas-phase phototransformation of polychlorinated dibenzo-p-dioxins. Organohalogen Compounds 19:349-353.

Sivils, L.D.; Kapila, S.; Yan, Q.; Zhang, X.; Elseewi, A.A. (1995) Studies on vapor phase phototransformation of polychlorinated dibenzo-p-dioxins (PCDDs): effect of environmental parameters. Organohalogen Compounds 24:167-172.

Smith, D.G.; Chaudhuri, I.S.; Heinold, D.; Ruffle, B. (1995) An alternative approach for estimating plant uptake of dioxin vapors. Organohalogen Compounds 24:187-193.

Smith, R.M.; O'Keefe, P.; Aldous, K.; Briggs, R.; Hilker, D.; Connor, S. (1992) Measurement of PCDFs and PCDDs in air samples and lake sediments at several locations in upstate New York. Chemosphere 25(1-2):95-98.

Smith, R.M.; O'Keefe, P.W.; Hilkes, D.; Connor, S.; Posner, E. (1995) Direct and indirect contributions of atmospheric PCDDs and PCDFs to Hudson River National Estuarine Research Reserve sediment areas. Organohalogen Compounds 24:141-145.

SRC. (1991) Syracuse Research Corporation. Calculated values from Chemfate Database literature search.

Stowe, R.A. (1996) A needle in a haystack. Environmental Protection. August 1996. pp. 22-25.

Takada, S.; Nakamura, M.; Matsueda, T.; Kurokawa, Y.; Fukamati, K., Kondo, R.; Sakai, K. (1994) Degradation of PCDDs/PCDFs by ligninolytic fungus *Phanerochaete sordida YK-624*. Organohalogen Compounds. 20:195-198.

Takada, S.; Nakamura, M.; Matsueda, T.; Kondo, R.; Sakai, K. (1996) Degradation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans by the white rot fungus *Phanerochaete sordida YK-624*. Applied and Environmental Microbiology 62(12):4323-4328.

Tien, M.; Kirk, T.K. (1983) Lignin-degrading enzyme from the Hymenomycete *Phanerochaete chrysosporium* Burds. Science 221:661-663.

Tien, M.; Kirk, T.K. (1984) Lignin-degrading enzyme from *Phanerochaete chrysosporium*: purification, characterization, and catalytic properties of a unique H_2O_2-requiring oxygenase. Proc. Natl. Acad. Sci. USA 81:2280-2284.

Towara, J.; Kaupp, H.; McLachlan, M.S. (1993) Distribution of airborne PCDD/F in relation to particle size. Organohalogen Compounds 12:115-119.

Trapp, S.; Matthies, M. (1995) Generic one-compartment model for uptake of organic chemicals by foliar vegetation. Environ. Sci. Technol. 29:2333-2338.

Travis, C.C.; Hattemer-Frey, H.A. (1987) Human exposure to 2,3,7,8-TCDD. Chemosphere 16(10-12):2331-2342.

Travis, C.C.; Hattemer-Frey, H.A. (1991) Human exposure to dioxin. Sci. Total Environ. 104:97-127.

Tysklind, M.; Rappe, C. (1991) Photolytic transformation of polychlorinated dioxins and dibenzofurans in fly ash. Chemosphere 23(8-10):1365-1375.

Tysklind, M.; Carey, A.E.; Rappe, C.; Miller, G.C. (1992) Photolysis of OCDF and OCDD on soil. Organohalogen Compounds 8:293-296.

Tysklind, M.; Fangmark, I.; Marklund, S.; Lindshog, A.; Thaning, L.; Rappe, C. (1993) Atmospheric transport and transformation of polychlorinated dibenzo-p-dioxins and dibenzofurans. Environ. Sci. Technol. 27(10):2190-2197.

United National Environment Programme (UNEP) (1999) Dioxin and furan inventories--national and regional emissions of PCDD/PCDF. Geneva, Switzerland: UNEP.

U.S. Environmental Protection Agency. (1988) Drinking water criteria document for polychlorinated biphenyls (PCBs). Cincinnati, OH: U.S. Environmental Protection Agency, Office of Health and Environmental Assessment. ECAO-CIN-414.

U.S. Environmental Protection Agency. (1990) Background document to the integrated risk assessment for dioxins and furans from chlorine bleaching in pulp and paper mills. Washington, D.C.: U.S. Environmental Protection Agency, Office of Toxic Substances. EPA 560/5-90-014.

U.S. Environmental Protection Agency. (1993) Interim report on data and methods for assessment of 2,3,7,8-tetrachlorodibenzo-p-dioxin risks to aquatic life and associated wildlife. Duluth, MN: U.S. Environmental Protection Agency, Office of Research and Development. EPA/600/R-93-055.

U.S. Environmental Protection Agency (1995) Great Lakes Water Quality Initiative technical support document for the procedure to determine bioaccumulation factors. Washington, D.C.: U.S. Environmental Protection Agency, Office of Water. EPA-820-B-95-005.

Van Dort, H.M.; Bedard, D.L. (1991) Reductive ortho and meta dechlorination of a polychlorinated biphenyl congener by anaerobic microorganisms. Appl. Environ. Microbiol. 57:1576-1578.

Wagenaar, W.J. Boelhouwers, E.J.; de Kok, H.A.M.; Groen, C.D.; Govers, H.A.J.; Olie, K.; de Gerlache, J.; Rooij, C. (1995) A comparative study of the photolytic degradation of octachlorodibenzofuran (OCDF) and octachlorodibenzo-p-dioxin (OCDD). Chemosphere 31(4):2983-2992.

Wallenhorst, T.; Krauss, P.; Hagenmaier, H. (1995) PCDD/F in ambient air and deposition in Baden-Wurttenburg, Germany. Organohalogen Compounds 24:157-161.

Walters, R.W.; Guiseppi-Elie, A. (1988) Sorption of 2,3,7,8-tetrachlorobenzo-p-dioxin to soils from water/methanol mixtures. Environ. Sci. Technol. 22(7):819-825.

Walters, R.W.; Ostazeski, S.A.; Guiseppi-Elie, A. (1989) Sorption of 2,3,7,8-tetrachlorodibenzo-p-dioxin from water by surface soils. Environ. Sci. Technol. 23:480-484.

Watanabe, I.; Kawano, M.; Tatsukawa, R. (1994) The photolysis of halogenated dibenzofurans in hexane solution and on airborne dust by sunlight. Organohalogen Compounds 19:239-338.

Webster, G.R.B.; Friesen, K.J.; Sarna, L.P.; Muir, D.C.G. (1985) Environmental fate modelling of chlorodioxins: determination of physical constants. Chemosphere 14(6/7):609-622

Webster, G.R.B.; Muldrew, D.H.; Graham, J.J.; Sarna, L.P.; Muir, D.C.G. (1986) Dissolved organic matter mediated aquatic transport of chlorinated dioxins. Chemosphere 15(9-12):1379-1386.

Welsch-Pausch, K.; Umlauf, G.; McLachlan, M.S. (1993) An investigation of the deposition pathways of atmospheric PCDD/F to a standardized grass culture. Organohalogen Compounds 12:99-102.

Welsch-Pausch, K.; McLachlan, M.S. (1995) Photodegradation of PCDD/Fs on pasture grass. Organohalogen Compounds 24:509-512.

Welsch-Pausch, K.; McLachlan, M.S.; Umlauf, G. (1995) Determination of the principal pathways of polychlorinated dibenzo-p-dioxins and dibenzofurans to *Lolium multiflorum* (Welsh Ray Grass). Environ. Sci. Technol. 29:1090-1098.

Wevers, M.; De Fre, R.; Rymen, T. (1992) Dioxins and dibenzofurans in tunnel air. Organohalogen Compounds, pp. 123-126.

Yan, Q.; Kapila, S.; Sivils, L.D.; Elseewi, A.A.; Yanders, A.F. (1995) Polychlorinated dibenzo-p-dioxins (PCDDs): effects of sensitizers and inhibitors on phototransformation. Organohalogen Compounds 24:173-178.

Yanders, A.F.; Orazio, C.E.; Puri, R.K.; Kapila, S. (1989) On translocation of 2,3,7,8-tetrachlorodibenzo-p-dioxin: time dependent analysis at the Times Beach experimental site. Chemosphere 19(1-6):429-432.

Yalkowsky, S.H.; Valvani, S.C.; Mackay, D. (1983) Estimation of the aqueous solubility of some aromatic compounds. Res. Rev. 85:43-55.

Young, A.L. (1983) Long-term studies on the persistence and movement of TCDD in a natural ecosystem. In: Human and environmental risks of chlorinated dibenzodioxins and related compounds. Tucker, R.E.; Young, A.L.; Gray, A.P., Eds. Plenum Press.

Table 2-1. Possible Number of Positional CDD (or BDD) and CDF (or BDF) Congeners

Halogen Substitution	Number of Congeners		
	CDDs (or BDDs)	CDFs (or BDFs)	PCBs
Mono	2	4	3
Di	10	16	12
Tri	14	28	24
Tetra	22	38	42
Penta	14	28	46
Hexa	10	16	42
Hepta	2	4	24
Octa	1	1	12
Nona	0	0	3
Deca	0	0	1

Table 2-2. Ranking Scheme for P-Chem Property Evaluation

Ranking	Factors				
	1	2	3	4	5
1	✓	✓	✓	x	x
2	x	✓	✓	x	x
3	✓	x	✓	✓	x
4	x	x	✓	✓	x
5	x	x	x	x	✓

Notes:

✓ indicates all specifications of the Factor have been met.
x indicates the specifications of the Factor have not been met, or the Factor does not apply.

Table 2-3. Selected Physical-Chemical Property Values for the "Dioxin-Like" CDD, CDF, and PCB Congeners

Chemical	Melting Point		Water Solubility			Vapor Pressure			Henry's Constant		Log K$_{ow}$	
CAS No. (IUPAC No.)	**Value (°C)^{a}**	**Ref.**	**Value (mg/l)^{a,c}**	**Temp. (°C)**	**Ref. [R]^{b}**	**Value (mm Hg)^{a,c}**	**Temp. (°C)**	**Ref. [R]^{b}**	**Value (atm-m^{3}/mol)^{a}**	**Ref. [R]^{b}**	**Value**	**Ref. [R]^{b}**
Tetrachlorodibenzo-p-dioxins (MW=321.98)												
2,3,7,8-TCDD 1746-01-6	305-306	9	1.93E-05	25	4,53 [1]	(1.50E-09)	25	9,53 [2]	(3.29E-05)	53 [4]	6.80	53 [1]
Congener Group Average			(3.3E-04)	25	20	(1.4E-08)	25	20	(1.7E-05)	20	(6.5)	20
Pentachlorodibenzo-p-dioxins (MW=356.42)												
1,2,3,7,8-PeCDD 40321-76-4	240-241	9				(4.4E-10)	25	9 [4]			6.64	10 [2]
Congener Group Average			(1.18E-04)	20	20	(5.6E-10)	25	20	(2.6E-06)	20	(6.6)	20
Hexachlorodibenzo-p-dioxins (MW=390.87)												
1,2,3,4,7,8-HxCDD 39227-28-6	273-275	9	4.42E-06	25	6,53 [2]	(3.8E-11)	25	53 [4]	(1.07E-05)	53 [4]	7.80	53 [4]
1,2,3,6,7,8-HxCDD 57653-85-7	285-286	9				(3.6E-11)	25	9 [5]				
1,2,3,7,8,9-HxCDD 19408-74-3	243-244	9				(4.9E-11)	25	9 [5]				
Congener Group Average			(4.4E-06)	25	20	(4.4E-11)	25	20	(1.1E-05)	20	(7.3)	20
Heptachlorodibenzo-p-dioxins (MW=425.31)												
1,2,3,4,6,7,8-HpCDD 35822-46-9	264-265	9	2.40E-06	20	6,53 [2]	(5.6E-12)	25	9,53 [4]	(1.26E-05)	53 [4]	8.00	53 [4]
Congener Group Average			(2.4E-06)	20	20	(3.2E-11)	25	20	(1.26E-05)	20	(8.0)	20
Octachlorodibenzo-p-dioxins (MW=460.76)												
1,2,3,4,6,7,8,9-OCDD 3268-87-9	325-326	6	7.4E-08	25	5,53 [2]	(8.25E-13)	25	9,53 [2]	(6.75E-06)	5,53 [4]	8.20	5,53 [2]

Table 2-3. P-Chem Properties for the Dioxin-Like Congeners (continued)

Chemical CAS No. (IUPAC No.)	Melting Point		Water Solubility			Vapor Pressure			Henry's Constant		Log K_{ow}	
	Value (°C)[a]	**Ref.**	**Value (mg/l)[a,c]**	**Temp. (°C)**	**Ref. [R][b]**	**Value (mm Hg)[a,c]**	**Temp. (°C)**	**Ref. [R][b]**	**Value (atm-m^3/mol)[a]**	**Ref. [R][b]**	**Value**	**Ref. [R][b]**
Tetrachlorodibenzofurans (MW = 305.98)												
2,3,7,8-TCDF 51207-31-9	227-228	21	4.19E-04	22.7	11 [2]	(1.5E-08)	25	21,53 [4]	(1.44E-05)	53 [4]	6.1	53 [2]
Congener Group Average			(4.2E-04)	22.7	20	(2.5E-08)	25	20	(1.4E-05)	20	(6.2)	20
Pentachlorodibenzofurans (MW = 340.42)												
1,2,3,7,8-PeCDF 57117-41-6	225-227	21				(1.7E-09)	25	21 [4]			6.79	10 [2]
2,3,4,7,8-PeCDF 57117-31-4	196-196.5	21	2.36E-04	22.7	11 [2]	(2.6E-09)	25	21,53 [4]	(4.98E-06)	53 [4]	6.5	53 [2]
Congener Group Average			(2.4E-04)	22.7	20	(2.7E-09)	25	20	(5.0E-06)	20	(6.4)	20
Hexachlorodibenzofurans (MW = 374.87)												
1,2,3,4,7,8-HxCDF 70648-26-9	225.5-226.5	21	8.25E-06	22.7	11 [2]	(2.4E-10)	25	21,53 [5]	(1.43E-05)	19 [5]	(7.0)	53
1,2,3,6,7,8-HxCDF 57117-44-9	232-234	21	1.77E-05	22.7	11 [2]	(2.2E-10)	25	21 [5]	(7.31E-06)	53 [5]		
1,2,3,7,8,9-HxCDF 72918-21-9	246-249[d]	21										
2,3,4,6,7,8-HxCDF 60851-34-5	239-240	21				(2.0E-10)	25	21 [5]				
Congener Group Average			(1.3E-05)	22.7	20	(2.8E-10)	25	20	(1.1E-05)	20	(7.0)	20
Heptachlorodibenzofurans (MW = 409.31)												
1,2,3,4,6,7,8-HpCDF 67562-39-4	236-237	21	1.35E-06	22.7	11 [2]	(3.5E-11)	25	21,53 [4]	(1.41E-05)	53 [4]	(7.4)	53 [2]

Table 2-3. P-Chem Properties for the Dioxin-Like Congeners (continued)

Chemical CAS No. (IUPAC No.)	Melting Point		Water Solubility			Vapor Pressure			Henry's Constant		Log K_{ow}	
	Value (°C)[a]	**Ref.**	**Value (mg/l)[a,c]**	**Temp. (°C)**	**Ref. [R][b]**	**Value (mm Hg)[a,c]**	**Temp. (°C)**	**Ref. [R][b]**	**Value (atm-m^3/mol)[a]**	**Ref. [R][b]**	**Value**	**Ref. [R][b]**
1,2,3,4,7,8,9-HpCDF 55673-89-7	221-223	21				1.07E-10 (4.7E-11)	25	21,53 [4]				
Congener Group Average			(1.4E-06)	22.7	20	(4.7E-11)	25	20	(1.4E-05)	20	(7.4)	20
Octachlorodibenzofurans (MW = 444.76)												
1,2,3,4,6,7,8,9-OCDF 39001-02-0	258-260	21	(1.16E-06)	25	11 [2]	3.75E-12	25	21 [2]	(1.88E-06)	19 [4]	8.0	53 [4]
Tetrachloro-PCB (MW = 291.99)												
3,3',4,4'-TCB 32598-13-3 (77)	180-181	58	1.0E-03	25	56 [2]	4.47E-07	25	56 [2]	1.70E-05	56 [2]	6.5	56 [2]
3,4,4',5-TCB 70362-60-4 (81)	160-163	58	2.92E-03	25	17 [5]	(7.85E-07)	25	18 [4]	1.28E-04	41 [4]	(6.36)	15 [5]
Pentachloro-PCB (MW = 326.44)												
2,3,3',4,4'-PeCB 32598-14-4 (105)	116.5- 117.5	56	(1.90E-03)	25	35 [5]	(8.28E-07)	25	18 [4]	(9.93E-05)	35 [5]	(6.0)	56 [2]
2,3,4,4',5-PeCB 74472-37-0 (114)	98-99	58	(2.58E-03)	20	41 [2]	(4.18E-07)	20	41 [2]	6.90E-05	41 [4]	(6.65)	15 [5]
2,3',4,4',5-PeCB 31508-00-6 (118)	111-113	58	(1.59E-03)	20	41 [2]	(3.14E-07)	20	41 [2]	8.50E-05	41 [4]	7.12	31 [4]
2',3,4,4',5-PeCB 65510-44-3(123)	134-135	58	(1.64E-03)	25	17 [5]	(8.78E-07)	25	18 [4]	1.74E-04	35 [5]	(6.74)	15 [5]
3,3',4,4',5-PeCB 57465-28-8 (126)	160-161	58	(1.03E-03)	25	17 [5]	(2.96E-07)	25	18 [4]	(5.40E-05)	35 [5]	(6.89)	15 [5]
Hexachloro-PCB (MW = 360.88)												

Table 2-3. P-Chem Properties for the Dioxin-Like Congeners (continued)

Chemical	Melting Point		Water Solubility			Vapor Pressure			Henry's Constant		Log K_{ow}	
CAS No. (IUPAC No.)	**Value ($^{\circ}$C)^{a}**	**Ref.**	**Value (mg/l)^{a,c}**	**Temp. ($^{\circ}$C)**	**Ref. [R]^{b}**	**Value (mm Hg)^{a,c}**	**Temp. ($^{\circ}$C)**	**Ref. [R]^{b}**	**Value (atm-m^{3}/mol)^{a}**	**Ref. [R]^{b}**	**Value**	**Ref. [R]^{b}**
2,3,3',4,4',5-HxCB 38380-08-4 (156)	129.5-131	58	(4.10E-04)	20	41 [2]	(1.47E-07)	25	18 [2]	8.70E-04	43 [4]	7.16	14 [3]
2,3,3',4,4',5'-HxCB 69782-90-7 (157)	161-162	58	(3.61E-04)	25	17 [5]	(5.47E-08)	25	18 [4]	5.80E-04	43 [4]	7.19	14 [3]
2,3',4,4',5,5'-HxCB 52663-72-6 (167)	125-127	58	(3.61E-04)	25	17 [5]	(1.95E-07)	25	18 [4]	(1.10E-04)	35 [5]	7.09	14 [3]
3,3',4,4',5,5'-HxCB 32774-16-6 (169)	208-210	58	(3.61E-05)	25	17 [5]	(1.81E-07)	25	56 [5]	(6.52E-05)	35 [5]	7.46	14 [3]
Heptachloro-PCB (MW=395.33)												
2,3,3',4,4',5,5'-HpCB 39635-31-9 (189)	162-163	58	(6.26E-05)	25	17 [5]	(1.31E-08)	25	18 [4]	(6.65E-05)	35 [5]	(7.71)	15 [5]
2,2',3,3',4,4',5-HpCB 35065-30-6 (170)	136.5-138.5	58	(2.27E-04)	20	41 [2]	(6.46E-09)	25	41 [2]	1.50E-05	41 [4]	(7.27)	15 [5]
2,2',3,4,4',5,5'-HpCB 35069-29-3 (180)	112.5-114	58	(4.40E-04)	20	41 [2]	(2.72E-08)	25	41 [2]	3.20E-05	41 [4]	(7.36)	15 [5]

Footnote References

a Values are presented as they appeared in the referenced article. Values in ( ) are either estimated or are calculated/extrapolated from experimental values.

b [R] is the ranking of the value from the cited reference.

c For several PCB congeners, subcooled liquid values were converted to solid values using the melting points presented in this table and the conversion methodology presented in Eitzer and Hites (1988) and Mackay et al. (1992).

$\ln (P_{sc}/P_s) = 6.79\ (T_m\text{-}T)/T$

where:
P_{sc} = subcooled value
P_s = solid value
T_m = melting point ($^{\circ}$K)
T = ambient temperature ($^{\circ}$K)

d The melting point value for this congener obtained from Ref. 21; however, it was attributed through a probably typographical error to 1,2,3,6,8,9-HxCDF.

1. Marple et al. (1986a)
2. USEPA (1990)
3. Podoll et al. (1986)
4. Marple et al. (1986b)
5. Shiu et al. (1988)
6. Friesen et al. (1985)
8. Burkhard and Kuehl (1986)
9. Rordorf (1987)
10 Sijm et al. (1989)
11. Friesen et al. (1990b)
13. Dunnivant and Elzerman (1988)
14. Risby et al. (1990)
15. Hawker and Connell (1988)
16. Sabljic and Gusten (1989)
17. Abramowitz and Yalkowsky (1990)
18. Foreman and Bidleman (1985)
19. Calculated by the VP/WS ratio technique
20. Average of all literature values (measured and calculated)
21. Rordorf (1989)
22. Dulin et al. (1986)
23. Choudhry and Webster (1987)
25. Choudhry et al. (1990)
30. Orth et al. (1989)
31. Rapaport and Eisenreich (1984)
33. Eitzer and Hites (1988)
35. Dunnivant et al. (1992)
41. Murphy et al. (1987)
43. Murphy et al. (1983)
45. Webster et al. (1986)
50. Marple et al. (1987)
51. Santl et al. (1994)
52. Rordorf et al. (1990)
53. Mackay et al. (1992a)
54. Eitzer and Hites (1989)
55. Sacan and Inel (1995)
56. Mackay et al. (1992b)

Table 2-3. P-Chem Properties for the Dioxin-Like Congeners (continued)

within a homologue group

42. EPRI (1990)

58. Bolgar et al. (1995)

Table 2-4. Summary of Selected Deposition Measurements Reported in the Literature

Author	Year[a]	Sampling Method	Analytes	Sampling Locations	Range of Results
Horstmann and McLachlan	1996	Bergerhoff	CDD/CDF	Germany Rural	0.2-2.3 ng I- TEQ_{DF}/m^2-yr
Smith et al.	1995	Wet deposition; Ambient air samples	CDD/CDF	New York, USA	Total CDD/CDF flux wet: 94 ng/m^2-yr dry: 100 ng/m^2-yr total: 194 ng/m^2-yr
Wallenhorst et al.	1995	Bergerhoff	CDD/CDF	Germany Urban Rural	 11 ng I-TEQ_{DF}/m^2-yr 2-3 ng I-TEQ_{DF}/m^2-yr
DeFré et al.	1994	Bergerhoff	CDD/CDF	Flanders, Belgium Background <1 km from MSWI Urban	 0.7-5.1 ng I-TEQ_{DF}/m^2-yr 39-374 ng I-TEQ_{DF}/m^2-yr 13-77 ng I-TEQ_{DF}/m^2-yr
Hiester et al.	1993	Bergerhoff	CDD/CDF/PCB	Germany Urban Rural	 3.6-30.3 ng I-TEQ_{DF}/m^2-yr 4.4 ng I-TEQ_{DF}/m^2-yr
Liebl et al.	1993	Bergerhoff	CDD/CDF	Germany Urban Rural/Industrial Rural	 7.6 ng I-TEQ_{DF}/m^2-yr 1.5 ng I-TEQ_{DF}/m^2-yr 1.1 ng I-TEQ_{DF}/m^2-yr
Andersson et al.	1992	Cotton cloth; snow collector	CDD/CDF	Umea, Sweden	1 ng I-TEQ_{DF}/m^2-yr
Fernandez	1992	Wet and dry frisbee collector	CDD/CDF	United Kingdom Urban-Semiurban	 13-17 ng I-TEQ_{DF}/m^2-yr
Koester and Hites	1992a	Frisbees; flat glass plates; wet-only collector	CDD/CDF	Indiana, USA	Total CDD/CDF flux wet: 210-220 ng/m^2-yr dry: 160-320 ng/m^2-yr total: 370-540 ng/m^2-yr

a Year represents year of publication, not measurement.

Table 2-5. Percentages of CDD/CDFs in Particulate Phase Measured in Air Monitoring Studies

Reference	Temp. (°C)	Percent of Total Congener Group Mass in Particulate Phase									
		TCDD	PeCDD	HxCDD	HpCDD	OCDD	TCDF	PeCDF	HxCDF	HpCDF	OCDF
A	20	23	37	66	87	96	14	31	64	87	91
B	3	40	87	100	100	100	100	60	88	100	98
B	16 - 20	8	28	45	88	100	ND	28	30	93	100
B	>28	5	13	45	60	100	ND	0	38	78	98
C		21	20	24	70	85	23	26	29	59	94
C		3	5	12	64	90	7	12	15	43	91
D	18	NR	NR	92	100	78	14	42	73	100	100
D	18	NR	NR	100	100	100	5	43	100	100	NR
E (urban)	NR	ND	0	65	82	100	20	71	100	100	100
E (rural)	NR	ND	ND	100	100	100	ND	ND	ND	ND	ND
F	18	10	28	45	77	93	9	22	48	77	89
G	9.5	31	59	82	>96	>97	18	55	79	>93	>94

NR = Not reported.
ND = Not detected.
Source: Volume 3. References are as follows:
Reference A: Eitzer and Hites (1989)
Reference B: Hites and Harless(1991)
Reference C: Harless and Lewis (1992)
Reference D: Hunt and Maisel (1992)
Reference E: Bobet et al. (1990)
Reference F: Welsch-Pausch et al. (1995) (data provided by authors); values presented for HpCDD, OCDD, HpCDF, and OCDF represent lower limits.
Reference G: Hippelein et al. (1996); values represent annual means for six sites in the outskirts of Augsburg, Germany.

Table 2-6. Predicted Fractions of CDD/CDF Congeners in Particulate Phase at 20°C in Four Airsheds

Congener	Fraction in Particulate Phase by Airshed Type			
	Clean Continental	Average Background	Background Plus Local Sources	Urban
2,3,7,8-TCDD	0.10	0.29	0.49	0.75
1,2,3,7,8-PeCDD	0.44	0.74	0.87	0.95
1,2,3,4,7,8-HxCDD	0.78	0.93	0.97	0.99
1,2,3,6,7,8-HxCDD	0.78	0.93	0.97	0.99
1,2,3,7,8,9-HxCDD	0.78	0.93	0.97	0.99
1,2,3,4,6,7,8-HpCDD	0.93	0.98	0.99	>0.99
OCDD	0.98	>0.99	>0.99	>0.99
2,3,7,8-TCDF	0.09	0.27	0.47	0.73
1,2,3,7,8-PeCDF	0.27	0.57	0.75	0.91
2,3,4,7,8-PeCDF	0.38	0.69	0.84	0.94
1,2,3,4,7,8-HxCDF	0.63	0.86	0.93	0.98
1,2,3,6,7,8-HxCDF	0.63	0.86	0.93	0.98
1,2,3,7,8,9-HxCDF	0.74	0.91	0.96	0.99
2,3,4,6,7,8-HxCDF	0.74	0.91	0.96	0.99
1,2,3,4,6,7,8-HpCDF	0.86	0.96	0.98	0.99
1,2,3,4,7,8,9-HpCDF	0.92	0.98	0.99	>0.99
OCDF	0.98	>0.99	>0.99	>0.99

Source: Chapter 3 of Volume 3.

Table 2-7. Factors Influencing the Dry Deposition Removal Rate in the Atmosphere

Micrometeorological Variables	Characteristics of Particles	Characteristics of Gases	Surface Variables
Aerodynamic roughness Mass transfer of Particles Gases Heat transfer Momentum transfer Atmospheric stability Diffusion Friction velocity Inversion layer Pollutant concentration Relative humidity Seasonal variation Solar radiation Surface heating Temperature Terrain effects Turbulence Wind velocity Zero plane displacement effect Mass transfer of Particles Gases Heat transfer Momentum transfer	Agglomeration Diameter Diffusion effects Brownian Eddy Particle Momentum Heat Electrostatic effects Attraction Repulsion Gravity settling Hygroscopicity Impaction Interception Momentum Physical properties Resuspension Solubility Thermophoresis	Chemical Activity Diffusion effects Brownian Eddy Partial pressure in equilibrium with the surface Solubility	Accommodation: Exudates Trichomes Pubescence Wax Biotic surface Canopy growth Dormant Expanding Senescent Canopy structure Areal density Bark Bole Leaves Porosity Soils Stem Type Electrostatic properties Water Pollutant penetration of canopy

Source: Adapted from Sehmel (1980).

Table 2-8. Rain Scavenging Ratios (W) and Percent Washout Due to Particulates (%P) for CDDs and CDFs in Bloomington and Indianapolis Ambient Air

Congener Group	Bloomington, IN		Indianapolis, IN	
	W	%P	W	%P
TCDD	a	a	a	a
PeCDD	10,000	50	30,000	67
HxCDD	10,000	88	26,000	69
HpCDD	62,000	93	91,000	78
OCDD	90,000	80	150,000	60
TCDF	22,000	21	33,000	24
PeCDF	14,000	54	18,000	35
HxCDF	11,000	77	15,000	74
HpCDF	34,000	88	32,000	79
OCDF	21,000	52	41,000	87
Total CDD/CDF	---	68	---	64

[a] Rarely detected; no calculations performed.

Sources: Hites and Harless (1991); Koester and Hites (1992a).

Table 2-9. Log BCF Values for CDD/CDFs in Fish

Congener	Measured Log BCFs Various Species (Reference A)	Measured Log BCFs Guppy (Reference B)	Calculated Log BCFs Guppy (Reference C)
2,3,7,8-TCDD	3.73-5.90	5.24	5.48
1,2,3,7,8-PeCDD		5.27	5.34
1,2,3,4,7,8-HxCDD	3.23-4.00	5.01	5.07
1,2,3,6,7,8-HxCDD		4.94	5.08
1,2,3,7,8,9-HxCDD		4.93	5.18
1,2,3,4,6,7,8-HpCDD	2.71-3.32	4.68	4.79
OCDD	1.90-3.97	4.13	4.39
2,3,7,8-TCDF	3.39-4.82		4.93
1,2,3,7,8-PeCDF			4.84
2,3,4,7,8-PeCDF	3.70	5.14	4.79
1,2,3,4,7,8-HxCDF			4.57
1,2,3,6,7,8-HxCDF		4.95	4.58
1,2,3,7,8,9-HxCDF			4.71
2,3,4,6,7,8-HxCDF			4.59
1,2,3,4,6,7,8-HpCDF		4.46	4.26
1,2,3,4,7,8,9-HpCDF			4.32
OCDF	2.77	3.90	3.88

Reference A: Mackay et al. (1992a); wet weight BCFs.
Reference B: Govers and Krop (1996); lipid-adjusted BCFs.
Reference C: Govers and Krop (1996); values calculated with the Solubility Parameters for Fate Analysis model.

Table 2-10. CDD/CDF BSAFs and BEFs for Lake Ontario Lake Trout

Congener	Estimated Log K_{ow}[a]	BSAF	BEF
2,3,7,8-TCDD	7.02	0.059	1.0
1,2,3,7,8-PeCDD	7.50	0.054	0.92
1,2,3,4,7,8-HxCDD	7.80	0.018	0.31
1,2,3,6,7,8-HxCDD	7.80	0.0073	0.12
1,2,3,7,8,9-HxCDD	7.80	0.0081	0.14
1,2,3,4,6,7,8-HpCDD	8.20	0.0031	0.051
OCDD	8.60	0.00074	0.012
2,3,7,8-TCDF	6.5[b]	0.047	0.80
1,2,3,7,8-PeCDF	7.0[b]	0.013	0.22
2,3,4,7,8-PeCDF	7.0[b]	0.095	1.6
1,2,3,4,7,8-HxCDF	7.5[b]	0.0045	0.076
1,2,3,6,7,8-HxCDF	7.5[b]	0.011	0.19
2,3,4,6,7,8-HxCDF	7.5[b]	0.040	0.67
1,2,3,7,8,9-HxCDF	7.5[b]	0.037	0.63
1,2,3,4,6,7,8-HpCDF	8.0[b]	0.00065	0.011
1,2,3,4,7,8,9-HpCDF	8.0[b]	0.023	0.39
OCDF	8.80	0.001	0.016

Source: U.S. EPA (1995).

[a] Burkhard and Kuehl (1986).
[b] Estimated based on degree of chlorination and Burkhard and Kuehl (1986).

Table 2-11. Photolysis Rates of CDDs/CDFs in Water and Water:Acetonitrile Mixtures

CONGENER	LIGHT SOURCE	REACTION MEDIUM	PHOTOLYSIS RATE CONSTANT (1/day)	HALF-LIFE (days) DURING SUMMER	REFERENCE
			CDDs		
1,2,7,8-TCCDD	sunlight	water from 7 ponds/lakes	4.06	0.17	Kim and O’Keefe (1998)
1,3,6,8-TCDD	Hg lamp	pond water	0.198	3.5	Choudry and Webster (1989)
2,3,7,8-TCDD	sunlight	water:acetonitrile (1:1 v/v)	0.255	2.7	Podoll et al. (1986)
2,3,7,8-TCDD	Hg lamp	water:acetonitrile (1:1 v/v)	0.78	0.9	Podoll et al. (1986)
1,2,3,4,7,8-HxCDD	Hg lamp	water:acetonitrile (2:3 v/v)	0.111	6.3	Choudry and Webster (1989)
1,2,3,4,6,7,8-HpCDD	Hg lamp	water:acetonitrile (2:3 v/v)	0.0148	47	Choudry and Webster (1989)
OCDD	Hg lamp	water:acetonitrile (2:3 v/v)	0.0397	18	Choudry and Webster (1989)
OCDD	sunlight	water from 7 ponds/lakes	1.04	0.67	Kim and O’Keefe (1998)
			CDFs		
2,3,7,8-TCDF	sunlight	water from 7 ponds/lakes	3.87	0.18	Kim and O’Keefe (1998)
1,2,7,8-TCDF	sunlight	HPLC water	1.96	0.35	Dung and O'Keefe (1992)
1,2,7,8-TCDF	sunlight	distilled water	2.18	0.32	Dung and O'Keefe (1992)
1,2,7,8-TCDF	sunlight	Saratoga Lake	3.53	0.20	Dung and O'Keefe (1992)
1,2,7,8-TCDF	sunlight	Hudson River	3.96	0.18	Dung and O'Keefe (1992)
1,2,7,8-TCDF	Hg lamp	HPLC water	24.5	0.03	Dung and O'Keefe (1992)
2,3,7,8-TCDF	sunlight	water:acetonitrile (1:2.5 v/v)	0.106	6.5	Friesen et al. (1993)
2,3,7,8-TCDF	sunlight	lake water	0.58	1.2	Friesen et al. (1993)
2,3,7,8-TCDF	sunlight	distilled water	1.49	0.47	Dung and O'Keefe (1992)
2,3,7,8-TCDF	sunlight	HPLC water	1.56	0.44	Dung and O'Keefe (1992)
2,3,7,8-TCDF	sunlight	Saratoga Lake	2.64	0.26	Dung and O'Keefe (1992)
2,3,7,8-TCDF	sunlight	Hudson River	2.83	0.25	Dung and O'Keefe (1992)
2,3,7,8-TCDF	Hg lamp	HPLC water	16.8	0.04	Dung and O'Keefe (1992)
2,3,4,7,8-PeCDF	sunlight	water:acetonitrile (1:2.5 v/v)	0.015	46.2	Friesen et al. (1993)
2,3,4,7,8-PeCDF	sunlight	lake water	3.59	0.19	Friesen et al. (1993)
OCDF	sunlight	water from 7 ponds/lakes	1.19	0.58	Kim and O’Keefe (1998)

Table 2-12. Estimated Tropospheric Half-Lives of CDDs/CDFs with Respect to Gas-Phase Reaction with the OH Radical

Congener Group	2,3,7,8-Substituted Congener	Estimated OH Reaction Rate Constant (cm^3/molecule-sec)	Estimated Tropospheric Lifetime[a,b] (days)	Estimated Tropospheric Half-Life[a,c] (days)
TCDD	2,3,7,8-TCDD	7.08E-13	17	12
PeCDD	1,2,3,7,8-PeCDD	4.59E-13	26	18
HxCDD	1,2,3,4,7,8-HxCDD	1.97E-13	61	42
	1,2,3,6,7,8-HxCDD	2.95E-13	40	28
	1,2,3,7,8,9-HxCDD	2.95E-13	40	28
HpCDD	1,2,3,4,6,7,8-HpCDD	1.30E-13	92	64
OCDD	OCDD	5.09E-14	234	162
TCDF	2,3,7,8-TCDF	4.26E-13	28	19
PeCDF	1,2,3,7,8-PeCDF	2.65E-13	45	31
	2,3,4,7,8-PeCDF	2.49E-13	48	33
HxCDF	1,2,3,4,7,8-HxCDF	1.06E-13	113	78
	1,2,3,6,7,8-HxCDF	1.51E-13	79	55
	1,2,3,7,8,9-HxCDF	1.62E-13	74	51
	2,3,4,6,7,8-HxCDF	1.40E-13	85	59
HpCDF	1,2,3,4,6,7,8-HpCDF	6.04E-14	198	137
	1,2,3,4,7,8,9-HpCDF	6.78E-14	176	122
OCDF	OCDF	2.58E-14	462	321

a Calculated using a 24-hour, seasonal, and global tropospheric average OH radical concentration of 9.7×10^5molecule/cm^3 (Prinn et al., 1995).

b Lifetime = [(reaction rate constant)(OH concentration)]$^{-1}$.

c Half-life = 0.693/[(reaction rate constant)(OH concentration)].

Source: Based on Atkinson (1996).

Table 2-13. BAFs, BCFs, and BSAFs for Dioxin-Like PCBs

PCB Congener/ Congener Group	Log BAFs[a]				Log BCFs[b] Various Species	BSAFs[c] Lake Trout
	Zooplankton	Sculpin	Alewive	Salmonids		
77					3.24-4.15	0.29
81[d]	7.47	7.48	7.79	7.96		0.67
105	7.36	7.82	7.72	8.13		2.70-4.49
118	7.37	7.86	7.71	8.15		1.72-4.09
126						3.21
156						3.97
167						0.69
170[e]	8.20	9.15	8.84	9.20		2.06-4.17
180	7.66	8.45	8.15	8.58		3.26-3.78
189						0.71
TeCB					3.95-4.79	
PeCB					5.0-5.30	
HxCB					5.39	
HpCB					5.80	

[a] U.S. EPA (1995); citing data from Oliver and Niimi (1988).

[b] Mackay et al. (1992b)

[c] U.S. EPA (1995).

[d] Includes congeners 81, 56, and 60.

[e] Includes congeners 170 and 190.

Table 2-14. Estimated Tropospheric Half-Lives of Dioxin-Like PCBs with Respect to Gas-Phase Reaction with the OH Radical

Congener Group	Dioxin-Like Congener	Estimated OH Reaction Rate Constant (10^{-12} cm^3/molecule-sec)	Estimated Tropospheric Lifetime (days)[a]	Estimated Tropospheric Half-Life (days)[a]
TCB	3,3',4,4'-TCB	0.583	20	14
	3,4,4',5-TCB	0.710	17	12
PeCB	2,3,3',4,4'-PeCB	0.299	40	28
	2,3,4,4',5-PeCB	0.383	31	22
	2,3',4,4',5-PeCB	0.299	40	28
	2',3,4,4',5-PeCB	0.482	25	17
	3,3',4,4',5-PeCB	0.395	30	21
HxCB	2,3,3',4,4',5-HxCB	0.183	65	45
	2,3,3',4,4',5'-HxCB	0.214	56	39
	2,3',4,4',5,5'-HxCB	0.214	56	39
	3,3',4,4',5,5'-HxCB	0.266	45	31
HpCB	2,2',3,3',4,4',5-HpCB	0.099	121	84
	2,2',3,4,4',5,5'-HpCB	0.099	121	84
	2,3,3',4,4',5,5'-HpCB	0.125	95	66

cm^3 = cubic centimeters.

[a] Calculated using a 24-hour, seasonal, annual, and global tropospheric average OH radical concentration of 9.7×10^5 molecule/cm^3 (Prinn et al., 1995).

Source: Atkinson (1995) [Based on Atkinson (1991) and Kwok et al. (1995)].

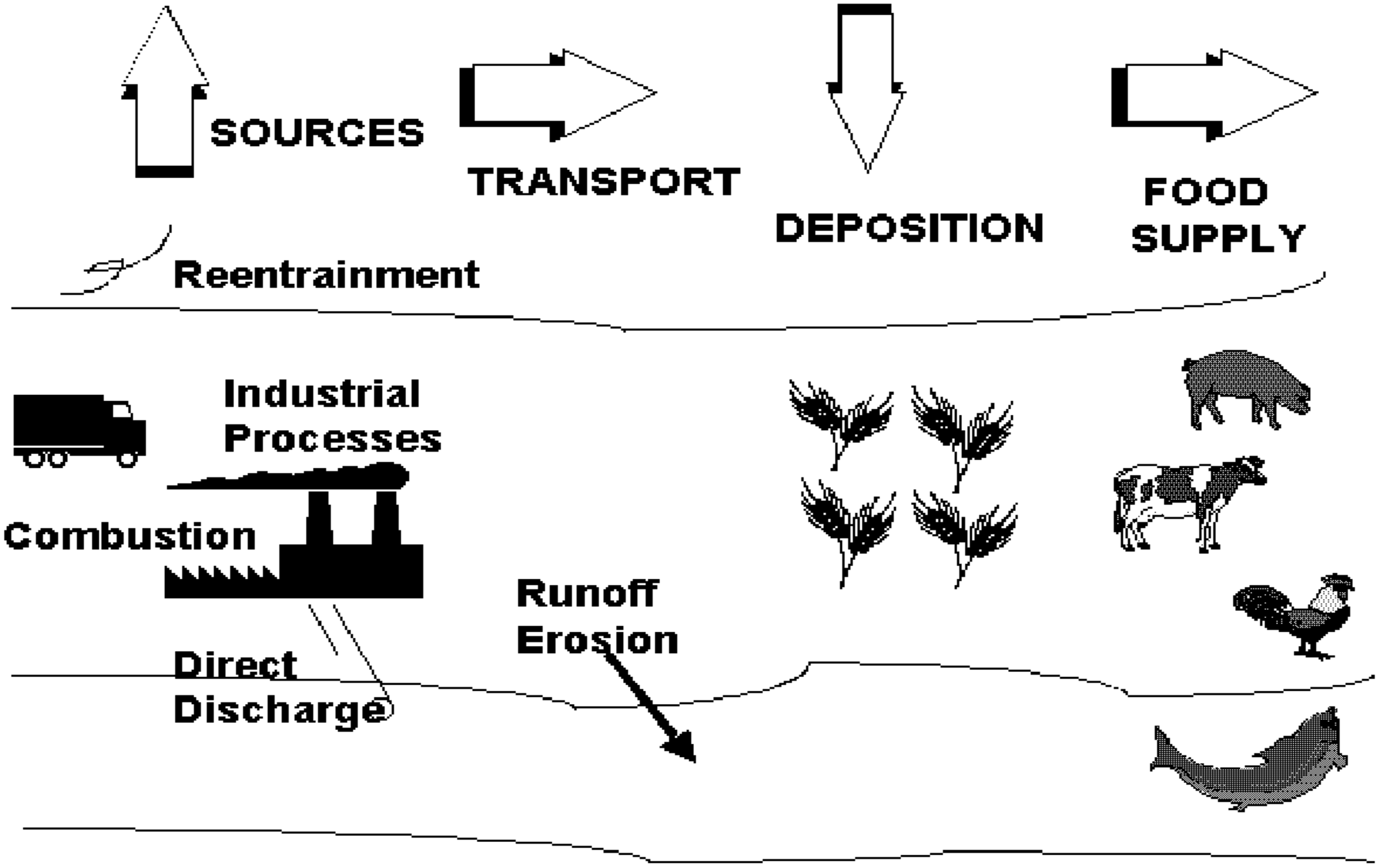


Figure 2-1. Pathways for Entry of Dioxin-like Compounds into the Terrestrial and Aquatic Food Chains

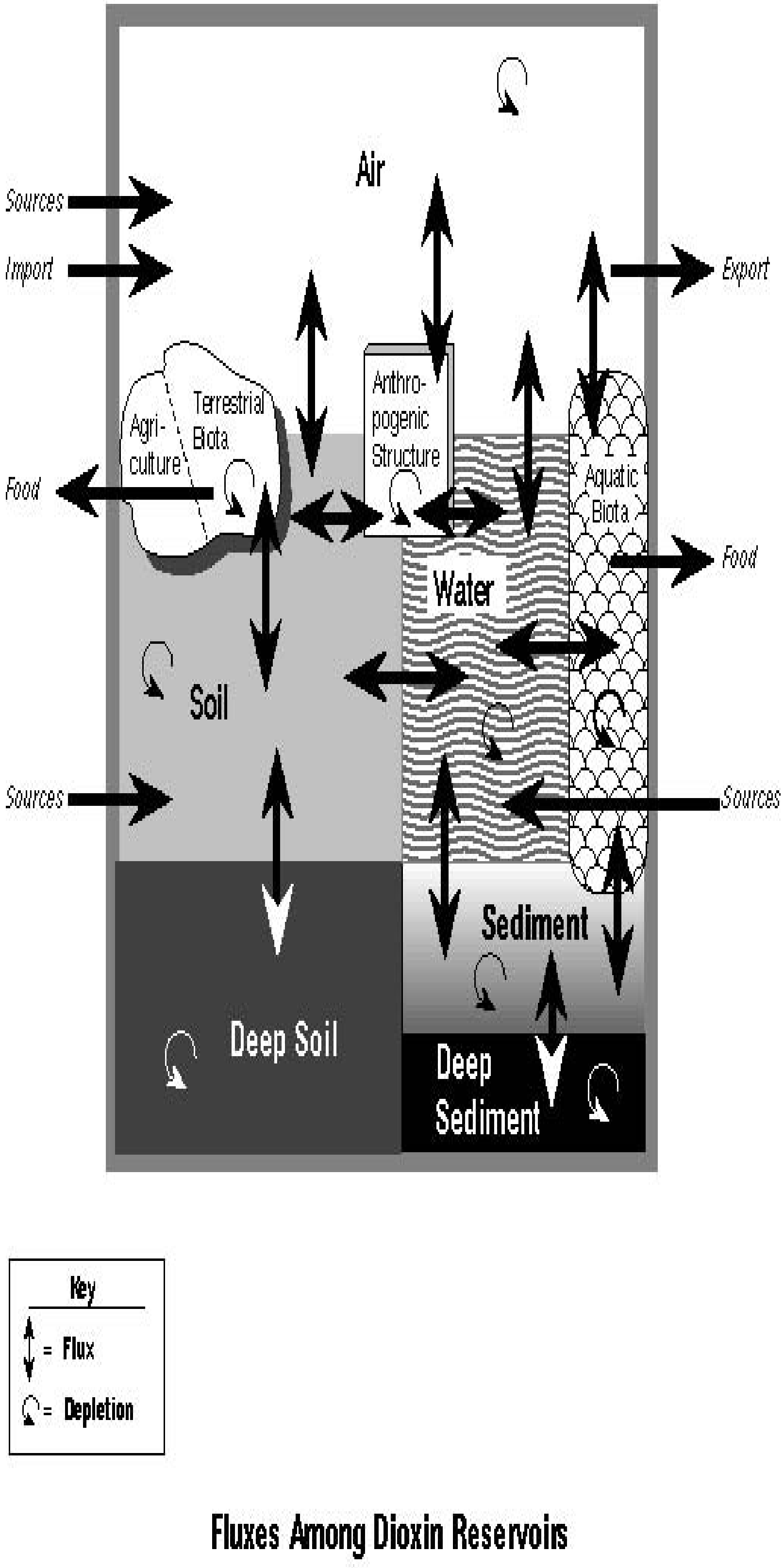


Figure 2-2. Intermedia Movement of CDD/CDFs and PCBs Among Major Environmental Media