PROPERTY OF THE
OFFICE OF SUPERFUND

United States
Environmental Protection
Agency

Office of Pesticides
and Toxic Substances
Washington, DC 20460

December 1983
EPA 560/5-83-025

Toxic Substances

Environmental Transport and Transformation of Polychlorinated Biphenyls

U.S. Environmental Protection Agency
Region 5, Library (PL-12J)
77 West Jackson Boulevard, 12th Floor
Chicago, IL 60604-3590

ENVIRONMENTAL TRANSPORT AND TRANSFORMATION OF POLYCHLORINATED BIPHENYLS

by

Asa Leifer, Robert H. Brink, Gary C. Thom, and
Kenneth G. Partymiller

U.S. Environmental Protection Agency
Office of Toxic Substances
Washington, DC 20460

DISCLAIMER

This report has been reviewed by the Office of Environmental Processes and Effects Research, Office of Research and Development, EPA, and the Office of Pesticide Programs, Office of Pesticides and Toxic Substances, EPA and has been approved for publication. Mention of trade names or commercial products does not constitute endorsement.

CONTENTS

		Page NO.
ABSTRACT		iv
INTRODUCTION	Asa Leifer	1
CHAPTER 1:	WATER SOLUBILITY AND OCTANOL/WATER PARTITION COEFFICIENT OF POLYCHLORINATED BIPHENYLS Gary C. Thom	1-1
CHAPTER 2:	VAPOR PRESSURE OF POLYCHLORINATED BIPHENYLS Kenneth G. Partymiller	2-1
CHAPTER 3:	HENRY'S LAW CONSTANT AND VOLATILITY FROM WATER OF POLYCHLORINATED BIPHENYLS Asa Leifer and Kenneth G. Partymiller	3-1
CHAPTER 4:	ADSORPTION (SORPTION) OF POLYCHLORINATED BIPHENYLS TO SOILS AND SEDIMENTS Asa Leifer	4-1
CHAPTER 5:	BIOCONCENTRATION OF POLYCHLORINATED BIPHENYLS IN FISH Asa Leifer	5-1
CHAPTER 6:	ATMOSPHERIC OXIDATION OF POLYCHLORINATED BIPHENYLS Asa Leifer	6-1
CHAPTER 7:	HYDROLYSIS AND OXIDATION OF POLYCHLORINATED BIPHENYLS Asa Leifer	7-1
CHAPTER 8:	PHOTOLYSIS OF POLYCHLORINATED BIPHENYLS Asa Leifer	8-1
CHAPTER 9:	BIODEGRADATION OF CHLORINATED BIPHENYLS Robert H. Brink	9-1

ABSTRACT

This report summarizes the environmental transport and transformation of polychlorinated biphenyls and contains nine separate chapters describing water solubility and octanol/water partition coefficient, vapor pressure, Henry's law constant and volatility from water, adsorption (sorption) to soils and sediments, bioconcentration in fish, atmospheric oxidation, hydrolysis and oxidation in water, photolysis, and biodegradation. In the preparation of each of these chapters, the emphasis has been on obtaining experimental data on environmentally relevant rate constants and equilibrium constants for these processes/properties for individual PCB congeners and Aroclors. If no experimental data were found, then estimation techniques were used wherever possible to obtain values for the rate constants or equilibrium constants for each individual congener or for groups of congeners (i.e., for monochloro-, dichloro-, trichloro-, etc., biphenyls). These parameters are in a form suitable for environmental fate modeling.

Since water solubility (C_s) and octanol/water partition coefficeint (K_{ow}) are key parameters in chemical fate analyses, work was sponsored by the Chemical Fate Branch of the EPA's Office of Toxic Substances to obtain precise values for a number of individual PCB congeners using the very reliable coupled generator column-chromatographic method. Based on all the experimental data, regression equations were developed relating these two key parameters to the parachor. In addition, a

regression equation was developed correlating C_s with K_{ow} so that if the precise experimental value of one of them is known, then a precise experimental value for the other one can be obtained for a specific PCB congener.

Adsorption (sorption) to soils and sediments (K_{oc}) and bioconcentration in fish (K_B) are related to K_{ow}. Based on the available experimental data published in the literature, linear regression equations were developed for a wide range of chemicals correlating K_{oc} and K_B to K_{ow}. The precise values of K_{ow} were then used to obtain the best estimate of K_{oc} and K_B for a number of the individual PCB congeners and all the groups of congeners.

For most of the other transport and transformation processes, estimation techniques were used to obtain environmentally relevant rate constants and half-lives. For example, the structure/reactivity method of Hendry and Kenley was modified to estimate the second-order rate constant (k_{OH}) for the reaction of OH radicals with the various PCB congeners in the gas phase. Using these rate constants, half-lives were estimated for the various congeners in reasonably polluted air. For aqueous photolysis in sunlight, the available photolysis data for a few specific PCB congeners [molar absorptivities and quantum yield] were used along with solar irradiance data in pure water and at shallow depths to estimate rate constants and half-lives at 40° north latitude and for the winter and summer solstices. Based on an analysis of the available biodegradation literature, some general conclusions have been deduced about potential

biodegradation half-lives for the mono- and dichloro-, trichloro-, tetrachloro-, penta- and higher chlorinated biphenyls in various environments [i.e., aerobic fresh and oceanic surface waters, activated sludge, soil, and anaerobic environment], but it must be emphasized that these are broad generalizations and that half-lives in particular environments for specific chlorinated biphenyls may be much larger due to certain limiting environmental variables [e.g., low temperatures, low moisture, pH extremes] or the specific PCB structure.

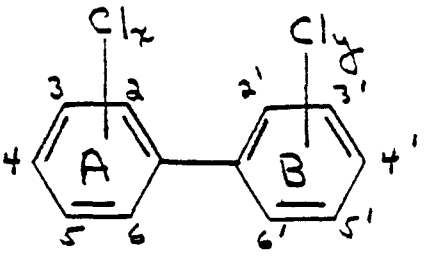
It must be emphasized that these estimates of rates for transport and transformation involved simplifying assumptions and thus these data should not be regarded as precise but rather as a best estimate based on the available data. Precise environmentally relevant experimental data are needed to confirm these rate constants and half-lives.

INTRODUCTION

Polychlorinated biphenyls (PCBs) represent a class of chlorinated aromatic compounds which have found widespread industrial application because of their stability and inertness, excellent dielectric properties, and their excellent solvent characteristics. There are 209 possible PCB congeners when biphenyl is chlorinated [Hutzinger et al. (1974)]. Figure A lists the possible distribution of the chlorines on the two rings and the number of congeners while Figure B lists a few congeners and their names. Monsanto, the only U.S. manufacturer, has sold a number of industrial grade PCBs called Aroclors and the approximate molecular composition of these products are listed in Figure C.

The fate of PCBs in the environment is a function of a number of chemical, physical, and biological processes/properties. These processes/properties are: water solubility, octanol/water partition coefficient, vapor pressure, Henry's law constant, volatility from water, adsorption (sorption) to soils and sediments, bioconcentration in fish, atmospheric oxidation, hydrolysis and oxidation in water, photolysis, and biodegradation. These processes/properties can be divided into two principal categories: transport and transformation. The first seven are transport processes/properties while the remaining ones are transformation processes. The transformations can be further subdivided into abiotic and biological processes. Whenever possible, these processes/properties have been expressed as rate constants or equilibrium constants which are suitable for environmnental fate modeling.

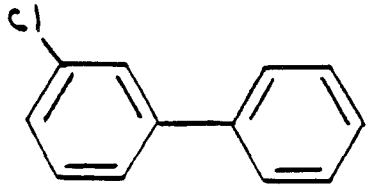
Figure A: Possible Distribution of Chlorines on the Two Biphenyl Rings and the Number of Congeners



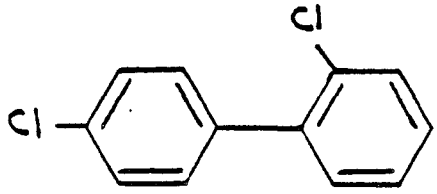
NUMBER OF CHLORINE ATOMS ON RING A (x)

		0	1	2	3	4	5
	0	1	3	6	6	3	1
	1		6	18	18	9	3
NUMBER OF	2			21	36	18	6
CHLORINE ATOMS	3				21	18	6
ON RING B (y)	4					6	3
	5						1

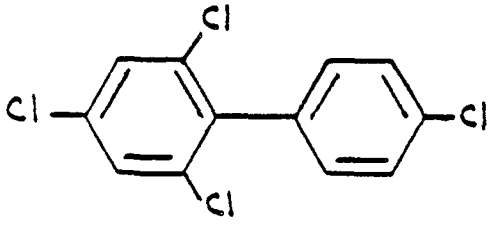
Figure 3: Molecular Structure and Names of a Few Selected Polychlorinated Biphenyls



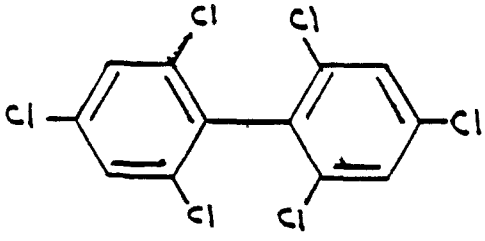
3-chlorobiphenyl



2,4'-dichlorobiphenyl



2,4,4',6-tetrachlorobiphenyl



2,2',4,4',6,6'-hexachlorobiphenyl

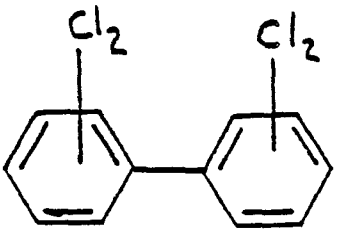
Figure C: Approximate Molecular Composition of Aroclors (Percent) [Hutzinger *et al.* 1974]

Empirical Formula	Aroclor Number						
	1016	1221	1232	1242	1248	1254	1260
$C_{12}H_{10}$	<0.1	11	<0.1	<0.1	ND*	<0.1	ND
$C_{12}H_9Cl$	1	51	31	1	ND	<0.1	ND
$C_{12}H_8Cl_2$	20	32	24	16	2	0.5	ND
$C_{12}H_7Cl_3$	57	4	28	49	18	1	ND
$C_{12}H_6Cl_4$	21	2	12	25	40	21	1
$C_{12}H_5Cl_5$	1	<0.5	4	8	36	48	12
$C_{12}H_4Cl_6$	<0.1	ND	<0.1	1	4	23	38
$C_{12}H_3Cl_7$	ND	ND	ND	<0.1	ND	6	41
$C_{12}H_2Cl_8$	ND	ND	ND	ND	ND	ND	8
$C_{12}H_1Cl_9$	ND	ND	ND	ND	ND	ND	ND
Average Molar Mass	257.9	200.7	232.2	266.5	299.5	328.4	375.7

*ND denotes none detected.

In describing the environmental fate of PCBs, this report has been divided into nine separate chapters describing these physical, chemical, and biological processes/properties in detail, Figure D. Chapters 1-5 are devoted to a discussion of the transport processes/properties, Chapters 6-8 are devoted to a discussion of abiotic transformation processes, while Chapter 9 is devoted to a discussion of biological degradation.

In the preparation of each of the chapters, the emphasis has been on gathering the available experimental data on these processes/properties for individual PCB congeners and Aroclors. If no experimental data were found, then estimation techniques were used wherever possible to obtain values for rate constants or equilibrium constants for each individual PCB congener. In many cases, these estimation techniques were unable to distinguish between congeners containing the same number of chlorines on the two rings. For example, for the PCBs with four chlorines on the two rings,



there are 21 possible congeners (Figure A)

Figure D: A List of the Chapters Describing the Transport and Transformation of PCBs in the Environment

CHAPTER 1: Water Solubility and Octanol/Water Partition Coefficient of Polychlorinated Biphenyls

CHAPTER 2: Vapor Pressure of Polychlorinated Biphenyls

CHAPTER 3: Henry's Law Constant and Volatility from Water of Polychlorinated Biphenyls

CHAPTER 4: Adsorption (Sorption) of Polychlorinated Biphenyls to Soils and Sediments

CHAPTER 5: Bioconcentration of Polychlorinated Biphenyls in Fish

CHAPTER 6: Atmospheric Oxidation of Polychlorinated Biphenyls

CHAPTER 7: Hydrolysis and Oxidation of Polychlorinated Biphenyls in Water

CHAPTER 8: Photolysis of Polychlorinated Biphenyls

CHAPTER 9: Biodegradation of Chlorinated Biphenyls

but only one value of a specific property could be obtained for all the possibilities. Thus, all the possible congeners were grouped together as the tetrachloro PCB congener and a single value of the specific property was listed.

Since water solubility (C_s) and octanol/water partition coefficient (K_{ow}) are key parameters, work was sponsored by the Chemical Fate Branch of the EPA's Office of Toxic Substances to obtain precise values for a number of PCB congeners using a coupled generator column-chromatographic method (Chapter 1). Based on the experimental data, regression equations were developed relating these two key parameters to the parachor. These equations were then used to estimate and obtain precise values for other groups of congeners.

Adsorption (sorption) to soils and sediments (K_{oc}) and bioconcentration in fish (K_B) are related to the octanol/water partition coefficient (K_{ow}). Based on the available experimental data published in the literature, linear regression equations were developed for a wide range of chemicals correlating K_{oc} and K_B to K_{ow} (Chapters 4 and 5, respectively). The precise values of K_{ow} developed in Chapter 1 were then used to obtain the best estimate of K_{oc} and K_B for a number of the individual PCB congeners and all the groups of congeners (i.e., dichloro, trichloro, tetrachloro, etc).

For other transport and transformation processes, estimation techniques were used to obtain environmentally relevant rate constants and half-lives. It must be emphasized that these estimation techniques involved simplifying assumptions and thus these data should not be regarded as precise but rather as a best estimate based on the available data.

REFERENCE

Hutzinger O, Safe S, and Zitko V. 1974. The Chemistry of PCBs. CRC Press.

CHAPTER 1

WATER SOLUBILITY AND OCTANOL/WATER PARTITION COEFFICIENT OF POLYCHLORINATED BIPHENYLS

by
Gary C. Thom

Contents

Page No.

I. INTRODUCTION AND SUMMARY 1-1

II. LITERATURE DATA ON THE WATER SOLUBILITY OF PCBs.....1-8

III. LITERATURE DATA ON THE OCTANOL/WATER PARTITION COEFFICIENT OF PCBs 1-10

IV. DETERMINATION OF C_s AND K_{ow} FOR SOME POLYCHLORINATED BIPHENYLS 1-12

V. CONCLUSION 1-22

VI. REFERENCES 1-23

I. INTRODUCTION AND SUMMARY

This chapter discusses the water solubility (C_s) and octanol/water partition coefficient (K_{ow}) of PCBs and gives experimental and/or estimated values for all PCB congeners.

C_s and K_{ow} are fundamental physicochemical properties that significantly affect the transport and transformation of a chemical in the environment. For hydrophobic chemicals such as PCBs, the water solubility can affect the rate at which the chemical is distributed in the environment and can influence the rate and extent of chemical and biological transformations such as aqueous photolysis and biodegradation. In addition, the water solubility can be correlated to the octanol/water partition coefficient. The partition coefficient is important because it is useful in predicting biological uptake, lipophilic storage and soil adsorption (i.e., properties that quantify the distribution of a chemical between the hydrophobic and hydrophilic compartments in the environment). With PCBs so widespread in the environment, their water solubility and octanol/water partition coefficients have become of critical importance in assessing their transport and transformation in the environment.

The availability of precise, reliable data on the water solubility and octanol/water partition coefficient of PCBs is limited. There are two principal reasons for this lack of data. First, the highly hydrophobic nature of PCBs makes the determination of their concentration in water (a measurement that is required for both C_s and K_{ow}) difficult from an analytical

standpoint because they are present in such low concentrations. Second, with the exception of the work of Wasik et al. (1981) that will be discussed below, all methods for C_s and K_{ow} use a "shake-flask" procedure that leads to the formation of emulsions or colloids in the equilibration step. For very hydrophobic chemicals, such as PCBs, colloid formation is difficult to control and leads to erroneously high and/or erratic PCB concentrations in water.

Wasik et al. (1982a,b) have circumvented the colloid problem by using a generator column or column leaching method coupled with a gas chromatograph/election capture detector. This method gives reliable, precise values of C_s and K_{ow} for even the most hydrophobic PCBs. In addition, Wasik has correlated both the C_s and K_{ow} of PCBs with the Sugden parachor (Par) for each PCB congener. Thus, in the absence of experimental values, the C_s and/or K_{ow} of a PCB can be estimated from its calculated parachor.

Although there are other methods for estimating these parameters [e.g., Hansch and Leo's (1979) fragment constant method and the linear regression correlations summarized by Lyman et al. (1982)], the Wasik correlations are much more reliable because they represent the direct correlation of precise C_s or K_{ow} data with the parachor.

Tables 1 and 2 summarize the data on the water solubility and octanol/water partition coefficient; C_s is given in $\mu g/L$ (ppb) and moles/liter (M) while K_{ow} is given in log units (log K_{ow}).

Table 1. Water Solubility of PCB Congeners at 25°C

PCB Congener	Generator Column Method[b] μg/L (ppb)	Generator Column Method[b] moles/liter (M)	Literature[c] μg/L (ppb)	Literature[c] moles/liter (M)	Estimated[a] μg/L (ppb)	Estimated[a] moles/liter (M)
Biphenyl	6710	4.35×10^{-5}	6620 (7)	4.29×10^{-5}	11270	7.31×10^{-5}
Monochloro-					2900	1.54×10^{-5}
2	4130	2.19×10^{-5}	5020 (2)	2.66×10^{-5} (2)		
3			2400 (2)	1.27×10^{-5} (2)		
4			1040 (2)	5.51×10^{-6} (2)		
Dichloro-					721	3.23×10^{-6}
2,5	1940	8.70×10^{-6}	580	2.60×10^{-6}		
2,2'			1140 (2)	5.11×10^{-6} (2)		
2,4			1400	6.28×10^{-6}		
2,4'			1050 (3)	4.71×10^{-6} (3)		
2,6	1390	6.23×10^{-6}	332[d]	1.49×10^{-6}[d]		
4,4'			66 (3)	2.96×10^{-7} (3)		
Trichloro-					175	6.80×10^{-7}
2,4,5	163	6.32×10^{-7}	92	3.57×10^{-7}		
2,4,6	226	8.76×10^{-7}	119[d]	4.62×10^{-7}[d]		
2,2'5			444 (2)	1.72×10^{-6} (2)		
2'3,4			78	3.03×10^{-7}		
2,4,4'			172 (2)	6.68×10^{-7} (2)		
3,4,4'			15.2	5.90×10^{-8}		
Tetrachloro-					41.8	1.43×10^{-7}
2,2',3,3'			34.0	1.16×10^{-7}		
2,2',3,5			170	5.82×10^{-7}		
2,2',4,4'			68.0	2.33×10^{-7}		
2,2',4',5	16.4	5.63×10^{-8}				
2,2',5,5'			26.2 (3)	8.97×10^{-8} (3)		
2,3',4,4'			58.0	1.99×10^{-7}		
2,3,4,5	20.9	7.17×10^{-8}	19.2	6.58×10^{-8}		
2,3',4',5			41.0	1.40×10^{-7}		
3,3',4,4'			175	5.99×10^{-7}		

Table 1. Water Solubility of PCB Congeners at 25°C (Cont.)

PCB Congener	Generator Column Method[b] μg/L (ppb)	moles/liter (M)	Literature[c] μg/L (ppb)	moles/liter (M)	Estimated[a] μg/L (ppb)	moles/liter (M)
Pentachloro-					9.83	3.01×10^{-8}
2,2',3,4,5			9.8	3.00×10^{-8}		
2,2',3,4,5'			4.5	1.38×10^{-8}		
2,2',3,4,6			12.0	3.68×10^{-8}		
2,2',4,5,5'	19.3	5.92×10^{-8}	11.9(5)	3.65×10^{-8} (5)		
2,3,4,5,6	5.48	1.68×10^{-8}	6.8	2.08×10^{-8}		
Hexachloro-					2.29	6.35×10^{-9}
2,2',3,3',4,4'	0.283	7.54×10^{-10}	0.44	1.22×10^{-9}		
2,2',3,3',4,5			0.85	2.36×10^{-9}		
2,2',3,3',5,6			0.91	2.52×10^{-9}		
2,2',3,3',6,6'	6.02	1.67×10^{-8}				
2,2',4,4',5,5'			3.00(4)	8.32×10^{-9} (4)		
2,2',4,4',6,6'	0.408	1.13×10^{-9}	0.90	2.49×10^{-9}		
Heptachloro-					0.527	1.33×10^{-9}
2,2',3,3',4,4',6	2.17	5.49×10^{-9}				
2,2',3,4',5,5',6			0.47	1.19×10^{-9}		
Octachloro-					0.121	2.82×10^{-10}
2,2',3,3',4,4',5,5'			0.272	6.33×10^{-10}		
2,2',3,3',4,4',5,5',6	0.393	9.15×10^{-10}	0.180	4.19×10^{-10}		
Nonochloro-					0.0274	5.90×10^{-11}
2,2',3,3',4,5,5',6,6'	0.0180	3.88×10^{-11}				
2,2',3,3',4,4',5,5',6			0.112	2.41×10^{-10}		
Decachloro-	0.00743	1.49×10^{-11}	0.0160	3.21×10^{-11}	0.00619	1.24×10^{-11}

[a]Estimated using $\log \frac{1}{C_s(M)} = 0.0182\ Par - 2.78$ from Wasik, S., et al., 1982.

[b]Wasik, S. et al., 1982.

[c]Average of values from Mackay, D. et al., 1980, unless otherwise noted; number in parentheses is the number of values included in average.

Table 2. Log Octanol/Water Partition Coefficients of PCB Congeners at 25°C

PCB Congener	Generator Column Method[b]	Literature Values	Estimated[a]
Biphenyl	3.74 3.89[c]	4.04[d] 3.75[e] 4.03[f]	4.09
Monochloro-			4.51
2	4.50 4.38[c]		
3	4.58[c]		
4	4.49[c]	4.28	
Dichloro-			4.94
2,2'	4.90[c]		
2,4'	5.14[c]		
2,5	5.16		
2,6	4.93		
3,4	5.29		
4,4'	5.33	5.18[g] 5.58[h]	
Trichloro-			5.37
2,2',5	5.60[c]		
2,4,5	5.51 5.81[c]		
2,4,5	5.77[c]		
2,4,6	5.47		
Tetrachloro-			5.90
2,2',3,3'		4.63[g]	
2,2'4',5	5.73		
2,3,4,5	5.72		
2,3,5,6		5.46[g]	
Pentachloro-			6.24
2,2'4,5,5'	5.92	611[h]	
2,3,4,5,6	6.30		
Hexachloro-			6.67
2,2',3,3',4,4'	6.98		
2,2',3,3',6,6'	6.65		
2,2',4,4',5,5'		6.72[h]	
2,2',4,4',6,6'	7.55[m]	6.34[k]	

Table 2. Log Octanol/Water Partition Coefficients (Cont.d)

PCB Congener	Generator Column Method[b]	Literature Values	Estimated[a]
Heptachloro-			7.10
2,2',3,3',4,4',6	6.68		
Octachloro-			7.53
2,2',3,3', 5,5',6,6'	7.11		
Nonochloro-			7.96
2,2',3,3',4, 5,5',6,6'	8.16		
Decachloro-	8.26		8.39

[a]Estimated using log K_{ow} - 0.0116 Par - 0.33 from Wasik, S. et al., 1982.

[b]Wasik, S., et al., 1982.

[c]Woodburn, K.B., 1982.

[d]Banerjee, S., et al., 1980.

[e]Veith, G.D., et al., 1979.

[f]Yalkowsky, S.H. and S.H. Valvani, 1979.

[g]Sugiura, K. et al., 1978.

[h]Chiou, C.T., et al., 1977.

[i]Mackay, D., et al., 1980.

[k]Karickhoff, SW, et al., 1979.

[m]It should be noted that the generator column value of 7.55 for the 2,2',4,4',6,6'-PCB is not consistent with the values of the other hexachloro congeners or with the other classes of congeners. That is, the value for the 2,2'4,4',6,6'-PCB is too high.

Furthermore, the generator column value for this congener is to high relative to the literature value obtained by the shake-flask method. Thus, the value of 7.55 for this congener should be used with caution until further experimentation can confirm the generator column value.

Both tables give values as determined by three methods: (1) estimated from the parachor; (2) experimentally determined using Wasik's generator column method, and; (3) experimentally determined using other methods published in the literature. In selecting a value from these tables, the value determined by the generator column method is preferred, if one exists for the particular congener of interest; if not then the literature value can be used. If neither of these values are given, the estimated value should be used. It should be noted, however, that the estimated value applies to all congeners, i.e., all tetrachloro congeners have an estimated C_s of 41.8 ppb. This is because the parachor calculation does not distinguish between different positions that the chlorine can occupy on the biphenyl ring.

II. LITERATURE DATA ON THE WATER SOLUBILITY OF PCBs

A comprehensive summary of the water solubility data on PCBs has been made by Mackay et al. (1980). It is these data (as individual values or averages) that are included in Table 1 as the literature value. These values were measured using various modifications of the standard shake-flask method along with a variety of analytical techniques for determining the aqueous concentration of the PCB.

A comparison of the literature values with those obtained using the generator column method show considerable discrepancies. Wide variation also exists between the individual literature values used in computing the average values given in Table 1. For example, the average C_s value of 1140 ppb for the 2,2' congener represents the average of two significantly different values - 790 and 1500 ppb. The Mackay summary shows many other similar discrepancies that lead one to question the reliability of the procedures used to determine the water solubility, and of the analytical techniques employed. The major factor responsible for these discrepancies is the formation and failure to remove emulsified or colloidal PCB from the aqueous solution. Another factor is the use of an insufficiently reliable and sensitive analytical technique, particularly for the more hydrophobic PCBs, where, for example, values range over a factor of ten for 2,2',4,4',6,6'-PCB. Thus, it seems clear that an alternate method is needed for determining PCB water solubility -- a method that avoids the problems of colloid

formation and removal, and contains a reliable and precise analytical procedure. To fulfill this need the Chemical Fate Branch of EPA's Office of Toxic Substances sponsored research work at the National Bureau of Standards (Wasik et al. 1981) to develop a coupled generator column/chromatographic method that could be used to obtain reliable and precise measurements of C_s (and K_{ow}) particularly for very hydrophobic chemicals such as PCBs. The results of this research are discussed in Section IV.

III. LITERATURE DATA ON THE OCTANOL/WATER PARTITION COEFFICIENT OF PCBs

As shown in Table 2, few experimental values of the octanol/water partition coefficient for PCBs have been determined. Of those values published in the literature, most have been estimated from retention time on a high pressure liquid chromatograph (Sugiura, 1978). Because so little data are available on the partition coefficient of PCBs, most values must be obtained from the several methods available for estimating log K_{ow}. The most widely used method for estimating this parameter is that of Hansch and Leo (1979), who have compiled over 10,000 log K_{ow} values for a wide variety of chemicals. Their method sums the "fragment constants" for each atom in a molecule to give the log K_{ow} for the entire, intact molecule. This method has been computerized by Chou and Jurs (1979).

Another method for estimating log K_{ow} is through correlation with water solubility. There are a number of equations correlating log K_{ow} with solubility. These are reviewed and summarized by Lyman et al. (1982). Each equation has been obtained for certain classes of compounds thus making the correlation as good as possible. Two of these equations are:

$$\log K_{ow} = -1.085 \log C_s + 4.538 \qquad (1)$$

and

$$\log K_{ow} = -0.73 \log C_s + 5.30 \qquad (2)$$

Equation (1) was developed to correlate the two parameters for a large number of pesticides and PCBs and, therefore, should give more "accurate" values of log K_{ow} than equation (2) which applies to chlorinated benzenes.

Although these estimation techniques enable the log K_{ow} of any PCB congener to be calculated, most values are only accurate to within a factor of ± 1 log units, due to scatter around the regression line and to the fact that these equations do not contain a lattice energy correction term for solids. In addition, it should be noted that none of the estimation techniques distinguish between congeners; that is, all dichlor - PCB's have the same log K_{ow}, regardless of the positions of the chlorines on the two phenyl rings. This problem has recently been addressed by Woodburn (1982), who developed an additional " π " factor that accounts for the position of the chlorine. However, his technique does not have the broad applicability or the advantage of obtaining precise experimental data afforded by the generator column method discussed in the next section.

IV. DETERMINATION OF C_s AND K_{ow} FOR SOME POLYCHLORINATED BIPHENYLS BY THE GENERATOR COLUMN METHOD

Because of the lack of reliable, precise data on the K_{ow} and C_s of PCBs, EPA's Chemical Fate Branch recently sponsored a laboratory research program at the National Bureau of Standards to experimentally determine the values of these parameters for a series of 16 representative PCBs, ranging from the mono- to decachloro congeners. The measurements were made using the generator column method developed by Wasik et al. (1981) which is ideally suited for obtaining reliable, precise data on very hydrophobic chemicals such as PCBs. The principal advantage of this method is that it avoids the formation of solute emulsions and colloids that introduce considerable error in both the K_{ow} and C_s measurements. The method accomplishes this by eliminating the agitation used to attain solute-solvent equilibrium in the shake-flask method. Instead, a column is used to generate equilibrium saturated solute-solvent solutions by the aqueous leaching of the solute from an appropriate column support; the concentration of the solute is then determined using a gas chromatograph equipped with an electron capture detector.

The results of this work have been reported (Wasik et al. 1982) and the values for the C_s and K_{ow} at 25°C are given in Table 3. As a part of this study Wasik was able to show that both parameters are correlated to the solute parachor, Par. The parachor was first demonstrated to be directly related to K_{ow} and C_s by McGowan (1966) through the equation:

$$\log K_{ow} = k'_m \, Par$$

where k'_m is a constant that is characteristic of the octanol/water solute system. The parachor is an ideal parameter to correlate with K_{ow} and C_s because it can be easily calculated by summing the individual parachor values of the atoms and structural units that make up the molecule. An example of how the parachor is calculated for 1-chlorobiphenyl is given below:

Atom or Structure	Sugden Parachor*
C	4.8
H	17.1
Cl	54.3
double bond	23.2
six-membered ring	6.1
For 1-chlorobiphenyl	
12 C	57.6
9 H	153.9
1C 1	54.3
6 double bonds	139.2
2 six-membered rings	12.2
TOTAL	417.2

*From Dreisbach compilation [1955].

The major disadvantage of the parachor estimation method is that it does not distinguish between congeners. For example, the

two monochlorobiphenyl congeners, 1-CBP and 2-CBP have the same parachor (417) and therefore, the same estimated water solubility. However, the experimental data (Table 1) show that these two congeners have very different water solubilities: 5020 and 2400 ppb, respectively. As a consequence, the log C_s - Par correlation does not give unique values for each congener, but the same value for both congeners. The same problem applies to the log K_{ow} - Par correlation.

The parachor for each of the 16 PCB's along with the experimentally determined values of log K_{ow} and C_s are given in Table 3. Correlation of K_{ow} and C_s with the parachor using linear regression analysis gave the following results that are shown graphically in Figures 1 and 2.

For the octanol/water partition coefficient:

$$\log K_{ow} = 0.0116 \text{ Par} - 0.33$$

with a coefficient of determination, $r^2 = 0.936$; for the water solubility given in moles/liter:

$$\log 1/C_s = 0.0182 \text{ Par} - 2.78$$

with a coefficient of determination, $r^2 = 0.954$.

Table 3. Aqueous Solubilities and Octanol/Water Partition Coefficients of Polychlorinated Biphenyls at 25°C as Measured Using the Generator Column Method

Compound	Parachor	C_s^w (M)[a]	Log K_{ow}[a]
1. Biphenyl	380.0	$(4.35 \pm 0.14) \times 10^{-5}$	3.74 ± 0.01
2. 2-Chlororbiphenyl	417.2	$(2.68 \pm 0.03) \times 10^{-5}$	4.50 ± 0.01
3. 2,5-Dichlorbiphenyl (liquid)	454.4	$(8.70 \pm 0.21) \times 10^{-6}$	5.16 ± 0.01
4. 2,6-Dichlorobibiphenyl	454.4	$(6.23 \pm 0.13) \times 10^{-6}$	4.93 ± 0.02
5. 2,4,5-Trichlorobiphenyl	491.6	$(6.32 \pm 0.31) \times 10^{-7}$	5.51 ± 0.11
6. 2,4,6-Trichlorobiphenyl	491.6	$(8.76 \pm 0.47) \times 10^{-7}$	5.47 ± 0.03
7. 2,3,4,5-Tetrachlorobiphenyl	528.8	$(7.17 \pm 0.34) \times 10^{-8}$	5.72 ± 0.07
8. 2,2',4',5-Tetrachlorobiphenyl	528.8	$(5.63 \pm 0.33) \times 10^{-8}$	5.73 ± 0.09
9. 2,3,4,5,6-Pentachlorobiphenyl	566.0	$(1.68 \pm 0.08) \times 10^{-8}$	6.30 ± 0.05
10. 2,2',4,5,5'-Pentachlorobiphenyl	566.0	$(5.92 \pm 0.27) \times 10^{-8}$	5.92 ± 0.01
11. 2,2',3,3',6,6'-Hexachlorobiphenyl	603.2	$(1.67 \pm 0.08) \times 10^{-8}$	6.65 ± 0.06
12. 2,2',3,3',4,4'-Hexa chlorobiphenyl	603.2	$(7.84 \pm 0.36) \times 10^{-10}$	6.98 ± 0.04
13. 2,2',4,4',6,6'-Hexachlorobiphenyl	603.2	$(1.13 \pm 0.05) \times 10^{-9}$	7.55 ± 0.21
14. 2,2',3,3',4,4'6-Heptachlorobiphenyl	640.4	$(5.49 \pm 0.24) \times 10^{-9}$	6.68 ± 0.20
15. 2,2',3,3',5,5',6,6'-Octachlorobiphenyl	677.6	$(9.15 \pm 0.50) \times 10^{-10}$	7.11 ± 0.30
16. 2,2',3,3',4,5,5',6,6'-Nonchlorobiphenyl	714.8	$(3.88 \pm 0.17) \times 10^{-11}$	8.16 ± 0.22
17. 2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	752.0	$(1.49 \pm 0.19) \times 10^{-11}$	8.26 ± 0.10

[a]The uncertainty is the standard deviation for three replicate measurements.

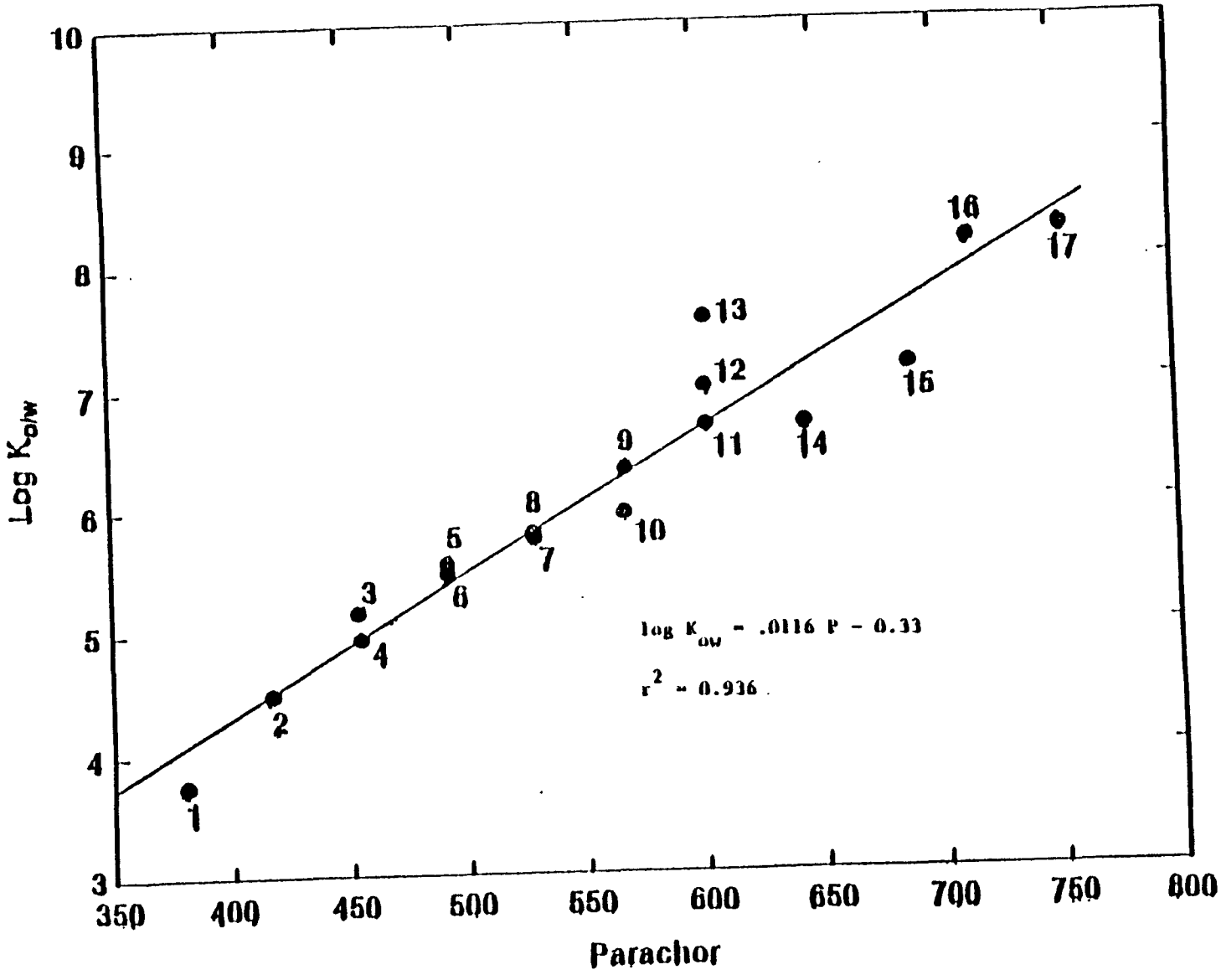


Figure 1. Log $K_{o/w}$ versus Parachor for the PCB experimental data given in Table 1.

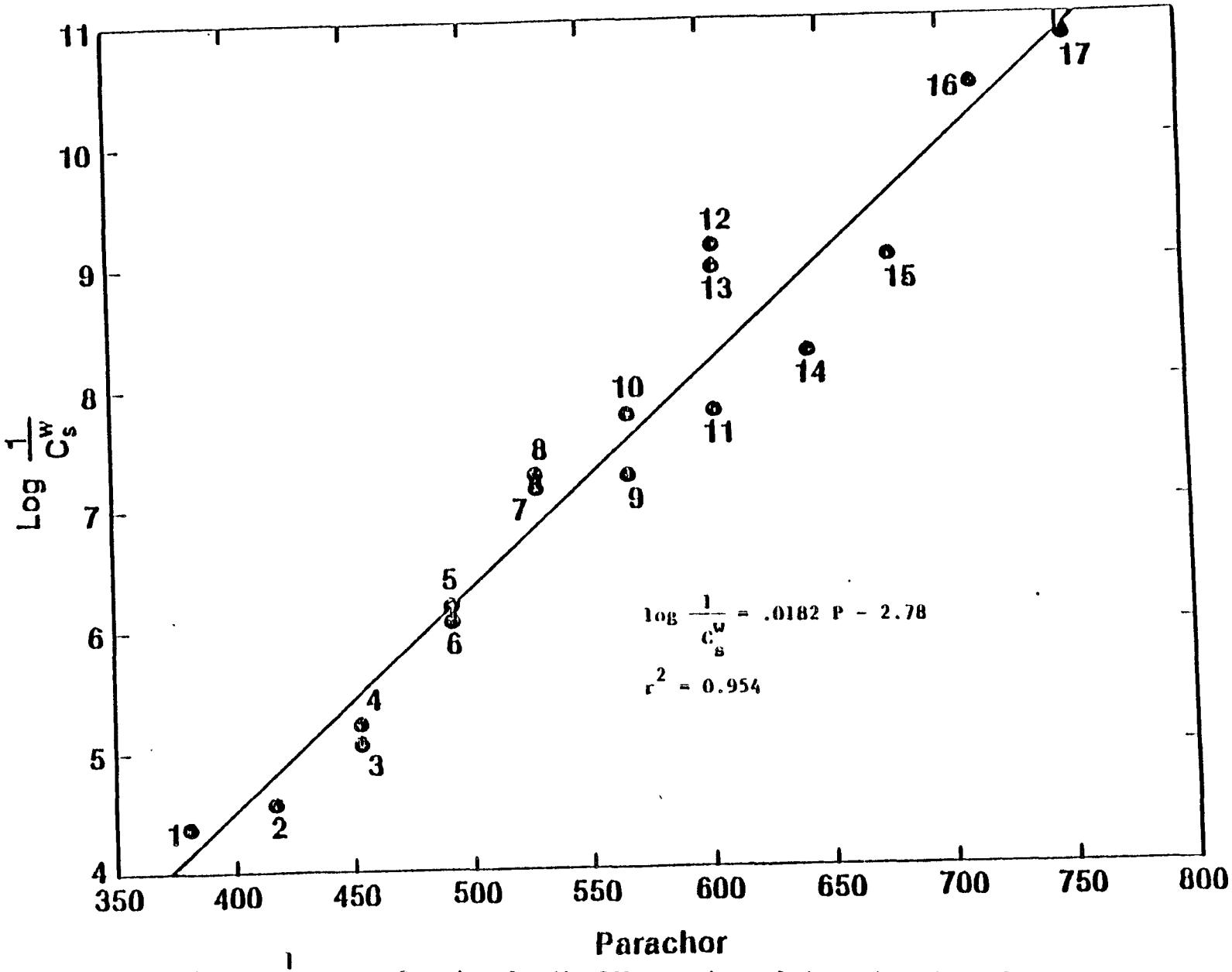


Figure 2. Log $\frac{1}{C_s^w}$ versus Parachor for the PCB experimental data given in Table 1.

Figure 3 shows the correlation between the number of chlorines on the biphenyl and log K_{ow}. The resulting regression equation:

$$\log K_{ow} = 0.43\ n_{Cl} + 4.08$$

has a coefficient of determination, $r^2 = 0.936$. This figure also shows the error that would result if Hansch and Leo's fragment constant method were used to calculate log K_{ow}. The slope, or π value, of their curve differs significantly. Recently however, Woodburn (1982) has shown that a series of π factors could be developed for PCBs based on chlorine position. Use of these new π factors is limited to estimating log K_{ow} values of less than 6.

Thus, it appears that the parachor parameter is, at the present time, the most reliable method for estimating the octanol/water partition coefficient and water solubility of those PCBs for which no experimental data are available. As an equally good alternative one can estimate either C_s or log K_{ow} if the other is known, from the regression equation derived from correlating these two parameters. Using the data in Table 3, the form of the regression equations are:

$$\log K_{ow} = 0.594 \log 1/C_s + 1.80$$

that can be rearranged to give:

$$\log 1/C_s = 1.68 \log K_{ow} - 3.03$$

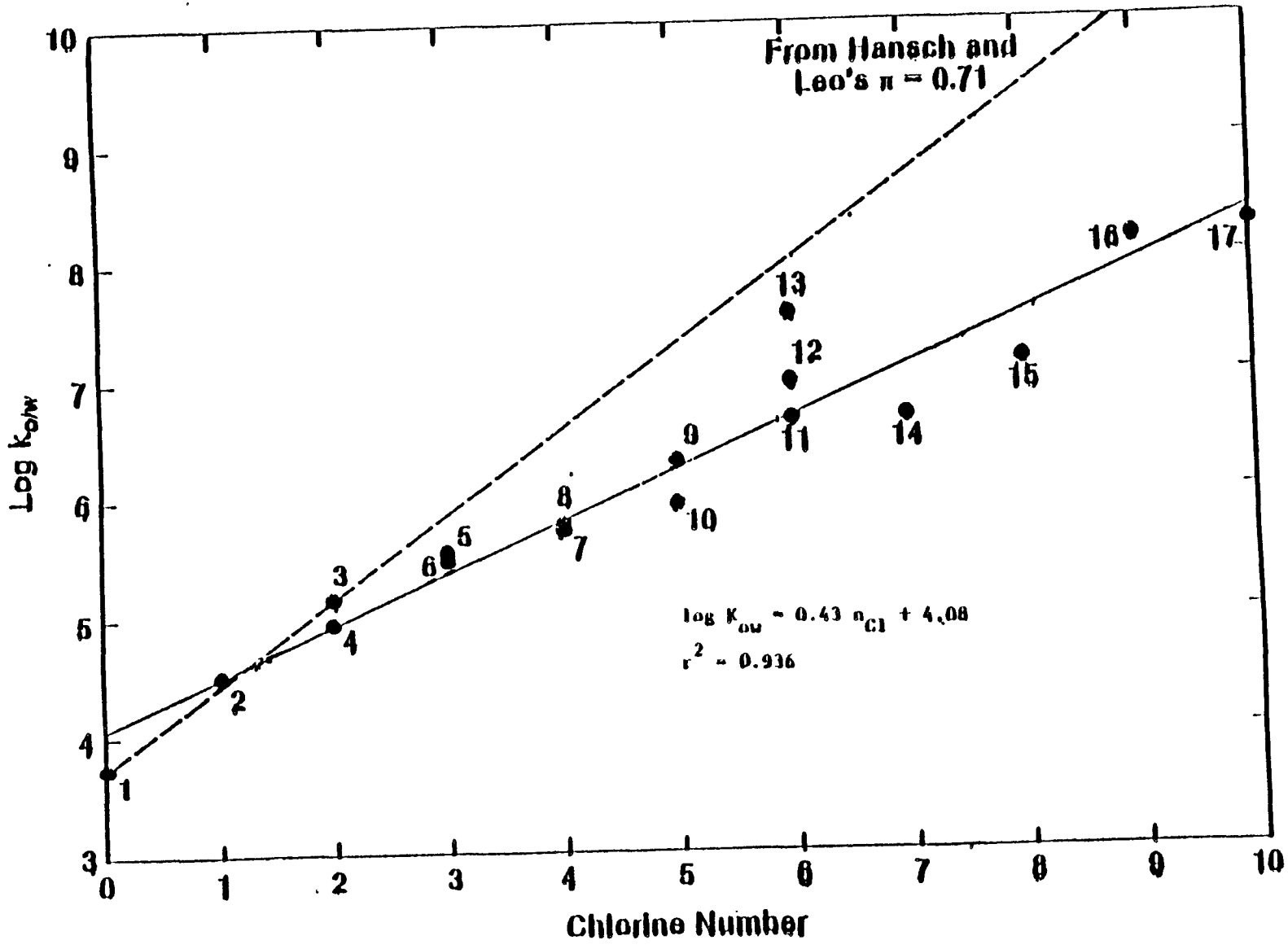


Figure 3. Log $K_{o/w}$ versus chlorine number (n_{Cl}) for the PCB experimental data given in Table 1.

For both equations, C_s is expressed in moles/liter and the coefficient of determination is 0.980. An advantage of using these regression equations is that, unlike the parachor-C_s-K_{ow} correlations, unique values are obtained for each PCB congener.

Finally, if the melting point of the PCB congener is known, the water solubility can be estimated from the following equation:

$$\log 1/C_s = 2.82 \log K_{ow} + 0.0147\ t_m - 1.91$$

where C_s is given in moles per liter and t_m is the melting point in °C of the PCB; the coefficient of determination for this equation is, $r^2 = 0.972$. Inclusion of the melting point term corrects for heat of fusion or crystal lattice energy that increases as the solubility of a substance decreases. As indicated by the value of r^2, this equation does not necessarily give a better estimation of the water solubility than the other equations because only one of the PCBs used in developing the equation was not a solid (i.e., was a liquid). Thus, the melting point factor has already been "included" in the other two regression equations.

Table 4 summarizes the various regression equations that have been described in this paper for estimating the water solubility and octanol/water partition coefficients of PCBs.

Table 4. Summary of Regression Equations for Estimating the Water Solubility and Octanol/Water Partition Coefficients of Polychlorinated Biphenyls.

Water Solubility (given in moles/liter)	
$\log 1/C_s = 0.0182\ Par - 2.78$	$r^2 = 0.954$
$\log 1/C^s = 1.68 \log K_{ow} - 3.03$	$r^2 = 0.980$
$\log 1/C_s = 2.82 \log K_{ow} + 0.0147\ t_m(°C) - 1.91$	$r^2 = 0.972$
Octanol/Water Partition Coefficient	
$\log K_{ow} = 0.0116\ Par - 0.33$	$r^2 = 0.936$
$\log K_{ow} = 0.594 \log 1/C_s(M) + 1.80$	$r^2 = 0.980$
$\log K_{ow} = 0.43\ n_{Cl} + 4.08$	$r^2 = 0.936$

V. CONCLUSION

A summary of the available and most recent data on the water solubility (C_s) and octanol/water partition coefficients (K_{ow}) of polychlorinated biphenyls (PCBs) has been made. Those PCBs for which no experimental data exist can have their C_s and K_{ow} estimated using regression equations recently developed at the National Bureau of Standards (NBS). In addition, the NBS has used a new more reliable and precise method to experimentally determine the C_s and K_{ow} for 16 PCBs. The data and information contained in this report can be used to obtain the C_s and K_{ow} for all PCB congeners.

VI. REFERENCES

Banerjee S, Yalkowsky S, and Valvani S. 1980. Water solubility and octanol/water partition coefficients of organics. Limitations of the solubility-partition coefficient correlation. Environ Sci and Tech 14: 1227-1229.

Chiou C, Freed V, Schmedding D, and Kohnert R. 1977. Partition coefficient and bioaccumulation of selected organic chemicals. Environ Sci and Tech 11:475-478.

Chou JT and Jurs PC. 1979. Computer assisted computation of partition coefficients from molecular structures using fragment constants. J Chem Inf Comput Sci 19:172-175.

Dexter RN and Parlou SP. 1978. Mass solubility and aqueous activity coefficients of stable organic chemicals in the marine environment: Polychlorinated biphenyls. Marine Chem 6:41-53.

Dreisbach RR. 1955. Physical Properties of Chemical Compounds. American Chemical Society, Washington, DC.

Hansch C and Leo A. 1979. Substituent Constants for Correlation Analysis in Chemistry and Biology. John Wiley and Sons. New York.

Karickhoff SW, Brown DS and Scott TA. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res 13:241-248.

Lyman WJ, Reehl WF and Rosenblatt DH. 1982. Handbook of Chemical Property Estimation Methods. McGraw-Hill Book Co. New York, NY.

Mackay D, Mascarenhas R and Shiu WY. Aqueous solubility of polychlorinated biphenyls. Chemosphere 9:257-264.

McGowan JC, Atkinson PN and Ruddle LH. 1966. The Physical Toxicity of Chemicals. V. Interaction Terms for Solubilities and Partition Coefficients. J Appl Chem 16:99-102.

Sugiura K, Ito N, Matsmoto N, Mihara Y, Murata K, Tsukakoshi Y and Goto M. 1978. Accumulation of polychlorinated biphenyls and polybrominated biphenyls in fish: Limitation of "Correlation between partition coefficients and accumulation factors." Chemosphere 9: 731-736.

Veith GD, Austin NM and Morris RT. 1979. A rapid method for estimating log P for organic chemicals. Water Res 13:43-47.

Wasik SP, Tewari YB, Miller MM and Martire DE. 1981. Octanol/Water partition coefficients and aqueous solubilities of organic compounds. National Bureau of Standards, NBSIR 81-2406. Washington, DC.

Wasik SP, Tewari YB, Miller MM and Purnall JH. 1982a. Measurements of the octanol/water partition coefficient by chromatographic methods. NBS J Res 87:311-315.

Wasik SP, Tewari YB, Miller MM, Martire DE and Ghodbane S. 1982b. Water solubility and octanol/water partition coefficient of polychlorinated biphenyls and other selected substances - Task IC" Final Report to Office of Toxic Substances, Chemical Fate Branch, USEPA, Washington, DC.

Woodburn KB. 1982. Measurement and application of the octanol/water partition coefficient for selected polychlorinated biphenyls. Master's Thesis. University of Wisconsin - Madison.

Yalkowsky SH and Valvani SC. 1979. Solubilities and partitioning. 2. Relationships between aqueous solubilities, partition coefficients, and molecular surface areas of rigid aromatic hydrocarbons. J Chem Eng Data 24:127-129.

CHAPTER 2

VAPOR PRESSURE OF POLYCHLORINATED BIPHENYLS

by
Kenneth G. Partymiller

Contents

Page No.

I. INTRODUCTION AND SUMMARY 2-1

II. MEASURED VALUES OF PCB VAPOR PRESSURE 2-6

III. ESTIMATED VALUES OF PCB VAPOR PRESSURE 2-7

IV. REFERENCES 2-10

I. INTRODUCTION AND SUMMARY

A knowledge of the vapor pressure of various PCB congeners is important in predicting the behavior and fate of these compounds in the environment. A knowledge of the vapor pressure of the various PCBs will allow the estimation of rates of evaporation of PCBs from spills, the rate of volatilization of PCBs from water, and possible maximum levels of PCBs in the air.

Very little data exists in the literature on the vapor pressure of Aroclors (mixtures of PCBs). Even less data are available on the vapor pressure of individual PCBs. Vapor pressure data on Aroclor mixtures are presented in Table 1. This table also lists the main PCBs which are present in each Aroclor and their percent in the mixture. Table 2 lists all measured vapor pressure data for individual PCB congeners which could be found in the open literature.

Due to the apparent paucity of vapor pressure data on PCBs, it was necessary to consider other methods for obtaining the vapor pressure of the various congeners. Lyman et al. (1982) describe a number of estimation techniques in a handbook which are useful for estimating physicochemical properties of organic chemicals. Several methods for estimating vapor pressure are included in Chapter 14 [Lyman et al. (1982)]. These methods require a boiling temperature as an input. However, this property also had to be estimated since none of these data are available in the published literature. Therefore, the boiling temperature was estimated by the method recommended by Lyman et al. (1982). Both of the above mentioned estimation techniques

Table 1. Vapor Pressures of Aroclors at 25°C

Aroclor	Vapor Pressure (Torr)	Primary PCBs Present and Percent Composition[c]	
1016	4×10^{-4} (estimate)[a]	57%	$C_{12}H_7Cl_3$
1221	6.7×10^{-3} (estimate)[a]	51%	$C_{12}H_9Cl$
1231	4.06×10^{-3} (estimate)[a]	31%	$C_{12}H_9Cl$
		24%	$C_{12}H_8Cl_2$
		28%	$C_{12}H_7Cl_3$
1242	4.06×10^{-4} (measured)[b]	49%	$C_{12}H_7Cl_3$
1248	4.94×10^{-4} (measured)[b]	40%	$C_{12}H_6Cl_4$
		36%	$C_{12}H_5Cl_5$
1254	7.71×10^{-5} (measured)[b]	48%	$C_{12}H_5Cl_5$
1260	4.05×10^{-5} (measured)[b]	38%	$C_{12}H_4Cl_6$
		41%	$C_{12}H_3Cl_7$

[a]USEPA (1979).

[b]Monsanto (1974) Extrapolated to 25°C from higher temperatures.

[c]Table C, of the Introduction, lists the complex composition of the Aroclors.

Table 2. Measured Vapor Pressures of PCBs

PCB	Temperature(°C)	Vapor Pressure (Torr)
2',3,4	25	0.8×10^{-4} [a]
	25	1.0×10^{-4} [b] (extrapolated from 30°C)
	30	1.3×10^{-4} [b]
2,2',5,5'	25	5.5×10^{-5} [a]
	25	1.9×10^{-5} [b] (extrapolated from 30°C)
	30	3.6×10^{-5} [b]
2,2',4,5,5'	25	9.2×10^{-6} [a]
	25	7.2×10^{-6} [b] (extrapolated from 30°C)
	30	1.3×10^{-5} [b]
3,3'	25	2.0×10^{-4} [a]
2,2',4,4',6,6'	25	1.2×10^{-5} [a]

[a] Westcott and Bidleman (1981).

[b] Westcott et al. (1981).

are insensitive to location of chlorine atoms on the biphenyl rings so that, for example, all pentachloro biphenyls will be predicted to have identical vapor pressures and boiling points. Table 3 lists estimated vapor pressures of all possible PCB congeners (with the above mentioned caveat) as estimated, using estimated boiling temperatures, by the method preferred for PCBs.

In summary, it is apparent that there is only limited experimental data on vapor pressures of a few PCBs. Furthermore, the estimation techniques used to estimate the vapor pressures of the various PCB congeners have two limitations:

1) these estimation techniques cannot distinguish between congeners of PCBs containing the same number of chlorines; and
2) the estimation techniques for the vapor pressure of the PCB congeners containing 7 to 10 chlorine atoms are not reliable since these PCBs have vapor pressures below the useful limit of the estimation technique.

It is thus obvious that carefully conducted experiments must be performed on a series of PCB congeners to obtain reliable vapor pressures. With these data, one should be able to develop empirical correlations for determining the vapor pressure of all PCB congeners.

Table 3. Estimated Vapor Pressures of PCB Congeners [a]

# of Cl's	Estimated Vapor Pressure (Torr @ 25°C)	Physical State
0	7.3×1^{-2}	Liquid
1	2.8×10^{-2}	Liquid
2	1.1×10^{-2}	Liquid
3	8.5×10^{-5}	Solid
4	3.7×10^{-6}	Solid
5	7.6×10^{-7}	Solid
6	1.7×10^{-7}	Solid
7	(3.6×10^{-8})[b]	Solid
8	(7.6×10^{-9})[b]	Solid
9	$(1.9. \times 10^{-9})$[b]	Solid
10	(4.0×10^{-10})[b]	Solid

[a]Predicted by vapor pressure estimation method 2 as described in Lyman et al. (1982).

[b]Values in parentheses are outside of the useful range of the estimation technique and must be used with caution.

II. MEASURED VALUES OF PCB VAPOR PRESSURE

The vapor pressure data on Aroclors (PCB mixtures) is given in Table 1 [USEPA (1979), Monsanto (1974)]. These data were either estimated or measured. It should be noted that Monsanto was the only US manufacturer and supplier of PCBs for a number of years.

The PCB vapor pressure data listed in Table 2 has been determined by two techniques. Westcott et al. (1981) measured the vapor pressure of a few PCBs by the gas saturation method at temperatures of 30, 35, and 40°C and the data were then extrapolated to 25°C using the Clapeyron or Antoine equation. The gas saturation technique which was used is very similar to the one published by EPA as an OTS Test Guideline [USEPA (1982)]. In the method used by Westcott et al. (1978), air was used as the carrier gas rather than the nitrogen recommended in the EPA procedure. The second technique used by Westcott [Westcott and Bidleman (1981)] utilized a capillary gas chomatographic technique which determines vapor pressure by measuring the PCB retention times relative to a reference compound of known pressure.

III. ESTIMATED VALUES OF PCB VAPOR PRESSURE

Several of the Aroclor vapor pressure values listed in Table 1 were estimated [USEPA (1979)]. The exact source and/or method of estimation of these values is unknown. These values appear to be in agreement with expected values.

Vapor pressures of the pure PCB congeners were estimated by the methods recommended by Lyman et al. (1982). These methods require a boiling temperature as an input. Boiling temperatures were not found in the literature and thus they were estimated by the method recommended by Lyman et al. (1982). The recommended methods [Lyman et al. (1982)] for the estimation of both vapor pressure and boiling temperature are not sensitive to position of chlorine atoms on the biphenyl rings so that all congeners will have identical estimated vapor pressure and boiling temperature. Table 4 lists the calculated boiling points of the PCB congeners. Lyman et al. (1982) recommended two methods for estimating vapor pressures and these are designated as Method 1 and Method 2. Method 1 is applicable only to liquids or super-cooled liquids. Method 2 is applicable to both solids and liquids. Method 1 has a lower vapor pressure limit of 10^{-3} Torr while Method 2 is useful down to 10^{-7} Torr. Values less than 10^{-7} Torr are out of the useful range of the estimation techniques but have been included in both Tables 3 and 4 as they are only the available numbers. These values must be used with caution. Method 2 makes corrections for variations in $\Delta H_v/\Delta Z$ with temperature (ΔH_v is the heat of vaporization while ΔZ is the

compressability factor) while Method 1 assumes that this ratio is invariant. For the above three reasons, Method 2 values are preferred. Values estimated by both techniques are listed in Table 4.

Table 4. Estimated Boiling Temperatures and Vapor Pressures of PCBs

# of Cl's	Boiling Temp.[a] (°C at 1 atm)	Vapor Pressure Method 1[b]	Vapor Pressure Method 2[c]	Physical State[d]
0	247	5.2×10^{-2}	7.3×10^{-2}	Liquid
1	268	1.7×10^{-2}	2.8×10^{-2}	Liquid
2	288	5.6×10^{-3}	1.1×10^{-2}	Liquid
3	308	(1.8×10^{-3})[e]	8.5×10^{-5}	Solid
4	326	(5.9×10^{-4})[e]	3.7×10^{-6}	Solid
5	344	(1.9×10^{-4})[e]	7.6×10^{-7}	Solid
6	361	(6.4×10^{-5})[e]	1.7×10^{-7}	Solid
7	378	(2.1×10^{-5})[e]	$(3.6 \times 10^{8-})$[e]	Solid
8	395	(6.3×10^{-6})[e]	(7.6×10^{-9})[e]	Solid
9	410	(2.1×10^{-6})[e]	(1.9×10^{-9})[e]	Solid
10	426	(6.6×10^{-7})[e]	(4.0×10^{-10})[e]	Solid

[a]Estimated by method of Meissner as described by Lyman et al. (1982).

[b]Estimated by vapor pressure estimation method 1 as described by Lyman et al. (1982).

[c]Estimated by vapor pressure estimation method 2 as described by Lyman et al. (1982).

[d]Based upon estimated melting temperatures.

[e]Value out of range of usefulness of the estimation technique.

IV. REFERENCES

Lyman WJ, Reehl WF, and Rosenblatt DH. 1982. Handbook of Chemical Property Estimation Methods, McGraw-Hill. New York.

Monsanto. 1974. Aroclor Plasticizers. Technical Bulletin, O/PL-306A.

USEPA. 1979. Water-related Environmental Fate of 120 Priority Pollutants. Washington, D.C. EPA-440/4-79-029a.

USEPA. 1982. Chemical Fate Test Guidelines. EPA 560/6-82-003. NTIS publication PB 82-233008. Test Guideline CG-1600.

Westcott JW and Bidleman TF. 1981. J Chromatogr 210:331-6.

Westcott W, Simon CG, and Bidleman TF. 1981. Environ Sci Tech. 15:1375-1378.

CHAPTER 3

HENRY'S LAW CONSTANT AND VOLATILITY FROM WATER OF POLYCHLORINATED BIPHENYLS

by
Asa Leifer and Kenneth G. Partymiller

Contents

Page No.

I. INTRODUCTION AND SUMMARY 3-1

II. MEASURED VALUES OF PCB VAPOR PRESSURE 3-7

A. Background 3-7
B. Henry's Law Constant 3-9
C. Rates and Half-Lives of Volatilization from Water 3-12

III. REFERENCES 3-17

I. INTRODUCTION AND SUMMARY

Volatilization from water bodies to the atmosphere can be a significant environmental pathway for hydrophobic chemicals such as polychlorinated biphenyls. Volatilization rate data is needed to estimate the amount of chemical that enters the atmosphere and the change in concentration of pollutants in the water bodies. The mass transfer of chemical from water to the atmosphere is dependent upon chemical and physical properties (e.g., water solubility, vapor pressure, and thus Henry's law constant), the presence of other pollutants in the water body, and environmental properties (e.g., water body depth, flow rate, and turbulence; and the wind speed above the water).

Henry's law constant (H) is an important physical property of the chemical which is used in the calculation of rates of volatilization. Under equilibrium conditions, the value of H gives the direction of transfer. Chemicals having H in the range 3×10^{-7} to 1×10^{-3} atm m^3 $mole^{-1}$ are considered to be moderately volatile. Chemicals with higher or lower values of H are considered to be very volatile or nonvolatile, respectively.

Mackay and Leinonen (1975) estimated H from the vapor pressure and water solubility of Aroclors 1242, 1248, 1254, and 1260 and the results are summarized in Table 3, Section II.B. Doskey and Andren (1981), based on some experimental data, reported H for the Aroclor 1016 and this result is summarized in Table 3. The Aroclors are complex mixtures of PCBs and the composition of each Aroclor is defined in the Introduction, Figure C.

Mackay and Leinonen (1975) developed a model and equations to predict the liquid-phase mass transfer coefficient (K_L) and the half-lives ($t_{1/2}$). These equations were used to estimate K_L and $t_{1/2}$ at a depth of 100 cm for the Aroclors 1242, 1248, 1254, and 1260, Table 3, Section II.B. The half-lives ranged from 10-12 hours and thus they are quite volatile from pure water. Doskey and Andren (1981), based on experimental work published in the literature, estimated K_L for the Aroclors 1016, 1221, 1242, and 1254 and these results are summarized in Table 4, Section III.B.

No literature data has been found on the determination of rates and half-lives of volatilization for any of the PCB congeners. Hence, estimation techniques were employed to obtain these data. One of the best methods of estimating volatilization half-lives from water bodies is described by Lyman et al. (1982). The method is based on the two-film concept for estimating the flux of volatile chemicals across an air-water interface and the work of Mackay and Leinonen (1975). Detailed procedures are described by Lyman et al. (1982) to estimate the overall liquid-phase mass transfer coefficient (K_L) and half-lives ($t_{1/2}$) under environmental conditions.

Rates of volatilization from pure water and half-lives were estimated for all the PCBs listed in Tables 1 and 2. The environmental conditions were: depth in water body = 100 cm; river flow rate = 100 cm sec^{-1}; wind speed = 300 cm sec^{-1}. The volatilization half-lives for the PCBs listed in Table 1, in

Table 1. Henry's Law Constant and Estimated Volatilization Half-Lives (Based on Measured Water Solubilities and Vapor Pressures)

PCB Congener	C_s[a] (mole m^{-3})	VP[b] (atm)	H[c] (atm m^3 $mole^{-1}$)	K_L[d] (cm hr^{-1})	$t_{1/2}$[e] (hrs)
2',3,4-trichloro-	3.0×10^{-4}	1.2×10^{-7}	4.0×10^{-4}	8.5	8.2
2,2',5,5'-tetrachloro-	9.0×10^{-5}	4.9×10^{-8}	5.5×10^{-4}	8.9	7.8
2,2',4,5,5'-pentachloro-	5.9×10^{-5}	1.1×10^{-8}	1.9×10^{-4}	5.0	14.0
2,2',4,4',6,6'-hexachloro	1.1×10^{-6}	1.6×10^{-8}	1.4×10^{-2}	12	5.8

[a]Water solubility at 25°C. Measured values from Chapter 1 (Generator Column).

[b]Vapor pressure at 25°C. Measured values from Chapter 2.

[c]Estimated Henry's law constant at 25°C.

[d]Estimated liquid-phase mass transfer coefficient at 25°C.

[e]Estimated half-life by the recommended method of Lyman et al. (1982). The estimated half-lives correspond to a 100 cm deep river flowing at a speed of 100 cm sec^{-1} and the wind velocity is 300 cm sec^{-1}.

Table 2. Henry's Law Constant and Estimated Volatilization Half-Lives
(Based on Measured Water Solubilities and Estimated Vapor Pressures)

PCB Congener	C_s[a] (mole m^{-3})	VP[b] (atm)	H[c] (atm m^3 $mole^{-1}$)	K_L[d] (cm hr^{-1})	$t_{1/2}$[e] (hrs)
Monochloro					
2-	2.2×10^{-2}	3.7×10^{-5}	1.7×10^{-3}	15	4.6
Dichloro					
2,5-	8.7×10^{-3}	1.4×10^{-5}	1.7×10^{-3}	14	5.0
2,6-	6.2×10^{-3}		2.3×10^{-3}	14	5.0
Trichloro					
2,4,5-	6.3×10^{-4}	1.1×10^{-7}	1.8×10^{-4}	5.3	13
2,4,6-	8.8×10^{-4}		1.4×10^{-4}	4.6	15
Tetrachloro					
2,2',4',5-	5.6×10^{-5}	4.9×10^{-9}	8.6×10^{-5}	3.2	22
2,3,4,5-	7.2×10^{-5}		6.8×10^{-5}	2.6	27
Pentachloro					
2,3,4,5,6-	1.7×10^{-5}	1.0×10^{-9}	6.0×10^{-5}	2.2	32
Hexachloro					
2,2'3,3',4,4'-	7.8×10^{-7}	2.2×10^{-10}	2.9×10^{-4}	6.3	11
2,2',3,3',6,6'-	1.7×10^{-5}		1.3×10^{-5}	0.53	130

Table 2. Henry's Law Constant and Estimated Volatilization Half-Lives (Continued)

PCB Congener	C_s[a] (mole m^{-3})	VP[b] (atm)	H[c] (atm m^3 $Mole^{-1}$)	K_L[d] (cm hr^{-1})	$t_{1/2}$[e] (hrs)
Heptachloro					
2,2',3,3',4,4',6-	5.5×10^{-6}	(4.7×10^{-11})[f]	(8.6×10^{-6})[f]	(0.33)[f]	(210)[f]
Octachloro					
2,2',3,3',5,5',6,6'-	9.2×10^{-7}	(1.0×10^{-11})[f]	(1.1×10^{-5})[f]	(0.41)[f]	(170)[f]
Nonachloro					
2,2',3,3',4,5,5',6,6'	3.9×10^{-8}	(2.5×10^{-12})[f]	(6.4×10^{-5})[f]	(2.2)[f]	(32)[f]
Decachloro	1.5×10^{-8}	(5.3×10^{-13})[f]	(3.5×10^{-5})[f]	(1.1)[f]	(63)[f]

[a]Water solubility at 25°C. Measured values from Chapter 1 (Generator Column).

[b]Vapor pressure at 25°C. Estimated values from Chapter 2.

[c]Estimated Henry's law constant.

[d]Estimated liquid-phase mass transfer coefficient at 25°C.

[e]Estimated half-life by the recommended method of Lyman et al. (1982). The estimated half-lives correspond to 100 cm deep river flowing at a speed of 100 cm sec^{-1} and the wind velocity is 300 cm sec^{-1}.

[f]These values should be used with caution since they were based on vapor pressures which were outside the useful range of the vapor pressure estimation technique.

which H was estimated from the measured water solubility and vapor pressure, ranged from 5.7 hours to 14 hours. Thus, these PCBs are very volatile from pure water under these specific environmental conditions.

The volatilization half-lives for selected PCBs for each class of congeners (i.e., monochloro, dichloro,....., decachloro) under the specific environmental conditions are listed in Table 2. It must be emphasized that H, used in these calculations, was obtained from measured water solubility data but from estimated values of the vapor pressure for these congeners. For the mono to the hexachloro congers (exclusive of the 2,2',3,3',6,6' congener) $t_{1/2}$ ranged from 5-32 hours and thus they are very volatile to moderately volatile. The half-lives for the hepta to the decachloro congeners ranged from 31-210 hours and these are moderately volatile. However, the latter results must be used with caution since the vapor pressures of these congeners fell outside the useful range of the vapor pressure estimation techniques (Chapter 2) and thus H and $t_{1/2}$ are uncertain. In general, the data indicate that all PCBs are very volatile to moderately volatile in pure water. However, reliable volatilization data are needed on selected PCB congeners to confirm these results.

II. DISCUSSION OF RESULTS

A. Background

Volatilization from water bodies to the atmosphere is recognized as a significant environmental pathway for solutes such as gases and some hydrophobic organic pollutants such as hydrocarbons and chlorinated hydrocarbons. Volatilization rate data are necessary to estimate the amount of chemical that enters the atmosphere and the change in concentration of pollutants in the water bodies. The mass transfer of a chemical from water to the atmosphere is dependent upon (1) the chemical and physical properties of the chemical; (2) the presence of other pollutants present in the water body; and (3) environmental properties such as the water body flow velocity, depth, and turbulence and the atmospheric conditions above the water body (e.g., wind speed).

Henry's law constant H is an important physical property of a chemical used in calculating rates of volatilization. Under equilibrium conditions, the value of H immediately gives the direction of transfer. In most cases, the distribution of resistance to mass transfer between the atmosphere and a water body, and hence the overall rate of volatilization, depends on H.

Henry's law constant is defined as the ratio of the vapor pressure of a solute above an aqueous solution to the concentration of the solute in the water body at a fixed temperature at equilibrium. Mathematically, it is defined by the equation

$$H = VP/C_s \quad , \qquad (1)$$

where VP is the vapor pressure of the solute above the water phase and C_s is the water solubility. Mackay et al. (1979) describes one of the best methods for measuring H directly. Henry's law constant can also be estimated from the measured vapor pressure and the water solubility of a solute at a given temperature. H is often expressed in the units atm m^3 mole $^{-1}$ so that in equation 1, the vapor pressure (VP) is expressed in atmospheres and the water solubility (C_s) is expressed in moles m^{-3}. In addition, it is often convenient to express H as a dimensionless parameter H' defined by the equation

$$H' = H/RT \quad , \qquad (2)$$

where H is Henry's law constant in atm m^3 $mole^{-1}$, R is the gas constant and is equal to 8.21×10^{-5} atm m^3 mole $^{-1}$ °K^{-1} and T is the absolute temperature in °K.

A class of chemicals having a value of the H less than 3×10^{-7} atm m^3 $mole^{-1}$ is considered to be nonvolatile from water. Examples of chemicals that fall in this class are 3-bromo-1-propenol, Dieldrin, and ionic organic compounds. Another class of chemicals having H in the range $3 \times 10^{-7} < H < 1 \times 10^{-3}$ atm m^3 $mole^{-1}$ are considered to be moderately volatile. Examples of chemicals that fall in this class are Lindane, 4-t-butylphenol, nitrobenzene, and phenanthrene. The remaining class of chemicals having H in the range $> 1 \times 10^{-3}$ atm m^3 $mole^{-1}$ are considered to be highly volatile from water. Examples of chemicals that fall in this class are biphenyl, methylene chloride, o-xylene, and ethylene.

One of the best methods of estimating half-lives of volatilization from water bodies is described in detail by Lyman et al. (1982). The method is based on the two-film concept for estimating the flux of volatile chemicals across an air-water interface and the work of Mackay and Leinonen (1975). Detailed procedures are described by Lyman et al. (1982) to estimate half-lives for volatilization of chemicals in water bodies under environmental conditions. The detailed procedures require the following minimum data: (1) physical properties - vapor pressure, aqueous solubility, and molar mass; (2) environmental properties -- wind speed, current speed, and depth in a water body. The half-life for volatilization under environmental conditions is given by

$$t_{1/2} = 0.693Z/K_L \quad , \qquad (3)$$

where Z is the depth in a water body in cm and K_L is the overall liquid-phase mass transfer coefficient in cm hr^{-1}. The method of estimating K_L under environmental conditions is described, and examples are given to illustrate how to use the method.

B. Henry's Law Constant

Mackay and Leinonen (1975) estimated Henry's law constant from the vapor pressure and water solubility of Aroclors 1242, 1248, 1254, and 1260, Table 3. Doskey and Andren (1981), based on experimental work of Paris et al. (1978), reported H for the Aroclors 1016 and 1242, Table 3. Aroclors are complex mixtures of PCBs, and the composition of each grade is defined in Figure C of the Introduction.

No literature data have been found on the direct determination of Henry's law constant for any of the PCB congeners. However, H can be estimated from the experimental values of the water solubility and vapor pressure in equation 1. H was estimated from the experimental data for a few PCBs [(2',3,4,-trichloro), (2,2',5,5'-tetrachloro), 2,2',4,5,5'-pentachloro), (2,2',4,4',6,6'-hexachloro)] from Chapters 1 and 2 and the results are summarized in Table 1. H for the tri-, tetra-, and pentachlorobiphenyls are in the range 1.9-5.5 x 10^{-4} atm m^3 $mole^{-1}$, and thus these PCBs are moderately volatile. H for the hexachlorobiphenyl is 1.4 x 10^{-2} atm m^3 $mole^{-1}$, and thus this PCB is highly volatile.

For a number of PCB congeners, the water solubility was determined experimentally (Chapter 1). However, experimental values of the vapor pressure for these congeners were not available; hence they were estimated by the procedure described in Chapter 2. Table 2 lists the values of H for selected PCBs for each class of congeners (i.e., monochloro, dichloro, trichloro,....., decachloro) using the measured water solubilities and estimated vapor pressures. H for all the congeners are in the range 10^{-3} to 10^{-5} atm m^3 $mole^{-1}$ and thus they are moderately volatile. However, the values of H for the heptachloro to the decachloro congeners must be used with caution since the estimated vapor pressure of these congeners fell outside the useful range of the vapor pressure estimation technique (Chapter 2).

Table 3. Estimated Henry's Law Constant, Rates, and Half-Lives for Several Aroclors

Aroclor	H (atm m^3 $mole^{-1}$)	K_L (cm hr^{-1})	$t_{1/2}$ hrs
1016	$(1.4 \pm 0.7) \times 10^{-2}$	-	-
1242	5.73×10^{-4}	5.7	12.1
1248	3.51×10^{-3}	7.2	9.5
1254	2.76×10^{-3}	6.7	10.3
1260	7.13×10^{-3}	6.7	10.2

C. Rates and Half-Lives of Volatilization from Water

Mackay and Leinonen (1975) developed a model and equation to predict the liquid-phase mass transfer coefficient K_L and the half-life, and this model formed the basis of the method of Lyman et al. (1982) as described in Section II.A. These equations were used by Mackay and Leinonen to estimate K_L and $t_{1/2}$ at a depth of 1 meter (100 cm) for the Aroclors 1242, 1248, 1254, and 1260, Table 3. The half-lives ranged from 10-12 hrs, and thus these Aroclors are quite volatile.

Doskey and Andren (1981), based on experimental data published in the literature, estimated K_L for the Aroclors 1016, 1221, 1242, and 1254, and these results are summarized in Table 4.

Paris et al. (1978) studied the volatilization of Aroclors 1016 and 1242 in the presence of sediments in three pond waters by the reaeration rate method developed by Smith et al. (1979, 1980). Thus, volatilization and adsorption were taking place simultaneously. These researchers determined the ratio of the rate coefficients k/k_2, where k is the rate coefficient for PCB loss and k_2 is the reaeration rate constant, and compared these results with the theoretically estimated ratio.

Table. 4 Experimentally Derived Values of K_L From Various Research Workers for Some Aroclors

	K_L (cm hr^{-1})			
Research Scientist	Aroclor: 1221	1016	1242	1254
Paris		7.9 ± 8.3	8.3 ± 2.5	
Hetling	$(8.9 \pm 0.6) \times 10^{-2}$	$(8.7 \pm 1.6) \times 10^{-2}$		
Doskey & Andren[a]			1.3×10^{-1}	2.8×10^{-2}
Doskey & Andren[b]			$(9.0 \pm 5.9) \times 10^{-3}$	$(4.1 \pm 2.1) \times 10^{-3}$

[a]*Determined from precipitation and air samples collected by Murphy and Rzeszutko.*

[b]Determined in unfiltered lake water solutions.

The results are given in Table 5, and the agreement is quite good. These researchers concluded that for water containing no sediments, volatilization would be an important pathway. For water containing sediments, in which Aroclors are highly adsorbed, these Aroclors would be transported within the aquatic environment in association with the sediments.

No literature data has been found on the determination of rates and half-lives of volatilization for any of the PCB congeners. Rates of volatilization (K_L) and half-lives ($t_{1/2}$) were estimated for all the PCB congeners listed in Tables 1 and 2 as described by the method outlined in Section II.A. These values are summarized in Tables 1 and 2. The environmental conditions were: depth of water body (Z) = 100 cm; river flow rate = 100 cm sec^{-1}; wind speed = 300 cm sec^{-1}. The volatilization half-lives for the PCBs listed in Table 1, in which H was estimated from the measured water solubility and vapor pressure, ranged from 5.7 hours for the congener 2,2',4,4',6,6'-hexachlorobiphenyl to 14 hours for the congener 2,2',4,5,5'-pentachlorobiphenyl. Thus, these PCBs are very volatile under these specific environmental conditions.

The volatilization half-lives for selected PCBs for each class of congeners (i.e., monochloro, dichloro, trichloro,....., decachloro) under the specified environmental conditions are listed in Table 2. It should be noted that H, used to estimate $t_{1/2}$, was obtained from measured water solubility data and estimated values of the vapor pressure for these congeners.

Table 5: Volatilization - Sorption for Arochlor 1242

Site	Dry Weight of Seston (mgL^{-1})	Calculated (k/k_2)	Experimental* (k/k_2)
Doe Run Pond	83.1	0.16	0.14-0.16
Hickory Hills Pond	95.1	0.16	0.12-0.15
USDA Pond	144.4	0.17	0.15-0.19

*Results of two determinations.

For most of the congeners, $t_{1/2}$ ranged from 5-32 hours for the monochloro to the hexachloro congeners (excluding the congener 2,2',3,3'3,6,6'-hexachlorobiphenyl). Thus, these PCBs range from very volatile to moderately volatile chemicals. The other PCB congeners from heptachloro to decachloro had half-lives ranging from 31-210 hours and are thus moderately volatile chemicals. However, these results must be used with caution since the vapor pressure of these congeners fell outside the useful range of the vapor pressure estimation techniques (Chapter 2) and thus H and $t_{1/2}$ are uncertain. In general, the data indicate that all PCBs are very volatile to moderately volatile in pure water. However, reliable volatilization rate data are needed for selected PCB congeners to confirm these results.

III. REFERENCES

Doskey PV and Andren AW. 1981. Modeling the flux of atmospheric polychlorinated biphenyls across the air/water interface. Environ Sci Tech 15:705.

Lyman WJ, Ruhl WF, and Rosenblatt DH. 1982. Handbook of chemical property estimation methods. McGraw Hill Book Co. N.Y.

Mackay D and Leinonen PJ. 1975. Rates of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ Sci Tech 9:1178.

Mackay D and Wolkoff AW. 1973. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ Sci Tech 7:611.

Paris DF, Steen WG, and Baughman GL. 1975. Role of physico-chemical properties of Aroclors 1016 and 1242 in determining their fate and transport in aquatic environments. Chemosphere 4:319.

Smith JH and Bomberger DC. 1979. Prediction of volatilization rates of chemicals in water. Water: 1978. AICHE Symposium Series, 190, 75:375.

Smith JH, Bomberger DC, Haynes DL. 1980. Prediction of the volatilization rates of high volatility chemicals from natural water bodies. Environ Sci Tech 14:1332.

CHAPTER 4

ADSORPTION (SORPTION) OF POLYCHLORINATED BIPHENYLS TO SOILS AND SEDIMENTS

by
Asa Leifer

Contents

Page No.

I. INTRODUCTION AND SUMMARY.....4-1

II. DISCUSSION OF RESULTS 4-7

A. Background 4-7
B. Experimental Data on Soil/Sediment Adsorption (Sorption) and Mobility of Polychlorinated Biphenyls 4-9
C. Estimation of Adsorption (Sorption) to Soils and Sediments from the Octanol/Water Partition Coefficient and Water Solubility 4-15

III. REFERENCES 4-21

I. INTRODUCTION AND SUMMARY

The extent to which an organic chemical partitions itself between water and soil or sediment is determined by several physical and chemical properties of both the chemical and the soil or sediment. In most cases, it is possible to express the tendency of a chemical to be adsorbed (or sorbed) in terms of the equilibrium constant K_d derived from the Freundlich isotherm equation. It is generally accepted that for a given soil or sediment, the sorption of neutral organic molecules can be well correlated with the organic matter content in the soil or sediment [Karickhoff (1981), Karickhoff et al. (1979), Lyman et al. (1982)]. Consequently, the adsorption constant K_d can be converted to the more generally useful constant K_{oc}, defined by the relationship $K_{oc} = K_{d/oc}$, where oc is the fractional mass of organic carbon in the soil or sediment.

There are very little published data on the experimental determination of log K_{oc} for the PCBs adsorbed to soils or sediments. What experimental data are available is discussed in section II.B. and all these results are summarized in Tables 4 and 5.

Since there are very little data available on the adsorption (sorption) of PCBs to soils and sediments, estimation techniques were used to determine log K_{oc}. Chiou et al (1979) reported the correlation of log K_{oc} with the log water solubility for 15 chlorinated hydrocarbons, including three PCBs. However, even though a good correlation was obtained, the correlation was

deficient in that several of the compounds were crystalline solids at 25°C and a crystal energy correction term must be added to the correlation [Karickhoff (1981)].

Karickhoff carried out two adsorption (sorption) studies and correlated log K_{oc} with log K_{ow} [Karickhoff et al. (1979), Karickhoff (1981)]. In the research work published in 1981, Karickhoff chose five reference compounds (benzene, naphthalene, phenanthrene, anthracene, and pyrene) and the K_{ow} and K_{oc} data were fitted to give the equation

$$\log K_{oc} = \log K_{ow} - 0.386 \quad , \qquad (1)$$

with a correlation coefficient (r^2) of 0.994. Karickhoff also expressed the correlation in the more traditional form and obtained the equation

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346 \quad , \qquad (2)$$

with a correlation coefficient (r^2) of 0.997. It should be noted that for these five reference compounds, k_{ow} and K_{oc} varied by only three orders of magnitude.

Karickhoff (1981) listed the published experimental values of K_{ow} and K_{oc} for 17 hydrocarbons and chlorinated hydrocarbons (including two hexachloro PCBs), six chloro-s-triazines, three carbamates, four organophosphates, six phenyl ureas and six miscellaneous compounds. The predicted values of K_{oc} were within

0.48 log units or within a factor of three except for certain classes of compounds. That is, compounds for which solute speciation could be expected were excluded. The phenyl urea class was also excluded for either speciation or for poor experimental data.

In developing a regression equation which would have more widespread applicability to more different hydrocarbons and chlorinated hydrocarbons, it was decided to use all 22 hydrocarbons including Karickoff's five reference compounds and the four high molar mass chlorinated compounds (i.e., DDT, methoxychlor, and the two hexachloro-biphenyls). Linear correlation analysis on all 22 compounds gave the relationship

$$\log K_{oc} = 0.942 \log K_{ow} - 0.144 \quad , \qquad (3)$$

with a correlation coefficient (r^2) of 0.986. This equation is more applicable to a larger set of hydrocarbons and chlorinated hydrocarbons (N=22) and both K_{ow} and K_{oc} vary by 4.5 and 4.7 orders of magnitude, respectively, in comparison to equations 1 and 2 which only apply to a data set of 5 compounds and both K_{ow} and K_{oc} only vary by three orders of magnitude.

Equation 3 was then used to estimate log K_{oc}. Whenever precise experimental values of log K_{ow} were available for specific PCB congeners (see Chapter 1), these values were used to estimate log K_{oc}. In addition, log K_{ow} was estimated for all other congeners of a given type [e.g., monochlorobiphenyls,

dichlorobiphenyls, trichlorobiphenyls, etc.] using the method outlined in Chapter 1. These values were used to estimate log K_{OC} from equation 3. All these data are summarized in Table 1. Inspection of all the data indicates that PCBs are strongly adsorbed (sorbed) to soils and sediments high in organic content and are immobile.

Table 1. Log K_{oc} for the PCB Congeners from Estimated and Experimental Values of Log K_{ow} Using Equation 3

PCB Congener	log K_{ow} Est.	log K_{ow} Exp.	Log K_{oc}
Monochloro-	4.51		4.10
2-		4.44[a]	4.04
3-		4.58	4.17
4-		4.49	4.09
Dichloro-	4.94		4.51
2,2'-		4.90	4.47
2,4'-		5.14	4.70
2,5-		5.16	4.72
2,6-		4.93	4.50
3,4-		5.29	4.84
4,4'-		5.33	4.88
Trichloro-	5.37		4.92
2,2',5-		5.60	5.13
2,4,5-		5.66[a]	5.19
2,4',5-		5.79	5.31
2,4,6-		5.47	5.01
Tetrachloro-	5.80		5.32
2,2',3,3'-		4.63[b]	4.22
2,2',4',5-		5.73	5.25
2,3,4,5-		5.72	5.24
2,3,5,6-		5.46[b]	5.00
Pentachloro-	6.24		5.73
2,2',4,5,5'-		5.29	5.43
2,3,4,5,6-		6.30	5.79
Hexachloro-	6.67		6.14
2,2'3,3',4,4'-		6.98	6.43
2,2',3,3',6,6'-		6.65	6.12
2,2',4,4',6,6'-		7.55	6.97
		6.34[c]	5.83

Table 1. Log K_{oc} for the PCB Congeners (Continued)

PCB Congener	log K_{ow} Est.	log K_{ow} Exp.	Log K_{oc}
Heptachloro-	7.10		6.54
2,2',3,3',4,4',6-		6.68	6.15
Octachloro-	7.53		6.95
2,2',3,3',5,5',6,6'-		7.11	6.55
Nonachloro-	7.96		7.35
2,2',3,3',4,5,5',6,6'-		8.16	7.54
Decachloro-			
2,2',3,3',4,4',5,5',6,6'-		8.26	7.64

Almost all experimental data were obtained from the coupled column generator--chromatographic method, Chapter 1.

a. These values represent the average of the experimental results of NBS and Woodburn.

b. These values were measured by the reverse-phase liquid chromatographic method.

c. This value was measured by the conventional shake-flask method. method discussed in Chapter 1.

All estimated by K_{ow} values for the PCB Congeners were obtained by the method discussed in Chapter 1.

II. DISCUSSION OF RESULTS

A. Background

The extent to which an organic chemical partitions itself between water and soil or sediment is determined by several physical and chemical properties of both the chemical and the soil or sediment. In most cases, it is possible to express the tendency of a chemical to be adsorbed (or sorbed) in terms of the equilibrium constant, K_d, in the Freundlich isotherm equation

$$x/m = K_d C^{1/n} \quad , \qquad (4)$$

where x/m is the μgm of chemical adsorbed/gm of soil or sediment, C is the concentration of chemical in the acqueous solution, and n is a constant. In general, 1/n is close to unity [Karickhoff (1981), Karickhoff et al (1978), Lyman et al. (1982)] and equation becomes

$$x/m = K_d C \quad . \qquad (5)$$

It is generally accepted that for a given soil or sediment type, the sorption of neutral organic molecules can be well correlated with the organic matter content in the soil or sediment [Karickhoff (1981), Karickhoff et al. (1978), Lyman et al. (1982)] and the adsorption constant K_d can be converted to the more general and useful constant K_{oc} defined by the relationship

$$K_{oc} = K_d/oc \quad , \qquad (6)$$

where oc is the fractional mass of organic carbon in the soil or sediment.

The conventional method for measuring adsorption coefficients is to determine an adsorption isotherm with one or more soils or sediments with well defined characteristics. Specific soil/solution ratios of soil or sediment are prepared in water using at least six different initial concentrations of the chemical being studied. The mixture is generally shaken for at least 48 hours to achieve equilibrium and the concentrations in the water and on the soil or sediment are then measured. The amount adsorbed (x/m) and the equilibrium solution concentration are fitted to equation 4 to determine K_d and n. Using the fractional mass of organic carbon in the soil or sediment, K_{oc} is obtained from equation 6.

Helling and Turner (1968) introduced an alternative method for measuring the mobility of chemicals on soils which is related to adsorption. This method is called soil thin-layer chromatography (soil TLC) and is analogous to conventional TLC with the use of soils instead of silica gels, oxides, etc. as the adsorbent phase. The term designating movement in the soil TLC method is R_f, defined as the furthest distance traveled by a chemical on a soil TLC plate divided by the distance traveled by the solvent front (arbitrarily set at 10.0 cm in soil TLC studies). Based on considerable research work, a relationship

has been established between K_d, R_f, and mobility on soils, and the results are summarized in Table 2. The details of this work and soil TLC are discussed in depth in an EPA test guideline and support document [US EPA (1981)].

B. Experimental Data on Soil/Sediment Adsorption (Sorption) and Mobility of Polychlorinated Biphenyls

Griffin et al. (1978) measured R_f values for the Aroclors 1242 and 1254 on four soils and the results are given in Table 3. The principal PCB components in these two commercial products are (49 percent trichloro, 25 percent tetrachloro, 16 percent dichloro) and (48 percent pentachloro, 23 percent hexachloro, 21 percent tetrachloro), respectively. Figure C of the Introduction gives the complete composition of these two Aroclors. The R_f values with water as the solvent is in the range 0.02-0.03. For landfill leachates as the solvent, the range was 0.02 to 0.04. Thus, these two Aroclors are highly adsorbed and are immobile, Table 2. However, it should be noted that this method does not give precise measures of adsorption for R_f values less than 0.1.

Haque et al. (1974) reported the adsorption coefficients for Aroclor 1254 on Woodburn soil. The values for the constants n and K_d from equation 4 are given in Table 4. The composition of Aroclor 1254 has been described previously. Haque and Schmedding (1976) continued these studies with the PCB congeners (2,4'-dichloro), 2,2',5,5'-tetrachloro), and 2,2',4,4',5,5'-hexachloro) on Woodburn soil and humic acid at 24 ± 2°C and the values of n and K_d are given in Table 4.

Table 2. The General Relationship Between the Soil/Solution Partition Coefficient K_d, R_f, and Soil Mobility

K_d	R_f	Mobility class	Distance surface applied chemical may leach
0.1	0.95	Very Mobile	Much of chemical leaches through top 20 cm soil into subsoil.
1	0.60	Very Mobile	
10	0.25	Mobile	Much of chemical leached into soil, but peak concentration in top 20 cm soil.
10^2	0.10	Low Mobility	Only small amount of leaching and peak concentration normally in top 5 cm soil.
$10^{2.5}$	0.00	Immobile	
10^3	0.00	Immobile	No significant leaching.
10^4	0.00	Immobile	

Table 3. R_f Values for Two Aroclors on Four Different Soils with the Solvents Water and Landfill Leachate

Aroclor	Soil Type	R_f (Water)	R_f (Landfill Leachate)
1242	Ottawa Sand	0.03	0.03
	Catlin loam C	0.02	0.03
	Ava silty clay loam B_2	0.02	0.02
	Catlin silt loam A_p	0.02	0.04
1254	Ottawa Sand	0.03	0.03
	Catlin loam C	0.02	0.03
	Ava silty clay loam B_2	0.02	0.02
	Catlin silt loam A_p	0.02	0.04

Table 4. Freudlich Isotherm Constants for Aroclor 1254 and Three PCB Congeners on Woodburn Soil and Humic Acid

PCB	Solvent	Adsorbent	K_d	n	K_d*
Aroclor 1254	H_2O	Woodburn Soil	26.3	0.81	26.3
2,4'-dichloro-	H_2O	Woodburn Soil	7.00	1.18	7.00
	H_2O	Humic Acid	3.98×10^3	0.86	3.98×10^3
2,2'5,5'-tetrachloro-	H_2O	Woodburn Soil	48.9	1.00	4.89×10^1
	H_2O	Humic Acid	4.36×10^4	3.82	4.36×10^4
2,2'4,4'5,5'-hexachloro-	H_2O	Woodburn Soil	3.20×10^2	1.25	3.20×10^2
	H_2O	Humic Acid	3.39×10^9	3.78	3.39×10^9

*Assuming C=1ppm, Kd is in μg/gm adsorbent

In general, the dichloro congener showed some adsorption to soil and humic acid and some mobility on these soil profiles may be expected. The tetrachloro congener exhibits less mobility while the hexachloro congener should be immobile.

Karickhoff et al. (1979) determined K_{OC} for 2,2'4,4'6,6'-hexachlorobiphenyl from adsorption isotherm experiments using Doe Run Pond and Hickory Run Pond sediments at 25°C. The average K_{OC} value for both of these sediments is listed in Table 5.

Karickhoff (1981), using the experimental data of Haque and Schmedding (1976), calculated K_{OC} for the congener 2,2',4,4',5,5'-hexachlorobiphenyl and found that log K_{OC} was equal to 5.62.

Paris et al. (1978) carried out a simple adsorption experiment for Aroclor 1016 and 1242 on three different pond sediments at 25°C and characterized adsorption by the equation

$$K = C_A/C_W \quad , \qquad (7)$$

where C_A is the concentration of the component on the sediment and C_W is the concentration of the component in water at equilibrium. These results are summarized in Table 5.

Table 5. Adsorption Constants of Some PCBs on Pond Sediments

PCB	Sediment Type	$K \times 10^{-3}$	$K_{oc} \times 10^{-3}$
Aroclor 1016	Doe Run Pond	1.29	
	Hickory Hills Pond	1.30	
	USDA Pond	1.37	
Aroclor 1016	Doe Run Pond	1.09	
	Hickory Hills Pond	1.25	
	USDA Pond	1.21	
2,2',4,4',6,6'-hexachloro-biphenyl	Doe Run Pond and Hickory Hills Pond		1200

C. Estimation of Adsorption (Sorption) to Soils and Sediments from the Octanol/Water Partition Coefficient and Water Solubility

Since there are very little experimental data on the adsorption to soils and sediments, estimation techniques were used to evaluate adsorption (sorption) to these substrates.

Using thermodynamic concepts, Karickhof (1981) showed that for liquids

$$\log K_{oc} = -\alpha \log X_{sol} + \beta \quad , \qquad (8)$$

where X_{sol} is the mole fraction water solubility and α and β are constants. However, for crystalline solids at room temperature, a crystal energy must be added. That is

$$\log K_{oc} = -\alpha \log X_{sol} + \text{"crystal energy term"} + \beta. \qquad (9)$$

Chiou et al. (1979) reported the correlation of K_{oc} with the water solubility for 15 chlorinated hydrocarbons including the PCB congeners (2,4'-dichloro), (2,2',5,5'-tetrachloro) and (2,2',4,4',5,5'-hexachloro) by the regression equation

$$\log K_{oc} = 4.040 - 0.557 \log S \quad , \qquad (10)$$

where S is the solubility in μ moles/L and with a correlation coefficient (r^2) of 0.988. Though the correlation is good, several of the compounds are crystalline at 25°C and a crystal

energy correction term must be added to equation 10 as described above.

Karickhoff (1981) clearly showed the improvement in the correlation for five liquid and solid hydrocarbons [benzene, naphthalene, phenanthrene, anthracene, and pyrene] when using equation 9 in comparison to equation 8. Linear regression analysis of the K_{ow} and K_{oc} data in equation 8 gave

$$\log K_{oc} = -0.594 \log X_{sol} - 0.917 \quad , \qquad (11)$$

with a correlation coefficient (r^2) of 0.945. Linear regression analysis of the same data in equation 9 containing the crystal energy term gave

$$\log K_{oc} = -0.921 \log X_{sol} - 0.00953\ (mp-25) - 1.405, \qquad (12)$$

where mp is the melting point of the compound (in °C) and the correlation coefficient (r^2) was 0.995. Thus, the crystal energy term significantly improves the correlation.

Octanol/water partitioning provides a much better estimator for soil or sediment-water partitioning than does water solubility. This is because in octanol/water partitioning, the partitioning already involves the distribution of monomers between the two phases. However, in water solubility, the formation of a saturated solution involves the equilibration between monomers in solution with the crystalline solid. As a

result, crystal energy contributions enter into the formation of saturated solutions in water but do not affect the distribution of the species between octanol and water or soil/sediment and water since the molecules are already present in the monomeric state.

Karickhoff et al. (1979) carried out adsorption isotherm experiments at 25°C with 15 aromatic compounds using Doe Run and Hickory Pond sediments and determined K_{oc}. These researchers correlated K_{oc} with K_{ow} using linear regression analysis to give the equation

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21 \quad , \qquad (13)$$

with a correlation coefficient (r^2) of 1.00.

Using thermodynamic concepts, Karickhoff (1981) showed that

$$\log K_{oc} = \log K_{ow} + A \quad , \qquad (14)$$

where A is a constant. Five compounds [benezene, naphthalene, phenanthrene, anthracene, and pyrene] were chosen as reference compounds based on the following criteria:

1. they form a hydrocarbon framework for a large percentage of aromatic organic compounds and thus constitute a good reference set from which to extrapolate to other compounds;

2. they hydrophobically sorb with little potential for sorption involving solute dipoles or hydrogen bonds;
3. k_{ow} and K_{oc} span three orders of magnitude; and
4. there is good agreement for the experimental values of K_{ow} and K_{oc} published by other research scientists.

Fitting the experimental data for these five reference compounds to equation 14 gave

$$\log K_{oc} = \log K_{ow} - 0.386 \quad , \qquad (15)$$

with a correlation coefficient (r^2) of 0.994.

A more general equation correlating K_{oc} with K_{ow} traditionally has taken the form

$$\log K_{oc} = C \log K_{ow} + D \quad , \qquad (16)$$

where C and D are constants. Applying linear correlation analysis to the experimental data for the five reference hydrocarbons gave

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346 \quad , \qquad (17)$$

with a correlation coefficient (r^2) of 0.997.

Karickhoff listed the published experimental values of K_{ow} and K_{oc} for a number of pesticides and other organic compounds including: (a) 17 hydrocarbons and chlorinated hydrocarbons, including two hexachloro PCBs [the two hexachlorobiphenyl congeners are (2,2',4,4',6,6'-) and (2,2',4,4',5,5'-)]. The log K_{ow} values for these two congeners are 6.34 and 6.72, respectively (Table 2, Chapter 1); the log K_{oc} values for these two congeners are 6.08 and 5.62, respectively (Section II.B of this Chapter)]; (b) six chloro-s-triazines; (c) three carbamates; (d) four organophoshates; (e) six phenyl ureas; (f) six miscellaneous compounds including heterocyclics, a ketone, and a brominated quinone. The predicted values of K_{oc} from equation 15 were then compared to the experimental values. Compounds for which solute speciation could be expected were excluded (e.g., organic bases with pK_a greater than 3). The phenyl ureas were excluded as a class because the predicted K_{oc} values were an order of magnitude less than the measured values. This could be due to speciation but Karickhoff attributed the deviation to poor experimental data. Overall, the agreement between estimated and measured K_{oc} for the remaining compounds agreed to within 0.48 log units or within a factor of 3.

In developing a regression equation which has more widespread applicability to more different hydrocarbons and chlorinated hydrocarbons, it was decided to use the K_{ow} and K_{oc} data for all twenty-two hydrocarbons including the five reference compounds and the four high molar mass chlorinated compounds (DDT, methoxychlor, and the two hexachlorobiphenyls). Linear

correlation analysis on all the data for the set N=22 using equation 16 gave

$$\log K_{oc} = 0.942 \log K_{ow} - 0.144 \quad , \qquad (18)$$

with a correlation coefficient (r^2) of 0.986. This equation is now applicable to be a larger set of hydrocarbons and chlorinated hydrocarbons (22) and K_{ow} and K_{oc} vary by 4.5 and 4.7 orders of magnitude, respectively, in comparison to equation 17 which applies to a data set of 5 compounds and both K_{ow} and K_{oc} only vary by 3 orders of magnitude.

Precise values of K_{ow} and PCBs have been obtained by the coupled column generator-chromatographic method, Chapter 1. These values (log K_{ow}) are summarized in Table 1, Section I, for the various PCB congeners measured and those estimated for the various congeners of a given type [e.g., dichloro-, trichloro-, etc.]. These values were substituted into equation 18 to estimate log K_{oc} and the results are summarized in Table 1. All PCB congeners are immobile.

III. REFERENCES

Chiou CT, Peters LJ, and Freed VH. 1979. A physical concept of soil-water equilibria for nonionic organic compounds. Science 206:831.

Griffin R, Clark R, Lee M, and Chian E. 1978. Disposal and removal of polychlorinated biphenyls in soil. In: Land and disposal of hazardous wastes proceedings. 4th annual research symposium. EPA-600/9-78-016:282.

Haque R, Schmedding D, and Freed VH. 1974. Aqueous solubility, absorption, and vapor behavior of polychlorinated biphenyl Aroclor 1254. Environ Sci Tech 8:139.

Haque R. and Schmedding D. 1976. Studies on the adsorption of selected polychlorinated biphenyl isomers on several surfaces. J Environ Sci Health B11:129.

Karickhoff S, Brown DS, and Scott TA. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res 13:241.

Karickhoff SW. 1981. Semi-empirical estimation of hydrophobic pollutants on natural sediments and soils. Chemosphere 10:833.

Lyman WJ, Reehl WF, Rosenblatt DH. 1982. Handbook of chemical property estimation methods. McGraw Hill Book Co., N.Y.

Paris, DF, Steen WC, and Baughman GL. 1978. Role of physico-chemical properties of Aroclors 1016 and 1242 in determining their fate and transport in aquatic environments. Chemosphere 4:319.

U.S. Environmental Protection Agency. 1982. Chemical fate test guidelines. EPA 560/6-82-003. NTIS publication PB 82-233008. Test Guideline CG-1700.

CHAPTER 5

BIOCONCENTRATION OF POLYCHLORINATED BIPHENYLS IN FISH

by
Asa Leifer

Contents

Page No.

I. INTRODUCTION AND SUMMARY 5-1

II. DISCUSSION OF RESULTS 5-5

A. Background 5-5
B. Experimental Data on Bioconcentration and Ecological Magnification of Polychlorinated Biphenyls 5-8
C. Estimation of Bioconcentration from the Octanol/Water Partition Coefficient 5-13

III. REFERENCES 5-19

I. INTRODUCTION AND SUMMARY

One very important aspect of the environmental fate of PCBs is the prediction of the extent to which these chemicals will achieve concentrations in fish which may be several orders of magnitude greater than the concentration of PCBs in the water phase. A convenient equilibrium constant which describes this process is the bioconcentration constant, K_B, defined as the ratio of the concentration of PCB in fish to the concentration in the water.

There is only a small amount of published data on the experimental determintion of log K_B of PCBs in fish. What experimental data are available is discussed in Section II.B. and all these results are summarized in Table 2 for the Aroclors and Table 3 for individual PCB congeners.

Since there is only a small amount of data available on the bioconcentration of most of the PCB congeners in fish, estimation techniques were used to estimate log K_B. Veith et al. (1981) developed a regression equation correlating log K_B with log K_{ow} for 122 different chemicals and 13 different species of fresh and marine water fish. This equation is

$$\log K_B = 0.79 \log K_{ow} - 0.40 \quad , \qquad (1)$$

and had a correlation coefficient (r^2) of 0.86. In a recent publication by Mackay (1982), the data of Veith et al. (1979) were carefully analyzed, suspect data were eliminated, and the regression equation

$$\log K_B = \log K_{ow} - 1.32 \qquad (2)$$

was developed with a correlation coefficient of 0.95 for approximately fifty chemicals. One of the major differences between equations 1 and 2 is that the slope of equation one is 0.79 while the slope in equation two is 1.0. Furthermore, equation two is only valid for log K_{ow} less than 6.0. Clearly, there is a need for precise and reliable K_{ow} and K_B data in the region log $K_{ow} > 6.0$ to test equation two.

At present, the best correlation is given by equation one, since it is based on the most extensive data set (122 chemicals) for 13 different fresh or marine water fish. Thus, this equation was chosen to estimate log K_B for the various PCB congeners and the results are listed in Table 4, Section II.C. Whenever precise experimental log K_{ow} data were available for specific PCB congeners (see Chapter 1), these values were used to estimate log K_B. In addition, log K_{ow} was estimated for all other congeners of a given type [i.e., monochlorobiphenyls, dichlorobiphenyls, trichlorobiphenyls, etc.] using the method outlined in Chapter 1. These values were then used to estimate log K_B. All these data are given in Table 4 and are summarized in Table 1. For comparison purposes, the average experimental values of log K_B for each group of congeners, for all aquatic species (obtained from the data listed in Table 3), are listed in Table 1. Comparison of both sets of data for each group of congeners indicates that the agreement, in general, is very good and

further substantiates equation one and the data, for the PCBs presented in Table 4. It should be noted that there is an experimental spread in the data (Table 3) and thus the data are probably good to ± 0.5 log units or within a factor of 3.

All the data listed in Tables 1 to 4 indicate that PCBs have the potential to bioconcentrate to a large extent in fish. However, one must consider transformation of PCBs before making a final assessment of bioconcentration potential. For the higher chlorinated species, where transformation is most likely slow, these estimated values of log K_B should be reasonably reliable.

Table 1. Comparison of Estimated Log K_B Values of Groups of PCB Congeners (from Estimated Values of Log K_{ow} and Equation 1) with the Average Experimental Values.

PCB Congeners	Estimated Log K_{ow}	Log K_B Estimated	Log K_B Experimental
Monochloro-	4.51	3.16	3.26
Dichloro-	4.94	3.50	3.61
Trichloro-	5.37	3.84	3.56
Tetrachloro-	5.80	4.18	3.95
Pentachloro-	6.24	4.53	4.14
Hexachloro-	6.67	4.87	5.27
Heptachloro	7.10	5.21	a
Octachloro-	7.53	5.55	a
Nonochloro-	7.96	5.89	a
Decachloro-	8.26	6.13	5.10

a. No experimental data was found in the literature.

II. DISCUSSION OF RESULTS

A. Background

One very important aspect of the environmental fate of a chemical is the ability of a chemical to partition from the water phase into a hydrophobic phase. For example, consider the environmental scenario in which a fish is in a water body containing a dissolved organic chemical. If the chemical is hydrophobic, it will have a tendency to partition out of the water phase and into the fatty tissue of the fish (i.e., the hydrophobic phase). Thus, over a period of time, the hydrophobic chemical will bioconcentrate in the fish. A convenient equilibrium constant which describes this environmental process is the bioconcentration constant, K_B, defined by the relationship

$$K_B = C_B/C_M \quad , \qquad (4)$$

where C_B is the concentration of the chemical in the fish and C_M is the concentration of the chemical in water, at equilibrium. Since C_B and C_M are usually expressed in the same concentration units, K_B is a dimensionless constant. Hydrophobic chemicals have high values of K_B and will thus bioconcentrate in fish. Since K_B can span several orders of magnitude, a convenient expression for bioconcentration is log K_B.

The bioconcentration process is often viewed as a balance between two kinetic processes, uptake and depuration [Veith et al. (1979), Mackay (1982)]. If one defines the uptake

and depuration as first-order processes with rate contants K_1 and K_2, respectively, then the increase in concentration of a chemical in the fish (C_B) with time (t) is given by the differential equation

$$(dC_B/dt) = K_1C_M - K_2C_B \quad , \tag{5}$$

where C_M is the concentration of the chemical in water. Integrating equation 5 for the boundary conditons t=0, C_B=0 and t, C_B, yields

$$C_B = (K_1C_M/K_2)\ [1 - \exp(-k_2t)] \quad . \tag{6}$$

If K_B is defined by the ratio of the uptake and depuration rate constants

$$K_B = K_1/K_2 \quad , \tag{7}$$

then equation 6 becomes

$$C_B = K_BC_M\ [1 - \exp\ (-K_2t)] \quad . \tag{8}$$

After a long time (i.e., as $t \to \infty$), which corresponds to equilibrium conditions, equation 8 yields

$$C_B = K_BC_M \quad , \tag{9}$$

which is the expression for bioconcentration defined in equation

4. Values of K_B can be obtained from long term exposure measurements to give C_B or by kinetic measurements. It must be emphasized that this approach is only valid for chemicals which are not degraded to any appreciable extent in the aquatic environment by chemical or biological processes. This is true for the higher chlorinated biphenyls.

Mackay (1982) proposed an alternative approach to bioconcentration by viewing the fish as an inanimate volume of material that approaches thermodynamic equilibrium with the water as defined by the chemical potential or fugacity of the bioconcentrating-persistent solute. In this case, the differential equation (eq. 5) can be reformulated to give a first-order process in which C_B approaches $K_B C_M$ after long exposure ($\rightarrow \infty$), but has the attractive feature that K_B can be related to physical-chemical properties. Support for this approach has been demonstrated by the fact that K_B is well correlated with the octanol/water partition coefficient (K_{ow}). Traditionally, correlations of K_B and K_{ow} have taken the form

$$\log K_B = n \log K_{ow} + b \quad , \qquad (10)$$

where n and b are constants evaluated from a large body of experimental data on K_B and K_{ow} for a wide variety of chemicals. [Veith et al. (1979, 1981) and Mackay (1982)].

B. Experimental Data on Bioconcentration and Ecological Magnification of Polychlorinated Biphenyls

Hansen (1975) reported the uptake of two Aroclors, 1016 and 1254, in oysters, shrimp, and fish in a laboratory estuarine environment. The principal PCB components in these two commercial products were: (57 percent trichloro, 20 percent dichloro, and 21 percent tetrachloro) and (48 percent pentachloro, 21 percent tetrachloro, and 23 percent hexachloro), respectively. Figure C of the Introduction gives the complete composition of these Aroclors. Considerable bioconcentration was observed for these two Aroclors and the log K_B is given in Table 2. Bioconcentration factors were estimated from Escambria Bay data for Aroclor 1254 for oysters, shrimp, and fish, Table 2. Again, the data indicated considerable bioconcentration in these estuarine species. A comparison of the field data with the laboratory data indicated that the laboratory experiments underestimated bioconcentration. More experimental data is needed to verify these results.

Veith et al. (1979) reported laboratory bioconcentration data in fathead minnows in fresh water for several Aroclors [1016, 1254, 1248 and 1260], Table 2. The principal PCB components of the first two Aroclors have been given above and the principal PCB components of the last two Aroclors are (40 percent tetrachloro, 18 percent trichloro, and 36 percent pentachloro) and (41 percent heptachloro, 38 percent hexachloro, and 12 percent pentachloro), respectively. Figure C of the Introduction gives the complete composition of these two

Table 2. Experimental Bioconcentration Factors for Several Aroclors in Aquatic Species

Aroclor	Lab.	Field	Aquatic Species	Reference
1254	5.00 - 5.02	>5[a]	Oyster	Hansen (1975)
1254	4.42	5.36[a]	Shrimp	Hansen (1975)
1254	4.51	5.82[a]	Fish	Hansen (1975)
1016	4.53	-	Fish	Hansen (1975)
1016	4.63		Fathead Minnow	Veith et al. (1979)
1048	4.85		Fathead Minnow	Veith et al. (1979)
1254	5.00		Fathead Minnow	Veith et al. (1979)
1260	5.28		Fathead Minnow	Veith et al. (1979)
1254	4.60		Brook Trout	Veith et al. (1981)
1254	4.43		Spot	Veith et al. (1981)

[a]Calculated from Escambria Bay data.

Aroclors. Since the log k_{ow} values reported in Table 2 are greater than 4.4, bioconcentration is considerable in these fresh water species.

Veith et al. (1981) reported laboratory bioconcentration data for Aroclor 1254 in the fresh water species Brook Trout and Spot, Table 2. Since the log k_{ow} values reported in Table 2 are greater than 4.4, bioconcentration was substantial.

Sugiura et al. (1978) measured the uptake of several PCBs [(4-chloro), (2,2'-dichloro), (4,4'-dichloro), (2,2',3,3'-tetrachloro), (2,3,5,6,-tetrachloro), (3,3',4,4'-tetrachloro) and (3,3',5,5'-tetrachloro)] in killifish (Oryzias latipes) and calculated K_B from the data. However, these researchers used Tween 20^R at 1 or 100 ppm to prepare solutions of PCBs. They claimed that Tween 20^R had no effect on the uptake of these PCBs which is quite surprising since the Tween concentrations were considerably greater than the concentration of the PCBs.

Sanborn et al. (1975) measured the uptake of three chlorinated biphenyls [(2,2',5-trichloro-), (2,2',5,5'-tetrachloro-, and (2,2',4,5,5'-pentachloro-)] in green sunfish [Leponis cyanellus Raf] in tap water in the laboratory and found substantial bioconcentration for all three congeners. Table 3 lists the log K_B for these three PCBs.

An extensive literature review has been recently made by Nabholz (1983) on the determination of bioconcentration or ecological magnification (EM) in the laboratory for various PCB congeners and the results are summarized in Table 3 together with the literature references. It should be noted that EM is

Table 3. Experimental Bioconcentration Factors for Several PCB Congeners in Aquatic Species

PCB Congener	log K_B	Species	Reference
Monochloro-			
2-	3.30	unknown fish sp.	Moolenar (1982)
3-	3.02	unknown fish sp.	Moolenar (1982)
4-	3.72	Golden Orfe	Sugiura et al. (1979)
	2.95	Carp.	Sugiura et al. (1979)
	3.60	Brown Trout	Sugiura et al. (1979)
	3.26	Guppy	Sugiura et al. (1979)
	2.98	unknown species	Moolenar (1982)
Dichloro-			
2,3-	3.08	Oyster	Vreeland (1974)
2,5-	4.14	Goldfish	Bruggeman et al. (1981)
Trichloro-			
2,2',5-	1.73	Green Sunfish	Sanborn et al. (1975)
	3.76*	Snail	Metcalf et al. (1975)
	2.91*	Mosquito Larvae	Metcalf et al. (1975)
	4.30	Goldfish	Bruggeman et al. (1981)
	3.81*	Gambusia (fish)	Metcalf et al. (1975)
2,4',5-	4.63	Goldfish	Bruggeman et al. (1975)
2',3,4-	3.79	Oyster	Vreeland (1974)
Tetrachloro-			
2,2',3,5'-	4.04	Oyster	Vreeland (1974)
2,2',4,4'-	3.98	Rainbow Trout	Branson et al. (1975)
2,2',5,5'-	4.60*	Snail	Metcalf et al. (1975)
	4.02*	Mosquito Larvae	Metcalf et al. (1975)
	4.69	Goldfish	Bruggeman et al. (1981)
	4.07*	Gambusia (fish)	Metcalf et al. (1975)
	3.87	Oyster	Vreeland (1974)
	2.66	Green Sunfish	Sanhorn et al. (1979)
2,3,4,5	4.29	Golden Orfe	Sugiura et al. (1979)
	3.57	Carp	Sugiura et al. (1979)
	3.94	Brown Trout	Sugiura et al. (1979)
	3.90	Guppy	Sugiura et al. (1979)

Table 3. Experimental Bioconcentration Factors for Several PCB Congeners in Aquatic Species (Continued)

PCB Congener	log K_B	Species	Reference
2,3',4',5-	4.62	Goldfish	Bruggeman et al. (1979)
3,3',4,4'-	3.85	Rainbow Trout	Stalling et al. (1979)
	3.90	Golden Orfe	Sugiura et al. (1979)
	3.24	Carp	Sugiura et al. (1979)
	3.63	Brown Trout	Sugiura et al. (1979)
	4.15	Guppy	Sugiura et al. (1979)
Pentachloro-			
2,2',3,4,5'-	4.43	Oyster	Vreeland (1974)
2,2',4,5,5'-	4.78*	Snail	Metcalf et al. (1975)
	4.24*	Mosquito Larvae	Metcalf et al. (1975)
	4.09*	Gambusia (fish)	Metcalf et al. (1975)
	3.18	Green Sunfish	Sawborn et al. (1975)
Hexachloro-			
2,2',4,4',5,5'-	5.00	Snail	NRC (1979)
	5.02	Mosquito Larvae	NRC (1979)
	4.62	Gambusia (fish)	NRC (1979)
	4.68	Oyster	Vreeland (1974)
	5.67	Benthic Amphipod	Lynch and Johnson (1982)
	6.03	Benthic Amphipod	Lynch and Johnson (1892)
	5.20	Benthic Amphipod	Lynch and Johnson (1982)
	5.93	Benthic Amphipod	Lynch and Johnson (1982)
Decachloro			
2,2',3,3',4,4',5,5',6',6'	5.97	Snail	NRC (1979)
	4.34	Mosquito Larvae	NRC (1979)
	4.99	Gambusia (fish)	NRC (1979)

*log (Ecological Magnification) or log (EM).

determined from laboratory model ecosystems and is defined as the increase in concentration of the PCB over the concentration in the water and the uptake is bioconcentration and biomagnification. These EM data are starred in Table 3. The average values of the log bioconcentration for the different species within a class of congeners is summarized in Table 1. Inspection of the data in Table 3 indicates that there is a spread in the results and thus these data are probably good to ± 0.5 log units or within a factor of 3. The spread in these data can be attributed to: (1) both EM and bioconcentration are reported and EM data involves both bioconcentration and biomagnification and (2) the inherent difficulties in measuring precise values of bioconcentration or ecological magnification. Inspection of all the data indicates that bioconcentration in all cases is substantial.

C. Estimation of Bioconcentration from the Octanol/Water Partition Coefficient

Since there is only a small amount of experimental data on the bioconcentration of individual PCB congeners in fish, estimation techniques were used to estimate the bioconcentration factor K_B from the octanol/water partition coefficient. In Section IIA., it has been shown that K_B is related to K_{ow} (equation 10). Veith et al. (1979) determined log K_B for 30 different chemicals in fathead minnows (*Pimephales promelas*) and found a relationship between log K_B and log K_{ow}. This relationship is given by the equation

$$\log K_B = 0.85 \log K_{ow} - 0.70 \quad ,(11)$$

where the constants in equation 10 were found to be n=0.85 and b= -0.70. The correlation coefficient (r^2) for the linear regression analysis was 0.90.

Veith et al. (1981) expanded the work to include 122 different chemicals with 13 different species of fresh and marine water fish. Linear correlation analysis of these data gave the equation

$$\log K_B = 0.79 \log K_{ow} - 0.40 \quad , \qquad (12)$$

with a correlation coefficient (r^2) of 0.86. An important conclusion of the evaluation of the relationship of K_B to K_{ow} is that the prediction limits of the regression did not change significantly (i.e., r^2 only changed from 0.90 to 0.86) by quadrupling the number of test chemicals and increasing the number of species from one to thirteen.

In a recent publication by Mackay (1982), the physical-chemical factors influencing bioconcentration were studied in detail. Using purely thermodynamic concepts, Mackay showed that

$$\log K_B = \log K_{ow} + \log A \quad , \qquad (13)$$

where A is a constant. In this case the slope n is equal to one. Using equation 13 and the data by Vieth et al. (1979), Mackay eliminated suspect chemicals and found that

$$\log K_B = \log K_{ow} - 1.32 \quad , \qquad (14)$$

with a correlation coefficient (r^2) of 0.95. Mackay concluded that this correlation will satisfactorily predict K_B using one constant and that indeed n=1.

Since the reliability of K_B and K_{ow} measurements is often suspect, it is apparent that it is difficult to determine n precisely and reliably. Mackay indicated log K_{ow} values in excess of 6.0 may be suspect since many were measured using HPLC technique and extrapolated outside the range of values measured under equilibrium conditions. However, the HPLC technique is one of the best and most precise methods for estimating high log K_{ow} values for hydrophobic compounds. This method measures the retention time of a chemical on a hydrophobic column to estimate the value of log K_{ow}. Given the nature of the experimental procedure for measuring K_B, it is apparent that the K_B data is far less precise. Clearly, there is a need for precise and reliable K_{ow} and K_B data in this region to test the linearity hypothesis proposed by Mackay.

At present, the most extensive set of data and the most reliable correlation equation is the one proposed by Veith et al. (1981), given by equation 12, and this one was chosen to estimate log K_B from K_{ow} data.

Very precise values of K_{OW} for PCBs have been obtained from the coupled column generator-chromatographic method, Chapter 1. These values are summarized in Table 4 for the various PCB congeners measured and for those estimated for all the other congeners of a given type [i.e., monochloro, dichloro, trichloro, etc.]. These values were substituted in equation 12 to estimate log K_B and the results are summarized in Table 4.

The log K_B values for all the congeners of a given type (i.e., monochloro, dichloro, trichloro, etc.) are given in Table 4 and have been summarized in Table 1, Section I, for convenience of presentation of the data. In addition, the average experimental values of log K_B for each group of congeners, for all aquatic species (obtained from Table 3), are also listed in Table 1. Comparison of both sets of data for each group of congeners indicates that the agreement, in general, is very good and further substantiates equation 12 and the data for the PCBs presented in Table 4. It should be noted that there is a spread in the experimental data (Table 3) and thus the data are probably good to ± 0.5 log units or within a factor of 3.

All the data indicates that PCBs have the potential to bioconcentrate to a large extent in fish. However, one must consider the transformation of PCBs before making a final assessment of bioconcentration potential. For the higher chlorinated species, where transformation is most likely very slow, these estimated values should be reasonably reliable.

Table 4. Log K_B for the PCB Congeners from Estimated and Experimental Values of Log K_{ow} Using Equation 12.

PCB Congener	log K_{ow} Est.	log K_{ow} Exp.	Log K_B
Monochloro-	4.51		3.16
2-		4.44[a]	3.11
3-		4.58	3.22
4-		4.49	3.15
Dichloro-	4.94		3.50
2,2'-		4.90	3.47
2,4'-		5.14	3.66
2,5-		5.16	3.68
2,6-		4.93	3.50
3,4-		5.29	3.78
4,4'-		5.33	3.81
Trichloro-	5.37		3.84
2,2',5-		5.60	4.02
2,4,5-		5.66[a]	4.07
2,4',5-		5.79	4.17
2,4,6-		5.47	3.92
Tetrachloro-	5.80		4.18
2,2'3,3'-		4.63[b]	3.26
2,2',4',5-		5.73	4.13
2,3,4,5-		5.72	4.12
2,3,5,6-		5.46[b]	3.91
Pentachloro-	6.24		4.53
2,2',4,5,5'-		5.92	4.28
2,3,4,5,6-		6.30	4.58
Hexachloro-	6.67		4.87
2,2',3,3',4,4'-		6.98	5.11
2,2',3,3',6,6'-		6.55	4.85
2,2',4,4',6,6'-		7.55	5.57
		6.34[c]	4.61

Table 4. Log K_B for the PCB Congeners from Estimated and Experimental Values of Log K_{ow} Using Equation 12 (Continued)

PCB Congener	log K_{ow} Est.	Exp.	Log K_B
Heptachloro-	7.10		5.21
2,2',3,3',4,4',6-		6.68	4.88
Octachloro-	7.53		5.55
2,2'3,3',5,5',6,6'-		7.11	5.22
Nonachloro-	7.96		5.89
2,2',3,3',4,5,5',6,6',		8.16	6.05
Decachloro-			
2,2',3,3',4,4',5,5',6,6'-		8.26	6.13

Almost all experimental data were obtained from the coupled column generator--chmomatographic method, Chapter 1.

a. These values represent the average of the experimental results from NBS and Woodburn.

b. These values were measured by the reverse-phase liquid chromatographic method.

c. This value was measured by the conventional shake-flask method.

All estimated by log K_{ow} values for the PCB congeners were obtained by the method discussed in Chapter 1.

III. REFERENCES

Branson DR, Blau GE, Alexander HC, Neeley WB. 1975. Bioconcentration of 2,2',4,4'-tetrachlorobiphenyl in rainbow trout as measured by an accelerated test. Amer Fish Soc 104:785-792.

Bruggeman WA, Martron LBJM, Kooiman D, Hutzinger O. 1981. Accumulation and elimination kinetics of di-, tri-, and tetrachlorobiphenyls by goldfish after dietary and aqueous exposure. Chemosphere 10:811-832.

Hansen D. 1975. PCBs: Effects on accumulation by estuarine organisms. National Conference on Polychlorinated Biphenyls. Chicago, Illinois. pp. 282-283. EPA-560/6-75-004.

Mackay D. 1982. Correlation of bioconcentration factors. Env Sci Technol 16:274.

Metcalf RL, Sanborn JR, Lu P-Y, Nye D. 1975. Laboratory model ecosystem studies of the degradation and fate of radiolabled tri-, tetra-, and pentachlorobiphenyl compared with DDE. Arch Environ Contam Toxic 3:151-165.

Moolenar RJ. 1982. Environmental behavior of MCBs. Unpublished Manuscript. The Dow Chemical Co., Midland, MI.

Nabholz JV. 1983. Bioconcentration factors for selected polychlorinated biphenyl isomers in aquatic organisms. Memorandum to Irwin Baumel, Director, Health and Environmental Review Division/Office of Toxic Substances/U.S. Environmental Protection Agency, Washington, D.C.

National Research Council. 1979. Polychlorinated biphenyls. Washington, D.C. National Academy of Sciences.

Sanborn JR, Childers WF, and Metcalf RL. 1975. Uptake of three polychlorinated biphenyls, DDT, and DDE by the green sunfish, Leponis cyanellus RAF. National Conference on Polychlorinated Biphenyls. Chicago, Illinois. PP. 236-242. EPA-560/6-75-004.

Sugiura K, Ito N, Matsumoto N, Mihara Y, and Goto M. 1978. Chemosphere 7:731.

Sugiura K, Washino T, Haltori M, Sato E, Goto M. 1979. Accumulation of organochlorine compounds in fishes. Difference of accumulation factors by fishes. Chemosphere 6:359-364.

Veith GD, DeFoe, DL, and Bergsdedt BV. 1979. Measuring and estimating bioconcentration factor of chemicals in fish. J Fish Res Board Can 36:1040.

Veith GD. 1981. State-of-the-art report on structure-activity methods development (II). Draft EPA report.

Vreeland V. 1974. Uptake of chlorobiphenyls by oysters. Environ Poll 6:135-140.

CHAPTER 6

ATMOSPHERIC OXIDATION OF POLYCHLORINATED BIPHENYLS

by

Asa Leifer

Contents

		Page No.
I.	INTRODUCTION AND SUMMARY	6-1
II.	OXIDATION OF POLYCHLORINATED BIPHENYLS BY HYDROXYL RADICALS	6-8
III.	STRUCTURE-REACTIVITY RELATIONSHIPS FOR HYDROXYL RADICAL REACTION WITH POLYCHLORINATED BIPHENYLS	6-9
IV.	CALCULATION OF THE SECOND-ORDER RATE CONSTANTS (k_{OH}) FOR POLYCHLORINATED BIPHENYLS USING STRUCTURE-REACTIVITY RELATIONSHIPS	6-13
	A. 2-Chlorobiphenyl	6-14
	1. OH Addition to the Rings	6-14
	a. Ring (A)	6-14
	b. Ring (B)	6-14
	c. Total $k^{add.}_{arom.}$	6-14
	2. H Abstraction on the Rings	6-15
	a. Ring (A)	6-15
	b. Ring (B)	6-16
	c. Total $k_{abs.}$	6-16
	3. Total k_{OH}	6-16
	B. 2,2-Dichlorobiphenyl	6-17
	1. OH Addition to the Rings	6-17
	a. Rings (A) and (B)	6-17
	b. Total $k^{add.}_{arom.}$	6-17
	2. H Abstraction on the Rings	6-18
	a. Rings (A) and (B)	6-18
	b. Total $k_{abs.}$	6-18
	3. Total k_{OH}	6-18

Page No.

C. 2,4-Dichlorobiphenyl..... 6-19

1. OH Addition to the Rings..... 6-19

a. Ring (A)..... 6-19
b. Ring (B)..... 6-19

c. Total $k_{arom.}^{add.}$ 6-20

2. H Abstraction on the Rings..... 6-20

a. Ring (A)..... 6-20
b. Ring (B)..... 6-21
c. Total $k_{abs.}$..... 6-21

3. Total k_{OH}..... 6-22

V. CALCULATION OF THE HALF-LIFE OF POLYCHLORINATED BIPHENYLS..... 6-22

VI. DISCUSSION OF RESULTS..... 6-24

VII. REFERENCES..... 6-27

I. INTRODUCTION AND SUMMARY

If polychlorinated biphenyls (PCBs) are transported into the atmosphere (i.e., the troposphere), then there are two principal modes of oxidation that can occur. PCBs may be transformed by reaction with the oxidants hydroxyl radicals or ozone. However, because of the chemical structure of PCBs, the dominant oxidative reaction occurs with hydroxyl radicals (OH). Consequently, this chapter is devoted to the determination of the rate of OH reaction with PCBs.

There are no experimental data published in the literature on the rates of transformation of PCBs in the atmosphere with OH radicals. Cupitt (1980), using structure-reactivity relationships developed by Hendry and Kenley (1979), estimated the second order rate constant (k_{OH}) for PCBs as less than 1×10^{-12} cm^3 $molecule^{-1}$ $sec.^{-1}$ and the atmospheric resonance time (τ) as greater than 11 days (note: the atmospheric resonance time is defined as the time required to reduce the chemical concentration to 1/e of its original value). These values of k_{OH} and τ represent composite values for all the congeners. Cupitt made no attempt to calculate k_{OH} for every possible PCB congener. Using the method of Hendry and Kenley (1979), which was updated by SRI [Mill et al. (1982)], k_{OH} was estimated for the various PCB congeners. The structure-

reactivity framework involves the calculation of the two major pathways for the reaction of OH with PCBs: H abstraction ($k_{abs.}$) and addition to the double bonds in the aromatic rings ($k^{add.}_{arom.}$). The second-order rate constant k_{OH} is then the sum of $k_{abs.}$ and $k^{add.}_{arom.}$. Detailed calculations were carried out for a large number of the PCB congeners and all the rate constants are summarized in Table 1. In addition, the half-lives were calculated for these congeners assuming that the average global concentration for reasonably polluted air was 1×10^6 molecules cm^{-3} [Hendry and Kenley (1979), Sprung (1977), and Crutzen and Fishman (1977)]. All the half-lives for the PCB congeners are summarized in Table 1.

From a detailed analysis of the data, the following generalizations can be made:

(1) The value of k_{OH} is not significantly affected by the position of the chlorines on the ring. For example, for three chlorines on one ring, k_{OH} was essentially the same for the various congeners.

(2) The dominant reaction pathway is the addition of OH radicals to the double bonds in the aromatic ring ($k^{add.}_{arom.}$).

(3) As the number of chlorines on a ring increases, $k^{add.}_{arom.}$ decreases. As a result, k_{OH} decreases and the half-life ($t_{1/2}$) increases.

Table 1. Second-Order Rate Constants (k_{OH}) and Half-Lives ($t_{1/2}$) for Polychlorinated Biphenyls Estimated from structure-Reactivity Relationships

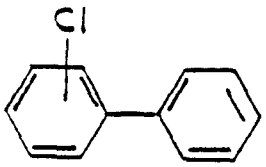
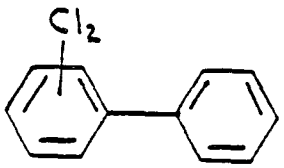
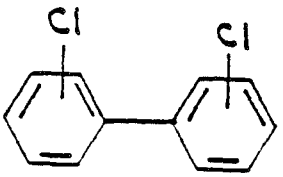
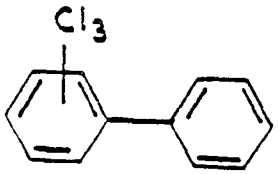
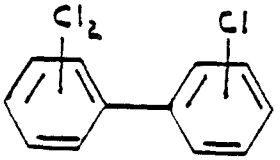
Structure	$10^{12}k_{OH}$ (cm^3 $molec^{-1}$ sec^{-1})	$t_{1/2}^{a}$ (days)
1. 	2.7	3.0
2. 	2.3	3.5
3. 	1.3	6.2
4. 	2.1	3.8
5. 	0.86	9.3

Table 1. Continued

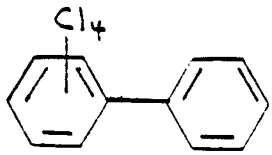
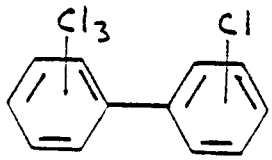
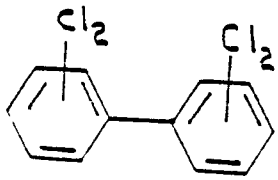
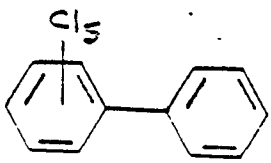
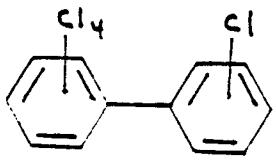
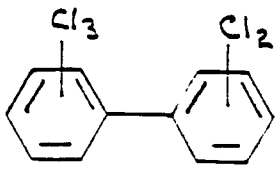
Structure	$10^{12}k_{OH}$ (cm^3 $molec^{-1}$ sec^{-1})	$t_{1/2}^{a}$ (days)
6. 	2.1	3.8
7. 	7.0	11
8. 	0.41	20
9. 	2.1	3.8
10. 	0.65	12
11. 	0.26	31

Table 1. Continued

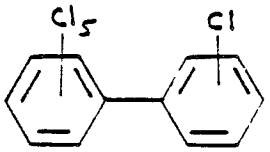
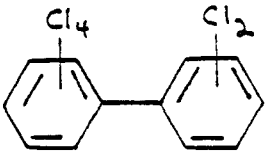
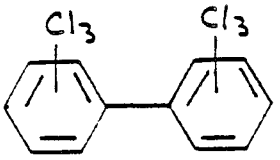
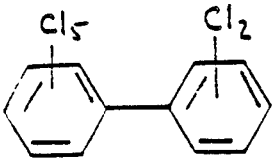
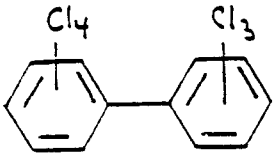
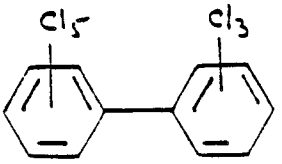
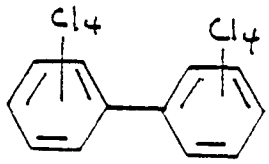
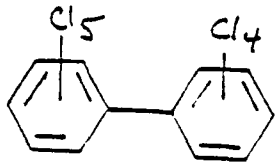
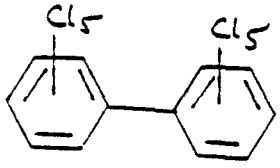
Structure	$10^{12}k_{OH}$ (cm^3 $molec^{-1}$ sec^{-1})	$t_{1/2}^{a}$ (days)
12. 	0.64	13
13. 	0.22	36
14. 	0.13	62
15. 	0.21	38
16. 	0.085	94
17. 	0.069	120

Table 1. Continued

Structure	$10^{12}k_{OH}$ (cm^3 $molec^{-1}$ sec^{-1})	$t_{1/2}^{a}$ (days)
18. 	0.039	210
19. 	0.024	330
20. 	0.0049	1700

a. The half-life was calculated based on an average value of [OH] = 1 x 10^6 molecules cm^{-3} for the global concentration of OH radicals produced by sunlight in reasonably polluted air.

(4) For unsymmetrical chlorinated biphenyls with all the chlorines on one ring, k_{OH} is dominated by the rate of addition of OH to the double bonds of the unsubstituted ring. Therefore, k_{OH} and $t_{1/2}$ are approximately the same regardless of the number of chlorines on the one ring.

(5) For a given group of chlorinated congeners (e.g., the tetrachlorobiphenyls) the totally unsymmetrical chlorinated congener has the largest k_{OH} and the smallest $t_{1/2}$. As the number of chlorines becomes more symmetrically distributed between the two rings, k_{OH} decreases and $t_{1/2}$ increases. For the congeners with the most symmetrical distribution of chlorines on the rings, k_{OH} has the lowest value and $t_{1/2}$ has the largest value (and therefore these congeners are the most persistent).

(6) For symmetrically distributed chlorinated congeners with both rings containing high numbers of chlorines (e.g., Cl_x, Cl_y, with $x + y = 7, 8, 9, 10$), as the total number of chlorines increase, k_{OH} decreases rapidly and $t_{1/2}$ increases rapidly. For example, the nonachlorobiphenyl has a half-life of 330 days while the decachlorobiphenyl has a half-life of 1700 days. Hence, these compounds are reasonably persistent.

For a large number of the PCB congeners especially those containing a small number of chlorines and those with all or most of the chlorines on one ring, atmospheric transformation occurs

at a reasonable rate by reaction with OH radicals. These results are based on the structure-reactivity relationships developed by Hendry and Kenley (1979) and Mill et al. (1982). It should be emphasized that these results are tentative and must be verified experimentally. Experiments should be carried out to measure k_{OH} by flash photolysis and flow through techniques on selected PCBs at room temperature and elevated temperatures. The OH radicals should be produced by the flash photolysis of HONO or N_2O in the presence of H_2O or H_2. The OH decay should be monitored by fluorescence spectroscopy or resonance absorption.

II. OXIDATION OF POLYCHLORINATED BIPHENYLS BY HYDROXYL RADICALS

The reaction of PCBs with OH can be treated mathematically in the following manner:

$$\text{PCB} + \text{OH} \rightarrow \text{Products} \qquad (1)$$

$$-\frac{d[\text{PCB}]}{dt} = k_{OH}[\text{OH}][\text{PCB}] \quad , \qquad (2)$$

where k_{OH} is the second-order rate constant in cm^3 $molecule^{-1}$ $sec.^{-1}$ and [OH] and [PCB] are the concentrations of hydroxyl radicals and polychlorinated biphenyls, respectively. Since very low concentrations of PCBs exist at any given time in the atmosphere and a steady-state concentration of OH radicals is

produced by sunlight in polluted air, the hydroxyl radical concentration can be treated as a constant and equation 2 becomes a pseudo first-order rate equation.

$$-\frac{d[PCB]}{dt} = k[PCB] \quad , \tag{3}$$

where

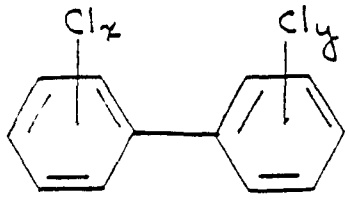
$$k = k_{OH}[OH] \quad . \tag{4}$$

The pseudo first-order rate constant k is in the units of reciprocal time (usually in seconds). Since equation 3 is a pseudo first-order rate equation, the half-life (i.e., the time to reduce the initial concentration of PCBs by one half) is

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{k_{OH}[OH]} \quad . \tag{5}$$

III. STRUCTURE-REACTIVITY RELATIONSHIPS FOR HYDROXYL RADICAL REACTION WITH POLYCHLORINATED BIPHENYLS

Hendry and Kenley (1979) developed a structure-reactivity method for estimating values of the second-order rate constant, k_{OH}, for the reaction of OH radicals with an organic molecule. There are three major reaction pathways in the gas phase: (1) H atom abstraction; (2) addition to olefinic bonds; and (3) addition to aromatic rings. Since the structure of PCBs is



(6)

where x and/or y is equal to 0 to 5, only H abstraction and addition to aromatic rings need to be considered. Each of these reaction pathways has an intrinsic reactivity constant for each reaction center, $k_{abs.}$ and $k^{add.}_{arom.}$. These reactivity constants are modified by substituents at the reaction center (α position) and adjacent to the reaction center (β position) and these substituent constants are denoted by α and β. Thus, the general expresssion for the second-order rate constant, k_{OH}, in terms of the two reactivity constants is

$$k_{OH} = k_{abs.} + k^{add.}_{arom.} \quad . \tag{7}$$

The rate of hydrogen atom abstraction is affected by substitution on the same and adjacent functional groups. The total reactivity rate constant for hydrogen abstraction, $k_{abs.}$, may be expressed as the summation of the rate constants for each reactive hydrogen according to equation

$$k_{abs.} = \sum_{i=1}^{p} n_i \alpha_{Hi} \beta_{Hi} k_{Hi} \quad , \tag{8}$$

where k_{Hi} is the reactivity of the ith hydrogen atom towards OH and depends on the degree of substitution on the adjacent functional group and whether a vinyl or phenyl group is attached. The term α_{Hi} represents the effect of substituents in the α position for atoms other than hydrogen (for hydrogen $\alpha_{Hi} = 1$) and β_{Hi} represents the effect of the substituents in the β position for atoms other than hydrogen (for hydrogen $\beta_{Hi} = 1$). The term α_{Hi} represents the product for each α substituent or $\prod\alpha_{Hi}$. For example, for the group $H\text{-}CX_2$, the two α substituents are X and $\prod\alpha_{Hi} = \prod\alpha_{Xi} = (\alpha_{Xi})^2$. Similarly, β_{Hi} represents the product of each β position or $\prod\beta_{Hi}$. For example, for the group

$$\begin{array}{c} C - (Y_a)_3 \\ | \\ H - C - (Y_b)_3 \\ | \\ C - (Y_c)_3 \end{array} ,$$

where Y_a, Y_b, and Y_c can represent the different β positions, there are a maximum of nine β substituents and $\prod\beta_{Hi} = (\beta_{Y_a})^3(\beta_{Y_b})^3(\beta_{Y_c})^3$. Hendry and Kenley (1979) developed the values of k_H for various hydrogens on different functional groups and the values of α and β for various substituents. The term n_i represents the number of times the same type of hydrogen with the same α and β substituents appear in the molecule. The development of the values of these constants was based on a detailed study of an extensive list of published rate constants

for each kind of reaction or composite reactions which were dissected into the contributory constants for each pathway [Table 4, Hendry and Kenley (1979)].

The rate of addition of OH to aromatic rings is given by the equation

$$k^{add.}_{arom.} = \sum_{l=1}^{\delta} \alpha_{Al} k_{Al} \quad , \qquad (9)$$

where k_{Al} is the reactivity of the lth aromatic ring towards OH and depends on the degree of substitution on the ring (e.g., alkyl, methoxy, or aldehyde groups). The term α_A is a factor which takes into account the effect of halogen atoms substituted on the ring and α_{Al} represents the product of α_A for each lth halogen atom on the ring. Hendry and Kenley (1979) developed values for k_A and α_A based on a detailed analysis of published rate constants for aromatic compounds and these results are summarized in Table 6 of the Hendry and Kenley report.

Further work was carried out by SRI to further validate the method of Hendry and Kenley [Mill et al. (1982)]. Detailed kinetic studies were carried out for the model compounds 2-chlorobutane, 2,3-dichlorobutane, 2-chloropropene, 3-chloropropene, chlorobenzene, and p-dichlorobenzene and the precisely measured second-order rate constants (k_{OH}) were compared to the calculated values using the method of Hendry and Kenley. The results for the first four compounds were, in general, good. However, the values of k_A and α_A for the aromatic

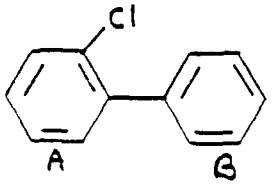
compounds had to be adjusted to obtain a better fit between the experimental and the estimated values from the structure-reactivity method. SRI found that $k_A = 2.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ $sec.^{-1}$ for an aromatic ring (Hendry and Kenley listed a value of 1.4×10^{-12} cm^3 $molecule^{-1}$ $sec.^{-1}$) and $\alpha_{Cl} = 0.30$ (Hendry and Kenley listed a value for $\alpha_{Cl} < 1.0$). All the updated values for the reactivity constants for hydrogen abstraction, OH addition to aromatic rings, and OH addition to olefinic double bonds are summarized in the report by Mill et al. (1982), Tables 9-12, of the Section on Oxidation in Air. Detailed calculations are given for each of the model compounds to illustrate the application of the Hendry and Kenley method of estimating k_{OH}.

IV. CALCULATION OF THE SECOND-ORDER RATE CONSTANTS (k_{OH}) FOR POLYCHLORINATED BIPHENYLS USING STRUCTURE-REACTIVITY RELATIONSHIPS

The method outlined in Section III was used to calculate the second-order rate constant, k_{OH}, for the congeners of the polychlorinated biphenyls (PCBs). A few examples are included in this Section to illustrate how the method of Hendry and Kenley was used to estimate k_{OH}. Since no experimental rate constant data are available for PCBs, the assumption was made that there is no interaction between the two rings and that each ring could be treated separately. The second-order rate constants k_{OH} were then calculated as the sum of the rate constants for each separate ring.

A. 2-Chlorobiphenyl

The structure of 2-chlorobiphenyl is:



where A and B designate each ring.

1. OH Addition to the Rings

a. Ring A

Since ring A contains one chlorine, $\alpha_{Cl} = 0.30$; $k_A = 2.0 \times 10^{-12}$ cm^3 molec.$^{-1}$ sec^{-1}. Using these results in equation 9 yields

$$k^{add.}_{(1)\,arom.} = 0.30(2.0 \times 10^{-12}) = 0.60 \times 10^{-12} \quad .$$

b. Ring B

Since ring B does not contain a chlorine

$$k^{add.}_{(2)\,arom.} = 2.0 \times 10^{-12} \quad .$$

c. Total $k^{add.}_{arom.}$

$$k^{add.}_{arom.} = k^{add.}_{(1)\,arom.} + k^{add.}_{(2)\,arom.}$$

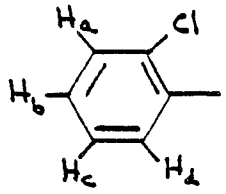
$$k^{add.}_{arom.} = 0.60 \times 10^{-12} + 2.0 \times 10^{-12}$$

$$k^{add.}_{arom.} = 2.60 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1} \quad (10)$$

2. <u>H Abstraction on the Rings</u>

a. Ring A

Ring A has the structure



(i) H_a has a β chlorine substituent and no α substituent. Therefore $\beta_{Cl} = 0.4$; $n = 1$; $k_H = 0.01 \times 10^{-12}$ cm^3 molec.$^{-1}$ sec.$^{-1}$. Using these values in equation 8 yields

$$k_{abs.}(1) = 1(0.4)(0.01 \times 10^{-12}) = 0.004 \times 10^{-12} \quad .$$

(ii) H_b, H_c, H_d are equivalent hydrogens. There are no α substituents and only β hydrogens. Therefore, $n = 3$; $\beta_H = 1$; $k_H = 0.01 \times 10^{-12}$ cm^3 molec.$^{-1}$ sec.$^{-1}$.

$$k_{abs.}(2) = 3(1)^2(0.01 \times 10^{-12}) = 0.03 \times 10^{-12}$$

$$k'_{abs.} = k_{abs.}(1) + k_{abs.}(2) = 0.004 \times 10^{-12} + 0.03 \times 10^{-12}$$

$$k'_{abs.} = 0.034 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1} \qquad (11)$$

b. Ring B

There are five hydrogens on the ring with no α substituents, no halogen substitution, and only β hydrogens. Therefore, n = 5; $\beta_H = 1$; $k_H = 0.01 \times 10^{-12}$ cm^3 molec.$^{-1}$ sec.$^{-1}$.

$$k''_{abs.} = 5(1)^2(0.01 \times 10^{-12})$$

$$k''_{abs.} = 0.05 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1}. \qquad (12)$$

c. Total $k_{abs.}$

$$k_{abs.} = k'_{abs.} + k''_{abs.} = 0.034 \times 10^{-12} + 0.050 \times 10^{-12}$$

$$k_{abs.} = 0.084 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1} \qquad (13)$$

3. <u>Total k_{OH}</u>

$$k_{OH} = k_{abs.} + k^{add.}_{arom.}$$

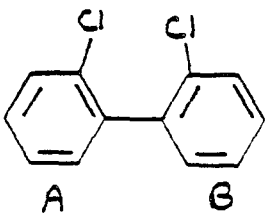
Using equations 10 and 13 yields

$$k_{OH} = 0.084 \times 10^{-12} + 2.60 \times 10^{-12}$$

$$k_{OH} = 2.68 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1} \quad . \qquad (14)$$

B. 2,2′-Dichlorobiphenyl

The structure of 2,2′-dichlorobiphenyl is



where A and B designate each ring.

1. OH Addition to the Rings

a. Rings A and B

Since rings A and B are identical and the same as the ring in Section IV.A.1.a, the same $k^{add.}_{arom.}$ is obtained. Therefore,

$$k^{add.}_{arom.} = 0.60 \times 10^{-12} \quad .$$

b. Total $k^{add.}_{arom.}$

$$k^{add.}_{arom.} = 2\ k^{add.}_{arom.} = 2(0.60 \times 10^{-12})$$

$$k^{add.}_{arom.} = 1.20 \times 10^{-12}\ cm^3\ molec.^{-1}\ sec.^{-1} \qquad (15)$$

2. H Abstraction on the Rings

a. Rings A and B

Since rings A and B are identical and the same as the ring in Section IV.A.2.a., the same $k'_{abs.}$ is obtained (equation 11). Therefore

$$k'_{abs.} = 0.034 \times 10^{-12} \quad .$$

b. Total $k_{abs.}$

$$k_{abs.} = 2k'_{abs.} = 2(0.034 \times 10^{-12})$$

$$k_{abs.} = 0.068 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1} \qquad (16)$$

3. Total k_{OH}

$$k_{OH} = k_{abs.} + k^{add.}_{arom.}$$

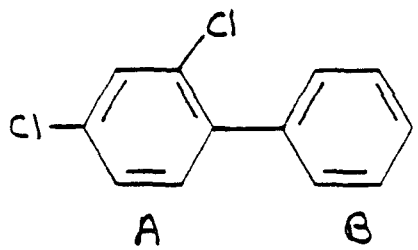
Using equations 15 and 16 yields

$$k_{OH} = 0.07 \times 10^{-12} + 1.20 \times 10^{-12}$$

$$k_{OH} = 1.27 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1} \quad . \qquad (17)$$

C. 2,4-Dichlorobiphenyl

The structure of 2,4-dichlorobiphenyl is



1. OH Addition to the Rings

a. Ring A

Since ring A contains two chlorines, $\alpha_{Cl} = 0.30$; $k_A = 2.0 \times 10^{-12}$ cm^3 molec.$^{-1}$ sec.$^{-1}$. Using these results in equation 9 yields

$$k^{add,}_{arom.(1)} = (0.30)^2(2.0 \times 10^{-12})$$

$$k^{add,}_{arom.(1)} = 0.18 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1} .$$

b. Ring B

Since ring B does not contain a chlorine

$$k^{add,}_{arom.(2)} = 2.0 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1} .$$

c. Total $k^{add.}_{arom.}$

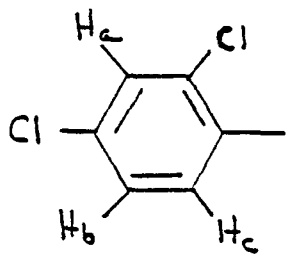
$$k^{add.}_{arom.} = k^{add.}_{arom.(1)} + k^{add.}_{arom.(2)} = 0.18 \times 10^{-12} + 2.0 \times 10^{-12}$$

$$k^{add.}_{arom.} = 2.18 \times 10^{-12}\ cm^3\ molec.^{-1}\ sec.^{-1} \qquad (18)$$

2. <u>H Abstraction on the Rings</u>

a. Ring A

Ring A has the structure



(i) H_a; n = 1; there are two β chlorines and no α substitution; $\beta_{Cl} = 0.4$; $k_H = 0.01 \times 10^{-12}$. Using these results in equation 8 yields

$$k'_{abs.(1)} = 1(0.4)^2(0.01 \times 10^{-12})$$

$$k'_{abs.(1)} = 0.0016 \times 10^{-12}\ cm^3\ molec.^{-1}\ sec.^{-1}\ ,$$

(ii) H_b; n = 1; there is no α substitution, only one β hydrogen, and only one β-chlorine; $\beta_{Cl} = 0.4$; $\beta_H = 1$; $k_H = 0.01 \times 10^{-12}$

$$k'_{abs.(2)} = 1(1)(0.4)(0.01 \times 10^{-12})$$

$$k'_{abs.(2)} = 0.004 \times 10^{-12} \quad .$$

(iii) H_c; n = 1; there is no α substitution and only a β hydrogen; $\beta_H = 1$; $k_H = 0.01 \times 10^{-12}$

$$k'_{abs.(3)} = 1(1)(0.01 \times 10^{-12})$$

$$k'_{abs.(3)} = 0.01 \times 10^{-12}$$

$$k'_{abs} = k'_{abs.(1)} + k'_{abs.(2)} + k'_{abs.(3)}$$

$$k'_{abs.} = 0.0016 \times 10^{-12} + 0.004 \times 10^{-12} + 0.01 \times 10^{-12}$$

$$k'_{abs.} = 0.0156 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1} \quad . \qquad (19)$$

(b) Ring B

This ring is the same as in Section IV.A.2.b. Therefore, from equation 12

$$k''_{abs.} = 0.05 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1} \quad . \qquad (12)$$

(c) Total $k_{abs.}$

$$k_{abs.} = k'_{abs.} + k''_{abs.}$$

Using equations 12 and 19 yields

$$k_{abs.} = 0.016 \times 10^{-12} + 0.050 \times 10^{-12}$$

$$k_{abs.} = 0.066 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1} \quad . \qquad (20)$$

3. Total k_{OH}

$$k_{OH} = k_{abs.} + k^{add.}_{arom.}$$

Using equations 18 and 20 yields

$$k_{OH} = 0.07 \times 10^{-12} + 2.18 \times 10^{-12}$$

$$k_{OH} = 2.25 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1} \quad . \qquad (21)$$

The rate constants for these PCB congeners are summarized in Table 1.

V. CALCULATION OF THE HALF-LIFE OF POLYCHLORINATED BIPHENYLS

Hydroxyl radicals are formed as a result of a complex set of chemical reactions in the atmosphere in the presence of sunlight. The concentration is a function of the solar light intensity (which is a function of time of day, or zenith angle, and season of the year), latitude, pollutant concentrations, temperature, and altitude. Based on the research work of several scientists, a global

average for the OH concentration for reasonably polluted air in the troposphere is 1×10^6 molecules cm^{-3} [Hendry and Kenley (1979), Sprung (1977), Crutzen and Fishman (1977)]. Using these results in equation 5 yields a half-life of

$$t_{1/2} = \frac{0.693}{k_{OH}[OH]}$$

$$t_{1/2} = \frac{0.693}{k_{OH}[1 \times 10^6 \text{molecules cm}^{-3}][8.64 \times 10^4 \text{sec. day}^{-1}]}$$

$$t_{1/2}(\text{day}) = \frac{8.02 \times 10^{-12}}{k_{OH}(\text{cm}^3 \text{ molec.}^{-1} \text{ sec.}^{-1})} \quad . \qquad (22)$$

Consider the calculation of the half-life of 2-chlorobiphenyl. From Section VI.A.3, the second-order rate constant, k_{OH}, is 2.68×10^{-12} cm^3 molec.$^{-1}$ sec.$^{-1}$ (equation 14). Substitution of this result in equation 22 yields

$$t_{1/2} = \frac{8.02 \times 10^{-12}}{2.68 \times 10^{-12}}$$

$$t_{1/2} = 2.99 \text{ days}$$

$$t_{1/2} = 3.0 \text{ days} \quad . \qquad (23)$$

This half-life is listed in Table 1.

VI. DISCUSSION OF RESULTS

Section III discusses in detail the general framework for calculating the rate constants for the two major pathways for the reaction of hydroxyl radicals with chlorinated biphenyls: H abstraction ($k_{abs.}$) and addition to double bonds in the aromatic rings ($k^{add.}_{arom.}$). The second-order rate constant (k_{OH}) for the reaction of OH radicals with chlorinated biphenyls is then the sum of $k_{abs.}$ and $k^{add.}_{arom.}$ (equation 7). Detailed calculations were carried out for a large number of the chlorinated congeners and the rate constants are summarized in Table 1. Section IV illustrates the methods of calculating k_{OH} for a few selected PCB congeners.

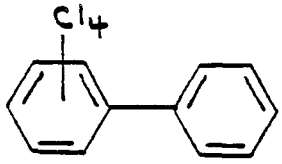
Section V illustrates the method of calculating the half-life ($t_{1/2}$) for PCB congeners and specifically for 2-chlorobiphenyl. The calculated values of $t_{1/2}$ for all the congeners are summarized in Table 1. A detailed analysis of the data indicates that the following generalizations can be made.

(1) For a given class of chlorinated biphenyls, for example, the tetrachlorobiphenyls, obvious trends were observed. For the congeners with four chlorines on one ring:

2,3,4,5-tetrachlorobiphenyl $k_{OH} = 2.1 \times 10^{-12}$ cm^3 molec.$^{-1}$ sec^{-1}

2,3,5,6-tetrachlorobiphenyl $k_{OH} = 2.1 \times 10^{-12}$ cm^3 molec.$^{-1}$ sec.$^{-1}$.

That is, changing the positions of the chlorines on the ring did not change the value of k_{OH}. Hence, all these congeners can be grouped together as the tetrachloro PCB congener using the general expression:

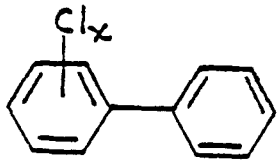


$k_{OH} = 2.1 \times 10^{-12}$ cm^3 molec.$^{-1}$ sec.$^{-1}$,

(2) The dominant reaction pathway is addition of OH radicals to the double bonds of the aromatic ring ($k^{add.}_{arom.}$). This leads to cleavage of the ring or the formation of hydroxy PCBs.

(3) As the number of chlorines on the rings increase, $k^{add.}_{arom.}$ decreases and consequently k_{OH} decreases. Since k_{OH} decreases, $t_{1/2}$ increases.

(4) For unsymmetrical chlorinated biphenyls

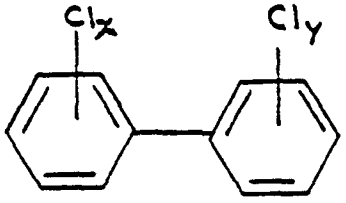


, where x = 1, 2, 3, 4, 5,

it is evident that k_{OH} is dominated by the rate of attack on the unsubstituted ring and this process controls the value of k_{OH}. For example, for the congener with x = 1, $k_{OH} = 2.7 \times 10^{-12}$ cm^3 molec.$^{-1}$

sec.$^{-1}$ and $t_{1/2}$ = 3.0 days while for the congeners with x = 3 or 5, k_{OH} = 2.1 x 10^{-12} cm^3 molec.$^{-1}$ sec.$^{-1}$ and $t_{1/2}$ = 3.8 days. In other words, the presence of chlorines on one ring deactivates this ring relative to the unsubstituted ring and the overall k_{OH} is dominated by the rate of reaction on the unsubstituted ring.

(5) Consider the pentachlorobiphenlys:



x	y	$10^{12}k_{OH}$(cm^3 molec.$^{-1}$ sec.$^{-1}$)	$t_{1/2}$(days)
5	0	2.1	3.8
4	1	0.65	12
3	2	0.26	31

(a) The unsymmetrically chlorinated congener with x = 5 and y = 0 has the largest k_{OH} and the smallest $t_{1/2}$. This occurs because the rate of addition is dominated by the extremely large reactivity of the unsubstituted ring (rule 4).

(b) As the chlorines become more symmetrically distributed between the two rings, k_{OH} decreases and $t_{1/2}$ increases.

(c) For the congener with the most symmetrical distribution of chlorines between the rings [i.e.,

three chlorines on one ring and two chlorines on the other ring], k_{OH} has the lowest value and $t_{1/2}$ is a maximum. This general pattern is true for all groups of chlorinated biphenyls: e.g., monochloro-, dichloro-, trichloro- etc. biphenyl classes of congeners.

(6) The data for the symmetrically distributed chlorinated congeners with high numbers of chlorines can be summarized as follows:

x	y	$10^{12}k_{OH}$ (cm^3 molec.$^{-1}$ sec.$^{-1}$)	$t_{1/2}$(days)
4	3	0.088	94
4	4	0.039	210
5	4	0.424	330
5	5	0.0049	1700

As the total number of chlorines increases, k_{OH} decreases rapidly and $t_{1/2}$ increases rapidly. The half-life for the last two congeners is fairly large and thus these two congeners are reasonably persistent.

VII. REFERENCES

Crutzen, PJ and Fishman J. 1977. Average concentration of OH in the troposphere and budgets of CH_4, CO, H_2, and CH_3CCl_3. Geophys Res Letters 4:321-324.

Cupitt LT. 1980. Fate of toxic and hazardous materials in the air environment. EPA-600/3-80-084.

Hendry DG and Kenley RA. 1979. Atmosphere reaction products of organic compounds. EPA-560/12-79-001.

Mill T, Winterle JS, Davenport JE, Lee GC, Mabey WR, Barich VP, Harris N, and Bawol R. 1982. Validation of estimation techniques for predicting transformation of chemicals in the environment. Unpublished [Draft Final Report for an EPA contract with SRI].

CHAPTER 7

HYDROLYSIS AND OXIDATION OF POLYCHLORINATED BIPHENYLS IN WATER

by
Asa Leifer

Contents

Page No.

I. INTRODUCTION AND SUMMARY 7-1

II. REFERENCES 7-2

I. INTRODUCTION AND SUMMARY

There are no experimental data published in the literature on the hydrolysis of polychlorinated biphenyls (PCBs) under environmental conditions. However, all the PCB congeners contain chlorines which are attached directly to the aromatic ring and as a result they should not hydrolyze under environmental conditions [Mabey and Mill (1978)]. Furthermore, PCBs are so hydrolytically stable that even under severe acidic and basic conditions, hydrolysis does not occur [Gustafson (1970), Hutzinger et al. (1974)]. Hydrolysis, therefore, is not an important environmental transformation process.

PCBs are extremely resistant to oxidation [Hutzinger et al. (1974)]. Gustafson references a Monsanto, technical bulletin on PCBs which states "they can be heated to 140°C under 260 psi of oxygen pressure without showing any evidence of oxidation as judged by the development of acidity or formation of sludge." Oxidation, therefore, is not an important environmental transformation process.

II. REFERENCES

Gustafson CG. 1970. PCBs - prevalent and persistent. Env Sci and Tech 4:814.

Hutzinger O, Safe S, and Zitko V. 1974. The chemistry of PCBs. CRC Press, Inc.

Mabey WR and Mill T. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. J Phys Chem Ref Data 7:383.

CHAPTER 8

PHOTOLYSIS OF POLYCHLORINATED BIPHENYLS

by
Asa Leifer

Contents

Page No.

I. INTRODUCTION AND SUMMARY.....8-1

II. DISCUSSION OF RESULTS.....8-6

A. Ultraviolet Absorption Spectra.....8-6
B. Photolysis Data.....8-10

III. REFERENCES.....8-24

IV. APPENDIX: DETAILED REVIEW OF THE AVAILABLE PHOTOLYSIS LITERATURE.....8-26

I. INTRODUCTION AND SUMMARY

Two important factors must be considered when studying the photolysis of polychlorinated biphenyls (PCBs) in solution and estimating rates of photolysis in the environment. These factors are: (1) the absorption of ultraviolet light by the PCBs in the solar region (λ greater than 290 nm) and (2) the quantum yield (ϕ) in aqueous solution. Considerable work has been done on the study of the ultraviolet adsorption (uv) spectra of PCBs in nonaqueous solvents [Hutzinger et al. (1974)] and very useful information has been obtained on the relationship of the structure of PCBs to uv absorption. With caution, one can use these results to obtain some insight into the behavior of the absorption of uv light by PCBs in aqueous media. An analysis of the uv absorption spectra of PCBs in nonaqueous media indicates that the absorption maxima in the uv region 200-300 nm are affected by the location of chlorines on the rings, the number of chlorines on the rings, and, in particular, by the degree of substitution at the positions ortho to the Ph-Ph bond (i.e., at the positions 2,2',6,6'). For PCBs with one or no chlorines in an ortho position, the two principal absorption maxima shift to the red. For PCBs with two or more chlorines in the ortho positions, the two principal maxima shift to the blue and a series of weak absorption maxima appear in the spectral region 270-300 nm with absorption tails extending into the region beyond 290 nm. The significance of these changes in the absorption spectrum with respect to photolysis in the environment is that in the solar region of the spectrum ($\lambda > 290$ nm), highly chlorinated

biphenyls absorb most strongly, PCBs lacking ortho substitution are intermediate, and PCBs having one or two ortho chlorines are the least absorbing. Nevertheless, all the PCBs are weak absorbers at $\lambda > 290$ nm.

A number of papers have been published on the photolysis of PCBs in solution. Unfortunately, most of these experiments were carried out in nonaqueous media. However, an understanding of these data can be very useful and with caution, one can use these results to obtain some insight into the photolysis of PCBs in the environment; that is, photolysis in aqueous media in sunlight. Bunce et al. (1978) published a paper on the photolysis of some PCBs in the solvent system water-acetonitrile (1:4) containing oxygen. Quantum yields were reported for several PCBs along with molar absorptivities (ε_{300}). Using the method of Zepp and Cline (1977) and Mill et al. (1982), direct photolysis rate constants (k_{pE}) and half-lives ($t_{1/2E}$) were calculated for several PCBs and two Aroclors at 40° north latitude on the summer and winter solstices at shallow depths (less than 0.5 meters) and under clear sky conditions. All the results are summarized in Table 1. Inspection of the data indicates that in general, as the chlorine content increases, the photolysis rate constant increases and the half-life decreases. Decachlorobiphenyl photolyzes rapidly on the summer and winter solstices. A few of these PCBs decompose at a moderate rate on the summer solstice. However, it must be emphasized that these results must be used with caution since the solvent is predominantly acetonitrile (75 percent) and therefore does not correspond to environmental conditions.

Table 1. Sunlight Photolysis Rate Constants and Half-Lives for the Summer and Winter Solstices

PCB	Summer Solstice k_{PE} ($days^{-1}$)	Summer Solstice $t_{1/2E}$ (days)	Winter Solstice k_{PE} ($days^{-1}$)	Winter Solstice $t_{1/2E}$ (days)
4-chloro-	3.3×10^{-3}	210	5.2×10^{-4}	1300
2,4-dichloro-	4.0×10^{-2}	17	6.4×10^{-3}	100
2,4,6-trichloro-	1.3×10^{-2}	53	2.0×10^{-3}	350
Aroclor 1232[a]	3.0×10^{-2}	23	5.4×10^{-3}	128
2,2',5,5'-tetrachloro	3.9×10^{-3}	180	6.3×10^{-4}	1100
Aroclor 1268[b]	5.0	0.1	0.43	1.6
Decachloro-	>11	<0.06	>1.1	<0.6

a. Composition: 31 percent monochloro; 24 percent dichloro; 28 percent trichloro obtained from Figure C, Introduction.

b. The composition of Aroclor 1268 was not found. The composition of Aroclor 1260 is: 41 percent heptachloro; 38 percent hexachloro; 12 percent pentachloro (Figure C Introduction). The higher the Aroclor number, the greater the percent of higher chlorinated congeners. Thus, Aroclor 1268 must be predominantly the octa and heptachloro congeners.

Based on all the available PCB photolysis data in the literature, dechlorination at 300 ± 10 nm is the predominant reaction in nonaqueous solvents including methanol containing oxygen, a solvent which is somewhat similar to water. Thus, PCBs, especially the more highly chlorinated congeners and those that contain ortho chlorines, photodechlorinate. All PCBs containing ortho chlorines yield products arising from the loss of these ortho chlorines. In their absence, meta chlorines are cleaved. Para chlorines do not cleave to any significant extent. The differences in photolability are due to the fact that almost all ortho chlorinated biphenyls have high quantum yields ($\phi \sim 0.1$ or greater). PCBs lacking ortho chlorines generally have low quantum yields ($\phi \sim 10^{-2}$ to 10^{-3}) [Bunce (1982)]. These results are significant, for if aqueous photolysis is an important transformation process, then photodechlorination results in the formation of lower chlorinated congeners and congeners with less chlorine content are more readily biodegradable (Chapter 9). Furthermore, PCBs with ortho chlorines are the most readily removed by photolysis and thus the resulting dechlorinated PCBs are more readily biodegradable. Hence, over a period of time, a combination of photolysis and biodegradation could remove PCBs from the environment.

More reliable photolysis data is needed on selected PCBs to estimate rates of photolysis in aqueous media in sunlight and to predict the transformation products and the mechanism of this transformation process. Photolysis experiments should be carried out in water - acetonitrile (99:1) to determine the uv absorption

spectra, the molar absorptivities (ε_λ), and the quantum yield (ϕ).

Hutzinger et al. (1974) discusses the photolysis of PCBs in the gas phase but there are no relevant data published to predict rates of photolysis in the atmosphere or the nature of the decomposition products.

II. DISCUSSION OF RESULTS

A. Ultraviolet Absorption Spectra

As a prelude to the discussion of the photolysis of PCBs in the environment and specifically to environmentally relevant photolysis rates, it is necessary to consider the absorption of light by polychlorinated biphenyls (PCBs) in aqueous media. Information on the absorption of light by PCBs can be obtained from the ultraviolet (uv) absorption spectrum. Unfortunately, very little data is available on the uv spectra of PCBs in aqueous media and one has to resort to data from the uv spectra in nonaqueous solvents [Hutzinger et al. (1974)]. An analysis of these data indicates that there are several very useful correlations on uv absorption and PCB structure. With caution, one can use these results to obtain insight into the behavior of the absorption of uv light by PCBs in aqueous media.

The uv spectrum of biphenyl contains two important absorption maxima: one band is at 202 nm (ε = 44000) and is designated as the main band; the other absorption maxima is at 242 nm (ε = 17000) and is called the κ band. The κ band is attributed to the conjugated biphenyl system with contributions from both rings. The effects of chlorine substitution on the rings on λ_{max} are given in Tables 2 and 3 [Hutzinger et al. (1974)]. Table 2 lists λ_{max} for the PCBs with one or no chlorine in the ortho position while Table 3 lists λ_{max} for the PCB congeners with two or more ortho chlorines. An analysis of

Table 2. UV Spectra of Chlorobiphenyls (None or One Ortho Chlorine)

Chlorinated biphenyl Congener	UV Maxima and Extinction Coefficients (x 10^{-3}) "Main band" (nm)	ϰ band (nm)
4	199 (43.3)	253 (20.5)
3	205 (42.8)	248 (16.0)
2	204 (39.2)	240 (10.2)
4,4'	200 (41.9)	258 (22.9)
3,3'		248 (23.4)
2,4	204 (42.2)	255 (12.8)
2,4,4'	205 (42.5)	250 (14.8)
2,3',4	210 (44.9)	246 (12.0)
2,3',4',5	214 (42.0)	248 (11.3)
3,3',4,4'		260 (22.9)
2,3',4,4'		253 (15.9)
2,4,4',5		257 (15.1)
2,3,4,4'		250 (12.6)
2,3,4',4,5		253 (2.5)
2,3,3',4,4'		253 (2.5)
3,3',4,4',5,5'	222 (51.7)	265 (27.7)

Table 3. Ultraviolet Spectra of Chlorobiphenyls (Two or More Ortho Chlorines)

Chlorinated biphenyl Congener	UV Maxima and Extinction Coefficients ($\times 10^{-3}$) "Main band" (nm)	α band (nm)	"β bands" (nm)
2,2'	208 (36.0)	230 (6.6)	273 (.54)
			266.5 (.74)
2,2',5	197 (62.5)		267 (1.10)
			275 (1.17)
			283 (0.82)
2,2',4,4'	207 (51.2)	220 (29.4)*	273 (1.49)
			282 (0.83)
2,2',5,5'	204 (43.3)	214 (34.9)*	276 (1.32)
			284 (1.25)
2,2',6,6'	197 (88.9)		272 (0.78)
			280 (0.65)
2,2',4,4',5,5'	211 (45.5)		282 (1.60)
			290 (1.12)
2,2',4,4',6,6'	202 (93.1)		267 (0.50)
			275 (0.59)
			288 (0.46)
2,2',3,4,5,5',6	214 (100)		268 (1.37)
			277 (1.76)
			286 (1.82)
			297 (0.63)
2,2',3,3',4,4',5,5'	210 (57.5)		285 (0.69)
			294 (0.59)
2,2',3,3',5,5',6,6'	210 (91.6)		285 (2.04)
			295 (2.31)
2,2',3,3',4,4',5,5',6,6'	216 (108)		291.5 (1.10)
			301.5 (1.22)

*Shoulder

these data indicate that these absorption maxima are affected by the location of chlorines on the rings, the number of chlorines on the rings and, in particular, by the degree of substitution at the positions ortho to the Ph-Ph bond (i.e., at the positions 2,2',6,6').

Consider the spectra of PCBs with less than two chlorines ortho to the Ph-Ph bond, Table 2. For the monochlorobiphenyls, the main absorption band only changed slightly in comparison to the same band in biphenyl. However, the 3- and 4-chloro groups induced a bathochrochromic or red shift (i.e., a shift to higher wavelengths) of the κ band with the 4-chloro groups showing the larger shift. The κ band for the 2-chloro congener is shifted to a slightly lower wavelength (i.e., a blue shift) with a lowering of ε. This effect has been attributed to some steric inhibition of resonance between the two phenyl rings.

Similarly, for the 4,4'- and the 3,3'-congeners, the magnitude of the red shift of the κ band is greater for the para disubstituted derivative.

For the more highly substituted PCBs, both the main absorption and κ bands shift to the red and exhibit appreciably more absorption tailing in the solar region beyond 290 nm.

Upon the introduction of two or more chlorines in the ortho positions to the Ph-Ph bond, major changes in the uv spectrum occur, Table 3. The κ band shifts to lower wavelengths and the molar absorptivity ε is lowered markedly; on the other

hand, the ε value for the main band increases significantly. In addition, these highly ortho substituted congeners exhibit a series of weak absorption maxima, called β bands, between 268 and 302 nm with tailing absorptions in the region beyond 290 nm. In the same manner as encountered in 2-chlorobiphenyl, it is generally accepted that these highly hindered PCBs are hindered to free rotation about the Ph-Ph bond and this results in the loss of coplanarity between the two rings. Thus, these β bands have been attributed to the contributions from the individual phenyl rings.

The significance of these changes in the absorption spectrum with respect to photolysis in the environment is that in the solar region of the spectrum ($\lambda > 290$ nm), highly chlorinated biphenyls absorb most strongly, PCBs lacking ortho substitution are intermediate and PCBs having one or two other chlorines are the least absorbing. Nevertheless, all the PCBs are weak absorbers at $\lambda > 290$ nm.

B. Photolysis Data

A number of papers have been reviewed which pertain to the photolysis of PCBs in solution [Safe and Hutzinger (1971), Hustert and Korte (1972), Hutzinger et al. (1972), Ruzo et al. (1972), Ruzo et al. (1974), Nordblom and Miller (1974), Hutzinger et al. (1974), Ruzo et al. (1975), Safe et al. (1976), Wagner and Schere (1977), Bunce and Kumar (1978), Bunce (1982)]. Unfortunately, almost all of these photolysis experiments were

carried out in nonaqueous media. However, a study of these data can provide some potential insight into the photolysis of PCBs in the environment in sunlight. The following paragraphs highlight these results and Appendix IV discusses these papers in greater detail.

All the experiments on the photolysis of PCBs were carried out in the laboratory by irradiation in the spectral region 290-310 nm; and these results are environmentally relevant with respect to solar radiation since the wavelengths of photolysis occur beyond the solar cutoff ($\lambda > 290$ nm). As discussed in Section II.A., many of the PCB congeners, especially those which contain several chlorines on the rings, have weak absorption tails beyond 290 nm. Furthermore, the PCB congeners with more than one chlorine in an ortho position exhibit weak absorption maxima in the region 270-300 nm (β absorptions) and the absorptions tail beyond 290 nm. As a result, these PCBs all have the potential to undergo photolysis in the solar region at wavelengths greater than 290 nm.

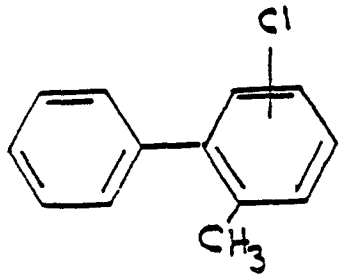
Based on a review of all the available literature, PCBs undergo photodechlorination when exposed to radiation in the spectral region 290-310 nm. For example, Ruzo et al. (1974) carried out a series of photolysis experiments with the tetrachloro PCB congeners [(3,3',4,4'), (2,2',4,4'), (3,3',5,5'), (2,2'3,3'), (2,2'5,5') and (2,2',6,6')] in degassed cyclohexane. The major reaction undergone by these congeners was the stepwise dechlorination to yield tri- and dichlorobiphenyls as

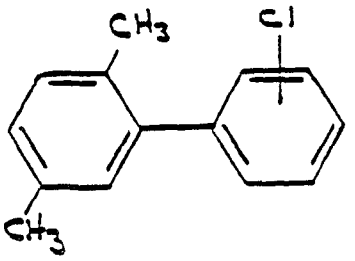
the major products. All PCBs containing ortho chlorines yielded products arising from the loss of the ortho chlorines. In their absence, meta chlorines were cleaved. Chlorine in the para position did not cleave to any significant extent. Similar experiments were carried out by photolyzing these compounds in undegassed and degassed methanol at 290 - 310 nm. Again, the major reaction undergone by these compounds was stepwise dechlorination to yield tri- and dichlorobiphenyls as the major products. The order of removal of the chlorines was ortho chlorines > meta chlorines >> para chlorines. The differences in photolability are due to the fact that almost all ortho chlorinated biphenyls have high quantum yields ($\phi \sim 0.1$ or greater). PCBs lacking ortho chlorines generally have low quantum yields ($\phi \sim 10^{-2}$ to 10^{-3}) [Bunce (1982)]. Minor amounts of the methoxylated products were also observed (<3 percent of reacted PCBs in all cases). It should be noted that methanol is a hydroxylated solvent, similar in some respects to water. Thus, one might expect a similar pattern of photodechlorination in water, especially for the PCB congeners with chlorines in the ortho positions. Furthermore, these results were applicable to methanol containing oxygen. Water in the environment usually contains oxygen.

In order to elucidate the mechanism of photodechlorination described above, Ruzo et al. (1974) carried out more detailed photolysis experiments: the quantum yield (ϕ_r) was determined for several congeners in cyclohexane, Section IV, Table 9; the quantum yield of intersystem crossing (ϕ_{isc}),

corresponding to the conversion of the excited singlet state to the excited triplet state, was measured for the congeners (3,3',4,4'), (2,2'4,4'), (3,3',5,5') and was found to be 1 ±0.05; and the triplet lifetimes (τ) were measured in cyclohexane and methanol for all the congeners [Section IV, Table 9]. The lifetimes of all the ortho congeners were approximately three times smaller than the congeners containing no ortho chlorines. Because of the presence of the ortho chlorines, the ground state is non-planer while the excited triplet state is planar [Wagner (1967), Wagner and Scheve (1977)]. Triplet lifetime shows a definite variation between the ortho congeners and the others. This is undoubtedly due to the greater steric hindrance to the preferred excited state geometry. Crowded conditions created by the ortho chlorines result in a greater twisting of the Ph-Ph bond with the subsequent decrease in its double band character. The products obtained in the greatest yield arise from the loss of ortho chlorines; thus, the strain on that bond is relieved.

In some recent work, Bruce (1982) reported the results of photolysis experiments using a series of compounds of the type





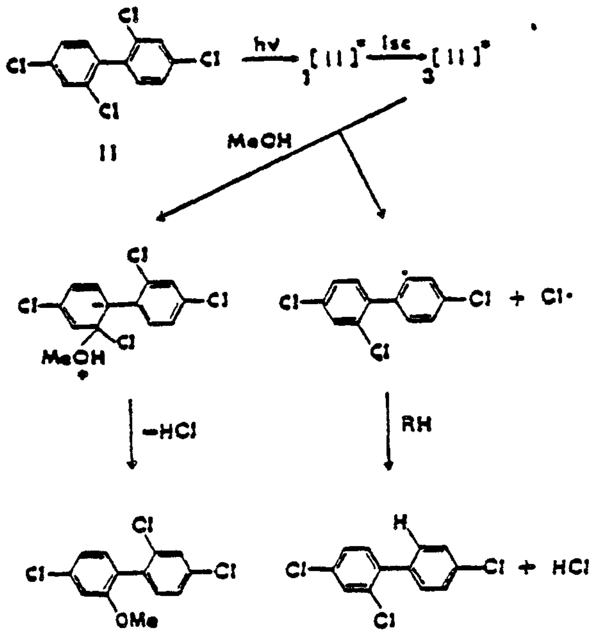
Compounds with these structures were more photolabile than the analogous compounds lacking the ortho methyl substituents, but were not as photolabile as the ortho chlorine compounds. Bunce

concluded that the relief of strain when an ortho chlorine departs must be important. However, the extraphotolability arises because the ortho chlorine substituent raises the energy of the excited state and hence provides the extra energy for dissociation.

Based on all the data, Ruzo et al. (1974) postulated the mechanism of photodechlorination of PCBs. As an example, the mechanism is illustrated in Figure 1 for the congener 2,2'4,4'-tetrachlorobiphenyl (congener II, Table 7, Section IV). The dechlorination products obtained from the uv irradiation result from the cleavage of the C-Cl bond in the ortho position to form a biphenyl free radical. This free radical then abstracts a hydrogen from the solvent to form the dechlorinated product and HCl. Photolysis of congener II in methanol yielded a small amount of the methoxylated products (Table 8, Section IV). These methoxylated products would be formed by nucleophilic displacement of chlorine by methanol. In the latest publication by Bunce (1982), this researcher summarized the status of the photolysis of PCBs and supported the mechanism postulated by Ruzo et al. (1974).

Hutzinger et al. (1972) attempted to carry out photolysis experiments on selected PCB congeners under environmental conditions (i.e., photolysis in sunlight). Unfortunately, these experiments were poorly designed and no useful data were obtained.

Figure 1. Mechanism of Photodecomposition of 2,2',4,4'-Tetrachlorobyphenyl



Bunce et al. (1978) carried out photolysis experiments on selected PCBs to assess the impact of solar degradation of PCBs in the aquatic environment. These researchers obtained extinction coefficients at 300 nm and quantum yields at 254 nm (at less than 10 percent conversion) for a series of PCB congeners and two Aroclor samples in the oxygenated solvent system water-acetonitrile (1:4). All their results are summarized in Table 4. In general, the quantum yield for complex molecules in solution is wavelength independent so that the quantum yield at 254 nm is the same in the spectral region greater than 290 nm [Zepp and Cline (1977)]. These data can be used to estimate rates of photolysis by the method of Zepp and Cline (1977) and Mill et al. (1982) to see if photolysis would be important in an aquatic environment in sunlight.

Zepp and Cline (1977) published a paper on the rates of direct photolysis in aquatic environments. The rates of direct photochemical processes in a water body are affected by solar spectral irradiance at the water surface, radiative transfer from air to water, and the transmission of sunlight in the water body. It has been shown that in dilute solution (i.e., the absorbance of a chemical is less than 0.02 in the reaction cell at all wavelengths greater than 290 nm) at shallow depths (>0.5m), the kinetic expression for direct photolysis of a chemical at a molar concentration C is

$$- dC/dt = \phi_E k_a C = k_{pE} C \quad , \qquad (1)$$

Table 4. Photochemical Data on Some PCBs[a]

PCBs	ε_{300} ($M^{-1}cm^{-1}$)	ϕ
4-chlorobiphenyl	120	0.0037
2,4-dichlorobiphenyl	25	0.22
2,4,6-trichlorobiphenyl	7	0.25
2,2',5,5'-tetrachlorobiphenyl	30	0.017
decachlorobiphenyl	1200[b]	0.21
Aroclor 1232	60	0.036
Aroclor 1268	770	0.16

[a]Measured in water-acetonitrile (1:4).

[b]Molar absorptivity at 301 nm.

with

$$k_{pE} = \phi_E k_a \quad , \tag{2}$$

where ϕ_E is the reaction quantum yield of the chemical in dilute solution and is independent of the wavelength, and $k_a = \sum k_{a\lambda}$, the sum of $k_{a\lambda}$ values of all wavelengths of sunlight that are absorbed by the chemical. The term k_{pE} represents the photolysis rate constant for water bodies in sunlight in the units of reciprocal time. Integrating equation 1 yields

$$\ln(C_o/C) = k_{pE}t \quad , \tag{3}$$

where C is the molar concentration of chemical at time t during photolysis and C_o is the initial molar concentration. By measuring the concentration of chemical as a function of the time t during photolysis in sunlight, k_{pE} can be determined using equation 3. In addition, equation 3 can be solved for the condition $C_t = C_o/2$ and the half-life of the chemical is given by

$$t_{1/2E} = 0.693/k_{pE} \quad . \tag{4}$$

Furthermore, under the same conditions cited above [i.e., for homogenous chemical solution with absorbance less than 0.02* in a reaction cell at all wavelengths greater than 290 nm

*At an absorbance of 0.05, equation 5 is in error by only 11%.

and at shallow depths (less than 0.5 m)], the first-order direct photolysis rate constant, k_{pE}, is

$$k_{pE} = \phi_E \Sigma \varepsilon_\lambda L_\lambda \quad , \qquad (5)$$

where ϕ_E is the quantum yield which is independent of the wavelength, ε_λ is the molar absorptivity in the units molar $^{-1}$ cm^{-1}, and L_λ is the solar irradiance in water in the units 2.303 x 10^{-3} einsteins cm^{-2} day $^{-1}$ [Mill et al. (1981, 1982a, 1982b)]. L_λ is the solar irradiance at shallow depths for a water body under clear sky conditions and is a function of latitude and season of the year.

Calculations were carried out for all the PCBs listed in Table 4 to see if sunlight photolysis would be important. The following assumptions were made in the calculations.

1. The molar absorptivity reported by Bunce et al. (1978) in the solvent water-acetonitrile (1:4) was used. It was assumed that the molar absorptivity decreased uniformly as the wavelength increased:

   $\varepsilon_{305} = (1/2)\ \varepsilon_{300}$; $\varepsilon_{310} = (1/2)\ \varepsilon_{305}$; $\varepsilon_{315} = (1/2)\ \varepsilon_{310}$;.....; $\varepsilon_\lambda = 0$.
2. A latitude of 40°N was chosen since this latitude is approximately in the center of the United States.
3. Calculations were made on the summer and winter solstices.

4. The solar irradiance values (L_λ) were obtained from Mill et al. (1982) and interpolations were made to estimate L_λ at 300, 305, 310, 315,.....nm on the summer and winter solstices.
5. The quantum yield reported by Bunce et al. (1978) in the solvent water-acetonitrile (1:4) was used.
6. The calculations correspond to water bodies under clear sky conditions and at shallow depths.

The following calculation for 2,4-dichlorobiphenyl illustrates the method of determining the rate constant (k_{pE}) and half-life ($t_{1/2E}$) for the summer and winter solstices. Table 5 summarizes the data for $\sum \epsilon_\lambda L_\lambda$ for the summer and winter solstices. Substituting the values of $\sum \epsilon_\lambda L_\lambda$ from Table 5 in equation 5 yields

Summer solstice: $k_{pE} = 0.040 \text{ days}^{-1}$

Winter solstice: $k_{pE} = 0.0064 \text{ days}^{-1}$.

Substituting these results in equation 4 yields

Summer solstice: $t_{1/2E} = 17$ days

Winter solstice: $t_{1/2E} = 110$ days .

The results for all the PCBs are summarized in Table 1 of Section I. Inspection of the data indicates that in general, as the chlorine content increases, the photolysis rate constant increases and the half-life decreases. Decachlorobiphenyl

Table 5. Summary of Photolysis Data for 2,4-Dichlorobiphenyl at 40° North Latitude

Summer Solstice

λ (nm)	ε_λ ($M^{-1}cm^{-1}$)	L^*_λ	$\varepsilon_\lambda L_\lambda$ (day^{-1})
300	25.0	0.66×10^{-3}	0.017
305	12.3	3.4×10^{-3}	0.042
310	6.2	0.99×10^{-2}	0.061
315	3.1	2.0×10^{-2}	0.062
320	0.0	--	0.000
		$\Sigma\ \varepsilon_\lambda L_\lambda =$	0.18_2

Winter Solstice

λ (nm)	ε_λ ($M^{-1}cm^{-1}$)	L^*_λ	$\varepsilon_\lambda L_\lambda$ (day^{-1})
300	25.0	0.35×10^{-4}	0.001
305	12.3	0.33×10^{-3}	0.004
310	6.2	1.6×10^{-3}	0.010
315	3.1	4.5×10^{-3}	0.014
320	0.0	--	0.000
		$\Sigma\ \varepsilon_\lambda L_\lambda =$	0.029

*The units of L_λ are in 2.303×10^{-3} einsteins cm^{-2} day^{-1}.

photolyzes rapidly in the summer and winter solstices. A few of these PCBs decompose at a moderate rate on the summer solstice. However, it must be emphasized that these results must be used with caution since the solvent is predominantly acetonitrile (75 percent) and therefore does not correspond to environmental conditions. It should be noted that ϕ_E and the molar absorptivities were obtained in oxygenated solvent.

Based on all the photolysis data available, dechlorination is the predominant reaction. Thus PCBs, especially the more highly chlorinated congeners and those that contain two or more chlorines in the ortho positions, photodechlorinate. This is a significant result, for if aqueous photolysis is an important transformation process in the environment, then photolysis results in the formation of lower chlorinated congeners and the lower chlorinated congeners biodegrade more readily (Chapter 9). Furthermore, PCBs with ortho chlorines biodegrade very slowly (Chapter 9). However, ortho chlorines are the most readily removed by photolysis and thus the resulting dechlorinated PCBs are more readily biodegradeable. Hence, over a period of time, a combination of photolysis and biodegradation could remove PCBs from the environment. Since this could represent a viable mechanism for the removal of PCBs from the environment and a number of the PCB congeners have the potential to undergo photolysis at a moderate rate in the summer, it is important that laboratory studies be carried out in the solvent water-acetonitrile (99:1). Reliable molar absorptivities and quantum yields are needed in this

solvent saturated with oxygen to verify if PCBs can transform photolytically in the environment.

III. REFERENCES

Bunce NJ. 1982. Photodechlorination of PCBs: current status. Chemosphere 11:701.

Bunce NJ, Kumar Y, and Brownlee BG. 1978. An assessment of the impact of solar degradation of polychlorinated biphenyls in the aquatic environment. Chemosphere No. 2:155.

Hustert K and Korte F. 1972. Beitrage zur okologischen chemie XXXVIII. Synthese polychlorierter biphenyle und ihre reaktionen bei uv - bestrahlung. Chemosphere No. 1:17.

Hutzinger O, Safe S, and Zitko V. 1972. Photochemical degradation of chlorobiphenyls (PCBs). Env Health Persp 1:15.

Hutzinger O, Safe S, and Zitko V. 1974. The chemistry of PCBs. Chapter 6. Photodegradation of chlorobiphenyls. Chapter 10. Ultraviolet spectroscopy of chlorobiphenyls. CRC Press.

Mill T, Mabey WR, Bomberger DC, Chou T-W, Hendry DG, and Smith JH. 1982. Laboratory protocols for evaluating the fate of organic chemicals in air and water. Chapter 3. EPA 600/3-82-022.

Nordblom GD and Miller LL. 1974. Photoreduction of 4,4'-dichlorobiphenyl. J Agri Food Chem 22:57.

Ruzo LO, Zabik, MJ, and Scheutz RD. 1972. Polychlorinated biphenyls: Photolysis of 3,4,3',4'-tetrachlorobiphenyl and 4,4'-dichlorobiphenyl in solution. Env Cont and Tox 8:217.

Ruzo LO, Zabik MJ, and Scheutz RD. 1974. Photochemistry of bioactive compounds. Photochemical processes of polychlorinated biphenyls. J Am Chem Soc 96:3809.

Ruzo LO, Safe S, and Zabik MJ. 1975. Photodecomposition of unsymmetrical polychlorobiphenyls. J Agri Food Chem 23:595.

Safe S and Hutzinger O. 1971. Polychlorinated biphenyls: photolysis of 2,4,6,2',4',6'-hexachlorobiphenyl. Nature 232:641.

Safe S, Bunce NJ, Chittim B, Hutzinger O, and Ruzo LO. 1976. Chapter 3. Photodecomposition of halogenated aromatic compounds. In: Identification and analysis of pollutants in water. L.H. Keith, Editor. Ann Arbor Press.

Wagner PJ. 1967. Conformational changes involved in the singlet-triplet transitions of biphenyl. J Am Chem Soc 89:2820.

Wagner PJ and Scheve BJ. 1977. Steric effects in the singlet-triplet transitions of methyl- and chlorobiphenyls. J Am Chem Soc 99:2888.

Zepp RG and Cline DM. 1977. Rates of direct photolysis in aquatic environment. Environ Sci and Technol 11:359.

IV. APPENDIX: DETAILED REVIEW OF THE AVAILABLE PHOTOLYSIS LITERATURE

Safe and Hutzinger (1971) carried out some of the earliest experiments on the photolysis of PCBs. Specifically, the PCB congener 2,2',4,4',6,6'-hexachlorobiphenyl was photolyzed at 310 nm in the solvents hexane and methanol. Although the structures of the products were not determined, the mass spectra of the products indicated that dechlorination took place.

Laboratory experiments were carried out by Ruzo et al. (1972) on the photolysis of 4,4'-dichlorobiphenyl (DCB) and 3,3',4,4'-tetrachlorobiphenyl (TCB) in hexane at wavelengths greater than 286 nm and λ_{max} at 310 nm. DCB decomposed to a small extent to 4-chlorobiphenyl and no biphenyl was detected in the reaction products. The absence of biphenyl is not surprising since 4-chlorobiphenyl shows no tailing beyond 290 nm while DCB exhibits marginal tailing absorption at $\lambda > 290$ nm which results in a low yield of 4-chloribiphenyl. The photolysis of TCB yielded stepwise dechlorination: TCB decomposed to 3,4,4'-trichlorobiphenyl which photolyzed to 4,4'-dichlorobiphenyl. Thus, the meta chlorines were the most labile and were removed in a stepwise sequence to form DCB. A similar pattern was observed for the photolysis of several hexa- and tetrachlorobiphenyls [Hustert and Korte (1972)].

Several unsymmetrical PCBs were photolyzed in degassed cyclohexane in the wavelength region 300 ± 10 nm [Ruzo et al. (1975)]. GC/MS analysis of the products indicated the loss of

one or two chlorines followed by hydrogen abstraction from the solvent. The products and yields are listed in Table 6. The quantum yield was determined for each PCB at less than 10 percent conversion to avoid sensitization or quenching of the reaction by the photoproducts and these results are summarized in Table 6. The reactivity of the PCBs depends upon the position of the chlorines on the rings: ortho chlorines cleaved first and at a considerably faster rate than meta chlorines; para chlorines did not cleave.

In another set of photolysis experiments, a series of symmetrical tetrachlorobiphenyls were photolyzed in degassed hexane and methanol and in methanol containing oxygen at 300 ± 10 nm [Ruzo et al. (1974)]. The compounds studied are listed in Table 7 and are designated as compounds I-VI. The photodegradation products are listed in Table 8. The major reactions of compounds I-VI in cyclohexane were stepwise dechlorinations to yield tri- and dichlorobiphenyls as the major products. Very little monochlorobiphenyl was detected after 20 hours of radiation (less than 1 percent of reacted PCB). All PCBs containing ortho chlorines yielded products with the loss of ortho chlorines. In the absence of ortho chlorines, meta chlorines were cleaved. Para chlorines were not cleaved after 20 hours of photolysis.

In methanol, dechlorination was also found to be the major reaction, Table 8. However, minor amounts of methoxylated

Table 6. Photoproducts and Quantum Yields of Unsymmetrical PCB's in Cyclohexane

PCB		Product	T_r Min.	% Yield[a]
2,4,6-Trichloro-biphenyl (I)	0.02	2,4-Dichloro	1.25	85
		4-Chloro	0.85	15
2,4,5-Trichloro-biphenyl (II)	0.05	3,4-Dichloro	1.80	98
		4-Chloro	0.85	2
2,3,4,5-Tetrachloro-biphenyl; (III)	0.04	3,4,5-Trichloro	3.60	95
		3,4-Dichloro	1.80	5
2,3,5,6-Tetrachloro-biphenyl (IV)	<0.01	2,3,5-Trichloro	2.20	50
		3,5-Dichloro	1.50	50
2',3,4-Trichloro-biphenyl (V)	0.02	3,4-Dichloro	1.80	100

[a]Based on total product formation.

Table 7. Tetrachlorobiphenyls

PCB	Designation
3,3',4,4'-Tetrachlorobiphenyl	I
2,2',4,4'-Tetrachlorobiphenyl	II
3,3',5,5'-Tetrachlorobiphenyl	III
2,2',3,3'-Tetrachlorobiphenyl	IV
2,2',5,5'-Tetrachlorobiphenyl	V
2,2',6,6'-Tetrachlorobiphenyl	VI

Table 8. Photoproducts in Hexane and in Methanol[a]

PCB	Dechlorinated products	Methoxylated products[b]
I	3,4,4'-Trichlorobiphenyl 4,4'-Dichlorobiphenyl	Trichloromethoxybiphenyl
II	2,4,4'-Trichlorobiphenyl 4,4'-Dichlorobiphenyl 4-Chlorobiphenyl[c]	Trichloromethoxybiphenyl Dichlorodimethoxybiphenyl[c]
III	3,3',5-Trichlorobiphenyl[c]	
IV	2,3,3'-Trichlorobiphenyl 2,2',3-Trichlorobiphenyl[c] 3,3'-Dichlorobiphenyl	Trichloromethoxybiphenyl Dichlorodimethoxybiphenyl[c]
V	2,3,5'-Trichlorobiphenyl 3,3'-Dichlorobiphenyl 3-Chlorobiphenyl[c]	Trichloromethoxybiphenyl Dichlorodimethoxybiphenyl[c]
VI	2,2'6-Trichlorobiphenyl 2,2'-Dichlorobiphenyl[c]	Trichloromethoxybiphenyl[c]

[a]Nondegassed solutions: Twenty hours irradiation.
[b]Only major products are shown.
[c]Compound represented less than 1 percent of reacted starting material.

products were observed (less than 3 percent of reacted PCB in all cases). These results are important because methanol is a hydroxy solvent, similar in some respects to water, and thus one might expect that dechlorination would be the major photolytic process in aqueous media. In addition, the photolysis experiments were carried out in methanol containing oxygen. In general, water bodies in the environment contain oxygen.

Quantum yields for reaction (ϕ_r) were determined in degassed cyclohexane for compounds I-VI at 300 nm, Table 9. Maximum conversion (of PCB reacted) was kept below 10 percent to avoid sensitization or quenching of the reaction by the photoproducts.

Quantum yields of intersystem crossing (ϕ_{isc}), corresponding to the conversion of the singlet excited state to the triplet excited state, were determined by measuring the phosphorescence emission intensity of biacetyl at 516 nm sensitized by either benzophenonone or PCB. Compounds I, II, and III were tested and ϕ_{isc} was found to be 1 ± 0.05 compared to benzophenone (ϕ_{isc} = 1). Thus the conversion to the triplet state is extremely efficient.

Quenching studies were performed on the photolysis of compounds I-VI in degassed methanol and cyclohexane. Degassed solutions of PCB containing various concentrations of 1,3-cyclohexadiene (E_t < 55 kal/mol) were irradiated to conversion < 20 percent. Based on an analysis of the data, the triplet lifetimes (τ) were calculated and are listed in Table 9. The

Table 9. Summary of Triplet State Reactivities of Polychlorobiphenyls in Cyclohexane

PCB	ϕ_T	τ, 10^{-8} sec	$1/\tau$, 10^7 sec^{-1}	k_T, 10^7 sec^{-1} [a]	k_d, 10^7 sec^{-1} [b]
I	0.005	2.20	4.54	0.023	4.52
II	0.100	0.78	12.82	1.282	11.54
III	0.002	1.91	5.23	0.010	5.22
IV	0.007	0.77	12.99	0.091	12.90
V	0.010	0.67	14.92	0.149	14.77
VI	0.006	0.70	14.28	0.086	14.20

values of τ were essentially the same within experimental error in both solvents.

The properties of biphenyl and its derivatives in the ultraviolet indicate that the ground state is nonplanar. The excited triplet state of biphenyl is planar [Wagner (1967), Wagner and Scheve (1977)]. Based on an analysis of the data, it was postulated that the triplet excited states of the PCBs studied are planar [Ruzo et al. (1974), Bunce (1982)]. Triplet lifetimes show a definite variation between ortho substituted PCBs and the others, Table 9. This is undoubtedly a result of the greater steric hindrance to the preferred excited state geometry. Crowded conditions created by the ortho substituents result in a greater twisting of the Ph-Ph bond with a decrease in its double bond character. The products obtained in the greatest yields arise from the loss of ortho chlorine; thus, the strain in the Ph-Ph bond is relieved.

Ruzo et al. (1974) postulated the following mechanism based on all results

$$[\text{P-Cl}] \xrightarrow[I_a]{h\nu} {}^1[\text{P-Cl}]^* \xrightarrow[\Phi_{isc}=1]{isc} {}^3[\text{P-Cl}]^* \quad , \qquad (6)$$

$$ {}^3[\text{P-Cl}]^* \xrightarrow{kd} {}^0[\text{P-Cl}] \quad , \qquad (7)$$

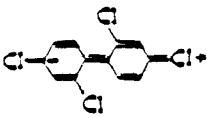
$$ {}^3[\text{P-Cl}]^* \xrightarrow{kr} (\text{products}) \quad , \qquad (8)$$

where $^{0}[P\text{-}Cl]$, $^{1}[P\text{-}Cl]^{*}$, and $^{3}[P\text{-}Cl]^{*}$ represent the PCB in its ground state, excited singlet state, and excited triplet state, respectively. I_a is the quanta of light absorbed by the ground state PCB and ϕ_{isc} is the quantum yield for conversion of the excited singlet state to the excited triplet state. Kinetic analysis of reactions 6-8 yielded

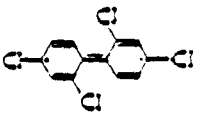
$$\tau^{-1} = k_d + k_r \quad , \tag{9}$$

$$\phi_r = \phi_{isc} k_r \tau \quad . \tag{10}$$

From the experimental data of τ^{-1}, ϕ_r, and ϕ_{isc}, k_d and k_r have been calculated and these results are summarized in Table 9. The value of k_r is much greater for II, IV, V, and VI than for I and III. Thus, the presence of ortho chlorines decreased the lifetime and increased the reactivity of the excited triplet state. As a result, the ortho substituted PCBs react much more rapidly. This has been ascribed directly to the destabilizing effect of ortho substitution. The large differences in k_r between compound II and the others may be attributed to the increased double bond character of the Ph-Ph bond as a result of the para chlorine. Since it has been postulated that a para substituent may increase conjugation between the phenyl rings by election donation, the excited state of PCB II may be represented by structures 1 and 2.



1



2

This effect would bring about greater conjugation with increasing driving force to planarity resulting in a faster chlorine cleavage.

Ruzo et al. (1974) postulated the mechanism of the photodechlorination of 2,2'4,4'-tetrachlorobiphenyl (II) and this mechanism is depicted in Figure 1, Section II.B. The dechlorination products obtained from the uv irradiation result from the cleavage of the C-Cl bond in the ortho position to form a biphenyl free radical species. This free radical species then abstracts a hydrogen atom from the solvent. HCl was detected as a reaction product in support of this mechanism. Photolysis of compounds I-VI in methanol yielded a small amount of the methoxylated products, Table 8. These methoxylated products would be formed by nucleophilic displacement of chlorine by methanol.

The photolysis of 4,4'-dichlorobiphenyl was performed in degassed methanol and isopropyl alcohol at 310 nm [Nordblom and Miller (1974)]. The reaction yielded exclusively 4-chlorobiphenyl which was stable. Photolysis in CH_3OD did not lead to the incorporation of deuterium indicating that the hydrogen atom is donated from the methyl group and is typically a free radical reaction where the weaker C-H bond is broken in preference to the O-H bond.

All the data on the photolysis of PCBs in solution can be summarized as follows. PCBs with chlorines in the ortho position decompose more readily than congeners without ortho substitution. This is a direct result of the fact that, in general, ortho substituted biphenyls have higher quantum yields than PCBs without ortho chlorines. The ortho substituted PCBs have a nonplanar configuration due to steric hindrance of the ortho chlorines. The mechanism of photodecomposition involves the triplet state which is planar. Crowded conditions created by the ortho substituents result in greater twisting of the Ph-Ph bond with a decrease in its double bond character. The products obtained in the greatest yields arise from the loss of ortho chlorines, thereby relieving the strain in the Ph-Ph bond. Thus, the ortho substituted PCBs decompose photolytically in a stepwise fashion by removal of the ortho chlorines.

CHAPTER 9

BIODEGRADATION OF CHLORINATED BIPHENYLS

by

Robert H. Brink

Contents

		Page No.
I.	INTRODUCTION AND SUMMARY	9-1
II.	MONITORING EVIDENCE	9-3
III.	BIODEGRADATION RATES	9-4
	A. General	9-4
	B. Anaerobic	9-5
	C. Aerobic Aquatic	9-5
	D. Biological Waste Treatment	9-8
	E. Soil	9-11
IV.	ANAEROBIC BIODEGRADATION	9-12
V.	PURE CULTURE STUDIES	9-13
VI.	SORPTION	9-15
VII.	VOLATILIZATION	9-16
VIII.	OTHER FACTORS	9-17
IX.	REFERENCES	9-19

I. INTRODUCTION AND SUMMARY

A review of the available literature on the degradation of chlorinated biphenyls by microorganisms discloses many conflicting findings and conclusions. There are, however, some discernable patterns. It is quite clear that there are numerous aerobic microorganisms in the environment that are capable of degrading most of the chlorinated biphenyls present in commercial PCB products and that such organisms are widely distributed in the environment. It is also evident that rates of biodegradation are related to both the degree of chlorination of the biphenyl structure and the positioning of those chlorines on the biphenyl rings.

There is no evidence for biodegradation of PCBs under anaerobic conditions and this might be quite important given the high degree of sorption to solids and the likelihood that many of those solids will reside in the environment under anaerobic conditions.

With respect to the degree of chlorination, as a broad generalization biodegradation proceeds more slowly as more chlorines are added to the biphenyl. Given the information in section III on biodegradation rates, it is possible to arrive at some general conclusions about potential biodegradation rates in various environments, but it must be emphasized that these are

broad generalizations and that half lives in particular environments for specific chlorinated biphenyls may be much larger due to certain limiting environmental variables (e.g. low temperatures, low moisture, pH extremes) or the specific PCB structure.

	Half Lives Resulting from Biodegradation			
	Mono- & dichloro	Trichloro	Tetrachloro	Pentachloro and higher
Aerobic				
Surface Waters				
Fresh	2-4 days	5-40 days	1 wk-2+mos.	>1 year
Oceanic	several months		>1 year	
Activated Sludge	1-2 days	2-3 days	3-5 days	*
Soil	6-10 days	12-30 days		>1 year
Anaerobic	∞			

* It is not clear how long the highly chlorinated PCBs would last under activated sludge treatment but there appears to be no significant biodegradation during typical residence times.

These half-life approximations also must be tempered by the knowledge that positioning of the chlorine atoms on the biphenyl rings can be important. It has been shown, for example, that (1) PCBs containing all of the chlorines on one ring are degraded faster than PCBs containing all of the chlorines distributed over both rings, (2) PCBs containing chlorine on 2 or more ortho

positions degrade very slowly, (3) the resistance of tetrachloro PCBs is greater when there are 2 chlorines on each ring and, (4) the initial biodegradation step occurs on the biphenyl ring with the fewest chlorines.

Biodegradation possibilities are also complicated by the fact that much of the PCBs released to the environment is likely to become tightly bound to sewage solids and sediments that are under anaerobic conditions where biodegradation will not be significant and by the possibility that a substantial portion of the more highly-chlorinated, less water-soluble PCBs will evaporate into the atmosphere.

II. MONITORING EVIDENCE

Among the most convincing evidence for the persistence of the more highly chlorinated biphenyls in the environment is actual monitoring data on various samples. There is a large number of reports, mostly on samples of biota, that might be cited and those presented here are not intended as a comprehensive listing.

Tucker et al. (1975) noted that the PCBs generally found in the environment are those containing 5 or more chlorine atoms per molecule. This is strong evidence that the less highly chlorinated biphenyls degrade more rapidly because the less highly chlorinated isomers constituted about 65% of all of the PCBs manufactured.

Ballschmiter et al. (1978) identified more than 80 PCBs in marine fish and found the ratios of ten major PCB components (pentachloro and higher) in the fish were the same as the ratios of those congeners found in Aroclor 1254 and Aroclor 1260. They speculated that this is true because the differences in the degradation rates of these highly chlorinated PCBs are too small to produce any changes in their relative occurrence during the time that they have been in the environment (up to 40 years).

Wszolek et al. (1979) analyzed lake trout in 1970 and again in 1978, from the same lake. They found PCBs similar to Aroclor 1254, but with a higher proportion of more chlorinated congeners at about 13 ppm at both sampling times. Moein et al. (1976) reported no reduction in Aroclor 1254 concentration over a 2-year period in a soil contaminated by a spill of transformer fluid.

III. BIODEGRADATION RATES

A. General

Biodegradation studies that report rates of degradation come in many sizes and shapes. Some used commercial mixtures, some pure congeners and some used both. PCB concentrations employed range from 5 ug/l up to 500 mg/l. Many analyzed only for the disappearance of parent compound(s), some for potential intermediates, and a few for mineralization to CO_2 and water. Studies have been conducted using lake water, sea water, soils and sewage, as well as various synthetic media, with a variety of

microbes and culture conditions. This hodge-podge of approaches makes it difficult to compare results and leads to skepticism about some of the procedures and conclusions. Nevertheless, it is possible to arrive at some conclusions with respect to biodegradation rates. Those conclusions, presented below, are mostly based on studies that used mixed microbial populations obtained from the environment and not those that employed pure cultures. The pure culture work is discussed in section V.

B. Anaerobic

Biodegradation of the PCBs under anaerobic conditions is probably very slow or nonexistent. This is discussed in more detail in section IV.

C. Aerobic Aquatic

Biodegradation of mono-, di- and trichlorinated biphenyls is probably moderately fast in most surface waters. Clark et al. (1979), using bacteria isolated from soils in shake flask cultures, found 100% primary biodegradation (loss of parent compound) in less than 5 days for monochlorobiphenyl and 90 to 99% degradation of dichlorobiphenyl, 42 to 87% degradation of trichlorobiphenyls and 6 to 61% degradation of tetrachlorobiphenyls after 5 days incubation. They also examined the biodegradation of Aroclor 1242 and presented data on the percent biodegradation of 38 congeners (identified by gc peaks) showing very substantial loss of most of the mono-, di- and trichlorinated biphenyls

within a 48-hour incubation time. Some of the trichloro isomers did not degrade rapidly and these may be isomers with chlorines in the ortho positions. Baxter et al. (1975), in shake flask studies, found that most dichlorinated biphenyls had half lives of less than 10 days and the trichlorobiphenyls were half gone in 20 to 40 days. Wong and Kaiser (1975), using lake water in stoppered shake flasks found that Aroclor 1221 was degraded completely, in about one month, to lower molecular weight metabolites. They also demonstrated that biphenyl degraded faster than 2-chlorobiphenyl which, in turn, degraded faster than 4-chlorobiphenyl. Shiaris and Sayler (1982), however, have shown that the biodegradation of the lesser chlorinated biphenyls in natural waters may lead to the accumulation of chlorobenzoic acid transformation products.

While the evidence is that the less chlorinated biphenyls degrade readily in aerobic freshwater, the same may not be true for seawater. Carey and Harvey (1978) found very low rates of biodegradation of 2,5,2'-trichlorobiphenyl with only 1 to 4% loss after 25 days in stoppered shake flasks. And Reichardt et al. (1981), using closed bottles of seawater at 10°, estimated the half-lives of biphenyl, 2-chlorobiphenyl, 3-chlorobiphenyl and 4-chlorobiphenyl. The biphenyl half-life, in their seawater, was about 3 months, and that for the monochlorobiphenyls was about 8 months. Observations of considerably slower biodegradations in the oceans are not confined to biphenyls and may be related to the low concentrations in seawater of certain essential elements, especially nitrogen.

With respect to those PCBs with 5 or more chlorines, it appears that biodegradation is very slow in all environments including surface waters. Oloffs et al. (1972) incubated Aroclor 1260 in river water for up to 12 weeks and found no evidence of biodegradation. They did, however, observe significant losses by evaporation. Shiaris et al. (1980) used reservoir water and found no apparent biodegradation of Aroclor 1254 during 2 months incubation. They used sealed vessels and did observe that significant amounts of the Aroclor sorbed tightly to the glass vessel walls and to the suspended solids. Only about 20% of the PCBs, initially added to a concentration of 0.1 mg/l, remain in the aqueous phase. Wong and Kaiser (1975) compared Aroclors 1221, 1242 and 1254 and found that the microorganisms in lake water samples could use 1221 and 1242 for growth but were not able to utilize 1254. In contrast to most reports, Sayler et al. (1977), using a pure culture of Pseudomonas sp., reported 70 to 85% biodegradation of 2,4,5,2,'4,',5'-hexachlorobipnenyl in 10 to 15 days. This finding does not seem to be consistent with the evidence from other studies.

There is little information on the biodegradation of tetrachlorobiphenyls in surface waters. In other media the tetrachloro congeners on the average, have biodegradation rates that are intermediate to those with fewer chlorines, most of which degrade quite readily, and those with 5 or more chlorines, which are quite persistent. The data presented by Clark et al. (1979) show that most of the tetrachloro congeners did not degrade significantly in 48 hours in shake flasks. The work by

Carey and Harvey (1978) included 2,5,2',5'-tetrachlorobiphenyl and they found little, if any, biodegradation after 25 days in seawater. Given the results of studies using other media, it is probably safe to assume that the biodegradation rates of the tetrachloro congeners are highly dependent upon the positioning of the chlorines on the biphenyl rings.

D. Biological Waste Treatment

Studies using activated sludge or sewage organisms and simulating biological waste treatment processes have shown that the biodegradation rates of PCBs are dependent upon both the degree of chlorination and the location of the chlorines. As might be expected, however, the rates of biodegradation, for the readily biodegradable PCBs, are higher under waste treatment conditions than in surface waters or soil.

Tucker et al. (1975) studied primary biodegradation by activated sludge microorganisms using Aroclors 1016, 1221, 1242 and 1254 plus a non-commercial mixture, MCS-1043, containing about 30% chlorine. After several weeks of acclimation, the PCBs were tested in semi-continuous activated sludge units operated on two 48-hour and one 72-hour cycles per week. They observed 100% biodegradation of biphenyl, 80% for 1221, 55% for MCS-1043, 35% for 1016, 25% for 1242 and 15% for 1254 in 48 hours. They also claim no significant losses of 1221, 1043 or 1016 through

volatilization. Zitco (1979) noted that the data of Tucker et al. (1975) show a decreasing rate of biodegradation with increasing chlorine content that has the following relationship-

$$R = 106\ (\pm\ 6) - 1.7\ (\pm\ 0.2)D$$

where R = % degraded in 48 hours and D = % chlorine

The evidence, however, indicates that those PCBs with 5 or more chlorines degrade too slowly to allow any practical application of that relationship to them. Also, it must be noted that individual tri- and tetrachloro congeners degrade at rates that are highly dependent upon the location of the chlorines on the biphenyl rings.

In contrast to the work of Tucker et al. (1975), Kaneko et al. (1976), using semi-continuous activated sludge units, following 3 months of acclimation, found no biodegradation of Kanechlor-500 (KC-500), a Japanese PCB product with an average chlorine content of 50%. In this paper the authors claim that the PCBs sorbed rapidly to the sludge solids and that losses of PCBs from their units were due almost entirely to losses by evaporation and losses of material sorbed to wasted sludge solids. Herbst et al. (1977) also concluded that there was little biodegradation of Aroclor 1221 in activated sludge and that the PCBs were distributed unchanged between the water and

sludge solids. However, they used relatively short test periods of 6 hours and there is no discussion of prior acclimation, which may be important.

Tulp et al. (1978) described the use of activated sludge inocula in shake flask and PCBs at 50 mg/l (well above the water solubility). Some of the flasks were supplemented with 500 mg/l additions of other carbon sources such as glucose, peptone or humic acid. They reported that the microbial populations did not degrade any of the PCBs during 14 days of incubation when there were three or more chlorines on the biphenyl rings. They also noted that the additions of other carbon sources dramatically reduced the biodegradation of 4,4'-dichlorobiphenyl. There are too few details on their experimental work to permit a good evaluation of their findings, but it is interesting to note that their test PCBs with three or more chlorines were the 2,4'5-trichloro-, 2,2',5,5'-tetrachloro-, 2,2',3,4,5,5'-hexachloro- and decachlorobiphenyls. Other evidence (Furukawa et al. 1978b) shows that those congeners with chlorines in any two ortho positions are degraded poorly.

Liu (1981), using a bench-scale fermentor and sewage inoculum, found that the half-life of Aroclor 1221 was highly dependent on the rate of mixing in the fermentor. His data show that the half-life was a logarithmic function of impellor speed between 0 and 800 rpm. At the top speeds, the half-life of 1221 was about 2 days. Liu also claimed no more than 10% loss of Aroclor 1221 through volatilization, over a 10-day test period.

E. Soil

As in water and sewage sludge, the biodegradation of PCBs in most soils appears to be rapid for the less chlorinated ones and increasingly difficult with increasing chlorination. In their review on the fate of PCBs, Pal et al. (1980) categorized decomposition rates in soils in three groups. Group 1 is for chlorinated biphenyls with 2 or fewer chlorines per molecule and Baxter et al. (1975) have shown that these degrade rapidly with half-lives of about 8 days. The second group contains the tri- and tetrachloro PCBs which have half-lives of 12 to 30 days. The third group, those with 5 or more chlorines, have half-lives in excess of one year. As with the biodegradation of any chemical in soils, biodegradation rates will vary greatly and depend upon the nature and viability of the microbial populations, the presence of other degradable organic matter, the moisture and oxygen content of the soils, pH, temperature and other environmental variables.

Griffin et al. (1978) also described the fate of PCBs in soils but the section on biodegradation is not easy to follow and presents data indicating a high percentage of biodegradation of tetrachloro PCB congeners (up to 99%) in only 20 hours. This seems unlikely. Fries and Marrow (1982), on the other hand, reported that only about 20% of labelled biphenyl and monochlorobiphenyls could be accounted for as $^{14}CO_2$ after 98 days in silt loam soil.

IV. ANAEROBIC BIODEGRADATION

There is no evidence in the literature that the PCBs are degraded by microorganisms under anaerobic conditions. Carey and Harvey (1978), Kaneko et al. (1976) and Pal et al. (1980) discuss anaerobic studies with PCBs, and there is no indication of anaerobic biodegradation. This seems somewhat surprising since dehalogenation is a commonly observed reaction for other organics under anaerobic conditions, for example with DDT and heptachlor. On the other hand, when DDT is transformed anaerobically to DDE or DDD, the dehalogenation removes only one chlorine from the ethane group and the products are more stable than the original DDT. It may be that, even if there is some reductive denalogenation with PCBs, the transformation product would be very stable and that the investigations conducted to date have not looked for those kinds of transformations. At any rate, the resistance to biodegradation under anaerobic conditions is probably quite significant. It is likely that much of the PCBs released to the environment are rapidly bound to particulate matter and stored under anaerobic conditions in sewage sludges and sediments. McIntyre et al. (1981b) found that about 83% of Aroclor 1260 found in digested sludge was retained on that sludge after chemical conditioning and dewatering steps and, as discussed in section VI, there is considerable evidence that PCBs can sorb rapidly to the sludge solids in sewage and waste treatment plants. Overall, it appears from the evidence that an important fraction of the PCBs released to the environment will

become tightly bound to particulate matter in sewage sludges, in sediments and in flooded soils, where anaerobic conditions will prevent or greatly slow degradation by microorganisms.

V. PURE CULTURE STUDIES

Much of the literature on the biodegradation of PCBs describes studies made using pure cultures of microorganisms. Those studies are of considerable value in elucidating the potential pathways of biodegradation and the relative rates of biodegradation of various isomers. They do not provide much of value in assessing the environmental biodegradation rates of specific congeners.

Lunt and Evans (1970), using pure cultures of gram-negative bacteria, described the transformaton of biphenyl into 2,3-dihydroxybiphenyl. Ahmed and Focht (1973) subsequently demonstrated the biodegradation of 3-chloro-, 4-chloro-, 2,2' dichloro- and 4,4'-dichlorobiphenyl by Achromobacter sp. and proposed a hypothetical pathway going from the PCB to a dihydroxychlorobiphenyl followed by ring opening and degradation to chlorinated benzoic acids. Other pure culture studies (Furukawa and Matsumura 1976, Furukawa et al. 1978a, Yagi and Sudo 1980, Ballschmiter 1977, Ohmori et al. 1973, and Wallnofer et al. 1973) tend to confirm this general pathway and have supplied additional details. The potential pathways of aerobic biodegradation are not very relevant to this review and will not be described in any detail. It does appear, however, that the

dihydroxylation requires oxygen and occurs on the less chlorinated ring when there is uneven distribution of the chlorines. It may be that the appearance of chlorines in two or more ortho positions sterically hinders the dihydroxylation step. It also seems that the dihydroxylation may be accomplished by an electrophilic form of oxygen and that the electron-withdrawing nature of the chlorines supresses that initial biodegradation step.

Pure culture studies have also helped in demonstrating not only that increasing levels of chlorine lead, in general, to decreasing rates of biodegradation, but also that the biodegradability is influenced by the positioning of the chlorines on the biphenyl rings. Furukawa et al. (1978b) studied 31 PCB congeners and demonstrated that (1) the resistance of tetrachloro PCBs is greater when there are two chlorines on each ring, (2) PCBs containing chlorine on 2 or more ortho positions (of either ring or both) are very resistant, (3) PCBs containing all of the chlorines on one ring are degraded faster than those with the same number of chlorines distributed over both rings, and (4) hydroxylation and ring fission occur preferentially on the biphenyl ring with the fewest chlorines. Furukawa et al. (1979), using Alcaligenes and Acinetobacter sp., have also shown that the positioning of chlorines has an effect on the metabolic pathways and kinds of degradation products formed. Liu (1982), using a Pseudomonas species in a closed fermentor, also observed

that the number of chlorines and the position of the chlorines on the rings are important factors in the relative biodegradation rates of PCBs.

VI. SORPTION

The preceding sections on biodegradation in various environments are complicated by the fact that a large proportion of the PCBs released to the environment will sorb tightly to the surfaces of sewage solids, suspended matter in surface waters and various sediments and may not be available for degradation by microorganisms in sewage treatment plants or in natural waters. While the subject of adsorption of PCBs is covered in detail elsewhere in this review, it is important to keep this phenomenon in mind when considering biodegradation potential and to consider some of the findings of those who were primarily investigating biodegradation.

Furukawa et al. (1978a), Bourquin and Cassidy (1973), Gresshoff et al. (1977), Kaneko et al. (1976) and McIntyre et al. (1981b) all noted, in connection with microbial studies, the highly sorptive nature of the PCBs. Gresshoff et al. (1977) speculated that much of the PCBs in the environment would tend to adsorb to rocks or sand or soil surfaces and to resistant organisms. They go on to suggest that those sorbed PCBs might be remobilized by other organic pollutants, such as oil spills. Colwell and Sayler (1977) noted that PCBs in the environment will be partitioned into suspended sediments, oils and surface

films. Studies at sewage treatment plants have shown that PCBs are principally removed form wastewater during sludge settling steps. McIntyre et al. (1981b) demonstrated that PCBs will be closely associated with the settled solids in sewage treatment and that those PCBs will be retained on the solids during chemical conditioning and dewatering steps. Fifty percent or more of the PCBs in raw sewage may be associated with the solids removed in primary sedimentation. (McIntyre et al. 1981a, Garcia-Gutierrez et al. 1982). Shiaris et al. (1980), in a study on extraction techniques for residual PCBs, found that when 0.1 mg/l preparations of Aroclor 1254 were incubated for 4 to 8 weeks, most of the PCB became tightly bound to vessel walls and particulates in the water. Marinucci and Bartha, in a study on the accumulation of Aroclor 1242 in percolators containing a shredded marshgrass (Spartina sp.) demonstrated that PCB accumulation in the litter was significantly enhanced by the presence of litter - decaying microbes and concluded that a significant fraction of the PCB in the litter was contained in the microbiota.

VII. VOLATILIZATION LOSSES

There are many questions that come to mind when reviewing the literature on PCB biodegradation. An important one concerns the possibility that losses due to volatilization may have been reported as losses due to biodegradation. Baxter et al. (1975) and Tucker et al. (1975) assert that their studies contained checks on volatilization losses and that there were no

significant losses to the air. Liu (1981) demonstrated no more than 10% loss of Aroclor 1221 due to volatilization during 10 days of stirring in a bench-top fermentor. It should be noted, however, that their claims for no significant volatilization losses are limited to the less-chlorinated, more water-soluble PCBs. On the other hand, Kaneko et al. (1976) and Oloffs (1972) reported very high levels of evaporative losses of Kanechlor-500 and Aroclor 1260 in their studies. Many of the biodegradation studies in the literature (e.g. Furukawa et al. 1978b, Sayler et al. 1977, Tulp et al. 1978) are not described in sufficient detail to allow the reader to determine whether or not the investigators accounted for potential evaporative losses.

VIII. OTHER FACTORS

There are several other factors in the literature on PCB biodegradation that raise questions about the validity of certain studies or present the reviewer with conflicting conclusions. Most of them do not alter significantly the general conclusions presented above, but they should be kept in mind by those who might attempt to obtain better evaluations of biodegradation possibilities or more reliable rate predictions.

Among the more interesting factors is the indication that PCBs can affect the metabolic processes of microorganisms. Kaneko et al. (1976) and Wong and Kaiser (1975) reported the stimulation of microbial respiration by PCBs at concentrations as low as 1 ug/l. Kaneko et al. (1976) suggested that the PCBs

might act as uncouplers of oxidative phosphorylation. These findings cast some doubt on the work of others who used respirometric techniques to study PCB biodegradation (e.g. Ahmed and Focht 1973 and Sayler et al. 1977).

Other unresolved factors include the influence of other degradable organic matter. Clark et al. (1979) and Yagi and Sudo (1980) found that PCBs degraded better in the presence of other substrates (acetate, meat extract or peptone). Tulp et al. (1978), on the other hand, found that the presence of other carbon sources (glucose, peptone, glycerol, yeast extract or humic acid) led to dramatically reduced biodegradation. Some researchers have observed faster biodegradation by pure cultures than by mixed cultures (Tulp et al. 1978 and Sayler et al. 1977) while others have noted the opposite (Clark et al. 1979). Liu (1981) reported the isolation of a Pseudomonas sp. that degraded Aroclor 1221 ten times faster than sewage organisms, and he proposed the use of that strain to seed biological treatment plants.

One area that needs to be investigated more fully is the role that acclimation may play in enhancing the rate and extent of biodegradation of those PCBs that are relatively biodegradable. It would also be very interesting to investigate anaerobic processes more fully to find out if reductive dechlorinations do occur and what would happen to PCBs in environments exposed to alternating aerobic and anaerobic conditions.

IX. REFERENCES

Ahmed M, Focht DD. 1973. Degradation of polychlorinated biphenyls by two species of Achromobacter. Can J Microbiol 19:47-52.

Ballschmiter K, Unglert Ch, Neu HJ. 1977 Abbau von chlorierten aromaten: mikrobiologischer abbau der polychlorierten biphenyle (PCB). III. Chlorierte Benzoesauren als metabolite der PCB. Chemosphere 1:51-56.

Ballschmiter K, Zell M, Neu HJ. 1978. Persistence of PCB's in the ecosphere: will some PCB-components "never" degrade? Chemosphere 2:173-176.

Baxter RA, Gilbert PE, Lidgett RA et al. 1975. The degradation of polychlorinated biphenyls by micro-organisms. Sci of Total Environ 4:53-61.

Bouquin AW, Cassidy S. 1975. Effect of polychlorinated biphenyl formulations on the growth of estuarine bacteria. Appl Microbiol 29:125-127.

Carey AE, Harvey GR. 1978. Metabolism of polychlorinated biphenyls by marine bacteria. Bull Environ Contam Toxicol 20:527-534.

Clark RR, Chian ESK, Griffin RA. 1979. Degradation of Polychlorinated Biphenyls by mixed microbial cultures. Appl Environ Microbiol 37:680-685.

Colwell R, Sayler G. 1977. Effects and interactions of polychlorinated biphenyl (PCB) with estuarine microorganisms and shellfish. EPA-600/3-77-070.

Fries GF, Marrow GS. 1982. Metabolism of chlorinated biphenyls in soil. Paper presented at third annual meeting of the Society for Environmental Toxicology and Chemistry, Arlington VA, Nov. 14-17, 1982.

Furukawa K, Matsumura F. 1976. Microbial metabolism of polychlorinated biphenyls. Studies on the relative degradability of polychlorinated biphenyl components by Alkaligenes sp. J Agric Food Chem 24:251-256.

Furukawa K, Matsumura F, Tonomura K. 1978a. Alcaligenes and Acinetobacter strains capable of degrading polychlorinated biphenyls. Agric Biol Chem 42:543-548.

Furukawa K, Tonomura K, Kamibayashi A. 1978b. Effect of chlorine substitution on the biodegradability of polychlorinated biphenyls. Appl Environ Microbiol 35:223-227.

Furukawa K, Tomizura N, Kamibayashi A. 1979. Effect of chlorine substitution on bacterial metabolism of various polychlorinated biphenyls. Appl Environ Microbiol 38:301-310.

Garcia-Gutierrez A, McIntyre AE, Perry R et al. 1982. The behavior of polychlorinated biphenyls in the primary sedimentation process of sewage treatment: a pilot plant study. Sci of Total Environ 22:243-252.

Gresshoff PM, Mahanty HK, Gartner E. 1977. Fate of polychlorinated biphenyl (Aroclor 1242) in an experimental study and its significance to the natural environment. Bull Environ Contam Toxicol 17:686-691.

Griffin R, Clark R, Lee M et al. 1978. Disposal and removal of polychlorinated biphenyls in soil. In: Land Disposal of Hazardous Wastes. EPA-600/9-78-016, pp. 169-181.

Herbst E, Scheunert I, Klein W et al. 1977. Fate of PCBs-^{14}C in sewage treatment - Laboratory experiments with activated sludge. Chemosphere 11:725-730.

Kaneko M, Morimoto K, Nambu S. 1976. The response of activated sludge to a polychlorinated biphenyl (KC-500). Water Res 10:157-163.

Liu D. 1981. Biodegradation of Aroclor 1221 type PCBs in Sewage Wastewater. Bull Environ Contam Toxicol 27:695-702.

Liu D. 1982. Assessment of continuous biodegradation of commercial PCB formulations. Bull Environ Contam Toxicol 29:200-207.

Lunt D, Evans WC. 1970. The microbial metabolism of biphenyl. Biochem J 118:54-55.

Marinucci AC, BArtha R. 1982. Biomagnification of Aroclor 1242 in decomposing Spartina litter. Appl Environ Microbiol 44:669-677.

McIntyre AE, Perry R, Lester JN. 1981a. The behaviour of polychlorinated biphenyls and organochlorine insecticides in primary mechanical wastewater treatment. Environ Pollution 2:223-233.

McIntyre AE, Lester JN, Perry R. 1981b. The influence of chemical conditioning and dewatering on the distribution of polychlorinated bipenyls and organochlorine insecticides in sewage sludges. Environ Pollution 2:309-320.

Moein GJ, Smith AJ Jr, Stewart ML. 1976. Follow-up study of the distribution and fate of PCBs and benzenes in soil and groundwater samples after an accidental spill of transformer fluid. In: Proc of 1976 Nat'l Conf on Control of Haz Mat'l Spills. Information Transfer Inc. Rockville, MD. pp.368-372.

Ohmori T, Ikai T, Minoda Y et al. 1973. Utilization of polyphenyl and polyphenyl-related compounds by microorganisms. Agr Biol Chem 37:1599-1605.

Oloffs PC, Albright LJ, Szeto SY. 1972. Fate and behavior of five chlorinated hydrocarbons in three natural waters. Can J Microbiol 18:1373-1398.

Pal D, Weben JB, Overcash MR. 1980. Fate of Polychlorinated biphenyls (PCBs) in soil-plant systems. In: Residue Reviews, vol. 74, Springer-Verlag New York Inc. pp.52-69.

Reichardt PB, Chadwick BL, Cole MA et al. 1981. Kinetic study of the biodegradation of biphenyl and its monochlorinated analogues by a mixed marine microbial community. Environ Sci Technol 15:75-79.

Sayler GS, Shon M, Colwell RR. 1977. Growth of an estuarine Pseudomonas sp. in polychlorinated biphenyl. Microbiol Ecology 3:241-255.

Shiaris MP, Sherril TW, Sayler GS. 1980. Tenax-GC extraction technique for residual polychlorinated biphenyl and polyaromatic hydrocarbon analysis in biodegradation assays. Appl Environ Microbiol 39:165-171.

Shiaris MP, Sayler GS. 1982. Biotransformation of PCB by natural assemblages of freshwater microorganisms. Environ Sci Technol 16:367-369.

Tucker ES, Saeger VW, Hicks O. 1975. Activated sludge primary biodegradation of polychlorinated biphenyls. Bull Environ Contam Toxicol 14:705-713.

Tulp MThM, Schmitz R, Hutzinger O. 1978. The bacterial metabolism of 4,4'-dichlorobiphenyl and its suppression by alternative carbon sources. Chemosphere 1:103-108.

Wallnofer PR, Engelhardt G, Safe S et al. 1973. Microbial hydroxylation of 4-chlorobiphenyl and 4,4'-dichlorobiphenyl. Chemosphere 2:69-72.

Wong PTS, Kaiser KLE. 1975. Bacterial degradation of polychlorinated biphenyls. II. Rate studies. Bull Environ Contam Toxicol 12:249-256.

Wszolek PC, Lisk DT, Wachs T et al. 1979. Persistence of polychlorinated biphenyls and 1,1-bis (p-chlorophenyl) ethylene (p,p'-DDE) with age in lake trout after 3 years. Environ Sci Technol 13:1269-1271.

Yagi O, Sudo R. 1980. Degradation of polychlorinated biphenyls by microorganisms. J Water Poll Cont Fed 52:1035-1043.

Zitko V. 1979. Role of biodegradability in the environmental evaluation of polychlorinated biphenyls and chemicals in general. In: Biotransformations and fate of chemicals in the Environment. Maki AW, Dickson KL, Cairns, JC Jr, eds. Washington DC: American Society for Microbiology, pp 120-125.

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO. EPA 560/5-83-025	2.	3. Recipient's Accession No.
4. Title and Subtitle Environmental Transport and Transformation of Polychlorinated Biphenyls			5. Report Date December 1983
			6.
7. Author(s) Asa Leifer, Robert H. Brink, Gary C. Thom, and Kenneth G. Partymiller			8. Performing Organization Rept. No.
9. Performing Organization Name and Address U.S. Environmental Protection Agency Office of Pesticides and Toxic Substances 401 M Street, S.W. Washington, D.C. 20460			10. Project/Task/Work Unit No.
			11. Contract(C) or Grant(G) No. (C) (G)
12. Sponsoring Organization Name and Address U.S. Environmental Protection Agency Office of Pesticides and Toxic Substances 401 M Street, S.W. Washington, D.C. 20460			13. Type of Report & Period Covered
			14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

This report summarizes the environmental transport and transformation of polychlorinated biphenyls and contains nine separate chapters describing water solubility and octanol/water partition coefficient, vapor pressure, Henry's law constant and volatility from water, adsorption (sorption) to soils and sediments, bioconcentration in fish, atmospheric oxidation, hydrolysis and oxidation in water, photolysis, and biodegradation. In the preparation of each of these chapters, the emphasis has been on obtaining experimental data on environmentally relevant rate constants and equilibrium constants for these processes/properties for individual PCB congeners and Arochlors. If no experimental data were found, then estimation techniques were used wherever possible to obtain values for the rate constants or equilibrium constants for each individual congener or for groups of congeners (i.e., for monochloro-, dichloro-, trichloro-, etc., biphenyls). It must be emphasized that these estimates of rates for transport and transformation involved simplifying assumptions and thus these data should not be regarded as precise but rather as a best estimate based on the available data.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms Toxic Substances, water solubility and octanol/water partition coefficient of PCBs, vapor pressure of PCBs, volatilization of PCBs from water, soil and sediment sorption of PCBs, fish bioconcentration of PCBs, photolysis of PCBs, atmospheric oxidation of PCBs by OH radicals, hydrolysis and oxidation of PCBs in aqueous media, biodegradation of PCBs.

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Released Unlimited	Unclassified	204
	20. Security Class (This Page)	22. Price

(See ANSI-Z39.18) See Instructions on Reverse OPTIONAL FORM 272 (4-77) (Formerly NTIS-35) Department of Commerce

U.S. Environmental Protection Agency
Region 5, Library (PL-12J)
77 West Jackson Boulevard, 12th Floor
Chicago, IL 60604-3590