PCBs and the Environment

Volume I

Editor

John S. Waid, D. Phil.(Oxford), F.I.Biol., M.A.S.M.
Chairman and Head
Department of Microbiology
La Trobe University
Bundoora, Victoria, Australia

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Chapter 5

SOLUBILITY AND SOIL MOBILITY OF POLYCHLORINATED BIPHENYLS

S. F. J. Chou and R. A. Griffin

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I. ABSTRACT

Aqueous solubilities of polychlorinated biphenyls (PCBs) are low, ranging from 2.7 ppb for Aroclor® 1260 to 3500 ppb for Aroclor® 1221. Water-soluble PCBs are reported to be richer in lower chlorinated isomers than were the original PCB fluids.

PCBs are strongly sorbed by earth materials. There is a very high direct correlation between the total organic carbon content of the soil and the amount sorbed. The sorption and retention of PCBs by soils and soil constituents are influenced by the number of chlorine atoms in the molecule, the more highly chlorinated derivatives being more tenaciously held. A linear regression relation for sorption of PCBs expressed on a unit carbon basis as a function of water solubility is presented. The correlation of sorption with compound *n*-octanol/water partition coefficients is also examined.

PCBs are not readily mobile in soils when leached with aqueous solutions such as water or sanitary landfill leachates but are highly mobile when leached with organic solvents. Mobility of PCBs is proportional to their solubility in the leaching solvent and to the soil organic matter content.

II. INTRODUCTION

PCBs are a class of chlorinated aromatic hydrocarbons that are thermally and chemically stable. They have been widely used as a dielectric fluid in transformers and as an impregnating agent for capacitors and condensers. The occurrence of PCBs in the environment and their consequences on environmental quality have been well emphasized.[1-4] The Toxic Substances Control Act (TSCA), Public Law 94-469, specifically prohibits production of PCBs within the U.S., regulates disposal of materials contaminated by PCBs, and restricts the use of any such materials already in service. The effect of these measures should be to eliminate further releases into the environment and eventually, to reduce quantities existing in the environment. However, because of the extreme stability of PCBs, environmental levels will not be reduced substantially for many years, and the problem of dealing with existing reservoirs of mobile PCBs will remain.

The disposal of PCBs and related materials in landfills is of great concern[5,6] because of the possibility of ground water contamination if these compounds are leached from landfills. The limited amount of available information indicates that PCBs have a strong affinity for soil[7-9] and are not readily leached by percolating water.[10] Briggs[11] reported that adsorption of nonionic organic compounds by soils was related to the organic matter content of soils and to their octanol/water partition coefficient. He predicted that PCBs would be immobile in soils. The water solubility, sorption, mobility, translocation, and plant uptake of PCBs will be discussed in this review. The correlation of the sorption constant of PCBs with soil and compound properties will also be examined.

III. AQUEOUS SOLUBILITY

The aqueous solubility of hydrophobic compounds such as PCBs is a valuable indictor of its environmental fate, for example, its tendency to sorb to soil or to bioaccumulate in organisms. A considerable volume of data has been published on PCB solubilities,[10,12-27] but discrepancies exist because of the experimental difficulty of generating and handling such dilute solutions. The aqueous solubilities of some individual PCB isomers and commercially available mixtures of PCBs are listed in Table 1. The soil sorption constant (K_{oc}) is also listed in Table 1. Aqueous solubilities of PCBs are very low ranging from 0.95 ppb for 2,4,5,2′,4′,5′-hexachlorobiphenyl to 5900 ppb for 2-chlorobiphenyl and 2.7 ppb for Aroclor® 1260 to 3500 ppb for Aroclor® 1221. The composition of Aroclors® is given in

Table 1
SOLUBILITY, K_{oc}, AND K_{ow} OF SEVERAL PCBs

Compound	Solubility (ppb)	log S	Ref.	K_{oc}	log K_{oc}[a]	Ref.	K_{ow}	log K_{ow}[b]	Ref.
Biphenyl	7,500	3.88	43	2,512	(3.40)		7,540	3.88	18
Monochlorobiphenyls									
2-	5,900	3.77	27	2,951	(3.47)		14,790	(4.17)	
3-	3,500	3.54	27	4,168	(3.62)		21,877	(4.34)	
4-	1,190	3.08	26, 27	7,943	(3.90)		79,400	4.90	50
Dichlorobiphenyls									
2,4-	1,400	3.15	27	7,244	(3.86)		41,686	(4.62)	
2,2'-	1,500	3.18	27	6,918	(3.84)		39,810	(4.60)	
2,4'-	1,260	3.10	23, 27	8,000	3.90	8	45,708	(4.66)	
4,4'-	80	1.90	27	42,658	(4.63)		346,736	(5.54)	
Trichlorobiphenyls									
2,4,4'-	85	1.93	27	40,738	(4.61)		323,593	(5.51)	
2',3,4-	78	1.89	27	43,652	(4.64)		346,736	(5.54)	
Tetrachlorobiphenyls									
2,2',5,5'-	36	1.56	23, 27	47,000	4.67	8	602,559	(5.78)	
2,2',3,3'-	34	1.53	27	72,443	(4.86)		645,654	(5.81)	
2,2',3,5'-	170	2.23	27	26,915	(4.43)		194,984	(5.29)	
2,2',4,4'-	66	1.82	24, 25, 27	47,863	(4.68)		158,400	5.20	49
2,3',4,4'-	58	1.76	27	52,480	(4.72)		436,555	(5.64)	
2,3',4,5'-	41	1.61	27	64,565	(4.81)		562,341	(5.75)	
3,3',4,4'-	180	2.26	27	25,633	(4.41)		186,208	(5.27)	
Pentachlorobiphenyls									
2,2',3,4,5'-	22	1.34	27	95,324	(4.98)		870,693	(5.94)	
2,2',4,5,5'-	31	1.49	27	76,948	(4.89)		691,830	(5.84)	
Hexachlorobiphenyl									
2,4,5,2',4',5'-	0.95	−0.02	23	1,200,000	6.08	43	5,248,000	6.72	15
Aroclors									
1221	3,500	3.54	19	4,123	(3.62)		12,300	4.09	25
1232	1,450	3.16	12	7,092	(3.85)		41,686	(4.62)	
Used capacitor fluid	698	2.84	19	10,725	4.03		70,794	(4.85)	
1016	332	2.52	10, 12, 14	17,684	(4.25)		202,000	5.31	14, 18

Table 1 (continued)
SOLUBILITY, K_{oc}, AND K_{ow} OF SEVERAL PCBs

Compound	Solubility (ppb)	log S	Ref.	K_{oc}	log K_{oc}[a]	Ref.	K_{ow}	log K_{ow}[b]	Ref.
1242	288	2.46	12, 13, 16, 17, 20	12,400	4.09	44	196,500	5.29	14, 18
1248	54	1.73	27	54,626	(4.74)		562,000	5.75	12
1254	42	1.62	15, 20, 21, 22	63,914	(4.81)		1,288,000	6.11	15
1260	2.7	0.43	12	349,462	(5.54)		4,073,800	(6.61)	

[a] Data in parentheses were estimated using the method of Hassett et al.[44]
[b] Data in parentheses were estimated using Equation 9.

Table 2
APPROXIMATE MOLECULAR COMPOSITION (%) OF AROCLORS® [24]

Empirical formula	Aroclor® no. 1221	1232	1016	1242	1248	1254	1260
$C_{12}H_{10}$	11	<0.1	<0.1	<0.1	ND	<0.1	ND
$C_{12}H_9Cl$	51	31	1	1	ND	<0.1	ND
$C_{12}H_8Cl_2$	32	24	20	16	2	0.5	ND
$C_{12}H_7Cl_3$	4	28	57	49	18	1	ND
$C_{12}H_6Cl_4$	2	12	21	25	40	21	1
$C_{12}H_5Cl_5$	<0.5	4	1	8	36	48	12
$C_{12}H_4Cl_6$	ND	<0.1	<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 mol wt	200.7	232.2	257.9	266.5	299.5	328.4	375.7

Note: ND means none detected.

Table 3
SUMMARY OF ISOMER COMPOSITION (%) OF WATER-SOLUBLE AROCLORS® [19]

Empirical formula	Aroclor® no. 1221	1016	1242	Capacitor fluid	1254
$C_{12}H_9Cl$	92	12	19	18	ND
$C_{12}H_8Cl_2$	7	34	35	32	ND
$C_{12}H_7Cl_3$	1	35	31	36	20
$C_{12}H_6Cl_4$	<0.1	19	14	13	56
$C_{12}H_5Cl_5$	ND	ND	1	1	24
$C_{12}H_4Cl_6$	ND	ND	ND	ND	<0.1
$C_{12}H_3Cl_7$	ND	ND	ND	ND	<0.1

Note: ND means none detected.

Table 2. The overall compositions of chlorobiphenyl isomers in the water-soluble fraction of these Aroclors® are listed in Table 3. Representative GC chromatograms of water-soluble Aroclors®[19] are shown in Figure 1. In comparing the composition of the water-soluble Aroclors® reported by Thurston[28] and Lee et al.,[19] the water-soluble fractions were found to be richer in the lower-chlorinated isomers than were the original PCBs. Aroclor® 1254 is reported to contain isomers from tetra- to heptachlorobiphenyl in the original fluid. The GC traces of hexane-soluble Aroclor® 1254 reported by several researchers[29,30] show some small peaks in the position of trichlorobiphenyl; this has also been confirmed by Lee et al.[19] Because trichlorobiphenyls are more water-soluble than the more highly chlorinated biphenyls, detection of trace amounts in water is reasonable. The hexa- and heptachlorobiphenyls are enriched in the Aroclor® 1254 fluid and do not dissolve readily in water. The low solubility of these highly chlorinated isomers in water is apparently the reason.

IV. SORPTION OF PCBs BY EARTH MATERIALS

Sorption of PCBs by earth materials is the major nondestructive physicochemical process

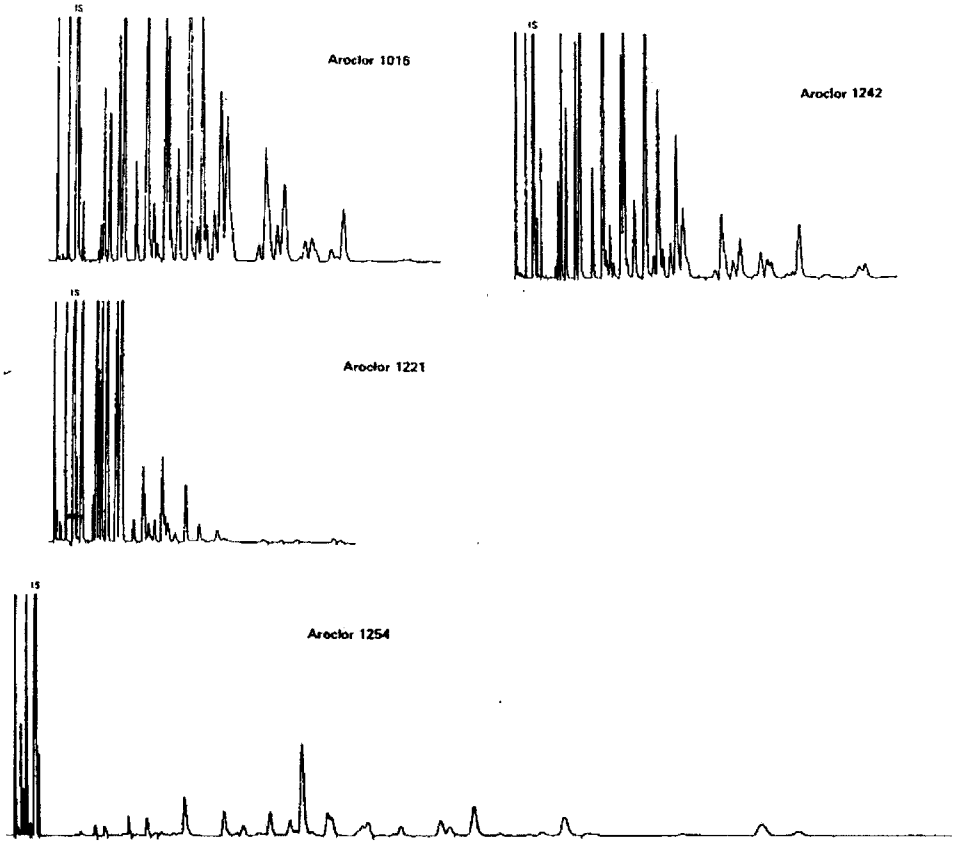

FIGURE 1. GC chromatograms of water-soluble Aroclors® [19] (IS means internal standard).

affecting PCB concentrations after introduction into the aquatic environment. The combination of low water solubility and high octanol/water partition coefficients (see Table 1) indicates that PCBs have a high affinity for suspended solids, especially those high in organic carbon.[31] This has been confirmed by a number of experiments which have shown that PCBs are rapidly sorbed and that the greatest amounts of PCBs are usually associated with the soils or sediments in soil-water systems.[7,14,32,33] Griffin and Chou[34] reported adsorption of water soluble PCBs by soil materials and coal chars. Data for PCB sorption by various earth materials are given in Table 4. Representative sorption isotherms are shown in Figures 2 and 3. The amount of PCBs sorbed by the earth materials was related to the equilibrium solution concentration of PCBs, and could be described by the simple linear relation[35]

$$x/m = KC \tag{1}$$

where x = micrograms of compound sorbed, m = weight of adsorbent (g), C = the equilibrium concentration of the PCBs in solution (μg/mℓ), and K = the sorption constant (mℓ/g).

The PCB sorption data reported here are a special case of the Freundlich equation where $1/n = 1$, K_f, and K are thus identical and Freundlich K_f values reported in the literature for other compounds can be compared with the K values for PCBs reported in Table 4. The data presented in Table 4 illustrate the wide differences in sorption by the various earth materials. Sorption of PCBs followed the series Medium Temperature Coal Char > High

Table 4
EARTH MATERIALS USED IN SORPTION STUDIES, THEIR SORPTION CONSTANT (K), THEIR TOTAL ORGANIC CARBON (TOC) CONTENT, AND SURFACE AREA (SA)[35]

Sorbent	K	TOC (%)	SA (m^2/g)
Ottawa silica sand	22	<0.1	0.4
Montmorillonite clay	172	0.93	20.1
Montmorillonite clay (LTA)	145	0.13	20.2
Catlin silt loam	532	4.73	26.5
Catlin, 6 hr (LTA)	472	4.37	25.4
Catlin, 12 hr (LTA)	310	3.64	24.5
Catlin, 336 hr (LTA)	239	1.84	23.8
Medium temp. coal char 650°C	1,938	74.04	253
Medium temp. coal char 650°C (LTA)	1,432	64.00	214
High temp. coal char 980°C	1,220	76.62	44
High temp. coal char 980°C (LTA)	1,174	32.14	120

Note: LTA denotes low temperature ashed samples.

Temperature Coal Char > Catlin Soil > Montmorillonite Clay > Ottawa Silica Sand. Low-temperature ashing reduced the amounts of PCBs sorbed by all samples. For the samples of Catlin soil (CS), PCB sorption decreased as ashing time increased; this corroborates the observations of Briggs[11] that there is a relationship between organic matter content and sorption.

The sorption of isomers from water-soluble Aroclor® 1242 solutions by different sorbents was investigated by Lee et al.[9] They found that higher chlorinated isomers were sorbed more than the lower chlorinated isomers. Haque and Schmedding[8] indicated that the extent of sorption for the surfaces they studied followed the sequence hexachloro- > tetrachloro- > dichlorobiphenyl for the isomers studied. The sorption of the water-soluble isomers of Aroclor® 1242 by coal char was reported by Griffin and Chian.[35] The average sorption of all isomers in groups such as monochloro- or dichloro-isomers were considered together. Griffin and Chian[35] concluded that the higher chlorinated were preferentially sorbed over the lower-chlorinated isomers which agreed with the sequence found by Haque and Schmedding.[8]

The relationship between total organic carbon (TOC) content, surface area, and PCB sorption were investigated by Lee et al.[9] A highly significant ($p = 0.001$ level) correlation was found with a linear regression relation of the PCB sorption constant (K) and TOC of:

$$K = 255 + 18.5\ TOC$$
$$r^2 = 0.87 \qquad (2)$$

Thus, the PCB sorption constant (K) can be estimated from a knowledge of the TOC content of the earth material. A highly significant ($p = 0.001$ level) correlation was also found with a linear regression relation of the PCB sorption constant (K) with surface area (SA, measured by using CO_2 gas adsorption):

$$K = 230 + 6.64\ SA$$
$$r^2 = 0.82 \qquad (3)$$

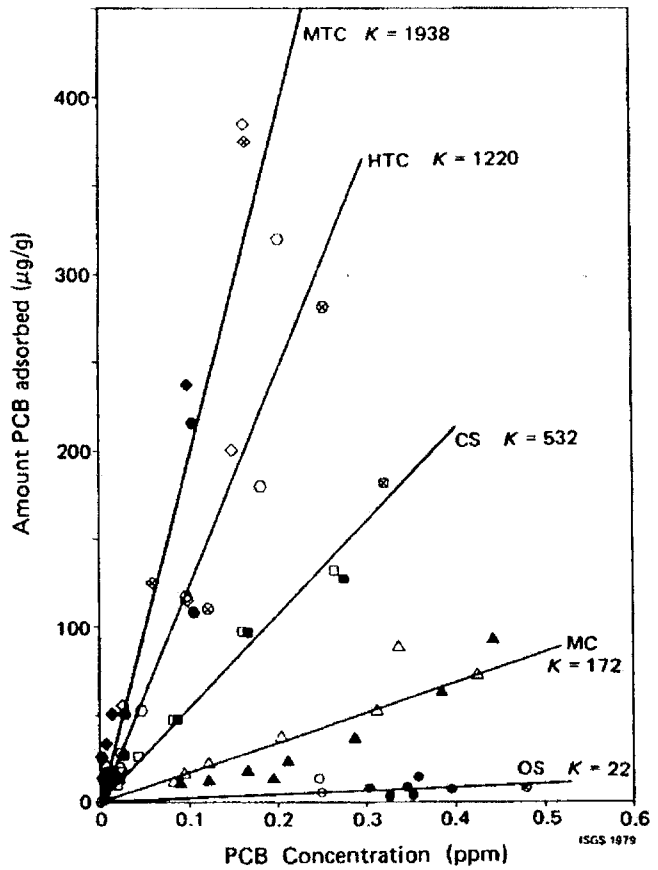

FIGURE 2. PCB adsorption by earth materials.[34] Solid symbols represent data for capacitor fluid, open symbols represent data for Aroclor® 1242, and Xs in open symbols indicate analysis using capillary column.

A three-variable regression analysis of the PCB sorption constant (K), TOC, and SA was investigated by Lee et al.[9] A very highly significant ($p = 0.001$ level) correlation was obtained with a linear regression relation of:

$$K = 188 + 3.36\,SA + 11.4\,TOC$$
$$r^2 = 0.94 \qquad (4)$$

The magnitude of the coefficients for SA and TOC indicate that TOC is the dominant factor in sorption. The best estimates of K were obtained by incorporating both SA and TOC; however, if only one earth material property must be chosen to estimate K, and TOC would be the most useful property.

The relation between the Aroclor® 1242 sorption constant, K, and the TOC content of the seven soil materials in Table 4 is illustrated in Figure 4. A linear relation was obtained and the slope of the line was used to estimate the K_{oc} value for Aroclor® 1242. The K_{oc} is the sorption constant normalized for the organic carbon content of soil and was found to have a value of 10,725. A three-variable regression analysis of the Aroclor® 1242 sorption constant, K, TOC, and SA was investigated using the data for soil materials (i.e., excluding coal chars) reported in Table 4 and is shown in Figure 5. A very highly significant correlation was obtained with a linear regression relation of:

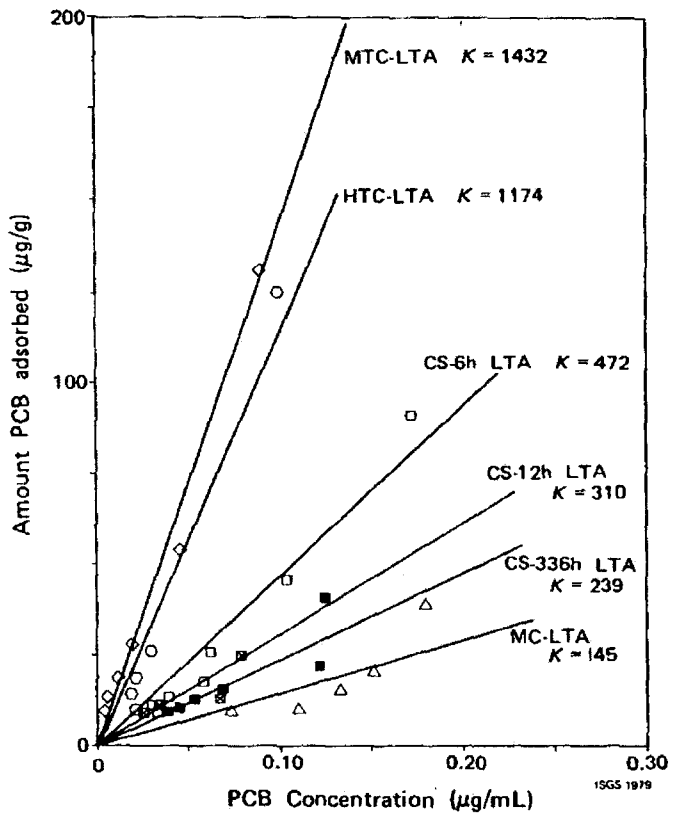

FIGURE 3. PCB adsorption by low-temperature ashes of earth materials.[34]

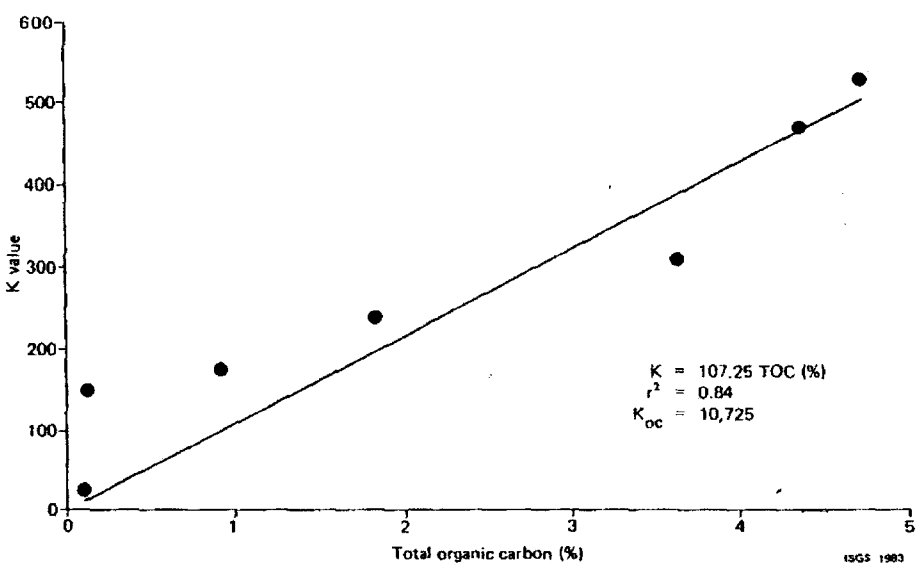

FIGURE 4. Aroclor® 1242 soil sorption constant (K) vs. soil material TOC content.

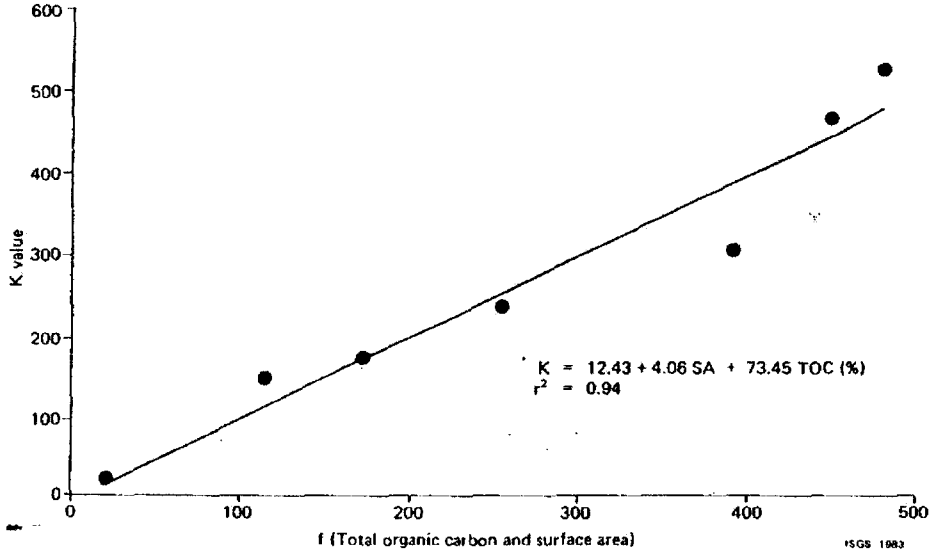

FIGURE 5. Multiple variable regression analysis of the Aroclor® 1242 soil sorption constant (K) plotted as a function of the TOC content and SA of 7 soil materials.

$$K = 12.43 + 4.06\ SA + 73.45\ TOC$$
$$r^2 = 0.94 \qquad (5)$$

The magnitude of the coefficients for SA and TOC indicates that TOC is the dominant soil property in sorption. The best estimates of K are obtained by a knowledge of both S and TOC; however, TOC is again, the single most important property controlling PCB sorption. When the PCB contamination level of soils or sediments becomes large, these materials may serve as a reservoir for desorption.[36] This is illustrated by Equation 1 which indicates that K is a ratio of x/m to C and as x/m becomes large, C also grows in relation to K. This fact has important ramifications to situations where PCBs are spilled or disposed in high concentrations because release of PCBs by soil materials can cause long-term pollution. For example, oysters still contained measurable levels of PCBs 7 years after a spill, even though the concentrations in the water were below detection limits.[37]

V. MECHANISM OF SORPTION

The sorption of PCBs by earth materials is suggested to be a hydrophobic sorption, which is the partitioning of the nonpolar solute out of the polar aqueous phase onto hydrophobic surfaces on the earth materials. The hydrophobic surfaces are primarily associated with soil organic matter but may also include ≡Si–O–Si≡ bonds at mineral surfaces.[38] The primary feature of hydrophobic sorption is the very weak interaction between the solute and the solvent. As the term hydrophobic suggests, the solvent water plays a major role in the interaction. Although not strictly the case, the interaction may be so weak as to acquire the nature of a repulsion of the PCB molecule from the water. The more hydrophobic the PCB molecule (lower in water solubility), the greater the repulsion from the water phase and the greater the sorption on a hydrophobic surface. In a stricter treatment, hydrophobic sorption is thought to be an entropy driven process governed by the basic thermodynamic relation:

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

where ΔG is the change in free energy of the system, ΔH is the heat of sorption (enthalpy), T is temperature, and ΔS is the change in entropy of the system. Sorption results when there is a negative free energy change. The primary driving force in hydrophobic sorption appears to be the large entropy change resulting from the removal of the organic molecule from solution and sorption onto a hydrophobic surface.[39,40] The entropy change is the primary driving force due to the destruction of the cavity occupied by the PCB molecule in the solvent and the destruction of the highly structured water shell surrounding the solvated PCB molecule.[40,41]

The role of the solute-solvent interaction in determining the degree of sorption of hydrophobic compounds was demonstrated by a soil thin-layer chromatography study using solutes and solvents (mobile phase) of different polarities.[42] When the mobile phase was 100% water, the polar compounds were weakly sorbed and moved with the solvent front, and the less polar compounds were strongly sorbed and showed little movement. As the mobile phase was made less polar by additions of ethanol, it became a better solvent for the nonpolar compounds and their sorption decreased. With ethanol additions, the mobile phase became a poorer solvent for the polar compound and its sorption increased and movement decreased. Similar results for Aroclors® 1242, 1254, and dicamba have also been reported.[35]

VI. CORRELATION OF K VALUES WITH EARTH MATERIAL AND COMPOUND PROPERTIES

Sorption experiments with nonpolar organic compounds and different earth materials produce a different K value for each earth material and organic compound. Hydrophobic sorption has been highly correlated with the organic carbon content of the earth material while at the same time being relatively independent of other sorbent properties.[43-46] When sorption of a hydrophobically sorbed compound is examined relative to the organic carbon content of the earth material, a constant, K_{oc}, is generated which is a unique property of the compound being sorbed. The K_{oc} can be determined graphically as shown in Figure 4 or computed as follows:

$$K_{oc} = K_f \times 100/(\%)\text{TOC} \tag{7}$$

where K_f is the Freundlich constant and TOC is the percent organic carbon in the respective soil material. K_{oc} values are compound properties, not soil properties, and have been related to other compound properties such as water solubility (S) and *n*-octanol/water partition coefficients (K_{ow}). Figure 6 shows the K_{oc}-S relation for the PCBs for which data are tabulated in Table 1. The linear regression equation obtained was

$$\log K_{oc} = 5.85 - 0.64 \log S \text{ (ppb)} \tag{8}$$

The data indicate that a good approximation of sorption of PCBs by soil materials can be made based on their water solubility. Water solubilities have been also shown to predict the K_{oc} values of a wide range of other hydrophobic compounds.[43,44,47]

The octanol/water partition coefficient (K_{ow}) measures the tendency of a compound to partition between an organic solvent and water. The octanol/water partition coefficient is usually obtained by measuring the concentration of the compound in equilibrium with *n*-octanol and water.[48] However, a satisfactory linear relationship is also observed between the log K_{ow} and log S, which extends over more than eight orders of magnitude in solubility (10^{-4} to 10^3 ppm) and four orders of magnitude in partition coefficient (10^2 to 10^6). The *n*-octanol/water partition coefficients of several PCBs are listed in Table 1. A plot of log

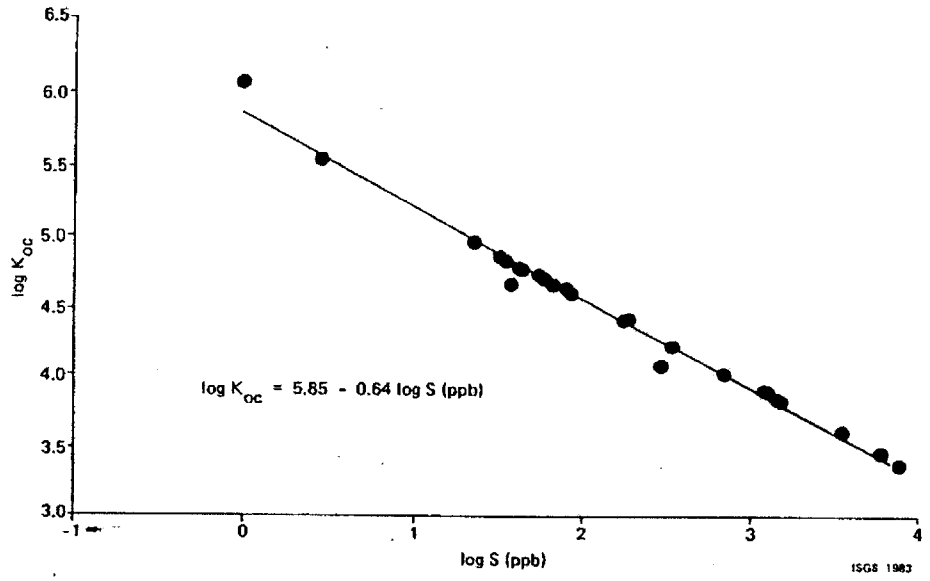

FIGURE 6. PCB soil sorption vs. water solubility.

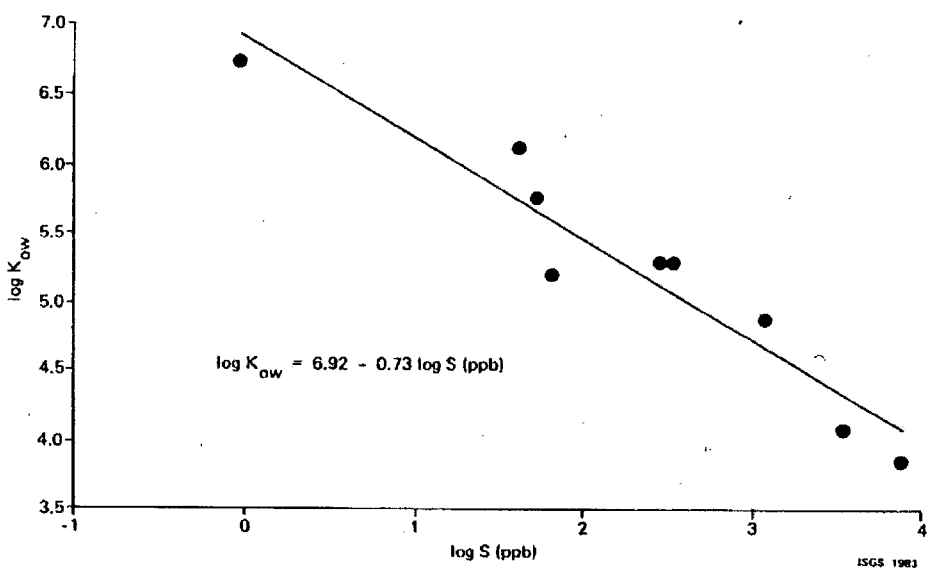

FIGURE 7. Relation of K_{ow} and the water solubility (S) of several PCBs.

K_{ow} vs. log S using the values cited in Table 1 is shown in Figure 7. The regression equation is

$$\log K_{ow} = 6.923 - 0.730 \log S \text{ (ppb)}$$
$$r^2 = 0.91 \qquad (9)$$

Equation 9 allows an estimation of the partition coefficient of a given compound from its aqueous solubility. The reliability of these relationships suggests that they may be very

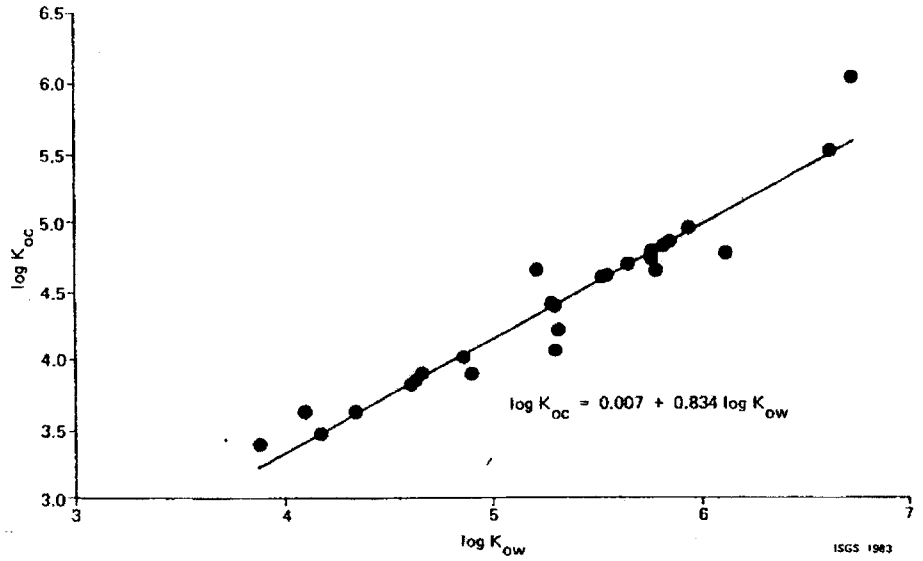

FIGURE 8. PCB K_{oc} vs. the K_{ow}.

useful in estimating the sorption of PCBs under many circumstances of soil and sediment conditions as well as bioaccumulation potential.

The sorption of nonionic organics has been related to the partitioning of an organic compound between an organic solvent (*n*-octanol) and water.[11,18,43,44,49] It follows therefore, that K_{ow} should be related to the tendency of the same compound to partition between water and soil organic matter. Figure 8 illustrates the relationship between K_{oc} and K_{ow} for PCBs. There is a high linear correlation between the two yielding the regression equation:

$$\log K_{oc} = 0.007 + 0.834 \log K_{ow} \tag{10}$$

VII. MOBILITY OF PCBs IN SOILS

The migration and vertical distribution of PCBs in soil profiles is a topic of much interest. A soil thin-layer chromatography (TLC) technique has been used to measure mobility of PCBs.[51] Soil TLC is a laboratory method of measuring the migration of a particular compound or element through a soil by using the soil as the sorbent phase and a developing solvent (water, landfill leachate, organic solvent, etc.) in a TLC system. The results are reported as R_f values, defined as the ratio of the distance the compound moved relative to the distance the solvent moved. The R_f value is a quantitative indication of the movement of a given compound in a soil-solvent system and a reproducible index of mobility.[52] The mobility of Aroclor® 1242 and Aroclor® 1254 in several earth materials was studied by Griffin and Chian[35] and expressed as frontal R_f values which are given in Table 5. The data indicate that under the conditions tested, Aroclor® 1242 and Aroclor® 1254 stayed immobile in these soil materials when leached with water and sanitary landfill leachates, but were highly mobile when leached with carbon tetrachloride. Similar results for polybrominated biphenyls (PBBs) and hexachlorobenzene (HCB) were also reported by Griffin and Chou.[53]

PCBs are nonpolar and are only very slightly soluble in polar solvents like water. Solubilities of Aroclor® 1242 and Aroclor® 1254 in distilled water have been determined to be approximately 288 and 42 ppb (see Table 1), respectively. However, PCBs are much more

Table 5
MOBILITY OF AROCLORS® 1242 AND 1254 IN SEVERAL SOIL MATERIALS LEACHED WITH VARIOUS SOLVENTS AS MEASURED BY SOIL-THIN-LAYER CHROMATOGRAPHY[35]

	R_f values					
	Water		Landfill leachate		Carbon tetrachloride	
Soil materials	1242	1254	1242	1254	1242	1254
Ava silty clay loam	0.02	0.02	0.02	0.02	1.00	0.96
Bloomfield loamy sand	0.03	0.03				
Catlin silt loam	0.02	0.02	0.04	0.04	1.00	1.00
Catlin loam	0.02	0.02	0.03	0.03	1.00	1.00
Cisne silt loam	0.03	0.02	0.03	0.02	1.00	1.00
Coal char (650°C)	0.03	0.03	0.04	0.04	1.00	1.00
Drummer silt loam	0.03	0.03			1.00	1.00
Flanagan silt loam	0.02	0.02	0.06	0.05	1.00	1.00
Ottawa silica sand	0.03	0.03	0.03	0.03	1.00	1.00

soluble in organic solvents such as acetone, methanol, benzene, or carbon tetrachloride. Griffin et al.[51] also tested the mobility of Aroclor® 1242 and Aroclor® 1254 in silica gel leached with acetone, methanol, benzene, carbon tetrachloride, and mixtures of water-acetone and water-methanol. They found the data consistent with the soil TLC data obtained by leaching with carbon tetrachloride; R_f values of 1.00 were obtained using the organic solvents. It is quite clear that mobility of PCBs in soil materials and silica gel is highly related to the solubility of PCBs in the solvent with which the TLC plates were being leached. In a soil column leaching study, Griffin and Chou[53] found that related compounds such as PBBs and HCB were not retained in the columns when ethanol was percolated through the soil columns. These data confirmed previous findings from soil TLC studies.

Leaching of water through soil containing PCBs may lead to the downward movement of PCBs, depending on the soil type and clay content. Moza et al.[54] incorporated ^{14}C-labeled 2,2′-dichlorobiphenyl in the top centimeter of a loamy sand at a concentration of approximately 1 ppm under field conditions. They found that the PCB dispersed to a depth of 30 cm during the first year and no radioactivity was detectable in the 30- to 40-cm layer. At the end of 1 year, when carrots grown on the test plots were harvested, concentrations of PCBs and their metabolites were highest in the 0- to 10-cm layer (0.24 ppm), intermediate in the 10- to 20-cm layer (0.17 ppm), and lowest in the 20- to 30-cm layer (0.03 ppm). Below 30 cm, the concentration of PCB and metabolites were less than 0.001 ppm. At the end of the second year, when sugar beets had been harvested, total PCB concentrations in the soil were 0.15 ppm in the top 10-cm layer, 0.04 ppm in the 10- to 20-cm layer, 0.02 ppm in the 20- to 30-cm layer, 0.008 ppm in the 30- to 40-cm layer, and 0.002 ppm in the leached water below the 40-cm depth. This study indicates that very small amounts of dichlorobiphenyls (or quite possibly a metabolite) moved below 40 cm in the soil; only 0.2% of the PCB-radioactivity applied to the soil appeared in leached water at the 40-cm depth over a period of 2 years.

Tucker et al.[10] studied the migration of PCBs in soil columns treated with Aroclor® 1016 and subjected to water percolation. The PCB application rate was 2.5% of soil weight, a very high rate for a land application system but more representative of landfill operations. The soils used were Norfolk sandy loam, Ray silty loam, and Drummer silty loam; the water application rates for each soil were 0.26, 0.53, and 0.32 ℓ/day, creating an essentially saturated flow. They concluded that soils containing more clay retained larger amounts of

Table 6
AROCLOR® 1016 FOUND IN PERCOLATING WATER FROM SOIL COLUMNS[10]

Norfolk sandy loam		Ray silty loam		Drummer silty clay loam	
Effluent vol. (ℓ)	PCBs (ppb)	Effluent vol. (ℓ)	PCBs (ppb)	Effluent vol. (ℓ)	PCBs (ppb)
1.3—8.1	ND	2.7—16.4	ND	1.6—9.9	ND
10.1	ND	20.7	65	12.5	ND
13.5	23	27.6	92	31.4	ND
48.1	63	51.9	153	59.2	ND

Note: ND means none detected.

Table 7
CLASSIFICATION OF SOIL MOBILITY POTENTIAL OF PCBs BY R_f, K_{ow}, OR K_{oc}[11,56]

Class	R_f	K_{ow}	K_{oc}
Very mobile	0.90—1.00	<1.2	0—50
Mobile	0.65—0.89	1.2—23	50—150
Medium	0.35—0.64	23—245	150—500
Low	0.10—0.34	245—6000	500—2000
Slight	—	—	2000—5000
Immobile	0.0—0.09	>6000	>5000

PCBs. The ease of leaching of Aroclor® 1016 from the different soil types (Table 6) was in the order: Norfolk sandy loam > Ray silty loam > Drummer silty clay loam. It should also be noted that this order of retention follows the organic matter content of these soils, as well as their clay content; the conclusion of the authors may be in error regarding the active fraction of the soil that caused the observed retention. Regardless of the mechanism involved, approximately 0.05% of total Aroclor® 1016 in the soil column was leached from the soil during the 4-month period when 50 to 100 ℓ of water had passed through the soil. This high percolation rate is equivalent to 15 to 30 m of rainfall, assuming no runoff or evaporation. Tucker et al.[10] also observed that the less chlorinated and more degradable species leached from soils more readily than highly chlorinated and more resistant PCBs. This was later confirmed by Suzuki.[55] Thus, the more resistant PCBs are retained in the surface soil layers.

The vapor loss of PCBs from soils depends strongly upon their adsorption characteristics by soils. Haque et al.[7] have shown that the vapor loss of Aroclor® 1254 from a sand surface was significant which could have been due to the poor sorption capacity of sand. When, similar experiments were carried out with a soil, the loss was very low.

The relative mobility of PCBs in soils can be classified using the parameters of R_f, K_{ow}, and K_{oc} discussed above. The soil mobility classes assigned to the various values of these three parameters are given in Table 7. The values of the various parameters assigned to each mobility class are somewhat arbitrary, but have been chosen from experience based on the relative mobility of these compounds in the environment.[11,56]

VIII. SURFACE RUNOFF

There are several ways by which PCBs get into the environment. One of these is by

runoff from industrial wastes, dumps, and spills. Other sources are the points of manufacture and the plants where PCBs are processed into other products. PCBs can escape through the plant ventilation and exhaust system into the atmosphere and through its waste treatment system into sewers or directly into waterways. PCB input into fresh water by industries has been high in the past, and PCBs have accumulated in sediments.[57,58] Even if PCB input were stopped today, these sediments could continue to release PCBs into freshwater systems for years to come.

Nisbet and Sarofim[59] estimated that 4000 to 5000 tons/year of PCB were discharged into fresh and coastal waters in the peak year of PCB use. This estimate was based upon figures and industrial and disposal practices in effect at that time. Of the total PCBs, about 1000 tons may be assumed to have consisted of pentachlorobiphenyls. Analysis of waste waters and of surface water runoff entering the Southern California Bight since 1971 has shown that trichlorobiphenyls have constituted the majority of the total PCB residues. In this area, PCB input into the sea from waste waters is considerably higher than the input from surface runoff.

Martel et al.[66] reported that PCBs were found in the suburban watershed of Reston, Va. PCB concentrations in the Lake Anne basin increased going from water (<0.05 to 0.2 ppb), to bed sediment (<2.5 to 105 ppb), to fish (140 to 700 ppb) in an average ratio of 1:500:3000. The highest concentrations were observed in the lake itself, which is 10 years old, and receives no sewage or industrial waste discharges. Evidence indicates that the PCBs originated from diffuse sources associated with urban development and urban living and entered the hydrologic system through storm-water runoff. They also found that the PCB concentrations in sediment samples from two areas which were receiving rainfall runoff from two active construction sites were much higher than those from other streams feeding the lake. In the early 1970s, PCBs were commonly used in the formulation of plasticizers, adhesives, surface coatings, sealants, and fire-retardant compositions.[4,27] This suggests that building materials would be one possible source of PCBs.

In the summer of 1976, a serious spill of PCBs and chlorobenzenes was detected in Regina, Saskatchewan, Canada.[61] Approximately 6800 to 9100 ℓ of transformer oil containing PCBs (Aroclor® 1254) and chlorobenzene were spilled when an underground pipe broke at a transformer manufacturing plant. Large quantities of PCBs were found to have migrated both vertically and horizontally at the site. There was also strong evidence that the contaminants were being redistributed by surface processes. At the plant site, Roberts et al.[61] reported that PCB levels were up to 1000 ppm along some of the routes of surface drainage and zones of sediment accumulation after rainstorms. The sludge obtained from the catch basin in the street, which received the runoff, contained 20 ppm PCBs. The PCB levels at the surface in one area, which received the runoff from the highly contaminated area of the plant site ranged from less than 2 to 250 ppm.

A similar incident of a PCB spill occurred in a rural area near Kingston, Tenn. in 1973.[62] The spill resulted in the environmental contamination of two watersheds because the spill site was situated on the crest of a hill. Through the influence of rainfall, geological factors, and characteristics of the overlying stratum of soil, the chemical was subsequently dispersed through the soil both horizontally and vertically. The spread of the Askarel (a commercial mixture of Aroclor® and chlorinated benzenes) was also affected by the movement of contaminated surface water resulting from mass rainfall in the weeks immediately following the spill.

There are two potential means for PCBs to be transported at the surface: as a dissolved phase in water or as a sorbed phase on sediments. In the above cases of chemical spills, chlorobenzenes may play an important role in the movement of PCBs through soils. In previous soil-thin-layer chromatography studies,[34,35] it has been demonstrated that the mobilities of PCBs, PBBs, and HCB in soils were directly proportional to the solubility of the compounds in the leaching solvents.

Horn et al.[58] reported that measurable quantities of PCBs were leaching or eroding from some landfills and dredge spoil sites in the Upper Hudson River Basin. PCB losses to groundwater at the dredge spoil sites and at the landfills and dumps were approximately 44.4 kg/year and 172 kg/year, respectively. The results indicated that the landfills and dumps appeared to be larger contributors to the surrounding environment than the dredge-spoil areas. The erosion losses of PCBs from the same sites were 32.2 kg/year and 172 kg/year, respectively. The upper Hudson Basin delivered approximately 2.6 t of PCBs to the estuary in 1977.[58]

IX. PLANT UPTAKE

Since PCBs are strongly sorbed on carbonaceous materials and sediments, it is not surprising to observe that they are sorbed onto plant roots as well. Using Aroclors® 1242 and 1254, Suzuki[55] observed that soybean sprouts accumulated more lower chlorinated biphenyls than the higher chlorinated isomers during the first 2 weeks of exposure from a sandy soil containing 100 ppm PCBs. This may be due to the higher solubility and mobility of these isomers, thus allowing them to move to the plant root. A few gardeners in Indiana who used PCB contaminated sludge found that their vegetables had also picked up PCBs. Beets contained 0.6 ppm PCBs when grown in soil containing 4 ppm PCBs.[5] Grass clipped from a field with 8.5 ppm in the soil contained 1.16 ppm PCBs.[5]

Moza et al.[54] applied radioactive 2,2-dichlorobiphenyl to soils at a concentration of approximately 1 ppm. Carrot roots contained 0.24 ppm of 2,2′-dichlorobiphenyl while the phenolic metabolites from this PCB were found at a concentration of 0.012 ppm. In a similar study, Iwata et al.[63] found that 97% of the total absorbed Aroclor® 1254 remained on the carrot peel and very little was translocated into the plant tissue. Fries and Marrow[64] also reported that soybean plants grown on PCB contaminated soil would not be contaminated by root uptake and translocation, but some foliar contamination could occur from vapor sorption.

X. SUMMARY AND CONCLUSIONS

The aqueous solubility of PCBs is very low, ranging from 2.7 ppb for Aroclor® 1260 to 3500 ppb for Aroclor® 1221. Water-soluble PCBs were found to be richer in the lower-chlorinated isomers than were the original PCB fluids.

PCBs are strongly sorbed by soil materials. There is a very high direct correlation between the TOC content of the soils and the amount sorbed. The sorption and retention of PCBs by soils and soil constituents are influenced by the number of chlorine atoms in the molecule; the more highly chlorinated derivatives are more tenaciously held. The K_{oc} can be estimated from the water solubility of a PCB.

The higher-chlorinated isomers are preferentially sorbed to the organic matter of soils and suspended solids. Significant amounts of PCBs have been redistributed in the environment by surface-water runoff containing PCB contaminated soil particles. Sorption of PCBs onto suspended solids and their subsequent incorporation into sediments is considered the major mechanism for their immobilization in aquatic systems. However, the persistence of PCBs in sediments makes desorption a possibility for years after incorporation.

The vapor loss of PCBs from soils depends strongly upon their sorption to soils. The vapor loss of PCBs from a soil surface was very low but was significant from sand. The sorption of PCBs greatly influences their dynamics in soils. The diffusion, leaching, and vapor loss of PCBs in soils is retarded as the extent of sorption increases. The degree of sorption increases directly with an increase in organic matter content of a soil.

Highly chlorinated PCBs are not degraded or leached through soil by water to any sig-

nificant extent. They are also apparently not taken up by plants and are thus not readily mobile in surface soil systems. However, PCBs do have a moderate vapor pressure and a likely path for redistribution or migration in soils may be by vapor phase transport through the unsaturated pores.

The above findings are significant to the land disposal of PCBs and related wastes. To prevent potential migration of PCBs from a landfill, PCB wastes and organic solvents should not be disposed of in the same landfill location, and should not be allowed to come in contact with leaching organic solvents.

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