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Attenuation of Polychlorinated Biphenyls in Soils: Literature Review

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SUMMARY

Polychlorinated biphenyls (PCBs) have found their way into a wide variety of industrial applications, a major one being coolant-insulation in transformers. Perceived toxicity to humans and other organisms in conjunction with environmental persistence has led to a highly regulated climate of PCB use. Due to the ubiquity and persistence of PCBs, the ability to predict their long-term mobility in the soil-water environment is of particular interest to the electric utility industry and regulatory agencies.

This report reviews the current literature on 1) PCB attenuation in soils and subsoils, and 2) conceptual and mathematical models that deal with hydrophobic sorption in soils and subsoils and thus may be applicable to PCB studies. Because recent research has suggested that toxicity attributed to PCBs may be caused or enhanced by other closely associated compounds such as polychlorinated dibenzodioxins (PCDDs) or polychlorinated dibenzofurans (PCDFs), this report also briefly reviews the available literature on PCDD and PCDF attenuation in soils (PCDF attenuation data were virtually absent in the literature at the time of this review). The report identifies key issues where conflicting information exists; gaps or deficiencies in available data or in an understanding of the sorption/desorption processes; and models and estimation techniques that have not yet been tested quantitatively but may be applicable for describing the role sorption/desorption plays in determining the mobility of PCBs and related hydrophobic compounds such as PCDDs and PCDFs. Based on this review, the following conclusions were reached.

1. For aqueous solvents and soils containing 'typical' organic carbon (OC) concentrations ($0.1\% < OC < 15\%$ by weight), insufficient equilibrium sorption data exist for PCBs to 1) reliably test the applicability of sorption models for sorption of individual PCB isomers or Aroclor mixtures (although a few preliminary tests may be made), and 2) make accurate, scientifically defensible predictions of PCB mobility in soils.

2. Conflicting information and active debate exist regarding the rates and reversibility of the PCB sorption/desorption process for typical OC soils in aqueous solvents. The rates at which equilibrium conditions are achieved and the existence of sorbed PCB fractions, which are desorbed rapidly (hours), desorbed very slowly (months) or not

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desorbed at all, must be understood and quantitatively modeled if we are to predict PCB soil/subsoil mobility.

3. No data or models exist for PCB sorption/desorption/reversibility under equilibrium or nonequilibrium conditions for aqueous-soil systems where the soils contain less than 0.1% OC. These "low" organic carbon levels are typical of subsoils and subsurface ground water aquifer materials. Polychlorinated biphenyls mobility in these materials may differ significantly from that in typical OC soils.

4. Models are currently under development for describing sorption/desorption/reversibility of organic compounds (pesticides) on various sorbents in miscible aqueous-organic or pure organic solvent systems; however, these models have not been used or tested for PCBs. Research in this area along with investigation of the effects of cationic and anionic surfactants on sorption processes would provide a sound basis of understanding and possible improvements for soil washing methodologies.

5. Volatilization and chemical degradation of PCBs in soils have not received sufficient attention. The effect of different soils with a wider range of OC and clay mineral content should be examined under different water saturation conditions. It is also important to determine the degradation products and not merely the extent of 'loss' since loss can be due to a number of nondegradation processes.

6. Migration of PCBs as an adsorbed phase (i.e., transport on particles) and as an immiscible phase (i.e., as a pure compound or as a compound/organic solvent phase) also should be considered in any attempt to predict the transport of these compounds.

Future work on PCB sorption, volatilization, and abiotic degradation is needed to establish a more comprehensive data base. Attenuation models, when incorporated into solute and multiphase transport models, will yield predictive tools for describing migration of PCBs and related nonionizable hydrophobic compounds from the near-field region of initial contact with the soil to the far-field region of the adjacent groundwater aquifer and beyond. Based on these predictive tools for describing migration, the associated risk assessment and subsequent decisions can be made as to whether cleanup is required.

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Section 1

INTRODUCTION

Polychlorinated biphenyls (PCBs) have been manufactured and used industrially since the early 1930's. Their thermal stability, chemical stability (e.g., general inertness to oxidation and hydrolysis), and dielectric properties have made them very useful in a variety of industrial applications. They have been used as coolant-insulation fluids in capacitors and transformers; for impregnation of cotton and asbestos in braided insulation of electrical wiring; as plasticizer in wire, cable coatings, and vinyl chloride polymer films; as lubricants and gasket sealers; as high-pressure hydraulic fluids; as heat transfer agents; as machine tool cutting oils; as protective coatings for wood, metal, and concrete; for adhesives; and for carbonless reproducing paper (Gustafson 1970).

Polychlorinated biphenyls have been found in environmental and biological samples in many locations and are thought to have a tendency to bioaccumulate (Pal et al. 1980). Their widespread distribution has been attributed to volatilization or aerosol formation and atmospheric transport followed by wet or dry deposition. Evidence of chronic toxicity in birds and in man has been presented (Gustafson 1970), though recent research has questioned whether the toxicity may be caused or enhanced by other compounds such as polychlorinated dibenzodioxins (PCDDs) or polychlorinated dibenzofurans (PCDFs) (Josephson 1984; Vuceta et al. 1983).

The properties and environmental persistence of PCBs depend on their degree of chlorination. For example, PCBs with fewer than four chlorine atoms can be biodegraded fairly readily by a number of microorganisms, whereas PCBs with greater than four chlorine atoms are resistant to biodegradation (Callahan et al. 1979). Less chlorinated PCBs tend to be more volatile, while the more chlorinated PCBs tend to be more readily sorbed to suspended solids or sediments or incorporated into biota. Polychlorinated biphenyls are extremely resistant to oxidation and to acidic and basic hydrolysis. The more highly chlorinated species have been shown to undergo photolysis in organic media, with the possible formation of PCDFs as well as dehalogenated products (Safe et al. 1976 in Callahan et al. 1979). However, photolysis is probably not a significant factor affecting PCBs sorbed on soils in natural systems. PCBs are sorbed rapidly onto soils because of their low water solubilities

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and high octanol-water partition coefficients. Of even more environmental significance is the evidence that PCBs are desorbed slowly from sediments and may contribute to long-term degradation of water quality (Callahan et al. 1979). Much less is known about the environmental behavior of PCDDs and PCDFs; both are susceptible to photolysis, but, as with PCBs, this mode of degradation is relatively unimportant in soils. Tetrachlorodibenzodioxin (TCDD) is strongly sorbed by and is very persistent in soils, is resistant to biodegradation, is not bioaccumulated, and is thought to be immobile in all but very sandy soils (Yuceta et al, 1983).

Because of the ubiquity and persistence of PCBs, and the toxicity and persistence of PCDDs and PCDFs, it would be useful to be able to quantitatively predict their behavior in the soil-water environment so that their potential for environmental migration can be determined. Based on these predictions and on associated risk assessments, a decision can be made as to whether clean-up is required and is cost-affective. To attain this goal, specific data are needed for a variety of soil and water conditions as well as predictive models. In this report the literature on PCBs has been reviewed, and the available data are summarized in Section 2 in a format that will be useful for modeling efforts. In addition, information related to PCDD attenuation in soils is included at the end of Section 2. Because of the virtual absence in the literature at the time of this review of attenuation data on PCDFs in soils, no discussion for PCDF attenuation is included. The literature on available models is reviewed in Section 3 to determine which may be applicable to PCBs and other related hydrophobic organic compounds. Based on the findings in Sections 2 and 3, Section 4 recommends an integrated program of experimental work and model development.

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Section 2

LITERATURE REVIEW OF PCB ATTENUATION IN SOILS

This section reviews the available literature on PCB attenuation in soils, with an emphasis on sorption. Additional information was sought on two closely associated hydrophobic compounds, namely the PCDDs and PCDFs, however because of the dearth of published literature on PCDD sorption and an almost total lack of literature concerning PCDFs in soils, this report focuses on PCB data in soils. The available published PCDD data are discussed separately at the end of this section.

The general topics covered in this section for PCBs include linear partition coefficients or distribution ratios in soils and sediments; Freundlich isotherms; Langmuir isotherms; organic carbon partition coefficients (K_{OC}); water solubility; octanol-water partition coefficients (K_{OW}); reversibility of sorption; kinetics of sorption; mobility studies in aqueous and organic solvent systems (soil thin layer chromatography, soil column, and other migration studies); field studies; and the effect of soils on volatilization, plant uptake, and degradation. In some cases, the published literature deals with individual PCB congeners; in others, with mixtures, usually one or more of the Aroclors; and for still other cases, with spills of actual capacitor fluids. In this section the available information is sorted and summarized so that contradictions and deficiencies in the data can be determined and the data can be organized in a format that makes it more readily accessible for modeling.

EQUILIBRIUM SORPTION: PARTITION COEFFICIENTS AND SORPTION ISOTHERMS

Reasonable agreement between theoretically derived partition coefficients and actual (laboratory or field) values suggests that equilibrium sorption is a good method for describing accumulation of nonpolar organic compounds on soils, sediments, and particles (Pavlou 1980). Almost all of the PCB sorption data in the literature have been described in terms of the Freundlich isotherm, the partition coefficient or the distribution ratio. In one exception, Weber et al. (1983) also apply the Langmuir model, though they conclude that this model fits the data poorly, especially at "high" solution concentrations.

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The partition coefficient (K_p) is defined as the ratio between the amount of compound sorbed on a sorbent surface and that in solution at equilibrium:

$$K_p = \frac{S}{C} \quad (2\text{-}1)$$

where S is the amount of compound sorbed per unit weight of sorbent (μg/g) and C is the equilibrium concentration of compound in solution (μg/mL). When such ratios are determined for a range of solution concentrations, the plot of S versus C is termed a sorption isotherm.

The distribution ratio, K_D, is the appropriate sorption parameter for describing a mixture of congeners and is defined by

$$K_D = \frac{S_{an}}{C_{an}}$$

where S_{an} and C_{an} are the total analytical concentrations of all sorbed and solution congeners, respectively.

The Freundlich isotherm model represents an empirically derived relationship between the amount sorbed and the equilibrium solution concentration:

$$S = K_F C^{1/n} \quad (2\text{-}2)$$

where K_F is the Freundlich sorption coefficient and 1/n is an empirical constant. When 1/n = 1, the Freundlich isotherm reduces to a linear partition coefficient.

The Langmuir isotherm is theoretically derived by assuming that the sorption at a given site is independent of the number of other sites already occupied. Its mathematical expression is

$$S = \frac{S^{max} K_L C}{1 + K_L C} \quad (2\text{-}3)$$

where S^{max} is the monolayer sorption capacity and K_L is the Langmuir sorption coefficient (Weber et al. 1983).

Partition coefficients are frequently normalized to the organic carbon content of the soil (Karickhoff et al. 1979). In this report we have calculated the organic carbon partition coefficient, K_{OC}, from both K_p and K_D values according to the formula $K_{OC} = \frac{K \times 100}{\%OC}$, where K is either K_p or K_D. For more information about the derivation and characteristics of these various partition coefficients, see Section 3 of this report.

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Table 2-1

SORPTION COEFFICIENTS OF PCBs

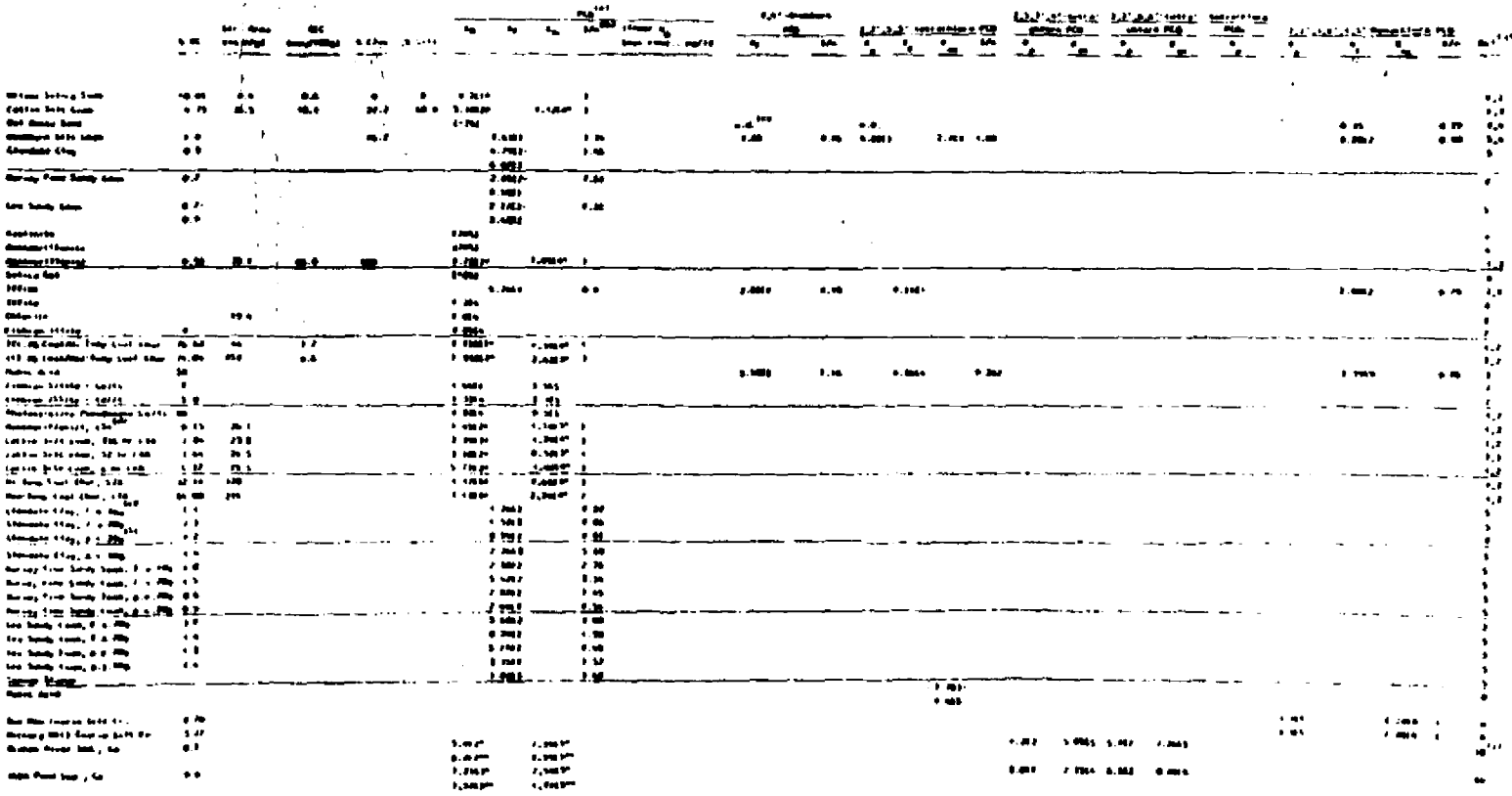

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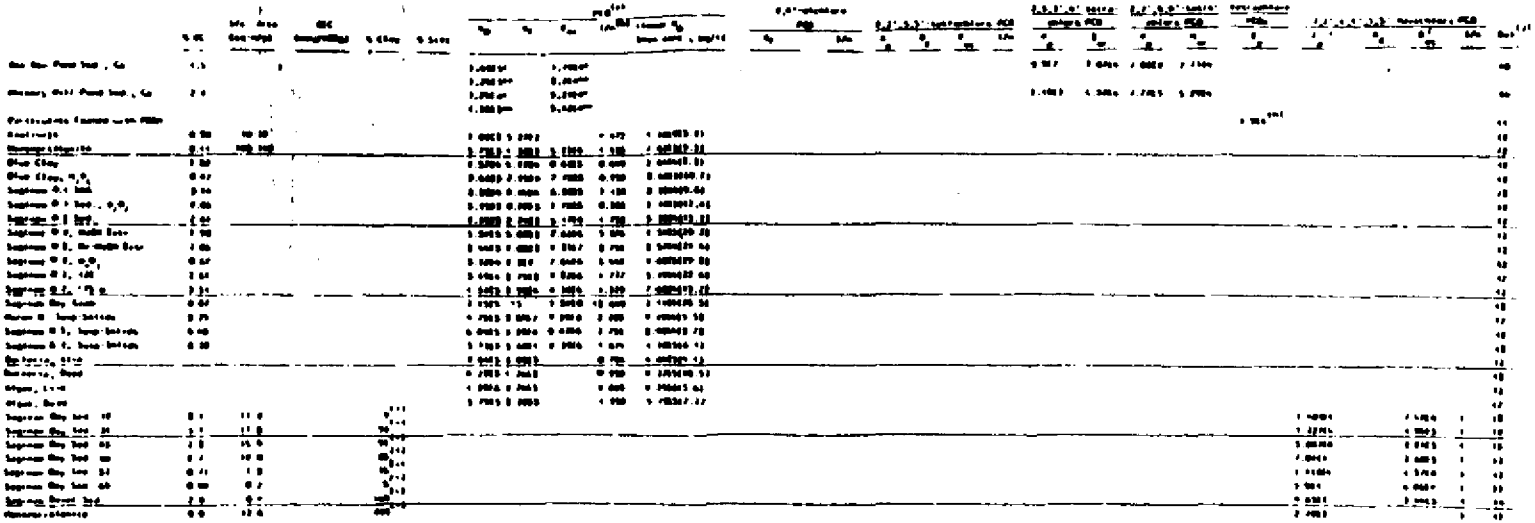
Table 2-1

(cont'd)



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The results of studies designed to determine the sorption coefficients of various PCB isomers or mixtures are shown in Table 2-1. The sorbent matrices studied include soils, sediments, clays, coals, sewage sludge, and biological organisms. Some of the sorbents have been treated by a variety of means (low-temperature ashing, solvent extraction, peroxidation) in an attempt to vary their organic carbon content. Unfortunately, such treatments may also affect the inorganic constituents and other properties of the sorbents (such as surface area, pore distributions). Because most of these parameters are not usually determined or reported in the reviewed papers, changes in sorption coefficient cannot be attributed solely to changes in organic carbon content. Thus, results with such treated sorbents must be interpreted with caution.

The organic carbon contents of the sorbents in Table 2-1 varied from <0.01% for a silica sand to 76.6% for a coal char; most soils were above 0.5%. The organic carbon contents were not given for most of the clays. Surface areas (SA) were noted in four references and ranged from 0.2 to 253 m^2/g. Cation exchange capacity was determined in two references and ranged from 0.0 to 85.0 meq/100 g. The observed variations in K_0, Freundlich parameters, and K_{oc} for the PCB mixtures in Table 2-1 are summarized in Table 2-2a. Isotherm linearity generally applied at low solution concentrations, the exact concentration depending on the sorbent (Weber et al. 1983). At higher concentrations, the nonlinear relationship fits the Freundlich model (Weber et al. 1983). K and K_{oc} increased with decreased temperatures (Weber et al. 1983). It should be noted that most of the PCB sorption data in Table 2-1 were obtained for PCB mixtures (Aroclors) containing several PCB congeners. Because

Table 2-2a

RANGE OF DISTRIBUTION RATIOS FOR PCB MIXTURES

Parameters	Range	Number of Sorbents[a]
K_{oc}	1.6E3 to 1.6E7	32
K_0	2.2E1 to 6.1E5	36
K_F	<1 to 4.2E4	34
1/n	0.39 to 12.4	45

[a]Organisms are excluded.

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the partition coefficients for individual congeners differ, the use of K_{OS} to describe the PCB mobility in the environment must be interpreted with caution (see page-3-5 of this report).

A few cases are shown in Table 2-1 where individual congeners were studied. The range of partition coefficients and other sorption model parameters for these congeners are summarized in Table 2-2b. The organic carbon content in the sorbents in Table 2-2b ranged from 0.06% to 58%. The variation in K_{oc} values is smaller than for K_p or K_F values. This decreased variability is consistent with the hypothesis that soil organic carbon is a dominant factor in sorption of hydrophobic organic compounds (Karickhoff et al. 1979). While K_{oc} values show some overlap among the different congeners because of the wide range of soil types used, K_{oc} tends to increase with increased degree of chlorination. The relative sorption of individual congeners as part of Aroclor mixtures was also observed using gas chromatography (GC) (Griffin and Chou 1981; Lee et al. 1979). The congeners with fewer chlorine atoms tended to be sorbed less than those with more chlorine atoms (Griffin and Chou 1981; Lee et al. 1979). A comparison was also made between sorption of Aroclor 1242 and used capacitor fluids that had the same congener distribution patterns; no significant differences in sorption were found in the five soils studied (Griffin and Chian 1980).

Table 2-2b

RANGE OF PARTITION COEFFICIENTS FOR INDIVIDUAL CONGENERS

Parameters	Dichloro PCB	Tetrachloro PCB	Hexachloro PCB
K_{oc}	--	2.7E3-1.3E5 (n=5)[a]	6.1E4-7.4E6 (n=9)
K_p	--	4.9E1-1.3E3 (n=5)	3.6E1-1.5E4 (n=10)
K_F	7.0-4.0E3 (n=3)	2.1E1-4.4E4 (n=2)	3.5E1-3.4E9 (n=4)
1/n	0.85-1.19 (n=3)	0.26-1.09 (n=2)	0.26-0.80 (n=4)

[a] n = number of sorbents studied.

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Further analysis of Table 2-1 points out a number of gaps in the sorption data available for PCBs. (Also, see Section 4 of this report for recommendations.) First, few data are available dealing with sorption of the individual congeners or the congeners as part of the mixture (with the exceptions noted above). Such data are needed both for a single soil as a function of chlorine number and for a number of soils with varying organic carbon and swellable clay contents. Second, while most authors include numbers for sorbent organic carbon content, these data are generally lacking for the clays. Other potentially important soil parameters, such as surface area measurements (including determination of the appropriate methodology to use for these measurements) and clay mineralogy, are too frequently unavailable. And third, while the sorbent organic carbon content covers a wide range of values above 0.5%, very few soil samples with organic carbon <0.1% have been examined. Such low organic carbon soils are typical in the subsurface environment or in highly oxidized surface soils, both of which may influence the transport of PCBs. In these low carbon soils, the presence of swellable clays is considered especially important in sorption (see Section 3 of this report).

The information presented in Table 2-1 may be used to determine whether initial attempts (with even smaller data sets) (Griffin and Chou 1981; Lee et al. 1979; Steen et al. 1978) to correlate K_p for PCBs with sorbent organic carbon content and surface area are valid. These studies show that linear correlations for PCBs exist between K_p and OC for the soil types examined (usually four to five soils, sometimes of limited OC range): for example, $K_p = 255 + 18.5$ OC ($r^2 = 0.87$) (Lee et al. 1979). Steen et al. (1978) observed that partitioning of two tetrachlorobiphenyl isomers was linear with OC for four soils (0.4% to 2.5% OC). However, using the same soils, Steen et al. (1978) observed that partitioning of the Aroclors was independent of OC, which he attributed to the narrow OC range. Data in the available literature are too limited for any definite conclusions to be drawn, but one can speculate that correlations that are valid for individual PCB isomers may not be applicable to Aroclor mixtures. In general, the sorbent organic carbon content is thought to be the dominant factor controlling PCB sorption. It is not known at what threshold levels of organic carbon this relationship breaks down for PCBs. The existence of such a threshold dependant on the ratio of organic carbon content to clay mineral content has been suggested by Karickhoff (1984) for hydrophobic organic compound sorption (see Section 3 of this report). This hypothesis needs further examination specifically directed at PCBs.

Parameters other than the OC may also be important in sorption. Significant linear correlations were also found between K_p and sorbent surface area (measured by the

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BET gas-adsorption method with CO_2 as adsorbate, which gives a measure of external surface area as well as micropore area) (Griffin and Chian 1980); for example, $K_p = 230 + 6.64\ SA$ ($r^2 = 0.82$) (Lee et al. 1979). It is interesting to note that the correlation was much weaker when sorbent surface area was measured by the BET gas-adsorption method with N_2 as adsorbate. Strek (1980) observed that the quantities of sorbent required to sorb 50% of the applied PCBs increased in the following order: a peaty muck < montmorillonite < sand < peroxide-treated sand. This sequence incorporates variations in both organic carbon content and specific surface area. The relative amounts of sorbent required indicate that while both parameters play a role, the OC predominates, a relationship also observed by Griffin and Chian (1980); for example, $K_p = 188 + 3.36SA + 11.4\ OC$ ($r^2 = 0.82$) (Lee et al. 1979). Hassett et al. (1984) point out that the molecular weight of the organic matter (humic acids in water) may also make a difference in the degree of sorption; these authors showed a general increase in K_{oc} with molecular weight above 50,000 daltons. Scharpenseel et al. (1978) similarly showed that PCBs attach preferentially to humic acid rather than to fulvic acid but also indicated that PCBs bind to nonhumic organic constituents. Fairbanks and O'Connor (1984) also observed that sorption properties of sewage sludge differ from native soil organic matter; therefore, correlations of K_{oc} with organic carbon content for sewage sludge may not be at all valid for use with soils. Thus, a knowledge of the properties of the organic matter (molecular weight, functional groups, hydrophobicity, structure) is also important in studying sorption characteristics.

PHYSICAL CONSTANTS: WATER SOLUBILITY, K_{ow}, VAPOR PRESSURE

A number of studies deal with determination of the physical constants of PCBs that influence their migration in soils. Attempts have been made to use some of these physical constants such as water solubility (S) and octanol-water coefficients (K_{ow}) to predict partition coefficients and environmental migration (see Section 3). The largest amount of data is available for K_{ow}, less is available for water solubility, and still less for vapor pressure. The octanol-water partition coefficient, K_{ow}, is defined as the ratio of the concentration of a chemical in octanol to that in water in an equilibrated octanol-water system:

$$K_{ow} = \frac{\text{concentration in octanol phase}}{\text{concentration in aqueous phase}} \qquad (2\text{-}4)$$

It has been measured for a large number of PCB congeners by a reverse-phase high-pressure liquid chromatography (RPHPLC) technique (Rapaport and Eisenreich 1984). Water solubilities are given in mg/L or ppm, vapor pressures are in torr, and K_{ow}s

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are dimensionless. Literature values found for these physical constants are summarized in Table 2-3 for the various individual congeners and mixtures of PCBs.

The reported water solubilities of the congeners range from 0.40 to 5.9 ppm for the three monochloro isomers, from 0.06 to 1.9 ppm for four dichloro isomers, from 0.08 to 0.25 ppm for four trichloro isomers, from 0.027 to 0.17 ppm for seven tetrachloro isomers, from 0.01 to 0.031 ppm for three pentachloro isomers, from 0.00095 to 0.0088 ppm for one hexachloro isomer, 0.007 ppm for one octachloro isomer, and 0.015 ppm for the decachloro isomer (Chiou et al. 1977; Griffin and Chian 1980; Haque and Schmedding 1976; Kalmaz and Kalmaz 1979; Kilzer et al. 1979). Although there is considerable overlap in the solubilities from one set of isomers to the next, the general trend is for a decrease in water solubility with an increase in number of chlorine atoms as expected. In each set of congeners with the same number of chlorines, certain congeners were relatively soluble compared to others (Griffin and Chian 1980). These include 2-monochloro-, 2,4'-dichloro-, 2,2',5-trichloro-, 2,2',3,5'-tetrachloro-, and 3,3',4,4'- tetrachloro-biphenyls. The water solubilities of a few congeners as components of Aroclor 1242 were also measured (Griffin and Chian 1980). The water solubilities of these 'component congeners' were typically less than the corresponding solubilities of the individual congeners, sometimes by as much as one and one-half orders of magnitude. The Aroclor solubilities themselves ranged from 3×10^{-3} to 15.0 ppm, depending on the relative amounts of PCB congeners (Griffin and Chian 1980; Kalmaz and Kalmaz 1979; Pal et al. 1980). One problem with some of these data is that the temperature at which the water solubility was measured is not always given in the literature.

The log K_{ow} values for the individual congeners follow a similar pattern as the water solubilities; that is, while there is considerable overlap from one group of isomers to the next, the general trend is for an increase in log K_{ow} with increasing chlorine content starting from ~4.4 for the monochloro isomers and continuing to 7.75 for one hexachloro isomer (Chiou et al. 1977; Rapaport and Eisenreich 1984). The Aroclor trend is also similar, with the less chlorinated Aroclor 1221 having a log K_{ow} of 2.81 and the more highly chlorinated Aroclor 1260 having a log K_{ow} of 4.34 (Pal et al. 1980). Octanol-water coefficients have been correlated with water solubilities for 34 organic compounds with a range of structures, including three PCBs (Chiou et al. 1977); for example, log K_{ow} = 5.00 - 0.670 log S (r^2 = 0.97). Organic carbon partition coefficients for a range of organic compounds have also been correlated with K_{ow} values and with water solubilities for ten hydrophobic compounds including one PCB using a coarse silt sediment (Karickhoff et al. 1979); for example, K_{OC} = 0.63 K_{ow} (r^2 = 0.96); log K_{OC} = -0.54 log S + 0.44 (r^2 = 0.94).

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Table 2-3

PHYSICAL PROPERTIES OF PCBs

	Water Solubility (ppm) [Temperature in (°C)]				Log K_{ow}	Vapor Pressure (mm Hg) [Temperature in °C]
	Ref. [1]a	Ref. [2]	Ref. [3]	Other Refs.	[Ref.]a [Ref.]	
Aroclor 1221		15.0	1.5[23C]		3.01[3]; 4.14[7]	1E-5[2]
Aroclor 1232		1.45			3.23[3]; 4.8-5.2[7]	
Aroclor 1242	2.4E+1	2.4E+1	7.03E+1[23C]		3.94[3]; 4.9-5.8[7]	4.06E-4[1]
Aroclor 1248	5.4E-2	5.4E-2			4.17[3]; 5.0-6.5[7]	4.9E-4[1]; 1.15E-4[25C][2]
Aroclor 1254	1.2E-2	1.2E-2	7.9E-3[23C]	1.0E-2[6]	4.18[3]; 5.1-6.5[7]	7.71E-5[1]
Aroclor 1260	2.7E-3	2.7E-3			4.34[3]; 5.8-7.5[7]	4.05E-4[1]; 4E-5[2]
Aroclor 1016		3.4E-1	9.08E+1[23C]		3.40[3]; 4.5-5.6[7]	
PCB, general				7.0E-1[5]		
2-chloro	5.9				4.80	
3-chloro	1.8				4.42	
4-chloro	4.19		4.0E-1	1.3E-2[6]	4.60	
2,2'-dichloro	1.50		9.0E-1	2.1E-2[6]	4.89	
2,6'-dichloro	1.00		6.37E-1	1.30E+1[6]	5.10	
3,3'-dichloro					4.89	
3,5-dichloro	1.40				5.30	
2,5-dichloro					5.30	
2,6-dichloro					5.31	
4,4'-dichloro	0E-2			6.0E+2[23C][7]	4.89;5.50[6][7]	
2,2',3-trichloro					5.21	
2,2',4-trichloro					5.76	
2,3',5-trichloro	7.40E-1		7.4E-1	6.1E-2[6]	5.50	
2,3',6-trichloro					5.40	
2,3,6-trichloro					5.89	
2',3,4-trichloro					5.57[8]	
2,3,4'-trichloro					5.62	
2,3,5'-trichloro					5.76	
2',3,5-trichloro	7.0E-2					
2,4,6'-trichloro	0.5E-2				5.00	
2,4,5-trichloro					0.25	
2,4',5-trichloro				1.4E-1[25C][9]	5.69	4E-4[8]
2,5',6-trichloro					5.75	
3,3',5-trichloro					5.15	
3,4,4'-trichloro					5.96	
2,2',5,5'-tetrachloro	3.4E-2				5.96	
2,3',4,5-tetrachloro					6.11	
2,3',5,5'-tetrachloro	7.7E-1				5.81	
2,2',6,6'-tetrachloro	6.0E-2				5.20	
2,3',4,4'-tetrachloro					6.22	
2,3',4,5'-tetrachloro	9.0E-2		2.05E-1	2.23E-2[10]	6.00	
2,3',4',5-tetrachloro					5.86	
2,3',4,4'-tetrachloro	5.0E-2				6.21	
2,3',6,5'-tetrachloro	6.1E-2				6.25	
2,4,6,5'-tetrachloro					6.07	
2,3,3',6',6-pentachloro	1.75E-1				5.82;6.53[8]	
2,3',4,6,6'-pentachloro					6.61	
2,3',5,6,5'-pentachloro	2.2E-2				6.37	
2,3',5',6,5-pentachloro					6.07	
2,3',6,6'-tetrachloro					6.51;5.45[8]	
2,3',3,5,5'-pentachloro					6.91	
2,3',3,3',6'-pentachloro					6.38	
2,2',6,6',3-pentachloro					7.21	
2,3',6,5,5'-pentachloro	3.4E-3			1.0E+2[23C][7]	7.07;8.11[6][7]	
2,3',6,6',6-pentachloro				3.1E-2[25C][9]		
2,3',6,6',5-pentachloro					7.13	
2,3',3,3',6-pentachloro					6.66;6.76[8]	
2,3',5,3',6-pentachloro					6.86	
2,3',3,3',6,6'-hexachloro					6.56	
2,3',3,3',6,3-hexachloro					7.53	
2,2',3,3',6,5'-hexachloro					7.39	
2,3',3,3',5,6'-hexachloro					7.15	
2,3',3,3',6,6'-hexachloro					6.81	
2,2',3,6,6',3-hexachloro					7.64;7.71	
2,3,3',5,5',6-hexachloro					7.32	
2,2',6,6',5,5'-hexachloro	0.0E-0			0.5E+0[23C][7;10]	7.75;8.72[6;7]	
2,2',3,6',3',6-hexachloro					7.28	
2,3',3,6,3,5'-hexachloro					7.59[8]	
2,2',3,3',6,6',5,5'-octachloro	7.0E-0					
decachloro	1.5E-2					
biphenyl				7.48[23C][9]	3.79	9.0E-3[25C][10]
cyclohexyl ring			6.99E+1			

[a] Reference for log K_{ow} is [6] unless specified

[b] Water solubility or isomer in Aroclor 1242 [Ref. 5]

[c] References for Table 2-3:

1. Kelmas and Kalmab (1979)
2. Pal et al. (1980)
3. Griffin and Chou (1981)
4. Rapaport and Eisenreich (1984)
5. Griffin and Chou (1981)
6. Hague et al. (1976)
7. Chiou et al. (1977)
8. Rapaport & Eisenreich (1985)
9. Miller et al. (1979)
10. Hague and Swimmering (1976)
11. Mackay et al. (1986)

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Similar correlations have not yet been attempted for an extensive series of PCBs (see Section 4). Because PCBs constitute a much more closely related group of compounds than was used in the previous correlation studies, it would be valuable to determine whether these correlations remain valid. Such correlations may yield a useful method for extrapolating sorption data from a small number of PCB congeners to the full complement of PCB congeners found in Aroclors.

Very few vapor pressure data appear to be available in the literature studied. The Aroclors have vapor pressures of 7×10^{-3} to 7×10^{-5} torr (Kalmaz and Kalmaz 1979), though one reference (Griffin and Chou 1981) indicates that Arocior 1248 has a vapor pressure of 0.375 torr, illustrating considerable disagreement in the literature.

KINETICS/REVERSIBILITY OF SORPTION

As discussed in Section 3 of this report, kinetics and reversibility of sorption of hydrophobic compounds such as PCBs is an open, controversial issue. While the background and theory are discussed in Section 3, the conflicting results of research on PCBs are summarized in this section.

Several authors have noted that the amount of desorption of PCBs from various sediment types was minimal. For example, in Haque and Schmedding (1976), the maximum desorption of 2,4'-dichloro-, 2,2',5,5'- tetrachloro-, and 2,2',4,4',5,5'-hexachloro-biphenyl isomers is 4%. Desorption of PCBs from Glendale soil with or without sludge treatment was <2% at the two lowest equilibrium solution concentrations (0.3 and 0.6 µg/L) and 4.4% to 9.5% at the highest equilibrium solution concentration (5 µg/L) (Fairbanks and O'Connor 1984). The partition coefficient for sorption (K_a) is thus less than that for desorption (K_d), again suggesting incomplete reversibility of sorption. For example, Horzempa and DiToro (1983) show a range in K_a between 9,000 and 14,000 for 2,2',4,4',5,5'-hexachloro-biphenyl, while the corresponding range of K_d is 20,000 to 30,000. One exception is a washed sand in which K_a ~40 and K_d ~60. The same authors show a range of K_a from $2.1\ 10^3$ to 1.48×10^4 for another set of sediments and a corresponding range of K_d from 7.23×10^3 to 3.01×10^4. DiToro and Horzempa (1982) and DiToro et al. (1982) suggest that sorption can be divided into reversible and resistant components. The partition coefficient for the reversible component, K_r, corresponding to K_a above, ranges from 3.49×10^2 to 9.15×10^2, whereas the partition coefficient, K_0, for the resistant component ranges from 1.79×10^3 to 1.40×10^4. Their experiments suggest that the resistant component may decrease as a result of a large number of consecutive desorptions, suggesting in turn that the sorption is not irreversible, but instead desorption kinetics are very slow. Gschwend and Wu (1985), however,

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attribute the resistant component to an experimental artifact. The typical experimental protocol involves a sorption step, followed by the removal of the aqueous phase and its replacement by a fresh aqueous phase during the desorption step. When the original soil/aqueous phase is not centrifuged sufficiently, the aqueous phase contains nonsettling microparticles to which PCBs are bound; these bound PCBs are thus removed from the system before desorption under most experimental protocols used to date. Thus, this removal creates the appearance of decreased desorption and higher K_d (Gschwend and Wu 1985). This would explain why the K_d decreases as sorbent concentration (and suspended microparticles) increases (Weber et al. 1983). Gschwend and Wu (1985) found that in experiments with prewashed sediments, the sorption and desorption isotherms are essentially identical.

There is also disagreement concerning the rate of sorption. Several authors suggest that sorption and desorption equilibria are rapid. Equilibrium is reached within 3 hours (Nau-Ritter et al. 1982; Weber et al. 1983), though small increases may occur during the next 24 hours (Horzempa and DiToro 1983). Little subsequent change occurs thereafter, for up to 96 hours (Horzempa and DiToro 1983). However, Karickhoff (1984) suggests that equilibrium is not attained so rapidly. The rate of PCB desorption from illite and chlorite has been calculated as 0.029/hour, using a first-order rate constant (Nau-Ritter and Wurster 1983).

MOBILITY IN AQUEOUS AND ORGANIC SOLVENT SYSTEMS

Several experimental techniques have been used to study the mobility of PCBs in aqueous and organic solvent systems. These methods, discussed below, include soil thin layer chromatography, soil column studies, and microcosm studies.

Soil Thin Layer Chromatography

Soil thin layer chromatography (soil TLC) is a method for estimating the mobility of a compound through a soil using a specified leachate. It is analogous to the standard analytical TLC method except that the typical silica gel or cellulose adsorbent phase is replaced by a thin layer of soil. The leachate or developing solvent may be water, an organic solvent, a landfill leachate, etc. The distance moved by the compound relative to the distance moved by the solvent is defined as the r_f value or retardation factor, where

$$r_f = \frac{\text{distance compound moved}}{\text{distance solvent moved}} \qquad (2\text{-}5)$$

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This r_f value is indicative of the mobility of a compound in a given soil-solvent system. (It should be noted that this definition of r_f, commonly used in the chromatography literature, is the reciprocal of the retardation factor, R_f, defined in Eq. 3-3 below and used in the hydrologic literature describing solute transport in aquifer systems).

The mobility of PCBs as determined by soil TLC has been addressed by Griffin and Chian (1980) and Griffin and Chou (1981). The five soils studied had a range of organic carbon content between <0.01% and 74.04%, specific surface area between 0.4 and 253 m^2/g, cation exchange capacity between 0.0 and 29.4 meq/100 g, and a clay content between 0% and 31.6%. Despite the major differences among these soils, the r_f values of Aroclor 1242 and 1254 are close to 0 (0.02 to 0.06) using either deionized water or a landfill-derived (aqueous) leechate as the developing solvent (Griffin and Chien 1980; Griffin and Chou 1981). On the other hand, when carbon tetrachloride is the developing solvent, the r_f values are close to 1.00 (0.96 to 1.00) (Griffin and Chian 1980; Griffin and Chou 1981). Based on these experimental results, the Aroclors appear to be immobile in soils when water is the solvent, but are highly mobile when a (nonpolar) organic solvent is present. This is consistent with the solubility parameter model of desorption from soils discussed in Section 3 because the PCB is more soluble in the organic solvent and because the organic solvent swells the soil organic matrix thus speeding desorption. These results point out a potential problem in mixed waste landfill systems. Organic solvents may significantly mobilize PCBs that might otherwise remain fairly immobile if water were the only solvent.

Scharpenseel et al. (1978) also refer to this potential problem when they determined the sorption of PCBs by clays and humic acids from hexane solution. In contrast to PCBs in water solution, which have very high partition coefficients, PCBs in hexane solution were minimally sorbed onto clays and humic acids. Interestingly, the sorption of PCBs from hexane solution (in contrast to water solution) was greater onto clays than onto humic acid. This was attributed to the competition between solute (PCB) and solvent (hexane) for the humic acid surface (Scharpenseel et al. 1978). PCB sorption and mobility in the presence of organic solvents or mixed aqueous-organic solvent systems (see Section 3) is an important aspect of the problem which has not been sufficiently addressed (see Section 4).

Soil Column and Microcosm Studies

Soil column and microcosm studies are other sources of information about the mobility of PCBs. In soil column studies, a known weight of soil is packed in a

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column, a PCB component is added, and the column is then leached with successive amounts of water, simulating intermittent rainfall. In PCB soil column experiments, only minimal amounts of PCB were leached from the soil by percolating water. The highest values noted were 0.73% PCBs leached after 1700 mm of total rainfall equivalent; in this case, the PCBs consisted of 30.3% dichloro and 69.7% trichloro congeners (Scharpenseel et al. 1978). When Aroclor 1016 was used as the PCB, it was observed by gas chromatography that only the less chlorinated PCBs were leached (Tucker et al. 1975). Incremental leaching of PCBs by water results in decreasing amounts being leached (Farquhar et al. 1979). In the case of three soils with relatively similar organic carbon content (1% to 6%) but different clay contents (5.5% to 35.8%), breakthrough of the Aroclor 1016 decreased with increased clay content of the soil (Tucker et al. 1975). In a soil column that was extruded and analyzed by autoradiography, PCBs were found to be associated with rotting organic matter, mainly plant remnants, suggesting that PCBs were sorbed and retained by organic matter (Scharpenseel et al. 1978).

One microcosm study was done to determine the movement of PCBs from a silt/clay sediment (2.9% organic carbon) into overlying water (Fisher et al. 1983). Differences in mobility among the various congeners were attributed to differences in sorption. Surprisingly, the less chlorinated congeners (trichloro- and tetrachloro-) exhibited lower diffusivities than the more chlorinated congeners. The diffusivity values ranged from 1.2×10^{-9} to 8.5×10^{-7} cm^2/day for the different congeners, all very low values. At these rates, sedimentation would rapidly bury the PCB-contaminated surface layer, removing it from immediate contact with the overlying water. However, this does not take into account bioturbation or physical disturbance. In the case of such disturbances, the extent of PCB contamination of the overlying water would be dependent on the kinetics of desorption. As mentioned earlier, this topic is currently the subject of much debate.

FIELD STUDIES

Polychlorinated biphenyl spills from transformers have occurred at a number of sites. Several studies have monitored the soils and water at these sites in an attempt to determine and predict the migration and degradation patterns of the PCBs. In one of the earlier studies, Smith et al. (1976) and Moein (1976) observed the effects of an Askarel* spill in eastern Tennessee over a 2-year period (1500 gal of Askarel were spilled and cleaned up by excavation of soil). Soil cores, which consisted mainly of clays with chert (cryptocrystalline quartz) fragments, and well

*The Askarel transformer fluid consisted of Aroclor 1254 and chlorobenzenes.

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water samples from below and around the excavation site were analyzed for both PCBs (Aroclor 1254) and polychlorinated benzenes (the solvent in Askarel). The soil core samples contained 0 to 67 ppm PCB; the water samples contained < 0.5 ppb. These values remained approximately the same after 2 years, indicating no significant reduction in Aroclor 1254 resulting from migration, and no significant migration patterns were observed. Gas chromatography analysis indicated that the ratio of congeners remained the same; therefore, no dagradation occurred or all congeners degraded at the same rate. In contrast to the PCBs, the polychlorinated benzenes (solvent) did undergo migration. Specifically, the trichlorobenzenes migrated whereas the higher homologs were retained by the soil. Since this constitutes a mixed-solvent system, it is interesting to note that the PCBs apparently did not migrate with the organic solvent in this case. It is reasonable to assume that dilution effects played a major role here since the bulk of the spill had been cleaned up by excavation.

In another field study in which 6,800 to 21,000 L of Askarel were spilled when an underground pipe broke at a transformer manufacturing plant in Saskatchewan, the distribution and migration of PCBs were studied before major cleanup (Roberts et al. 1982; Schwartz et al. 1982). The study area consisted of granular fill which was underlain by Regina clay, Condie silt, till, glacial sands and gravels. The Regina clay and Condie silt both have an abundant fracture system. These authors found that the distributions of PCBs were extremely heterogeneous, both horizontally and vertically. Surface samples showed large concentrations of PCBs in a number of locations. The PCBs evidently seeped to the surface and were transported on particles during runoff--an important migration mechanism. The surface samples tended to show a decrease in the less chlorinated PCBs relative to the original Aroclor 1254, suggesting preferential degradation or other loss (e.g., resulting from volatilization or faster migration). These authors found that the contaminants spread more laterally than vertically, suggesting that the permeability of the fractured Regina clay was considerably less than the fill. They hypothesized that the Askarel moved as a separate liquid phase along the largest fractures. As an oily phase, Askarel would not wet the rock, but would form droplets that would be trapped as the fractures became smaller. Capillary forces would have to be overcome to force entry of this oily phase into pore openings saturated with water. The force needed would become greater as porosity and permeability decreased. A high head in the system would be needed to overcome this force, making it unlikely that the Askarel would continue to migrate downward as a distinct phase. However, the Askarel does have a finite, though low, solubility in water which would allow it to migrate slowly downward through the low-permeability zone as a dissolved phase in

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water. A field study such as this dramatically emphasizes the need to study PCB migration in three phases: as a dissolved phase (which is how most of the laboratory experiments have been performed), as a sorbed phase (transportation on particles during runoff), and as a pure PCB or PCB/organic solvent phase (an area which has barely been explored).

EFFECTS OF SOILS ON VOLATILIZATION, PLANT UPTAKE, AND DEGRADATION

The transport of PCBs in soils is affected by several processes that can lead to an attenuation of the PCBs in the soil environment. Such processes include volatilization of PCBs from soils, plant uptake, bioaccumulation, and chemical or biological degradation. In turn, the soil environment can significantly affect these removal processes.

Volatilization

Volatilization from soils is a function of the (air and soil) temperature and moisture content, the vapor pressure of the compound, concentration of the compound, the degree to which it is bound to the soil (Haque et al. 1974), and the gas velocity in the soil and air (Thibodeaux 1981). Volatilization is much lower from soils than from water (Kilzer et al. 1979); even the presence of soil particulates or soluble humic substances reduces the volatilization of PCBs from aqueous solution (Griffin and Chian 1980). The mass transfer coefficient is three and one-half orders of magnitude less in soil than in air, though it increases by an order of magnitude as gas is generated in a landfill and gas velocity is thereby increased (Thibodeaux 1981). Thus, for PCBs in a landfill, the greatest barrier to volatilization is the fill cover material. A calculated emission flux rate is on the order of 9×10^{-4} g/m^2/day (Thibodeaux 1981). At an uncontrolled landfill containing leaking capacitors, the fugitive emissions of PCBs into the air were found to be one to three orders of magnitude above background levels; at an unspecified distance downwind from these sites, the emissions were up to an order of magnitude above background (Lewis et al. 1984). At a controlled chemical waste landfill, the average PCB emission rate was determined to be 12.1 ng/s (under conditions of -1° to 14°C, 0.4 to 6.6 m/s wind speed, and 46% to 95% relative humidity). These concentrations were insufficient to be detected downwind (Lewis et al. 1984).

The vapor loss of Aroclor 1254 from soil surfaces was considered negligible during a 4-week interval (Haque et al. 1974). However, Pal et al. (1980) point out that while the volatilization rate is low, the total loss by volatilization over time may be significant because of the persistence and stability of the PCBs. These authors also reference a study in which 40% to 50% of Aroclor 1254 (0.05 to 5.0 ppm in soil)

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was lost from three soils in 2 to 4 months. The type of soil will also influence volatilization, with sands allowing more and humus less (Kilzer et al. 1979). Increasing amounts of organic matter, activated carbon, or clay in the soils may decrease volatilization loss as a result of increased sorption.

The different PCB congeners exhibit different volatilization rates. For example, Aroclor 1242 was found at higher concentrations than Aroclor 1260 above a landfill, even though it was present in the landfill in smaller quantities (Lewis et al. 1984). Hexachloro and heptachloro PCBs volatilize much more slowly than do pentachloro PCBs which, in turn, volatilize at half the rate of tetrachloro PCBs from a sand (Pal et al. 1980). A substantial percentage of dichlorobiphenyl was lost from soils after 1 and 2 years (54% and 79%, respectively), presumably as a result of volatilization (Haque et al. 1976). Kilzer et al. (1979) caution, however, that the relative ranking of volatilization of compounds from water is not predictive for volatilization from wetted soils. For example, while one trichlorobiphenyl isomer volatilized from sand at a rate two and one-half times that observed for a pentachlorobiphenyl, their volatilization rates from humus were very similar.

Plant Uptake

Plant uptake of PCBs is also influenced by soil properties. Addition of 10 to 1000 ppm of PCBs to the soil resulted in up to 100% inhibition of soybean, beet, and redroot pigweed growth (Strek 1980). However, if activated carbon is added to the soil, there is an 81% to 100% reduction in PCB uptake by the plants, and no inhibition occurs (Strek 1980). This result is consistent with the findings by Lawrence and Tosine (1976) that activated carbon added to waters strongly sorbs PCBs (though, incidentally, they found that PVC is a more effective sorbent of PCBs from raw sewage). Strek and Weber (1982) also demonstrated with a series of treated soils that removal of organic carbon from the soil causes greater inhibition of plant growth, addition of clay decreases inhibition, and addition of organic carbon decreases inhibition further. This is, of course, consistent with the relative degrees of sorption of PCBs by these treated soils. Bioaccumulation of PCBs in crops appears to be inhibited in aerobic soils. For example, carrot roots have a bioaccumulation factor of two and sugar beets exhibit no bioaccumulation (Haque et al. 1976). This is in marked contrast to flooded soils and aquatic areas where bioaccumulation is pronounced (Pal et al. 1980).

Degradation

Degradation of PCBs in soils is another mechanism of removal of PCBs from the soil that is affected by the soil environment. Iwata et al. (1973) showed major

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differences in losses of Aroclor 1254 congeners from six soil types in 1 year. In two soils (with 0.3% and 11.3% OC), 95% of the Aroclor 1254 was recovered with no preferential losses of different congeners. In the other four soils (with 0.06% to 1.9% OC), varying degrees of preferential loss of the less chlorinated congeners were observed. Losses were attributed to degradation or sorption since leaching and volatilization were minimized by experimental conditions. Strek (1980) found that the presence of activated carbon (3333 ppm) in soils decreased the loss of the applied PCB by a factor of almost two in 1.5 years.

Other studies have also observed the relative ease of degradation of less chlorinated congeners. For example, monochloro isomers in Aroclor 1242 were 100% degraded in 6 hours by a mixed culture of soil microorganisms, whereas tetrachloro isomers in Aroclor 1242 were ~42% degraded after 15 days (Griffin and Chian 1980). The position of the chlorine atoms also affects the rate of degradation; PCBs with a preponderance of chlorine atoms on one ring degrade more readily relative to those with equal numbers of chlorine atoms on both rings (Pal et al. 1980). Biodegradation is an important attenuation mechanism for monochloro, dichloro, and trichloro PCBs, but it is much less significant with pentachloro and more highly chlorinated PCBs; however, the presence of the less chlorinated congeners may help induce the degradation of the more chlorinated congeners (Pal et al. 1980). It should be noted that high concentrations of PCBs (on the order of 10,000 ppm) inhibit soil microbial activity. Metabolism of PCBs requires aerobic conditions (Pal et al. 1980).

For a dichlorobiphenyl, degradation in 1 year resulted in 8.8% soluble metabolites and 42% unextractable residues (Moza et al. 1976). Metabolites include monochlorobenzoic acids, monohydroxydichlorobiphenyls, and hydroxyoxo(chlorophenyl)chlorohexadienoic acid (Baxter and Sutherland 1984). Metabolism of Aroclor 1242 results in analogous metabolites that are more highly chlorinated. Photodegradation of PCB metabolites yields monochloroacetophenones (Baxter and Sutherland 1984). Photodegradation may also initiate the destruction of highly chlorinated PCBs (Pal at al. 1980). However, in soils, photodegradation would only be possible to a 1-mm depth (the penetration depth of UV radiation) and would require localized anaerobic areas to mitigate the quenching effect of oxygen (Pal et al. 1980).

PCDD ATTENUATION IN SOILS

Despite the tremendous amount of recent public attention to PCDDs, especially 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), in the environment, it appears from the published literature that relatively few laboratory studies have dealt with PCDD attenuation in soils. This may be because safety precautions and specially designed

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laboratories are required for this type of research. Field studies are rather more numerous, but, not surprisingly, are generally more concerned with cleanup and containment of spills than with controlled studies. Most work has dealt with TCDD, though a few studies have also considered 2,7-dibenzo-p-dioxin (DCDD).

Field Study

One fairly extensive field study has occurred in conjunction with the industrial accident in Seveso, Italy, which resulted in the TCDD contamination of a large area. In a series of studies, Di Domenico et al. (1980a, 1980b, 1980c, 1982) made the following observations:

- TCDD concentration was highly variable in the soil surface layer.
- The highest TCDD concentration was not in the top 0.5 cm of soil, but was usually found at 0.5- to 1.5-cm depth; this was postulated to be a result of photodegradation, volatilization, or penetration and binding of TCDD to the lower soil layers.
- The amount of TCDD found at depths greater than 8 cm was at least an order of magnitude lower than that found in the upper layer. The concentration at greater depths increased slightly in 1 year; this was considered significant.
- TCDD concentrations decreased rapidly in the first 5 months, dropping by about half; this was attributed to photodegradation or volatilization in the soil surface layer. After 5 months, the rate of decrease in TCDD concentration declined significantly, with little further decrease apparent. Thus, predictions of persistence of TCDD in the soil increased with elapsed time after the incident; for example, 1 month after the incident, persistence was thought to be 1 year, whereas by 17 months after the accident, persistence was thought to be 10 years.
- Wipf et al. (1982) observed that plant uptake was minimal for apples, pears, peaches, corn, and carrots, though the outer layers of the vegetation did accumulate TCDD from local dust.

Equilibrium Sorption

None of the papers reviewed have yielded any data on sorption isotherms or partition coefficients for PCDDs. However, Hutter and Philippi (1982) estimate a sorption coefficient of 1×10^6 from data in Isensee and Jones (1975). They observed that TCDD becomes strongly sorbed to soils during long-term incubations and becomes more difficult to extract with time, leading to potential experimental extraction artifacts. At least one study by Walters and Means is currently under way that deals with determination of kinetic and equilibrium characteristics of sorption and desorption of TCDD on soils.

Physical Constants: Water Solubility, K_{ow}, Vapor Pressure, Henry's Law Constant

Some physical constants for TCDD are summarized in Table 2-4.

Table 2-4

PHYSICAL PROPERTIES OF TCDD

Property	Value	References
Water Solubility (ppm)	2E-4	Kearney et al. (1972), Helling (1971)
	3.17E-4 (25°C)	Schroy et al. (1984)
Log K_{ow} (unitless)	6.15	Schroy et al. (1984)
Vapor Pressure (torr)	1.7E-6	Schroy et al. (1984)[a]
	1.49E-9 (25°C)	Schroy et al. (1984)
Henry's Law Constant ($atm\text{-}m^3$/mole)	2.1E-6 (25°C)	Schroy et al. (1984)[a]

[a]Estimated from the general literature.

Soil TLC

The mobility of TCDD and OCDD as determined by soil TLC has been addressed by Helling (1971) and Kearney et al. (1973a). The five soils studied had a range of organic carbon between 0.08% and 52.4%, a clay content between 0% and 39.5%, and a cation exchange capacity between 0.2 and 33.8 meq/100 g. As with the PCBs, the r_f values of both PCDDs, using water as the developing solvent, were 0.0 for all soils, despite their diversity.

Soil Leaching Studies

Five studies indicate that there is little or no leaching of TCDD in soils. For example, in an aquatic ecosystem, TCDD added to the water was found in only the uppermost organic soil layer after 2 years (Tsushimoto et al. 1982). In a highly porous sandy soil, Young (1983) observed that the TCDD remained in the top 15 cm of soil 14 years after application. Kearney et al. (1973a) claim that vertical movement of TCDD did not occur in a wide range of soil types; however, they do not document this statement. In a column study by Matsumura and Benezet (1973), almost no TCDD leached from sand to soil in 7 days. However, Yockim et al. (1978) did find some desorption of TCDD into water from a silt loam soil (0.9% OC, 12.2% clay) after

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1 day. During a period of 275 days, Nash and Beall (1980) also observed minor leaching of TCDD which reached a (low) concentration maximum in the leachate water after 126 days and then declined.

Degradation

Degradation studies include a determination of the half-lives of PCODs in soils and an attempt to explain their loss by mechanisms that include volatilization, photodegradation, and biodegradation. Half-lives of TCDD have been determined in soils as well as in a number of other media (see Table 2-5). In another study, Yockim et al. (1978) found that soil TCDD levels decreased by 18% in 5 months.

Table 2-5

HALF-LIVES OF TCDD

Matrix	Half-Life	References
sediment and water	600 days	Ward and Matsumura (1978)
soil and organic compost	2.5 years	Cameni et al. (1982)
loamy sand (0.5% OC)	420-540 days	Kearney et al. (1972)
silty clay loam (1.5% OC, 39.5% clay)	530-650 days	Kearney et al. (1972)
soils	10-12 years[a]	Young (1983)
soils (with high herbicide/ microbial concentrations)	< 200 days	Young (1983)
moist soils (1-100 ppm TCDD)	1 year	Kearney et al. (1973a)
soils	variable	Nash and Beall (1980)
grass	5 days	Nash and Beall (1980)
leachate water	57-65 days	Nash and Beall (1980)
air	7-24 days	Nash and Beall (1980)

[a]Measure of persistence rather than half-life.

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Volatilization

Hütter and Philippi (1982) summarize the conflicting information about TCDD volatilization by stating that it is negligible over short time periods, but that some TCDD losses have been attributed to volatilization (e.g., Camoni et al. 1982; Young 1983). Plimmer (1978) observed TCDD on thin layer chromatography plates in the dark. In his experiments, 16% of the applied TCDD was volatilized from silica gel plates in 8 hours (32% in 20 hours) and 6% was volatized in 8 hours from a plate coated with a silty clay loam. Young (1983) suggests the possibility of water-mediated evaporation from soils.

Photodegradation

Plimmer (1978) also compared the decomposition of TCDD on TLC plates in the dark and in sunlight. When the TLC plate was coated with silica gel, 31% of the TCDD decomposed in sunlight compared to 1% in the dark, suggesting substantial photodegradation. However, when the TLC plate was coated with a silty clay loam, negligible photolysis of the TCDD occurred. The photolysis products on the silica gel plate were more polar than the TCDD. Nash and Beall (1980) also found that TCDD on leaves, grass, and in air (but not in soil) degraded more readily in the sun than in the shade in a microagroecosystem chamber and field plot. More TCDD was also lost by volatilization from the nonshaded plot (50°C) than from the shaded plot (30°C). The photolysis reaction includes dechlorination to mono-, di-, and tri-chlorinated dibenzo-p-dioxins. Kearney et al. (1973b) also concluded that TCDD does not photodecompose on wet or dry soil surfaces. Both Crosby et al. (1973) and Liberti et al. (1978) suggest that the photodecomposition of TCDD is a reductive dechlorination process that requires a hydrogen donor. Thus, photodecomposition is negligible for thin films of pure TCDD on dry, irradiated soil surfaces (Crosby et al. 1973). However, the presence of organic solvents or other organic compounds may photosensitize TCDD. Liberti et al. (1978) treated a sieved soil with a hydrogen donor solvent and noted 100% decay to a depth of 10 mm and 40% to 60% decay to a depth of 30 mm after 9 days in the sun. (It is possible that part of this decay could be attributed to volatilization.)

Biodegradation and Plant Uptake

TCDD does not appear to be readily biodegradable (Hütter and Philippi 1982). Little CO_2 evolution was measurable from TCDD after 1 year. In a test of 100 microbial strains, Matsumura and Benezet (1973) found only five with some ability to degrade TCDD. DCDD, on the other hand, is metabolized to the extent of ~5% in 10 weeks; the major metabolite is more polar than the parent compound (Kearney et al. 1972).

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The uptake of TCDD from soil by oats and soybeans is negligible (Isensee and Jones 1971; Kearney et al. 1973a). As with PCBs, there seems to be a greater uptake of TCDD from solution than from soils. Oats and soybeans took up two to ten times as much TCDD from solution than from soils, averaging 13% in the roots, though little in other parts of the plants.

Section 3

SORPTION MODEL REVIEW

The objective of Task 2 of this study was to review available literature on models that describe the role sorption plays in the attenuation of hydrophobic organic compounds, specifically PCBs, in soils, sediments, and groundwater aquifer materials during the solute transport of these compounds in natural waters. This section documents the results of this review. Because PCBs fall within the broad class of hydrophobic organic compounds, models describing hydrophobic sorption are emphasized in this review. It was beyond the scope of this study to review the models describing attenuation of these compounds via volatilization or microbiological degradation processes, or models describing their transport via immiscible multiphase fluid flow and/or suspended particulate and sediment movement.

Hydrophobic organic compounds are typically those that are relatively insoluble in water (water solubility <100 ppm) and whose octanol/water partition coefficients, K_{ow}, (defined in Eq. 3-15 below) are greater than 10^2 to 10^3. For example, the water solubility and K_{ow}s of PCB isomers fall within the range 5.9 ppm < S (PCBs) < 7.0 ppb and 4.4 < log K_{ow} (PCBs) < 8.13. In general, hydrophobic solutes are not involved in strong specific interactions (e.g., coulombic attraction, ligand exchange, or hydrogen bonding) with the sorbent (Hamaker and Thompson 1972). Sorption of hydrophobic solutes results, not because of a large sorbate-sorbent bonding energy, but rather, because the sorbate-solvent and sorbent-solvent interaction is weak relative to the solvent-solvent (i.e., the tendency of water to bond to itself) interaction. Hydrophobic bonding is a long-range attraction which describes the enhanced interaction between sorbate and sorbent resulting from the presence of a solvent with strong self-bonding interactions (Adamson 1982). Hydrophobic sorption increases as the sorbete becomes less polar or as its water solubility decreases (Gustafson et al. 1968; Gustafson and Paleos 1971).

The models and related estimation methods for describing hydrophobic sorption reviewed in this section have been developed using, and are applicable to, a broad range of hydrophobic compounds. In most cases, these models have not been explicitly applied to PCB sorption, although in a few cases the hydrophobic compounds

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modeled included two or three PCB congeners. Thus, in this section examples taken from the literature consider other hydrophobic compounds as well as PCBs.

The soil/subsurface mobility and fate of organic compounds such as PCBs, PCDDs, and PCDFs are ultimately described by solute transport models. This section provides a brief description of how sorption models are incorporated into and used in solute transport models. Mathematical descriptions of sorption isotherm models, linear organic-carbon-referenced models, and gel models of equilibrium sorption are reviewed. The emphasis in the literature centers around sorption of dilute solutes from an aqueous solvent phase. However, where available, mathematical descriptions of sorption from nonaqueous or mixtures of aqueous/organic solvents are included. A mathematical description of sorption on low carbon soils, the reversibility of the sorption process, and sorption kinetics are also discussed.

SOLUTE TRANSPORT MODELS INCLUDING SORPTION

Currently, models used to predict or simulate the transport of organic and inorganic compounds through porous media are based on an advective-dispersive (AD) equation (described in Eq. 3-1 below). For most organic solutes, additional terms or equations which describe the chemical or microbiological reactions must be added to the AD equation. In general, these reactions retard or attenuate the advance of the solute relative to the movement of the bulk fluid. For PCBs, sorption is the dominant attenuation mechanism because these compounds are relatively resistant to chemical and microbiological transformation. Thus, to describe the transport of PCBs in soils, sediments, and groundwater aquifer materials (henceforth referred to as sorbents), it is necessary to incorporate a mathematical representation of the sorption/desorption process into the AD equation.

The AD equation used to describe one-dimensional advective-dispersion of a solute in uniform porous media at steady hydraulic flow with constant water content can be written as

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \frac{\rho}{\theta}\frac{\partial S}{\partial t} \qquad (3\text{-}1)$$

where C is the concentration of the mobile organic solute, S is the sorbed phase concentration, D is the dispersion coefficient in the direction of flow (Bear 1972), x is the direction of flow, v is the average velocity of fluid (solvent) phase, ρ is the bulk density of the porous media and θ is the volumetric water content,

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Sorption is usually incorporated into the AD equation by assuming that S is a function of C [i.e., by the sorption isotherm $S = f(C)$]. In general, sorption cannot be adequately represented by a single function because S depends on other variables in addition to C. This dependence on other variables can, in some cases, be highly complex (e.g., if the organic solute is ionizable and forms complexes with other ions in solution). However, PCBs are relatively inert and generally undergo no significant side reactions (ionization, complexion, etc.) with other constituents in solution. Thus, representation of PCB sorption with a single isotherm equation is valid.

Based on the local equilibrium assumption (James and Rubin 1979), it is possible to replace $\partial S/\partial t$ in Eq. 3-1 by $(dS/dC)\cdot(\partial C/\partial t)$. The last term on the right-hand side of Eq. 3-1 becomes

$$-\frac{\rho}{\theta} K' \frac{\partial C}{\partial t}$$

where $K' = dS/dC$ and is physically represented by the slope of the sorption isotherm. This expression represents the solute mass which is lost from solution as a result of sorption. The resultant AD equation is applicable only when sorption reactions are fast relative to the velocity, v, and sorption equilibrium is attained.

For many organic sorbates and PCBs in particular, the isotherm is linear for a wide range of soil types and typical environmental concentrations. In such cases the slope, K', of the isotherm is a constant and is typically referred to as the distribution coefficient, K_d, or partition coefficient, K_p. For PCBs the latter terminology is more appropriate. Under these circumstances the AD equation for PCB transport can be expressed as

$$\frac{\partial C}{\partial t} = D' \frac{\partial^2 C}{\partial x^2} - v' \frac{\partial C}{\partial x} \qquad (3\text{-}2)$$

where D' is the effective dispersion coefficient ($D' = D/R_f$) and v' is rate of advance of the PCB front ($v' = v/R_f$) in the absence of dispersion. This PCB front is retarded relative to the rate of advection of the front (v) of a nonreactive solute; R_f is the PCB retardation factor, defined as v/v' or as

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$$R_f = v/v' = 1 + \frac{\rho}{\theta} K_p \qquad (3\text{-}3)$$

Many types of sorption isotherms have been used to describe the sorption of organic compounds on soils, and a few of these are discussed in the following subsections.

ISOTHERM AND PARTITION CONSTANT (K_p) MODELS

Sorption isotherm models consist of 1) a functional relationship, or isotherm equation, relating the surface density of sorbed organic compound to its solution activity (C) at equilibrium; and 2) a set of assumptions on which the isotherm equation is based. Ideally, S could be expressed as the surface activity of the sorbent per unit mass of the solid sorbent. However, because no adequate theory exists for calculating the surface activities of organic compounds, S is typically expressed in units of concentration per unit mass of solid. The solution activity, C, can also be expressed in terms of concentrations rather than solution activities when the compound behaves ideally (e.g., in dilute sorbate solutions). A plot of S versus C is referred to as the sorption isotherm. The Linear, Langmuir, BET, Frumkin, and Freundlich models are briefly described below.

Linear Isotherm Model

By far the simplest model of sorption is the linear sorption model where the amount sorbed (S) is related to the equilibrium solution concentration (C) by a constant and a linear isotherm results. This constant is the slope of the isotherm and referred to as the partition coefficient,

$$K_p = \frac{S}{C} \qquad (3\text{-}4)$$

Applications of this model have been extensively described in the PCB sorption literature (see Section 2 of this report). Each of the models discussed below reduces to this linear relationship for low solution concentration of the sorbate. Low solution concentration is typically encountered for hydrophobic organic compounds, such as PCBs, under natural environmental conditions. Because of its mathematical simplicity, the linear isotherm model is easily incorporated into, and allows easy solution of, the advective-dispersive solute transport equations (Cherry et al. 1984).

When describing the sorption of organic compounds which consist of a number of individual species or congeners, a distinction must be made between the partition

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coefficient, K_p^i, for sorption of individual congeners and the distribution ratio, K_D, for PCB mixtures defined by,

$$K_D = \frac{\sum_i^1 S_i}{\sum_i^1 C_i} = \frac{\sum_i^1 K_p^i C_i}{\sum_i^1 C_i} = \frac{S_{an}}{C_{an}} \qquad (3\text{-}5)$$

where S_{an} and C_{an} are the total analytical concentrations of all sorbed and solution congeners, respectively, and the sum is over all congeners present.

This distinction is particularly important when describing PCB mobility in soils (e.g., Eq. 3-3). Since K_p^is for individual congeners differ, K_D changes as congeners are chromatographically separated from each other along the migration path of the Aroclor. When modeling PCB transport, K_D is not an adequate parameter for describing attenuation via sorption; individual K_p^is should be used.

Langmuir Model

The Langmuir model is based on the following assumptions: 1) the free energy of sorption (ΔG) is constant and independent of S (i.e., the extent of surface coverage); 2) no surface heterogeneity exists (i.e., all regions of surface are energetically identical); 3) no interactions occur between sorbed species; and 4) the maximum monolayer sorption density (S^m) is that of a complete monolayer. The Langmuir isotherm equation is described by the expression

$$S = \frac{K_L S^m C}{1 + K_L C} \qquad (3\text{-}6)$$

where the Langmuir constant K_L can be related to the free energy of sorption (ΔG) by the expression $K_L = \exp(-\Delta G/RT)$, where R is the gas constant and T is the temperature in degrees Kelvin.

If more than one organic sorbate is present in solution, the individual sorbates will compete for the available surface in relation to their individual binding constants, K_Ls. This competition reduces the sorption of each individual sorbate. For the case of two Langmuirian sorbates, '1' and '2', Eq. 3-6 can be generalized to account for the competitive effect of each sorbate on the sorption of the other, that is,

$$S_1 = \frac{K_{L1} S_1^m C_1}{1 + K_{L1} C_1 + K_{L2} C_2} \qquad (3\text{-}7)$$

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$$S_2 = \frac{K_{L2}\, S_2^m\, C_2}{1 + K_{L1}\, C_1 + K_{L2}\, C_2}$$

where S and C for sorbates '1' and '2' are as defined above, and the S^ms and K_Ls are the single-sorbate sorption maximum and Langmuir adsorption constants for each sorbate. The competitive Langumir Model (Eq. 3-7) has also been used for describing sorption of single sorbates onto heterogeneous soils containing more than one type of sorption site. For example, if two Langmuirian sites, 1 and 2, exist on the sorbent surface, with binding constants K_{L1} and K_{L2}, respectively, then S_1 and S_2 describe the amount of sorbate on each site.

In the single application of the Langmuir model to PCB (Aroclor 1254) sorption found in the literature, Weber et al. (1983) measured S_{an} and C_{an} and found that Eq. 3-6 did not provide a good fit to the data. This is not surprising, however, because Eq. 3-6 assumes a constant free energy of sorption (or a single K) and, as Eq. 3-5 shows, an Aroclor mixture by necessity is characterized by several K^is. Use of a 'competitive type' Langmuir model or a 'composite' K_D may have provided a better fit to the data. Weber et al. (1983) found that the Freundlich isotherm (described below) provided a good fit to the Aroclor 1254 data. The competitive Langmuir model (Eq. 3-7) has been used as the basis of a model that treats the 'apperent' irreversible sorption of single PCB isomers on soils that are presumed to possess two distinct sorption sites with K_{L1} and K_{L2} (Curl and Keolelan 1984).

BET Model

Ample evidence in the soils literature of non-Langmuirian sorption behavior suggests that one or more of the Langmuir assumptions are violated. If, for example, the monolayer assumption is relaxed, multilayer Langmuirian sorption can be described by the Brunauer, Emmett and Teller (BET) isotherm. The sorption of the first monolayer of sorbate molecules with a constant average heat of sorption, E, forms a new surface layer to which additional molecules sorb with an average heat of sorption, E_2. Each layer is assumed to follow a Langmuir equation. No limit to the number of successive layers is imposed, and thus, the adsorption density approaches that of a saturated vapor condensing on the surface of the saturated solution in contact with the solid. If the heats of adsorption on all successive layers are assumed equal, the BET equation is,

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$$S = \frac{K_B S^m C}{(C_s - C)[1 + (K_B - 1)(C/C_s)]} \qquad (3\text{-}8)$$

where C_s is the saturation concentration of the solute, S^m is the maximum adsorption density of the first layer corresponding to complete monolayer coverage, K_B is a constant related to the difference in sorption energies ($E_1 - E_2$) and the ratio of evaporation/condensation coefficients for sorbed layers (Bailey and White 1970). The BET equation reduces to the Langmuir equation if $K_B \gg 1$ and $C/C_s \ll 1$. The BET isotherm differs from the other isotherm equations considered in this section by allowing for the creation of new surface as the existing surface becomes occupied. We are not aware of any application of the BET model to PCB sorption data; however, at high solute concentrations, this model may be applicable. The curvature of the experimental isotherm at PCB concentrations greater than 50% of its solubility limit will provide an indication of whether the BET model is applicable.

Frumkin Model

If either attractive or repulsive interactions between sorbed species become significant as the fractional surface coverage ($\theta = S/S^m$) increases, the energy of sorption becomes an explicit function of surface coverage, S. Frumkin extended the original Langmuir formulation to include a term describing long-range surface interaction energy among surface species. The Frumkin isotherm equation can be expressed as

$$S = \frac{S^m K_f C \exp[-\alpha(S/S^m)]}{1 + K_f C \exp[-\alpha(S/S^m)]} \qquad (3\text{-}9)$$

where α is a parameter that expresses the way in which increased sorption changes the sorption energy of the sorbate (Parsons 1964; Bard and Faulkner 1980). If $\alpha > 0$, the interactions between two surface species are attractive and sorption is enhanced (i.e., the slope of the Frumkin isotherm is greater for all values of C than in the Langmuir case). Conversely, if $\alpha < 0$ (repulsive surface interactions), sorption is retarded with respect to the Langmuir case. As α approaches zero, Eq. 3-9 reduces to the Langmuir isotherm equation. The Frumkin isotherm model has been widely used to describe sorption of both polar and hydrophobic compounds onto electrode surfaces. It has been applied to the modeling of the sorption to soils of hydrophobic organic compounds by Koopal (1984). We find no evidence that it has

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been applied to PCB sorption on soils, although at high sorption densities where lateral attractive hydrophobic interactions may occur on the surface, this model may be useful.

Freundlich Model

Other possible isotherm equations can be derived if 1) the condition that a maximum sorption capacity, S, exists is relaxed and 2) the free energy of sorption (ΔG) decreases as S increases. This decrease in sorption energy could occur if the surface is heterogeneous in structure or composition and the most energetically favorable regions of the surface are initially occupied. For example, if we assume that the sorption energy varies as log (S) and that the distribution of ΔG on the surface is Gaussian, then the Freundlich isotherm equation can be derived (Sposito 1981; Adamson 1982) and expressed as

$$S = K_f C^{1/n} \qquad (3\text{-}10)$$

where K_f and n are empirical constants. For dilute solutions n is typically 1, but as the sorption density increases, $n > 1$. Examples of typical Freundlich isotherms are compared to a linear isotherm in Figure 3-1a. The linearized form of Eq. 3-10 (Figure 3-1b),

$$\ln (S) = \ln K_f + (1/n) \ln C \qquad (3\text{-}11)$$

is used to derive the parameters (1/n) and K_f from experimental data. Note that no physical basis exists for assuming the log (S) or the Gaussian energy distribution. Indeed, Eq. 3-10 was originally used by Freundlich because it frequently described experimental data better than Langmuir, BET, and other models. Repeated attempts to attach physical significance to the constants, K_f and n, have generally been unsuccessful. However, K_f has been considered by some to be a relative indicator of sorption capacity (Weber 1972), although this interpretation is questionable. The literature shows that the Freundlich model has been widely used for describing PCB sorption (see Section 2 of this report).

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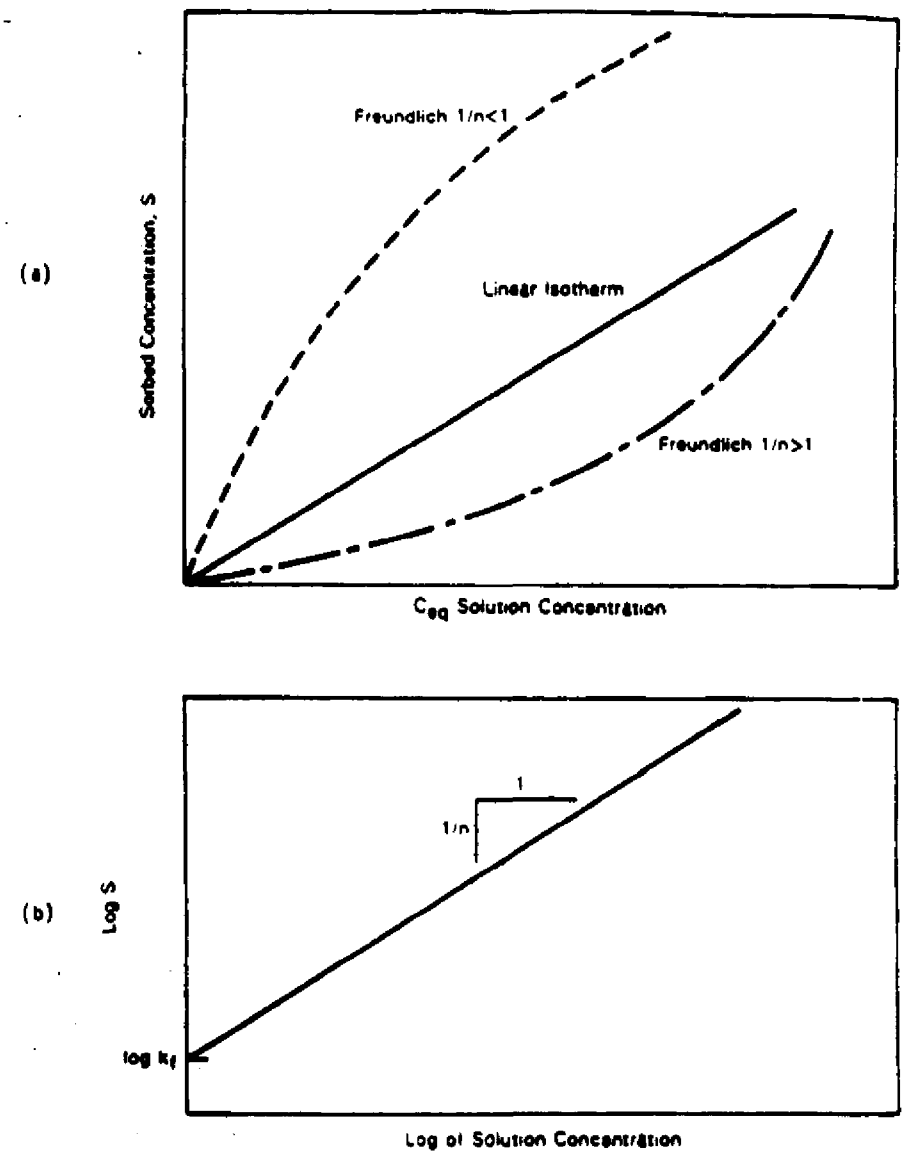

Figure 3-1. (a) Examples of Linear and Freundlich isotherm commonly used to describe PCB sorption/desorption data. (b) Linearized Freundlich isotherm from which Freundlich constants K_F and n may be determined.

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It should be emphasized that the empirical observation that a given set of adsorption data can be fitted to a Langmuir, Freundlich, or Frumkin equation does not necessarily establish a constant or logarithmic dependence of adsorption energy on adsorption density, S, nor the existence of interactions between surface sorbate species.

The isotherms or partition coefficients described above are expressed in terms of the concentration of the total sorbate (C) in solution. This implicitly assumes that the free energy of adsorption for all solution species is equal. For ionizable organic sorbates, this assumption may not be correct. However, for individual PCB congeners, this assumption is valid. The use of sorbate activities, rather than concentrations, in the above isotherms would, however, extend their applicability to higher solute concentrations and to mixed aqueous/organic solvents where variations in the ratio of miscible components may significantly alter the activities of the sorbate species (Chiou et al, 1982).

CARBON-REFERENCE SORPTION MODEL

The linear isotherm model discussed by Karickhoff (1981, 1984) describes sorption of hydrophobic organic solutes at low environmental concentrations for a wide variety of soils and sediments. This model, which is probably the most applicable model for existing PCB data, can be derived from the following thermodynamic condition: the sorbate fugacities (F)* in the solution and sorbed phases are equal at equilibrium (i.e., $F_s = F_w$). The subscripts "s" and "w" refer to the sorbent and solution phases, respectively. In each phase, the fugacity and concentration are related; in aqueous solution, for example,

$$F_w = \gamma_w F_w^0 C_w = \phi_w C_w$$

where γ_w is the activity coefficient, F_w^0 is the corresponding reference state fugacity and their product is termed the fugacity coefficient, ϕ_w. For hydrophobic compounds the reference state is usually taken as the pure liquid solute at STP or the supercooled liquid when the solute has a melting point greater than 0°C (as is

*The fugacity can be thought of as the 'escaping tendency' of a chemical compound from a phase and has units of pressure. In terms of a thermodynamic driving force, fugacity is to mass diffusion as temperature is to heat diffusion. At equilibrium, the fugacities of a compound in air, solution, soil, and biotic phases are equal (Macksy 1979).

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the case for PCB congeners). This relation is valid for mole fraction units; however, for low concentrations conventional units (moles/L) can be used. Using a similar expression for F_s, the equality of fugacities yields the isotherm:

$$S = K_p C \tag{3-12}$$

where,

$$K_p = \frac{\gamma_w F_w}{\gamma_s F_s} = \frac{\phi_w}{\phi_s} \tag{3-13}$$

More generally, for composite sorbents consisting of several components (e.g., organic carbon, expandable clay), K_p can be expressed as a linear combination of the sorption onto individual components

$$K_p = \phi_w \sum_j (Y^j/\phi_s^j) \tag{3-14}$$

where Y^j denotes the weight-fraction of component j. This combination assumes no interactions among components exist, and $K_p^j = \phi_w/\phi_s^j$ varies linearly with the quantity of each component. In general, because the activity coefficients, and thus K_p, are functions of solute concentration, this sorption isotherm, Eq. 3-12, is nonlinear. However, for dilute conditions, the values of ϕ_s^j approach limiting values, and Eq. 3-12 reduces to a linear isotherm with a constant partition coefficient, K_p.

Organic sorption on natural sediments and soils usually yields linear isotherms when the organic sorbate is present in solution at concentrations below 10^{-5} M or below 50% of the compound water solubility, whichever is lower (Karickhoff et al. 1979; Rogers et al. 1980; Brown and Flagg 1981; Chiou et al. 1982; Hassett et al. 1980a, 1980b; Means et al. 1980, 1982). This is typically the case for PCBs in natural waters. Solute speciation changes (protonation, chemical complexion, coagulation, or degradation) represent a significant source of isotherm nonlinearity for ionizable hydrophobic compounds. PCBs however, are relatively resistant to degradation and undergo virtually no chemical side reactions in solution. In this respect, the linear isotherm model is ideally suited to the description of PCB sorption.

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Based on extensive data for pesticides and neutral hydrophobic organic compounds Karickhoff (1984) concluded that soil organic carbon content (OC) dominates observed variations in K_p for surface soils, while particle size distribution and swellable clay content (CM) are of secondary importance, for most sorbents with OC > 0.1% (by weight). Thus, to a first approximation, K_p in Eq. 3-14 reduces to

$$K_p = \phi_w \frac{f_{oc}}{\phi_{oc}} \approx K_{oc} f_{oc} \qquad (3\text{-}15)$$

where f_{oc} is the weight fraction of organic carbon in the soil, ϕ_{oc} is the fugacity coefficient of the sorbate in the soil organic carbon, and the carbon-referenced partition coefficient, K_{oc}, is

$$K_{oc} \approx \frac{\phi_w}{\phi_{oc}} \approx \frac{K_p}{f_{oc}} \qquad (3\text{-}16)$$

Based on extensive data for a wide variety of hydrophobic organic compounds and natural sorbents, Karickhoff (1984) concluded that for nonionizable, hydrophobic organic compounds, whose water solubility is $<10^{-3}$ M, sorption is typically 'controlled' by soil organic carbon (humin-kerogen), and sorption can be adequately described using the carbon-referenced partition coefficient K_{oc} (i.e., for this class of sorbate, K_{oc} is essentially independent of soil type).

Estimation of K_{oc}

In Eq. 3-16, the dominant variation in K_{oc} is due to the variation in the fugacity coefficient of the sorbate in the solvent, ϕ_w. On the other hand, the fugacity coefficient of the sorbate in the soil organic carbon, ϕ_{oc}, remains relatively constant (Karickhoff 1981). For the case of dilute hydrophobic organic sorbates in an aqueous or mixed aqueous/organic solvent, existing techniques for estimating K_{oc} from basic physical properties of the sorbate are described below.

Relations Between K_{oc} and Water Solubility. Based on the reciprocal relationship between ϕ_w and mole-fraction solubility (X_w), Karickhoff (1981, 1984) has shown that for hydrophobic sorbates

$$\log K_{oc} = -a \log X_w - \frac{\Delta S_f (T_m - T)}{2.303\ RT} + b \qquad (3\text{-}17)$$

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where a and b depend on ϕ_{oc} but are treated as regression parameters, ΔS_f is the entropy of fusion, T_m is the melting point of the sorbate in °K, R is the gas constant, T is absolute temperature. The ΔS_f term is a "crystal energy" or "melting point" correction to the solubility for sorbates which, like PCBs, are solids at ambient temperatures. For solutes that are liquids at temperature T, the ΔS_f term approaches zero. Reasonable estimates of ΔS_f can be made for families of structurally similar compounds (Yalkowsky and Valvani 1980; Yalkowsky 1981). Karickhoff (1981) evaluated the parameters in Eq. 3-20 using a set of K_{oc}-solubility data for a sequence of condensed ring aromatic compounds. Estimates based on this correlation equation agreed within a factor of 2 to 3 with independent data for several families of hydrophobic compounds. However, using the same correlation equation for highly chlorinated, high molecular weight compounds, such as DDT or hexachlorobiphenyl, yielded estimates that were high by as much as an order of magnitude. In general, it is not advisable to use a correlation equation for estimation outside the immediate class of compounds for which it was derived. Within the family of 209 PCB congeners, this approach should be useful but has not appeared in the literature.

Relation Between K_{oc} and K_{ow}. The octanol-water partition coefficient (K_{ow}) is the ratio of the solute concentration in octanol to that in water. Because fugacities in the two phases are equal, this ratio can be expressed in terms of either fugacity or activity coefficients,

$$K_{ow} = \frac{C_o}{C_w} = \frac{\phi_w}{\phi_o} = b\,\frac{\gamma_w}{\gamma_o} \qquad (3\text{-}18)$$

where b is a constant for converting molar to mole fraction units, and "o" refers to octanol. The partition coefficient, K_{oc}, can be related to K_{ow} by combining Eqs. 3-16 and 3-18,

$$K_{oc} = \frac{\phi_o'}{\phi_{oc}'} K_{ow} \qquad (3\text{-}19)$$

Here the primes on the solute fugacity coefficient for the octanol and the organic carbon sorbent refer to water-saturated octanol and sorbent, respectively. It is important to note here that the ratio (ϕ_o'/ϕ_{oc}') must not depend on the solute if a linear relation between K_{oc} and K_{ow} is to exist. Regression equations of the form,

$$\log K_{oc} = a \log K_{ow} + b \qquad (3\text{-}20)$$

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based on this assumption of linearity have been extensively used in the literature (Hassett et al. 1980a; Karickhoff 1981; Schwarzenbach and Westall 1981; Rao et al. 1982). The values of a and b, as data-fitted coefficients, and the accuracy of this linear regression differ depending on the structure and functionality of the sorbate included in the regression. The accuracy of K_{oc} estimated using Eqs. 3-19 and 3-20 depends on 1) the predominance of organic carbon as the soil sorbent and hydrophobic interactions as the dominant sorbate-sorbent interaction and 2) sorption isotherm linearity. The applicability and accuracy of Eqs. 3-19 and 3-20 should be established among PCBs.

Structural Estimates from Molecular Fragments. In general, linear free energy theory treats the solute molecule as an array of fragments and assumes that each of these fragments make independent (linear) contributions to the total free energy, ΔG, of the molecule. The linear free energy relations (LFERs) of interest here describe the partitioning coefficients, K_{ow} and K_{oc}, for solutes in terms of the contributions of individual structural components of the solute.

The incremental change in K_{ow} or K_{oc}, caused by the substitution of a functional group X for a hydrogen atom on the base molecule R-H can be written

$$\pi_{oc}^{X} = \log K_{oc}^{(R-X)} - \log K_{oc}^{(R-H)} \qquad (3\text{-}21)$$

$$\pi_{ow}^{X} = \log K_{ow}^{(R-X)} - \log K_{ow}^{(R-H)}$$

The substituent constants, π_{oc}^{X} and π_{ow}^{X}, for X are derived from experimental sorption data and octanol-water partitioning data. These πs are relatively constant within a family of structurally similar organic compounds. For a family of compounds, say PCBs, Eq. 3-21 can be used to extrapolate values of K_{ow} or K_{oc} for isomers for which no Ks are available using the πs for that family and values of experimentally determined Ks for other isomers.

Because K_{oc} and K_{ow} are linearly related via Eq. 3-19, π_{ow}^{X} can be shown to be proportional to π_{oc}^{X} if the ratio (a_o'/a_{ow}') is independent of solute (sorbate). This result is very useful because existing data for π_{ow}^{Cl} (Leo 1975; Leo et al. 1971) could be used to estimate K_{oc}s for PCBs without developing a separate body of data for substituent constants for chlorine, π_{oc}^{Cl} (Karickhoff 1984).

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The application of K_{oc}-K_{ow} and K_{oc}-solubility relations defined above and the use of Eq. 3-21 in practical problems has been described by Lyman et al. (1982) in a handbook of estimation methods. In general, it is advised that estimation of K_{oc} for a given compound should be derived from a correlation equation derived for a family of structurally similar compounds. A similar caveat applies to substituent constant equations for π. We find no evidence that K_{oc}-K_{ow} and K_{oc}-solubility relations for PCBs, as a family of compounds, have been derived or the linearity of π_{ow}^{Cl}, as a function of the number of substituted Cl atoms, has been examined among PCB congeners.

MIXED SOLVENTS

The K_{oc}-solubility relation, Eq. 3-17, expresses sorption of dilute solute (or sorbate) from aqueous solvents. This relation has been generalized for other solvents and mixed aqueous/organic solvents by Amidon et al. (1974) and Yalkowsky et al. (1975) using a solviphobic cavity model. This model describes the solubility of hydrophobic solute molecules which may contain distinct hydrophobic and polar fragments or moieties. Although this approach has not been applied to estimate aqueous PCB solubility, it may be applicable to the estimation of PCB solubility/sorption from aqueous, nonaqueous, and miscible aqueous/organic solvents.

In the cavity model, solubility is dominated by the energy required to create a cavity in the solvent. This energy depends on the molecular surface area of solute hydrophobic and polar moieties and the interfacial surface tensions between the solvent and these moieties. The mole fraction solubility (X_w) in aqueous solvent is expressed by Amidon, Yalkowsky and coworkers by

$$\log X_j = - \frac{[\gamma_j (HSA) + \phi_j (PSA)]}{2.303\ kT} - \frac{\Delta S_f}{2.303\ RT} (T_m - T) \qquad (3\text{-}22)$$

where j denotes the solvent, k is Boltzman constant, T and R have been defined above, γ_j and ϕ_j are interfacial free energies at the aqueous interface with the hydrophobic and polar segments of the sorbate molecule, whose respective interfacial surface areas are (HSA) and (PSA). The ΔS_f term is the same crystal energy term used in Eq. 3-17. Substitution of Eq. 3-22 into Eq. 3-17 results in a generalization of the expression for K_{oc}^w.

$$\log K_{oc}^w = a \frac{[\gamma_j (HSA) + \phi_j (PSA)]}{2.303\ kT} + b \qquad (3\text{-}23)$$

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where w refers to water as the solvent. Based on the work of Yalkowsky et al. (1975, 1976) for binary solvent mixtures, Rao et al. (1982) showed that for a mixture of water and water-miscible organic solvent, the K_{oc} for sorbate j in the mixture can be written

$$\log K_{oc}^{m} = \log K_{oc}^{w} - a P_c f_c \tag{3-24}$$

where a is a constant, the superscript m refers to the mixed solvent, and K_{oc}^{w} is defined in Eq. 3-23 for an aqueous solvent that does not contain the organic cosolvent C. The fraction of organic cosolvent is denoted by f_c ($0 < f_c < 1$). The expression for P_c is given by

$$P_c = \frac{[\Delta\gamma_c\ (HSA) + \Delta\phi_c\ (PSA)]}{2.303\ kT} \tag{3-25}$$

where $\Delta\gamma_c$ and $\Delta\phi_c$ are the differences in surface tension between water and the cosolvent

$$\Delta\gamma_c = (\gamma_w - \gamma_c) \text{ and } \Delta\phi_c = (\phi_w - \phi_c) \tag{3-26}$$

Note the PSA term in Eqs. 3-23 and 3-25 vanishes for sorbates containing no polar moieties, as is the case with PCBs. For this reason this description of K_{oc} for mixed solvents should be applicable to PCBs. A further generalization to ternary or quaternary aqueous-organic mixtures was proposed by Rao et al. (1982),

$$\log K_{oc}^{m} = \log K_{oc}^{w} - \sum_k a_k P_k f_k \tag{3-27}$$

where the summation is over cosolvents k, and $f_w + \Sigma f_k = 1$. The theoretical approach on which these mixed-solvent expressions for K_{oc} are based assumes, as Yalkowsky and coworkers do, that solubility can be treated as a linear combination of pair-wise interactions of each solvent with each moiety of the solute molecule. Based on this development, the sorption coefficients, log K_{oc} or log K_p, would be expected to decrease linearly as a function of the cosolvent fraction f_c or Σf_k. This linear decrease has significant implications for the mobility of PCBs in soils contacting mixed solvents.

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Nkedi-Kizza et al. (1982), Hornsby et al. (1982) and Rao et al. (1983) have reported data for the sorption of unsubstituted and substituted polycyclic aromatic hydrocarbons from mixed aqueous-organic solvents using reversed-phase high-performance liquid chromatography, batch, and column techniques, which are consistent with the formal description of mixed-solvent sorption presented above. The applicability of this formalism for describing PCB sorption data and/or the a priori estimation of PCB sorption from physical solubility data and surface areas should be evaluated.

The sorption of hydrophobic organic compounds from mixed solvents is being actively researched; however, we found no evidence of current or past research on PCB sorption from mixed solvents.

GEL PARTITION MODEL

Sorption/desorption on soil organic matter (gel) has been described by Freeman and Cheung (1981) using solubility parameter theory for solute-gel and solvent-gel interactions. The humin-kerogen particles and coatings on mineral surfaces responsible for the K_p-f_{oc} correlation in soils are considered to be arrays of highly branched polymer chains that form a three-dimensional network. Interaction of this polymer lattice with the solvent(s) controls the initial polymeric swelling to form a porous gel phase (polymer-solvent system) and its subsequent expansion and contraction. This expansion and contraction, in turn, influences 1) sorption (desorption) rates of solutes into (out of) the gel via diffusion through the gel matrix and 2) apparent reversibility of sorption reactions via 'trapping' or 'lock-in' mechanisms (Johnson and Starr 1972; Ogner and Schnitzer 1971).

Hydrophobic (lipophilic) solutes diffusing into the gel phase will be sorbed depending on the relative solute affinities for the bulk solvent and gel phases. By combining both molecular sieve effects with a solubility theory description of solvent-gel and solute-gel interactions (Hildebrand et al. 1970), Freeman and Killion (1977) are able to describe equilibrium and kinetic sorption processes. An expression for K_{oc} was derived for solute, i:

$$\ln K_{oc} = A - B L_i + \frac{V_i}{RT} f(\delta) \qquad (3\text{-}28)$$

where A and B are soil parameters describing gel phase pore structure; L_i and V_i are the size and molar volume of solute, 'i', respectively; and the solubility parameter function

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$$f(\delta) = (\delta_l - \delta_s)^2 - (\delta_l - \delta_s)^2 \qquad (3\text{-}29)$$

describes the solute preference for the solvent versus the gel phases, based on competing solute-solvent and solute-gel attractive interactions (hydrophobic bonding). Here, δ is the solubility parameter (Hildebrand et al. 1970; Shinoda 1978) and subscripts s and g refer to solvent and gel, respectively.

Maximum gel expansion is expected when gel and solvent solubility parameters are matched, (i.e., $\delta_s = \delta_g$). Diffusion of the solute through the gel will be a maximum for this matched condition and will decrease as the difference between δ_s and δ_g increases (mismatched). The rate of desorption of the solute from the sorbent gel will be a maximum for a solute-gel matched system (i.e., $\delta_l = \delta_g$). However, desorption of a solute is also a function of its solubility in the solvent phase (extracting liquid) and will be favored when solute and solvent are matched. The rate and the extent of the desorption process is maximized when $\delta_l \simeq \delta_s \simeq \delta_g$.

Freeman and Cheung (1981) show that desorption of di(2-ethylhexyl) phthalate (DEHP, $\delta_l = 8$) from a single clay-silt sediment (obtained from an industrial wastewater holding pond, assumed $\delta_g = 10$) into several organic solvents of variable δ_s is consistent with their gel partition model. When δ_s was within the band $\Delta\delta$, whose limits are defined by δ_l and δ_g, rapid and complete desorption of DEHP was observed. When δ_s differed by one or more units from $\Delta\delta$, an initial rapid desorption step occurred, followed by a slow diffusion-controlled desorption step that plateaued well below 100% desorption. Kitchens et al. (1984) reported Aroclor 1260 desorption from a "clay-soil" (2.0% OC) to be between 90% to 92% complete after two successive extractions (10 min each) with an isopropanol solvent ($\delta_s = 11.4$) depending on whether the soil was air-dry or wet (23% water by weight).

For water, $\delta_s = 23$ (Burrell and Immergut 1975), while for natural soil organic carbon (humin) δ_g values of between 10 and 13 have been estimated (Freeman and Cheung 1981; Chiou et al. 1983). Because of magnitude of $\delta_g - \delta_s$ and the formulation of the gel model, it can be concluded that in aqueous systems (or mixed aqueous-organic solvent systems where water is the major cosolvent), sorption equilibrium may be particularly difficult to obtain, requiring days to months. For shorter time periods, the sorption process would appear to be irreversible. In successive batch desorption experiments of PCBs from a "high-clay" soil and a "potting soil" Weitzman (1984) concluded that desorption into aqueous and mixed aqueous/isopropanol solvents was linear with time, extremely slow (days to months), and would be incomplete after

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several hundred successive extractions; desorption of PCB from "pure sand" was more rapid, but still on the order of days to weeks. Indeed, for grossly mismatched solvents, a sorbed component which is highly resistant to desorption may exist similar to that reported by DiToro and Horzempa (1982) for PCBs and by other investigators for a variety of pesticides and hydrophobic sorbates.

Although a δ_i data base for hydrophobic pollutants such as PCBs is not currently available and the variability of the A, B, and δ_g parameters for different soils has not been established, a major advantage of this gel model is its inherent ability to treat nonaqueous and mixed aqueous/organic solvents through variation of the solvent solubility parameter, δ_i.

SORPTION ON LOW-ORGANIC-CARBON SOILS

The sorption of hydrophobic solutes on low organic carbon soils ($f_{oc} < 0.001$) is not well understood, and thus, no qualitative predictive model is available. However, it has been repeatedly pointed out (Hassett et al. 1980a, 1981a; Mingelgrin and Gerstl 1983; Karickhoff 1984) that the influence of mineral surfaces, particularly expandable clay surfaces, cannot be neglected in low-organic-carbon soils, as they can be in the majority of cases in soils where $f_{oc} > 0.001$. The influence of expandable clay minerals and a description of a crude qualitative model describing their influence on K_p is summarized below.

It is known that surface area is an important parameter influencing sorption of hydrophobic solutes on minerals containing only trace amounts of organic carbon. The expandable clay minerals (e.g., montmorillonite) dominate sorption in natural mixed-mineral assemblages (Hassett et al. 1980a; Karickhoff and Brown 1978). Hassett et al. (1980a) found, for a wide range of soils and organic sorbates, that the large deviations in the observed K_p (K_p^{obs}) with respect to the carbon-referenced K_{oc} depend on the ratio of the expandable clay to organic carbon content of the soil (i.e., f_{cm}/f_{oc}), where f_{cm} is the weight fraction of expandable clays. For sorbates with polar moieties and varying hydrophobicity ($3 < \log K_{ow} < 5$), these deviations in K_p [$K_p = (K_p^{obs}/f_{oc} - K_{ow})$] have been observed when the ratio (f_{cm}/f_{oc}) exceeds some threshold value, f_T (Hassett et al. 1980a, 1981b; Means et al. 1982; Karickhoff 1984). An additional CM contribution to K_p becomes significant at this threshold value.

Examination of the relative importance of the OC and CM soil fractions is facilitated by the simple two compartment model discussed by Karickhoff (1984) in which

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soil organic carbon (humin) and expandable clay surfaces compete for the sorbate. Based on Eq. 3-14, Karickhoff expresses K_p as

$$K_p^{obs} = K_{oc} Y_{oc} + K_{cm} Y_{cm} \qquad (3\text{-}30)$$

$$= K_{oc} f_{oc} a_{oc} + K_{cm} f_{cm} a_{cm}$$

where K_{oc} and f_{oc} have been defined previously. K_{cm} is an expandable clay-referenced partition constant, f_{cm} is the fractional quantity of expandable clay in the soil, and a_{oc} and a_{cm} are availability fractions ($0 < a_i < 1$) indicating what fraction of the total mass of OC or CM is available for sorption. This simplistic model assumes that the two sorbent compartments act independently (i.e., there is no covariant interaction between sorbents). We have found no evidence of experimental data justifying this assumption for hydrophobic organic sorbates. However, for inorganic sorbates, it is known that mineral surfaces and natural polymeric organic coatings do not behave according to Eq. 3-30 (Altmann 1984). Nevertheless, insight can be obtained by making this assumption and rearranging Eq. 3-30 so that,

$$K_p' = \frac{K_p^{obs}}{f_{oc} a_{oc}} = K_{oc} + K_{cm} \frac{f_{cm}}{f_{oc}} \frac{a_{cm}}{a_{oc}} \qquad (3\text{-}31)$$

The ratio (a_{cm}/a_{oc}) can be considered as an availability or permeability parameter, λ, describing the ability of the solute to diffuse through the humin coating to the underlying mineral surface. λ can account for the "blockage or masking" (Walker and Crawford 1968; Edwards and Bremner 1967) of clay mineral surfaces by soil organic carbon, which renders them unavailable to organic sorbates. Using Eq. 3-31, Karickhoff analyzed published pesticide data and proposed that a possible threshold value, $f_T = 30$, exists for hydrophobic organic sorbates containing polar moieties. For soils below this threshold, the clay mineral components contribute little to sorption, and $K_p' = K_{oc}$. As f_{cm}/f_{oc} increased above this threshold, K_p' increased significantly relative to K_{oc}. This increase in K_p' is presumed to be a result of the increased accessibility of clay surfaces. Expandable clays are known to contain nonpolar hydrophobic surfaces, ≡Si-O-Si≡, in addition to polar surfaces, -OH (Chen 1976). One can hypothesize that both hydrophobic sorption [attraction of the non-polar solute moieties to hydrophobic clay surfaces (Hassett at al. 1981a) and specific sorption (attraction of polar solute moieties to polar mineral surfaces]

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would contribute to this increase in K_p'. For soils or unconsolidated aquifer materials where $f_{oc} < 0.001$ or $(f_{cm}/f_{oc}) > 30$, Karickhoff concluded that sorption on mineral-surfaces should be considered.

It should be emphasized that the value of this threshold must be regarded as tentative and probably depends on the structure and functionality of the solute. In addition, for mixed aqueous-organic solvents, the threshold for a given solute may vary with the fraction of organic cosolvent, f_c. This variation is plausible because 1) the availability parameter, λ, depends on swelling of the humin and thus on the solubility parameter, δ, (Freeman and Cheung 1981) which changes with f_c and 2) hydrophobic sorption on humin decreases exponentially with increasing f_c (see Eq. 3-24). Nothing is known about the sorption behavior of PCBs in low organic carbon soils. Because PCBs contain no polar moieties through which specific sorption to polar clay surfaces could occur, the intensity of hydrophobic sorption to hydrophobic clay surfaces, K_{cm}^{hyd}, may not differ substantially from that of the humin, K_{oc}^{hyd}. Thus, depending on the relative magnitude of K_{cm}^{hyd} and K_{oc}^{hyd} for individual PCB congeners, the observed K_p' may increase, remain constant, or decrease as a function of CM/OC among different soils. For mixed solvents, both the relative increase or decrease in K_p' and the CM/OC thresholds may depend on the type and fraction of the cosolvent. Therefore, an adequate description of sorption in low organic carbon soils of highly hydrophobic, nonpolar, nonionizable compounds such as PCBs may require that the carbon-referenced K_{oc} model be modified as for the less hydrophobic polar compounds described by Eq. 3-30.

SORPTION REVERSIBILITY AND ISOTHERM NONSINGULARITY

The reversibility of organic sorption processes on soils is an important unresolved issue typified by conflicting literature reports. The reversibility of sorption reactions on soils is a key factor both in developing a conceptual understanding of the underlying sorption/desorption mechanisms and incorporating a mathematical description of sorption/desorption into advective/dispersive solute transport equations. If, under equilibrium conditions, successive sorption/desorption experiments can be described by a single isotherm, the term singular isotherm is used and the sorption process is considered to be reversible. However, numerous studies have indicated that successive desorption experiments do not retrace the original sorption isotherm but rather follow a distinct isotherm (more sorption); the term nonsingular isotherm or nonsingularity is used to characterize the observed hysteresis on the plots, S versus C (Figure 3-2). When this nonsingularity is observed, as it often is, it can be attributed to 1) experimental artifacts [e.g., nonattainment of

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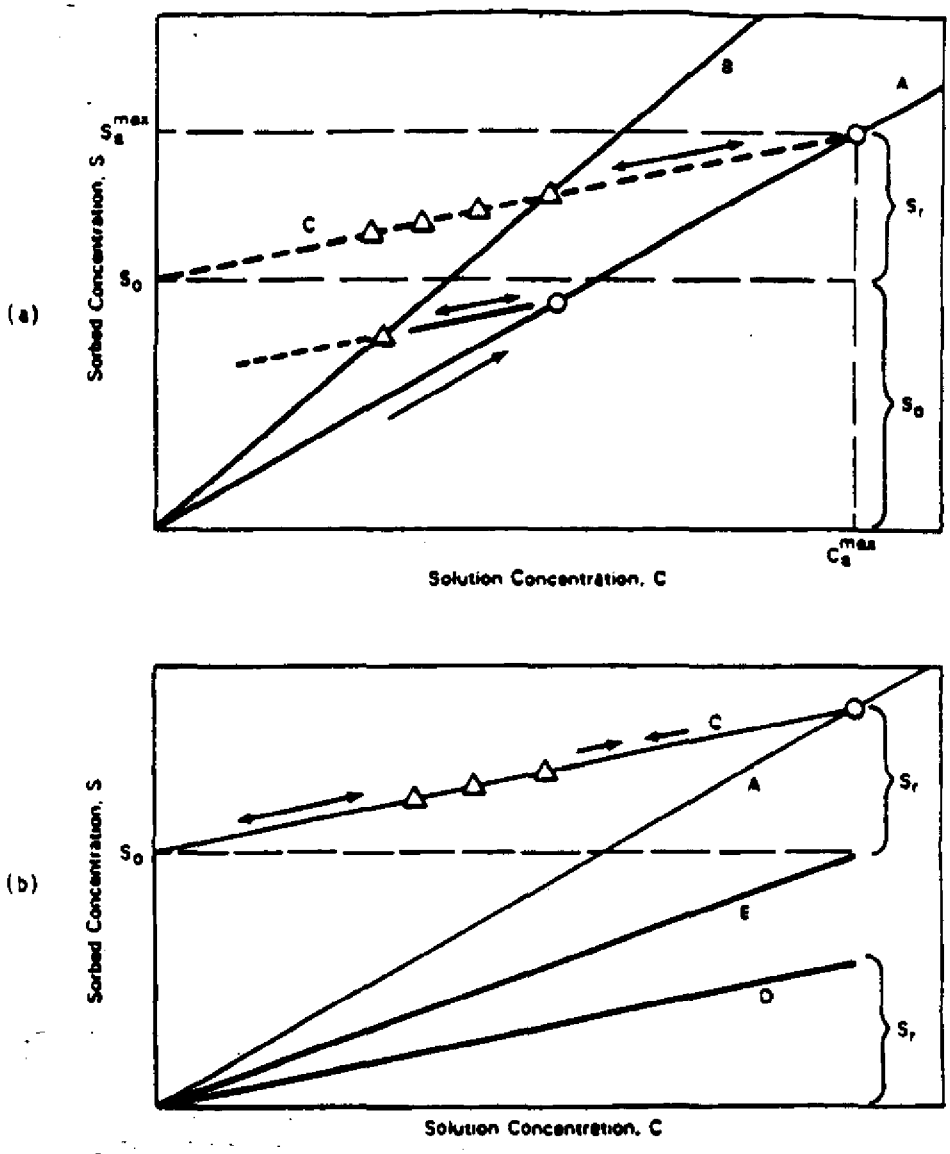

Figure 3-2. Linear sorption-desorption isotherms. (a) Curve A and B are the sorption and first desorption isotherms, respectively. Curve C is the consecutive desorption isotherm which describes the sorption/desorption path followed as the sorbate concentration, C, is cycled between 0 and C_s^{max}. (b) Curve D and E are the isotherms for the easily reversible (S_r) and resistant (S_o) sorbed components, respectively.

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equilibrium in the sorption and/or desorption experiment because diffusion-controlled migration of the sorbate through the porous or gel structure of the solid (Freeman and Cheung 1981; Karickhoff 1984)] 2) the existence of a nonsettleable fine-particulate or macromolecule phase in solution that competes with the settleable solids for the sorbate (Voice et al. 1983; Gschwend and Wu 1985), or 3) the existence of a fraction of the bound sorbate that is highly resistant to desorption (DiToro and Horzempa 1982). In the latter case, the sorption process would appear to be irreversible. Several approaches for describing nonsingular behavior are described below. However, resolution of divergent observations and the basic issue of reversibility remain topics of current research.

The degree of the nonsingularity in many cases is directly proportional to the amount of the sorbate sorbed before initiation of desorption (Van Genuchten et al. 1974), the rate of sorption, the hydrophobicity of the sorbate, and the duration of the desorption experiment (Mukhtar 1976). Karickhoff (1984) points out that the magnitude of the nonsingularity in K_p is inversely proportional to the rate of desorption (i.e., slow desorption results in a nonsingular isotherm unless the duration of the desorption experiment is sufficiently long to ensure that equilibrium is reached). For the first or single desorption step following the initial sorption step, this nonsingular behavior can be expressed using a pair of Freundlich isotherms,

$$S_a = K_a C^{N_a} \tag{3-32}$$

and

$$S_d = K_d C^{N_d} \tag{3-33}$$

where the subscripts a and d refer to sorption and desorption, respectively, where $K_d > K_a$ and the Freundlich constant 1/n in Eq. 3-10 has been redefined ($1/n = N$). As can be seen for the linear isotherms in Figure 3-2a, the magnitude of the hysteresis depends on the maximum amount of sorbate sorbed, S_a^{max}, at the maximum solution concentration, C_a^{max}, before initiation of desorption. Van Genuchten et al. (1974), among others, derived the useful relation

$$K_d = (K_a)^{\beta} (S_a^{max})^{1-\beta} \quad \text{or} \quad K_d = K_a (C_a^{max})^{N_a - N_d} \tag{3-34}$$

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Here, $\beta = N_d/N_a \simeq 1/2.3$ for a wide range of compounds. Using the latter expression for K_d, S_d can be written in terms of K_a and C

$$S_d = K_a (C_a^{max})^{N_a - N_d} C^{N_d} \tag{3-35}$$

Eqs. 3-32 and 3-35 constitute a simple model describing hysteretic sorption. This model has been incorporated into a solute transport model similar to Eq. 3-1 to describe pesticide sorption/desorption processes in soil column breakthrough and leaching studies (Van Genuchten et al. 1974). Good agreement was achieved between predicted and observed pesticide breakthrough curves at low, average pore-water velocity; however, for higher pore-water velocities, this simple sorption-transport model failed to describe experimental data.

DiToro and Horzempa (1982) report the existence of both a readily reversible component (S_r) and a highly resistant component (S_o) for PCB sorption to sediments (Figure 3-2). This highly resistant component does not desorb upon successive desorption steps, lasting up to 48 hours each. Within the context of DiToro's model, these successive desorption steps are assumed to trace a linear path intercepting the S-axis at a point which defines S_o. This path is termed the consecutive desorption isotherm (curve C Figure 3-2). The linear sorption isotherm and linear first desorption isotherm are labeled A and B, respectively, in Figure 3-2a and given by

$$S_a = k_a C \tag{3-36}$$

$$S_d = k_d C \tag{3-37}$$

Here, k_a and k_d are the sorption and desorption partition constants, respectively. When cycling the solution concentration such that $C < C_a^{max}$, DiToro and Horzempa found that the system traced out a path along curve C with only minor hysteresis. This line, with respect to an origin located at S_o along the S-axis in Figure 3-2a, is referred to as the reversible component isotherm:

$$S_r = k_r C \tag{3-38}$$

The partition coefficient for the reversible component, k_r, is given by

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$$k_r = \frac{k_a}{1 + m\,(k_d - k_a)}$$

where m is the mass of sorbent in solution. Alternatively, this reversible isotherm can be viewed as curve D in Figure 3-2b. The resistant component isotherm is shown as curve E and given by

$$S_0 = k_0\, C_a^{max} \tag{3-39}$$

where C_a^{max} is defined as above and k_0, the partition coefficient for the resistant component is given by

$$k_0 = \frac{m\, k_a\, (k_d - k_a)}{1 + m\,(k_d - k_a)}$$

which remains constant as long as $C < C_a^{max}$. The consecutive desorption isotherm (curve C) is simply the sum of Eqs. 3-38 and 3-39 (curves D and E) and is given by

$$S = S_0 + k_r\, C \tag{3-40}$$

Isotherm Eqs. 3-38 and 3-40, together with the constants k_a and k_d and the definitions of k_r and k_0, define a model for describing nonsingular PCB sorption/desorption cycling on natural sediments. If, after successive cycling the solvent phase concentration C exceeds C_a^{max}, S_0 is no longer constant, and Eq. 3-40 must be replaced by $S = (k_0 + k_r)\, C$. This model is easily incorporated into the mass balance equations of a solute transport model, although we find no evidence that this has been done.

The expressions defining k_r and k_0 above are based on the assumption that the sorption and the first desorption isotherms are linear and that all of the adsorbate mass is associated with the solid at the start of desorption. If, however, the sorption and first desorption isotherms (Eqs. 3-32 and 3-33, respectively) are nonlinear, this analysis of nonsingular sorption can be generalized by substituting the Freundlich isotherms from 3-32 and 3-33 for the linear isotherms 3-36 and 3-37. Using Eqs. 3-32 and 3-33 and the approximation $N_a/N_d \approx 2.3$, k_0 and k_r can be redefined in terms of the Freundlich constants N_a, N_d, K_a, and K_d. This analysis is

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strictly limited, however, to that region of the consecutive desorption isotherm, (Eq. 3-40 or curve C in Figure 3-2), that is linear. If the consecutive desorption isotherm curves toward the origin as the sorbate concentration in the solvent decreases or approaches zero, the linear analysis fails. Then, either the magnitude of a highly resistant component depends on the solution concentration C, the number of desorption steps, and the time involved in each desorption step, or the concept of a highly resistant component loses its meaning (see discussion of Figure 3-3 on p. 3-27).

This analysis identifies a major research question: does a totally resistant component continue to exist as C approaches zero. That is, does a truly nonreversible sorbed component exist, and under what conditions does it exist? From a practical standpoint, the more important question for PCB-contaminated soils is the possibility of prolonged cleanup and treatment necessitated by slow desorption of the 'resistant' component. Without prolonged treatment or PCB source removal, PCBs would migrate from the near-field region of initial PCB contact with the soil to the far-field region of the adjacent groundwater aquifer and beyond.

The decrease in observed values of K_p with the increase in the solid to solution ratio (S:S) of the sediment/solvent suspension (O'Conner and Connolly 1980; Voice et al. 1983) and the nonsingularity or irreversibility of the hydrophobic sorption process (Swanson and Dutt 1973; Peck et al. 1980; Rao and Davidson 1980; DiToro and Horzempa 1982) represent two important examples of nonideal sorption behavior for hydrophobic organic solutes. The debate regarding the dependence of K_p on S:S and isotherm nonsingularity has for a long time centered on whether these observations are experimental artifacts or real behavior (Rao and Davidson 1980). Recently, Gschwend and Wu (1985) have presented new experimental evidence for PCB sorption on sediments that strongly suggests that both the S:S dependence of K_p and nonsingular behavior are indeed experimental artifacts.

Gschwend and Wu (1985) propose a model of sorption that includes the effects of sorbate bonding to nonsettling microparticulates and neutrally buoyant organic macromolecules, which in previous studies have not been distinguished from the sorbate that remains in true solution. These nonsettling particulates (NSP) are removed from natural sediments as the sediments are dispersed or suspended in the solution phase, and because of their small settling velocities or near-neutral buoyancy, resist separation from the true solution phase via centrifugation, which is by far the most common method of solid-solution phase separation in organic sorption studies.

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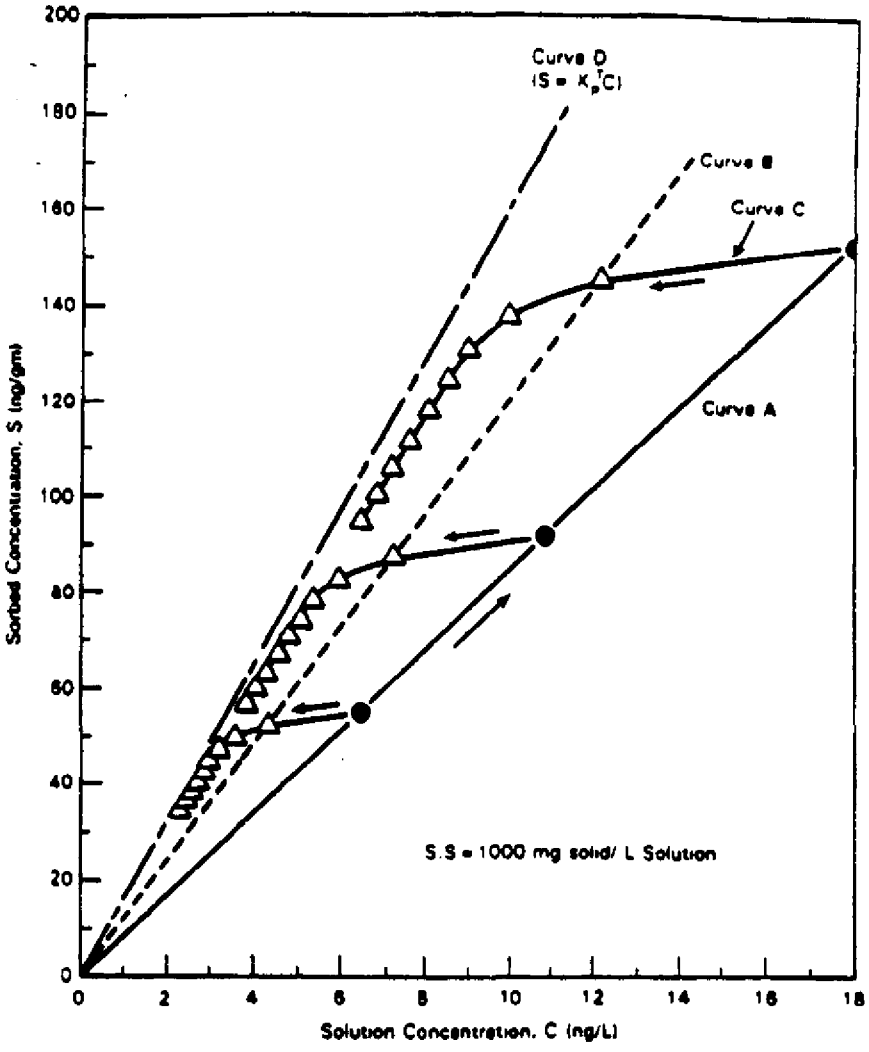

Figure 3-3. Sorption/desorption isotherms when sorption to nonsettling particulates and neutrally buoyant macromolecules (NSP) is accounted for. Curves A, B and C are the sorption, first desorption and consecutive desorption isotherms, respectively. Curve D is the 'true' isotherm in the absence of NSP.

Gschwend and Wu show that a noncentrifugable NSP phase typically occurs in batch sorption experiments unless precautions are taken to minimize NSP effects. This may be particularly important for the highly hydrophobic PCBs. Determination of partitioning constants must include not only the fraction of the sorbate associated with

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the true dissolved and settleable solid phases but also with this NSP phase. They express the observed partition coefficient K_p^{obs} as

$$K_p^{obs} = \frac{S}{C(dis) + C(NSP)} \tag{3-41}$$

where C(dis) and C(NSP) are the true dissolved concentration of the sorbate and the concentration of the sorbate bound to the NSP, respectively. The true partition coefficient is defined as

$$K_p^T = \frac{S}{C(dis)} \tag{3-42}$$

These two equations can be combined to yield

$$K_p^{obs} = \frac{K_p^T}{1 + K_{NSP}^T \left(\frac{\text{wt. NSP}}{\text{volume of solvent}}\right)} \tag{3-43}$$

or in terms of K_{oc} ($K_p = f_{oc} K_{oc}$)

$$K_{oc-p}^{obs} = \frac{K_{oc}^T}{1 + K_{oc-NSP}^T (DOC)} \tag{3-44}$$

where the dissolved organic carbon (DOC) is

$$DOC = \frac{(f_{oc})\ (\text{wt. NSP})}{(\text{volume of solvent})}$$

From Eq. 3-41 it can be seen that when C(NSP) << C(dis) K_p^{obs} approaches K_p^T. Eqs. 3-43 and 3-44 suggest that this condition occurs when [(wt. NSP)/volume] or DOC are such that $[K_{NSP}^T[(\text{wt. NSP})/\text{volume}]]$ or $(K_{oc-NSP}^T\ DOC) << 1$. In addition, when the S:S ratio or the hydrophobicity of the sorbate increases, C(NSP) will increase and K_p^{obs} will decreese relative to K_p^T. This apparent dependency of the partitioning coefficient on S:S is not a property of the sorption or partitioning mechanism, but rather an artifact resulting from failure to account for sorbate bonding to the NSP

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phase. The value of K^T_{NSP} or K^T_{OC-NSP} can be established by independent experiment or set equal to K^T_p. K^T_p or K^T_{OC-p} are determined from data at low values of S:S (curve D Figure 3-3).

Apparent irreversible or hysteretic sorption behavior is also shown by Gschwend and Wu (1985) to result from neglect of the NSP phase. They found that for the first, and each successive desorption experiment, C(NSP) decreases relative to the original quantity of NSP present during the original sorption experiment in which K^e_p is determined. Hence, by transposing Eq. 3-41 for desorption, it can be seen that the observed K^d_p will be greater than the initial K^e_p, which has often been interpreted as irreversible binding of the sorbent. Further, the extent of this hysteresis was thought to be a function of the initial dissolved concentration (Figure 3-2 and 3-3). With the consideration of NSP, Gschwend and Wu show that the consecutive desorption isotherm (curve C in Figure 3-3) bends towards the origin and asymptotically approaches the true isotherm which has slope K^T_p (curve D). This true isotherm is obtained using low S:S suspensions.

Although this model provides a reasonable interpretation of two important types of nonideal sorption behavior, it was developed and tested for two PCB congeners using only two natural sediments. Additional PCB congeners, organic compounds, and soils must be examined before any general resolution of the divergent observations regarding the reversibility and rates of hydrophobic sorption on natural sediments will emerge.

SORPTION KINETICS

Karickhoff (1984) noted that "a great deal of confusion exists in the sorption literature regarding the speed of attainment of sorption equilibrium." Reports abound which claim rapid and readily reversible organic sorption reactions in aqueous suspensions. Yet, others report highly release-resistant 'nonlabile' fractions, comprising 50% to 80% of the sorbed organic (Di Toro and Horzempa 1982), that require extended and often harsh extractions for complete removal of the sorbant from the solid phase (Karickhoff and Brown 1978; Karickhoff 1980; Freeman and Cheung 1981). These reports and others note that the nonlabile fraction and the difficulty of extraction usually increase with the duration of the sorption step.

The nonlabile component may indeed result not from the actual nature of the sorption/desorption process but rather from mass transfer or diffusion processes that control the migration of the sorbate between the bulk solvent phase and regions of the sorbent not in direct contact with the bulk solvent (Van Genuchten et al. 1974;

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Van Genuchten and Wierenga 1976a, 1976b; Rubin 1984). Based on observations that magnitude of the kinetic rate coefficients for 2,4-D sorption on kaolinite and montmorillonite were typical of those observed for diffusion coefficients (0.2 to 0.05 $days^{-1}$), Haque et al. (1968) concluded that the rate-limiting step in sorption/desorption was diffusion of the pesticide to the reactive sites within the clay matrix and not the kinetics of reaction at the site. Leenheer and Ahlrich (1971) suggest that for times exceeding a few minutes, the rate-limiting step was pesticide diffusion to sorption sites in the interior of the soil organic matter. Observations of initial rapid reactions (for both sorption and desorption reactions), followed by a slow reaction over long times, have been reported by many authors (Hamaker et al. 1966; Freeman and Cheung 1981). It is likely that both mass transfer of the sorbate to reactive sites and reaction kinetics of the sorbate at the sites contribute to the general macroscopic observation that sorption (or desorption) is a combination of a fast plus a slow step. Experimentally, mass transfer and reaction kinetics contributions cannot be distinguished. Examples of each approach are presented below.

Mass Transfer as the Rate-Limiting Step

A two-stage kinetic model of sorption was proposed by Karickhoff (1980) where sorption was considered to be the sum of a 'labile' component (S_ℓ) and a 'nonlabile' component (S_n). The labile component reaction, which occurs rapidly (usually within an hour), is treated as an equilibrium process and characterized by an equilibrium constant, K_L. The migration of the sorbate to and from the 'nonlabile' compartment is described by a mass transfer coefficient (k_n). The combined process is denoted

$$C \underset{K_L}{\rightleftharpoons} S_\ell \underset{k_n}{\rightleftharpoons} S_n$$

where C is the concentration of the sorbate in the bulk solvent phase and S_ℓ and S_n are the quantities of bound sorbate associated with labile and nonlabile sorbent sites. Karickhoff (1984) notes that the magnitude of k_n varies widely among sediments; however, he concludes that, as a rule, "the characteristic time ($1/k_n$) for diffusive release from the 'nonlabile' compartment approximates the K_{OC} (in minutes)." This model is limited in that it will not describe changes in sorption for times that are short relative to the characteristic time of nonlabile sorbate exchange.

A similar diffusion-limiting model for treating sorption was proposed by Van Genuchten and Wierenga (1976a,b) in which the soil-water phase was assumed to

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consist of mobile and immobile phases. The mobile phase (phase 1) participated in the advective-dispersive movement of the soil water through the soil. The immobile phase (phase 2) was considered stationary, residing for example in stagnant or dead-end pore spaces. Solute movement between phases 1 and 2 was assumed to be diffusion controlled:

$$\frac{\delta C_2}{\delta t} \propto d\,[C_1 - C_2]$$

where d is the diffusion coefficient and C_1 and C_2 are the solute concentrations in phases 1 and 2. In each phase, sorption/desorption was considered to be instantaneous and described in both regions by either linear or Freundlich isotherms. This treatment was applied by the authors to simulate pesticide migration through soil columns.

Reaction Rate as the Rate-Limiting Step

Selim et al. (1976) describe a mixed, nonlinear, equilibrium-kinetic model in which the soil was assumed to consist of two types of reaction sites or compartments: Type 1, which react rapidly relative to the average velocity of the bulk solvent and Type 2, which react slowly. Sites where the reaction rate is limited by diffusion are assumed to be Type 2. For Type 1 sites, the local equilibrium assumption is valid and a linear Freundlich was used to describe sorption

$$S_1 = KC^N \qquad (3\text{-}46)$$

The rate of change of Type 2 sites is described by a first-order reversible kinetic equation

$$\frac{\delta S_2}{\delta t} = \frac{\theta}{\rho} k_1 C^N - k_2 S_2 \qquad (3\text{-}47)$$

where k_1 and k_2 are the forward and reverse (sorption and desorption) rate coefficients ($days^{-1}$) and θ and ρ are the volumetric water content and the density of the porous media (soil), respectively. The total quantity sorbed, S_T, is assumed to be the sum on S_1 and S_2 (i.e., the equilibrium and kinetic processes are assumed to be independent). The mecroscopic rate of total sorption can be written

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$$\frac{\partial S_T}{\partial t} = \frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t} \tag{3-48}$$

Combining this with Eqs. 3-46 and 3-47 yields

$$\frac{\partial S}{\partial t} = (KNC^{N-1}) \frac{\partial C}{\partial t} + \frac{\theta}{\rho} k_1 C^N - k_2 S_2 \tag{3-49}$$

Substitution of Eq. 3-49 into the advective-dispersive mass balance equation (Eq. 3-1) constitutes a one-dimensional solute transport model that contains a nonlinear, combined equilibrium-kinetic description of sorption. Cameron and Klute (1977) used linear sorption isotherms (N = 1) in Eqs. 3-46 to 3-49. They obtained analytical solutions for the transport model (Eq. 3-1 and 3-49) and used these to describe soil column breakthrough and leaching data. Numerical and analytical solutions for the case where N = 1 have also been obtained for various boundary and initial conditions (Ogata 1964; Cho 1971; Lindstrom and Boersma 1978). If $k_2 S << (\theta/\rho)k_1 C$, and N = 1, Eq. 3-47 reduces to an irreversible, first-order kinetic model where $\partial S/\partial t$ is dependent only on the forward rate constant and C and independent of S. Analytic solutions for Eq. 3-1 containing this equilibrium-kinetic irreversible sorption model have been obtained (Ogata 1964; Cho et al. 1970). This nonlinear ($N \neq 1$), mixed, equilibrium-kinetic model was used by Selim et al. (1976) and Rao et al. (1979) to model pesticide breakthrough data in saturated soil column experiments.

Rao et al. (1979) have compared the ability of the mass transfer model (Van Genuchten and Wierenga 1976a) and the reaction kinetics model (Selim et al. 1976; Cameron and Klute 1977) to describe both batch sorption uptake-rate data and soil column breakthrough data at various initial concentrations of three pesticides on three soils. These authors concluded that for the soil column experiments, the sorption/desorption processes were diffusion-controlled and not limited by reaction kinetics at individual sites within the solid/solution interface. On the other hand, the concept of mobile and immobile soil-water phases in the mass transfer model was not a reasonable hypothesis because the fraction of immobile water differs for the nonadsorbing tritium tracer and the pesticides. It may be concluded that adequate descriptions of nonequilibrium organic sorption/desorption during organic solute transport do not currently exist. This is an area of active debate and research from both the chemical and hydrologic perspective.

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Yet another approach to describing nonequilibrium sorption that allows sorption and desorption energies to vary as a function of surface coverage was proposed by Lindstrom et al. (1970). This first-order, reversible kinetic model of sorption is expressed by

$$\frac{\partial S}{\partial t} = [k_2 \exp(\alpha S)] \left[\frac{k_2}{k_3} \frac{\theta}{\rho} C \exp(-2\alpha S) - S\right] \quad (3\text{-}50)$$

where α is related to surface stress coefficients. At equilibrium ($\partial s/\partial t = 0$), this equation reduces to

$$S = \left[\frac{\theta k_2}{\rho k_3}\right] [C \exp(-2\alpha S)] \quad (3\text{-}51)$$

which can be rearranged into

$$\ln (S/C) = \ln \left[\frac{\theta k_2}{\rho k_3}\right] - 2\alpha S \quad (3\text{-}52)$$

Plots of (S/C) versus S for different equilibrium sorbate concentrations provide a means to evaluate the parameters α and $(\theta k_2)/(\rho k_3)$. This model has been used to describe pesticide breakthrough and leaching in saturated soil columns (Van Genuchten et al. 1974). To our knowledge, these models for describing nonequilibrium sorption/desorption processes along with others described in reviews by Travis and Etnier (1981) and Kirackhoff (1980) have not been applied to PCB sorption/desorption in flow-through soil systems.

Returning finally to Eq. 3-49 for the mixed linear equilibrium-kinetic model ($N = 1$), the total sorption at equilibrium (i.e., for prolonged contact times) becomes

$$S = \frac{\theta}{\rho} (k_1/k_2 + K) C \quad (3\text{-}53)$$

This equation basically represents a linear isotherm. After some critical time, t_c (the value of which will depend upon both the sorbate and sorbent and experimental conditions), the equilibrium component can be shown to begin to dominate. At that

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point, equilibrium will appear to have been reached, when in fact the kinetic component continues to contribute. This is consistent with the observation of Karickhoff (1984) that "if one measures simply changes in aqueous phase and sorbed phase concentrations, the [sorption] process appears to be complete after a few hours, but in reality [it] may proceed indefinitely." This issue of sorption equilibrium (i.e., the time to reach equilibrium) is at the center of the confusion regarding reversibility of sorption reactions. This and the related issue of adequately describing nonequilibrium sorption/desorption processes remain topics of active research.

Section 4

RECOMMENDATIONS

The two preceding sections have described the data in the literature on PCB attenuation in soil and the conceptual models that may be applicable for describing PCB sorption/desorption in soils. The second section also provided a brief review of the PCDD data available in the literature. Data have been tabulated for water solubility, K_{ow}, K_p, K_F, and K_{oc} (Section 2). Equations have been presented linking these parameters for hydrophobic organic compounds, in general (Section 3). Using a much more limited data set than that described in Tables 2-1 and 2-3, several empirical equations have been found to describe the correlation among some of these parameters for PCBs (Section 2). For example, K_{ow} has been used to estimate K_{oc} values which, in turn, can be used to determine K_p values when the fraction of organic carbon in the soil is known. The K_p values are related to the retardation factor (p. 3-4), which relates PCB movement to solvent movement. While several empirical or derived relationships have been proposed, available data are insufficient to accurately predict PCB movement in soils.

Furthermore, results of both laboratory and field studies present conflicting conclusions regarding PCB attenuation within soils, subsoils, and groundwater systems. The commonly held belief that PCBs are environmentally immobile is overly simplistic. Transport models describing PCB migration within these environmental systems must include adequate descriptions of dominant attenuation processes (e.g., sorption, volatilization, etc.) if they are to serve as accurate predictive tools upon which risk assessments can be based. Quantitative risk assessments are an essential part of the process for evaluating environmental contamination and deciding whether and what site remediation is warranted. However, quantitative predictive models and the requisite data for describing these attenuation processes for PCBs, are not currently available.

The review of the available literature on PCB attenuation in soils discussed in Section 2 revealed a number of deficiencies or gaps in the data. Even less data were found for PCDD and virtually no data were found for PCDF attenuation in soils. The review of sorption models and semiquantitative methods for estimating sorption constants in Section 3 described a number of conceptual and mathematical approaches,

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as well as their strengths and limitations that are available for describing hydrophobic organic compound sorption in soils. Some of these models have been used for PCBs; many have not or have only incorporated one or two PCBs along with other hydrophobic compounds. Conditions for which models are needed, but for which none are available, are also identified. In both Sections 2 and 3, issues for which conflicting information exists in the literature are discussed. Based on the observations in these sections, we recommend a combined program of experimental and model development work. The basic goals of this program are to 1) amplify the PCB data base by filling in some of the data gaps on their attenuation in soils, and 2) determine and test the appropriate models for quantitative prediction of their sorption in soils, using both currently available data as well as data to be generated in the future. As in Sections 2 and 3, the recommendations in this section emphasize sorption data and models, though research needs in other areas related to abiological attenuation are addressed. Because EPRI is currently examining the role of biological degradation as part of a separate study, it has not been addressed here. Our recommendations for PCBs can be divided into several categories as described below.

STUDY OF PCBs IN AQUEOUS SOLVENT/SOIL* SYSTEMS

1. Establish the applicability and accuracy of models and estimation techniques of the type described in Section 3 to PCB congeners using both the limited data currently available and new data as it becomes available. Examples of models that should be tested include the relationships between K_p and percent of OC, K_{oc} and K_{ow}, K_{oc} and water solubility, and K_{oc} and surface area.

2. Because low organic carbon soils are typical in subsurface aquifer materials, it is important to determine the sorption/desorption behavior [K_ps, rates, reversibility, dominant soil parameters: e.g., surface area, expandable clay content (CM), etc.] for a broad range of low organic carbon (OC < 0.1%) sorbents. Appropriate estimation and modeling techniques for sorption/desorption on low-carbon soils should be developed. The levels of OC at which these other parameters become important for PCBs should be determined.

3. The related and controversial issues of reversibility/hysteresis/rate of approach to equilibrium for soils where OC > 0.1% (and possibly for low organic carbon soils, if similar effects are found to exist) need to be resolved. The dependence of reversibility/kinetics on soil aggregation properties, contact time, and other parameters should be established. Models are needed for describing sorption/desorption cycling. A major research question must be considered here; that is, is there a truly nonreversible sorbed component? For PCB contaminated soils, this addresses the important question of whether prolonged cleanup and treatment, or source

*The term soil is used here in a general sense to indicate soils, sediments, subsurface aquifer materials, and engineered backfill materials.

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removal is necessitated by slow desorption of the 'resistant' component. If this theory regarding slow desorption of the resistant component is accurate, PCBs might migrate in the presence of water from the near-field region of initial PCB contact with the soil to the far-field region of the adjacent groundwater aquifer and beyond, unless source removal is performed. On the other hand, if the sorption is truly irreversible, source removal may not be necessary.

4. The existing limited data base for PCBs should be enhanced by measuring K_p for 1) a range of individual isomers varying in chlorine number on a single soil; 2) repeating (1) for a wide range of soil types (e.g., differing OC/CM); and 3) repeating (1) and (2) for PCB mixtures, paying special attention to individual congeners that are part of the PCB mixtures. Model and estimation techniques should then be tested using these data.

5. The dependence of K_p or K_{ow} on temperature and the salt concentration of the solute should be determined because these geochemical parameters may vary in groundwater systems and from site to site.

6. Because differences in organic matter in soils have been observed to influence K_{oc}, the role of molecular weight, functional groups, structure, hydrophobicity of the soil organic matter, and the origin of the soil organic matter should be examined as they affect the ability to sorb PCBs.

STUDY OF PCBs IN ORGANIC OR MIXED AQUEOUS-ORGANIC SOLVENT-SOIL SYSTEMS

1. The sorption/desorption and reversibility/hysteresis behavior needs to be examined for selected mixed solvent/soil systems as outlined in recommendations 1, 2, and 3 for PCBs in aqueous solvent/soil systems. The role of expandable clays may be of special interest here.

2. The applicability of the generalized K_{oc}/solubility relationships and the gel model approach for describing hydrophobic sorption for organic and mixed-solvent systems described in Section 3 should be tested.

3. Estimation techniques and models should be generalized or new ones developed for describing sorption in organic solvent and mixed solvent/soil systems because the nature of the solvent plays a major role in PCB attenuation and transport. Adequate estimation techniques and models are either untested or nonexistent.

GENERAL PCB SORPTION RECOMMENDATION

The applicability and utility of 'C-18' or 'soil column' reverse-phase, high-pressure liquid chromatography techniques for rapid measurement of PCB solvent/soil partitioning parameters should be investigated. This method allows flow rate effects on sorption to be determined.

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RESEARCH NEEDS IN OTHER AREAS OF ATTENUATION

1. A wide disparity exists in literature values for water solubility, vapor pressure, and octanol-water partition coefficients for individual PCB congeners. A critical review and evaluation of literature data are urgently needed to determine 'best' values of these physical constants and to determine where additional experimental effort is most needed to correct this situation.

2. Volatilization data from soils are needed for a wider range of PCB congeners, especially those that are more highly chlorinated. The effect of different soils with a wider range of organic carbon content and clay mineral content should be examined under different water saturation conditions. The effect of the presence of organic solvents on volatilization from soils should also be determined because organic solvents will likely be present in a surface spill.

3. The effect of soils on chemical degradation is another area that has not received sufficient attention. Here, it is important to determine the degradation products and not merely the extent of loss of the PCBs, because loss can be due to a number of processes not related to degradation. These studies should be done on single congeners or simple mixtures of congeners whose decomposition can be more readily followed experimentally. Again, a number of soils with a wide range of organic carbon and clay mineral contents should be examined under different water saturation conditions.

4. The migration of PCBs as a sorbed phase (i.e., transport on particles) and as an immiscible phase (i.e., as pure compound or as a compound/organic solvent phase) also should be considered in any attempt to predict PCB transport.

SUMMARY OF RECOMMENDATIONS

The recommendations made above are presented with the needs of the electric utility industry in mind. Polychlorinated biphenyls while of themselves important to the utility industry, also represent an ideal tool for investigating the important hydrophobic interactions which play a major role in the attenuation process of a wide variety of organic compounds significant to a much broader spectrum of researchers and industries. Results from PCB research may be 1) applied to other nonionizable hydrophobic compounds with relatively unreactive functional groups, and 2) potentially extrapolated to the hydrophobic component of interaction associated with polar and/or slightly ionizable organic compounds. Model compounds other than PCBs might require a greater effort in the separation of sorption phenomena from other pathways of loss, e.g., biodegradation, chemical reaction, or volatilization.

A coordinated experimental and modeling approach should be used to address this series of recommendations. The development of predictive tools for describing the attenuation mechanisms governing PCB movement in soils, sediments, and subsurface aquifer materials must, by necessity, include both laboratory studies and field

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testing. During the initial laboratory phase, batch sorption/desorption experiments, soil column breakthrough, leaching and volatilization experiments, and degradation studies should be conducted. These experiments should study aqueous, mixed aqueous-organic and organic solvents, and a range of congeners (e.g., those found in utility Aroclor mixtures should be emphasized). In addition, well-characterized soils should be used which cover a range of organic carbon and expandable clay content and which typify soils where utility cleanup may be an issue. Information obtained at contaminated sites that further defines the practical limits of attenuation processes should be integrated into laboratory studies during all stages of research.

Field testing of the data base and attenuation models developed during the initial phase should begin as soon as feasible and technically profitable at well-characterized field sites. The objective of this testing is to identify deficiencies in the predictive capability resulting from inadequacies in the process models (e.g., sorption, volatilization, etc.) and/or in the requisite data base and site characterization. These deficiencies should, in turn, be resolved by either laboratory or field experiments or a combination of both.

Future work on PCB sorption, volatilization, and abiotic degradation will establish the date base. Attenuation models can be incorporated into solute and multiphase transport models to yield predictive tools. Such models can then be used to describe migration of PCBs and related nonionizable hydrophobic compounds in the presence of solvents from the near-field region of initial contact with the soil to the far-field region of the adjacent groundwater aquifer and beyond. Then based on these predictive tools for describing migration, the associated risk assessment and subsequent decisions can be made as to whether cleanup is required and/or cost-effective.

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Section 5

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REPORT SUMMARY

SUBJECTS	Hazardous/toxic substances / Solid-waste studies / T&D: Substations
TOPICS	PCBs Hydrology Adsorption Mathematical models Literature reviews
AUDIENCE	R&D scientists / Environmental engineers

Attenuation of Polychlorinated Biphenyls in Soils: Literature Review

Computer models that accurately predict the long-term behavior and transport of PCBs in soils would help utilities make correct and cost-effective decisions about cleaning up contaminated sites. However, inconsistencies and deficiencies in the data on PCB sorption processes hinder the development of such models.

BACKGROUND

Regulatory agencies restrict the use of polychlorinated biphenyls (PCBs) because of their perceived toxicity to humans and other organisms and their persistence in soil and water. However, the degree of concern with which PCB-contaminated soil should be regarded remains unclear because little is known about the behavior and long-term migration of these compounds in various types of soil and water. The utility industry is particularly interested in resolving this question, since these chemicals are widely used as insulating fluids and coolants in capacitors and transformers.

OBJECTIVES

To review and summarize the scientific literature on the attenuation of polychlorinated biphenyls in soils and on conceptual and mathematical approaches to modeling PCB sorption and desorption in soils.

APPROACH

Researchers reviewed laboratory and field measurements of PCB behavior in soils, identified mechanisms of interaction between PCBs and soils, and identified and evaluated several mathematical approaches to modeling PCB sorption and desorption. Because recent research suggests that toxicity attributed to PCBs may be caused or intensified by chlorinated dibenzofurans and dioxins, project personnel reviewed literature on the attenuation of those compounds also.

RESULTS

The study findings indicate that further research is required for a clear understanding of the mechanisms of PCB sorption and the differences in behavior of the 209 possible PCB compounds.

- The collected data support the qualitative conclusion that PCBs are sorbed into the organic carbon in the soil. However, insufficient quantitative data exist on PCB sorption under equilibrium conditions in aqueous solvents and soils containing typical concentrations of organic carbon. It is therefore not

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yet possible to verify existing sorption models for the 209 individual PCB compounds or to make accurate, scientifically defensible predictions of PCB mobility in soils.

- Conflicting information exists on the rates and reversibility of the PCB sorption and desorption process in typical organic compound soils and aqueous solvents. Such conflicts hinder modeling.

- The literature contains no data on PCB sorption, desorption, and reversibility under equilibrium and nonequilibrium conditions in aqueous solvents and soils containing organic carbon levels of less than 0.1%. Nor do verified mathematical models exist. Such low organic carbon levels are typical of subsoils and subsurface groundwater aquifer materials. The mobility of PCBs in such materials may differ significantly from that in typical organic carbon soils.

- The report includes a summary of existing PCB data on sorption coefficients.

EPRI PERSPECTIVE

This study shows that utilities are addressing the cleanup of PCB spills and contaminated sites on the basis of very limited data on PCB behavior in the environment and little understanding of the molecular processes involved in PCB interaction with soil. Models that accurately predict PCB migration in soil would enable utilities and regulators to agree on the proper corrective action for a specific PCB spill. Before such models become a reality, utilities need reliable data on the long-term behavior of PCBs in a variety of soil and water conditions.

PROJECT

RP1263-22
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Attenuation of Polychlorinated Biphenyls in Soils: Literature Review

CS-4396
Research Project 1263-22

Final Report, January 1986

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ABSTRACT

Polychlorinated biphenyls (PCBs) have found their way into a wide variety of industrial applications, a major one being coolant-insulation in capacitors and transformers. Perceived toxicity to humans and other organisms in conjunction with environmental persistence has led to a highly regulated climate of PCB use. Because of the ubiquity and persistence of PCBs, the ability to predict their long-term mobility in the soil-water environment is of particular interest to the electric utility industry and regulatory agencies.

This report has two main objectives: to review and summarize available literature data on the attenuation of PCBs in soil and to review the current literature on the conceptual and mathematical approaches that may be applicable to modeling PCB sorption/desorption in soils. Because research has suggested that toxicity attributed to PCBs may be caused or enhanced by other closely associated hydrophobic compounds such as polychlorinated dibenzodioxins (PCDDs) or polychlorinated dibenzofurans (PCDFs), literature on PCDD and PCDF attenuation data in soils has also been briefly reviewed; these data are amenable to the same modeling approaches as described for PCBs. Sorption/desorption data have been emphasized, but information on other attenuation mechanisms has been included as well. Major deficiencies in the data are identified and, based on these deficiencies, recommendations are made for a combined program of experimental work and model development. These recommendations identify specific areas for research which in the near future would allow the development of a predictive capability.

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