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Influence of Colloids on Sediment-Water Partition Coefficients of Polychlorobiphenyl Congeners in Natural Waters

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■ Laboratory studies have shown that speciation of hydrophobic organic pollutants in aquatic systems is too complex to model as a linear, two-phase sorption equilibrium due to ill-defined phases and slow kinetics. This complexity is manifested in an inverse variation in sediment-water partition coefficients with the concentration of solids. Measurements of the sediment-water partitioning of polychlorobiphenyl (PCB) congeners in Lake Superior provide some of the first field evidence demonstrating the importance of colloids to the fates of highly hydrophobic organic pollutants. Laboratory-derived correlations between sediment-water distribution coefficients and properties of both the contaminant (octanol-water partition coefficient) and the suspended solids (organic carbon content, concentration) do not accurately predict PCB speciation in Lake Superior. This failure can be explained by the presence of colloidal matter with which contaminants may associate and the very low solids concentrations in oligotrophic surface waters. A surprising consequence of such colloid associations is that the observed sediment-water distribution coefficients are independent of properties of highly hydrophobic compounds. A three-phase model including nonfilterable microparticles and macromolecular organic matter shows that colloidal-associated contaminants may be the dominant species in most surface waters. Colloidal associations are therefore likely to significantly impact the geochemistry of hydrophobic pollutants.

Introduction

The aquatic fate of hydrophobic organic contaminants is tightly linked to chemical and physical interactions at the air-water and sediment-water interfaces. The residence time of trace elements (e.g., ref 1 and 2) and organic contaminants (3-5) depends on the fraction bound to suspended particles and the rate of particle settling through the water column (or the sediment accumulation rate). Thus, the affinity of hydrophobic organic compounds for biotic and abiotic phases is an important determinant of both the rate of a lake's detoxification and its response time to changing loadings.

The sorption of organic compounds to sediment has been viewed as an equilibrium and linear process (6) described by a partition coefficient, $K_p = C_{\text{part}}/C_{\text{aq}}$ (kg/L), where C_{part} and C_{aq} are particulate and dissolved (aqueous) contaminant concentrations, respectively. K_p has been correlated to the fractional organic carbon content of the solids phase (foc) through the equation $K_p = K_{oc} \text{foc}$.

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Table I. Distribution Coefficients of Total PCB in Surface Waters

	range in log K_d	ref
Lake Michigan	4.55-7.0	15
Lake Michigan	5.15-5.40	16
Saginaw Bay, Lake Huron	4.60-4.97	17
Lake Superior	4.65-7.0	18
Lake Superior, western	4.16-5.76	19
Puget Sound	4.0-5.4	20
Crystal and Emrick Lakes, WI	4.48-5.95	15

Values of K_{oc} of nonpolar organic contaminants may be predicted for many sediments and soils through correlations with octanol-water coefficients (K_{ow} ; 7, 8). These correlations are consistent with a partitioning of the hydrophobic organic compound into the organic matter (OM) of the sediment. Laboratory data (ref 9 and references cited therein, 10-12) suggest that the value of K_p or K_{oc} is inversely proportional to the solid/solution ratio. This observation may be attributed to nonequilibrium effects, nonlinear sorption isotherms, slow rates of desorption (6, 12, 13), particle-particle interactions (14), and imperfect separation of particulate and dissolved species (10, 11). Gschwend and Wu (11) and others (10) suggest that non-settling colloids and microparticles are not separated from the dissolved species and thus contribute to the apparent dissolved fraction. In this manner, log K_d for hydrophobic organic contaminants (the operationally defined distribution coefficient between dissolved and particulate phases) may artificially decrease with increasing suspended solids concentration (SS).

Although numerous investigators have studied sorption of hydrophobic compounds to soils and sediments in the laboratory, there are only a few cases where organic contaminant sorption has been measured in the field under ambient conditions. Field partition data available for total polychlorobiphenyl (PCB) (Table I) suggest K_d may vary several orders of magnitude. This paper presents results from a detailed field investigation of contaminant partitioning. The specific objective of this work is to evaluate the hypothesis that colloidal particles binding PCB congeners in an aquatic field setting may explain the anomalous log K_d -log SS relationship. The data selected for study are distribution coefficients for 28 PCB congeners obtained in 1980 and 1983 from oligotrophic Lake Superior.

Materials and Methods

Concentrations of 28 PCB congeners were measured in water samples collected throughout Lake Superior in 1980 and in western Lake Superior in 1983. Sampling and analytical techniques are presented in detail elsewhere

(21–23) and will be summarized here. Water samples in 1980 were collected with a 30-L Teflon-lined Go-Flo bottle (General Oceanics). Chlorinated hydrocarbons were isolated from the bulk water by passage through XAD-2 resin in a 2 cm × 15 cm glass column at 100–200 mL/min. Particles were isolated from bulk water samples with a precombusted 293-mm glass fiber filter (0.6-μm pore size) in a stainless steel filtration unit. Nonfilterable PCB concentrations were determined by difference. Samples were collected from surface water throughout the lake. In 1983, a submersible pump delivered water from depth through equilibrated Tygon tubing to the surface (flow rate = 10 L/min), where the water passed through a precombusted 0.6-μm glass fiber filter. In general, samples were obtained from the surface, at middepth below the thermocline, and in the benthic nepheloid layer 2–3 m from the bottom at several stations in the western end of the lake. Sampling began prior to thermal stratification (early June) and continued biweekly through fall turnover in October 1983. The water depth in the sampling area was 25–36 m. Nonfilterable chlorinated hydrocarbons were isolated by passing 20 L of filtrate through XAD-2 resin as in 1980.

Chlorinated hydrocarbons in samples from both years were analyzed in an identical manner. Filter and resin samples were extracted with 1:1 (v/v) hexane–acetone, and the resulting extracts were concentrated by solvent removal, fractionated on Florisil columns, concentrated, and analyzed by capillary gas chromatography with electron-capture detection (GC–EC). Individual PCB congeners were identified and quantified by comparison to standard Aroclor mixtures by the procedure of Capel et al. (23). Briefly, Capel et al. (23) identified 70 congeners in Aroclors 1242, 1254, and 1260 by comparison to published Aroclor chromatograms and relative retention times (24, 25). These identities were independently confirmed with single congener standards, gas chromatography/mass spectrometry (GC/MS), and high-performance liquid chromatography with GC–EC detection. The weight percents of each congener in each Aroclor mixture were then determined by GC/MS. In this study, 28 congeners were quantified by comparison of their peak areas to corresponding peak areas in Aroclor 1242 and 1254 standards. PCB in these environmental samples retained the characteristic Aroclor pattern and consisted primarily of congeners found in Aroclors 1242 and 1254. A congener's peak was considered contaminated and discarded if its area was significantly larger than that expected in the Aroclor "fingerprint". Several GC–EC peaks contain two unresolved congeners, which were considered to consist only of the dominant congener. In most cases, the coeluting congeners had an equal number of chlorines and similar physical properties.

Recoveries of PCB congeners from spiked XAD-2 resins were 75–85%, and propagated analytical uncertainties in congener concentrations and distribution coefficients were estimated to be 25–30% and ca. 40%, respectively (18, 19). Reported concentrations are not corrected for recovery. Field blanks were generally free of PCB congeners, but samples were corrected for occasional contamination of the blanks.

Suspended solids (SS) concentrations were determined by filtering 1–2 L of bulk lake water through tared glass fiber or membrane filters (0.6-μm pore size), followed by freeze-drying and reweighing. Uncertainty in SS values is ca. 0.1 mg/L at 5 mg/L. Total and dissolved organic carbon were measured with a Barnstead Photochem organic carbon analyzer. Particulate organic carbon (POC) was determined for some 1983 samples with the persulfate

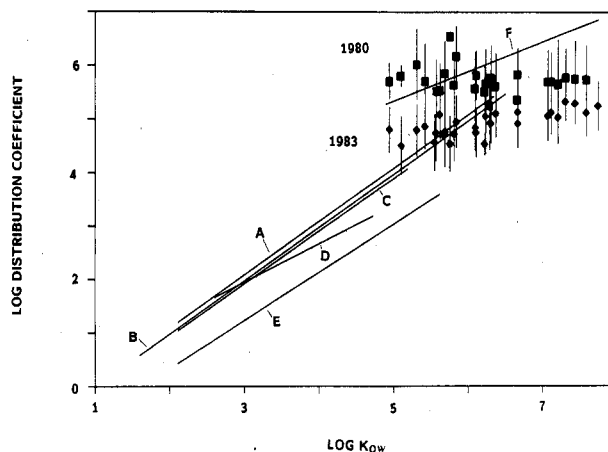


Figure 1. Mean PCB congener distribution coefficients measured in Lake Superior, 1980 (■) and 1983 (◆). Vertical lines represent ± 1 SD. Solid lines indicate empirical relationships between K_d and K_{ow} plotted over the range in K_{ow} from which they were derived, assuming $f_{oc} = 0.2$. (A) $\log K_d = 1.00 \log K_{ow} - 0.909$, ref 7; (B) $\log K_d = 1.00 \log K_{ow} - 1.02$, ref 29; (C) $\log K_d = 0.989 \log K_{ow} - 1.045$, ref 27; (D) $\log K_d = 0.72 \log K_{ow} - 0.21$, ref 8; (E) $\log K_d = 0.904 \log K_{ow} - 1.48$, ref 43; (F) $\log K_d = 0.55 \log K_{ow} + 2.7$, ref 30.

oxidation technique of Menzel and Vaccaro (26) on an Oceanographic International carbon analyzer. Estimated analytical uncertainty in POC measurement was 10–20%.

Results

Concentrations and distributions of 28 PCB congeners measured in Lake Superior in 1980 and 1983 are summarized in Table II. Samples were collected from surface waters throughout the lake in 1980 and from an approximately equal number of surface, middepth, and near-bottom depths in the western end of the lake in 1983. Lower congener concentrations in 1983 reflect the decreasing PCB load in the Great Lakes resulting from the ban on PCB use (3) and higher sedimentation rates (and thus removal efficiencies) in the western end. Distribution coefficients (K_{ds}) are uniformly higher in 1980 than in 1983 (Figure 1). Although this could be due to artifacts introduced by collecting total and particulate PCB in 1980 vs. dissolved and particulate PCB in 1983, we believe these higher K_{ds} in 1980 result from sampling in areas of lower suspended solids concentrations (22; also see discussion below).

One of the most surprising results of these field measurements is that the observed K_d values for individual PCB congeners vary 1–3 orders of magnitude (Figure 1). The goal of the following discussion is to examine whether the presence of PCB-binding colloids can explain the variations in PCB distribution coefficients observed in a "real" aquatic system.

Congener K_{ds} did not systematically vary with either sampling depth or date. As particle and contaminant residence times in the water column are ≤ 1 year and less than or equal to a few years, respectively (4, 21, 22), it seems likely that local sorptive equilibrium is achieved at low SS concentrations (6). Also, desorption induced by interparticle interactions (14) is probably unimportant at the low suspended solids concentrations observed in Lake Superior (0.1–5 mg/L).

Observed distribution coefficients varied slightly with congener K_{ow} in 1983 and not at all in 1980 (Figure 1): for 1980

$$\log K_d = -0.024 (\pm 0.046) \log K_{ow} + 5.86 (\pm 0.29) \quad (1)$$

$$r^2 = 0.4760 \quad N = 363$$

for 1983

$$\log K_d = 0.230 (\pm 0.023) \log K_{ow} + 3.50 (\pm 0.14) \quad (2)$$

$$r^2 = 0.1113 \quad N = 807$$

Also shown in Figure 1 are relations between $\log K_d$ and $\log K_{ow}$ determined in five laboratory sorption studies (7, 8, 27, 28, 29) and in one marine sediment/porewater system (30). Each line is plotted over the range of $\log K_{ow}$ from which it was derived in laboratory or field studies. These relationships predict more variation in K_d with K_{ow} by a factor of 2–4 than was observed in this study, suggesting that either K_d values asymptotically approach a maximum at $\log K_{ow} > \text{ca. } 5$ or that contaminant speciation in surface waters is impacted by other processes. Oliver and Charlton (31) reported K_{oc} values in Lake Ontario that were also less variable with K_{ow} than predicted by Karickhoff's empirical equation (27).

The variations of K_d with the fractional organic carbon content (foc) of the suspended solids for four PCB congeners are shown in Figure 2. Values of foc are available for only half of the 1983 samples, resulting in limited data in Figure 2. Considerable scatter observed for all four congeners suggests only a weak relationship between K_d and foc. Organic carbon normalized distribution coefficients ($K_{oc} = K_d/\text{foc}$) obtained from Figure 2 are within those calculated from empirical relationships between K_{oc} and K_{ow} (8, 27) (Table III). Particles in Lake Superior had foc values 5–10 times those of sediments used in these laboratory studies. The relationship between K_d and foc observed in oligotrophic lake waters is weaker than empirical relationships derived from laboratory studies at much higher suspended solids concentrations.

Variations in observed K_d s for PCB congeners were most strongly dependent on the suspended solids concentrations. Plots of $\log K_d$ vs. $\log \text{SS}$ (Figure 3) and linear regression analysis (Table IV) demonstrate an inverse correlation with slopes ranging from -0.54 to -1.62 for the 28 PCB congeners. On the basis of the coefficient of determination (r^2), linear regressions with $\log \text{SS}$ explain 20–73% of the variation in $\log K_d$. Prior to combining the 1980 and 1983 data sets, we tested the hypothesis that differences in K_d values between the two years were due only to differences in SS concentrations. Samples collected in 1980 had lower SS concentrations (generally $< 1 \text{ mg/L}$) and higher K_d s than those in 1983, when $\text{SS} \geq 1 \text{ mg/L}$. When the two data sets were analyzed separately, regressions of $\log K_d$ vs. $\log \text{SS}$ yielded slopes and y intercepts that were not different between years ($p = 0.05$, Figure 4). The y intercept, the predicted $\log K_d$ at 1 mg/L SS concentration, is particularly useful to compare the data sets since they overlay at this point. Note that the one high SS concentration sample collected in 1980 ($\text{SS} = 5 \text{ mg/L}$) falls within the range of observed K_d s at similar SS concentrations in 1983 (Figure 3). We conclude that the 1980 and 1983 data differ primarily due to their SS concentrations and that other potential biases introduced by sampling differences are relatively unimportant.

The data presented in Figure 3 and Table IV show the observed K_d s for PCBs decrease 10–1000 times as the SS concentration increases from 0.1 to 10 mg/L . In addition, the y intercepts of the $\log K_d$ vs. $\log \text{SS}$ regressions are remarkably constant for the 28 PCB congeners (3.3% relative standard deviation). Although their aqueous solubilities and K_{ow} s vary ca. 100-fold and ca. 600-fold, respectively, K_d values of the PCB congeners normalized to 1 mg/L SS (i.e., the y intercept) are invariant. This implies that contaminant partitioning in surface waters is not controlled by a simple two-phase partitioning, since

the extent of such partitioning should depend directly on K_{ow} .

Multiple regression analysis was employed to simultaneously evaluate the influences of $\log K_{ow}$ and $\log \text{SS}$ on $\log K_d$ for the 28 PCB congeners:

$$\log K_d = -0.85 (\pm 0.04) \log \text{SS} + 0.23 (\pm 0.20) \log K_{ow} + 3.69 (\pm 0.11) \quad (3)$$

$$r^2 = 0.4579 \quad N = 807$$

Samples from 1983 for which foc values were available yielded

$$\log K_d = -0.92 (\pm 0.10) \log \text{SS} + 0.29 (\pm 0.02) \log K_{ow} - 0.09 (\pm 0.23) \text{foc} + 3.31 (\pm 0.16) \quad (4)$$

$$r^2 = 0.4581 \quad N = 374$$

More than half of the variation in K_d explained by these regressions is attributable to variations in the SS concentrations. Because SS and foc inversely covary, adding foc to the regression provides no additional predictive ability.

Discussion

The variations in the K_d s of PCB congeners observed in Lake Superior raise questions as to the applicability of two-phase equilibrium models describing the aquatic speciation of hydrophobic contaminants. The strong inverse variation of K_d with SS concentration suggests the presence of colloidal-sized, nonsettling microparticles (NSPs), which effectively complex contaminants. Recently, Gschwend and Wu (11) described pollutant speciation as a three-phase equilibrium, incorporating a colloidal phase into the calculation of observed K_d . Here, their model is modified and calibrated to the inverse correlation between K_d and SS concentration observed in Lake Superior. These calculations show that colloids contributing to the "dissolved" concentration can explain PCB partitioning in natural waters.

Colloids (NSPs) that complex contaminants and are not separated by filtration or centrifugation decrease the contaminant's K_d :

$$K_d = (P/M)/[(D+N)/V] \quad (5)$$

where P , N , and D are masses of organic contaminant sorbed to filterable solids, sorbed to NSPs, and dissolved in solution, respectively, and M and V are mass of particles and volume of water. Rearranging eq 5 and defining a NSP equilibrium partition coefficient analogous to K_p , $K_{NSP} = (N/M_{NSP})/(D/V)$, yields (eq 6 of ref 11)

$$K_d = K_p[1 + K_{NSP}(M_{NSP}/V)]^{-1} \quad (6)$$

Direct measurement of NSPs in natural waters proves elusive. However, the mass concentration of NSPs is likely related to the SS concentration because particle size distributions are continuous across the operational cut-offs of either filtration or centrifugation (32). As a first approximation, NSP concentration was assumed to be a linear function of SS concentration; $M_{NSP}/V = f_{NSP}(M/V)$. This assumes that the particle size distribution is independent of SS concentration. Surficial Lake Superior sediments contain 5% of NSPs by weight ($f_{NSP} = 0.05$) (11). Since colloids are slower to settle and more easily reentrained, f_{NSP} in the water column is likely greater than that in the underlying sediments. Dissolved organic carbon concentration (DOC) provides an alternate estimate of M_{NSP}/V , assuming NSPs are primarily organic macromolecules and colloids (33). DOC in western Lake Superior

Table II. Partitioning of PCB Congeners in Lake Superior in 1980 (18, 22) and 1983 (19, 21)

congener	IUPAC no.	log K_{ow} ^a	year	dissolved			particulate					log K_d		
				pg/L			pg/L		ng/g		N			
				mean	SD	N	mean	SD	mean	SD		mean	SD	N
2,4'	8	5.10	1980	68	22	6	31	21	81	95	16	5.8	0.2	4
			1983	104	110	25	4	4	4	7	28	4.5	0.5	20
2,2',3	16	5.31		24	19	18	11	8	38	51	19	6.0	0.7	16
				26	14	37	3	2	3	4	34	4.8	0.5	32
2,2',4	17	5.76		22	7	2	19	3	84	39	2	6.5	0.1	2
				44	40	39	3	3	3	6	34	4.6	0.5	33
2,2',5	18	5.55		15		1	38	6	167	79	2	7.2		1
				74	69	38	5	5	5	9	35	4.6	0.5	33
2,3,4'	22	5.42		18	9	18	6	4	14	16	17	5.7	0.7	15
				12	7	37	1	1	1	1	28	4.9	0.4	24
2,4,4'	28	5.69		46	23	17	12	12	47	76	19	5.5	0.6	17
				50	25	41	5	6	4	6	38	4.7	0.5	38
2,4',5	31	5.69		72	41	19	7	4	22	24	20	5.9	0.6	19
				66	36	41	6	8	5	7	38	4.8	0.7	38
2,3,3'	33	5.57		ND			22	13	67	75	20	ND		
				38	20	35	5	11	4	9	35	4.8	0.5	30
3,4,4'	37	4.94		20	13	15	8	13	34	83	16	5.7	0.3	12
				16	10	40	2	2	2	2	37	4.8	0.4	36
2,2',3,4	41	6.11		31	15	15	6	4	23	27	7	5.8	0.5	4
				18	8	39	2	2	2	2	37	4.8	0.5	35
2,2',3,5'	44	5.81		37	14	18	9	5	30	35	18	5.6	0.4	16
				26	15	41	3	3	2	3	34	4.7	0.5	34
2,2',4,4'	47	6.29		38	15	18	6	9	25	57	17	5.3	0.5	16
				9	5	26	2	4	2	3	26	4.9	0.5	21
2,2',4,5'	49	6.22		22	7	18	5	3	14	16	18	5.5	0.5	16
				16	6	10	3	1	1	0	3	4.5	0.2	3
2,2',5,5'	52	6.09		76	32	19	17	14	65	92	20	5.6	0.7	19
				40	26	35	5	4	4	5	34	4.9	0.4	29
2,3,4,4'	60	5.84		45	51	17	20	23	74	90	13	6.2	0.5	11
				13	9	37	2	2	2	2	35	5.0	0.5	32
2,3',4,4'	66	6.31		42	27	19	16	10	58	76	20	5.8	0.6	19
				26	22	38	4	3	3	3	37	4.9	0.4	34
2,3',4',5	70	6.23		73	74	19	18	12	61	72	20	5.7	0.6	19
				33	23	39	6	4	4	4	37	5.1	0.7	35
2,4,4',5	74	6.67		8	6	19	3	2	10	12	19	5.8	0.5	18
				9	6	33	2	2	1	1	30	4.9	0.5	26
2,2',3,4,5'	87	6.37		15	10	19	4	4	17	27	20	5.6	0.6	19
				13	9	33	2	4	2	3	29	5.1	0.5	22
2,2',3',4,5	97	6.67		25	16	5	3	2	9	9	18	5.4	0.9	5
				7	5	36	2	2	1	2	37	5.1	0.4	32
2,2',4,4',5	99	7.21		29	27	19	8	8	32	51	19	5.7	0.8	18
				11	10	9	3	3	2	1	12	5.1	0.5	7
2,2',4,5,5'	101	7.07		65	44	18	18	13	65	81	20	5.7	0.6	18
				38	39	35	7	8	5	6	36	5.1	0.5	30
2,3,3',4',6	110	5.62		59	38	18	20	28	88	199	20	5.6	0.5	18
				28	23	40	7	8	4	6	38	5.1	0.5	37
2,3',4,4',5	118	7.12		65	50	18	14	9	44	55	18	5.7	0.5	17
				35	25	40	9	9	6	8	38	5.1	0.4	37
2,2',3,4,4',5	138	7.44		39	29	17	12	7	43	44	14	5.8	0.7	11
				20	16	34	8	10	5	7	34	5.3	0.4	28
2,2',3,4,5,5'	141	7.59		25	23	16	8	7	32	46	17	5.8	0.6	14
				12	8	19	3	3	2	4	27	5.1	0.4	18
2,2',3,4',5,5'	146	7.31		36	34	19	11	8	40	48	20	5.8	0.5	19
				15	10	38	6	6	4	5	37	5.3	0.3	35
2,2',4,4',5,5'	153	7.75		ND			ND		ND			ND		
				17	13	35	6	5	4	4	34	5.3	0.5	29

^aRef 42.Table III. Organic Carbon Normalized Distribution Coefficients (K_{oc} s) of Four PCB Congeners in Lake Superior, 1983

congener	IUPAC no.	mean log K_d	obsd log K_{oc} (% SD) ^a	calcd log K_{oc} ^b	calcd log K_{oc} ^c
2,4,4'	28	4.66	5.28 (33)	5.30	4.59
2,2',5,5'	52	4.87	5.35 (28)	5.70	4.87
2,2',4,5,5'	101	5.09	5.65 (32)	6.68	5.58
2,2',3,4',5,5'	146	5.40	5.88 (35)	6.92	5.75

^aPercent standard deviation of the slope of K_d vs. foc. ^b $K_{oc} = 0.411K_{ow}$; ref 27. ^c $\log K_{oc} = 0.72 \log K_{ow} + 0.49$; ref 8.

in 1983 ranged from 1.8 to 3.8 mg of C/L (19). To calculate NSP concentration, DOC values are first converted to

dissolved organic matter concentrations (DOM, mg/L) by dividing by the fraction organic carbon content of DOM

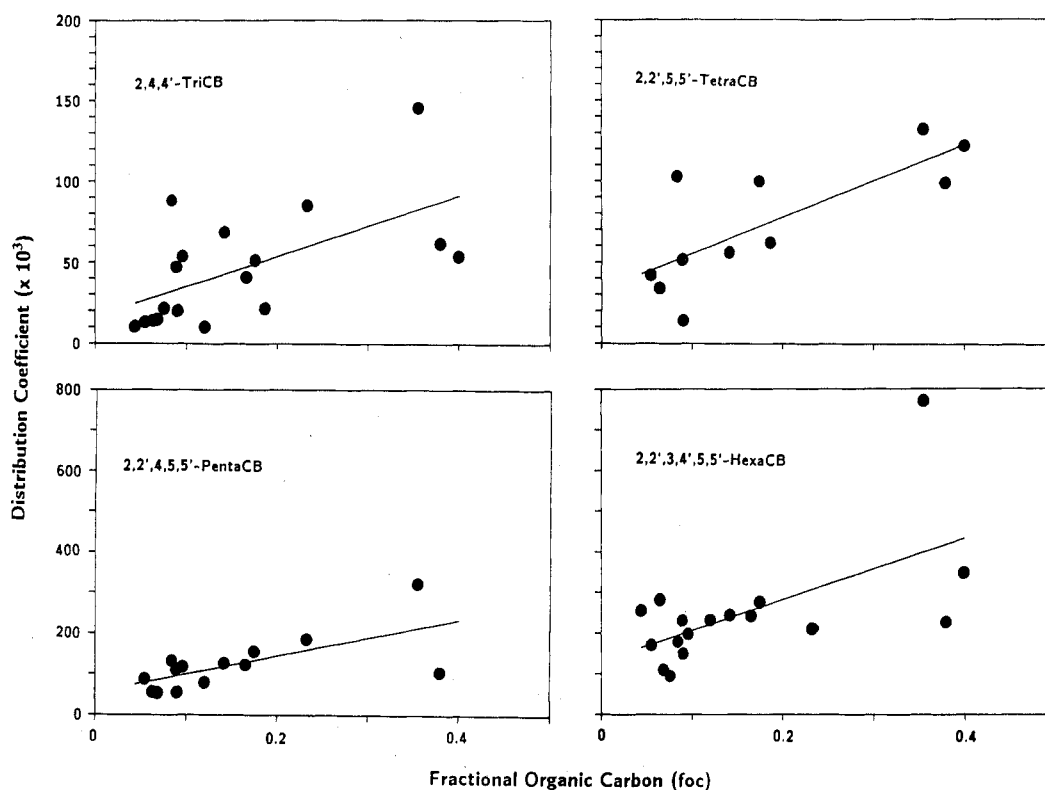


Figure 2. PCB congener distribution coefficients vs. fractional organic carbon content of suspended solids, Lake Superior, 1983. Slope of linear regression analysis equals K_{oc} . (2,4,4'-TriCB) $K_d = (1.89 \pm 0.62) \times 10^5 \text{foc} + (1.6 \pm 1.2) \times 10^4$, $r^2 = 0.36$, and $N = 18$; (2,2',5,5'-TetraCB) $K_d = (2.25 \pm 0.62) \times 10^5 \text{foc} + (3.3 \pm 1.4) \times 10^4$, $r^2 = 0.59$, and $N = 11$; (2,2',4,5,5'-PentaCB) $K_d = (4.47 \pm 1.41) \times 10^5 \text{foc} + (5.5 \pm 2.6) \times 10^4$, $r^2 = 0.45$, and $N = 14$; (2,2',3,4',5,5'-HexaCB) $K_d = (7.59 \pm 2.62) \times 10^5 \text{foc} + (1.3 \pm 0.5) \times 10^5$, $r^2 = 0.36$, and $N = 17$.

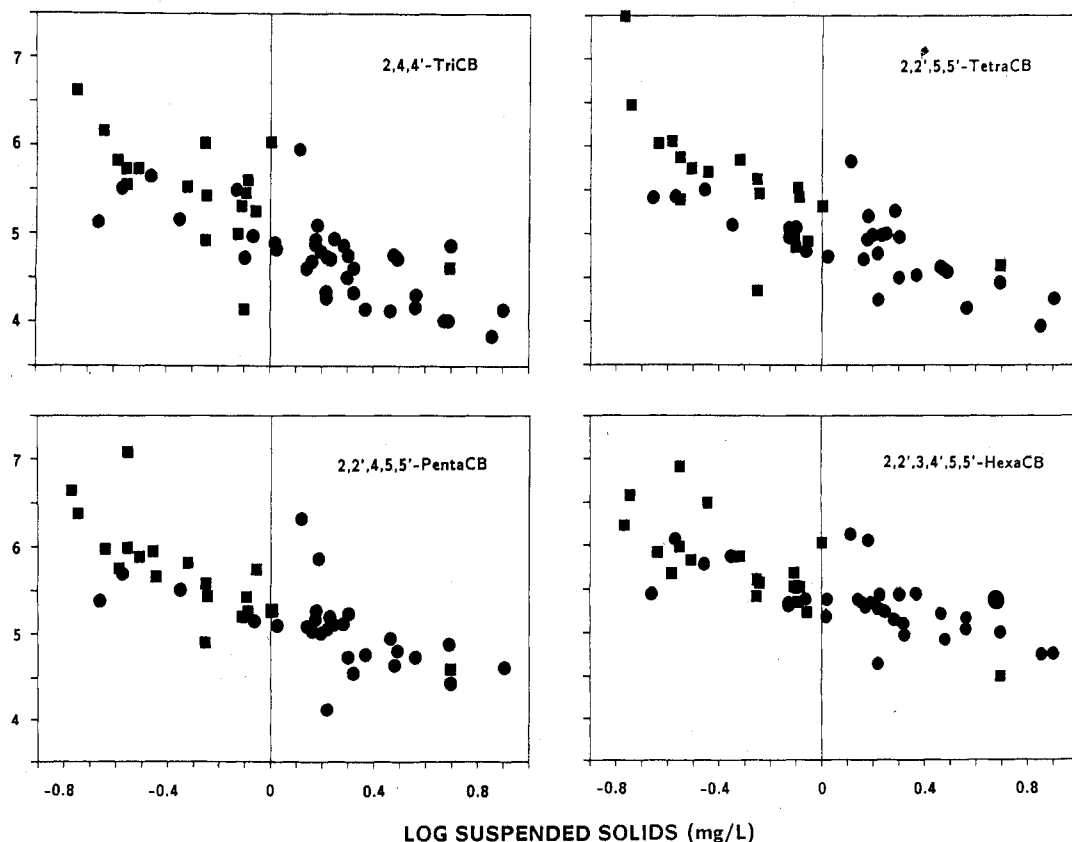


Figure 3. Log observed distribution coefficient vs. log SS concentration for four PCB congeners in Lake Superior, 1980 (■) and 1983 (●). (foc_{om}). DOM concentrations are then multiplied by the fraction of DOM that is colloidal (a_{NSP}), resulting in the equation

$$M_{NSP}/V = \text{DOC}(a_{NSP}/\text{foc}_{om}) \quad (7)$$

Values of foc_{om} and a_{NSP} are perhaps 0.3–0.5 and <1, re-

spectively. For the present discussion, the colloid concentration is assumed to be numerically equal to DOC (e.g., approximately 50% of DOM is colloidal).

Values of K_{NSP} have been measured for a few contaminant/colloid systems (34–40). In general, distribution coefficients describing contaminant-colloid binding are of

Table IV. Linear Regression Analysis of PCB Distribution Coefficients as a Function of Suspended Solids Concentration

congener	IUPAC no.	slope	SD	intercept	SD	r ²	N
2,4'	8	-1.36	0.20	4.86	0.09	0.667	24
2,2',3	16	-1.62	0.15	5.31	0.06	0.723	48
2,2',4	17	-1.45	0.15	4.92	0.07	0.735	35
2,2',5	18	-1.48	0.16	4.94	0.07	0.726	34
2,3,4'	22	-1.06	0.19	5.20	0.08	0.450	39
2,4,4'	28	-1.21	0.13	5.06	0.05	0.629	55
2,4',5	31	-1.36	0.19	5.20	0.08	0.495	57
2,3,3'	33	-1.04	0.20	4.98	0.08	0.480	30
3,4,4'	37	-1.22	0.13	5.18	0.05	0.670	48
2,2',3,4	41	-1.14	0.12	5.05	0.05	0.700	39
2,2',3,5'	44	-1.04	0.16	5.29	0.07	0.513	41
2,2',4,4'	47	-0.79	0.16	5.28	0.07	0.411	37
2,2',4,5'	49	-1.43	0.28	5.31	0.12	0.542	25
2,2',5,5'	52	-1.08	0.13	5.33	0.05	0.617	48
2,3,4,4'	60	-0.75	0.13	5.28	0.06	0.387	55
2,3',4,4'	66	-0.97	0.11	5.36	0.05	0.590	54
2,3',4',5	70	-0.81	0.14	5.51	0.06	0.502	38
2,4,4',5	74	-1.04	0.16	5.38	0.07	0.598	32
2,2',3,4,5'	87	-1.04	0.16	5.29	0.07	0.513	41
2,2',3',4,5	97	-0.79	0.16	5.28	0.07	0.411	37
2,2',4,4',5	99	-1.43	0.28	5.31	0.12	0.542	25
2,2',4,5,5'	101	-1.08	0.13	5.33	0.05	0.617	48
2,3,3',4',6	110	-0.75	0.13	5.28	0.06	0.387	55
2,3',4,4',5	118	-0.97	0.11	5.36	0.05	0.590	54
2,2',3,4,4',5	138	-0.81	0.14	5.51	0.06	0.502	38
2,2',3,4,5,5'	141	-1.04	0.16	5.38	0.07	0.598	32
2,2',3,4',5,5'	146	-0.83	0.10	5.52	0.04	0.564	54
2,2',4,4',5,5'	153	-0.54	0.21	5.37	0.09	0.201	29
average		-1.08		5.25		0.548	
RSD		24.5		3.3		22.0	

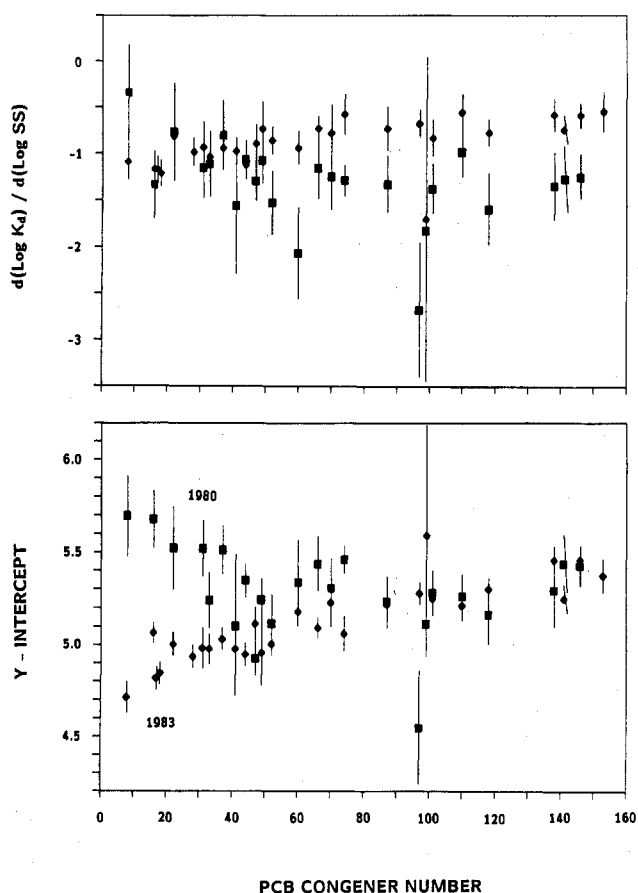


Figure 4. Slope and y intercept resulting from linear regression analysis of $\log K_d$ vs. $\log SS$, Lake Superior, 1980 (■) and 1983 (◆). Vertical lines represent ± 1 SE from linear regression analysis.

the same magnitude as those of sorption to solids containing identical foc values. Gschwend and Wu (11) assumed $K_{NSP} = K_p$ because the isolated colloids and sedi-

ments had similar foc values. Colloids have greater specific surface areas (m^2/g) and may have more accessible organic matter than sediments. Means and Wijayarathne (29) measured K_{NSP} s for atrazine and linuron, which were 10–35 times their K_p s to sediment organic matter. In Great Lakes sedimentary pore water, however, K_{NSP} s of PCB congeners are approximately half the corresponding K_p s describing sorption to bottom sediment when both are normalized to organic carbon (41). For the calculations presented here, K_{NSP} is assumed to be directly proportional to K_p ; $K_{NSP} = x_{NSP}K_p$, where x_{NSP} is a proportionality constant. Values of x_{NSP} may be close to 1 but may range from 0.5 to ca. 35 (29, 41).

Substituting for NSP and K_{NSP} in eq 6 results in an expression for the observed K_d that is inversely proportional to the SS concentration (M/V):

$$K_d = K_p / [1 + x_{NSP}K_p f_{NSP}(M/V)] \quad (8)$$

At low values of K_p , K_d approaches K_p and is independent of SS concentration. Surprisingly, even though eq 8 describes three-phase equilibrium partitioning, the observed distribution coefficient becomes independent of K_p and approaches a value of $1/[x_{NSP}f_{NSP}(M/V)]$ when K_p is large. Figure 5 shows $\log K_d$ predicted by eq 8 as a function of $\log SS$ for several values of K_p ($x_{NSP}f_{NSP} = 5$, see below). Partitioning of more hydrophobic compounds (large K_p) is less dependent on K_p and more variable with SS concentration than that of more soluble, less hydrophobic compounds. At high SS (and therefore high colloid) concentrations, observed K_d s of compounds with K_p s greater than 10^5 are predicted to converge. This result is consistent with our observations of virtually constant K_d s for PCB congeners in Lake Superior. Brownawell and Farrington (30) also observed a leveling of K_d s of PCB congeners with K_{ow} s above 10^6 in sedimentary pore waters.

Figure 6 compares observed distribution coefficients of 2,2',4-trichlorobiphenyl and 2,2',3,4',5,5'-hexachlorobiphenyl in Lake Superior with the K_p -independent limiting

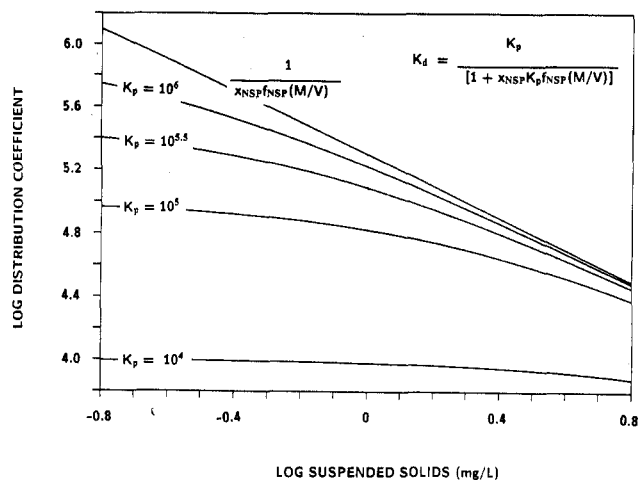


Figure 5. Variation in log K_d with log SS concentration predicted by eq 8 for different values of the sediment-water partition coefficient, K_p . The product $x_{NSP}f_{NSP}$ was assumed equal to 5 (see text).

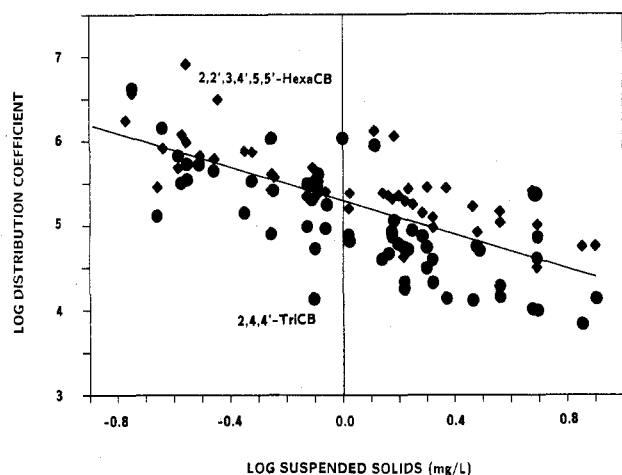


Figure 6. Observed (symbols) and predicted (solid line) relationship between log K_d and log SS for 2,4,4'-triCB (●) and 2,2',3,4',5,5'-hexaCB (◆). Solid line results from the noncompound-specific limit of eq 8 for large values of K_p .

prediction of eq 8 for highly hydrophobic compounds (e.g., $K_d = 1/[x_{NSP}f_{NSP}(M/V)]$). A value of 5 for $x_{NSP}f_{NSP}$ qualitatively fits the field data. Although there is a small amount of difference between the two congeners' behaviors, their variation with SS concentration is adequately described by the noncompound-specific model. Changing the value of the product $x_{NSP}f_{NSP}$ shifts the intercept but does not change the slope of the K_d vs. SS relationship.

The above analysis demonstrates the potential importance of colloidal matter in the speciation of hydrophobic organic pollutants in low SS waters. The relative amounts of dissolved, colloid-associated, and particle-bound contaminant are readily calculated from a three-phase equilibrium speciation model as follows:

$$\% \text{ dissolved} = \frac{100}{1 + 10^6 K_p (M/V) + 10^6 K_{NSP} (M_{NSP}/V)} \quad (9)$$

$$\% \text{ colloidal} = 100 / \{1 + (10^6 / [K_{NSP} (M_{NSP}/V)]) + (K_p (M/V) / [K_{NSP} (M_{NSP}/V)])\} \quad (10)$$

$$\% \text{ particulate} = \frac{100}{1 + (10^6 / [K_p (M/V)]) + (K_{NSP} (M_{NSP}/V) / [K_p (M/V)])} \quad (11)$$

where M/V and M_{NSP}/V are expressed in mg/L. As

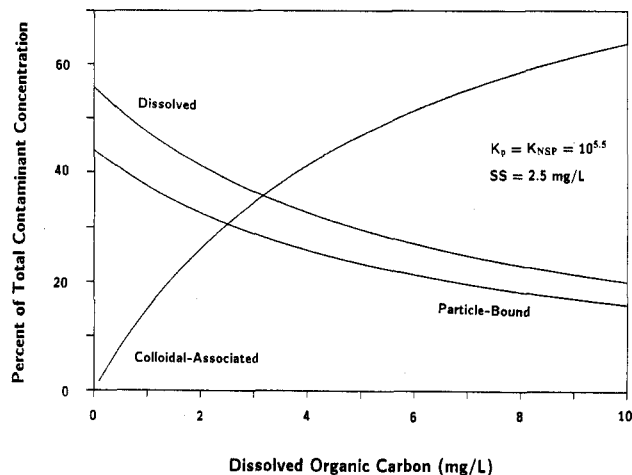


Figure 7. Three-phase speciation for hydrophobic pollutants in low suspended solids waters (eq 9-11).

discussed previously, M_{NSP}/V is roughly equivalent to the DOC concentration. At low SS concentrations typical of oligotrophic lakes, a significant fraction of the total concentration of a hydrophobic pollutant is associated with colloidal matter (Figure 7). In waters with moderately high DOC concentrations (>3.5 mg/L), colloid-associated material is likely to be the dominant fraction. Since contaminants associated with colloidal matter are subject neither to sedimentation nor to volatilization, they may have longer residence times in the water column. Aggregation and settling of destabilized colloids in the presence of larger particles may, however, rapidly remove this fraction under proper hydrodynamic conditions (32). Clearly, the geochemistry of trace organic pollutants in natural waters is closely tied to the behavior of colloids.

Conclusions

The importance of speciation in controlling the aquatic behavior of nonpolar organic contaminants has led to several attempts to relate speciation to properties of both the contaminants and the aquatic phases. These laboratory studies have shown that "sorption" to sediments is too complex to be modeled as a linear, reversible equilibrium due to inexact phase separations and slow kinetics. Analysis of distribution coefficients from Lake Superior presented here shows even greater deviations from a two-phase sorption model than encountered in laboratory studies. Laboratory-derived correlations between PCB distribution coefficients and properties of the contaminants and environmental phases do not accurately predict the trends in speciation observed in Lake Superior. Data from Lake Superior may be explained by the presence of contaminant-associating colloidal matter. The substantial impact of colloidal matter in controlling the aquatic behavior of chlorinated hydrocarbons points out the need for its further characterization in natural waters. Direct measurements of distribution coefficients between hydrophobic compounds and colloidal matter at typical environmental concentrations, accurate quantification of colloid concentrations in natural waters, and further elucidation of the sources, behaviors, and fates of colloids will aid attempts to describe the behavior of hydrophobic organic contaminants.

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Registry No. 2,4'-DiCB, 34883-43-7; 2,2',3'-TriCB, 38444-78-9; 2,2',4'-TriCB, 37680-66-3; 2,2',5'-TriCB, 37680-65-2; 2,3,4'-TriCB, 38444-85-8; 2,4,4'-TriCB, 7012-37-5; 2,4',5'-TriCB, 16606-02-3; 2,3,3'-TriCB, 38444-84-7; 3,4,4'-TriCB, 38444-90-5; 2,2',3,4-TetraCB, 52663-59-9; 2,2',3,5'-TetraCB, 41464-39-5; 2,2',4,4'-TetraCB, 2437-79-8; 2,2',4,5'-TetraCB, 41464-40-8; 2,2',5,5'-TetraCB, 35693-99-3; 2,3,4,4'-TetraCB, 33025-41-1; 2,3',4,4'-TetraCB, 32598-10-0; 2,3',4',5'-TetraCB, 32598-11-1; 2,4,4',5'-TetraCB, 32690-93-0; 2,2',3,4,5'-PentaCB, 38380-02-8; 2,2',3',4,5'-PentaCB, 41464-51-1; 2,2',4,4',5'-PentaCB, 38380-01-7; 2,2',4,5,5'-PentaCB, 37680-73-2; 2,3,3',4',6'-PentaCB, 38380-03-9; 2,3',4,4',5'-PentaCB, 31508-00-6; 2,2',3,4,4',5'-HexaCB, 35694-06-5; 2,2',3,4,5,5'-HexaCB, 52712-04-6; 2,2',3,4',5,5'-HexaCB, 51908-16-8; 2,2',4,4',5,5'-HexaCB, 35065-27-1.

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