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PARAMETERS AFFECTING PARTITIONING OF 6 PCB CONGENERS IN NATURAL SEDIMENTS

E. ALKHATIB and C. WEIGAND

Abstract. Polychlorinated biphenyls (PCBs) released by bottom sediments were determined by experiments in which the sediments were artificially resuspended using sediment contaminated with PCBs in a particle entrainment simulator (PES). Sediment cores, spiked with PCBs, were collected from the Housatonic River in Connecticut and run in the PES at simulated shear stresses from 0 to 0.6 N m^{-2}. Experimental results from these simulations have shown that mean concentration of PCBs in the solid phase for sites with high volatile organic carbon (VOC) were significantly greater than samples with low VOC; the reverse was true for the water phase. In addition, on a mass load basis, the amount of PCBs found in sediment increased when shear stresses were increased from 0 to 0.6 N m^{-2}, beyond which shear stress did not affect mass loads in the water column. Partition coefficients (K_p) were determined from PES sediment and water data for the following congeners: PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180. K_p was determined to be inversely proportional to total suspended solids (TSS), but directly proportional to chlorine content of the congener. Because of the strong influence of TSS and VOC concentrations on K_p values, agitation of samples using a PES better simulated real environmental conditions when compared to jar studies where no agitation was employed. Therefore, a device like the PES is more appropriate in obtaining K_p that would be found under real stream flow conditions when compared to the traditional way of measuring K_p using the jar study technique.

Keywords: *K_p, partition coefficients, PCBs, sediments, resuspension*

1. Introduction

PCBs are classified as 209 congeners that were used in commercial waxes, nonflammable transformer fluids, and resins. Congeners have the same structural backbone and differ only in the position and/or number of chlorine atoms. Since PCBs were produced by batch chlorination of biphenyl, not all 209 congeners were commercially available. These compounds are found to be ubiquitous throughout the biosphere and have been observed in the tissues of birds, fish, and mammals. Due to PCBs' resistance to chemical and biological degradation (Kimbrough and Jensen, 1989), their toxic effects to aquatic life, and their status as a probable human carcinogen (Brown, 1994), there has been considerable interest in the transport and fate of these hydrophobic compounds in the environment. Once released into the aquatic environment, PCBs bind to sediment and act as a natural sink for a variety of organic as well as inorganic contaminants. It is therefore vital to study the role that sediments play at the sediment-water interface.

Because PCBs are not affected by pH, redox, or acid base equilibria (Brannon *et al.*, 1991), their partitioning behavior can be generally described as:

$$K_p = 10^9 (p/m)/C \tag{1}$$

where 10^9 is a conversion constant, p is the pollutant concentration on particulates (mg L^{-1}), m is the suspended solids concentration (mg L^{-1}), C is the dissolved pollutant concentration in the water phase (μg L^{-1}), and K_p the partition coefficient (L kg^{-1}). Typical K_p values are on the order of 10^3 to 10^5 (L kg^{-1}) in sediment, but much higher values have been found in organic matter (Mackay *et al.*, 1996). Since humic acids and fine particles can interact with both water and solid phases, partitioning behavior, i.e., K_p, can be explained by colloidal particles which are less than 1 μm in diameter. Colloids can interact with both water and solid phases significantly changing the concentration of PCBs in either phase using a two-phase model. Recent experiments (Alkhatib and Castor, 2000) have suggested that the net effect of these colloids is to increase K_p since they are flocculated and trapped in the solid phase during resuspension events.

Another important and not completely understood factor that governs the fate of PCBs in the environment is resuspension and entrainment of natural sediments under actual flow conditions. Several methods have been used in the past to study sediment resuspension, including sediment traps, shaker devices, and annular flumes (Bloesch, 1994). These studies have improved our understanding of sediment properties by helping to define the various parameters that can affect entrainment of particles. These parameters include (Lee *et al.*, 1981): i) the applied force over a given area or shear stress at the sediment-water interface, which can be correlated to river flow rates, ii) the composition of the sediment, iii) water content in the sediment, iv) activity of bacteria and benthic organisms, and v) compaction of the sediment. Unfortunately, the amount of published data specifically relating PCBs partitioning behavior to sediment resuspension is fairly rare in the literature. This limited the possibility of studying a link between contaminant concentration and stream flow rates at the sediment-water interface. Most data were based on controlled sorption experiments where there was no agitation (Chiou *et al.*, 1983), or more recently, where the amounts of suspended solids were fixed (Borglin *et al.*, 1986). Although these studies provide important clues into the behavior of hydrophobic contaminants, they cannot be applied to real conditions because of the complex nature of sediment resuspension.

One method that has been used in the past is a device called a Particle Entrainment Simulator (PES). This device was used to study metals released by sediments (Alkhatib and Castor, 2000) and their relationship between contaminant and stream flow rates. By using a similar device, Raccanelli *et al.* (1989) determined the total mass of PCBs present in both the resuspended solid and in the salt water phases but he was unable to specifically evaluate PCB concentration in the aqueous phase mainly due to the low solubility of PCBs in salt water. In the present study, the amount of PCBs released by bottom sediments was evaluated by using a PES device similar to the one used by Lick (1986). Different stream velocities were selected in order to resuspend freshly contaminated sediments. Released PCBs were determined in solid as well as dissolved phases and flow rate was correlated with the amount of PCBs in resuspended sediments. Partition coefficients were calculated for various PCB congeners at different simulated flow rates that demonstrated the dynamic nature of the mechanism controlling sediment resuspension. These results were compared with those obtained from a static partition study, which was performed at the same time.

2. Experimental

2.1. PARTICLE ENTRAINMENT SIMULATOR

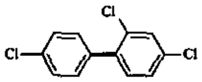
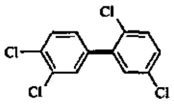
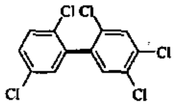
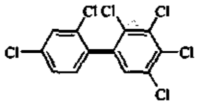
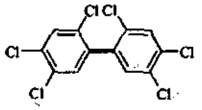
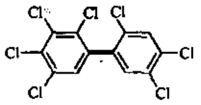
The Particle Entrainment Simulator (PES) is a device that has been used for quick and reasonably accurate simulation of sediment resuspension. Although the turbulence created by the PES is very different than that found in rivers and lakes, suspended solids in the PES can be measured and compared to annular flumes. Annular flumes are chambers through which water is allowed to flow over a bed of sediment and have been used to simulate sheer stress, but were often time consuming and difficult to use. By direct comparison of flume and PES resuspension data, it has been possible to find equivalent shear stresses which allow for calibration of the PES at various oscillation speeds. The PES used in this study (Figure 1) was constructed using the specifications from an EPA PES and the calibration was done, before the experiments, by performing analyses of the same cores with our PES and with another EPA PES instrument in a parallel fashion and then comparing the results of the two instruments.

2.2. SAMPLE COLLECTION

Sediment cores were collected from various locations situated along the lower Housatonic River in proximity to the river mouth in Connecticut. Acrylate cores which were 300 mm high, 127.5 mm and, 117.5 mm internal and external diameter, respectively, were used in order to sample the River sediment. A 12.5 mm beveled plate with a 150 mm circular groove was slid underneath the core. Each core, which had overlying river water, was transferred with minimal disturbance to a PES sample holder with a sealed bottom and brought to the laboratory. From each core, a sub-sample was dried at 105 °C for 30 min. These sub-samples were sieved in order to separate grain size fractions from 14 to 230 mesh (according to U.S. standard sieves). Their cumulative frequency distribution was plotted as a function of the grain size. In addition, 25 g of each dried sub-sample was heated in a muffle at 550 °C in order to measure VOC in the sample.

TABLE I

Physical properties and descriptive data of PCB congeners in PES study

Acronym	Chemical Name	Molecular Weight $g\ mol^{-1}$	Melting, Boiling Point °C	Water Solubility mg/L	Congener found in significant amounts in the following Aroclors	Structure
PCB 28	*2,4,4'-trichlorobiphenyl*	*257.54*	*57-58, 206-207*	*0.085-0.266*	*1221,1232,1242,* 1248	
PCB 52	2,4',5,5'-tetrachlorobiphenyl	291.99	86-89, 360	0.046-0.184	1232,1242,1248, 1254	
PCB 101	2,2'4,5',5-pentachlorobiphenyl	326.43	76.5-77.5, 381	0.009-0.164	1242,1248,1254, 1260	
PCB 138	2,2',3,4,4',5-hexachlorobiphenyl	360.88	78.5-80, 400	0.0015-0.0024	1248,1254,1260	
PCB 153	2,2',4,4',5,5'-hexachlorobiphenyl	360.88	102-104, 400	0.00095-0.0012	1248,1254,1260	
PCB 180	2,2',3',4,4',5,5'-heptachlrobiphenyl	395.32	109-110, 400	0.00031-0.00053	1254,1260	

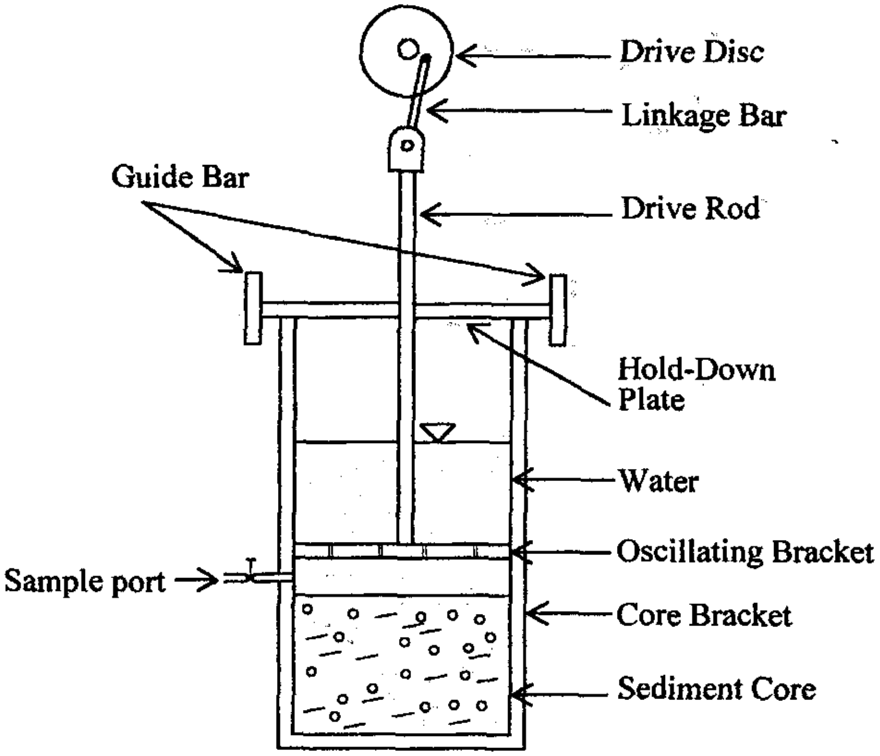


Figure 1. Particle Entrainment Simulator.

2.3. SAMPLE SPIKING

As shown in Table I, six PCB congeners, carrying from 3 to 7 chlorine atoms, were selected as a representative set of PCBs because of the presence in commercial Aroclor mixtures. A wide range in the degree of chlorination was selected since their solubilities in water, boiling points, and partitioning behavior vary considerably. Samples were prepared as follows: 0.5 mL of a standard mixture of 1000 mg L^{-1} of each congener was added to a 500 mL Teflon capped jar that was washed with detergent, rinsed with distilled water and pesticide grade acetone, and heated at 400 °C. Upon evaporation of the solvent, 500 g of each core sub-sample was added and the jar filled with water. These spiked samples, which contained 1 mg L^{-1} by dry weight as added for each congener, were sealed with zero head-space and agitated for 14 days. This ensured steady state conditions of PCBs between sediment and water as well as uniform distribution throughout the sediment. In addition, a sub-sample of this spiked sediment that contained both sediment and water was saved prior to reintroduction into a PES sample holder. This sub-sample was stored in Teflon lined 125 mL jar. Before each experiment, as part of the jar partition study, the sub-sample was subsequently used to determine partition coefficients. The contaminated sediment was then transferred uniformly to a PES sample holder which was washed with detergent and distilled water prior to each run. This required careful addition of the spiked sediment to a 50.8 to 76.2 mm thick layer of uncontaminated sediment from the same core with a 5 mm layer of overlying water. The transfer of spiked sediment translated into a 25.4 mm layer of contaminated sediment. The contaminated layer was considered sufficient to work with, since in prior experiments breakthrough did not occur to the underlying layer. The height of the oscillating grid was also adjusted so that it reached 50.8 mm above the sample surface at its lowest point of oscillation. River water was added from the same site to provide a 152.4 mm layer of overlying water prior to core agitation. After each core was allowed to settle for 2 days, the PES was subsequently run using the following oscillations per minute in order to vary shear stress: 0, 269, 357, 455, 547 and 694 oscillations per minute. This translates to shear stresses of 0, 0.2, 0.3, 0.4, 0.5, and 0.6 N m^{-2}, respectively. At each setting, the PES remained at the same oscillation rate for approximately 30 min to achieve equilibrium. At equilibrium a 100 mL sample was withdrawn into a graduated cylinder while the core was agitated. To compensate for this withdrawal, 100 mL of river water were added and each sample immediately vacuum filtered using preweighed Whatman 934-AH glass filters (1.2 μm) in order to separate water and sediment fractions. The filtered water samples were kept at 4 °C until extraction. The sediment samples were retained on the filters and dried at 105 °C for 30 min, and then weighed in order to determine dry weight and TSS using method 3540D (AWWA, 1995). Volatile Suspended Solids (VSS) was determined using a separate set of samples and the dried filters muffled at 550 °C for 20 min.

2.4. SAMPLE ANALYSIS

Sediment samples including each glass filter were extracted in hexane, sonicated in a Fisher FS-15 sonic water bath for 25 min, and concentrated to 5 mL in a Kuderna-Danish concentrator. Water samples were extracted according to EPA method 3510B (USEPA, 1986) with dichloromethane, the aqueous extracts were reduced to a volume of 1 mL, re-extracted with hexane, and the sample again concentrated to 1 mL. Cleanup was performed using Florisil on a 10 × 110 mm chromatography column to allow removal of undesired classes of compounds for both sediment and water samples. An external standard of decachlorobiphenyl of 100 μg L^{-1} and 200 μg L^{-1} calculated to final volume was added to sediment and water samples, respectively, to determine recoveries. Recoveries performed in this manner were 89.0±11.9 and 92.8±10.1% for water and sediment samples, respectively. Sample blanks run prior to each PES run were analyzed and found to be absent of PCBs. Quantification was performed by a Hewlett-Packard 6890 series GC interfaced with a Hewlett-Packard 7172 mass spectrometer. A 30 m × 0.25 mm

HP-5MS capillary column with a 0.25 μm film thickness was used at a helium flow rate of 1.0 mL min^{-1}. A 2 μL injection volume was used in the splitless mode at an injection temperature of 250 °C and a detector temperature of 280 °C. The temperature program was as follows: 90 °C isothermal for 2 min, then 20 °C min^{-1} to 170 °C, held for 3 min, then 6 °C min^{-1} to 280 °C and isothermal at 280 °C for 2 min. The desired peaks were quantified using EI-MS (electron impact mass spectrometry) and peaks areas calculated by computer.

2.5. JAR PARTITION STUDY SAMPLES

Sub-samples from each core were saved in 125 mL Teflon jars prior to introduction into the PES were stored at 4 °C. These sub-samples were vacuum filtered using Whatman 934-AH glass filters. Once separated, water and sediment fractions were subsequently extracted alongside their PES counterparts using the same methods outlined above for sediment and water samples.

3. Results and Discussion

3.1. SEDIMENT CHARACTERISTICS

Grain size data obtained from cores were plotted (data not reported) as a cumulative frequency distribution with the largest grain size assigned as the 100th percentile. As shown in Table II, sediments from each core were subsequently classified according to the 10th percentile into one of three types: fine sand, fine sand with silt, or silt. In addition to being classified by grain size, it was possible to group cores according to volatile organic content (VOC). Four of the cores (Table II) had VOC of between 0.77 to 1.1% while the remaining sites ranged from 0.28 to 0.39%. The four cores in the higher range were considered to contain 'high VOC' while the remainder was grouped together as 'low VOC' cores.

3.2. TOTAL SUSPENDED SOLIDS

Total suspended solids (TSS) and volatile suspended solids (VSS) were measures based on samples from each PES run. In Table II, TSS ranged from 74 to 12 318 mg L^{-1} while VSS varied from 23 to 785 mg L^{-1} at simulated shear stresses from 0.2 to 0.6 N m^{-2}. For comparative purposes, TSS was evaluated at 0.6 N m^{-2} which was the shear stress on the PES, and VSS was ignored since in general VSS is directly proportional to TSS.

3.3. DISSOLVED PCBs

Analysis of the dissolved fraction of PCBs in water demonstrated significant differences in concentration of PCBs depending on congener and simulated shear

TABLE II

Sediment characteristics by site

Site	Sediment characteristics	d_{10} (μm)	TSS (mg L^{-1}) 0 N m^{-2}	0.2 N m^{-2}	0.3 N m^{-2}	0.4 N cm^{-2}	0.5 N m^{-2}	0.6 N m^{-2}	VOC (%)
High VOC sites									
Sunnyside 1	Fine sand with silt	75	56	79	1401	4582	6592	7826	1.10
Sunnyside 2	Silt	<63	98	146	368	1763	4782	10023	0.77
Jackson Cove	Fine sand	110	39	263	391	2123	3186	6135	0.86
Route 34	Fine sand with silt	63	44	64	191	275	646	1822	0.83
Low VOC sites									
Indian Wells 1	Fine sand with silt	80	0	129	313	752	1446	1683	0.33
Lake Lillinonah 1	Fine sand with silt	80	59	537	743	1149	3069	12318	0.28
Lake Lillinonah 2	Silt	<63	46	275	461	6381	6422	8071	0.33
Lake Zoar	Fine sand	100	101	119	288	457	827	1557	0.33
Kettletown	Fine sand	100	10	74	115	146	1930	2204	0.39

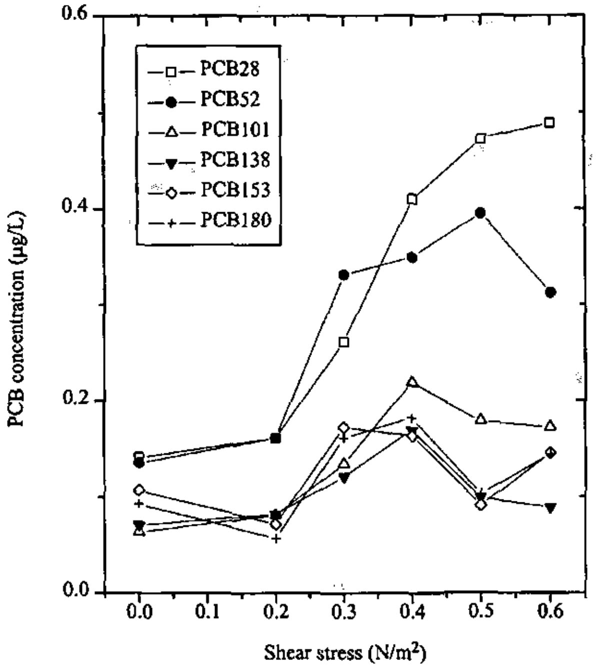


Figure 2. Variation of average dissolved PCB concentration with simulated shear stress.

stress. For 9 cores, overall concentrations of PCBs by congener varied from 20 to 489 ng L^{-1}. Average concentration of PCBs for each shear stress was obtained by averaging the data of all 9 cores for each shear stress. The results are shown in Figure 2. Based on these averages, there were two significant trends. First, mean PCB concentration decreased with increasing degree of chlorination regardless of shear stress in the following order from the most soluble in water to the least: PCB 28 > PCB 52 > PCB 101 > PCB 138 > PCB 153 > PCB 180. In Figure 2, this relationship is most clearly seen at 0.6 N m^{-2}. At this shear stress, the concentration for PCB 28, the least chlorinated congener, was 489 ng L^{-1} while PCB concentrations of the remaining congeners decreased steadily from 312 ng L^{-1} for PCB 52 to 144 ng L^{-1} for PCB 180. Second, the behavior of the 6 congeners at increasing shear stress was markedly different depending on congener. The two most water soluble congeners, i.e., PCB 28, and PCB 52, showed a large increase in the mean concentration when shear stress increased for 0 to 0.6 N m^{-2}. PCB 28 increased from 141 ng L^{-1} at 0 N m^{-2} to 489 ng L^{-1} at 0.6 N m^{-2} while PCB 52 increased from 135 to 312 ng L^{-1}. In contrast, for the four remaining congeners, there was no significant correlation between mean concentration and shear stress. In fact, when the other four congener slopes from Figure 2 were tested statistically, the parameter 'p' resulted to be always greater than 0.05. It is therefore assumed

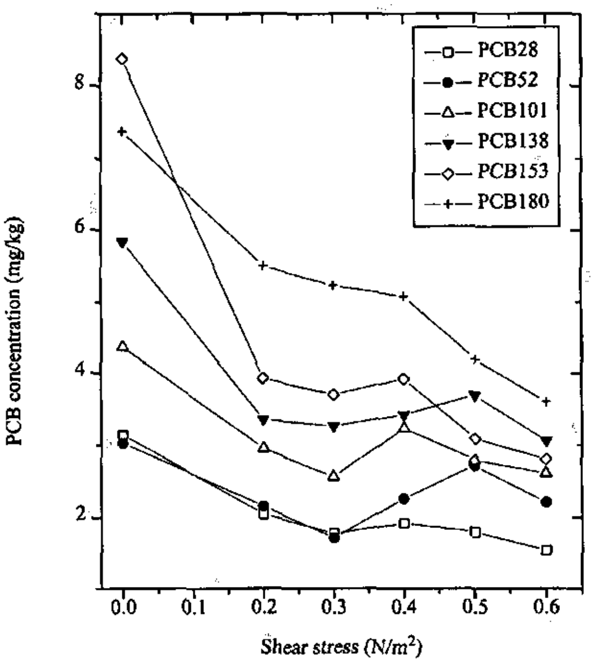


Figure 3. Changes in average PCB concentration on solid phase with simulated shear stress.

that the concentration in water of these four species to be constant and near 100 ng L^{-1}. This behavior can be explained by the fact that, in the case of PCBs, the partition coefficient, K_p, increases proportionally with chlorine content.

3.4. PCBS IN THE SOLID PHASE

Mean PCB concentrations for particulates from the solid phase were averaged for all 9 sites and plotted against shear stress (Figure 3). In most cases, particulates showed the opposite behavior of that found in water samples with the following trend: PCB 180 > PCB 153 > PCB 138> PCB 101> PCB 52 > PCB 28. This trend can be seen in Figure 3 at 0.2 N m^{-2} where the experimental concentration for PCB 180 was 5.5 mg kg^{-1}. The remaining congeners in the series at 0.2 N m^{-2} decreased steadily from to 3.9 mg kg^{-1} for PCB 138 to 2.0 mg kg^{-1} for PCB 28. There was also a significant decrease in concentration as shear stress increased, which was true for all congeners, although the decrease was most acute for PCB 138 and PCB 180. The significant decrease in PCB concentration for all congeners as shear stress increased can be explained by two factors. First, an increase of the proportion of larger particles was responsible for a decrease of PCB content mainly because these particles contained lower PCB concentrations per unit mass. This was corroborated by two observations: first, for one of the cores it

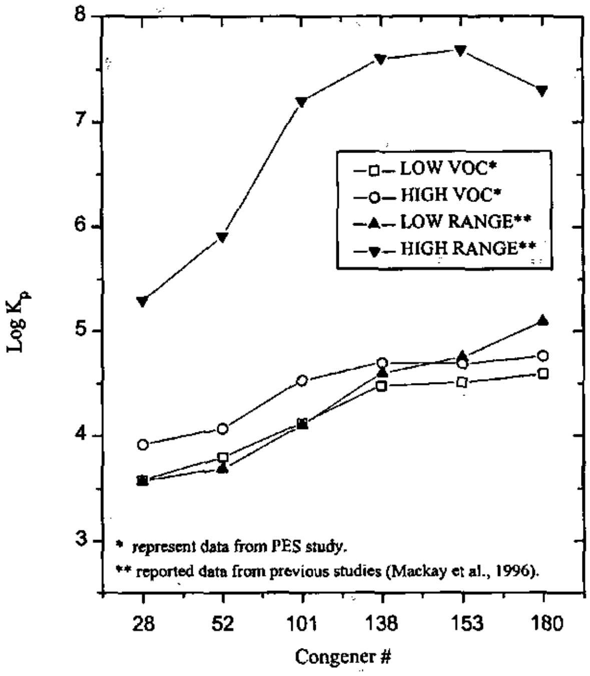


Figure 4. Variation of K_p between congeners for sites grouped according to volatile organic content.

was possible to see a change in the particle size distribution; second, a noticeable increase in sand content could be detected especially at higher simulated shear stress. The second contribution to the PCB concentration in the solid phase was due to a redistribution of some of the PCB to the water phase. This redistribution was due to the loss of absorption sites on particles as suspended solid concentrations increased resulting in the transfer of contaminants from absorption sites in particle flocs to the water phase.

3.5. PARTITION COEFFICIENTS IN PES STUDY

Partition coefficients were calculated based on particulate and water data for each simulated shear stress. Partition data were averaged within each sampling site along the Housatonic River and grouped by VOC content according to sediment characteristics outlined previously. This was repeated for all six shear stress levels and for each PCB congener. The corresponding K_p values, reported in Figure 4, are consistent, although generally lower than those reported as K_p values in previous studies (Mackay *et al.*, 1992). This is best illustrated by PCB 101 as plotted in Figure 4. The data from previous studies K_p ranged from 4.10 to 7.20. In contrast, for PCB 101 in the current study, average K_p ranged from 4.12 for low VOC cores to 4.53 high VOC cores. Clearly the data in the current study was in a much narrower interval and at the lower range of values reported in previous studies. Low values in the current study were attributed to the relatively low concentration of VOC (0.28 to 1.1%) for all sites sampled. It was also observed that K_p values were generally higher for sites characterized by elevated levels of VOC. Average K_p data for low VOC cores in Figure 4 for congeners 28, 52, 101, 138, 153, and 180 were 3.58, 3.8, 4.12, 4.48, 4.51, and 4.59, respectively. This was slightly lower than the corresponding K_p data, for high VOC cores which were as follows: 3.92, 4.07, 4.53, 4.70, 4.69, 4.76. In addition to comparing partition coefficient based on VOC content, partition data was averaged for all 10 sites and plotted against shear stress. The data in Figure 5 were comparable to a previous study by Voice and Weber (1985) in which solids concentrations were plotted against K_p. Voice and Weber studied Lake Michigan sediments and plotted K_p against solids concentration for two congeners: PCB 18 (2,2′,5-trichlorbiphenyl) and PCB 153 (2,2′, 4,4′, 5,5′-hexachlorobiphenyl). In both Voice and Weber's and our study K_p dropped dramatically at low TSS from 0 to 1000 mg L^{-1}, but leveled off to a single value at higher TSS for each congener. It was also observed from the PES data that changes in K_p were inversely proportional to chlorine content. For example, the most dramatic drop was for PCB 28, which had the lowest chlorine content. PCB 28 dropped from 4.34 at a TSS of 50 mg L^{-1} to 3.50 at a TSS of 6800 mg L^{-1}. On the other hand PCB 180, which had the highest chlorine content, changed from 4.83 to 4.39 over the same range of TSS. It is more than likely that observed changes in K_p in Figure 5 were a result of colloidal organic materials since VOC and colloidal organic materials would increase proportionally with shear stress and TSS. However, exact comparisons cannot be made between the aforementioned study and the PES study. The current study used averages instead of individual data points to obtain the curve as seen in Figure 6 due to the variability over 9 cores. In Figure 6, raw data for K_p at a TSS of 200 mg L^{-1} was 4.88±0.21 for PCB 180 and 4.10±0.16 for PCB 28.

3.6. PARTITION COEFFICIENTS IN JAR PARTITION STUDY

Data obtained from samples taken prior to each PES run where no continuous agitation occurred were compared with dynamic experiments from the PES study. Samples from this jar partition study were separated into water and solid phases and analyzed using the same methodology used for PES cores. The data obtained for both dissolved and solid fractions was subsequently used to calculate partition coefficients as shown in Table III. K_p values were in general significantly lower in jar tests for low VOC cores when compared to the same cores in the PES study. For example, the K_p value for Lake Lillinonah 1 for PCB 28 in the jar partition study was 2.07, which was well below minimum value of 3.37 found in the PES data for the same core. That was more than likely due to the absence of organic matter which in the jar partition study resulted in higher PCB concentrations in

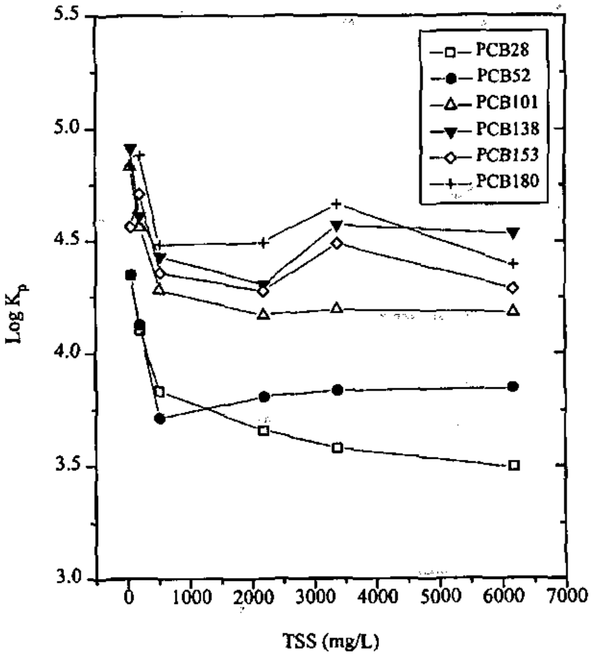


Figure 5. Deviation in mean total suspended solids with K_p for 9 sites at simulated shear stress from 0 to 0.6 N m^{-2}.

the water phase. This was possible because of higher concentrations of inorganic colloidal materials in the water phase since the volume in the water phase was approximately 1–10 of that found in the PES study. However, such a phenomenon was not observed in jar tests with sites containing high VOC. For instance, K_p for the jar partition study at Sunnyside 1 was 4.58 for PCB 28. This fell within the range of 3.40–4.78 reported for PCB 28 in the PES data for the identical core. Further, for the remaining sites with high VOC, the range of K_p values obtained in each jar test was approximately equal to that relative to the PES study. Collectively these results confirm the important role played by organic colloidal material in the partitioning process.

A second consideration in analyzing jar partition data when comparisons are made with shaker experiments is the wide variability in K_p values. K_p values varied dramatically when compared to the corresponding jar data for each core. In the case of Route 34 for PCB 28, K_p ranged from 4.00 to 4.64 while the value for the jar partition study was 4.13. A similar comparison of the remaining sites in Table III demonstrates the same behavior regardless of site or congener. The results of jar partition samples were different than PES samples since partition samples were based on relatively fixed concentrations of suspended solids. These findings

TABLE III

Jar partition study vs. PES partition coefficients (log K_p)

	High VOC				Low VOC				
	Sunnyside 1	Sunnyside 2	Jackson Cove	Route 34	Indian Well	Lake Lillinonah 1	Lake Lillinonah 2	Lake Zoar	Kettletown
Jar partition study data (log K_p)									
PCB 28	4.58	3.57	3.55	4.13	3.81	2.07	1.93	2.83	3.08
PCB 52	4.58	3.65	3.69	4.23	3.94	2.35	1.99	3.43	3.36
PCB 101	4.72	3.54	3.91	4.70	4.62	2.94	2.83	3.43	3.92
PCB 138	4.77	3.59	4.11	4.89	5.10	3.20	3.36	3.70	4.23
PCB 153	4.77	3.51	4.10	4.96	5.09	3.21	3.34	3.80	4.19
PCB 180	4.88	3.61	4.29	4.54	5.38	3.29	3.45	3.90	–[a]
PES partition data for 9 cores (log K_p)									
PCB 28	3.40–4.78	3.50–4.04	3.33–4.14	4.00–4.64	3.38–4.64	3.37–4.89	3.00–3.56	3.56–3.89	–
PCB 52	3.37–4.72	4.06–4.19	3.38–4.26	4.22–4.64	3.57–4.62	3.57–4.98	3.17–4.14	3.64–4.05	–
PCB 101	3.72–5.73	4.42–4.88	3.80–4.69	4.69–5.19	4.10–4.69	4.30–5.32	3.78–4.37	4.38–4.42	–
PCB 138	3.91–5.84	4.50–5.20	4.07–5.03	4.66–5.35	4.28–4.84	4.16–5.56	3.55–4.46	–	–
PCB 153	3.92–5.83	4.42–4.80	4.05–5.02	4.20–5.35	4.29–4.82	4.52–5.51	3.55–4.48	–	–
PCB 180	4.07–5.48	4.34–5.05	4.18–5.24	4.54–5.05	4.39–4.98	4.59–5.63	3.52–4.56	–	–

[a] – = Data not available.

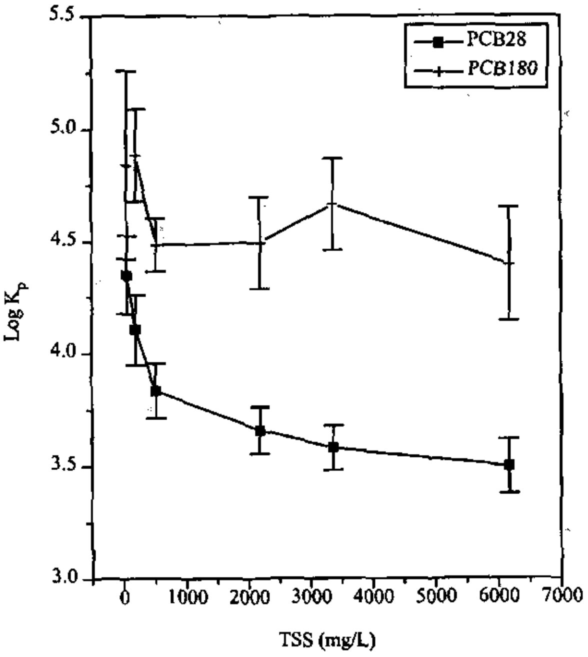


Figure 6. Mean and error bars for 2 of the 6 congeners shown in Figure 5.

demonstrate the limitations of jar tests since they ignore the resuspension and interaction of both phases in a dynamic environment. It is therefore clear that partition studies lacking agitation are not representative of actual stream flow conditions and should be used for approximate K_p values only.

3.7. BEHAVIOR OF PCBS IN NATURAL SEDIMENTS

Several aspects required consideration to properly interpret the results of this study. First, was the preferential exchange from the sediment to water phase of the more water-soluble congeners into the water fraction. Not only was this a favorable exchange of PCB 28 and PCB 52 over the other congeners since their concentrations were significantly higher than the other congeners, but also this was strongly dependent on shear stress over the range tested. This was not the case for the other congeners that remained at a constant concentration regardless of shear stress. The least chlorinated Aroclors such as Aroclor 1221, 1232, and 1242, which would have been released in water by sediments more easily than the other more highly chlorinated Aroclors, would result in them being transported downstream at low to moderate shear stress. These observations are confirmed based on previous studies by Frink *et al.* (1982) and Kulp (1991), which have shown a tendency for the pref-

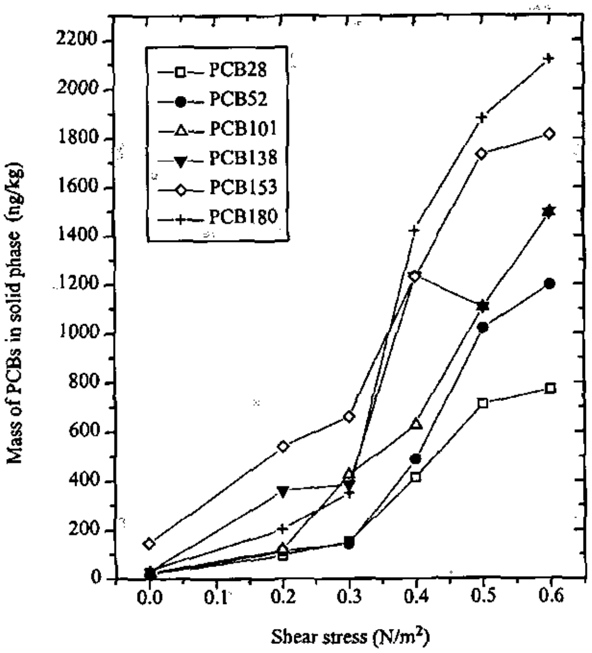


Figure 7. Variation in average PCB mass in solid phase with shear stress for 6 congeners in PES study.

erential transport of the more water soluble PCBs in the Housatonic River between 1979–1980 and again from 1984–1988 in the water phase.

Another consequence of the preferential exchange into the water phase of the most water-soluble congeners is that most of the remaining PCBs are bound to the solid phase. PCBs bound to sediment were shown in the PES study to be sensitive to changes at low to moderate shear stress. In Figure 7 as shear stress increased, the PCB quantity present in the solid phase increased rapidly from 100 ng kg^{-1} at 0 N m^{-2} to nearly 2000 ng kg^{-1} at 0.6 N m^{-2}. An extrapolation of this curve above 0.6 N m^{-2} suggests that the mass load of PCBs might reach a finite value at higher shear stresses. This hypothesis can be supported by a previous study by Raccanelli *et al.* (1989) where the mass load of PCBs in the solid phase was constant at shear stress rates between 0.6 and 0.9 N m^{-2}. Collectively, these facts are significant when considering the fate of PCBs downstream from contaminated sites, since contaminated sediments at the surface would transport a finite mass of PCBs at high shear stress. It is important to point out that average values of transport of PCBs in the Housatonic River and other rivers would greatly depend on what range these averages fall into. At high river flow rates which correspond to shear stresses well above 0.6 N m^{-2}, it would appear that averages are not as crucial, since mass load of PCBs would be far less sensitive to changes in flow rate.

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