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Precipitation of 78 PCB Congeners from Aqueous Solution by Clay

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The Hudson River south of the town of Fort Edward is contaminated by polychlorobiphenyls (PCB) throughout its length (Sloan et al. 1982; Bush et al. 1989). Records show that large quantities of Aroclor 1242, 1016, 1254 and 1260 were discharged into the river over a period of 30 years from a network of diffuse manufacturing sources, a detergent washing process and also via a municipal sewage treatment plant (Brown et al. 1988). Recent work using congener specific gas chromatographic PCB analysis has shown wide variations in composition of residues in different trophic levels in the river. Sediment-free water flowing slowly over contaminated sediment contains a high proportion (50%) of 2-chlorobiphenyl, 2,2'- and 2,6-dichlorobiphenyl (Bush et al. 1985b). Sediments fall roughly into two types, those with a distinguishable Aroclor-like type pattern and those in areas of active sedimentation which have patterns unrelated to commercial Aroclor products (Bopp et al. 1981). Macrophytes show a pattern similar to water and silty sediment (Bush et al. 1987). Macroinvertebrates and fish show a pattern very similar to the original pollutant mixture. A typical water pattern was produced by Wood et al. (1987) in the laboratory from sediment spiked with Aroclor mixtures using a continuous sediment release reactor. Distribution into the water column greatly enhanced the relative proportion of the least chlorinated PCB congeners. However, macroinvertebrates in this water bioaccumulated congeners so that their PCB residue resembled more closely the original spike in the sediment.

Comparison of gas chromatograph patterns has been accomplished previously by bar chart presentations (Baker et al. 1977) and by principal component analysis (Czmzwa and Hites 1986). The former treated only 18 chromatographic peaks while the latter gives no indication of peak-by-peak differences. So that differences between individual congeners can be observed, we have employed a packaged graphics program (Lotus, 123) to plot normalized bars for each of the 78 congeners measured in this study. We report here a simulation of an event where clean clay enters a polluted stream from a tributary and later settles out in a region of low turbulence, for example upstream from an impoundment or weir.

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Sediment (500 g) removed from a landfill containing Hudson River dredgings (from 1 m depth) was placed in a cylindrical glass tank (15 cm diameter, 15 cm deep: volume 2.65 L) with an overflow spout which flowed into a 5 L glass bottle with a self-priming siphon overflow. Albany City tap water was added to the sediment and stirred for ten minutes, the vessel was covered with aluminum foil and the contents were allowed to settle overnight. Tap water was pumped at 2 ml/min into the tank for six months, the PCB composition of the water from this generator was measured at monthly intervals.

Sediment from Owasco Lake, NY, which is unpolluted by PCB, was fractionated by selective sedimentation (Day, 1965). The sediment was suspended in distilled water at 25°C in a 250 mL measuring cylinder, and the material which was still suspended after 20 min was pipetted off and centrifuged to yield a silt and clay sized particle fraction. This fraction was resuspended in another 250 mL cylinder and the suspension was collected after 24 hr (<0.002 mm diameter) and centrifuged for use. The organic content was determined by ignition at 450°C. The wet clay-sized particles were added to water from the generator (500 ml) shaken vigorously and homogenized with a Tissuemizer (Tekmar Co., Cincinnati OH) for 3 min. After 24 hr, the slurry was centrifuged at 500 rpm for 20 min. The precipitate and supernatant were analyzed separately. The dry weight of clay was determined after extraction of PCB.

Water was analyzed by exhaustive extraction with hexane (Bush et al. 1985b). Sediment was extracted with acetone followed by hexane (Bush et al. 1987). Gas chromatography with electron capture detection was carried out with a Hewlett-Packard 5840 chromatograph with an Apiezon L coated glass capillary column (50 m) temperature programming from 70° to 250° at 1°/min (Bush et al. 1985a). The detector was calibrated using a 1:1:1:1 mixture of Aroclors 1221, 1016, 1254 and 1260 (EPA Pesticide Repository) at 200 ng/ml of each.

Data were transmitted to a VAX 780 computer where software previously reported (Bush et al. 1987) organized and labelled peaks with PCB congener structures. The finished data were transmitted to a personal computer (Leading Edge Model D, Canton MA) and were organized into bar charts (123, Lotus Development Corporation, Cambridge MA) for comparison of gas chromatograph patterns.

RESULTS AND DISCUSSION

The chromatogram of the water generated by the system at two dates six months apart is shown in Figure 1. There was a depletion of the more water soluble PCB congeners particularly 2,2'-dichlorobiphenyl, during six months. After six months, the sediment in the generator was resuspended by stirring, allowed to settle for two days and then water was allowed to flow for several days, little change in pattern was produced

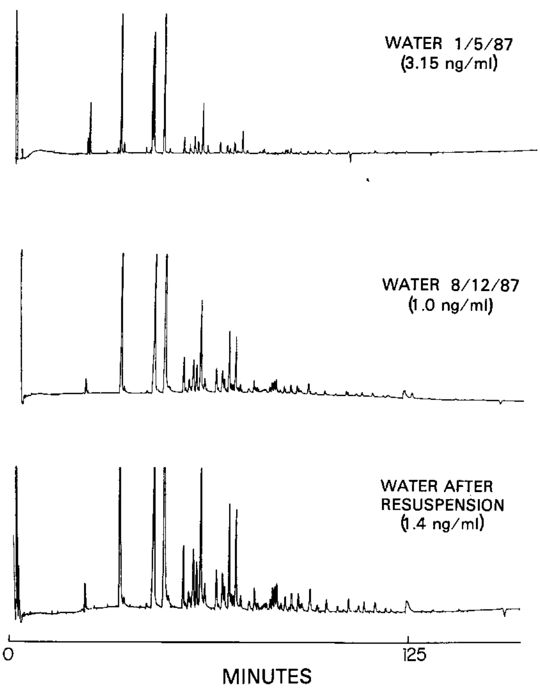

Figure 1. Chromatograms of water from generator in January and in August and in August after resuspension of the sediment.

(Fig 1). During this time, approximately 520 L of water had flowed over the sediment (surface area 177 cm^2) which is equivalent to 200 changes of the water in the generator vessel. Table 1 shows the composition of the water at the two times and after resuspension, also the composition of the sediment in January. A distribution factor is also given which, except for two congeners, is fairly constant. The cause of the high value for 2,4'-dichlorobiphenyl and the mixed chromatographic peak which contains 2,4,3'-trichlorobiphenyl is presently unknown, although similar anomalies were noted by Novak et al. (1989) during their uptake studies with caged, <u>Chironomus</u> <u>tentans</u> larvae (personal communications). Before landfilling, this sediment was dredged from the river, it may have reached partial equilibrium with the water column before deposition. The water PCB concentration is approximately ten times that of the upper Hudson River in summer, but the pattern is similar (Bush et al. 1985b).

The clay fraction of Owasco Lake sediment (dry weight 0.42 g; organic content 3.18%) was added to 500 mL of water from the generator, stirred, left overnight, centrifuged and analyzed. Figure 2 shows the chromatograms of the centrifuged clay and the supernatant water; the total PCB concentration of the water was reduced from 1.4 μg/L to 0.2 μg/L and the clay concentration was 1.3 μg/g (dry weight). Figure 2 shows normalized bar charts of the water pattern and the clay pattern. The resemblance of the two patterns is more striking after this

Table 1. PCB Congeners Present at >1% of Total Residue

Congener	Serial Sediment in Generator		Water Jan.		K_D[1] $x10^{-2}$	Water August		Water After Resuspension	
	ng/g	% of total	ng/ml	% of total		ng/ml	% of total	ng/ml	% of total
2,2'	107	9.1	0.17	5.9	6.3	ND[2]	-	0.04	3.0
2,6	9	0.8	0.20	6.9	0.5	0.02	2.1	0.03	2.3
2,6,2'[3]	94	8.0	0.74	26	1.3	0.21	22	0.27	20
2,4'	208	18	0.04	1.4	52	ND	-	0.01	0.8
2,4,2'	92	7.8	0.19	6.6	4.8	ND	-	ND	-
2,6,4'	148	13	0.59	20	2.5	0.27	28	0.33	25
4,4'	22	1.9	0.07	2.4	3.1	ND	-	0.06	4.5
2,4,6,2'	13	1.1	0.04	1.4	3.3	0.02	2.1	0.02	1.5
2,5,3'	21	1.8	0.04	1.4	5.3	0.05	5.2	0.03	2.3
2,4,3'[4]	143	12	0.06	2.1	24	0.02	2.1	0.02	1.5
2,5,4'	25	2.1	0.05	1.7	5.0	0.02	2.1	0.03	23
2,4,4'	52	4.1	0.11	3.8	4.7	0.07	7.3	0.10	7.5
2,3,4'	10	0.8	0.04	1.4	2.5	0.02	2.1	0.05	3.8
2,5,2'5'	18	1.5	0.06	2.1	3.0	0.02	2.1	0.02	1.5
2,4,2'5'	21	1.8	0.04	1.4	5.3	0.02	2.1	0.03	2.3
2,4,2'4'	49	4.2	0.07	2.4	7.0	0.05	5.2	0.06	4.5
2,3,6,3'	82	7.0	0.18	6.2	4.6	0.11	12	0.15	11
2,5,3'4'	12	1.0	0.02	0.7	6.0	0.01	1.0	0.02	1.5
2,4,3'4'	12	1.0	0.02	0.7	6.0	0.01	1.0	0.02	1.5
2,3,5,2'5'	8	0.7	0.01	0.3	8.0	0.03	3.1	0.01	0.8
2,3,4,2'3[5]	18	1.5	0.03	1.0	6.0	0.01	1.0	0.02	1.5
2,3,4,2'4'5'	13	1.1	0.12	4.2	1.1	ND	-	0.01	0.8
SUM:	1177	----	2.89	----	---	0.96	--	1.33	--
Total PCB	1430	82.3	3.15	91.7	---	1.0	96	1.4	95

[1] K_D distribution coefficient (conc in sediment)/(conc in generator water).
[2] ND - not detected (<0.01 ng/ml).
[3] contains 23;
[4] contains 24,2'6';
[5] contains 234 2'4' + 236,3'4'.

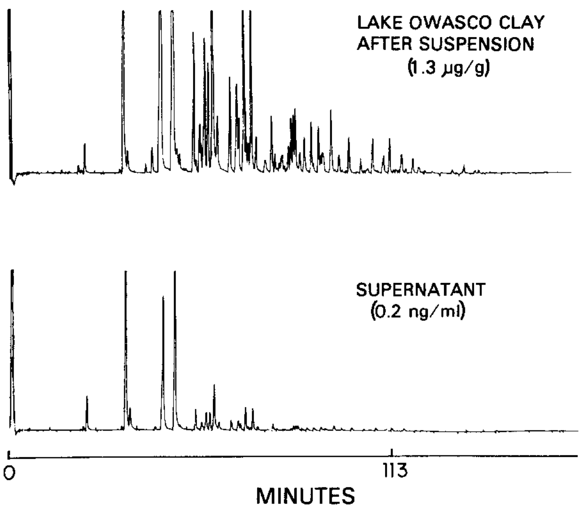

Figure 2. Chromatograms of clay after suspension in water from the generator and centrifugation, and the supernatant water after centrifugation.

enhancement than by comparing unenhanced chromatograms (Fig. 3).

Concentration of congeners comprising >0.3% of the residue in centrifuged clay, the corresponding congeners in the supernatant water and the distribution factor are given in Table 2. Since we are probably dealing with a predominantly adsorptive process, where the distribution coefficient is nonlinear with respect to concentration, it is unlikely that the factors will be the same as in Table 1: they are approximately 10 times greater in the generator than in the experiment scavenging with clean clay.

There are many factors which must be considered in equilibria of pollutants in natural aquatic systems, such as the quantity of colloidal organic matter in the water, the quantity of lipid type organic carbon in the particulate and the inorganic matrix of the particles themselves. These are beyond the scope of this report which attempts only to elucidate the congener pattern changes which occur during dissolution into the water column and subsequent deposition on previously uncontaminated particles. The logarithm of the average distribution factors for the dissolution and scavenging operations (Log_{10} K_D) are 3.8 and 2.8 respectively. These distribution factors are two orders of magnitude lower than reported for the Great Lakes (Baker et al. 1986) where water PCB concentrations are three orders of magnitude lower. Whereas Chironomus tentans larvae selectively bioaccumulated PCBs from contaminated water (Wood et al. 1987) clay has scavenged dissolved PCB fairly unselectively. The clay PCB pattern is very similar to that found in Hudson River sediments (Bush et al. 1987) and termed the sedimentation type of pattern. This strongly supports our hypothesis that the pattern in such sedimentary deposits is a result of adsorption

Table 2. PCB Congeners Present at >0.03% of the Total Residue Found on Owasco Lake Clay After Residence in PCB Containing Water.

	Centrifuged Clay		Supernatant Water		K_D $x10^{-3}$	PCB No.
	ng/g	% of T	ng/L	% of T		
2,2	3	0.2	3	1.3	1.0	2
2,6	12	1.0	12	5.2	1.0	3
2,6,2'	185	15	83	36	2.2	8
2,4'	8	0.7	7	3.1	1.1	9
2,5,2'	7	0.6	1	0.4	7.0	10
2,6,4'	280	23	55	24	5.1	14
4,4'	38	3.1	9	3.9	4.2	15
2,4,6,2'	18	1.5	2	0.9	9.0	16
2,5,3'	26	2.1	5	2.2	5.2	17
2,4,3'[1]	21	1.7	2	0.9	11	19
2,5,4	25	2.1	3	1.3	8.3	20
2,4,4'	92	7.6	10	4.4	9.2	22
2,3,4'	49	4.0	5	2.2	9.8	23
2,5,2'5'	20	1.7	2	0.9	10.	24
2,4,2'5'	26	2.1	2	0.9	13	25
2,3,2'5'	11	0.9	1	0.4	11	26
2,4,2'4'	60	5	5	2.2	12	27
2,3,2'4'	8	0.7	1	0.4	8.0	28
2,3,2'3'[2]	10	0.8	1	0.4	10	29
2,36,3'	130	11	11	4.8	12	30
2,3,6,4'	15	1.2	0.8	0.3	19	31
2,3,5,2'6'	4	0.3	<0.05	-	-	33
2,3,6,2'3'	12	1.0	2	0.9	6.0	35
2,5,3'4'	16	1.3	1	0.4	16	36
2,4,5,4'	13	1.1	1	0.4	13	37
2,4,3'4'	16	1.3	1	0.4	16	38
2,3,5,2'5'	10	0.8	1	0.4	10	39
2,4,5,2'5'	6	0.5	1	0.4	6.0	41
2,4,5,2'4'	9	0.7	1	0.4	9.0	42
2,4,5,2'3'	4	0.3	<0.05	-	-	43
2,3,4,2'5'	8	0.7	1	0.4	8.0	44
2,3,4,2'3'[3]	19	1.6	1	0.4	19	46
2,3,6,2'4'5'	4	0.3	<0.05	-	-	49
2,4,5,3'4'	8	0.7	1	0.4	8.0	54
2,3,5,2'4'5'[4]	19	1.6	<.05	-	-	56
2,4,5,2'4'5'	7	0.6	<.05	-	-	57
2,3,4,2'4'5'	7	0.6	1	0.4	7.0	61
2,3,4,5,3'4'	6	0.5	-	-	-	69
Total PCB	1210	-	229	-		

[1]Contains 24,2'6; [2]contains 234,2'; [3]contains 234,2'4' plus 236,3'4'; [4]contains 234,3'4'

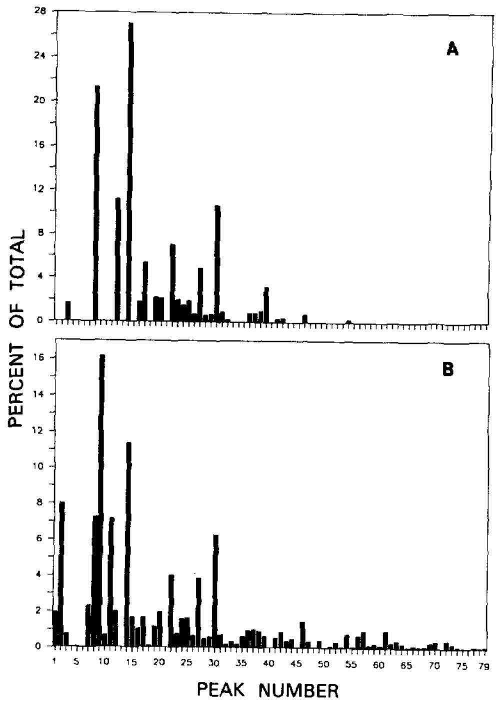

Figure 3. Normalized bar charts of the chromatograms of Lake Owasco clay after suspension in generator water and centrifugation (A) and the supernatant after centrifugation (B).

by uncontaminated sediment particles of PCB from the water column, followed by deposition. Brownaweh and Fanington (1986) note such pattern changes in sedimentary marine deposits.

Others have proposed anaerobic microbial dechlorination as a cause of the sedimentary pattern in the river sediments (Brown et al. 1987; Quensen et al. 1988). While this may be a contributing factor to PCB pattern modification in river sediments, the simple physicochemical mechanism illustrated here may well be the dominant factor in pattern modification during river transport.

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