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# Measuring Low Picogram Per Liter Concentrations of Freely Dissolved Polychlorinated Biphenyls in Sediment Pore Water Using Passive Sampling with Polyoxymethylene

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Studies into bioaccumulation of polychlorinated biphenyls (PCBs) have increasingly focused on congeners that are freely dissolved in sediment interstitial pore water. Because of their low water solubilities and their tendency to persist and concentrate as they progress in the food chain, interest has grown in methods capable of measuring individual PCB congeners at low part-per-quadrillion (picogram per liter) concentrations. Obtaining large volumes of pore water is difficult (or impossible), which makes conventional analytical approaches incapable of attaining suitable detection limits. In the present study, nondepletive sampling is used to achieve very low detection limits of freely dissolved PCBs, while requiring no separation of the sediment and water slurry. Commercially available 76  $\mu\text{m}$  thick polyoxymethylene (POM) coupons were placed directly into wet sediments and left to reach equilibrium with the pore water and sediment PCBs for up to 84 days, with 28 days found to be sufficient. Freely dissolved concentrations were then calculated by dividing the PCB concentration found in the POM by its POM/water partitioning coefficient ( $K_{\text{POM}}$ ). The  $K_{\text{POM}}$  values required for determining water concentrations were measured using two spiked sediments and two historically contaminated sediments for all 62 PCB congeners that are present at greater than trace concentrations in commercial Aroclors. Log  $K_{\text{POM}}$  values ranged from ca. 4.6 for dichloro-congeners to ca. 7.0 for octachloro-congeners and correlate well with octanol/water coefficients ( $K_{\text{OW}}$ ) ( $r^2 = 0.947$ ) so that a simple linear equation can be used to calculate dissolved concentrations within a factor of 2 or better for congeners having no measured  $K_{\text{POM}}$  value. Detection limits for freely dissolved PCBs ranged from ca. 20 pg/L (part-per-quadrillion) for dichloro-congeners down to ca. 0.2 pg/L for higher-molecular-weight congeners. Sorption isotherms were found to be linear ( $r^2 > 0.995$ ) over at least 3 orders of magnitude for all congeners, demonstrating good quantitative linearity of the method for determining freely dissolved PCB concentrations at environmentally relevant levels.

Several recent studies of sediments impacted by hydrophobic organic compounds (HOCs) such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) have demonstrated that biological effects are more strongly associated with freely dissolved concentrations than with sediment concentrations.<sup>1–7</sup> Even though present regulatory models and many scientific studies rely on being able to predict dissolved concentrations from sediment concentrations using equilibrium partitioning and standard organic carbon/water partitioning coefficients ( $K_{\text{OC}}$ ), these models have recently been shown to generally overpredict water concentrations compared to dissolved concentrations that are measured in the pore water. Studies by several different groups have shown that the basic assumption used in sediment/water partitioning models (and related regulatory practices), i.e., that a single  $K_{\text{OC}}$  value for each pollutant applies to all sediments is not valid.<sup>8–12</sup> In a recent comprehensive review of literature  $K_{\text{OC}}$  values and in-depth evaluation of the ability of equilibrium partitioning models to predict pore water concentrations of hydrophobic organics, Arp et al.<sup>12</sup> concluded that “...the only way to accurately obtain accurate porewater concentrations is to measure them directly, and not infer them from sediment concentrations.”

Although obtaining large volumes of most water samples is relatively trivial, measuring dissolved concentrations of HOCs in sediment pore water is greatly complicated by the difficulty of obtaining sufficient pore water for subsequent extraction and analysis, especially for sandy sediments and for the large number

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of samples required for field studies. In addition, methods must be able to eliminate the influence of colloid-bound HOCs and should be able to differentiate HOCs that are associated with the dissolved organic matter (DOM) and those that are “freely dissolved”. Recently, solid-phase microextraction (SPME) methods have been developed that can determine low nanogram per liter concentrations of freely dissolved PAHs and PCBs in only a milliliter of pore water, which makes the preparation and analysis of large numbers of sediments practical.<sup>13–15</sup> While these detection limits are sufficiently low for sediment sites where toxicity to benthic organisms is the regulatory driver of interest (e.g., PAH-caused hydrocarbon narcosis as applied by the U.S. Environmental Protection Agency’s hydrocarbon narcosis model<sup>5,16</sup>), lower detection limits (picogram per liter) are desired when human exposure via accumulation in the food chain is of concern, as is the case for PCBs. With the difficulty in obtaining large volumes of pore water, no conventional analytical approaches are suitable to make such measurements.

In an effort to achieve lower detection limits for freely dissolved HOCs, as well as to avoid the problems associated with obtaining large volumes of sediment pore water, several investigators have developed methods based on equilibrium sampling by directly inserting a “nondepletive” sorbent such as PDMS (polydimethylsiloxane), PE (polyethylene), or POM (polyoxymethylene) directly into the sediment water slurry.<sup>2,4–6,17–28</sup> These methods have the advantage of being useful in the lab or in the field but require long enough exposure times to allow equilibrium to be attained among the water, dissolved organic matter (DOM), sediment, and sorbent phases. After equilibrium, the sorbent concentrations of the HOCs are determined, and the freely dissolved concentrations are calculated using previously determined sorbent/water partitioning coefficients ( $K_{\text{SORBENT}}$  values,

**Table 1. Summary of Test Sediment Characteristics**

	contaminated sediments		spiked sediments	
	sed A	sed B	sed C	sed D
TOC, wt %	3.12	2.56	2.98	1.21
BC, wt % <sup>a</sup>	0.98	2.18	0.48	0.85
% BC vs TOC	31%	85%	16%	70%
texture	clay/silt	sand/clay	silt/sand	sand
total PCBs, $\mu\text{g/g}$	4.1	3.9	0.2 to 310	0.04 to 53

<sup>a</sup> Black carbon (BC) was determined using 375 °C oxidation.<sup>30</sup>

which must be measured for every individual target analyte). These methods have been applied by several research groups in an effort to measure low concentrations of freely dissolved PCBs but, unfortunately, there is little standardization in the various approaches, and the necessary  $K_{\text{SORBENT}}$  coefficients are available for only a few PCB congeners.

Of the several possible sorbents, the use of POM as a nondepletive sorbent for PCB determinations has gained increasing attention because it has appropriate  $K_{\text{SORBENT}}$  values, is inexpensive, has low background concentrations, and is easy to clean. It is also physically robust and has a smooth surface from which it is easy to remove interfering colloids and soot particles after exposure.<sup>19,21,27–29</sup> Earlier work used thicker (500  $\mu\text{m}$ ) POM material,<sup>27,28</sup> but more recent studies focus on thinner POM material (e.g., homemade 55  $\mu\text{m}$  strips) since Cornelissen et al. found that the 500  $\mu\text{m}$  sorbents were too thick to come to equilibrium even after several months of sampling time,<sup>29</sup> while the thinner material was found to equilibrate with PCBs in a few weeks. However, although there are 209 possible PCB congeners and more than 60 congeners that were present in significant concentrations in commercial Aroclors (and commonly found in sediments), the most extensive work to date has only reported the  $K_{\text{POM}}$  values necessary for determining freely dissolved concentrations for 12 PCB congeners.<sup>19</sup> In addition, the  $K_{\text{POM}}$  values that are reported by various workers for a single congener vary by as much as 2 orders of magnitude which, in essence, means that the freely dissolved concentrations determined by two laboratories will vary greatly, even with identical pore water samples.<sup>19,27,28</sup>

The goal of the present study is to develop an equilibrium partitioning method to determine the freely dissolved concentrations in the low part-per-quadrillion (picogram per liter) range for all PCB congeners that were produced in significant quantities during the use of commercial Aroclors. Commercially available POM sheets are used to help make the method robust, transferable among laboratories, and practical enough for the use of large numbers of sediment samples.

## EXPERIMENTAL SECTION

**Sediment Samples.** Four freshwater sediments (Table 1) were collected using a Ponar grab sampler or with a shovel, screened to 2 mm, and briefly mixed before subsampling into glass jars. Storage was at 4 °C in the dark. Two of the sediments (A and B in Table 1) had historical PCB contamination. The other two sediments had only background levels of PCBs and were used

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for spiking with either a mixture of Aroclors or PCB standards. Total organic carbon (TOC) was determined using a CHN analyzer after grinding and acidification of the sediment to remove inorganic carbonates. Black carbon (BC) was determined using 375 °C oxidation for 24 h.<sup>30</sup> Sediment PCB concentrations were determined using GC/MS with selected ion monitoring (SIM) after 18 h Soxhlet extraction with 1:1 acetone/isooctane.

**Target PCBs and Internal Standards.** Selection of the 62 target congeners was described in detail earlier.<sup>15</sup> In brief, the list of congeners was selected to include all congeners that were present at 1% or greater concentrations in any commercial Aroclors based on the analyses reported by Frame et al.<sup>31</sup> Although 13-C labeled congeners are available for GC/MS internal standards, they are prohibitively expensive. In addition, one goal of the method is to be compatible with both MS and ECD (electron capture detector), which eliminates the use of iso-topically labeled internal standards. Therefore, the congener distributions in commercial Aroclors reported by Frame et al.<sup>31</sup> and the retention times of all 209 congeners we determined were used to select internal standards from the list of PCB congeners that (1) were not present in significant concentrations in commercial Aroclors and (2) were well-resolved from all other PCB congeners. These criteria lead to the selection of 3,5-dichlorobiphenyl (PCB 14), 2,4,6-trichlorobiphenyl (PCB 30), 2,3,5,6-tetrachlorobiphenyl (PCB 65), 2,2',4,5',6-pentachlorobiphenyl (PCB 103), and 3,3',4,4',5,5'-hexachlorobiphenyl (PCB 169). Internal standards for the POM extract analyses were diluted to ca. 40 µg/mL in acetone, with ca. 200 ng (in 5 µL) added to the POM extracts, calibration standards, and solvent blanks.

**Selection of POM Material.** Previous studies showing reasonable equilibration time have utilized 55 µm POM material that was made from a solid rod on a precision lathe by Cornelissen et al.<sup>19,29</sup> This material was initially evaluated for our study but was found to be more difficult to handle than commercially produced POM sheets, since the lathe-produced material curled onto itself and was not rigid like commercial POM sheets. It was also not widely available. Therefore, the thinnest commercially produced (76 µm) POM material available from a major manufacturer was selected for subsequent method development.

**Preparation and Use of POM.** POM (polyoxymethylene, or "acetal") was purchased in sheets of 76 µm thick material from CS Hyde Company (Lake Villa, IL). The sheet was cut with scissors into 300 mg pieces (ca. 4 × 6 cm) and cleaned by sequential extraction in *n*-hexane followed by methanol for 2 h with the aid of sonication. The extracted POMs were then air-dried on clean tissues for a few hours and stored in a glass jar with a Teflon-lined lid. This procedure yielded POM blanks that had no detectable PCB congeners.

POM sorption studies are performed by inserting the POM directly into a glass vial or jar that has been filled with wet sediment and then mixing the sediment/water/POM slurry to attain equilibrium among the three phases as described below. After the mixing is complete, the POM coupon is removed from

the slurry and rinsed for a few seconds with a gentle spray of distilled water to remove particles of sediment. Recovery of sorbed PCBs is achieved by sonication with 1:1 acetone/*n*-hexane (20 mL per POM sorbent) for 3 h. After adding the extraction solvent to the POM, the internal standards listed above are spiked into the solvent prior to starting the sonication. In order to determine if this extraction procedure yielded good efficiencies, triplicate POM samples that had been equilibrated for 42 days during the sorption rate study (described below) were extracted for an additional 18 hours with a second fresh batch of solvent. Based on a comparison of the first and second extracts, the average recovery for all 62 congeners using the 3 h sonication was 99% with essentially 100% recoveries for all di- to pentachloro-congeners and 98, 97, and 95% for the hexa-, hepta-, and octachloro-congeners, respectively.

**Sediment/Water/POM Equilibrium Studies.** All sediment/water/POM equilibration studies were performed in 40 mL glass "VOA" vials equipped with Teflon-lined lids which contained 15 g (sediments A and B) or 10 g (sediments C and D) of the sediment, a 300 mg POM sheet, and 30 mL of water containing 0.2 mg/mL sodium azide. Vials were constantly mixed in a rotating box at ca. 6 rotations per min. At selected time periods, the vials were collected, and the PCB concentrations in the POM sorbent and the freely dissolved concentrations in the associated water sample were determined as described below. All determinations discussed below were based on duplicate or triplicate vials and POM coupons. Adams et al. reported only a minor temperature and salt concentration dependence on sorption into polyethylene (PE),<sup>20</sup> and previous investigators have shown that there is no significant dependence of POM sorption over the temperature range relevant to sediment/water systems.<sup>29</sup> Therefore, all experiments were performed at room temperature.

POM equilibration times were determined using sediment D which had been spiked with an Aroclor mix prepared using 27 mg of Aroclor 1242 and 18 mg of Aroclor 1260 in 30 mL of acetone. Dilutions of this mixture were used to obtain total PCB concentrations ranging from 0.04 to 53 µg/g (Table 1). Since the spiking solution was a mixture of Aroclors, the concentrations of individual congeners at each spike level varied by a factor of ca. 70, with the median concentrations of individual congeners ranging from ca. 0.5 ng/g for the lowest spiked concentration to ca. 670 ng/g for the highest level spike. Replicate vials were removed from the rotator at selected times, and the POM concentrations were determined as described below. After the equilibration time of 28 days was established, all four sediments were used to determine  $K_{\text{POM}}$  values for the 62 congeners. Sediments A and B were both historically contaminated and were used for  $K_{\text{POM}}$  determinations as received. Sediment C was spiked with known standards of the 62 congeners, and sediment D was spiked with the Aroclor mix. Sorption isotherms were investigated using sediments C and D spiked over the concentration ranges shown in Table 1. Attempts were made at all PCB concentrations to determine  $K_{\text{POM}}$  values. However, the ability to determine  $K_{\text{POM}}$  values was limited by the sensitivity of the SPME technique to determine freely dissolved concentrations as discussed later in the text.

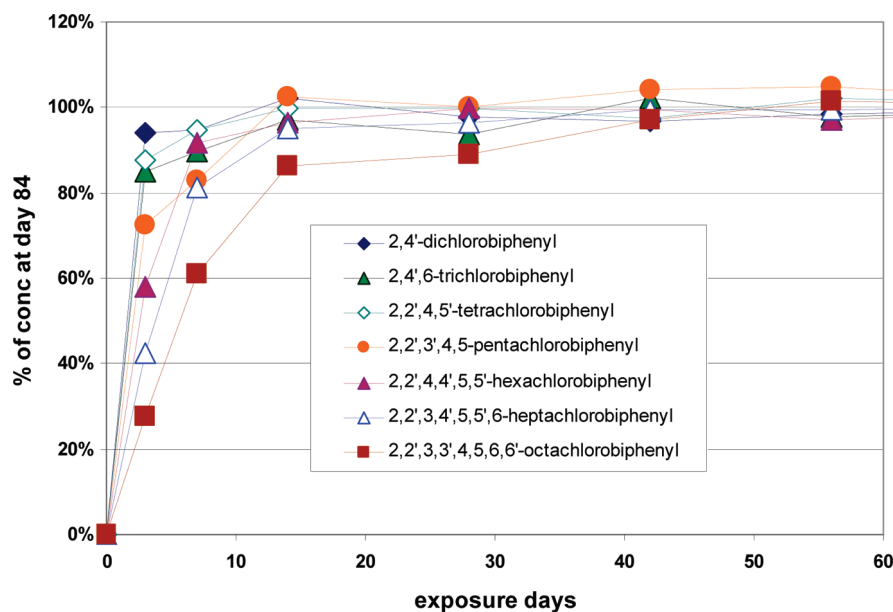
**PCB Analyses.** As noted above,  $K_{\text{POM}}$  values were determined by mixing sediment/water slurries with POM sheets and then determining the concentration of each congener that is freely dissolved in the water and comparing that to the

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**Figure 1.** Sorption rates of representative dichloro- to octachlorobiphenyl PCB congeners into 76  $\mu\text{m}$  thick POM sorbent coupons in sediment/water/POM slurries mixed for up to 84 days.

concentration found in the POM sorbent. Freely dissolved PCB concentrations in the pore water samples were determined using a SPME method capable of ca. 1 pg/mL detection limits.<sup>15</sup> In brief, a few milliliters of pore water were recovered from the wet sediment by centrifugation immediately after the POM sorbent had been removed. Colloids were removed by flocculation, the PCB internal standards (ca. 100 pg of each internal standard in 10  $\mu\text{L}$  of acetone) were added to the 1.5 mL flocculated pore water samples, and the freely dissolved concentrations were determined using SPME sorption and injection into a GC/MS operated in the selected ion monitoring (SIM) mode. Primary and confirmatory  $m/z$  ions for each PCB congener were optimized for the best signal-to-noise ratio and are listed in ref 15 along with the retention order of the 62 congeners. All SPME determinations on pore water samples were performed in duplicate.

The POM extracts (and Soxhlet extracts of the sediments) were analyzed using the same SIM  $m/z$  ions as optimized for the SPME pore water method. GC/MS analyses were performed using an Agilent model 5973 GC/MS. Separations were performed using a 60m Agilent HP-5 MS column (0.25  $\mu\text{m}$  film thickness, 250  $\mu\text{m}$  i.d.). The GC oven was held at 40  $^{\circ}\text{C}$  for 2 min after the injection, followed by a temperature ramp of 15  $^{\circ}\text{C}$  per min to 320  $^{\circ}\text{C}$  (hold for 10 min).

**Detection Limits and Calibration.** Four-point calibration solutions for the POM analyses were prepared in acetone and contained from 1.3 to 2000 ng/mL of each congener, which corresponds to a range in POM concentrations from 4 ng/g to 6700 ng/g POM for each congener. Detection limits (ng/g POM) for each congener were determined by analyzing increasingly dilute solutions until the signal-to-noise ratio no longer exceeded at least 3 to 1. No interferences in artifacts from blank POM extracts were found at the detection limits. Four-point calibration curves were also generated in water for the SPME determinations of freely dissolved concentrations as previously described.<sup>15</sup>

## RESULTS AND DISCUSSION

**Equilibration Time.** Figure 1 shows the progress toward equilibration for representative di- to octachloro-congeners from sediment D that had been spiked with the Aroclor mixture at a total PCB concentration of 5.3  $\mu\text{g/g}$ . As would be expected for a diffusion limited process, equilibration rates are slower for higher-molecular-weight congeners. As shown in Figure 1, all of the lower-molecular-weight congeners approach equilibrium in 14 days or less. However, 42 days is required before no change in the POM concentrations was observed for the octachloro-congeners. After 42 days, no further change could be detected for any congeners when POM sorbents that were equilibrated for 56 and 84 days were analyzed. After 28 days, the average concentration of the individual congeners of each molecular weight group of congeners compared to their concentrations after 84 days was  $103 \pm 3\%$  (mean of 4 dichloro-congeners),  $98 \pm 5\%$  (10 trichloro-congeners),  $98 \pm 6\%$  (13 tetrachloro-congeners),  $99 \pm 3\%$  (11 pentachloro-congeners),  $100 \pm 3\%$  (12 hexachloro-congeners),  $95 \pm 2\%$  (9 heptachloro-congeners), and  $87 \pm 3\%$  (3 octachloro-congeners). Since the analyses of POM sorbents from triplicate vials after each exposure time typically had relative standard deviations of  $<4\%$  for lower-molecular-weight congeners and increased to ca. 5 to 10% for octachloro-congeners, all congeners except the octachloro-congeners appear to be essentially at equilibrium with the POM after 28 days. Therefore, the 28 day exposure was chosen for the final method. These results are in agreement with those of Cornelissen et al. who reported that 55  $\mu\text{m}$  POM is equilibrated with higher-molecular-weight PAHs and PCBs in about a month for samplers placed in the field.<sup>19,29</sup>

The effect of spiked PCB concentrations on sorption rates was also evaluated by spiking sediment D with the Aroclor mixture at five different concentrations so that the total PCB concentrations on the sediment were 0.04, 0.21, 1.05, 5.28, 21.1, and 52.7  $\mu\text{g/g}$ . (These spiking levels resulted in sediment concentrations of individual congeners of ca. 0.2 to 200 ng/g for the less prominent congeners in the Aroclor mix and ca. 2 to 2000 ng/g for the more

**Table 2. Measured Log  $K_{\text{POM}}$  Values and Detection Limits for Individual Congeners**

sediment <sup>a</sup>	log $K_{\text{POM}}$				log Av $K_{\text{POM}}^b$	$n^c$	POM detection limit, ng/g	water detection limit, fg/mL
	sed A	sed B	sed C	sed D				
Dichloro-PCBs								
4			4.47	4.61	4.57	7	1.0	27.0
6	4.88		4.73	4.66	4.74	13	1.0	18.1
8			4.78	4.59	4.69	11	1.0	20.2
15			5.13		5.13	6	1.0	7.5
Trichloro-PCBs								
16 + 32	5.17		5.13	5.12	5.13	15	0.5	3.7
17	5.21		5.21	5.19	5.20	15	0.5	3.2
18	5.18		5.09	5.11	5.12	15	0.5	3.8
22	5.34		5.33	5.44	5.40	12	0.5	2.0
26	5.42		5.41	5.40	5.41	15	0.5	2.0
28	5.72		5.74	5.63	5.68	15	0.5	1.0
31	5.55		5.49		5.51	8	0.5	1.5
33	5.54		5.39	5.50	5.47	15	0.5	1.7
37	5.74		5.70	5.68	5.71	10	1.0	2.0
Tetrachloro-PCBs								
42	5.55		5.77	5.57	5.64	15	0.5	1.1
44	5.65		5.59	5.68	5.65	15	0.5	1.1
45	5.30		5.34	5.29	5.31	15	0.5	2.4
47 + 48	5.40		5.66	5.59	5.59	12	0.5	1.3
49			5.88	5.80	5.83	13	0.5	0.7
52	5.61		5.69	5.65	5.65	15	0.5	1.1
56 + 60	6.05		6.33	6.11	6.19	15	0.5	0.3
64			5.79	5.82	5.80	11	0.5	0.8
66	6.10		6.01	6.12	6.08	12	0.5	0.4
70	5.97		5.98	6.00	5.98	12	0.5	0.5
74	6.12		6.05	6.17	6.13	15	0.5	0.4
Pentachloro-PCBs								
82			6.09	5.89	6.00	5	0.5	0.5
84 + 101	5.84	5.92		5.91	5.90	11	0.5	0.6
85			6.20	5.98	6.07	7	0.5	0.4
O			6.08	6.04	6.05	7	0.5	0.4
95	5.86	5.90	5.84	5.92	5.89	14	0.5	0.6
97			6.04	6.29	6.23	7	0.5	0.3
99			6.20	6.15	6.17	7	0.5	0.3
105			6.38		6.38	3	0.5	0.2
110		6.21	6.09	6.23	6.20	12	0.5	0.3
118			6.21	6.41	6.32	5	0.5	0.2
Hexachloro-PCBs								
128			6.49	6.15	6.35	5	0.5	0.2
132		5.94	6.23	6.12	6.11	10	0.5	0.4
135	6.00	6.02	6.02	6.34	6.21	14	0.5	0.3
136			6.18	6.13	6.11	10	0.5	0.4
138 + 163				6.50	6.50	4	0.5	0.2
141			6.37	6.45	6.42	7	0.5	0.2
146			6.34	6.53	6.48	7	0.5	0.2
149	5.91	6.14	6.17	6.18	6.11	10	0.5	0.4
151	6.04	6.11	6.17	6.39	6.25	11	0.5	0.3
153		6.48	6.67	6.73	6.64	7	0.5	0.1
156			6.59		6.59	3	0.5	0.1
Heptachloro-PCBs								
170			6.54		6.54	3	0.5	0.1
171			6.56	6.75	6.67	5	0.5	0.1
174		6.52	6.41	6.62	6.57	12	0.5	0.1
177			6.53	6.73	6.68	7	0.5	0.1
179	6.14	6.25	6.21		6.23	7	0.5	0.3
180		6.76	6.64		6.67	8	0.5	0.1
183		6.35	6.50	6.70	6.59	9	0.5	0.1
187	6.39	6.40	6.48	6.48	6.44	10	0.5	0.2
191					6.99 <sup>d</sup>		0.5	0.1
Octachloro-PCBs								
194					7.18 <sup>d</sup>		1.0	0.1
199					6.71 <sup>d</sup>			0.2
203					7.07 <sup>d</sup>			0.1

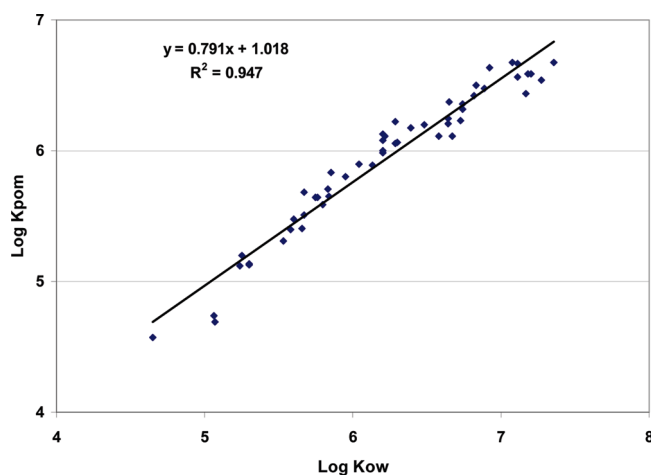
<sup>a</sup> Sediments A and B were historically contaminated. Sediment C was spiked with a mixture of the 62 target congeners. Sediment D was spiked with the mixture of Aroclors as described in the text. <sup>b</sup> The mean of all  $K_{\text{POM}}$  values determined for all sediments was calculated prior to taking its log. <sup>c</sup>  $n$  is the number of individual sediment/water/POM slurry vials for which  $K_{\text{POM}}$  values could be determined. <sup>d</sup> Values were estimated from the correlation with octanol/water coefficients shown in Figure 2.

prominent congeners.) Fortunately, no dependence on the spiking concentration of the POM sorption rates could be observed after 14, 28, and 42 days of sediment/water/POM equilibration (within the standard deviation of the analyses).

**Water/POM Partitioning Coefficients.** Measuring  $K_{\text{POM}}$  values is difficult because of the low water solubilities of PCB congeners (especially the higher-molecular-weight ones) and the difficulty in measuring low enough freely dissolved concentrations to allow  $K_{\text{POM}}$  values to be calculated. High water to POM ratios (ca. liters per gram) are normally used to avoid too much depletion of the water by sorption into the POM. Jonker et al. measured  $K_{\text{POM}}$  values of 11 congeners using water solutions with 500  $\mu\text{m}$  thick POM strips.<sup>27</sup> However, the  $K_{\text{POM}}$  values they measured varied with the POM/water ratio and sorption isotherms were very nonlinear, likely because of exceeding the water solubilities of the test PCBs at higher concentrations. Later studies have shown that the 28 day sorption time used was not sufficient to attain equilibrium and that 500  $\mu\text{m}$  POM did not attain equilibrium even after 119 days in a field deployment.<sup>19,21</sup> Similar difficulties in determining  $K_{\text{POM}}$  values for 500  $\mu\text{m}$  POM were experienced by McDonough et al.<sup>28</sup> In an effort to solve such problems in determining  $K_{\text{POM}}$  values, Cornelissen et al. used 10 to 50% methanol/water mixtures with 55  $\mu\text{m}$  “home-made” POM strips, and extrapolated the  $K_{\text{POM}}$  values to pure water.<sup>19</sup>

In the present study, we determined  $K_{\text{POM}}$  values in sediment/water slurries into which the POM is placed as described above. The presence of sediment ensures that the water saturation solubility of all congeners will not be exceeded since the sediment acts as a PCB reservoir. In addition, PCB molecules collected by the POM will be replenished in the water phase by the sediment/water equilibrium, so the final dissolved concentrations of PCBs will be higher than those remaining in a water/POM system, which makes determining water concentrations easier. Finally, assuming that sediment organic carbon/water partitioning ratios do not change with a reasonable range of spiked concentrations (i.e.,  $K_{\text{OC}}$  does not change for a particular congener on a sediment spiked at different concentrations), large ranges in water concentrations can be generated without fear of exceeding the water solubility limit of any congener. This assumption seems reasonable over the range of total PCB concentrations used (Table 1) for the spiked sediments C and D isotherm studies and is simple to demonstrate if the concentration of each congener in the POM sorbent after equilibration is proportional to its spiked concentration on the sediment. Finally, the SPME method to determine freely dissolved PCB concentrations only uses a few milliliters of water to measure low picogram per milliliter freely dissolved concentrations,<sup>15</sup> which eliminates the need for liter quantities of pore water that are required for more conventional extraction/analysis methods.

The mean  $K_{\text{POM}}$  values determined for each sediment are given in Table 2. For all samples, the ability to determine  $K_{\text{POM}}$  values depended on whether there were sufficient freely dissolved concentrations (greater than ca. 1 pg/mL) so they could be measured by the SPME method. Since the contaminated sediments A and B were used as received, the ability to measure  $K_{\text{POM}}$  values was limited by the contaminant congener



**Figure 2.** Correlation of measured  $K_{\text{POM}}$  values from Table 2 with  $K_{\text{OW}}$  (octanol/water) partitioning coefficients taken from Hawker et al.<sup>33</sup> for dichloro- to heptachloro-PCB congeners.

distribution. For the spiked sediments, C and D, pore water concentrations were high enough for SPME analyses at the highest one, two, or three spiking levels, depending on the congener. In the worst case, a minimum of three sediment/water/POM vials (from a single concentration on one sediment) were used for each  $K_{\text{POM}}$  determination reported, with as many as 15 vials from different sediments (and spike concentrations) used to determine  $K_{\text{POM}}$  values for some congeners.

The correlation of  $K_{\text{POM}}$  values with  $K_{\text{OW}}$  values is shown in Figure 2 and appears sufficiently strong ( $r^2 = 0.947$  for 59 congeners) so that  $K_{\text{POM}}$  values for congeners not reported in this study could be reasonably estimated on the basis of their  $K_{\text{OW}}$  values using the equation:

$$\log K_{\text{POM}} = 0.791 \log K_{\text{OW}} + 1.018$$

Similarly, since no sample had sufficient freely dissolved concentrations of congeners 191, 194, 199, and 203 to be directly measured, their  $K_{\text{POM}}$  values in Table 2 were estimated using this correlation with  $K_{\text{OW}}$ .

The accuracy of this correlation to predict  $K_{\text{POM}}$  values from  $K_{\text{OW}}$  values was investigated by comparing the measured  $K_{\text{POM}}$  values for the 59 congeners with those predicted using the equation above and literature  $K_{\text{OW}}$  values. The ability of the correlation to predict measured  $K_{\text{POM}}$  values was surprisingly accurate, with more than three-quarters of the predicted congener's linear (not log)  $K_{\text{POM}}$  values falling within 30% of the measured  $K_{\text{POM}}$  values, and all predicted values falling within a factor of 2 of the measured values. Therefore, the  $K_{\text{OW}}$  correlation above can be used to determine the freely dissolved concentrations within a factor of 2 (or better) for congeners that have no measured  $K_{\text{POM}}$  values.

As shown in Table 2, the log  $K_{\text{POM}}$  values that could be obtained from multiple sediments agree reasonably well, with the relative standard deviations (RSD) for log  $K_{\text{POM}}$  values typically less than 2%. When the reproducibility is calculated on  $K_{\text{POM}}$  values (not log  $K_{\text{POM}}$ ), 23 of the congeners had RSDs

(33) Hawker, D. W.; Connell, D. W. *Environ. Sci. Technol.* **1988**, *22*, 382–387.

**Table 3. Comparison of Log  $K_{\text{POM}}$  Values**

	congener #	log $K_{\text{POM}}$	
		this work 76 $\mu\text{m}$ POM	Cornelissen 55 $\mu\text{m}$ POM <sup>a</sup>
2,2',5-trichlorobiphenyl	18	5.12	4.83
2,4,4'-trichlorobiphenyl	28	5.68	5.09
2,2',5,5'-tetrachlorobiphenyl	52	5.65	5.52
2,3',4',5-tetrachlorobiphenyl	70	5.98	5.87
2,2',3,3',6-(2,2',4,4',6)-pentachlorobiphenyl	84 + 101 <sup>b</sup>	5.90	5.93
2,3,3',4,4'-pentachlorobiphenyl	105	6.38	6.32
2,3,3',4',6-pentachlorobiphenyl	110	6.20	5.93
2,3',4,4',5-pentachlorobiphenyl	118	6.32	6.32
2,2',3,4,4',5'-(2,3,3',4',5,6)-hexachlorobiphenyl	138 + 163 <sup>b</sup>	6.50	6.27
2,2',3,4',5',6-hexachlorobiphenyl	149	6.11	5.93
2,2',4,4',5,5'-hexachlorobiphenyl	153	6.64	6.40
2,2',3,4,4',5,5'-heptachlorobiphenyl	180	6.67	6.18

<sup>a</sup> Log  $K_{\text{POM}}$  values taken from ref 19. <sup>b</sup> Combined values are reported since these species coelute during GC/MS. Our values were determined using the ratio of congeners found in commercial Aroclors. Log  $K_{\text{POM}}$  values from Cornelissen et al.<sup>19</sup> are reported only for PCB 101 and 138.

less than 20% and nearly all of the remaining congeners had RSDs less than 30%. As might be expected, the reproducibility for replicate  $K_{\text{POM}}$  values from a single sediment were typically better than those measured using multiple sediments. For all subsequent studies, the average of the  $K_{\text{POM}}$  values shown in Table 2 will be used to calculate water concentrations from the PCB concentrations in POM after equilibrium.

Although few  $K_{\text{POM}}$  values for PCBs that were determined with the POM at equilibrium have been reported, Cornelissen et al. recently reported values for 12 trichloro- to heptachloro-congeners on 55  $\mu\text{m}$  POM equilibrated for 100 days.<sup>19</sup> A comparison of our values with theirs is shown in Table 3. In general, the values from the two studies agree well, especially when considering the wide range in values reported by earlier workers using 500  $\mu\text{m}$  POM.<sup>27,28</sup>

**Detection Limits.** Detection limits for freely dissolved PCBs depend on the detection limit for the POM extracts, i.e., the detection limit for the POM extract divided by the  $K_{\text{POM}}$  value equals the detection limit for the freely dissolved PCBs. For the POM extracts, the detection limits were determined using serial dilutions and were based on a minimum of 3:1 signal-to-noise ratio assuming that the POM extract was concentrated to 1 mL before a 1  $\mu\text{L}$  splitless injection. Under these conditions, the detection limit in POM extracts was ca. 1 ng/g POM for each individual congener, resulting in a range in freely dissolved concentrations from ca. 20 pg/L for low dichloro-congeners down to ca. 0.1 pg/L for the higher-molecular-weight congeners (Table 2).

**Method Linearity and Sorption Isotherms.** Although only the higher spiked concentrations on sediments C and D resulted in sufficient freely dissolved concentrations for SPME determinations, all of the spiking levels (Table 1) resulted in sufficient POM concentrations to allow sorption isotherms to be determined over 3 orders of magnitude. Therefore, the linearity of the POM method to determine freely dissolved PCB concentrations was investigated using POM sorption isotherms over the spiked concentration ranges shown in Table 1. (Freely dissolved concentrations were calculated from the  $K_{\text{POM}}$  values reported in Table 2 and the POM concentrations for each congener as described above).

Sorption isotherms for representative dichloro- to octachloro-congeners spiked at six different concentrations using the Aroclor

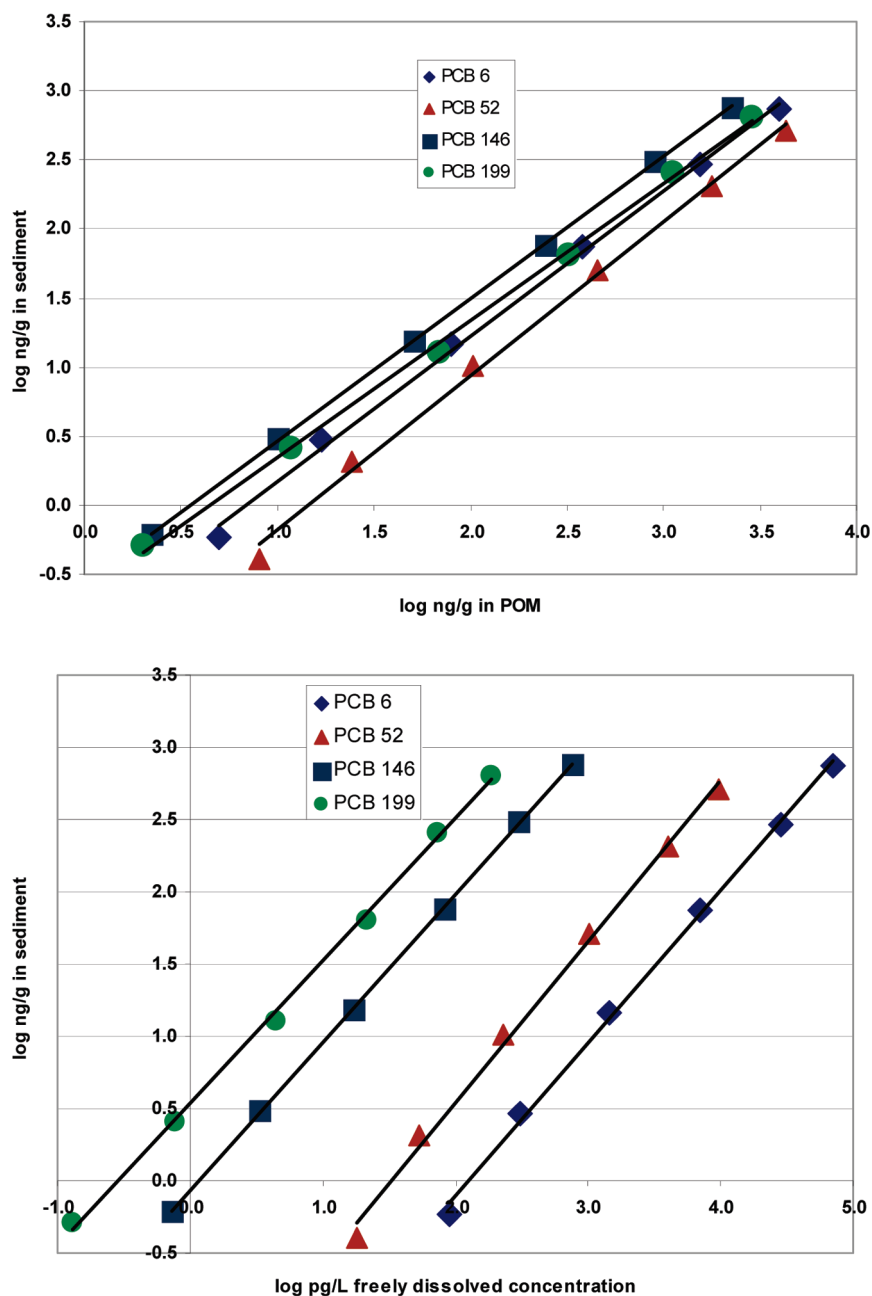
mix are shown in Figure 3. No deviations from linearity could be observed for any of the 62 congeners, and the linear correlation coefficient,  $r^2$ , was greater than 0.995 for all congeners. All intercepts on linear plots (not shown) were essentially zero. Similar results were obtained when sediment C was spiked with the 62 standard congeners at six different concentrations ranging (for each congener) from 4 to 5000 ng/g sediment, thus demonstrating that POM sorption isotherms for PCBs are linear over at least 3 orders of magnitude.

The linearity of the sorption isotherms demonstrates that the method should yield linear results over a wide range of environmentally relevant freely dissolved concentrations. The linearity also shows that the  $K_{\text{OC}}$  value for each isomer did not change with its spiked sediment concentration and that the concentration had no effect on establishing the sediment/water/POM equilibrium.

**Nondepletive Sampling.** As noted before, the use of POM to determine freely dissolved PCB concentrations requires that the sediment, water, and POM all come to equilibrium. In addition, the POM should not significantly deplete the PCB sediment reservoir so that the freely dissolved concentrations before the addition of POM are essentially the same after sediment/water/POM equilibrium is attained. The relative mass of each PCB congener in the POM, water, and sediment will depend on the ratio of POM mass to sediment mass, as well as the  $K_{\text{POM}}$  value for each congener and its sediment/water partitioning coefficient ( $K_{\text{D}}$ ). For example, for spiked sediment C, the relative mass (compared to spiked mass) of all 62 congeners in the POM after 28 days averaged  $8.2 \pm 0.7\%$ . Essentially, all of the PCBs not in the POM remain in the sediment, since the actual fractions of PCB molecules that are dissolved in the water are only ca. 0.002% (for dichloro-congeners) to 0.000002% (for the hepta- and octachloro-congeners).

As would be expected based on the linear isotherms shown in Figure 3, there is no trend in the PCB fraction in POM with spiking concentrations for any of the congeners tested. Interestingly, there is also no trend with the molecular weight of the 62 PCB congeners in the fraction found in POM, which clearly demonstrates that  $K_{\text{POM}}$  values parallel  $K_{\text{D}}$  (and  $K_{\text{OC}}$ ) values closely for this sediment, just as they parallel  $K_{\text{OW}}$  values as shown in Figure 3.





**Figure 3.** POM sorption isotherms for representative dichloro- to octachloro-PCB congeners (top) and converted to freely dissolved concentrations (picogram per liter) using the  $K_{\text{POM}}$  values from Table 2 (bottom). The low and high spiked sediment concentrations for the individual congeners shown are 0.6 to 730 ng/g (PCB 8), 0.4 to 510 ng/g (PCB 52), 0.6 to 770 ng/g (PCB 146), and 0.5 to 640 ng/g (PCB 199). Correlation coefficients ( $r^2$ ) are 0.998 for PCB 6 and PCB 199, 0.997 for PCB 52, and 1.000 for PCB 146.

In order to maintain “negligible depletion,” previous workers have suggested that less than 5% of the mass of each PCB should be found in the POM sorbent.<sup>27,32</sup> (Note that this criterion does not apply to determining the  $K_{\text{POM}}$  values reported in Table 2, since we directly measured the freely dissolved concentrations using the SPME technique from ref 15.) Since the fraction of PCBs dissolved in water is so small, controlling the fraction of PCBs collected by the POM is achieved by changing the ratio of sediment to POM mass. For sediment C, which has 3.0% organic carbon, the 30:1 sediment to POM ratio used resulted in ca. 8% depletion for all congeners. Therefore, the sediment/POM ratio should be increased to ca. 50:1 to achieve less than 5% depletion recommended by earlier workers.<sup>27,32</sup> However, sediments have different contents of natural and anthropogenic carbon sorbents,

which would affect the sediment/POM ratio needed. For example, sediment D, which has 1.2% organic carbon, averaged 25% of the PCBs found in the POM (again, with no distinction for the PCB molecular weight). Therefore, for general application of the POM method to determine freely dissolved PCB concentrations from a variety of sediments, we recommend that the sediment/POM ratio be greater than ca. 200 to 1 (dry sediment basis, or ca. 400 to 1 on a wet sediment basis) to maintain “nondepletive” conditions.

**Application to Field Sediments.** Methods developed on well-characterized and spiked sediments sometimes fail to perform adequately when a range of field sediments are tested, since interferences from nontarget organics and sediment characteristics (especially colloidal content) can both adversely affect the performance of methods based on nondepletive sorbents. In order

to further evaluate the POM method, freely dissolved PCB concentrations for 19 freshwater sediments having a range in total PCB concentrations (62 congeners) from ca. 80 to 1000 ng/g were determined. Duplicate vials containing the sediment/water/POM slurry for each sample were mixed for 28 days as before. Soxhlet extractions were also performed on duplicate 2 g sediment samples from each sediment jar.

Even with selected ion monitoring MS, interferences from nontarget species can adversely affect detection limits at these trace levels. However, for the 19 sediments tested, no significant interferences were found, and the method detection limits shown in Table 2 appear valid for field samples based on these 19 sediments.

The reproducibility of the POM method for freely dissolved PCBs will depend both on the analytical characteristics of the method and the sediment homogeneity. Our previous experience with ca. 250 PAH-contaminated sediments showed that ca. 20% of the samples had widely varying PAH concentrations in replicate samples taken from a single jar, even though those samples had been sieved and thoroughly mixed prior to storage. It was, therefore, not surprising to see a similar rate of heterogeneity in the PCB-contaminated sediments. For 12 of the sediments, about 1/2 (or more) of the congeners had freely dissolved concentrations from the duplicate slurries that agreed within 10% of each other, and the remaining congeners and sediments usually agreed within 15% (with the higher deviations occurring near the detection limits), results that show reasonably good method reproducibility given that two separate mixtures of sediment/water/POM were used. These sediments also showed similar reproducibility in the duplicate Soxhlet extracts. However, for a few sediments, the agreement was poorer, which is likely a result of sediment heterogeneity rather than method reproducibility, since the same sediment samples that showed heterogeneity in the duplicate POM coupons showed similar heterogeneity in their duplicate Soxhlet extracts.

**Practical Characteristics of the Method.** As noted above, a major goal of these investigations was to develop a robust method that could determine the freely dissolved concentrations of all relevant PCB congeners at low picogram per liter concentrations.

Although other sorbents such as PE and PDMS have been used for nondepletive sampling, we found the commercial POM material to be superior in its physical strength (no sorbent holder is needed, and it shows no abrasion even after mixing with sediment for 84 days) and lack of colloidal interference (especially compared to PDMS). The POM is also very inexpensive and easy to prepare as well as to recover sorbed PCBs. The major disadvantage of the method is that a 28 day equilibrium period is required for the higher-molecular-weight congeners to come to equilibrium, although this time does coincide with biological exposure tests often conducted with impacted sediments. Fortunately, once the  $K_{\text{POM}}$  values are established, the labor required to perform the determinations is fairly minimal, even compared to routine analytical procedures such as Soxhlet extraction. Thinner POM would shorten the time required, but we chose to use a common commercially available material so that the method could be transferrable to other laboratories without the need for each lab to measure  $K_{\text{POM}}$  values for every target PCB congener. Even though the method was developed for the 62 congeners that were present in any significant concentrations in commercial Aroclors, it is always possible that unexpected congeners (e.g., from degradation) could be present. However, since all 209 congeners are monitored during the GC/MS determinations, the freely dissolved concentrations of any unexpected congener found could be reasonably estimated using the  $K_{\text{POM}}/K_{\text{OW}}$  correlation discussed above. The method should be equally applicable to field deployment and lab determinations, and only relatively small (e.g., 100 mL) samples need to be shipped, which significantly reduces sample handling costs when large field surveys are performed.

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