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Polychlorinated Biphenyl Release from Resuspended Hudson River Sediment

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Three shear turbulence resuspension mesocosms (STORM tanks) were used to examine the release of polychlorinated biphenyls (PCBs) from resuspended Hudson River sediment. Twenty-two percent of the resuspended PCBs desorbed after 2 h, and $35\% \pm 8\%$ of PCBs were in the dissolved phase after apparent steady state was reached in 2 days. After the first resuspension event, the solids were allowed to settle and the quiescent time was varied to determine whether the labile pool of PCBs is recharged during sediment consolidation. The steady-state $\log K_{oc}$ values for the third subsequent resuspension were higher than for the first event due to lower dissolved PCB concentrations; the particulate PCB concentrations were constant between events. With 1 day of consolidation between resuspension events, the dissolved concentration of all congeners decreased an average of $8\% \pm 5\%$ between subsequent resuspension events. With 4 days between events, only the dissolved pentachlorinated PCBs decreased significantly ($p = 0.002$), suggesting that the easily desorbable PCBs recharge when there is sufficient time between resuspension events.

Introduction

The upper Hudson River is severely contaminated with polychlorinated biphenyls (PCBs). The river's sediments are the largest reservoir of PCBs in the system, and mass balances show that long-term, chronic releases of PCBs from the sediments account for the PCB inventory in the water column (1). Resuspension of surficial sediments occurs naturally during high river flows and tidal cycles as mediated by bottom shear stress. Understanding the release of PCBs during these events is critical for assessing remediation plans and evaluating their impact on dissolved PCB concentrations. However, most studies examining PCB partitioning to sediment do not mimic resuspension under realistic physical conditions. Typically, PCB desorption is studied by vigorously mixing, shaking, or rolling contaminated sediment in clean water (2–5).

It is difficult to realistically resuspend sediment in the laboratory, and few studies have simulated the bottom shear stress or water column turbulence levels typically encountered in a river. Latimer et al. (6) used a particle entrainment simulator (PES) to resuspend sediment at regulated shear stresses. The PES created realistic bottom shear stresses but the water column turbulence was unrealistically high. At a bottom shear stress of 2 dyn cm^{-2} the resuspended particles

were enriched in PCBs and organic carbon relative to the bulk sediment. As shear stress increased to 5 dyn cm^{-2} , both the organic carbon content and PCB concentration of the resuspended particles decreased to match those of the bulk sediment. This suggests that models which assume that the PCB concentration of particles resuspended at low shear stress is equal to the sediment concentration will underestimate PCB release into the dissolved phase.

Lick and colleagues (2, 7–10) examined the influence of particle flocculation on hexachlorobenzene (HCB) partitioning. As the suspended sediment concentration increased, flocs formed more quickly and apparent sorption equilibrium was reached more slowly. At a TSS concentration of 500 mg L^{-1} , steady-state floc formation was reached in 4.5 h but apparent sorptive equilibrium was not reached for 480 h (10). Lick and Rapaka (9) concluded that the time to reach equilibrium varied greatly with TSS because of the changes in the properties of the resuspended flocs.

Do resuspended particles remain in the water column long enough to reach sorptive equilibrium? Karickhoff et al. (11) observed that the partitioning of hydrophobic organic chemicals (HOCs) to a variety of sediment types depends on the octanol–water partition (K_{ow}) coefficient of the HOC and the fraction of organic carbon present in the sediment and formulated a new parameter, the organic carbon normalized partition coefficient (K_{oc}). Field measurements, however, have found only weak correlations between measured partition coefficients, suspended solids organic carbon content, and K_{ow} . Field measured K_{oc} s are highly variable and the K_{oc} for a single PCB congener may vary more than an order of magnitude at a given site (12–14). In the Hudson River, the deviation from Karickhoff's prediction is especially pronounced for the low molecular weight congeners (15), perhaps due to colloidal interference, nonequilibrium, or particle heterogeneity. Binding to dissolved organic carbon (DOC) may account for a significant fraction of the high molecular weight PCBs measured in filtered Hudson River water (15). However, correcting for DOC binding increases the observed deviation from Karickhoff's prediction. Nonequilibrium theory attributes the observed variability in partitioning to the amount of time the particles are resuspended in the water column (16). Finally, PCB partitioning measured in the field reflects interactions with the heterogeneous mixture of many types of particulate organic carbon, including black carbon, which strongly adsorbs many PCB congeners (17, 18). For some types of black carbon, K_{BC} values are not strongly correlated to K_{ow} (18).

Desorption of PCBs from particles can be modeled as a two-stage process; the first ("labile") is rapid and the second ("resistant") is slow. Much of the research into PCB desorption has focused on understanding and modeling the resistant pool (19–22). However, resuspension events typically last hours to days and riverine particles are likely not suspended into the water column long enough for desorption of the resistant fraction to contribute significant amounts of dissolved PCBs. Studies either assume a labile or easily desorbing pool that is at equilibrium with the water (3) or calculate a specific rate constant for the labile fraction (5, 23). Estimates of the percent of PCBs in the labile pool vary considerably among studies. Cornelissen et al. (24) found that the fraction of PCBs spiked into sediments remaining in the labile pool decreased from 70–85% after 2 days to 33–52% after 37 days. Carroll et al. (4) determined that 55–76% of the PCBs in Hudson River sediment were in the labile fraction.

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It is unclear whether a labile pool is replenished from a more resistant pool as sediments sit unmixed on the river bottom. If PCBs rapidly migrate from a resistant pool to a labile pool, then every time a particle is lifted from the sediment bed it will undergo the first rapid labile stage of the desorption process. On the other hand, if PCBs diffuse slowly into a labile pool, desorption during resuspension events will largely be a result of the second, slower resistant stage of desorption. Spectroscopic investigations of the binding of 1,2-dichloroethane (DCA) to humic and fulvic acids showed two different sorbed species (25). The first species was labile and sorbed to the organic matter within 30 min. The second species was detected only after several hours of sorption and increased in intensity throughout the experiment.

This study utilized 1000-L shear turbulence resuspension mesocosms (STORM tanks) to examine the release of PCBs from Hudson River sediment. Unlike previous laboratory experiments, the STORM tanks realistically mimic both bottom shear stress and water column turbulence (26). In this experiment, sediment was resuspended to TSS concentrations of about 80 mg L⁻¹ with minimal turbulence. Resuspended particles adhered to each other and formed flocs in the water column (27). Solid-phase microextraction (SPME) was used to measure dissolved PCBs so that colloids would not be included in the measurement of dissolved PCBs (28). The STORM tank's ability to easily start and stop resuspension events allowed us to explore the movement of PCBs between a labile and more resistant pool. We varied the quiescent time between resuspension events, allowing the sediment to sit on the bottom for various lengths of time to examine the recharge of the labile (rapidly desorbing) pool.

Materials and Methods

STORM Tanks. Resuspension events were conducted in three shear turbulence resuspension mesocosm (STORM) tanks (26), whose design evolved from 1000-L linked mesocosms (29). In each STORM tank a paddle rotated backward and forward just above the bottom around a central shaft, resuspending sediment without generating excessive water column turbulence. The maximum instantaneous bottom shear stress was about 1 dyn cm⁻² and the volume-weighted average water column turbulence intensity and energy dissipation rate were 0.55 cm s⁻¹ and 3.2 × 10⁻³ cm² s⁻³, respectively. Sediment was collected from the upper Hudson River near Griffin Island (43°12.246' N, 70°34.891' W, river mile 189.75), homogenized and added to the STORM tanks to a depth of 5 cm. In each tank the sediment surface area was 1 m² and the water column was 1 m deep with a total volume of 1000 L. To minimize biological growth, all experiments were conducted in the dark.

A series of three 3-day resuspension events were conducted in each tank. Mixing began on the morning of day 1 when the tanks were filled with clean well water and continued uninterrupted for the entire 3-day period. The slowly rotating paddle maintained the total suspended solids (TSS) concentration in the water column at a constant level. At the end of each 3-day resuspension event, mixing was stopped and the particles were allowed to settle through the water column for approximately 20 h. Following settling, the water was pumped out of the tank. The sediment sat at the bottom of the tank with only ~1 cm of overlying water until the start of the next resuspension event, when clean well water was slowly added back to the tank. In STORM tanks A, B, and C there were 1, 2, and 4 days of quiescence between resuspension events, respectively. A control tank identical to the resuspension tanks but without mixing was used to measure PCB diffusion from the sediment bed.

Dissolved PCB concentrations were measured and suspended solids were collected for particulate PCB, TSS, and particulate carbon and nitrogen (CHN) analyses. At the water

column turbulence levels of these experiments, the water column was well-mixed and samples were collected from 0.5 m depth. Laser in situ scattering and transmissometry (LISST 100C, Sequoia Scientific) measured the volume concentration (in microliters per liter) of particles 3.2–250 μm in diameter in 26 logarithmically spaced bins (27). In the diffusion control tank, dissolved PCBs were measured every third day for 30 days. Dissolved PCB concentrations were measured by nonequilibrium solid-phase microextraction (SPME), as detailed elsewhere (28). SPME fibers were deployed in the STORM tanks for 30 min to collect an integrated measurement of the dissolved PCB concentration. The SPME fibers were then spiked with PCB internal standards and injected into the cool on-column injection port of an Agilent 6890 gas chromatograph equipped with a 30 meter DB-5 column (J&W Scientific) and a ⁶³Ni electron capture detector. Each sample was analyzed for 10 PCB congeners based on retention time relative to a standard mixture of PCB Aroclor 1248. The mass quantified on the SPME fiber was calibrated to dissolved PCB concentrations by conducting both SPME and liquid/liquid extractions of deionized water spiked with various amounts of PCB Aroclor 1248 (28).

Particulate PCB samples were collected by filtering 150 mL of water through glass fiber filters (47 mm, 0.7 μm pore size). Sediment was collected in glass jars from the homogenized sediment added to each tank. All samples were frozen at -20 °C until analysis. The sediment was ground with cleaned anhydrous Na₂SO₄ and the filters were extracted without drying. The samples were transferred to Soxhlet flasks, spiked with PCB surrogate standards 3,5-dichlorobiphenyl (IUPAC 14), 2,3,5,6-tetrachlorobiphenyl (IUPAC 65), and 2,3,4,4',5,6-hexachlorobiphenyl (IUPAC 166), and extracted for 24 h in dichloromethane. The extract was concentrated, transferred into hexane, and eluted through a Florisil column (60–100 mesh, J. T. Baker Co.). The purified extracts were concentrated and analyzed on a Hewlett-Packard 5890 gas chromatograph with a 60-m DB-5 column (J&W Scientific) and a ⁶³Ni electron capture detector. Each sample was analyzed for 55 individual PCB congeners and 28 chromatographically unresolved congener groups. Internal standards (Ultra Scientific) consisting of 2,3,6-trichlorobiphenyl (IUPAC 30) and 2,2',3,4,4',5,6,6'-octachlorobiphenyl (IUPAC 204) were added to each sample prior to instrumental analysis. Each PCB congener was identified on the basis of its retention time relative to a standard mixture of PCB Aroclors 1232, 1248, and 1262 (Ultra Scientific).

Water was filtered through preweighed glass fiber filters (47 mm, 0.7 μm pore size) and dried overnight at 105 °C to measure the total suspended solids concentration. Particulate carbon and nitrogen was measured by filtering 50 mL of water through glass fiber filters (25 mm, 0.7 μm pore size) and combusting the dried filters in a CE-440 elemental analyzer (Exeter Analytical, Inc.).

Quality Control and Assurance. For the suspended particle samples, surrogate recoveries were 81% ± 9% for IUPAC 14, 83% ± 10% for IUPAC 65, and 85% ± 8% for IUPAC 166 (*n* = 100). For the sediment samples surrogate recoveries were 80% ± 10% for IUPAC 14, 87% ± 5% for IUPAC 65, and 85% ± 6% for IUPAC 166 (*n* = 13). Since analyte levels in field and laboratory matrix blanks were low relative to those in samples, no corrections were made. Detection limits for the various PCB congeners (defined as 3 times the mean blank mass of each PCB congener) ranged from 1 to 5 ng L⁻¹ in the dissolved phase, from 1 to 120 ng g⁻¹ in the particulate phase, and from 0.1 to 12 ng g⁻¹ in the sediment.

Results and Discussion

Flocculation and Disaggregation. In all three tanks, the TSS concentration rose rapidly and reached steady state by the

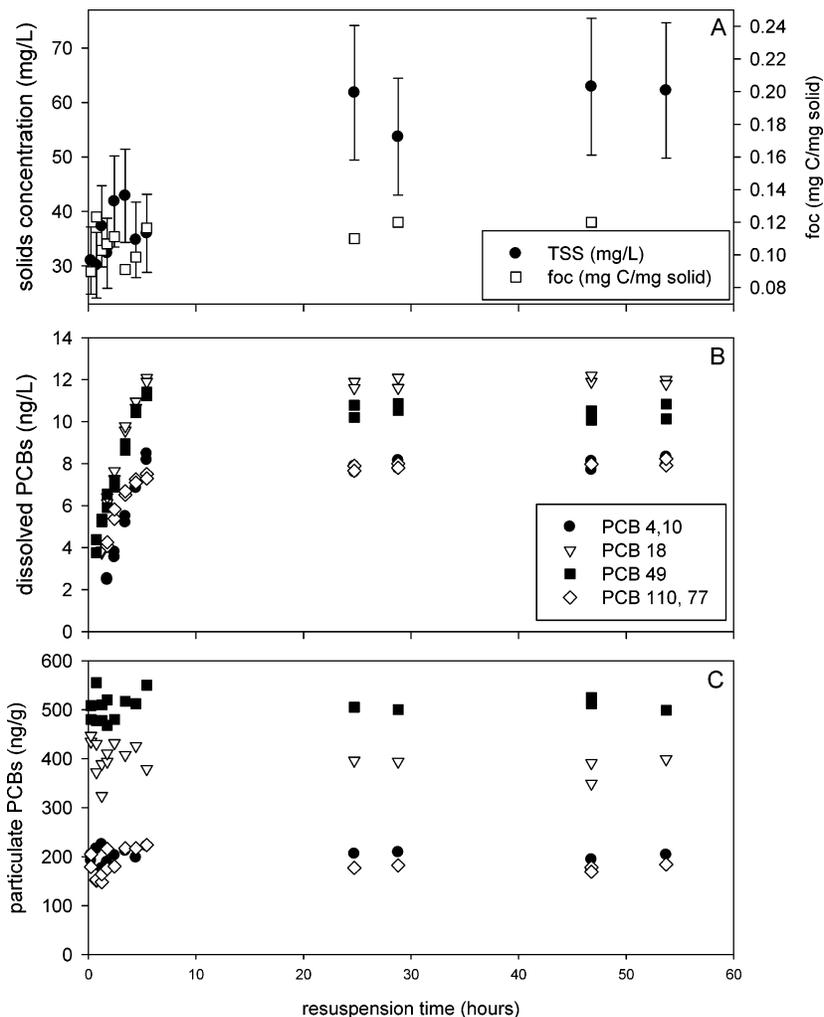


FIGURE 1. Total suspended solids (TSS) concentration and fraction organic carbon (A) and dissolved (B) and particulate (C) PCB congeners during the first resuspension event in tank 1. Duplicate symbols in panels B and C represent replicate measurements.

start of the second day of resuspension (Figure 1, 27). During the first resuspension event, the steady-state TSS concentration was $60 \pm 4 \text{ mg L}^{-1}$ in tank A and $79 \pm 5 \text{ mg L}^{-1}$ in both tanks B and C. Large flocs were lifted into the water column immediately following the initiation of resuspension, and the volume median diameter of the resuspended particles decreased with time as the flocs disaggregated. At steady state, the particle size distribution did not vary among tanks or events and the volume median particle diameter was $112 \pm 3 \mu\text{m}$ (27). If the solids density is assumed to be a linear combination of the density of minerals and organic matter, then the LISST data and TSS concentration can be used to calculate porosity and gross bulk density of the resuspended particles. At steady state, the particles had a porosity of 0.90 ± 0.02 and a gross bulk density of $1.13 \pm 0.02 \text{ g cm}^{-3}$ (27).

Sediment and Suspended Particles. At steady state, the organic carbon content of the particles resuspended at a maximum instantaneous bottom shear stress of 1 dyn cm^{-2} was $0.12 \text{ mg of C (mg of solid)}^{-1}$ in all three tanks and did not change during the course of each resuspension event (Figure 1). The resuspended particles were enriched in organic carbon relative to the bulk sediment [$0.05\text{--}0.06 \text{ mg of C (mg of solid)}^{-1}$, 27].

The total PCB concentrations in the bulk sediment were 12.6 ± 0.72 and $11.9 \pm 0.47 \mu\text{g g}^{-1}$ in tanks A and B respectively. Due to a handling error the tank C sediment was not analyzed, and the PCB concentration was assumed to be $12 \mu\text{g g}^{-1}$. The resuspended particles were enriched in PCBs by $50\% \pm 18\%$

relative to the bulk sediment and this enrichment was not correlated to PCB molecular weight. Under these realistic physical conditions, more PCBs were resuspended in the water column than predicted on the basis of bulk sediment PCBs measurements. Mass balance calculations utilizing sediment PCB concentration and TSS underestimate the mass of PCBs resuspended in the water column, a finding consistent with previous studies. In laboratory studies, resuspended sediments from Narragansett Bay (6) and the Housatonic River (30) were enriched in organic carbon and *t*-PCBs relative to the bulk sediment.

Initial Release during Resuspension Event 1. Since the initial conditions in all three tanks were the same, the first resuspension events in each tank are replicate treatments. This first event occurred 10–14 days after the sediment was added to each tank (27) and represents the initial release of PCBs from quiescent sediment resuspended after a long consolidation period. Some labile PCBs were probably lost when sampling the sediment from the Hudson River and transporting it to Maryland, so results of this study may underestimate the release caused by in situ resuspension.

The dissolved PCB concentration rose rapidly and reached steady state by the start of the second day of resuspension (Figure 1). Given the sensitivity limits of SPME, changes in dissolved PCB concentrations greater than $0.03 \text{ ng L}^{-1} \text{ h}^{-1}$ over the 3-day time period of each resuspension event could be detected. The flux of PCBs from the bedded sediment without resuspension in the diffusion control tank ranged

from 0.13 to 0.45 $\mu\text{g m}^{-2}\cdot\text{day}^{-1}$, which was 2 orders of magnitude lower than the 12–53 $\mu\text{g m}^{-2}\cdot\text{day}^{-1}$ flux due to resuspension and subsequent desorption measured during the first day of each resuspension event. Volatilization of PCBs from the tanks was estimated to average of 2.2 $\mu\text{g m}^{-2}\cdot\text{day}^{-1}$, an order of magnitude less than the flux caused by resuspension and subsequent desorption.

Several di-, tri-, and tetrachlorinated PCBs were detected after just 15 min of resuspension. This rapid initial release was on average 30% of the steady-state dissolved PCB concentration. Since the resuspension depth was less than 1 mm, less than 1 L of pore water was mixed into the 1000-L water column during resuspension. Assuming the pore water was in equilibrium with the sediment, resuspension of pore water accounts for dissolved PCB concentrations of only up to 8 pg L^{-1} for each congener, well below the detection limits of SPME and much less than the dissolved PCB concentrations measured after 15 min of resuspension. A similar evaluation was conducted to determine if this initial PCB release could be caused by the exchange of interstitial water during floc disaggregation. The LISST measured an initial volume of resuspended particles of 154 $\mu\text{L L}^{-1}$ and the calculated porosity of the flocs was 0.90. If all of the intrafloc water was released into the water column instantaneously, 138 $\mu\text{L}_{\text{floc water}} \text{L}^{-1} \text{water}$ would exchange with the water column. The release of this volume of water adds up to 5 pg L^{-1} of each congener into the water column, if equilibrium between the solid phase and pore water of the floc before resuspension is assumed. Neither of these mechanisms is sufficient to explain the rapid increase in dissolved PCBs, leaving desorption from a labile PCB pool within the resuspended sediments as the most likely process.

After 2 h of resuspension, all PCB congeners were detected and dissolved concentrations averaged 50% \pm 11% of their steady-state values. The dissolved phase comprised 20% \pm 8% of the water column PCB levels in all three tanks, and this did not vary with molecular weight. During the first 6 h of resuspension, the dissolved PCB concentration continued to increase with time and the particulate concentration was relatively constant, resulting in decreasing organic-normalized partition coefficients. After 6 h of resuspension, 31% \pm 10% of the resuspended PCBs were in the dissolved phase.

PCB Partitioning at Steady State during Resuspension Event 1. Apparent PCB steady state was reached by the start of the second day of resuspension, which was faster than observed in earlier studies (10). Tye et al. (10) found that sorptive equilibrium for 4,4'-dichlorobiphenyl to sediment was reached in 288 h at a TSS concentration of 100 mg L^{-1} . However, our study is consistent with the study of Carroll et al. (4) that found over 50% of the PCBs desorbed from Hudson River sediment during the first 24 h. The remaining fraction desorbed so slowly with time that the concentration appeared constant over a 2-day time period. Lamoureux and Brownawell (5) report that desorption of the lower molecular weight PCB congeners ($\log K_{\text{ow}} < 6.2$) from New York Harbor sediments occurred rapidly and equilibrium was reached after less than 100 h. Gong et al. (31) found that equilibrium was reached within 50 h when 2,2',5,5'-tetrachlorobiphenyl desorbed from laboratory-contaminated sediment.

The steady-state partition coefficients for the di-, tri-, and tetrachlorinated PCB congeners fell within the range observed in the Hudson River, but those for the pentachlorinated PCB congeners were lower (Figure 2, data from ref 15). Butcher et al. (15) calculated partition coefficients for the lower molecular weight PCBs using \sim 25 samples collected from the upper Hudson River but calculated partition coefficients for the pentachlorinated PCB congeners in only three samples. The Hudson River data set was generated by collecting suspended particles on glass fiber filters for the particulate measurement and then conducting a liquid/liquid

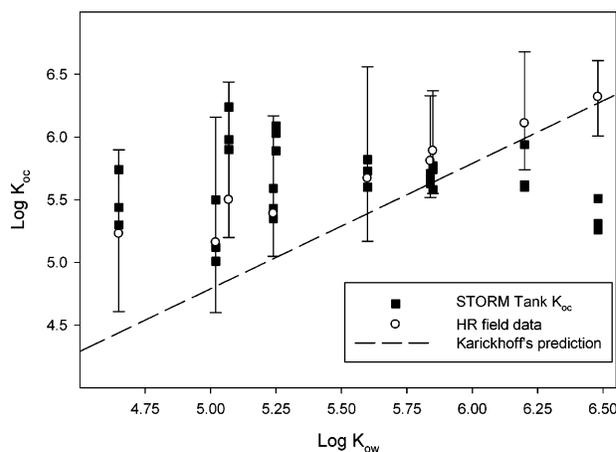


FIGURE 2. Log K_{oc} values measured in the Hudson River (average, maximum, and minimum data from ref 15) and in the STORM tanks at steady state for resuspension event 1.

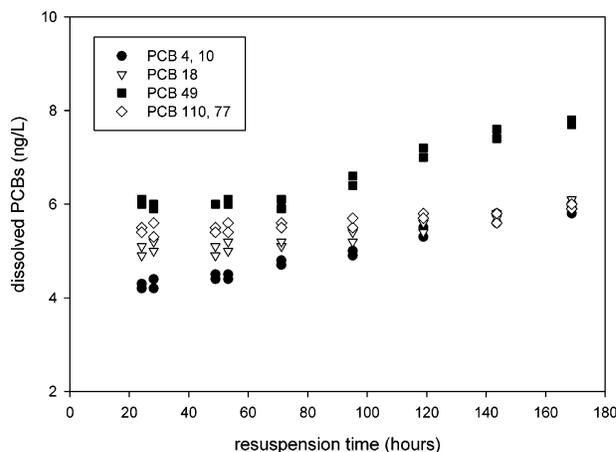


FIGURE 3. Dissolved PCB concentration in tank A when resuspension event 3 was extended for 7 days. Multiple dots represent replicate samples.

extraction of the water that passed through the filter for the dissolved measurement (15). The inclusion of PCBs bound to DOC in the estimate of Butcher et al. of dissolved PCBs suggests the actual partition coefficients were higher than reported.

Steady-state K_{oc} values observed in the STORM tanks are less variable than those measured in the field data (Figure 2, 12–14). Both in the field and in our experiments, the partition coefficients for low molecular weight PCB congeners are higher than predictions made by Karickhoff et al. (11) using the octanol water partition coefficient (12–14). This discrepancy is often seen in laboratory estimates of K_{oc} . For example, Jepsen and Lick (8) measured a $\log K_{\text{oc}}$ value of 5.73 for 4,4'-dichlorobiphenyl partitioning to sediment from the Detroit River compared to a value of 4.4 predicted from K_{ow} . Previously, unexpected trends in K_{oc} were explained by invoking dissolved organic carbon (DOC). Butcher et al. (15) estimated that up to 50% of measured dissolved mono- and dichlorinated PCBs in the Hudson River were bound to DOC. The use of SPME in these experiments limits DOC interference (28) and suggests the observed lack of trend with the octanol–water partition coefficient is not the result of this analytical bias.

PCB desorption is often modeled as a two-stage process, and it is likely that the steady-state dissolved concentration in the tanks was not the true equilibrium concentration with a resistant pool but rather represents equilibrium with a labile pool. Thus, one resuspension event (event 3 in tank A) was

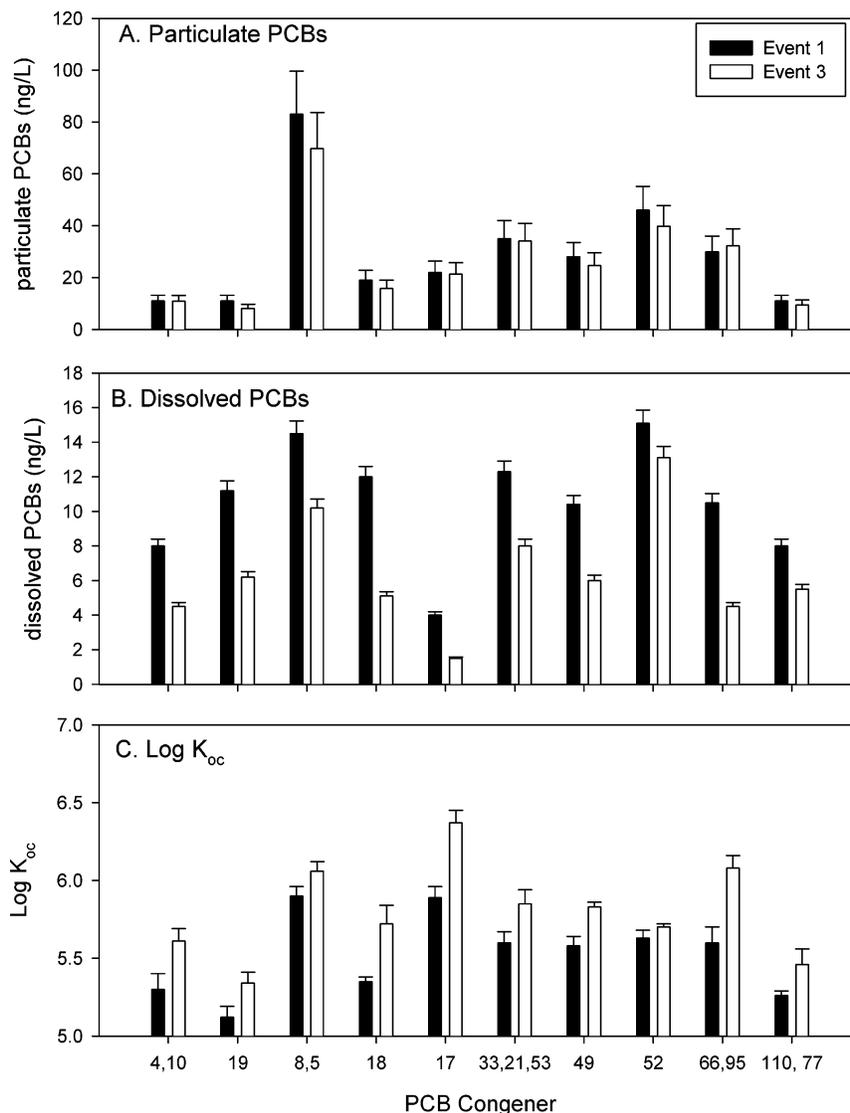


FIGURE 4. Particulate and dissolved PCB and log K_{oc} values at steady state for resuspension events 1 and 3 in tank A. K_{oc} increases between the events due to a decrease in the dissolved concentration. An error of 5% for the dissolved measurement and 20% for the particulate measurement was assumed and propagated through to determine the error on log K_{oc} .

extended for 7 days. After 3 days, the concentration of most congeners increased very slowly with time (Figure 3) and after 168 h of resuspension the dissolved concentration of every congener except PCB 110 was significantly greater than the dissolved concentration at 53 h ($p = 0.002$). Had the resuspension event continued, equilibrium partitioning as predicted by Karickhoff's K_{oc} may have been reached. However, the time scale for equilibrium is much greater than the time scale of a sediment resuspension event. In the STORM tanks, the steady state obtained after 3 days may represent equilibrium with a labile or readily desorbable pool rather than "true" equilibrium with a resistant pool.

Recharge of Labile Pool. After the first resuspension event, the three tanks had different quiescent times between resuspension events to examine the potential recharge of the labile PCB pool. By the third resuspension event, concentrations of several PCB congeners did not exceed detection limits until the second day of resuspension, and only the congeners that were detected in all three events are compared. In resuspension event 1, 22% \pm 3% of the resuspended PCBs were dissolved after 2 h. Event 2 and 3 had significantly less dissolved PCBs after 2 h of resuspension than event 1 ($p = 0.04$ for event 2 and $p = 0.005$ for event 3, Figure 3). Within the first 2 h of each successive resus-

pension event, there were no significant differences between tanks despite the different quiescence times between resuspension events ($p = 0.35$ for event 2 and $p = 0.54$ for event 3). By event 3, 16% \pm 8% of the resuspended PCBs were dissolved. There was no relationship between the percent of PCBs in the dissolved phase and congener molecular weight for any of the resuspension events.

During repeated resuspension events longer than a few hours, more PCBs are released from sediment as the time between resuspension events increases. However, in all cases less PCBs are released in successive events. In all three tanks 31% \pm 10% of the total resuspended PCBs were in the dissolved phase after 6 h of resuspension event 1. During events 2 and 3, 18% \pm 8% of resuspended PCBs were dissolved after 6 h of resuspension in tanks A and B. In these two tanks, repeated resuspension events resulted in significantly less PCB release into the dissolved phase ($p = 0.07$ for tank A and $p = 0.10$ for tank B) compared to the initial resuspension. In tank C, an average of 22% \pm 9% of the resuspended PCBs were dissolved after 6 h of resuspension events 2 and 3. Unlike in the other tanks, this change was not significant ($p = 0.39$). Each resuspension event resulted in a similar percentage of PCBs being released into the dissolved phase. This suggests

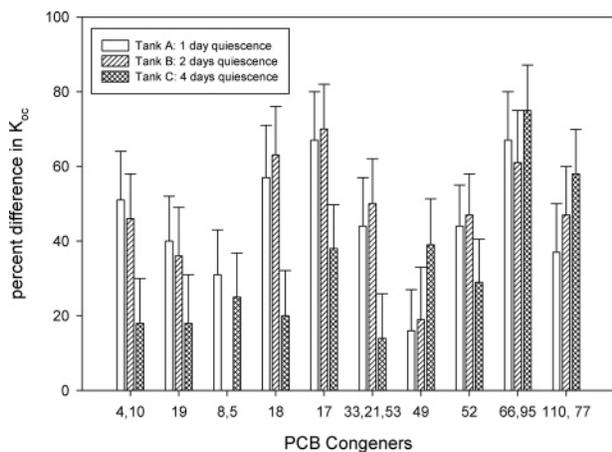


FIGURE 5. Percent difference in K_{oc} between the third and first resuspension events for STORM tanks A, B, and C.

that longer quiescent times result in similar PCB release during each event.

In all three tanks, the steady-state $\log K_{oc}$ values for the third resuspension event were higher than those for the first resuspension event due to lower steady-state dissolved PCB concentrations. In tanks A and B, with 1 and 2 days quiescence, respectively, the percentage of PCBs in the dissolved phase at steady state decreased by $9\% \pm 5\%$ from resuspension event 1 to event 3 ($p = 0.02$ for both tank A and tank B, Figure 4). In tank C, with 4 days quiescence between events, the percentage of low molecular weight PCBs ($\log K_{ow} \leq 5.85$) in the dissolved phase at steady state did not change significantly between events ($p = 0.44$). Only the percentage of higher molecular weight PCBs ($\log K_{ow} > 5.85$) in the dissolved phase decreased significantly ($p = 0.002$). The percent difference in K_{oc} values between the first and third resuspension event for low molecular weight, di-, tri-, and tetrachlorinated congeners ($\log K_{ow} \leq 5.85$) was significantly less for tank C than for tanks A and B ($p = 0.02$, Figure 5), indicating that a labile or easily desorbable pool recharged during the 4 days of quiescence. For higher molecular weight pentachlorinated PCB congeners ($\log K_{ow} > 5.85$), this labile pool did not recharge (Figure 5) and there were no significant differences between the tanks ($p = 0.63$).

Implications. After just 2 h of resuspension of Hudson River sediment, 20% of the resuspended PCBs were released into the dissolved phase. Resuspension could therefore add significant amounts of dissolved PCBs to the water column. In the Hudson River, where sediment PCB concentrations are as high as $50 \mu\text{g g}^{-1}$, a resuspension event of just 25 mg L^{-1} would add 250 ng L^{-1} dissolved PCBs to the water column. The amount of PCBs released into the dissolved phase decreased with subsequent resuspension events, suggesting the impact of resuspension events diminishes with their frequency. However, even after the third resuspension event an average of 16% of the resuspended PCBs were released into the dissolved phase after just 2 h. Current models that calculate PCB release on the basis of bulk sediment PCB concentrations will underestimate the amount of PCBs that enter the water column during resuspension events. The quiescence time between resuspension events affected PCB desorption on longer time scales. With only 1 or 2 days between resuspension events, the percentage of dissolved PCBs at steady state decreased with subsequent resuspension events. This suggests that recharge of an easily desorbable or labile pool does not occur fast enough for replenishment on the time scale of tidal cycle resuspension ($\sim 6 \text{ h}$). Extremely frequent resuspension events such as these might result in only minimal release of dissolved PCBs per event. However, if resuspension events occur infrequently (i.e., storms), the

time between events might be long enough to replenish a labile pool and result in a large release of PCB during each event. In the upper Hudson River, where storm events are the primary cause of sediment resuspension, the time between events might be long enough for the labile pool to be replenished.

Acknowledgments

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