

Assessing the Need to Clean Up Hudson River Estuary Sediments

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Abstract

In order to ascertain whether Hudson River estuary sediments should be cleaned up, we must evaluate the toxic chemical exposures that such contaminated deposits may cause. In this project, we focused on: (1) the impact of combustion-derived black carbon (BC) on the sorption of hydrophobic organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) to estuarine sediments, and (2) the importance of sediment resuspension on the bed-to-water column exchanges of PAHs and PCBs in the Hudson estuary.

The solid-water distribution ratios, K_d s, of PAHs, PCBs and dioxins for Hudson estuary sediments greatly exceeded expectations based on the assumption that these chemicals only absorb into natural organic matter in the solid phase (i.e., the $f_{oc}K_{oc}$ model). It was hypothesized that the black carbon fraction (f_{BC}), measured in the sediment at about 0.3% by weight, was responsible for the additional sorption as quantified with black carbon-normalized adsorption coefficients, K_{BC} s. The overall sorption was then attributed to absorption into the organic carbon plus adsorption onto the BC with an extended model: $K_d = f_{oc}K_{oc} + f_{BC}K_{BC}C_w^{n-1}$ where C_w ($\mu\text{g/L}$) is the dissolved concentration. Predictions based on published K_{oc} , K_{BC} and n values for phenanthrene and pyrene showed good agreement with observed K_d values. Assuming this dual sorption model applied to the other PAHs, PCBs, and dioxins, K_{BC} values were deduced for these contaminants. The inferred sorption to the sedimentary BC dominated the solid-water partitioning of these compound classes, so it is necessary to consider BC in these sediments to make accurate estimates of the mobility and bioavailability of PAHs, PCBs and dioxins.

Using this improved knowledge of the solid-water partitioning, we analyzed Hudson estuary sediment for PAHs and PCBs and estimated the levels expected in the overlying waters if they were at equilibrium with these muds. Then we used a new passive sampler made of polyethylene to measure a representative PAH, pyrene, and a representative PCB, 2,2',5,5'-tetrachlorobiphenyl (PCB #52), in the water of the lower Hudson estuary during weak and strong sediment resuspension events. In April 1999, soon after the arrival of large quantities of bed sediment with the spring freshet, resuspended sediments served as a source of pyrene to the estuary; surprisingly, PCB #52 was removed from the dissolved phase of the water column at that time. In contrast, in October 2000 the sediments and water column were close to equilibrium for both compounds. These results showed that sediment resuspension is important to the cycling of PAHs and PCBs in the lower Hudson River estuary, and consequently exposures of aquatic life to these toxic substances are spatially and seasonally varying.

Introduction

Once introduced to aquatic environments, hydrophobic compounds like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) tend to sorb to the sediments. Consequently, even after the inputs of these contaminants have diminished or even ceased, the sediment beds can remain a source of such pollutants to the surroundings.

Elevated concentrations of PAHs and PCBs have been found in the sediments from parts of the lower Hudson River estuary (Wolfe et al., 1996). The average total PAH sediment concentration for the Hudson-Raritan Estuary (40 ug/g; Wolfe et al. 1996) is ten times the typical “high” values reported in a national NOAA survey (2000). The average total PCB sediment concentration for the Hudson-Raritan Estuary [300 ng/g; Wolfe et al., 1996] was also greater than the “high” category reported in the NOAA survey (2000). Due to these large PAH and PCB concentrations in the sediments of the Hudson Estuary, understanding how bed sediments affect PAH and PCB exposures is necessary to evaluate the need to clean up those deposits.

The lower Hudson River estuary receives a very large quantity of sediment from upstream every year in association with the spring freshet. These solids initially accumulate as new deposits in the estuary, and then they undergo repeated resuspension as evidenced by the two estuarine turbidity maxima on the western side of the river. Geyer (1995) observed near-bottom suspended solids concentrations between 100 and 200 mg/L in the summer of 1992 and between 100 and 400 mg/L concentrations during high discharge in 1993 at the southern estuarine turbidity maximum site. During spring tides, near-bottom suspended sediment concentrations can reach values as high as 1800 mg/L, while near-bottom, suspended sediment levels during the weaker neap tides are about six times less. Suspended solid concentrations drop to below 20 mg/L at slack tides, indicating the strong tidal influence of sediment resuspension in this estuary.

In our study, we first examined the extent of sorptive disequilibrium between the bed sediment and the water column of a representative PAH, pyrene, and a representative PCB, 2,2',5,5'-tetrachlorobiphenyl (PCB #52). Subsequently, we ascertained whether dissolved concentrations of these compounds changed during neap and spring tides. Since dissolved levels reflect bioavailable species, this allowed us to assess the impact of sediment resuspension on controlling the exposures of aquatic life in the area to these toxic substances.

Approach

Polyethylene (PE) strips were used to deduce the dissolved concentrations of a representative PAH (i.e., pyrene) and a PCB congener (i.e., PCB #52) in both laboratory and field programs (Adams, 2003). To this end, we determined PE-water partition coefficients for numerous organic compounds and their dependencies on environmental factors (temperature and salinity). We also evaluated the rates at which thin PE sheets (ca. 50 um thick) accumulate target chemicals from stirred aqueous solutions, thereby allowing us to design PE deployments that achieved near equilibrium conditions.

In our laboratory sorption studies (Lohmann et al., 2005), we used small pieces of PE in sediment-water slurries of Hudson estuary sediment to discern equilibrium dissolved concentrations (i.e., concentration in the water = concentration in the PE divided by the PE-water partition coefficients.) In this way, we could desorb small quantities of PAHs, PCBs and dioxins from Hudson estuary sediments, and deduce the solid-water partition coefficients of each compound. Further, by showing that the observed coefficients were far greater than the product, $f_{oc}K_{oc}$, we provided evidence for the importance of another sorbing phase. Analyzing the sediments for BC (Gustafsson et al., 1997), we found typical levels of the weight fraction BC

(f_{BC}) between 0.1 and 1%. Using black carbon-water sorption coefficients reported in the literature, these f_{BC} values were sufficient to account for the additional sorption that we saw.

Next we sought to use this new understanding of sorption to evaluate the Hudson estuary sediments as potential sources of these organic contaminants to the overlying waters. Measuring PAH and PCB concentrations in sediment samples from the estuary, we normalized the data with our improved K_d values to estimate dissolved concentrations in the Hudson River estuary water if it were equilibrated with the bed sediment.

Subsequently, we used passive PE samplers in the lower Hudson Estuary during the neap and spring tides in April 1999 and again in October 2000 to measure PAH and PCB concentration changes as a function of position in the estuary. Water samples and hydrographic data were also collected. Water was analyzed for total suspended solids, particulate organic carbon, and BC. Sediment was also collected, and both sediments and TSS on filters were analyzed for organic carbon (f_{oc}) and BC (f_{BC}).

To interpret the distributions of PAH and PCB dissolved concentrations we saw in the estuary, we also performed laboratory observations of pyrene's desorption kinetics using Hudson estuary sediments. We used the "native" pyrene (i.e., without adding any pyrene to the sediment collected from the estuary). The use of native sediments allowed us to empirically include any effects of BC on PAH desorption, and the choice of pyrene stems from its uniquely long-lived fluorescence life time. Briefly, the dissolved pyrene was followed in Hudson River estuary suspensions over time using time-gated, laser-induced fluorescence. After 10 days, the water-sediment mixture was centrifuged, so that the water and sediment could be separated for subsequent solvent extraction and GCMS analysis.

Results

Laboratory Sorption Studies Using our knowledge of the equilibrium partitioning of PAHs, PCBs and dioxins between the dissolved phase and PE at the experimental temperatures, we used various sizes (0.27 g to 0.72 g) of PE in Hudson estuary sediment-water slurries to deduce the dissolved concentrations at equilibrium with the estuary's bed sediments (Lohmann et al., 2005). Aqueous PAH and PCB concentrations equilibrated with the Hudson estuary sample were generally much lower than those found using sediment from Boston. Then using our measured sediment concentrations and the dissolved concentrations inferred from the PE samplers, we calculated the observed sorption coefficients, $K_{d,obs}$ (Table 1). These $K_{d,obs}$ values with increased with sorbate hydrophobicity. Finally, these results were used to show the efficacy of the extended model: $K_d = f_{oc}K_{oc} + f_{BC}K_{BC}C_w^{n-1}$ where the dissolved level, C_w is in $\mu\text{g/L}$.

Table 1 Individual and average solid-water distributions ($K_{d,obs}$) for Hudson estuary sediment. Values preceded by a less than or equal sign may represent cases in which system equilibration was not achieved.

	phen	pyr	bap	# 44	# 66	# 95	2,7/8-Cl ₂ DD	2,3,7-Cl ₃ DD
log $K_{d,obs}$ (0.27g PE)	3.4	4.2	5.8	4.4	5.4	4.8	4.9	5.7
log $K_{d,obs}$ (0.43g PE)	3.6	4.4	5.9	4.4	5.3	4.8	4.9	5.8
log $K_{d,obs}$ (0.72g PE)	3.6	4.4	5.9	4.5	5.4	4.9	4.9	5.9
mean	3.5	4.4	≤ 5.9	4.4	5.4	≤ 4.8	4.9	5.8
stdev	0.1	0.1	0.1	0.1	0.0	0.1	0.0	0.1

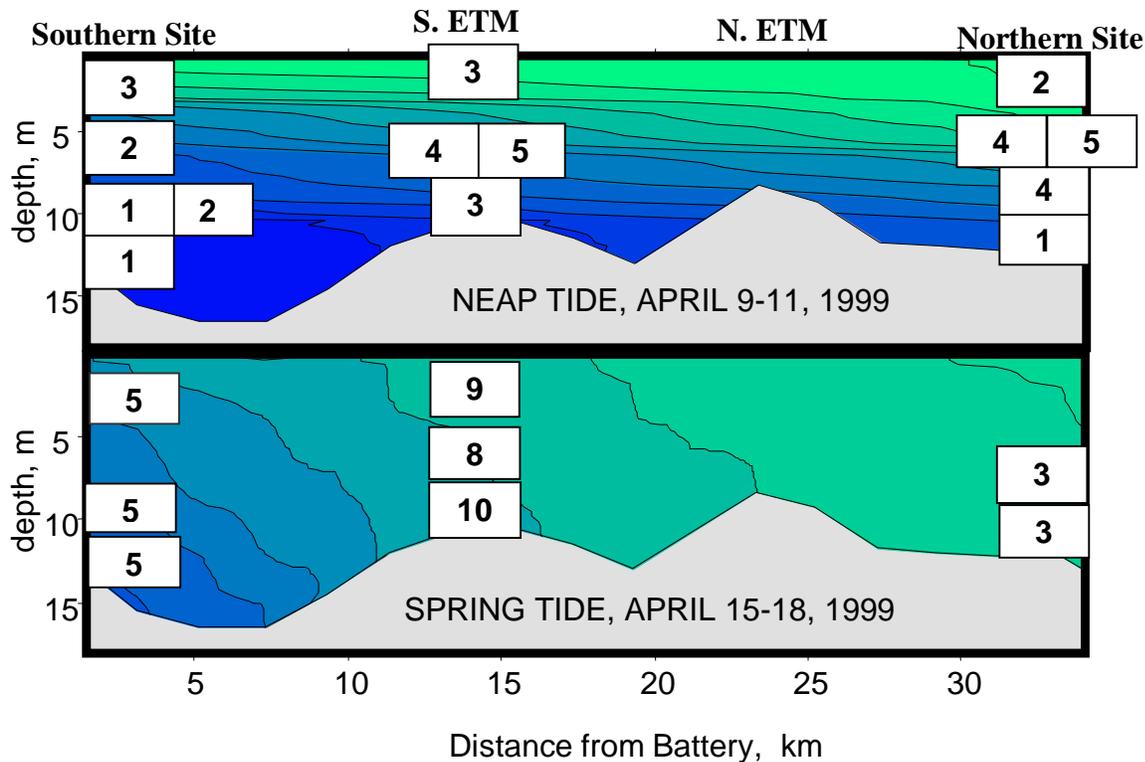


Figure 1. Dissolved concentrations of pyrene (ng/L) in the Hudson River estuary as a function of distance upstream of the Battery (kilometer 0) during neap and spring tides of April 1999. Spring tide-induced resuspension at the southern estuarine turbidity maximum (S. ETM) increased the dissolved pyrene loads significantly.

Field Data: Pyrene PE-measured dissolved pyrene concentrations in the lower estuary ranged from 1 to 10 ng/L during the April 1999 sampling campaign (Figure 1). The dissolved pyrene concentrations measured during the October 2000 campaign ranged from 5 to 60 ng/L (Figure 2), nearly an order of magnitude greater than the April concentrations in several locations within the estuary. The dissolved pyrene concentrations measured in this study are comparable to values measured in New York Harbor at the mouth of the Hudson River in July 1998 [10 & 16 ng/L; Gigliotti et al., 2002]. The results are also similar to “dissolved” pyrene measured in filtered water samples taken south of the Harlem River [nearest to the NETM; Litten, 2003] where pyrene values ranged from 11 to 19 ng/L in water samples collected between December 1998 and October 2001.

Two sediment samples from the SETM were collected in April and June 1999. The pyrene concentration was 1600 ng/g in both samples. Sediment at the Southern Site, the SETM, and the Northern Site were collected in October 2000 and measured to have pyrene concentrations ranging from 330 to 4200 ng/g. Consistent with a harbor source at that time, the sediment concentrations were greatest at the mouth of the river and decreased moving up river.

Based on the laboratory tests with Hudson estuary sediment, the bed should act as a source of pyrene to the water column driving the water concentrations toward an equilibrium value of about 30 ng/L. Consistent with this expectation, the dissolved pyrene in April in the mid-salinity region of the estuary increased in response to the energetic spring tides that cause large

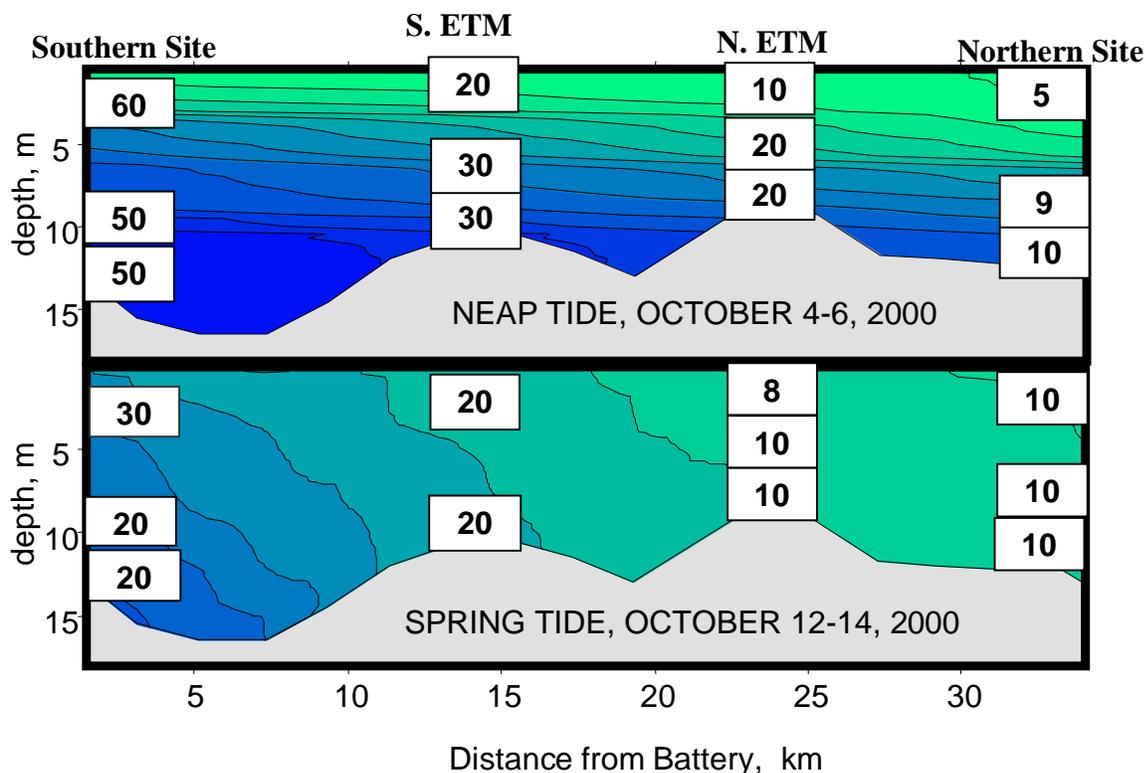


Figure 2. Dissolved concentrations of pyrene (ng/L) in the Hudson River estuary as a function of distance upstream of the Battery (kilometer 0) during neap and spring tides of October 2000. While dissolved pyrene concentrations in the fall were substantially higher than in the spring, tidally induced resuspension at the southern estuarine turbidity maximum (S. ETM) and the northern estuarine turbidity maximum (N. ETM) do not increase the dissolved pyrene loads significantly.

bottom sediment resuspension (Figure 1, lower panel). Such pyrene input was not clearly seen during the weaker sediment resuspension events associated with the neap tides only one week earlier (Figure 1, upper panel).

In contrast, pyrene behaved much more conservatively during its transport along-estuary in October (Figure 2). This was especially clear in plots of pyrene concentration vs. salinity (not shown). The largest dissolved concentration during October was in the water at the southern end of the estuary, not an area of significant sediment resuspension. Finally, one should note that the pyrene concentrations were much higher everywhere than seen in the spring, and they were near the value expected at equilibrium with the bed sediments. Hence, it appeared that between the spring and fall, sediments deposits derived from the freshet flow released this PAH until the estuarine water had built up near-equilibrium concentrations.

Field Data: PCB Congener #52 PE-measured PCB #52 concentrations in the Hudson river estuary ranged from 4 to 300 pg/L during the April 1999 sampling campaign (Figure 3). The October 2000 concentrations ranged from 100 to 400 pg/L (Figure 4). These values are comparable to measurements by Totten et al. (2001) in New York Harbor at the mouth of the

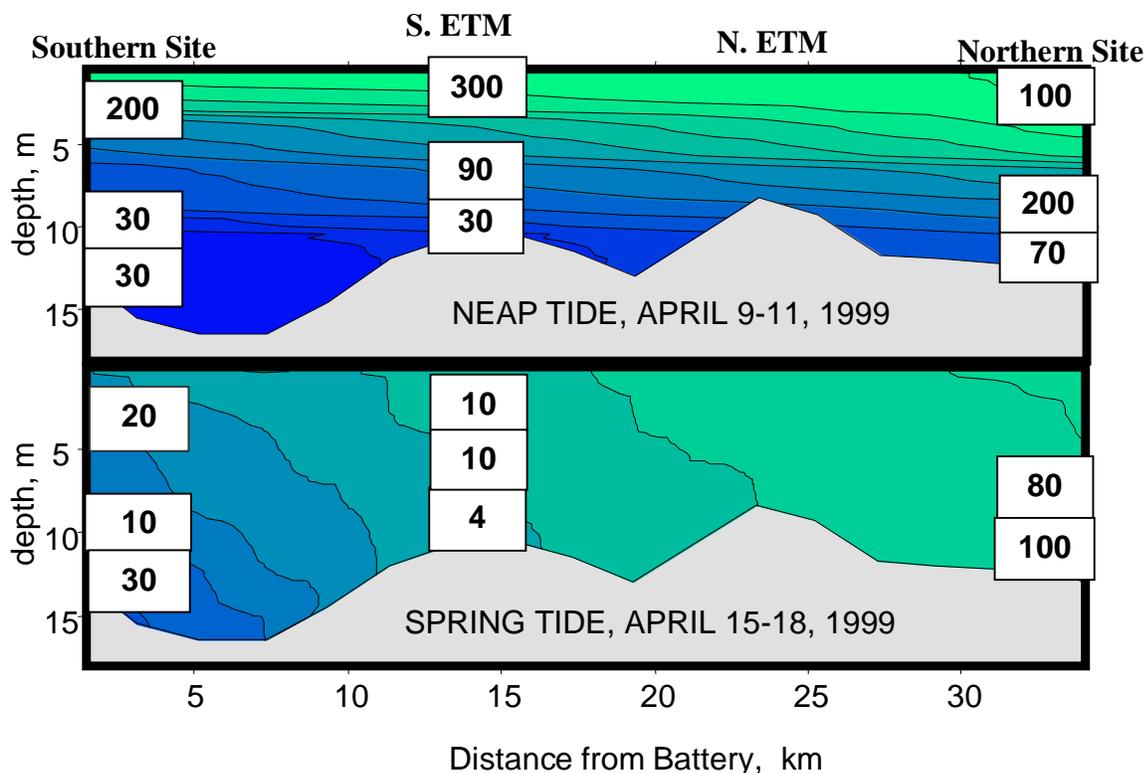


Figure 3. Dissolved concentrations of PCB #52 (pg/L) in the Hudson River estuary as a function of distance upstream of the Battery (kilometer 0) during neap and spring tides of April 1999. Spring tide-induced resuspension at the southern estuarine turbidity maximum (S. ETM) decreased the dissolved PCB #52 loads significantly.

Hudson River in July 1998 Totten et al. measured 237 pg/L for PCB # 52. PCB #52 water concentrations south of the Harlem River collected between December 1998 and October 2001 ranged from 11 to 340 pg/L (Litten, 2003).

PCB #52 sediment concentrations at the SETM were 32 and 31 ng/g in April and June, respectively. Sediment collected in October 2000 at the same site was found to have 16 and 18 ng/g of PCB #52. This may reflect spatial heterogeneity, or the difference may indicate a real decrease in the PCB #52 sediment concentration with time. PCB #52 porewater concentrations estimated from sediment measurements in April 1999 and our improved K_d values (~300 pg/L) are at least an order of magnitude greater than the PE-measured bottom water concentrations. This result implies that this PCB congener should be moving out of the sediments to the overlying water.

During April 1999 the PCB #52 concentration in the mid-salinity region of the estuary actually decreased between neap and spring tides (Figure 3). The surface water concentrations measured during the neap tide were also larger than the concentrations at depth, and the PCB #52 vs. salinity plots clearly showed removal of this compound from the water column at mid-estuary. These trends suggested that PCB #52 was being scavenged at this time by

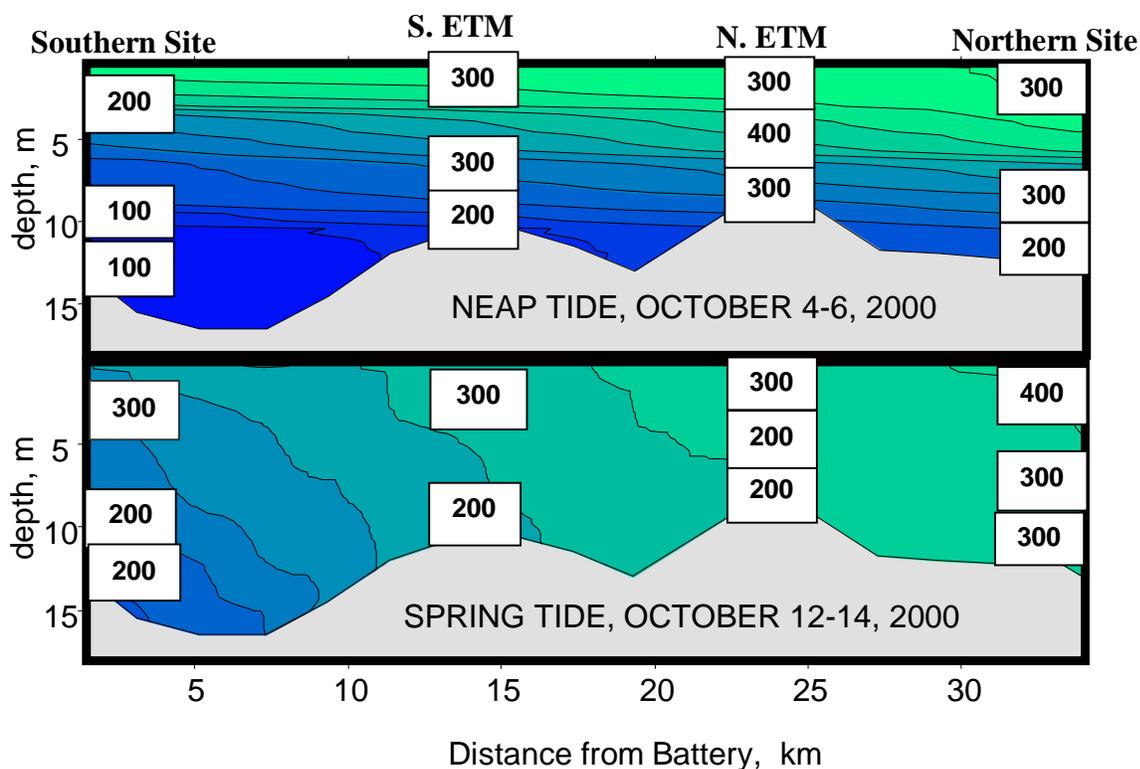


Figure 4. Dissolved concentrations of PCB #52 (pg/L) in the Hudson River estuary as a function of distance upstream of the Battery (kilometer 0) during neap and spring tides of October 2000. Tidally induced resuspensions at the southern estuarine turbidity maximum (S. ETM) and the northern estuarine turbidity maximum (N. ETM) do not increase the dissolved PCB #52 loads.

resuspended sediments, contrary to predictions based on sediment concentrations and sorption modeling. One possibility is that "cleaner" sediments that we did not sample were scavenging the compound from nearby positions (e.g., laterally displaced positions).

As for pyrene, the dissolved PCB #52 concentrations in the estuary were much greater in October than they were in April. Further, these concentrations approached those we would expect at sediment bed-water-column equilibrium. Finally, the PCB #52-salinity relation in October 2000 was linear. Consequently, PCB #52 appears to have exhibited little or no bed-water exchange at that time. Interestingly, for both April 1999 and October 2000 the upper river appears to be the source of PCBs to the estuary.

Sorption Kinetics

In light of the enhancement of dissolved pyrene concentrations during the April 1999 spring-tide resuspensions, we sought to understand the extent of this concentration increase. Noting that the water column concentrations never reached levels that would be at equilibrium with the bed sediments, we surmised that desorption kinetics limited pyrene build up. Our desorption experiments indicated that the pyrene reached equilibrium within hours (~ 15 ng/L; Figure 5). Using these data, we fit the time course to obtain an estimate of the mass transfer coefficient. These coefficients were interpreted as the ratio: D_{eff}/a^2 where D_{eff} is the effective diffusivity of pyrene moving through porous silty aggregates and a is the radius of suspended silty aggregates.

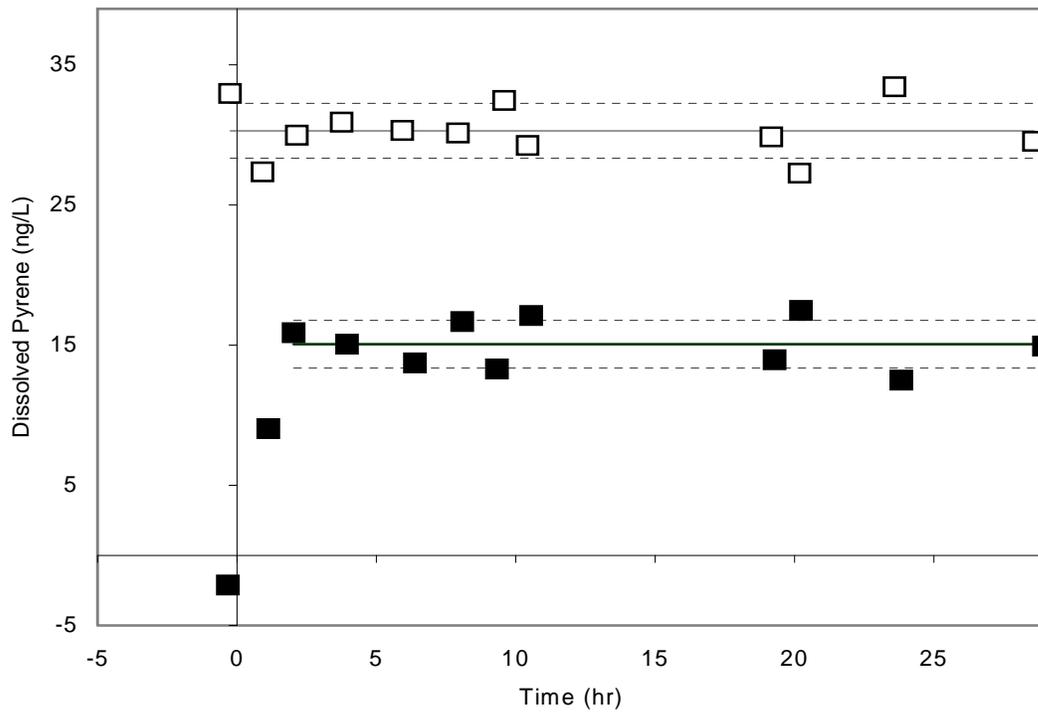


Figure 5. Pyrene water concentration vs. time measured in laboratory experiments with suspended Hudson River estuary sediment (solid squares) showing equilibrium within 22 hr with an average concentration of 15 ± 2 ng/L. The pyrene concentration in the control beaker (open squares) was stable at the 30 ± 2 ng/L initially added to the water.

The rate of system approach to equilibrium is dependent on the solid-to-water ratio as well as the solid-water partition coefficient, K_d . Using D_{eff}/a^2 measured in the laboratory, we estimated the time for 50% and 90% approach to desorption equilibrium for representative solid-to-water ratios measured in the lower Hudson Estuary. This approach assumes that the D_{eff}/a^2 for all of the sediments in the estuary are similar to the D_{eff}/a^2 measured for the 38 – 88 μ m size class that we used in the laboratory. If we assume the high-TSS bottom waters of the lower Hudson Estuary have 300 mg/L TSS on average, it is estimated that it will take between 5 and 30 min to reach 50% of the progress to sorptive equilibrium. Using the same approach, the time for 90% equilibrium ranges from 4 to 20 hr. However, if we assume an average 10 mg/L TSS for surface waters of the lower Hudson River estuary, the time for 50% equilibrium will range from 8 to 40 hr, while the time for 90% equilibrium is estimated to range from 3 to 10 days. Given the 2 to 7 day residence times for the waters of the lower Hudson Estuary, the sediment and water may not have enough time to reach equilibrium during repeated multi-hour resuspension events.

Major conclusions

Assuming the overall sediment-water partition coefficients, K_d , can be apportioned into the terms representing "OC"-adsorption and "BC"-adsorption in harbor sediments, we find that BC was responsible for over 80% of the total PAH sorption the Hudson River estuary sediments. For PCBs, adsorption to BC was also dominant for all congeners we assessed. Adsorption to BC explained 90% or more for the dichloro- and trichloro-dioxins considered here. Further, if the Freundlich coefficients are near 0.7, extrapolations of our observations to sorbate concentrations approaching their solubilities indicate this BC-adsorption would contribute at least half of the total sorption in the estuarine sediments.

In April 1999, soon after the delivery of sediments from upstream into the estuary with the spring freshet flow, the sediments within the lower Hudson River estuary were a source of pyrene to the overlying water column. This could be anticipated from measures of sediment pyrene concentrations normalized to pyrene's K_d . Consistent with this model calculation, bed-to-water transfer of pyrene in association with spring-tide resuspension events was observed at the southern estuary turbidity maximum. However, the sediments and water appear to have been become equilibrated by the fall based on our October 2000 field campaign.

With respect to PCB #52, mixing diagrams indicated the existence of a mid-estuary sink for this PCB congener in the spring (April) of 1999. This was not consistent with analyses of this congener's concentrations in our sediment samples when these were normalized by the corresponding sediment-water partition coefficient. One explanation for this discrepancy may be the scavenging of PCB #52 by cleaner sediments within the estuary. October 2000 PCB #52 findings indicate that, as with pyrene, the Hudson River estuary concentrations were consistently higher than in the spring and the sediments and waters of the lower Hudson are more closely equilibrated with respect to PCB #52.

These observations indicate that toxic organic compound "bioavailability" in the Hudson River estuary undergoes weekly and season cycles. This cycle is influenced by the arrival of new sediments from upriver in the spring and by repeated resuspensions of these solids throughout the following months. It appears that this dynamics causes the ecosystem to move toward sorptive equilibration by the succeeding autumn, steadily increasing toxic chemical exposures. Models that assume either (1) $K_d = f_{oc}K_{oc}$ or (2) sediment-water equilibrium is achieved will generally yield inaccurate estimates of the exposures of Hudson estuary aquatic life to the toxic substances examined in this work.

Finally, we future research must characterize the impact of sedimentary BC on sorption kinetics. Contact times between waters and sediments that occur in natural settings like the Hudson River estuary are short enough that chemical exchanges do not readily reach equilibrium. Hence, knowledge of exchange kinetics will be necessary to understand the solid-water partitioning, mobility, and bioavailability of PAHs, PCBs and dioxins in such an ecosystem.

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Adams, R.G. "Polyethylene Devices and the Effects of Sediment Resuspension on the Cycling of PAHs and PCBs in the Lower Hudson Estuary," PhD dissertation submitted to the Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, 186 pp., February 2003.

Lohmann, R.; MacFarlane, J.K.; Gschwend, P.M. Importance of black carbon to sorption of native PAHs, PCBs and PCDDs Boston and New York harbor sediments. *Environ. Sci. Technol.*, 39, 141-148, 2005.

In Preparation

Adams, R.G., R. Lohmann, L. Fernandez, and P.M. Gschwend. Polyethylene Devices: Samplers for Measuring Trace Dissolved Hydrophobic Organic Contaminants in the Aquatic Environment.

Adams, R.G., T.F.D. Kuo, J.K. MacFarlane, W.R. Geyer, and P.M. Gschwend. The Importance of Sediment Resuspension to the Sediment-Water Exchange of PAHs and PCBs in the Lower Hudson Estuary

Kuo, T.F.D., R.G. Adams, S. Rudnick, R. Chen, and P.M. Gschwend. Desorption Kinetics of Pyrene from Native Lower Hudson Estuary Sediments.