Paper B4-04, in: R.F. Olfenbuttel and P.J. White (Eds.), *Remediation of Contaminated Sediments—2005: Finding Achievable Risk Reduction Solutions.* Proceedings of the Third International Conference on Remediation of Contaminated Sediments (New Orleans, Louisiana; Jan 24–27, 2005). ISBN 1-57477-150-7, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

Relationship Between PAH Biodegradation and Transport in Estuarine Sediments

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ABSTRACT: Ambient polycyclic aromatic hydrocarbon (PAH) concentrations are often measured in estuarine sediments to evaluate risk of those chemicals to benthic infauna and adjacent ecosystems. Typical site investigations assume that PAHs are present in the sediment as a result of historical contamination despite overwhelming evidence of the dynamic nature of contaminants and associated sediment transport in estuaries. Although many processes may affect PAH concentration, we focused on two that were most likely to have to largest impact on PAH flux in the sediment; influx of PAH associated with settling water column particles and bacterial biodegradation within the surface sediments. We compared PAH associated with water column seston, in the benthic boundary layer and on settling particles with PAH biodegradation rates measured in the underlying sediments in the Cooper River in Charleston Harbor Estuary, USA. PAH concentration was generally higher in seston than in the benthic boundary particles and even lower in the underlying sediment for a given station. Bacterial mineralization of PAH was similarly rapid between nepheloid and surface sediment samples with turnover times for phenanthrene in the sediments of around 100 days. This data supports a site conceptual model where sediment in the lower Cooper River is a sink for PAH influx from particles from the water column and benthic boundary layer.

INTRODUCTION

Ambient PAH concentrations in estuarine sediment are the net result of many processes that can increase or decrease these values. Processes that can increase the ambient PAH concentration in the sediment include settling of particles from the water column, groundwater intrusion, and lateral particle transport in the benthic boundary layer. Processes that can deplete standing PAH mass include heterotrophic biodegradation, diffusion, and sediment resuspension. Because PAH compounds are hydrophobic, transport to the sediments would primarily occur on particles while degradation would occur in the water column, benthic boundary layer and within the aerobic portion of the sediments. There has been much recent interest in the benthic boundary layer with regards to transport and degradation of organic matter. Organic matter metabolism close to the seafloor may be as rapid as that which occurs in the euphotic zone (for review see Meyers, 2000).

Recently, Pohlman et al. (2002) examined independent measures of PAH fate in a tidally influenced riverine ecosystem including transport in the bottom boundary layer. They found that bacterial heterotrophy can seasonally degrade 50% of settling PAHs in a tidal basin that receives PAH from the adjacent Schuylkill River. During some portions of the year, the tidal basin and the associated sedimentary microflora acted as a sink for

PAH within this aquatic watershed. The flux of PAHs from the water column particles to the sediment supported a bacterial assemblage capable of relatively rapid PAH metabolism to carbon dioxide and bacterial biomass. By relying solely on ambient PAH concentration (up to 20 ppm) in the sediment, one may have mistakenly concluded that the tidal basin was a source of PAH to the water column or adjacent ecosystems. In a similar study, we compared PAH concentrations, and rates of deposition and degradation within the top cm of surface sediments in the Cooper River of Charleston Harbor to determine whether these sediments were PAH sources or sinks within the ecosystem.

Site Description. This study involved seasonal sampling of twenty-two stations through the Charleston Harbor and the three major rivers that are part of the watershed, the Ashley, Wando and Cooper (Figure 1). The former Charleston Navy Yard (CNY) is situated along the Cooper River about one mile upriver from the Charleston Harbor. Six of the stations were adjacent to the CNY in the Cooper River (6A, 6B, 6C, 6D, 6E, 9). Five stations were upriver of CNY (1-5). Two stations were downriver from CNY (13, 14). Three stations were in a tributary off the Cooper called Shipyard Creek (10, 11, 12). Two stations each were near the mouth of the Ashley River (16, 17), in the Wando River (A2

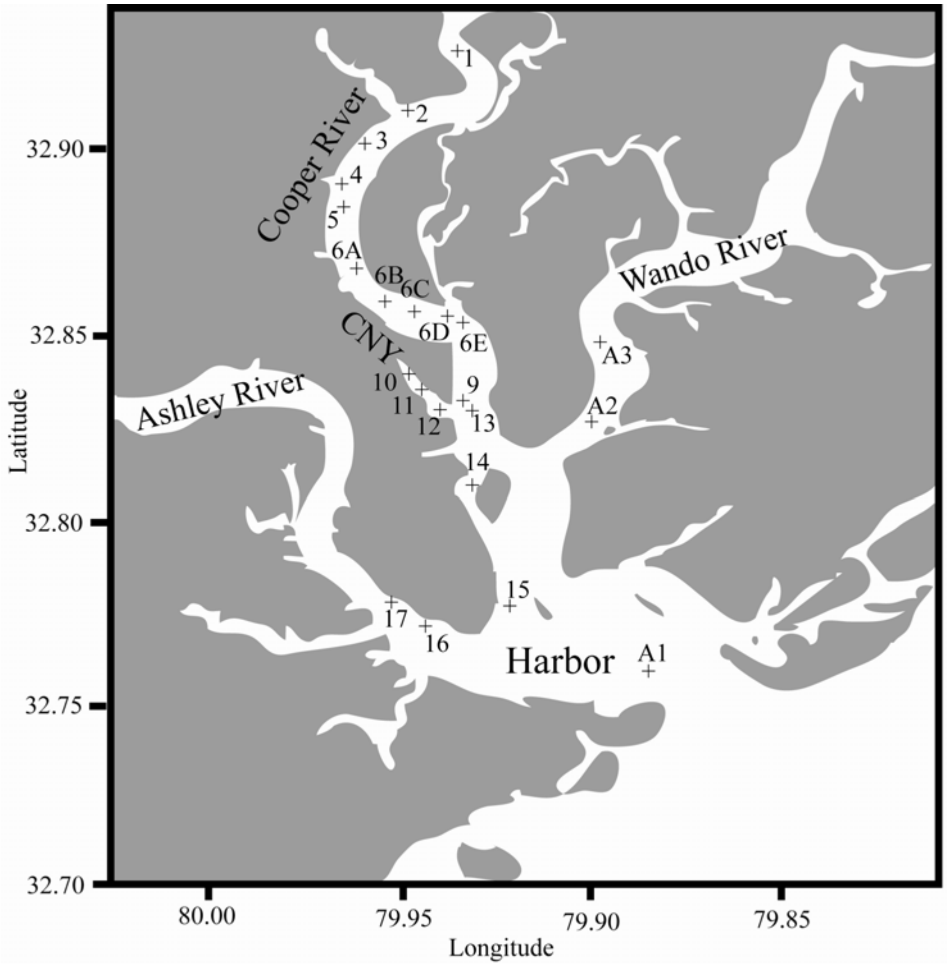

FIGURE 1. Sampling stations in the Charleston Harbor Estuary, SC, USA adjacent to the former Charleston Navy Yard (CNY).

and A3) and in the Charleston Harbor (15, A1). Surface sediment was collected with a Petite Ponor sediment grab. Seston was collected by filtration of 20 L of surface water onto 144-mm-diameter (0.22 µm nom. pore size) Nuclepore® polycarbonate filters. Benthic boundary particles were collected with a sampling device and methods described by Pohlman et al. (2002).

MATERIALS AND METHODS

Radiotracer mineralization assays were initiated within one hour of sediment sample collection using a modification of Boyd et al. (2004) and Pohlman et al. (2002). As radiotracers, we used three sentinel PAHs: UL-^{14}C-naphthalene (18.6 mCi mmol^{-1}), 3-^{14}C-fluoranthene (45 mCi mmol^{-1}), and 9-^{14}C-phenanthrene (47 mCi mmol^{-1}) that were purchased from Sigma Chemical. They were added in separate incubations to surface sediment samples (1 mL wet volume) in 100 × 16 mm test tubes to a final concentration of about 0.2 µg g^{-1} (depending on specific activity). Isotope dilution of PAH was calculated from the ambient PAH concentration and additions were intended to be <10% of ambient PAH concentration to minimize selective pressure on the natural bacterial assemblage. Samples were incubated no longer than 24 h at in situ temperature and evolved $^{14}CO_2$ was captured on NaOH-soaked filter papers suspended in the headspace of each tube. H_2SO_4 was added to end incubations and to partition any remaining CO_2 into headspace of the tube and to the filter paper trap. The filter paper traps containing metabolized $^{14}CO_2$ were removed, radioassayed and subsequently used to calculate substrate mineralization. Ambient PAH concentrations of 18 semi-volatile priority pollutants were determined. First, 10-15 g of sediment was dried with diatomaceous earth and then extracted in methanol using accelerated solvent extraction. The extracts were concentrated under a N_2 stream (Speedvap) and analyzed by GC/MS (Fisher et al., 1997). *p*-Terphenyl-d_{14} and 2-fluorobiphenyl were used as surrogate standards, following the method described in Pohlman et al. (2002).

The sediment trap construction and deployment strategy is similar to that described by Pohlman et al. (2002). Settling particles were collected in 5 to 72 h deployments of bands of three polycarbonate tubes sealed at the bottom and with 10 cm butyrate baffles at the top of their 6 cm-diameter mouth. Traps were attached to an anchor line and held upright with a mooring buoy and then deployed at the CNY stations 6A, 6C and 6E, upriver of CNY at station 5 and downriver at station 13.

RESULTS AND DISCUSSION

From November 1997 to October 1999, we examined PAH concentrations and degradation rates in sediment and on particles from the overlying waters in the Charleston Harbor Estuary, SC. In general, average PAH concentration was higher in suspended particles (seston, benthic boundary layer samples) than in sediments (Table 1). Differences in organic matter concentration between suspended particles in the Cooper River (nepheloid = 3.8-5.4%; seston = 4.9-5.1%) and sediments (4.9-5.3%) does not account for these differences in PAH concentration (see also Schneider et al., 2002). The two most likely explanations are that PAH mass on particles are being laterally transported out of the Cooper River or are degraded by bacteria in the benthic boundary layer and surface sediments.

TABLE 1. PAH concentration in water column particles verses sediments for the Cooper River in Charleston, SC, USA.

Total PAH Concentration (ppm)		
Cooper River (stations)	**Seston/Nepheloid**	**Sediment**
Upriver (1-5)	16.2 / 9.2	7.8
Navy Yard (6A-13)	20.2 / 5.0	4.2
Downriver (14-16)	17.7 / 4.6	1.8

During most of the year, there is no net flow out of the Cooper River though there is a large tidal movement of water (Van Dolah et al., 1990) and a well defined salt wedge with a vertical salinity gradient of 12 to 26‰ (based on shipboard CTD measurements). We measured changes in seston concentration from 45 mg L^{-1} upriver of the Navy Yard to 12-18 mg L^{-1} at the confluence of the Cooper River and the Charleston Harbor (downriver station 15). This change in seston concentration corresponded with an increase in transmissivity in the surface water from 3.9 to 24 RTU as measured with the shipboard CTD. These measurements appear to reflect the large scale settling of particles out of the surface water column in this area by the Navy Yard as has been documented by other studies (Van Dolah et al., 1990).

Tidal mixing can create conditions in the bottom water and bottom boundary layer that can accelerate bacterial degradation of organic matter. PAH degradation (based on wet volume) was similar between benthic boundary layer and sediment with phenanthrene mineralization being the highest relative to naphthalene and fluoranthene (Table 2). Without knowing the retention time for particles in the benthic boundary layer, we cannot determine the proportion of PAH degradation that is occurring as the particles are mixed tidally in this layer relative to that occurring in the surface sediments. The fact that turnover time for phenanthrene is rapid (ca. 100 days) and stable throughout the year in the sediment suggests that there is enough flux of PAH to the surface sediments to maintain selective pressure for PAH-degrading bacteria amongst the natural assemblage (Figure 2). Such rapid PAH turnover within the sediments decreases the likelihood that ambient PAH concentrations are the result of historical deposition.

PAH degradation with depth was not measured at Cooper River stations so one cannot necessarily extrapolate the rate measurement made in the top cm of aerobic sediment to depth unless the deeper sediments are aerated by benthic infauna (Montgomery et al., 2005). We calculated the bioturbation depth required to maintain aerobic rates of

TABLE 2. PAH degradation in the nepheloid and sediment samples (1 mL wet volume) at Cooper River station 6A.

PAH	**Nepheloid ($\mu g \times 10^{-4}$ mL^{-1} d^{-1})**		**Sediment ($\mu g \times 10^{-4}$ mL^{-1} d^{-1})**	
	AVG	**SD**	**AVG**	**SD**
Naphthalene	6.1	0.9	10.7	2.3
Phenanthrene	134	13	72	32
Fluoranthene	0.81	0.12	2.1	0.5

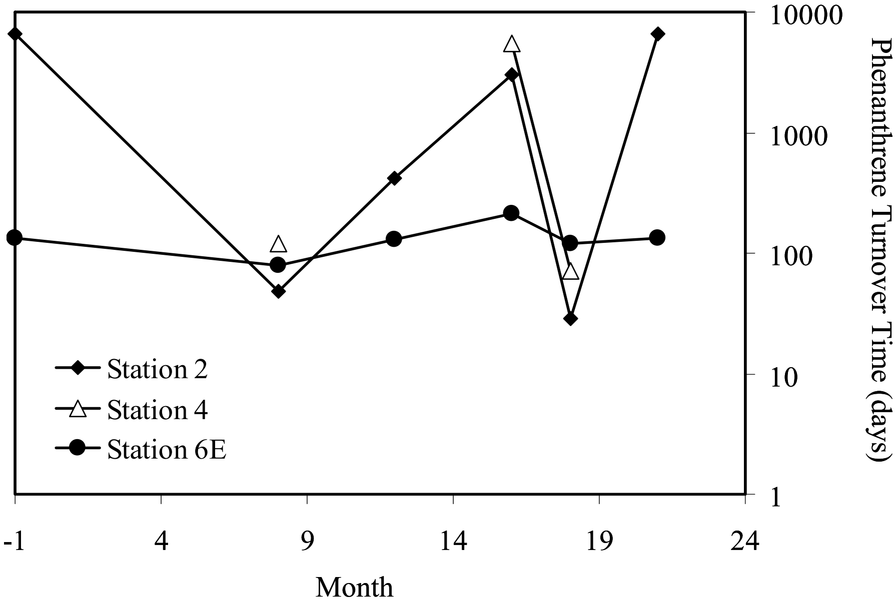

FIGURE 2. Phenanthrene turnover time in sediments of Cooper River, SC, USA from November 1997 to October 1999.

bacterial PAH degradation high enough to balance the PAH flux to the sediment from settling particles. In some cases, such as upriver of the Navy Yard, 367 cm of aerated (bioturbated) sediment would be needed to balance the PAH settling from the water column (Table 3). Such a deep bioturbation depth suggests that the settling PAH is either increasing the ambient PAH concentration in the local sediment (PAH concentration is several fold higher at this station) or the particle associated PAH is transporting laterally in the nepheloid layer. With the upriver sediments being only 3-4 ppm higher in ambient PAH concentration, the latter scenario is most likely. In contrast, the sediments adjacent to CNY (stations 6A-6E) would need only a 5 cm layer of bioturbation to increase the PAH degrading capacity enough to metabolize the PAH mass flux from settling particles. This does not take into account PAH flux transported in the benthic boundary layer from upriver so either a deeper layer of bioturbation is needed, PAH is degraded in the nepheloid layer, or PAH mass migrates past the CNY site to the Charleston Harbor. Rapid PAH turnover, low ambient concentration, and high flux suggest that the sediment adjacent to the CNY (stations 6A-6E) is acting as a sink for PAH in this estuarine system.

TABLE 3. Total PAH degradation verses deposition for Cooper River, SC, USA.

Location	**Total PAH Depositing (mg PAH m^{-2} d^{-1})**		**PAH Degrading* (mg PAH m^{-2} d^{-1})**	**Bioturbation Depth Needed (cm)**
	AVG	**SD**		
Upriver	7.35	1.62	0.02	367
CNY	6.09	0.35	1.30	5
Downriver	5.79	0.32	0.57	10

*1 cm deep

CONCLUSIONS

This paper used a strategy first described by Pohlman et al. (2002) for using independent measures of PAH transport, flux between media, and biodegradation, to determine the predominant source of PAH at an estuarine sediment site and its rate of intrinsic biodegradation. Pohlman et al. (2002) calculated that bacterial degradation in the top 10 mm could metabolize 25-50% of depositing PAHs annually. Bioturbation of just the top 4 cm would be enough to stimulate heterotrophic bacteria to degrade the entire mass of PAH depositing to the sediment at the Philadelphia Reserve Basin. In addition, Apitz and Chadwick (1999) compared various mechanisms of PAH transport and removal in San Diego Bay sediment and similarly concluded that ambient PAH concentration was a net result of particle settling and biodegradation by sedimentary bacteria (Montgomery et al., 2005). These studies demonstrate the importance of comparing independently derived measures of contaminant fate in estuarine systems.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research (to MTM, CLO, TJB & DCS) Contract # N0001499WX20525 and the NRL Shiptime Program (to TJB). Site support was provided by Matthew A. Hunt, P.E. at Naval Facilities Engineering Command, Environmental Field Division South for the former Charleston Navy Yard. The authors thank Dawn Castle, Mark Pyle and the crew of the R/V Cape Hatteras for assistance in sampling. The opinions and assertions contained herein are not to be construed as official or reflecting the views of the US Navy or the Federal Government at large. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

REFERENCES

Apitz, S.E., and D.B. Chadwick. 1999. "SERDP CU-1209: Pathway Ranking for In-place Sediment Management (PRISM)." *Final Report to the Strategic Environmental Research and Development Program.* http://www.serdp.org/ research/CU/CU-1209.pdf.

Boyd, T.J., M.T. Montgomery, J.K. Steele, J.W. Pohlman, S.R. Reatherford, B.J. Spargo, and D.C. Smith. 2004. "Dissolved oxygen saturation controls PAH biodegradation in freshwater estuary sediments." *Microbial Ecol.* (*Accepted 17 February*).

Fisher, J.A., M.J. Scarlett, and A.D. Stott. 1997. "Accelerated solvent extraction: An evaluation for screening of soils for selected U.S. EPA semivolatile organic priority pollutants." *Environ. Sci. Technol. 31*:1120-1127.

Meyers, S.P. 2000. "Developments in aquatic microbiology." *Internatl. Microbiol. 3*:203-211.

Montgomery, M.T., C.L. Osburn, W. Zeibis, C. Mahn, J. Do, and J.M. Gieskes. 2005. "Bacterial PAH mineralization with depth in estuarine sediments." *Marine Environ. Research* (*Submitted*).

Pohlman, J.W., Coffin, R.B., Mitchell, C.S., Montgomery, M.T., Spargo, B.J., Steele, J.K., and T.J. Boyd. 2002. "Transport, deposition, and biodegradation of particle bound polycyclic aromatic hydrocarbons in a tidal basin of an industrial watershed." *Environ. Monitor. Assess. 75*: 155-167.

Schneider, A.R., B.J. Eadie, and J.E. Baker. 2002. “Episodic particle transport events controlling PAH and PCB cycling in Grand Traverse Bay, Lake Michigan.” *Environ. Sci. Technol. 36*(6):1181-1190.

Van Dolah, R.F., P.H. Wendt, and E.L. Wenner. 1990. “A physical and ecological characterization of the Charleston Harbor Estuarine System.” *Final Report to the South Carolina Coastal Council.* 634 pp.