TRANSPORT, DEPOSITION AND BIODEGRADATION OF PARTICLE BOUND POLYCYCLIC AROMATIC HYDROCARBONS IN A TIDAL BASIN OF AN INDUSTRIAL WATERSHED

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Abstract. Polycyclic aromatic hydrocarbons (PAHs) are common contaminants in industrial watersheds. Their origin, transport and fate are important to scientists, environmental managers and citizens. The Philadelphia Naval Reserve Basin (RB) is a small semi-enclosed embayment near the confluence of the Schuylkill and Delaware Rivers in Pennsylvania (USA). We conducted a study at this site to determine the tidal flux of particles and particle-bound contaminants associated with the RB. Particle traps were placed at the mouth and inside the RB and in the Schuylkill and Delaware Rivers. There was net particle deposition into the RB, which was determined for three seasons. Spring and fall depositions were highest (1740 and 1230 kg of particles, respectively) while winter deposition was insignificant. PAH concentrations on settling particles indicated a net deposition of 12.7 g PAH in fall and 2.1 g PAH in spring over one tidal cycle. There was no significant PAH deposition in the winter. Biodegradation rates, calculated from 14C-labeled PAH substrate mineralization, could attenuate only about 0.25% of the PAH deposited during a tidal cycle in fall. However, in the spring, biodegradation could be responsible for degrading 50% of the settling PAHs. The RB appears to be a sink for PAHs in this watershed.

Keywords: biodegradation, deposition, PAHs, particle-associated contaminants, sediment transport

1. Introduction

PAHs (Polycyclic Aromatic Hydrocarbons) are common contaminants in aquatic ecosystems that, when present in significant quantities, pose a threat to human health and the environment (Fernandes et al., 1997; Menzie et al., 1992). Sources of PAHs are both natural and anthropogenic, with anthropogenic sources dominating environmental input (Wijayaratne and Means, 1984). PAHs are produced when hydrocarbon fragments from incomplete combustion of fossil fuels condense into multi-ringed aromatic structures (Witt, 1995). Industrial processes using coal or oil as a raw material and incidental oil releases at refineries produce effluents containing PAHs that enter streams, ground water and rivers. Atmospheric deposition, surface runoff and domestic wastes also deliver PAHs into the environment (Manoli...
and Samara, 1999). Identifying PAH sources and understanding their impact on watersheds is matter of scientific and public concern.

Because of their hydrophobic nature, PAHs rapidly adsorb onto nonpolar surfaces of particles and colloidal material in the water column (Bouloubassi and Saliot, 1991; Wijayaratne and Means, 1984). Although colloidal material is an important pool for PAH sequestration, the depositional nature of particles makes them the dominant source of PAH to aquatic sediments (Ko and Baker, 1995). Particles can be transported great distances before being deposited (Bouloubassi and Saliot, 1991). Thus, determining how far contaminants travel from a point source or from where contamination at a particular site originated, can be difficult. Numerous physical, chemical and biological factors must be considered to make an accurate assessment of the sources and fate of contaminants at an impacted site (Jaffe, 1991).

This study focuses on the concentration, distribution, transport and fate (biodegradation and burial) of particle bound PAHs in the Philadelphia Naval Reserve Basin (RB) and portions of the Schuylkill and Delaware Rivers (Figure 1A). The main issue is whether the RB serves as a watershed source or sink for contaminants. The RB is a semi-enclosed embayment covering approximately 10 900 m². Its depth ranges between 6.4 to 9.4 m (mean low water) and is subject to semi-diurnal 2 m tides. It is the Navy’s only freshwater reserve, and was once an area of active ship maintenance, storage and construction. Its semi-enclosed nature and location at the confluence of two rivers makes it an ideal study site for the modeling of contaminant and particle exchange, and biodegradation. The volume of water tidally exchanged each day is greater than 50% of the average volume of the entire basin. Runoff and stormwater discharge were determined to be a negligible source of contaminants to the RB (EA Engineering, 1997). Because of past activities within the RB, it is considered a potential contaminant source to adjacent areas within the watershed, with tidal flux of particle-attached PAHs the primary mechanism of exchange between the RB and surrounding watershed (EA Engineering, 1997). Because proximal sources of contamination (Naval activities) have been attenuated over the past 10 years (no releases) and the depositional accumulation of sedimentary material over time within the RB, we hypothesize that the RB may be a sink for contaminants in the watershed.

2. Experimental

2.1. Sampling

Sampling took place 17–20 September 1998 (Sep98), 14–16 December 1998 (Dec98) and 2–5 May 1999 (May99). Samples from the Schuylkill and Delaware River were taken aboard the R/V Cape Henlopen and samples from the RB were collected from an inflatable AVON boat.
Figure 1. Study site (A), showing current directions during maximum tides (B,C).
2.2. PARTICLE COLLECTION

During each sampling, particle traps were deployed on both flood and ebb tides within the mouth region of RB and other portions of the watershed to quantify particle dynamics. Suspended particles were trapped in polycarbonate tubes packed at the top with 10 cm tenite butyrate baffles (US Plastics, Ocean NJ). The baffles reduced the velocity of water passing across the 6 cm-diameter mouth of the trap, which caused particles from the water to fall into the trap. Because of lateral water flow (2 m tidal range with maximum flow rates up to ~0.2 m s\(^{-1}\)), both actively sinking and suspended particles were likely trapped. In the context of this paper, this collected material is termed suspended particulate matter (SPM). A trap set (3 traps banded together) was attached to an anchored line and held upright by a mooring buoy set below the low tide level. A small surface float was tied to mooring buoys and was used to haul the traps into the boat. One trap was placed in the Delaware River above the Schuylkill River convergence, and one was placed in the Schuylkill River upriver of the RB (Figure 1B, C). Two traps were placed at the mouth of the RB (Figure 2), and one trap was placed in the center of the RB (Figure 1B, C). Upon recovery, samples were drained into acid cleaned Nalgene carboys through a tube at the bottom of each trap and fixed with sodium azide to a concentration of 0.1% (w/v). After 5–7 days of settling, the supernatant was siphoned from the carboys. Samples were stored at 4°C until they were processed.
In addition to collecting suspended sediments from the water column, nepheloid material, the buoyant floc suspended above the sediments, was pneumatically pumped to the surface through an intake funnel and silicone tubing. The funnel was attached to an aluminum plate set 2-15 cm above a perforated base plate. The nepheloid layer depth determined the height the intake funnel was set above the base plate. Samples were collected in acid cleaned mason jars and were fixed to a final concentration of 0.1% (w/v) sodium azide.

Surface sediment samples were collected with a Petite Ponar sediment grab from the AVON in the RB and with a Smith-Mack grab from the R/V Cape Henlopen in the Delaware and Schuylkill Rivers. Samples were transferred to 50 mL centrifuge tubes and stored at 4 °C until processed.

The concentration of SPM was measured gravimetrically in Sept98 and by nephelometry with a Hydrolab Datasonde 4 (Hydrolab, Austin, TX) in Dec98 and May99. Nepheloid units (NTUs) registered by the Datasonde 4 were converted to concentration (mg L⁻¹) using a standard curve created by comparing gravimetrically determined concentrations against the in situ NTU measurement from the water samples (Dec98, \( r^2 = 0.99\); May99, \( r^2 = 0.94\)).

### 2.3. PAH ANALYSIS

Particle trap, sediment and nepheloid samples were processed for PAHs using Accelerated Solvent Extraction (Fisher et al., 1997) and GC/MS analysis. Samples were spiked with a surrogate standard (2-bromobiphenyl and \( P\)-Terphenyl) and extracted for 20 min (100 °C @ 2400 psi) with 1:1 acetone:methylene chloride. Post extraction cleanup was performed using silica gel columns (Supelco, Bellefonte, PA). Extracts were reduced to 1 mL under a gentle stream of purified N₂ gas. A Hewlett-Packard 6890 gas chromatograph (GC) with a 60 m 5% phenyl 95% methyl (SPB-5) 0.250 µm ID capillary column, coupled to a 5973 mass spectrometer (MS) was used for PAH analysis. Sample extracts were injected using an autosampler into a splitless mode inlet maintained at 250 °C. Pressure pulse programming was used to increase inlet pressure from 16 to 25 psi prior to the septum purge at 2 min into the run. Overall column flow was 1.0 mL min⁻¹ with helium as the carrier gas. The initial column temperature was 40 °C. The temperature was ramped as follows: 1) at 1 min run-time, ramp 4.0 °C min⁻¹ to 180 °C, hold 5 min, 2) ramp 4.0 °C min⁻¹ to 220, hold 5 min, 3) ramp 4.0 °C min⁻¹ to 280 °C, hold 5 min, 4) ramp 4.0 °C min⁻¹ to 300 °C, hold 10 min. The solvent delay was 7.0 min and the MS was set to scan from 35 to 300 amu. The MS was tuned with perfluortributylamine (PFTBA). The MS temperature was set to 106 °C, and the source was set to 230 °C.

There was very low recovery of surrogate standards from small nepheloid samples collected in Sept98 and Dec98. We conducted an experiment using varying amounts of initial sample with equal additions of surrogate standards. It was found that below roughly one gram starting material there was a linear relationship
between sample mass and surrogate standard recovery (Sep98, $r^2 = 0.89$; Dec98, $r^2 = 0.71$). This phenomenon artificially increased the calculation for PAH concentration in smaller samples. Smaller samples may not have had enough surface area and/or time to bind the surrogate with the same affinity as larger samples. Below one gram sample weight, the measured GC/MS responses were corrected to remove the variation caused by the loss of the surrogate standards during solvent extraction.

2.4. Mineralization Analyses

PAH mineralization assays were initiated within 1 hour of sediment sample collection using a modification of Boyd et al. (1996). UL-$^{14}$C-naphthalene (Sigma Chemical, 18.6 mCi mmol$^{-1}$), 3-$^{14}$C-fluoranthene (Sigma Chemical, 45 mCi mmol$^{-1}$), and 9-$^{14}$C-phenanthrene (Sigma Chemical, 47 mCi mmol$^{-1}$) were added to surface sediment samples (1 mL wet weight) in 100 × 16 mm test tubes to a final concentration of about 500 ng g$^{-1}$ (depending on specific activity) and, in all cases, below the ambient concentration. Isotope dilution was calculated from the ambient test PAH concentration. Samples were incubated no longer than 24 h at in situ temperature and evolved $^{14}$CO$_2$ was captured on NaOH-soaked filter papers. H$_2$SO$_4$ was added to end incubations and to force any remaining CO$_2$ into headspace of the tube to the filter paper trap. The filter papers containing metabolized $^{14}$CO$_2$ were removed, radioassayed and used to calculate substrate mineralization.

2.5. PAH and Particle Transport

The bathymetry across the RB pass was determined by taking depth soundings at 1 m intervals. The water column was divided into three equivalent depth bins (top, middle and bottom) and the relative area of each level determined. The top, middle and bottom levels, respectively, constituted 51.5%, 29% and 19.5% of the total cross sectional area of the pass (Figure 2, Bridge sampling point). Water transport through each bin was estimated by multiplying the fraction of each depth bin by the total transport (in L) coming in or going out of the RB during a tidal cycle. Total transport for the tidal cycle was calculated by multiplying the total area of the RB and tidal range (measured on the seawall). Suspended particulate matter (SPM) was measured hourly during flood and ebb tides and a time weighted averaged for total SPM coming in or going out of the RB per tide was calculated. In this way, any resuspension events within the sampling area would be detected and integrated into the net SPM flux. PAH concentrations were measured from particle trap samples collected during each phase of the tidal cycle. In Sep98 and Dec98, samples were collected only from the bottom layer. That concentration was assumed to be representative of the entire water column and was used in the PAH transport for each discreet level. In May99, samples were collected from each level to investigate the vertical variation of PAHs in the water column. PAH transport in each level was calculated using the PAH concentration measured at that depth.
The total transport of SPM into or out of the RB was calculated by the difference between \((\Sigma \text{H}_{2}\text{O}_{\text{flood tide}} \times \text{SPM}_{\text{flood tide}})\) and \((\Sigma \text{H}_{2}\text{O}_{\text{ebb tide}} \times \text{SPM}_{\text{ebb tide}})\). The PAH transport was calculated using the measured particle trap PAH concentrations and the following formula:

\[
\Sigma \text{PAH}_{\text{trans}} = \left\{ \Sigma \text{H}_{2}\text{O}_{\text{top}} \times [\text{SPM}_{\text{top}}] \times [\text{PAH}_{\text{top}}] \right\} + \\
\left\{ \Sigma \text{H}_{2}\text{O}_{\text{mid}} \times [\text{SPM}_{\text{mid}}] \times [\text{PAH}_{\text{mid}}] \right\} + \\
\left\{ \Sigma \text{H}_{2}\text{O}_{\text{bot}} \times [\text{SPM}_{\text{bot}}] \times [\text{PAH}_{\text{bot}}] \right\}
\]

3. Results and Discussion

3.1. SPM-attached PAH distribution

The SPM-attached PAH concentrations (those found on the collected particles) in the Delaware and Schuylkill Rivers were slightly higher than the mouth or interior of the RB during each sampling event (paired \(t\)-test; \(P = 0.03\)). The Schuylkill River \((n = 3)\) and Delaware River \((n = 3)\) traps had almost identical average SPM-attached PAH concentrations of 5.12 and 5.15 µg PAH g\(^{-1}\) particles, respectively \((P = 0.98)\). Average SPM-attached PAH concentrations collected over a complete tidal cycle at the mouth of the RB \(3.69 \mu\text{g PAH g}^{-1}\) particle; \(n = 6\) and interior of the basin \(3.47 \mu\text{g PAH g}^{-1}\) particle; \(n = 3\) were also similar \((P = 0.63)\).

Particles collected coming into the RB during rising tide \(3.77 \pm 1.88 \text{mg PAH g}^{-1}\) did not have a significantly different PAH concentration \((P = 0.08)\) than particles collected in the adjacent Schuylkill River \(5.12 \pm 1.64 \text{mg PAH g}^{-1}\). River traps collected particles during both phases of a tidal cycle that reverses the direction of flow in the Delaware and Schuylkill Rivers (NOAA on-line verified tide and current data). When the tide is at maximum flood, the major source of particles collected in river particle traps is the Delaware River below the confluence of the Delaware and Schuylkill Rivers (Figure 1B). When the tide is falling, the source of particles collected in the river traps is the upper Schuylkill River (see Figure 1C). Traps in the RB receive a higher proportion of particles from the Delaware River and lower Schuylkill River water, which is pushed into the RB by the rising tide. Particles from the upper Schuylkill River are partially excluded from the RB because it is draining when the upper Schuylkill River is flowing toward it. Particle traps in the rivers were deployed for an entire tidal cycle; thus their concentrations may represent a sum of a higher concentration period (when Schuylkill River is flowing downstream) and lower concentration period (when Delaware River water is flowing upstream). On the other hand, the particle traps at the mouth of the reserve basin only collected particles during the lower concentration period.
Because the particle traps placed in the rivers collected material over a period of several tidal cycles, the particle-attached PAH concentrations measured from those traps represents the time averaged concentration of particles passing through that region of the river. To constrain the regional distribution of the particle-attached PAHs, we measured nepheloid PAH concentrations. Nepheloid material is mobile, which makes nepheloid PAH data a useful proxy for particle attached PAHs. For both Sep98 and Dec98, the highest nepheloid PAH concentrations were from the upper Schuylkill River (Table I). Higher PAH concentrations in this region explains why particle traps deployed in the river had higher particle attached PAH concentrations than those deployed in the RB. Particles from the region with the highest PAH abundance do not enter the RB during the falling tide, when the RB is ebbing water.

### 3.2. Net Particle and PAH Transport

Total PAH transport depends upon the concentration of both the SPM and the SPM-attached PAH concentration. During the Dec98 and May99 sampling events, there was no difference between the average particle-attached PAH concentrations from the ebb and flood tides (Dec: \( P = 0.05 \), May: \( P = 0.71 \)) (see Table II). The SPM-attached PAH concentrations from samples collected in Sep98 were slightly higher during the flood tide than they were during the ebb tide (\( P = 0.02 \)).
To determine the total PAH transport, it was necessary to consider the SPM concentrations during each season. Seasonally variable factors such as phytoplankton production, soil erosion and sediment resuspension influence particle concentrations (Ko and Baker, 1995; Witt, 1995) in rivers and estuaries. During Dec98, when rainfall was low (2.5 cm during three weeks before sampling) and surface primary productivity is traditionally minimal (Coffin and Sharp, 1987), the average particle concentration was 0.6 ± 0.1 mg L\(^{-1}\) (\(n = 18\)). In Sep98 and May99, when detrital inputs were higher due to increased rainfall (3.8 and 4.2 cm, respectively, during three weeks prior to sampling) and perhaps due to higher plankton primary production, the average suspended particle concentrations were also higher (5.7 ± 2.2 mg L\(^{-1}\) (\(n = 29\)) in Sep98 and 5.5 ± 3.9 (\(n = 52\)) mg L\(^{-1}\) in May99).

In addition to seasonal differences in SPM concentrations water leaving the RB had a lower SPM concentration than water entering the RB during every sampling event at every depth sampled (Table II). The difference between the mass of particulate matter carried into the basin and the mass of the particulate matter exported from the basin is the amount deposited in the basin during each tidal cycle. There was a net deposition of 11.7 g PAH in Sep98 and 2.1 g PAH in May99 in the RB during each of the tidal cycles studied. There was no significant (\(P = 0.32\)) net deposition of PAH in the basin for the tidal cycle studied in Dec98. PAH removal from the incoming water was 43.8% in Sep98 and 21.7% in May99 (Table II).

In the RB’s associated watershed, SPM concentration was the dominant factor in determining PAH transport. During winter, when fossil fuel use at coal-fired power plants and private heating sources is higher and biodegradation may be lower, there may be a greater net input of PAHs into aquatic systems (Witt, 1995). Our data agree with this observation as particle attached PAH concentrations were highest in Dec98 (Table II). Nevertheless, because the SPM concentrations were so low, the net transport of PAHs into the RB at that time was the lowest of any sampling period.

### 3.3. Biodegradation of PAHs in the RB

Biodegradation of PAHs in settling particles was estimated by relating the PAH mineralization in the upper 10 mm of sediment surface to the amount of net sediment deposition over a given tidal cycle. Biodegradation rates were averaged for all RB stations for each sampling event. The mean biodegradation rate was multiplied by the SPM deposition (Table II) over a tidal cycle to arrive at a net PAH biodegradation (Table III). Because we only measured naphthalene, phenanthrene and fluoranthene mineralization, the total reflects only the sum of these PAHs. During the Sep98 sampling, PAH biodegradation could only account for a small percentage of potential PAH removal (0.25%). However, in May99, the average biodegradation rate may have been responsible for attenuating almost 50% of the PAH (naphthalene, phenanthrene and fluoranthene) deposition within the measured tidal cycle. Depending on in situ growth efficiencies, which have been shown to be
significant (Herbes and Schwall, 1978), higher total biodegradation (50%) may have actually occurred. Total PAH mass and biodegradation within the upper 10 mm of the RB was calculated by multiplying the area of the RB by the PAH concentration and biodegradation in the upper 10 mm of sediment surface. A turnover time was calculated by dividing the rate into the total PAH concentration (Table III). These data indicate temporal separation in the deposition:biodegradation dynamics of PAHs within the RB. There appears to be a median turnover time in Sep98 when net PAH deposition is highest. In Dec98, deposition is low and turnover time is high (160 days). In May99, there is low deposition (2.1 g), yet short turnover (6.1 days). We postulate that PAHs accumulate in fall and winter months and are attenuated by biodegradation in the spring. From a previous sampling in Jun98, we observed low dissolved oxygen above the sediment surface within the RB. We also noted lower PAH biodegradation rates than in other seasons. Perhaps, rapid biological activity depletes dissolved oxygen to a level that inhibits PAH biodegradation. Thus, net accumulation of PAH may also occur in summer months.

3.4. THREE-LAYER – VS – BOTTOM LAYER MODEL

In Sep98 and Dec98, PAH transport into the basin was calculated by assuming the particles collected 2 meters above bottom were representative of the entire water column. Suspended particle concentrations used in the calculations, however, were measured at three distinct levels – 2, 4 and 7 meters above bottom. Bottom SPM concentrations were notably higher than those at the middle and near surface depths during May99 and Sep98. This distribution could have lead to variations in the particle PAH binding capacity (Ko and Baker, 1995). Consequently, we
investigated the vertical stratification of the particle attached PAH concentrations in May99.

Three sets of traps were placed on the mooring line at the same levels suspended particle concentrations were measured to determine if the SPM-attached particle concentrations were vertically stratified. The shallowest samples (7 meters above bottom) for each treatment had the lowest SPM-attached PAH concentrations which ranged between 0.5 to 1.2 $\mu$g PAH g$^{-1}$ particles. The middle level (4 meters above bottom; 2.5 to 3.7 $\mu$g PAH g$^{-1}$ particle) and deepest level (2 meters above bottom; 2.1 to 2.7 $\mu$g PAH g$^{-1}$ particle) concentrations were a factor of 2-3 times higher than the surface samples.

Using only the bottom layer model with the May99 data, deposition of PAHs into the RB was 20.4% greater than calculated using the three-layer model. The difference in the two model calculations can be attributed to the relatively low SPM PAH concentrations in the shallow traps (7 meters above bottom). Despite seasonal differences in SPM composition (Asper et al., 1992; Thunell, 1997), it is reasonable to assume there may be similar variation in the net PAH transport values calculated in Sep98 and Dec98. Thus, the PAH deposition we have reported for each sampling event may be an overestimate of the actual deposition.

3.5. Fate of PAHs in the RB

Model calculations for maximum current velocities within the RB are thought to be below those necessary to scour the sediment surface (EA Engineering, 1997). Settling particles carry watershed contaminants like PAHs into the RB, a relatively quiescent body of water, where they likely stay. The net deposition of particles in the RB makes it a sink for PAHs in the watershed. The fate of particles (i.e. remaining suspended in the water column, aggregating in a nepheloid layers, or accumulating as sediment) may provide insight into the inter-sample differences observed in PAH deposition. There were clear differences in PAH concentrations in each of the particle reservoirs in the RB (Table IV). The sediments had the highest concentration of PAHs during all samplings, while the nepheloid layer had inter-
mediate concentrations in Sep98 and Dec98. Only during May99 did the nepheloid layer and water column suspended sediments have similar PAH concentrations ($P = 0.63$). The discrepancy between the PAH concentrations of the two mobile phases (nepheloid layer and water column) may explain why the sediment bound PAHs are more concentrated than the particle bound PAHs. Nepheloid material migrating into the reserve basin would elude capture by the traps deployed 2 meters above bottom.

Sediments are the likely reservoir for PAHs within the RB. Because biodegradation rates are too low to attenuate all of the settling SPM-associated PAHs (turnover times as long as 160 days), sediment PAHs will probably reach a steady state concentration (Table IV). The balancing of biodegradation (which is probably effective only during certain seasons) and burial into sediment most likely dictates the PAH concentration within an average RB sediment core. Evidence suggests that biodegradation of PAHs under anaerobic conditions within deeper sediments is very slow if significant at all (Coates et al., 1996; Coates et al., 1997). Because of low sulfate concentrations commonly found in freshwater sediments, one would not expect sulfate reduction, which has been identified as one of the major electron accepting processes associated with PAH biodegradation in marine sediments, to be the major factor in the freshwater RB.

4. Conclusions

Based on the results of this study, the RB appears to be a sink for particle-associated PAHs within its adjacent watershed. Although the PAH concentrations of settling particles were lowest within the RB, net particle deposition over tidal cycles indicates accumulation of PAHs within the RB. An estimate of biodegradation rates showed that during the spring season, PAH biodegradation may attenuate a significant fraction of the PAHs settling within the Basin. However, for other seasons sampled (fall and winter) PAH biodegradation was not rapid enough to attenuate PAH input. To validate our methods, we developed a three-layer model of transport that showed slightly lower accumulation of particles during incoming and outgoing tides. Because this error is most likely systematic, estimates of net particle deposition from Sep98 and Dec98 samplings were likely about 20% lower than reported.

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