*Environ. Sci. Technol.* **1999**, *33,* 2138−2144

# Diffusive Exchange of Polycyclic Aromatic Hydrocarbons across the Air−Water Interface of the Patapsco River, an Urbanized Subestuary of the Chesapeake Bay

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Air−water exchange fluxes of 13 polycyclic aromatic hydrocarbons (PAHs) were determined along a transect in the Patapsco River from the Inner Harbor of Baltimore, MD, to the mainstem of the northern Chesapeake Bay. Sampling took place at six sites during three sampling intensives (June 1996, February 1997, and July 1997) and at one site every ninth day between March 1997 and March 1998 to measure spatial, daily, and annual variability in the fluxes. The direction and magnitude of the daily fluxes of individual PAHs were strongly influenced by the wind speed and direction, by the air temperature, and by the highly variable PAH concentrations in the gas and dissolved phases. Individual fluxes ranged from 14 200 ng $m^{-2}$ $day^{-1}$ net volatilization of fluorene during high winds to 11 400 ng $m^{-2}$ $day^{-1}$ net absorption of phenanthrene when prevailing winds blowing from the northwest across the city of Baltimore elevated gaseous PAH concentrations over the water. The largest PAH volatilization fluxes occurred adjacent to the stormwater discharges, driven by elevated dissolved PAH concentrations in surface waters. Estimated annual volatilization fluxes ranged from 1.1 $\mu$g $m^{-2}$ $yr^{-1}$ for chrysene to 800 $\mu$g $m^{-2}$ $yr^{-1}$ for fluorene.

## Introduction

Air−water exchange of hydrophobic organic contaminants (HOCs) is an important process determining the transport, fate, and chemical loadings of these contaminants in the atmosphere and in large bodies of water (*1−7*). HOCs are transported long distances through the atmosphere from their original source and enter surface waters of lakes, estuaries, and oceans via air−water exchange (*2, 8−9*). Driven by HOC concentrations in the air and water and on meteorological conditions, many HOCs can cycle between air and water with intense periods of deposition followed by long periods of volatilization (*10*). The exchange of HOCs between the atmosphere and surface waters can be a dominant control of HOCs concentrations and residence times in the water, and the magnitude and direction of the fluxes can vary seasonally (*4, 5, 11*).

Studies conducted on the Great Lakes measured seasonal variations in fluxes of organic contaminants across the air−water interface (*2, 3,11−13*). Recently, Nelson et al. (*4*) estimated PAH gas exchange fluxes across the air−water interface of the Chesapeake Bay and determined that gaseous PAHs absorb from the atmosphere into the surface waters throughout most of the bay in early spring but revolatilize during the summer and early fall. Largest net absorption PAH fluxes were in the northern Chesapeake Bay due to high gaseous PAH concentrations, when prevailing winds transported elevated PAH concentrations from the Baltimore−Washington urban atmosphere over the water. Gustafson and Dickhut (*5*), who measured PAH gas exchange fluxes in the southern Chesapeake Bay, also observed seasonal and spatial variations in PAH gas transfer due to concentration gradients measured in both the atmosphere and surface waters, with levels decreasing from urban to rural areas. In the northern bay, however, the influence of the urbanized city of Baltimore on coastal waters via air−water exchange is unknown. The primary objectives of this study were to quantify the spatial and seasonal trends in PAH gas exchange fluxes in the Baltimore Harbor and Patapsco River (the subestuary that joins the Inner Harbor of Baltimore to the Chesapeake Bay) and to determine the contributions of urban source PAHs from Baltimore to these coastal waters through air−water exchange.

The direction and magnitude of air−water exchange fluxes of PAHs in the harbor and Patapsco River were calculated on daily, seasonal, and annual time scales using a gradient flux model dependent on gaseous and dissolved concentrations, wind speeds, and temperature-corrected Henry's law constants. Spatial and daily variations in PAH fluxes were quantified from samples collected during three sampling intensives, and annual gas exchange fluxes were estimated from samples collected on a regular basis between March 1997 and March 1998.

## Experimental Methods

**Sampling Sites.** Three intensive sampling cruises were conducted on the Patapsco River in June 1996, February 1997, and July 1997. During each cruise, surface water samples were collected at six sites along the river over a period of 3−4 days (June 3−5 and 9; February 18, 20, and 22; July 22, 25, and 26). Three of the water sites were located outside the city limits of Baltimore from the Key Bridge to the mainstem of the Chesapeake Bay (site 1 at 39°09.55′ N, 76°26.50′ W; site 2 at 39°09.30′ N, 76°29.72′ W; site 3 at 39°12.69′ N, 76°31.71′ W), and three were located within the city limits of Baltimore along the west and northwest branches of the harbor (site 4 at 39°15.33′ N, 76°36.36′ W; site 5 at 39°16.09′ N, 76°34.59′ W; site 6 at 39°17.00′ N, 76°36.32′ W; Figure 1). Air was sampled at three sites along the shores of the river (only two air sites were operated during the June 1996 cruise). One site was located within the city of Baltimore on the roof of the Maryland Science Center (39°16.45′ N, 76°36.40′ W; February and July, 1997) or at the Fort McHenry National Park (39°16.04′ N, 76°34.59′ W; June 1996). The second site was located 5 km south-southeast of the center of the city at USGG Station Curtis Bay (39°12.15′ N, 76°33.10′ W), and the third was 12 km east by Hart-Miller Island (39°14.30′ N, 76°21.55′ W). For the February and July intensives, additional air and water samples were collected from the EPA RV *OSV Anderson* stationed off the mouth of the Patapsco River in the main stem of the northern Chesapeake Bay. Between March 1997 and March 1998, one water sample was collected 100 m south of site 3 along the southern shoreline of the river (39°12.27′ N, 76°31.01′ W, near the Key Bridge; Figure 1) and one air sample from the roof of the Maryland Science

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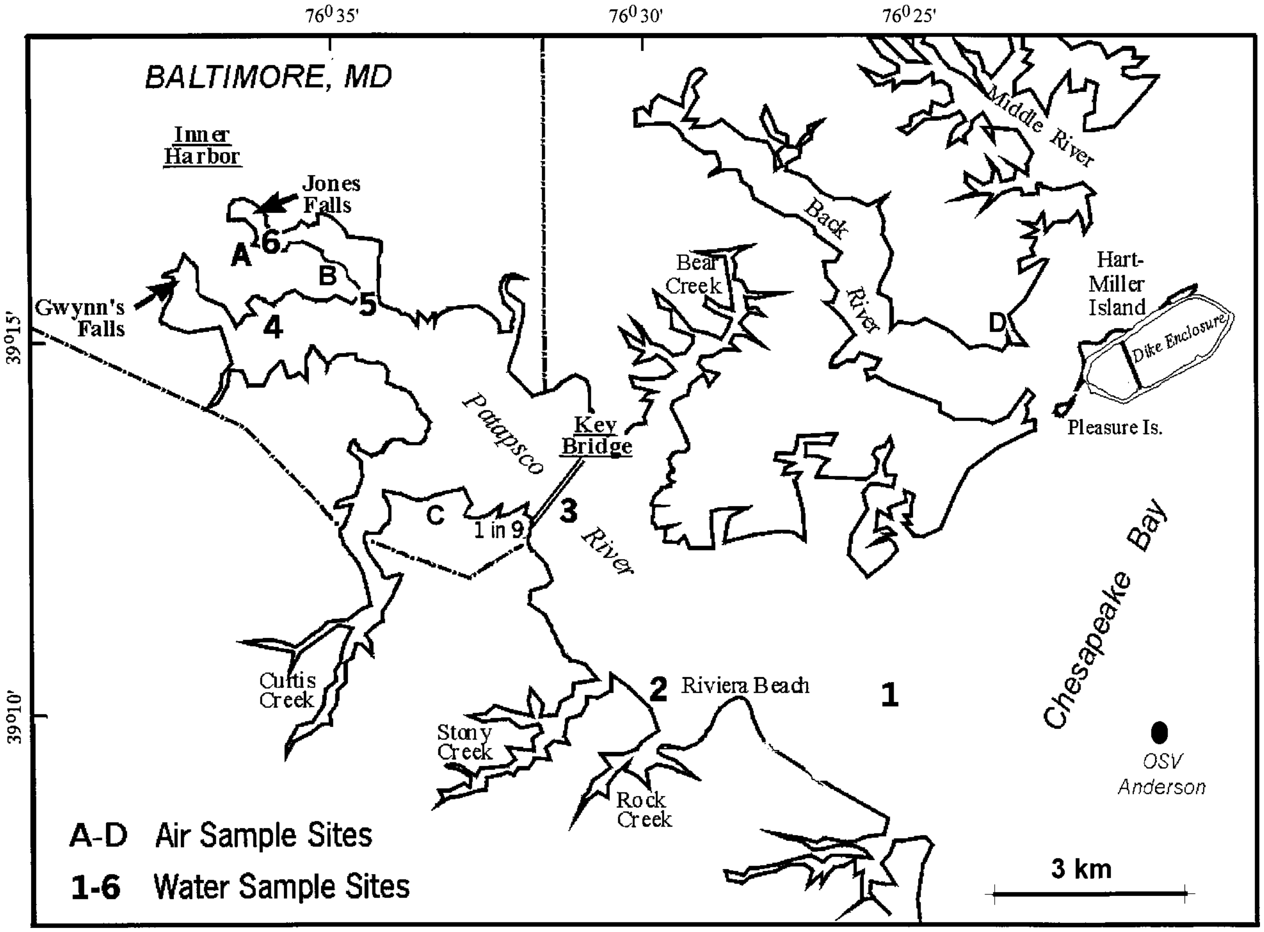

**FIGURE 1. Sampling sites for air and water samples.**

Center in Baltimore. Samples were collected every ninth day.

Water samples were collected in a polished stainless steel holding tank and pushed by pressurized clean air through a 293 mm diameter ashed (450 °C for 4 h) glass fiber filter (Schleicher & Schuell no. 25; 0.7 $\mu$m nominal pore size) placed inside an aluminum filter press. The filtered water was then pumped through a glass column (25 mm i.d.; 300 mm length) packed with 100 g of Amberlite XAD-2 macroresin (Sigma) at 200 mL/min to retain the dissolved PAHs in the water sample (*14*). PAHs quantified in a second XAD column in series were below detection limits or $<$1% of total PAH concentrations collected on the first column.

During the intensive sampling cruises, consecutive integrated 12-h air samples, beginning at 0700 were collected at each of the four sites (three on land plus the ship). Twenty-four hour integrated air samples were collected for the one in nine day samples. Details of air sampling are presented elsewhere (*4, 15, 16*) and briefly described below. Air was sampled using modified high-volume air samplers (model NY1 123; General Metal Works). The air sampler separates vapor and aerosol phases of atmospheric HOCs by pulling air through a 25 cm × 20 cm, 0.40 $\mu$m nominal pore size glass fiber filter (Schleicher and Schuell no. 25) and polyurethane foam (PUF) (8.5 cm by 10 cm) plug in series (*2−4, 16−20*). Meteorological data were collected from a sensor located on the Key Bridge (35 m above the water). For the February and July intensive sampling cruises, additional meteorological data were collected from the bridge of the *OSV Anderson*.

**Analysis.** Analytical procedures used here are described in detail elsewhere (*4, 15, 21*). In summary, dissolved phase samples collected on XAD resin were Soxhlet extracted for 24 h with 1:1 acetone and hexane. The extract was then washed three times with Nanopure water (30 mL) in a separatory funnel and concentrated to ≈4 mL by rotoevaporation and 1 mL under a nitrogen atmosphere. Vapor phase samples collected on PUFs were Soxhlet extracted with petroleum ether for 24 h, concentrated and transferred to hexane by rotoevaporation, and reduced to 1 mL by a stream of nitrogen. All PAHs were analyzed on a Hewlett-Packard 5890 series plus capillary gas chromatograph equipped with a Hewlett-Packard 5972 series mass selective detector. The mass spectrometer was run in selective ion monitoring mode. A total of 40 PAHs were identified for quantification. Analytes were identified by comparison of retention time of the parent mass ion to that of the retention times of a standard solution of all the analytes (Ultra Scientific). Five internal standards (acenaphthene-$d_{10}$, phenanthrene-$d_{10}$, benz[*a*]anthracene-$d_{12}$, benzo[*a*]pyrene-$d_{12}$, and benzo[*g,h,i*]perylene-$d_{12}$) were added to each sample and standard prior to instrumental analysis.

**Quality Assurance.** Four perdeuterated PAHs (naphthalene-$d_8$, fluorene-$d_{10}$, fluoranthene-$d_{10}$ and perylene-$d_{12}$) were added to both air and water samples prior to extraction in order to quantify procedural recoveries. For the dissolved phase samples, surrogate recoveries were 53% ± 21% ($n = 104$) for naphthalene-$d_8$, 92% ± 28% ($n = 98$) for fluorene-$d_{10}$, 76% ± 17% ($n = 104$) for fluoranthene-$d_{10}$, and 83% ± 23% ($n = 102$) for perylene-$d_{12}$. Vapor phase samples surrogate recoveries were 63% ± 42% ($n = 62$) for naphthalene-$d_8$, 77% ± 22% ($n = 54$) for fluorene-$d_{10}$, 84% ± 14% ($n = 64$) for fluoranthene-$d_{10}$, and 77% ± 19% ($n = 62$) for perylene-$d_{12}$. On the basis of fairly consistent percent recoveries among vapor and dissolved samples, PAH concentrations in each sample were not surrogate corrected.

Laboratory and field blanks were analyzed to quantify possible contamination due to collection, transport, and extraction. Field blanks were obtained by pushing deionized water through a glass fiber filter, followed by pumping through an XAD-2 column. These field blanks contained significantly more analyte than did the laboratory blanks due to impurities in the compressed air. Therefore, field blanks were used to calculated a mean blank concentration that represents the methodology detection limits. One to three PUF field blanks were also analyzed from each air site for setting the methodology detection limits.

The detection limits were set as three times the mean field blank concentration for each PAH (*4, 22*). The mean blank concentration is a more conservative method in quantifying analytes than using the blank concentration + 3 SD. For both vapor and dissolved samples, most of the lighter weight PAHs (<202 molecular weight) were above these detection limits. Detection limits for PAHs ranged from 0.01 to 3.4 ng/L in the dissolved samples and from 1 to 300 pg/m$^3$ in the air samples. PAHs that were consistently below the detection limits (>50%) were not used in air−water flux calculations. For compounds that were used in air−water flux calculations (13 compounds out of 40 analyzed) that had some samples with concentrations below the detection limit in either the vapor or dissolved phases, the detection limit concentration was used as the compounds' concentration in order to calculate the flux between these two phases.

**Air−Water Exchange Model.** Gas exchange rates were calculated using a modified version of the Whitman two-film resistance model (*4, 9, 11*). Details of these calculations are similar to that recently described by Nelson et al. (*4*). Flux measurements from this model are based on PAH measured dissolved and gaseous concentrations, estimated mass transfer coefficients, and temperature-corrected Henry's law constants:

$$F = K_{OL}\,(C_w - C_a/H') \qquad (1)$$

where $F$ is the flux (ng m$^{-2}$ day$^{-1}$), $K_{OL}$ is the overall mass transfer coefficient (m/day), $C_w$ and $C_a$ (ng/m$^3$) are the truly dissolved and gaseous phase concentrations, and $H'$is the dimensionless temperature-corrected Henry's law constant. PAH dissolved concentrations measured at each site were paired with vapor concentrations at that site interpolated by distance from the three measured PAH gaseous concentrations.

Correct assessment of the temperature dependence of the Henry's law constant is essential in order to determine the direction and magnitude of the flux. For many PAHs, an 8-fold increase in the Henry's law constant is measured with a 25 °C change (*23*). Therefore, each individual PAH was corrected for ambient temperatures using temperature dependence data from Bamford et al. (*23*):

$$\ln H' = -\Delta H/RT + \Delta S/R \qquad (2)$$

where $\Delta H$ (kJ/mol) is equal to the enthalpy of phase change or transfer across the air−water interface, $\Delta S$ (kJ mol$^{-1}$ K$^{-1}$) is the entropy of phase change, $R$ is the ideal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), and $T$ is temperature in kelvin. Because of the limited data on direct measurements of the temperature dependence of $H$, Nelson et al. (*4*) used a common $\Delta H$ and $\Delta S$ for all compounds to correct $H$ for temperature. The differences in the fluxes due to different $H$ values used in each study were evaluated by recalculating the fluxes from Nelson et al. (*4*) using the new temperature-corrected $H$ values used in this study (*23*). The recalculated fluxes yielded lower net absorption fluxes for all compounds (i.e., the fluorene flux changed from 99 to 45 ng m$^{-2}$ day$^{-1}$ net absorption) because $H$ varies less with temperature then previously thought.

**Error Analysis in Gas Exchange Fluxes.** Uncertainty in calculated daily gas exchange rates results from systematic and random measurement errors in the dissolved and gas phase, in the uncertainties in quantifying the temperature effect on H, and in uncertainties in estimating the mass transfer coefficient. The uncertainties in the fluxes were evaluated using a propagation of error analysis (*24*). Uncertainty in $K_{OL}$ was estimated by the errors in the air and water side mass transfer coefficients (*25*). The error associated with $C_a$ and $C_w$ was determined by replicate samples and the relative standard deviation of the surrogate recoveries, and the error associated with H was estimated as described in Bamford et al. (*23*). The estimated average percent error of all samples for $K_{OL}$, $C_a$, $C_w$, and $H$ was 40%, 20%, 20%, and 10% of the respective values. The $H$ term was removed from the overall error analysis because error in $H$ from incorrect temperature corrections are assumed to be systematic and not random errors.

The overall propagated error associated with daily gas exchange fluxes ranged between 43% and 910% with the average error equal to 64% (*21*). Higher percent errors were associated with small fluxes that were close to zero. Most of the errors associated with the fluxes were attributed to the $K_{OL}$ and the uncertainties due to the effect variations in wind speed has on the $k_w$ (*25*). Propagation of error demonstrates that improvement in estimating gas exchange rates will result from a better understanding of the mass transfer coefficient rather than that of the concentration gradients.

## Results and Discussion

**Dissolved and Gas Phase Concentrations.** Atmospheric PAH concentrations and their spatial and seasonal trends in the Baltimore area have been described in detail elsewhere (*16*) and are summarized below. PAH gas phase concentrations during June 1996 varied spatially, with high concentrations in the city as compared to the downwind site on Hart-Miller Island. Linear average air concentrations for $\sum_{13}$ PAHs equaled 42 ± 41 ng/m$^3$ at the downtown site and 5.1 ± 4.4 ng/m$^3$ on Hart-Miller Island. On June 5, 1996, the winds shifted to the northwest blowing over the city across the water, causing a 4-fold increase in PAH air concentrations in the city and an 8-fold increase in concentration at Hart-Miller Island, indicating that the urban plume of Baltimore extends over a spatial scale of 12 km affecting PAH air concentrations over the coastal waters (*16*). In contrast to June 1996, no spatial gradients in gaseous PAH concentrations were observed among the samples collected in the city and at Hart-Miller Island during the February and July 1997 sampling cruises. However, the air samples collected aboard the *OSV Anderson* had significantly lower PAH gas phase concentrations than the other sites. The average $\sum_{13}$ PAH gas phase concentrations in February were 27 ± 1.7 ng/m$^3$ at the downtown site, 20 ± 1.5 ng/m$^3$ at Curtis Creek, 28 ± 1.4 ng/m$^3$ at Hart-Miller Island, and 6.3 ± 5.8 ng/m$^3$ on the *OSV Anderson*. In July, gas phase $\sum_{13}$ PAH concentrations were 20 ± 0.65 ng/m$^3$ at the downtown site, 26 ± 1.8 ng/m$^3$ at Curtis Creek, 16 ± 0.49 ng/m$^3$ at Hart-Miller Island, and 6.4 ± 4.6 ng/m$^3$ on the *OSV Anderson*. During both the February and July 1997 sampling intensives, the winds were predominantly coming from the north-northeast direction, meaning air masses from the Baltimore area did not extend over the northern Chesapeake Bay to where the ship was located. Furthermore, the wind speeds in February were variable with speeds ranging from 1 to 11 m/s over the water. These high wind conditions may dilute the total PAH air concentration by dispersing the total mass of PAHs over a larger area, lessening the effect of the urban plume at the downwind sites.

The $\sum_{13}$ PAH dissolved phase concentrations at all sites averaged 29 ± 6.2 ng/L in June 1996 and 34 ± 5.8 ng/L in

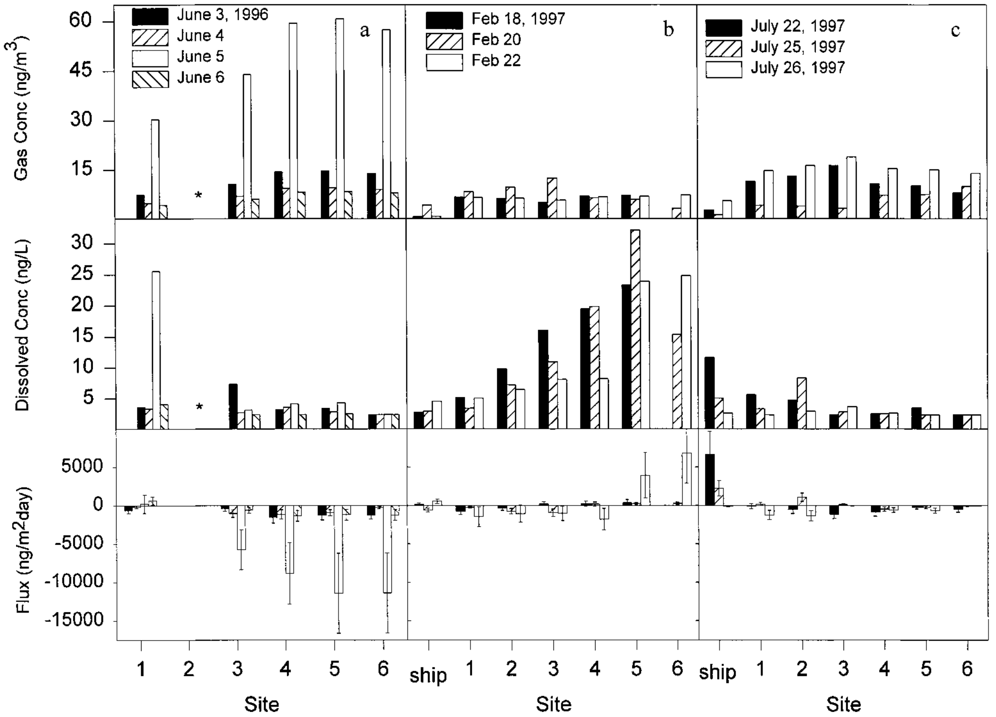

**FIGURE 2. Gaseous and dissolved phenanthrene concentrations and daily gas exchange rates measured during (a) June 1996, (b) February 1997, and (c) July 1997. Error bars represent the overall propagated error associated with the flux. An asterisk (*) indicates that no data are available.**

July 1997 with little spatial variation measured among sites during each cruise. In February 1997, however, the average $\Sigma_{13}$ PAH dissolved concentration was higher (77 ± 35 ng/L) as compared to June and July, with elevated dissolved concentrations in the harbor (110 ± 27 ng/L) relative to concentrations measured in the northern Chesapeake Bay (26 ± 15 ng/L). This concentration gradient may have resulted from high winds in February 1997, which may have resuspended contaminated bottom sediment in the harbor (*15, 26*) into the water column and elevated PAH concentrations in the water. Ashley and Baker (*26*) reported PAH concentrations in the sediments of the Patapsco River to range from 90 to 46 200 ng/g dry weight, with high concentrations localized around major stormwater discharges and Sparrow's Point industrial complex. Additionally, isolated precipitation events recorded around the city of Baltimore during this time may have increased urban runoff that discharges directly into the harbor via Jones Falls and Gwynn's Falls (Figure 1).

Overall, depending on atmospheric PAH concentrations and meteorological conditions, a spatial gradient was observed during independent sampling periods in both atmospheric gas and surface water dissolved PAH concentrations. In June 1996, prevailing northwesterly winds resulted in a PAH gas concentration gradient, with highest concentrations around the city; and in February 1997, high winds and isolated precipitation events caused a dissolved PAH concentration gradient with highest PAH concentrations in the harbor.

Air and water samples collected every ninth day between March 1997 and March 1998 had large variations in PAH concentrations throughout the sampling period. Gaseous concentrations of $\Sigma_{13}$ PAHs ranged between 4.1 and 76 ng/m$^3$, and $\Sigma_{13}$ PAHs in the dissolved phase ranged between 17 and 200 ng/L. For both gaseous and dissolved phases, lower PAH concentrations were measured in the spring between March and June 1997 and again between February and March 1998, as compared to the rest of the sampling period. The highest measured PAH air concentrations were in the fall and early winter between October and December 1997. The highest dissolved phase PAH concentrations were measured in the summer between July and October 1997 and again in January 1998.

**Daily Gas Exchange Fluxes.** Daily gas exchange rates were calculated for 13 PAHs at six sites along the Patapsco River (and an additional site in the northern bay during February and July 1997) for 4 days in June 1996 and 3 days each in February and July 1997. The main purpose of the sampling intensives was to measure the daily variation of air−water exchange fluxes and any spatial trends between fluxes measured at the different sites along the river. A total of 64 air and water pairs were used to calculate fluxes for all 13 compounds. Detailed information on compound-specific flux measurements, dissolved and vapor concentrations, and mass transfer coefficients are available in Supporting Information (see paragraph at end of paper).

The magnitude and direction of PAH fluxes varied widely on daily, seasonal, and spatial scales in the Patapsco River. The largest net absorption fluxes (negative fluxes) occurred in June as a result of high air concentrations, and the largest net volatilization fluxes (positive fluxes) occurred in February due to high dissolved phase concentrations and wind speeds. In June, the absorptive flux of phenanthrene increased from 0.24 to 11.4 $\mu$g m$^{-2}$ day$^{-1}$ between June 4 and June 5 (Figure 2a) despite water temperatures, dissolved phase concentrations, and wind speeds remaining relatively constant over the sampling period. The increase in the magnitude of the flux was driven by a large increase in the gaseous phenanthrene concentrations over the water as the winds shifted to the northwest blowing the air mass from around the city over the Patapsco River. An increase in net absorption for phenanthrene was also observed at the other sites along the river, with the largest fluxes in the harbor and decreasing away from the city. A spatial gradient was measured for other PAH compounds on this day, with the highest net absorption fluxes in the harbor. For lighter compounds such as fluorene that volatilized from the surface waters, elevated urban air concentrations on June 5 changed the direction of the flux (Figure 3a). For fluorene, the fluxes from the harbor changed

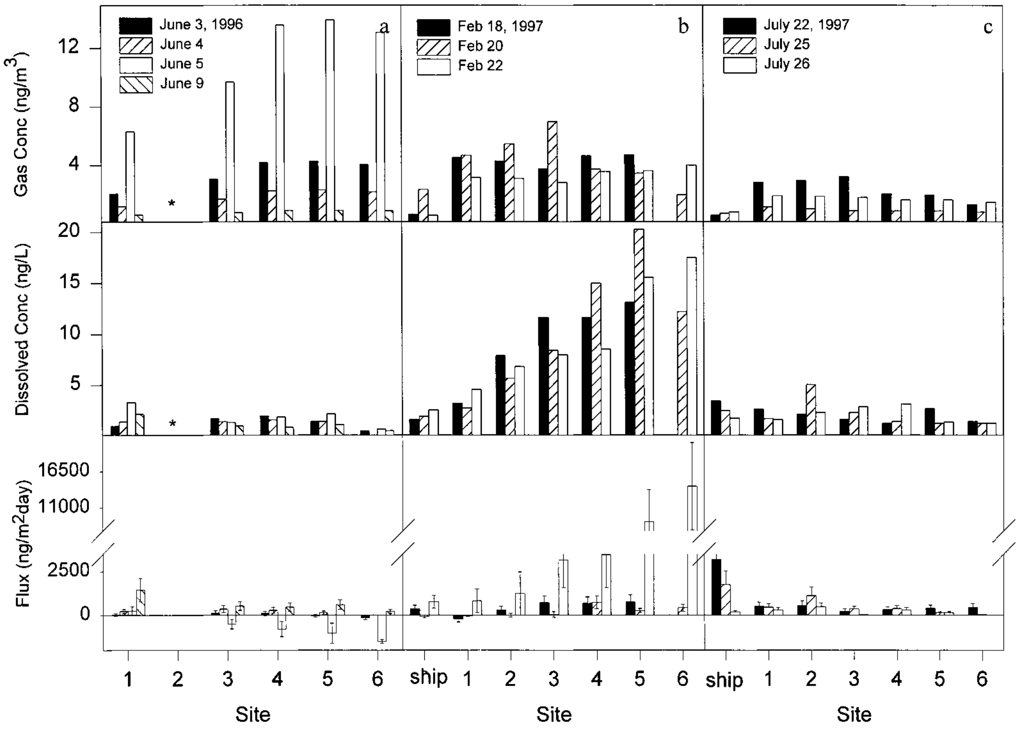

**FIGURE 3. Gaseous and dissolved fluorene concentrations and daily gas exchange rates measured during (a) June 1996, (b) February 1997, and (c) July 1997. Error bars represent the overall propagated error associated with the flux. An asterisk (*) indicates that no data are available.**

from near zero (a net volatilization of 1 ng m$^{-2}$ day$^{-1}$) on June 4 to net absorption of 1040 ng m$^{-2}$ day$^{-1}$ on June 5.

The highest daily fluxes for most compounds were measured in the harbor on February 22 as a result of elevated dissolved concentrations and high wind speeds, with the highest flux being 14.2 $\mu$g m$^{-2}$ day$^{-1}$ for fluorene (Figure 3b). The increase in daily fluxes between February 20 and February 22 was driven by higher wind speeds. The winds increased from an average of 3 m/s on February 20 to 11 m/s on February 22, resulting in a 20-fold increase in the mass transfer coefficient for most compounds and as high as a 45-fold increase in instantaneous fluxes measured in the harbor. A spatial gradient was also observed in February, with most compounds volatilizing from the surface waters to the atmosphere at sites close to the city and then reversing to net absorption in the northern Chesapeake Bay (Figures 2b and 3b). This trend was driven by the increase in dissolved concentrations around the harbor, possibly due to urban runoff discharged directly into the harbor or resuspension of contaminated bottom sediments (*26*).

For all three intensive sampling periods, all PAHs, except phenanthrene, mainly volatilized from the water to the atmosphere. Phenanthrene, which on average accounted for >50% of the total PAH gaseous concentrations measured, absorbed from the atmosphere to the surface waters with highest net absorption occurring in June due to elevated gaseous concentrations (Figure 2). Large variations in daily fluxes for most of the PAHs were measured in both June 1996 and February 1997 as a result of variations in air and water concentrations and wind speeds. However, in July 1997 when both PAH concentrations and wind speeds remained relatively constant, little daily and spatial variations were measured in fluxes (Figures 2c and 3c). Overall, there is large variations in the gas exchange fluxes for PAHs on both temporal and spatial scales with a common trend of the largest net volatilization and depositional fluxes occur closest to the city and decreasing down river.

**Annual Fluxes.** Annual air–water exchange fluxes were calculated from samples taken every 9 days between March 1997 and March 1998. From the intensive sampling cruises, large daily and seasonal variations in fluxes were observed; however, we are not able to accurately estimate the annual fluxes based on three cruises. Therefore, the overall goal of sampling every 9 days was to determine the direction and magnitude of air–water exchange rates in the Patapsco River on a seasonal and annual time scale. A total of 35 air and water pairs were used to calculate the fluxes (Figure 4). Compounds not illustrated are available in the Supporting Information.

The seasonal trend measured in PAH fluxes was a strong function of dissolved PAH concentrations and surface water temperatures. During most of the year, PAHs from the sampling site volatilized from surface waters to the atmosphere, with a period of high volatilization occurring between July and September 1997. During this period, water temperatures and dissolved PAH concentrations were elevated as compared to other times of the year. A period of net gas absorption was observed for most PAHs between November 1997 and January 1998 when water temperatures were lowest and dissolved concentrations decreased as compared to the previous months. Overall, for most PAH fluxes a seasonal trend of high net volatilization was measured between late summer and early fall when dissolved PAH concentrations and surface water temperatures were high and with a change to net absorption during the months of late November–January.

All PAHs measured, except phenanthrene, had a mean daily flux of net volatilization (Table 1). The mean daily fluxes were calculated by temporally extrapolating among the fluxes calculated every ninth day between March 1997 and March 1998 and the fluxes measured at site 3 during the sampling intensives. Each flux represented the 4 days before and 4 days after the sample was taken. The average daily fluxes ranged from 140 ng m$^{-2}$ day$^{-1}$ absorption for phenanthrene to 4500 ng m$^{-2}$ day$^{-1}$ volatilization for acenaphthlene.

Annual fluxes were calculated by multiplying the average daily fluxes by 365 days (Table 2). Annual gas exchange fluxes for fluoranthene in the Patapsco River are similar to the fluxes

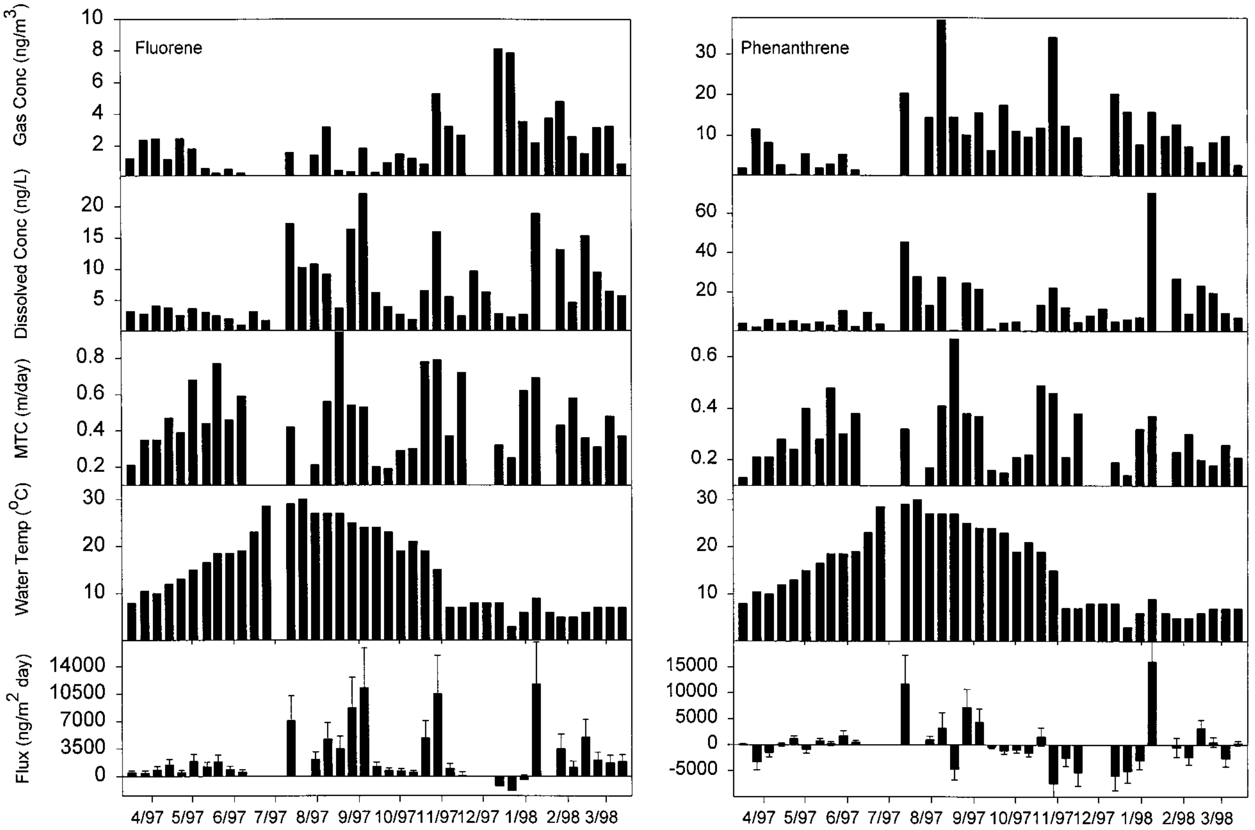

**FIGURE 4. Fluorene and phenanthrene concentrations in the air and water, surface water temperatures, mass transfer coefficients (MTC), and daily fluxes measured every 9 days between March 17, 1997, and March 13, 1998. Error bars represent the overall propagated error associated with the flux.**

**TABLE 1. Average and Range of Gaseous and Dissolved PAH Concentrations and Gas Exchange Fluxes Collected from the Patapsco River (Site 3) during Three Intensive Campaigns and Every 9 Days between March 1997 and March 1998**

| | gaseous concn (ng/m$^3$)$^a$ | | | dissolved concn (ng/L)$^b$ | | | flux (ng m$^{-2}$ day$^{-1}$)$^c$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | mean | min | max | mean | min | max | mean | min (↓) | max (↑) |
| 2-methylnaphthylene | 1.81 | 0.13 | 18.5 | 4.8 | 0.65 | 55 | +7 000 | −322 | +82 000 |
| acenaphthalene | 0.18 | <0.01 | 8.3 | 0.81 | 0.13 | 16 | +420 | −2 400 | +7 400 |
| acenaphthene | 0.20 | <0.01 | 2.5 | 5.5 | 0.86 | 39 | +4 500 | +9 | +39 000 |
| fluorene | 1.6 | 0.27 | 9.7 | 5.0 | 0.98 | 22 | +2 200 | −1 800 | +12 000 |
| phenanthrene | 7.8 | 0.28 | 44 | 7.4 | 0.38 | 70 | −140 | −7 500 | +16 000 |
| anthracene | 0.02 | <0.01 | 2.9 | 1.6 | 0.03 | 7.5 | +610 | −450 | +5 100 |
| 4,5-methylphenanthrene | 0.13 | <0.01 | 1.5 | 1.6 | 0.46 | 10 | +550 | −100 | +3 300 |
| 1-methylanthracene | 0.13 | 0.08 | 8.2 | 1.3 | 0.03 | 5.9 | +100 | −2 300 | +1 700 |
| 1-methylphenanthrene | 0.10 | 0.01 | 4.83 | 0.76 | 0.11 | 4.1 | +130 | −530 | +1 100 |
| fluoranthene | 1.5 | 0.12 | 6.8 | 8.9 | 2.2 | 53 | +1 100 | −850 | +10 000 |
| pyrene | 1.1 | <0.01 | 6.4 | 6.6 | 0.19 | 35 | +590 | −1 900 | +6 600 |
| benzo[*a*]fluorene | 0.10 | 0.01 | 0.56 | 0.58 | 0.23 | 5.5 | +120 | −94 | +1 300 |
| chrysene | 0.04 | <0.01 | 0.29 | 0.55 | 0.04 | 4.5 | +3 | −160 | +430 |

[a,b] Averages represent geometric means of samples collected every 9 days and samples collected at site 3 during each intensive. [c] Positive flux = net volatilization, and negative flux = net absorption.

measured by Gustafson and Dickhut (*5*) in the Elizabeth River (Table 2). The Elizabeth River, like the Patapsco River, is located in a heavily industrialized area with many coal-burning power plants and shipyards. Both rivers have elevated dissolved PAH concentrations as compared to those measured in the York River (*5*) and northern Chesapeake Bay (*4*). However, annual fluxes of lighter PAHs measured in the Patapsco River varied from other annual flux measurements made around the Chesapeake Bay. Fluorene volatilized from the Patapsco River but is deposited to the southern Chesapeake Bay (*5*) and the northern Chesapeake Bay (*4*). The difference in annual fluxes may be driven by the elevated dissolved fluorene concentrations measured in the Patapsco River and lower gaseous concentrations as compared to measurements made in the northern Chesapeake Bay (*4*).

To place the magnitude of these fluxes in perspective, the estimated annual fluxes were compared to the dissolved PAH inventory in the water column at the one in nine water site (depth was equal to 7 m). Annual PAH volatilization losses for compounds between 1-methylnaphthalene and anthracene are equal to or greater than 20 times the dissolved inventory in the water column. For heavier compounds such as fluoranthene, pyrene, and benzo[*a*]fluorene, the losses from volatilization are as high as 10 times the dissolved inventory. This suggests that the compounds have a short residence time (weeks to days) in the water column and that

**TABLE 2. Annual Gas Exchange Fluxes ($\mu$g m$^{-2}$ yr$^{-1}$) of PAHs From Surface Waters of the Chesapeake Bay[a]**

| | Patapsco River[b] ($\mu$g m$^{-2}$ yr$^{-1}$) | York River[c] ($\mu$g m$^{-2}$ yr$^{-1}$) | Elizabeth River[c] ($\mu$g m$^{-2}$ yr$^{-1}$) | N. Chesapeake Bay[d] ($\mu$g m$^{-2}$ yr$^{-1}$) |
|---|---|---|---|---|
| fluorene | +800 | −140 | −64 | −17 |
| phenanthrene | −51 | −740 | −480 | −78 |
| fluoranthene | +400 | −170 | +300 | −15 |
| anthracene | +220 | −25 | +4.8 | −3.3 |
| pyrene | +210 | −73 | +29 | −7.7 |
| chrysene | +1.1 | −1.5 | +31 | −0.37 |

[a] Positive flux = net volatilization, and negative flux = net absorption. [b] This study. [c] Ref *5*. [d] Ref *4*.

additional sources of PAHs to the river are replenishing the dissolved PAH concentrations. During high wind conditions, resuspension of contaminated bottom sediment (*26*) may replace water column PAH inventories, and during precipitation events, PAHs could enter the water column via wet deposition (*16*) or through discharge of urban runoff directly into the harbor. Phenanthrene's annual net absorption flux equaled 99% of the dissolved inventory of phenanthrene in that portion of the Patapsco River water column. This further supports the short residence time of a chemical in the water column where gas absorption has the potential to be a dominant source of phenanthrene concentrations to the water. With such short residence times and large inventories of PAHs being removed and absorbed through gas exchange, this is an extremely active system where air−water exchange has the potential to be a dominant source, transport, and removal process of PAHs to coastal waters.

**Comparing PAH Fluxes between Urban and Northern Chesapeake Bay.** The urban annual gas exchange rate of phenanthrene measured in the urban Patapsco River is similar (in both direction and magnitude) to that measured in the northern Chesapeake Bay (Table 2; *4*). Comparable phenanthrene exchange rates in the urban and northern bay do not imply similar concentrations of phenanthrene in the air and water but rather that both the urban atmosphere and the surface water are enriched in phenanthrene, resulting in a comparable gradient to that measured in the northern part of the bay. The annual urban gas exchange rates for other individual PAHs are much different in both direction and magnitude than those calculated by Nelson et al. (*4*) in the northern Chesapeake Bay. Many PAHs, including fluorene, fluoranthene, and pyrene, volatilize from surface waters in the urban area in contrast to annual absorptive fluxes measured in the northern bay (*4*). With relatively high average dissolved phase concentrations in the Patapsco River (5.0, 8.9, and 6.6 ng/L for fluorene, fluoranthene, and pyrene, respectively) as compared to average dissolved phase concentrations measured in the northern bay (1.4, 1.3, and 0.8 ng/L for fluorene, fluoranthene, and pyrene, respectively (*4*)), the differential gradient is driven by the dissolved PAH concentrations, resulting in net volatilization in the urban waters. As gaseous PAHs volatilize from the river via air−water exchange and are transported through the atmosphere, they can be redeposited into the northern Chesapeake Bay. This cycling of near-shore PAH volatilization and northern bay absorption suggests that the urban surface waters of Baltimore are a net source of gaseous PAHs to the surrounding atmosphere. This volatilization contributes to the total gaseous PAH concentrations in the regional atmosphere, which may redeposit into the mainstem of the northern Chesapeake Bay. Thus, with gas absorption contributing to greater than 90% of the total atmospheric loadings of selected PAHs to the Chesapeake Bay (*4*), air−water exchange may likely be the dominant process controlling the transport and fates of these chemicals from the urban atmosphere to open waters.

## Acknowledgments

We express our appreciation to Steve Eisenreich for guiding the AEOLOS project and to the crew of the EPA *OSV Anderson* for their help in sample collection. We also acknowledge Rick Hebert, Dan Liebert, and Carrie Dennenfelser for their laboratory assistance. The AEOLOS project was funded by a grant from the U.S. Environmental Protection Agency (EPA CR 822046-01-0). This is the University of Maryland Center for Environmental Science Contribution No. 3079.

## Supporting Information Available

PAH fluxes for all compounds and error analysis (30 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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*Received for review December 21, 1998. Revised manuscript received April 8, 1999. Accepted April 13, 1999.*

ES981324E