

# Seasonal and Annual Air–Water Exchange of Polychlorinated Biphenyls across Baltimore Harbor and the Northern Chesapeake Bay

HOLLY A. BAMFORD, FUNG CHI KO, AND JOEL E. BAKER\*

*Chesapeake Biological Laboratory, University of Maryland, Center for Environmental Science, Solomons, Maryland 20688*

As part of the Atmospheric Exchange Over Lakes and Oceans Study (AEOLOS), air–water exchange fluxes of polychlorinated biphenyls (PCBs) were determined along a transect in the Baltimore Harbor from the Inner Harbor of Baltimore, MD, to the mainstem of the northern Chesapeake Bay to assess the overall contributions of urban source PCBs through air–water exchange and their impacts on coastal waters. Six sites were sampled during three intensive sampling periods in June 1996, February 1997, and July 1997 and at two sites (urban and rural) every ninth day between March 1997 and March 1998 to measure spatial and temporal variability in the PCB air–water exchange fluxes. During the intensive sampling campaigns, net total PCB (*t*-PCBs) volatilization fluxes ranged between 5 and 2120 ng m<sup>-2</sup> day<sup>-1</sup>, varying on both temporal and spatial scales. Volatilization fluxes were highest in February, driven by high winds and elevated dissolved PCB concentrations. Throughout the annual sampling period, *t*-PCB volatilization fluxes were similar between urban (130 μg m<sup>-2</sup> yr<sup>-1</sup>) and rural (120 μg m<sup>-2</sup> yr<sup>-1</sup>) sites. Approximately 10% of the dissolved *t*-PCB inventory in the water column in Baltimore Harbor exchanges with the atmosphere each day. From air–water exchange alone, the estimated residence time of dissolved *t*-PCBs in the harbor is approximately 10 days (estimated hydraulic residence time of water in the harbor is between 7 and 14 days), indicating that air–water exchange is an efficient removal mechanism of *t*-PCBs from urban coastal waters. Furthermore, the annual flux of *t*-PCBs volatilizing from Baltimore Harbor is approximately 12% of the gas-phase *t*-PCB inventory over the water, and at the northern Chesapeake Bay site, the *t*-PCB flux is approximately 40% of the gas-phase *t*-PCB inventory. This suggests that air–water exchange of *t*-PCBs has the potential to be a significant source of PCBs to the rural atmosphere.

## Introduction

In coastal areas, large urban-industrial centers increase inventories of semivolatile organic contaminants in water through stormwater runoff, treated sewage discharge, riverine inputs, and wet and dry deposition and in air through vehicular and industrial emissions and reversible exchange of gaseous components across the air–water and air–soil

interfaces (1–8). The relative importance of each process depends directly upon the source of the contaminant, the physical–chemical properties of the compound, and the micro- and macroscale meteorological conditions of the region. For polychlorinated biphenyls (PCBs), air–water exchange between the atmosphere and surface waters is a dominant transport process, influencing the PCB concentrations, fate, and residence times in the water and regional atmosphere (9–13). A PCB mass balance study in Lake Michigan reported that the average mean PCB gross gas depositional fluxes were 30 times higher than the average PCB dry deposition flux and that the magnitude and direction of the fluxes varied seasonally (14). In the Chesapeake Bay region, Nelson et al. (15) estimated PCB gas exchange fluxes across the air–water interface of the mainstem of the Bay and determined that the annual loss of PCBs by volatilization was more than 10 times larger than inputs to the bay from wet and dry deposition. PCBs generally volatilize from the Chesapeake Bay throughout the year, demonstrating the importance of air–water exchange as a possible source of PCBs to the regional atmosphere (15). However, elevated atmospheric and water concentrations of PCBs observed around urban-industrial areas, which can lead to enhanced fluxes in coastal urban areas, were not investigated during the previous study.

Gas-phase PCB concentrations are significantly higher in Baltimore as compared to over bay and rural locations (16). PCB concentrations in Baltimore Harbor surficial sediments greatly exceed those measured in the mainstem of the Chesapeake Bay (17). While there is no doubt that organic contaminant concentrations are enriched in urban environments relative to remote locations, the spatial and temporal extent of the urban influence on air–water exchange in the northern Chesapeake Bay has not been quantified for PCBs. To specifically address the impact of urban areas on nearshore coastal water, the Atmospheric Exchange Over Lakes and Oceans Study (AEOLOS) was conducted in Chicago/southern Lake Michigan and Baltimore Harbor/northern Chesapeake Bay (2, 4, 13, 16, 18–23). Polycyclic aromatic hydrocarbon concentrations and air–water exchange fluxes have been reported for the Baltimore Harbor/northern Chesapeake Bay (4, 16). The primary objectives of this study were to determine the magnitude and direction of PCB gas exchange fluxes and to quantify the spatial and seasonal trends in these fluxes in the Baltimore Harbor/northern Chesapeake Bay area. Furthermore, our goal was to assess the overall contributions of urban source PCBs from Baltimore through air–water exchange and its impact on PCB inventories to these coastal waters and the regional atmosphere.

The strategy of this study was (i) to collect simultaneous air and water samples at multiple sites along a transect from the Baltimore Harbor to the northern Chesapeake Bay during seasonal intensive campaigns and (ii) to collect air and water samples at urban and rural locations on a regular basis for 1 yr. A gradient flux model that incorporated gaseous and dissolved concentrations, wind speeds, and temperature-corrected Henry's law constants was used to estimate air–water exchange fluxes for PCBs. Spatial and daily variations in PCB fluxes were quantified from the samples collected during three sampling intensives, while annual gas exchange fluxes were estimated from samples collected every 9 days between March 1997 and March 1998 at the urban and rural locations.

\* Corresponding author phone: (410)326-7205; fax: (410)326-7341; e-mail: baker@cbl.umces.edu.

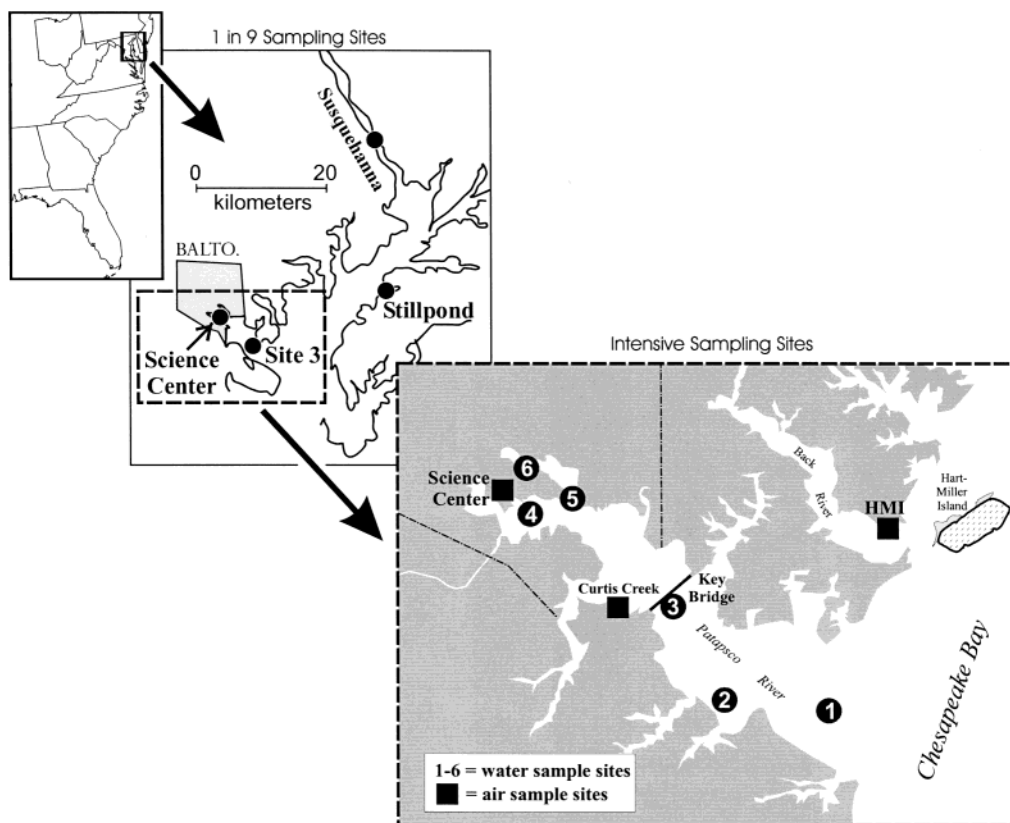


FIGURE 1. Map of northern Chesapeake Bay and Baltimore Harbor illustrating air and water collection sites during the three intensive sampling campaigns and annual sampling between March 1997 and March 1998.

## Experimental Methods

**Sampling Strategy.** Surface water and air samples were collected during the three sampling intensives conducted in the Baltimore Harbor in June 1996, February 1997, and July 1997 (4, 16). Two sets of air–water pairs (urban and rural) were also collected every ninth day between March 1997 and March 1998 (Figure 1). The urban set was collected within the Baltimore Harbor area, and the rural site was collected in the northern Chesapeake Bay region approximately 41 km north-northeast of the city along the eastern shore of the bay and the Susquehanna River (Figure 1). Latitudinal and longitudinal position of each air and water site are listed in Table 1S in Supporting Information.

During the intensives, consecutive 12-h air samples were collected at each of the sites. The 24-h air samples were collected for one in 9-day samples. Details of air sampling are presented elsewhere (4, 15, 16) and briefly described below. Modified General Metal Works high-volume air samplers were used, which housed a glass fiber filter and polyurethane foam (PUF) plug in series. Surface water samples were collected in 18-L polished stainless steel tanks. The particulate and dissolved phases were separated by pumping the raw water through a glass fiber filter (Schleicher & Schuell no. 25; 0.7  $\mu$ m nominal pore size) and Amberlite XAD-2 macroresin (Sigma) (4). Meteorological data including wind speed, wind direction, and air temperature were collected from the Key Bridge by the Maryland Department of Transportation, Key Bridge Authority (35 m above the water).

**Analytical Procedures.** Details of the analytical procedures were previously described and will be summarized here (4, 15, 16). Prior to extraction, two PCB congeners not found in industrial syntheses or in the environment (2,3,5,6-tetrachlorobiphenyl, IUPAC no. 65, and 2,3,4,4',5,6-hexachlorobiphenyl, IUPAC no. 166) were added as surrogates to each

PUF and XAD sample to monitor analytical recovery. After Soxhlet extraction, extracts were separated on a packed column of Florisil (60–100 mesh, J. T. Baker Co.) to remove polar interferences (24). The purified extracts were concentrated and analyzed using a Hewlett-Packard 5890 gas chromatography with a DB-5 column (J&W Scientific) and an electron capture detector (GC-ECD). Each sample was analyzed for 55 individual PCB congeners and 28 chromatographically unresolved congener groups. Many of the heavier PCB congeners were not above detection in both the dissolved and the gas phases. Therefore, total PCB (*t*-PCB) concentrations only included those congeners that were consistently quantified in both phases, which included 24 individual PCB congeners and 21 chromatographically unresolved congener groups. Internal standards (Ultra Scientific) consisting of 2,3,6-trichlorobiphenyl (IUPAC congener 30) and 2,2',3,4,4',5,6,6'-octachlorobiphenyl (IUPAC congener 204) were added to each sample prior to instrumental analysis to calculate relative response factors for each congener. Each PCB congener was identified based on its retention time relative to a standard mixture of PCB Aroclors 1232, 1248, and 1262 (Ultra Scientific) whose peaks were identified in Mullin (25).

**Quality Control and Assurance.** For the dissolved-phase samples, surrogate recoveries were  $72\% \pm 22\%$  ( $n = 130$ ) for IUPAC no. 65 and  $79\% \pm 24\%$  ( $n = 130$ ) for IUPAC no. 166. Vapor-phase samples surrogate recoveries were  $71\% \pm 16\%$  ( $n = 90$ ) for IUPAC no. 65 and  $89\% \pm 23\%$  ( $n = 90$ ) for IUPAC no. 166. On the basis of fairly consistent percent recoveries among vapor and dissolved samples, PCB congener concentrations in each sample were not surrogate corrected.

Laboratory and field blanks were incorporated in the analytical analysis to quantify possible contamination due to collection, transport, and extraction. The detection limits were derived from the blanks and defined as three times the mean concentration in the blank for each PCB congener.

TABLE 1. Mean and Range of Gaseous and Dissolved PCB Concentrations by Homologue Group and Gas Exchange Fluxes Collected from the Baltimore Harbor and Northern Chesapeake Bay Every 9 Days between March 1997 and March 1998

	gaseous concn (pg/m <sup>3</sup> ) <sup>a</sup>			dissolved concn (pg/L)			flux (ng m <sup>-2</sup> day <sup>-1</sup> ) <sup>b</sup>		
	mean	min	max	mean	min	max	mean	min	max
Baltimore Harbor									
dichloro	43	10	196	28	1.5	346	+33	-9.4	+257
trichloro	113	24	614	100	8.9	562	+77	-4.4	+467
tetrachloro	74	15	230	154	39	442	+119	+10	+393
pentachloro	51	7.8	191	81	19	261	+63	+7.4	+206
hexachloro	31	5.3	122	81	15	199	+51	+3.3	+125
<i>t</i> -PCBs	330	67	1400	500	100	1520	+350	+19	+1240
Northern Chesapeake Bay									
dichloro	5.7	0.6	37	23	2.0	196	+26	+0.94	+236
trichloro	17	0.8	121	58	21	120	+43	+6.2	+107
tetrachloro	17	0.64	105	116	46	237	+97	+15	+304
pentachloro	13	0.8	80	89	40	279	+75	+15	+240
hexachloro	7.8	0.9	44	104	70	244	+76	+17	+235
<i>t</i> -PCBs	70	5.1	370	430	246	940	+330	+90	+1150

<sup>a</sup> Averages represent geometric means. <sup>b</sup> Positive flux = net volatilization, and negative flux = net absorption.

Detection limits for individual PCB congeners ranged from 0.40 to 90 pg/L in the dissolved samples and 0.003 to 0.60 pg/m<sup>3</sup> in the air samples.

## Results and Discussion

**Gas-Phase Concentrations.** For the June 1996 intensive, the spatial and daily trends of the atmospheric PCB concentrations in the Baltimore area have been reported elsewhere (16) and are summarized below. PCB gas-phase concentrations during June varied spatially, with higher concentrations in Baltimore city at the Fort McHenry site as compared to the rural site on Hart Miller Island (HMI). Average gas-phase concentrations for *t*-PCBs at Fort McHenry were 1.3 ng/m<sup>3</sup> ( $n = 4$ ) and ranged between 0.3 and 2.9 ng/m<sup>3</sup>, and at HMI they were 0.39 ng/m<sup>3</sup> ( $n = 4$ ) and ranged between 0.14 and 0.62 ng/m<sup>3</sup>. During southeasterly winds, the *t*-PCBs air concentrations at Fort McHenry were the highest (June 9, *t*-PCBs = 2.9 ng/m<sup>3</sup>), indicating an emission source in the heavily industrialized section along the south shores of the harbor (16). Similar to June 1996, the *t*-PCB gas-phase concentrations in the city at the Science Center and Curtis Creek sites were consistently higher than the HMI site during the February and July 1997 sampling intensives. In February, the *t*-PCB concentrations at both Science Center and Curtis Creek sites were approximately 2.5 times higher than those at HMI. The *t*-PCB gas-phase concentrations in February at the Science Center and Curtis Creek sites ranged between 0.20 and 0.70 ng/m<sup>3</sup>, and at HMI they ranged between 0.12 and 0.19 ng/m<sup>3</sup>. In contrast to February, July *t*-PCB concentrations measured during the three sample days at Curtis Creek (1.1, 1.0, and 1.0 ng/m<sup>3</sup>) were higher than at the Science Center (0.51, 0.76, and 0.92 ng/m<sup>3</sup>) and at HMI (0.50, 0.24, and 0.54 ng/m<sup>3</sup>). Curtis Creek is centrally located along the industrialized section of the south shoreline, and volatilization from industrial/terrestrial sources, driven by higher ambient temperatures, may increase *t*-PCB concentrations (26, 27). During all three intensives, the congener distribution was dominated by the di-, tri-, tetra-, and pentachlorobiphenyls, accounting for approximately 90% of the *t*-PCB gas concentrations.

Overall, gas-phase concentrations in Baltimore were highest in June and lowest in February. Elevated *t*-PCB gas concentrations in June were partly driven by an increase in air temperature and by a change in wind direction. During the February and July 1997 sampling intensives, the winds were predominantly from the north-northeast direction, meaning air masses from the industrialized area of Baltimore

did not extend over the northern Chesapeake Bay toward HMI. The wind speeds during July were fairly constant, averaging 2 m/s. In February, the winds were more variable, with speeds ranging from 1 to 11 m/s over the water. High wind speeds coming from the north-northeast direction may dilute the *t*-PCB air concentrations measured around Baltimore, contributing to low gas-phase concentrations during this time of year.

Air samples collected every ninth day between March 1997 and March 1998 at the urban Science Center and the rural Stillpond site also showed a spatial gradient in *t*-PCB gaseous concentrations with significantly higher concentrations ( $\alpha = 0.01$ ;  $\rho < 0.001$ ) at Science Center relative to Stillpond (Table 1). The *t*-PCB gas-phase concentrations at both sites were log-normally distributed, and the geometric mean of *t*-PCBs at the Science Center was 0.33 ng/m<sup>3</sup> ( $n = 35$ ) and at Stillpond was 0.07 ng/m<sup>3</sup> ( $n = 28$ ). Significantly higher PCB concentrations at the Science Center is a strong indication of a gas-phase source of PCBs in Baltimore relative to background and rural locations. Gas-phase *t*-PCB concentrations from the Science Center are similar to those measured in the northern bay by Nelson et al. (15; range 0.20–0.92 ng/m<sup>3</sup>). Seasonal variability in *t*-PCB concentrations was observed at the Science Center, with higher concentrations measured during the late summer to fall months (geometric mean 0.68 ng/m<sup>3</sup> between July and November 1997) as compared to other times of the year (geometric mean 0.20 ng/m<sup>3</sup> between December and March). This seasonal trend is consistent with studies conducted in the Great Lakes region, where volatilization of PCBs from industrial/terrestrial sources increases during warmer months (13, 26, 27). The congener distribution measured in air at both sites was similar to the PCB gas distribution during the intensive sampling, with di- through pentachlorobiphenyls accounting for approximately 85% of *t*-PCB concentrations in air.

**Dissolved-Phase Concentrations.** During all three sampling campaigns, elevated surface water *t*-PCB concentrations were measured at site 4 (Middle Branch,  $1.2 \pm 0.26$  ng/L ( $n = 10$ )) relative to concentrations measured outside the Key Bridge away from the Inner Harbor ( $0.63 \pm 0.14$  ng/L ( $n = 16$ )). Site 4 is located near Gwynn's Falls, an urban outfall that discharges directly into Middle Branch. This spatial variability may have resulted from meteorological conditions (high wind speeds in February 1997; rain events in June and February), which resuspended contaminated sediments (17, 28–30) or increased urban runoff. PCB concentrations in



the sediments of the harbor range from 8 to 2150 ng/g dry weight, with higher concentrations localized around industrial outflows and urban runoffs (17).

Dissolved *t*-PCB concentrations did not vary seasonally among the intensives, with harbor concentrations ranging between 0.46 and 1.2 ng/L in June, between 0.57 and 1.4 ng/L in February, and between 0.20 and 1.7 ng/L in July. These concentrations are similar to average dissolved *t*-PCB concentrations measured in the Chesapeake Bay in 1993 ( $0.92 \pm 0.47$  ng/L; 15). Tri-, tetra-, and pentachlorobiphenyl congeners made up approximately 23%, 38%, and 14%, respectively, of the total dissolved PCB concentrations during the June and July intensives. The tri-, tetra-, and pentachlorobiphenyl congeners also dominated the homologue distribution during the February sampling intensive, making up approximately 28%, 23%, and 21%, respectively, of the total dissolved PCB concentration.

Dissolved-phase *t*-PCB concentrations collected from site 3 in Baltimore Harbor and in the Susquehanna River every ninth day between March 1997 and March 1998 ranged between 0.10–1.5 and 0.25–0.94 ng/L, respectively, with highest concentrations measured in the spring for both locations (Table 1). Annual average concentrations were statistically similar ( $\alpha = 0.01$ ;  $\rho = 0.12$ ) between site 3 in the harbor ( $0.5 \pm 0.17$  ng/L;  $n = 35$ ) and Susquehanna River ( $0.42 \pm 0.15$  ng/L;  $n = 28$ ) and were within the range of dissolved PCB concentrations measured previously in the northern Chesapeake Bay but higher than those in the southern Chesapeake Bay (15). Compared to other aquatic systems proximate to urban areas, the dissolved PCB concentrations in this study were significantly higher than recently reported for southern Lake Michigan (range 0.08–0.48 ng/L; 13) and Grand Traverse Bay, Lake Michigan ( $0.12 \pm 0.05$  ng/L; 31), but lower than those in Raritan Bay (range 1.4–1.8 ng/L; 32) and New York Harbor (range 3.5–4.2 ng/L; 32). The homologue distribution for site 3 in the harbor is similar to the homologue distribution observed during the intensive sampling, where the tri-, tetra-, and pentachlorobiphenyl congeners made up approximately 21%, 31%, and 17%, respectively. However, the Susquehanna River is enriched in heavier weight congeners as compared to site 3 in the harbor, with tetra-, penta-, and hexachlorobiphenyl congeners accounting for 28%, 21%, and 25%, respectively, of the total distribution.

**Air–Water Exchange Model.** The modified version of the Whitman two-film resistance model (10, 33) was used to calculate gas exchange rates for each PCB congener measured. Details of these calculations have previously been published (4, 15) and are briefly summarized here. The flux of each PCB congener across the air–water interface is modeled using estimates of mass transfer coefficients describing transfer through the gas and liquid phases and the concentration gradient between the paired dissolved- and gas-phase PCB congener measurements:

$$F = K_{OL}(C_d - C_a/K_H) \quad (1)$$

where  $F$  is the flux ( $\text{ng m}^{-2} \text{ day}^{-1}$ );  $K_{OL}$  is the overall mass transfer coefficient ( $\text{m/day}$ );  $C_d$  and  $C_a$  ( $\text{ng/m}^3$ ) are the measured dissolved- and gaseous-phase concentrations; and  $K_H$  is the dimensionless, temperature-corrected Henry's law constant.  $K_{OL}$  is empirically derived from field and laboratory studies, based on correlations with wind speed and molecular diffusivities (34), and determined here from the daily wind speed and surface water temperature measured during each sampling period (4, 12, 13, 15, 33). The concentration gradient is calculated from the dissolved- and gas-phase PCB concentrations and the temperature-corrected Henry's law constant. Fluxes were not calculated when the PCB concentration gradient was within two standard deviations of

zero. Individual PCB gas and dissolved concentrations, mass transfer coefficients, concentration gradients, flux, and error in the flux for all samples are listed in Tables 2S–6S in Supporting Information.

The magnitude and direction of gas exchange calculations are very sensitive to  $K_H$ . Correct assessment of the temperature dependence of  $K_H$  is essential in order to determine the direction and magnitude of the flux. For some PCB congeners, a 10-fold increase in  $K_H$  is measured with a 20 °C change (35, 36). Each individual PCB congener was corrected for ambient temperatures using temperature dependence data from Bamford et al. (36):

$$\ln K_H = -(\Delta H_H/RT) + (\Delta S_H/R) \quad (2)$$

where  $\Delta H_H$  ( $\text{kJ/mol}$ ) is the enthalpy of phase change or transfer across the air–water interface,  $\Delta S_H$  ( $\text{kJ mol}^{-1} \text{ K}^{-1}$ ) is the entropy of phase change,  $R$  is the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is temperature (K). Individual  $\Delta H_H$  values for PCBs that were experimentally measured or derived (36) were used. The previous study of PCB fluxes by Nelson et al. (15) estimated  $K_H$  using an empirical relationship derived by Brunner et al. (37) and corrected to ambient temperatures using an average  $\Delta H_H$  for all PCB congeners. The differences in the fluxes due to different  $K_H$  values and  $\Delta H_H$  used in each study were evaluated by recalculating the fluxes from Nelson et al. (15) using the new temperature-corrected  $K_H$  values used in this study. The recalculated fluxes of individual PCB congeners yielded higher net volatilization for most congeners because  $K_H$  for many PCB congeners varies more with temperature than previously thought. For example, the recalculated flux for PCB congener 52 from the northern Chesapeake Bay during March 1993 changed from 16 to 33  $\text{ng m}^{-2} \text{ day}^{-1}$  net volatilization. The differences among the  $\Delta H_H$  of individual congeners is as high as 91%, demonstrating the considerable variability in the  $K_H$  temperature dependence among individual congeners (36). Therefore, it was necessary to use  $\Delta H_H$  of individual congeners to accurately predict the temperature-specific  $K_H$  of PCB congeners.

**Uncertainty in Gas Exchange Fluxes.** The uncertainty in each of the fluxes was evaluated using a propagation of error analysis derived from Shoemaker et al. (38), which has been used in previous studies (4, 15, 23). For each congener (or congener groups), random measurement errors in  $C_a$  and  $C_d$  and in  $K_{OL}$  are taken into account. The summation of the various random errors in the flux are described by

$$\lambda^2(F) = \left(\frac{\partial F}{\partial K_{OL}}\right)^2 (\lambda K_{OL})^2 + \left(\frac{\partial F}{\partial C_d}\right)^2 (\lambda C_d)^2 + \left(\frac{\partial F}{\partial C_a}\right)^2 \quad (3)$$

where  $\lambda$  is the coefficient of error. The values of  $\lambda$  for  $C_d$  and  $C_a$ , determined by replicate samples and the relative standard deviations of sample surrogate recoveries, were  $\pm 15\%$  and  $\pm 20\%$ , respectively. The  $\lambda$  for  $K_{OL}$  was estimated by the uncertainty in the air and water mass transfer coefficients. Because of the large uncertainties in the air and water mass transfer coefficients (34) and the nonlinear effect of wind speed on the water mass transfer coefficient (39),  $\lambda$  was assumed to be  $\pm 40\%$  although it may be as high as 200% (4, 15). The  $K_H$  term was removed from the overall error analysis because errors in  $K_H$  from incorrect temperature corrections are assumed to be systematic and not random errors. For PCB congeners, the estimated average uncertainty in the fluxes were  $\pm 46\%$ . Most of the uncertainty associated with the fluxes was attributed to  $K_{OL}$  (74%) and the uncertainties due to the effect variations in wind speed have on the water-side mass transfer coefficient (39). The uncertainty in the flux calculations for each congener are listed in Tables 2S–6S in Supporting Information.

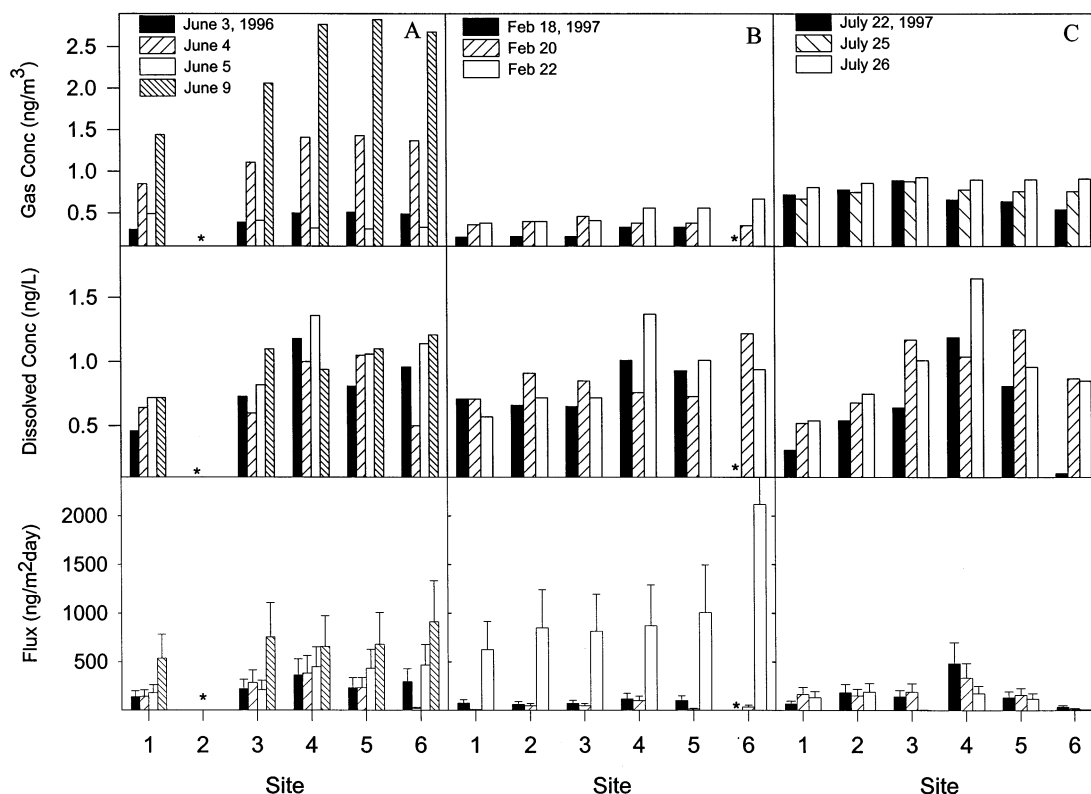


FIGURE 2. Gaseous and dissolved *t*-PCB concentrations and daily gas exchange rates measured during (A) June 1996, (B) February 1997, and (C) July 1997. Error bars represent the overall propagated error associated with the flux. An asterisk (\*) indicates that no data were available.

**Gas Exchange Fluxes During Intensive Sampling.** For the three intensives, instantaneous fluxes were calculated based on PCB dissolved concentrations measured at each of the six sites, which were paired with gas-phase concentrations interpolated by distance from the shoreline air sites. During all three intensives, *t*-PCBs volatilized from the surface waters to the atmosphere (positive fluxes) at all sampling sites along the harbor (Figure 2) because of relatively high dissolved PCB concentrations as compared to the gas phase. Despite elevated PCB gas-phase concentrations measured in Baltimore in June, the concentration gradient favored net PCB volatilization. By homologue, tri- through pentachlorobiphenyls accounted for approximately 80% of the total fluxes.

The magnitude of the PCB fluxes varied widely on daily, seasonal, and spatial scales in the harbor during all three intensives. The largest net volatilization flux occurred in Baltimore's Inner Harbor (site 6) during the February intensive, with *t*-PCB flux reaching  $2120 \text{ ng m}^{-2} \text{ day}^{-1}$  (Figure 2B). Despite dissolved- and gas-phase concentrations remaining relatively constant over the February sampling period, the magnitude of the flux was driven by high wind speeds recorded on February 22. Increased wind speeds from an average of 1 m/s on February 20 to 11 m/s on February 22 resulted in a 40-fold increase in the mass transfer coefficient for *t*-PCBs and a 57-fold increase in instantaneous *t*-PCBs fluxes measured in the Inner Harbor at site 6 (Figure 2B). On both February 18 and 20,  $K_{OL}$  was  $< 0.2$ , resulting in low gas exchange fluxes relative to February 22. The impact of wind speed on the magnitude of *t*-PCB fluxes was also observed during the June intensive. Highest net volatilization fluxes ( $910 \text{ ng m}^{-2} \text{ day}^{-1}$  on June 9) were calculated on days when  $K_{OL}$  increased above 0.6 m/day (Figure 2A). The majority of the PCB fluxes were controlled by the water-side mass transfer, and wind speed has a nonlinear effect on the water-side mass transfer coefficient. Turbulent mixing at the air-water interface facilitates the total mass transfer, increasing

the magnitude of the fluxes. The lowest net volatilization flux of  $5 \text{ ng m}^{-2} \text{ day}^{-1}$  was estimated during the July sampling intensive when very little turbulent mixing took place at the air-water interface.

A spatial gradient was observed in PCB fluxes during the June intensive, with smallest net volatilization fluxes typically measured outside the Key Bridge (sites 1–3) and increasing around sites 4–6. Volatilization fluxes also increased at site 4 near Gwynn's Falls during the July intensive (Figure 2A). This trend was driven by the changes in the measured dissolved concentrations at these sites, possibly due to urban runoff discharged directly into the harbor or resuspension of contaminated sediments (17). Overall, there were large variations in the gas exchange fluxes for PCBs on both a temporal and a spatial scale. PCB fluxes ranged between 20 and  $910 \text{ ng m}^{-2} \text{ day}^{-1}$  during the four days in June, between 10 and  $2120 \text{ ng m}^{-2} \text{ day}^{-1}$  during the three days in February, and between 5 and  $480 \text{ ng m}^{-2} \text{ day}^{-1}$  during the three days in July.

**Annual Gas Exchange Fluxes.** Annual air-water exchange fluxes were calculated from samples taken every 9 days between March 1997 and March 1998. The urban Baltimore Harbor sampling pair consists of the dissolved PCB concentrations measured at site 3 in the harbor and the PCB gaseous concentrations measured at the Science Center. The rural northern Chesapeake Bay sampling pair consists of the dissolved PCB concentrations measured from the Susquehanna River and the air samples collected at the Stillpond eastern shore site. The 35 and 28 air and water pairs were used to calculate the fluxes for the Baltimore Harbor and northern Chesapeake Bay sites, respectively.

Throughout the year, PCB volatilized from the surface waters at both the Baltimore Harbor and the northern Chesapeake Bay sites (Figure 3). The direction of the fluxes were strongly influenced by elevated dissolved PCB concentrations that remained relatively constant throughout the

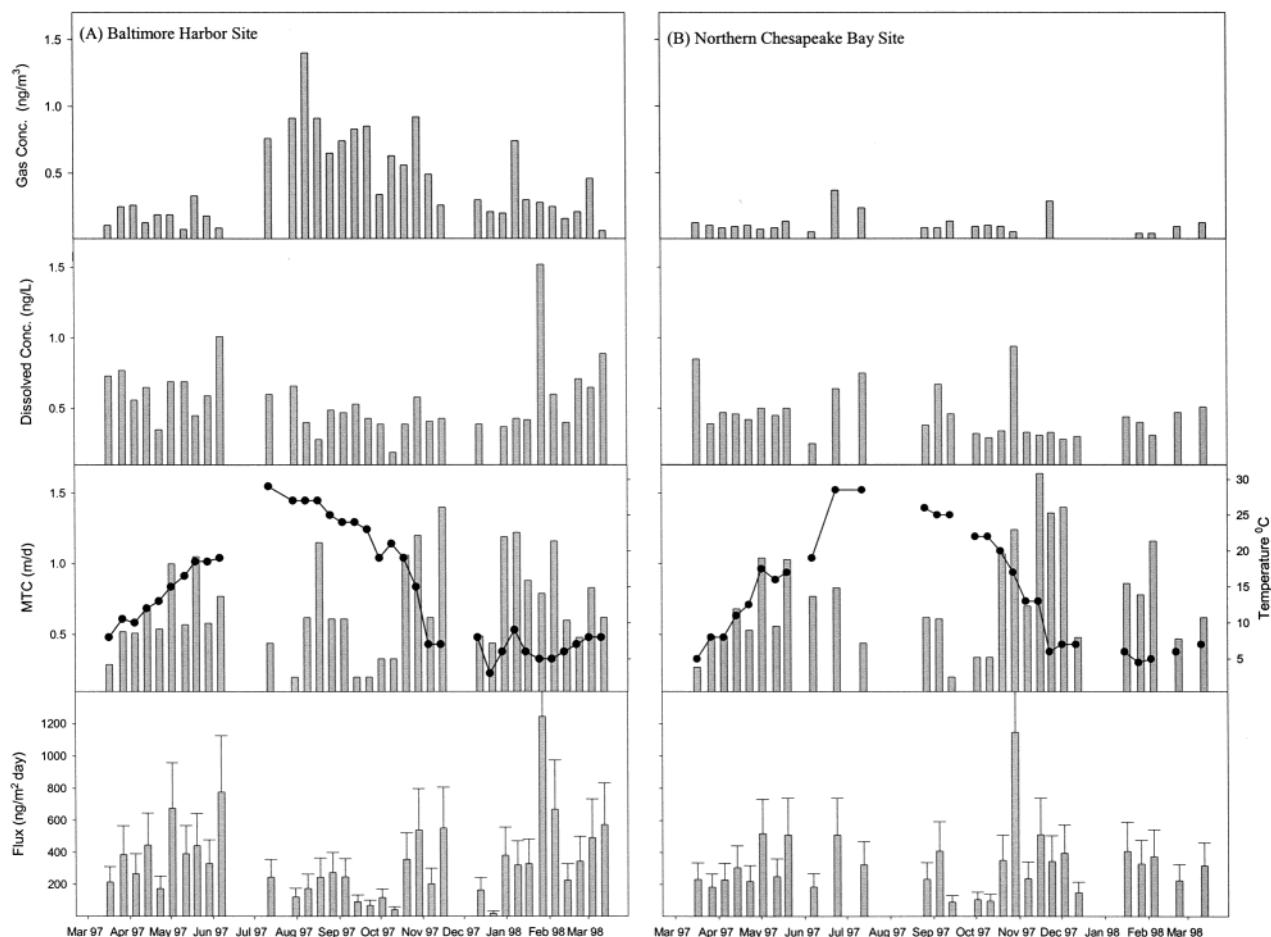


FIGURE 3. *t*-PCB concentrations in the air and water, mass transfer coefficients (MTC), surface water temperatures, and daily fluxes measured every 9 days between March 1997 and March 1998 in (A) Baltimore Harbor and (B) northern Chesapeake Bay. Error bars represent the overall propagated error associated with the flux.

year as compared to the gas-phase PCB concentrations. Despite increased PCB gas-phase concentrations measured during the summer months in Baltimore, net fluxes were positive, driven by the water-side gradient due to supersaturation of dissolved PCBs. The largest concentration gradient in favor of net volatilization was measured on October 29, 1997, at the northern Chesapeake Bay site and on January 27, 1998, in Baltimore Harbor resulting in the highest net fluxes measured during the year at both sites. To quantify the significance of the concentration gradient, the total net flux was divided into its gross volatilization and deposition fluxes and compared individually. Throughout the year, PCB gross volatilization and gross gas depositional fluxes in Baltimore Harbor ranged from +180 to +1300 ng m<sup>-2</sup> day<sup>-1</sup> and from -6 to -180 ng m<sup>-2</sup> day<sup>-1</sup>, respectively (Figure 4). At the northern Chesapeake Bay site, the PCB gross volatilization and gross gas deposition fluxes ranged from +92 to +1200 and from -1 to -93 ng m<sup>-2</sup> day<sup>-1</sup>, respectively. The ratio of volatilization fluxes to depositional fluxes ranged between 2 and 110 at Baltimore Harbor and from 5 to 400 at northern Chesapeake Bay, demonstrating the dominance of the water-side concentrations in the overall concentration gradient.

Lower PCB volatilization fluxes occurred during the late summer months between July and October 1997 in Baltimore Harbor due to elevated PCB gas concentrations in the city during the summer as well as lower recorded wind speeds during these months. A seasonal trend was not observed at northern Chesapeake Bay where both air and water concentrations remained relatively constant throughout the year. Overall, *t*-PCBs were volatilizing from the surface water

throughout the year at both Baltimore Harbor and northern Chesapeake Bay locations, and a seasonal trend in PCB fluxes was observed in Baltimore Harbor with lower net volatilization fluxes occurring in the late summer months.

Mean daily fluxes were calculated for *t*-PCBs by temporally extrapolating among the fluxes calculated every ninth day between March 1997 and March 1998. Assuming that each flux represented the 4 days before and 4 days after the sample was taken, the annual average daily fluxes were 350 ng m<sup>-2</sup> day<sup>-1</sup> volatilization for *t*-PCB for Baltimore Harbor and 330 ng m<sup>-2</sup> day<sup>-1</sup> volatilization for northern Chesapeake Bay (Table 1). Multiplying the average daily fluxes by 365 days, the annual PCB gas exchange fluxes from the surface waters to the atmosphere are 130 and 120 μg m<sup>-2</sup> yr<sup>-1</sup> for Baltimore Harbor and northern Chesapeake Bay, respectively. Comparable annual average *t*-PCB fluxes in Baltimore Harbor and northern Chesapeake Bay locations does not imply similar concentrations of *t*-PCBs in the air and water. The atmosphere in Baltimore is enriched in *t*-PCB during the summer months, reducing net volatilization fluxes in the summer, which results in a lower annual average similar to that measured in northern Bay. Average daily *t*-PCB fluxes at both Baltimore Harbor and northern Chesapeake Bay are higher than the average flux recalculated from Nelson et al. (15) for the mainstem of the Chesapeake Bay (+240 ng m<sup>-2</sup> day<sup>-1</sup>) but similar in both direction and magnitude to the average flux recalculated from Nelson et al. (15) for the northern Chesapeake Bay (+390 ng m<sup>-2</sup> day<sup>-1</sup>). The urban coastal region around Baltimore contributes to elevated *t*-PCB dissolved concentrations, generating higher net volatilization fluxes in the harbor and northern bay as compared to the

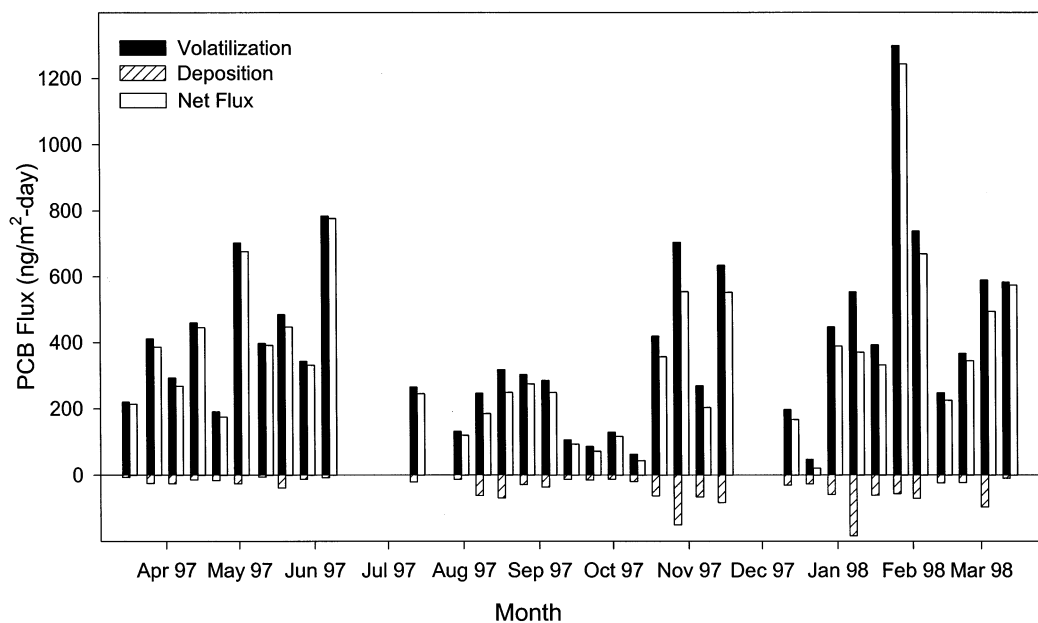


FIGURE 4. Absorption, volatilization, and net gas exchange flux of *t*-PCBs in Baltimore Harbor between March 1997 and March 1998. Net fluxes are positive, dominated by water-side concentration gradient.

mainstem bay average. These fluxes are also higher than the  $63 \text{ ng m}^{-2} \text{ day}^{-1}$  estimated for Lake Superior in 1992 (11) and the range of  $-32$  to  $+59 \text{ ng m}^{-2} \text{ day}^{-1}$  estimated for southern Lake Michigan in 1994–1995 (13). Average *t*-PCB fluxes from Raritan Bay and New York Harbor in 1998 were  $+400$  and  $+2100 \text{ ng m}^{-2} \text{ day}^{-1}$ , respectively (32), which are higher than both Baltimore Harbor and northern Chesapeake Bay fluxes.

On average, the congener distribution of the annual PCB volatilization fluxes from Baltimore Harbor were similar to the congener distribution of the intensive fluxes, with tri- (20%), tetra- (35%), penta- (19%), and hexachlorobiphenyl (17%) accounting for approximately 90% of the total flux. The tri-, tetra-, penta-, and hexachlorobiphenyls also accounted for approximately 90% of the total flux for northern Chesapeake Bay. However, unlike Baltimore Harbor, the contribution of the hexachlorobiphenyls to the total was higher than that of the trichlorobiphenyls. The total flux at northern Chesapeake Bay was approximately 29% tetra-, 23% penta-, and 23% hexa-, and the trichlorobiphenyls only accounted for 14% of the total flux. Congener distribution of volatilization fluxes at both sites followed the PCB distribution in the dissolved phase (see Figure 1S in Supporting Information).

**Implications of Air–Water Exchange to Coastal PCB Cycling.** To place the magnitude of these fluxes in perspective, the estimated daily fluxes of PCBs from Baltimore Harbor were compared to the dissolved PCB inventory in the water column. With an average water depth of 7 m and an average dissolved *t*-PCB concentration of  $0.5 \text{ ng/L}$ , the dissolved *t*-PCB inventory for this site is  $3500 \text{ ng/m}^2$ . Comparing this to the average daily *t*-PCB flux ( $350 \text{ ng m}^{-2} \text{ day}^{-1}$ ), approximately 10% of the dissolved *t*-PCB inventory exchanges with the atmosphere on a daily basis. If air–water exchange was the only loss process for *t*-PCBs from the water column, the residence time of *t*-PCBs in the Baltimore Harbor is 10 days. Totten et al. (32) estimated the residence time for PCBs in Raritan Bay via air–water exchange to range between 14 and 87 days, depending on the variations in PCB dissolved concentrations and wind speeds. The estimated residence time of *t*-PCBs in the Baltimore Harbor is similar to the hydraulic residence time of water in the harbor, which is estimated to be between 7 and 14 days (40–42). This suggests that removal of *t*-PCBs via air–water exchange is an important loss process of these contaminants from coastal waters.

Furthermore, it also suggests that additional sources of PCBs to the Baltimore Harbor are replenishing the dissolved PCB concentrations given that the dissolved *t*-PCB concentration remains relatively constant throughout the year. The Baltimore Harbor is a highly dynamic shallow system with a thin layer of water positioned between two large geochemical reservoirs of contaminants, atmosphere, and sediment (40). During high wind conditions, resuspension of contaminated sediment (17) may support water column *t*-PCB inventories, and during precipitation events *t*-PCBs may enter the water column via wet deposition (16) or by two major stormwater outfalls where urban runoff directly enters into the harbor. The surface waters are enriched with *t*-PCBs relative to the overlying atmosphere, resulting in net PCB volatilization throughout the year where the regional atmosphere is a sink for PCBs from Baltimore Harbor.

The annual flux of PCBs from the Baltimore Harbor site was also compared to the gas-phase *t*-PCB inventory to estimate the overall contribution of air–water exchange in controlling the gas-phase PCB concentrations in the atmosphere over the Baltimore Harbor using a simple well-mixed box model. Simple box models do not take into account complex mixing between the surface layer and higher altitudes, and the resulting predictions are in turn rough estimates, which vary depending on the environmental parameters used in the model. However, these models are quite useful as a first approach to predicting pollutant concentrations in an air mass over a region. We assumed a 1 km atmospheric mixing height, a 20 km (the average length of the harbor) by 3 km water surface over the Baltimore Harbor (the average width of the harbor), and that the only source of gas-phase *t*-PCBs to this area is from air–water exchange. With a wind speed of  $2 \text{ m/s}$  perpendicular to the box and an annual PCB volatilization rate of  $350 \text{ ng m}^{-2} \text{ day}^{-1}$ , the calculated steady-state air concentration in the box is  $0.04 \text{ ng/m}^3$  from air–water exchange. This is approximately 12% of the actual *t*-PCB gas-phase concentration ( $0.33 \text{ ng/m}^3$ ) measured in Baltimore. In the city where contributions of gas-phase PCBs from industrial/terrestrial sources exists, the contribution of gas-phase PCBs concentration from air–water exchange is relatively low. Using the box model for the northern Chesapeake Bay site away from local sources, the steady-state air concentration from air–water exchange is  $0.03 \text{ ng/m}^3$ . Comparing this to the average



PCB gas-phase concentration over the northern Chesapeake Bay ( $0.07 \text{ ng/m}^3$ ), air–water exchange accounts for approximately 40% of the actual *t*-PCB gas-phase concentration, suggesting that air–water has the potential to be a significant source of PCBs to the rural atmosphere. The exchange of PCBs from the water column to the overlying atmosphere is a relatively rapid process, resulting in the efficient exchange of PCBs between these two reservoirs. With a short residence time in the water column, this is an extremely active system where air–water exchange is an important loss mechanism controlling the transport, fate, and removal of *t*-PCBs from these urban coastal waters. It also has the potential to be a significant source of *t*-PCBs to the rural atmosphere where local emissions do not exist.

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## Supporting Information Available

Table 1S lists air and water sampling site descriptions; Tables 2S–6S list the PCB temperature-corrected Henry's law constant, gas and dissolved concentrations, mass transfer coefficients, concentration gradient, flux, and uncertainty in the flux for each congener for samples collected during the three intensives and the Baltimore and northern Chesapeake Bay annual sampling; Figure 1S illustrates the average percent total of gas phase, dissolved phase, and net flux for PCBs by homologue groups in Baltimore and northern Chesapeake Bay. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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