

Atmospheric Concentrations and Deposition of Polychlorinated Biphenyls to the Hudson River Estuary

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The first estimates of atmospheric deposition fluxes of polychlorinated biphenyls (PCBs) to the Hudson River Estuary are presented. Concentrations of PCBs were measured in air, aerosol, and precipitation at nine sites representing a variety of land-use regimes at regular intervals from October 1997 through May 2001. Highest concentrations in the gas phase were observed at urban sites such as Camden and Jersey City (Σ PCB concentrations averaged 3250 and 1260 pg m^{-3} , respectively). In great portions of the state encompassing forested, coastal, and suburban environments, gas-phase Σ PCB concentrations were essentially the same (averaging 150–220 pg m^{-3}). This spatial trend suggests that atmospheric PCBs arise from highly localized, urban sources which influence atmospheric concentrations and deposition fluxes over a distance of a few tens of kilometers. Atmospheric Σ PCB deposition fluxes (gas absorption + dry particle deposition + wet deposition) ranged from 7.3 to 340 $\mu\text{g m}^{-2} \text{yr}^{-1}$ and increased with proximity to urban areas. While the magnitude of the fluxes increased with urbanization, the relative proportions of wet, dry, and gaseous deposition remained largely constant. Because the Hudson River Estuary is adjacent to urban areas such as Jersey City, it is subject to higher depositional fluxes of PCBs. These depositional fluxes are at least 2–10 times those estimated for the Chesapeake Bay and Lake Michigan. Inputs of PCBs to the Hudson River Estuary from the upper Hudson River and from wastewater treatment plants are 8–18 times atmospheric inputs, and volatilization of PCBs from the estuary

exceeds atmospheric deposition of low molecular weight PCBs.

Introduction

Wet deposition via rain and snow, dry deposition of fine/coarse particles, and gaseous air–water exchange are major pathways for persistent organic pollutant (POP) input to the Great Waters such as the Great Lakes and Chesapeake Bay (1, 2). Many urban/industrial centers are located on or near coastal estuaries (e.g., the Hudson River Estuary, NY Bight, and Delaware River) and the Great Lakes (e.g., Chicago, IL, and southern Lake Michigan). Emissions of pollutants into the urban atmosphere are reflected in elevated local and regional pollutant concentrations and atmospheric deposition that are *not* observed in the regional signal (3, 4). The Hudson River Estuary has been impacted by anthropogenic inputs of polychlorinated biphenyls (PCBs) from many sources, including wastewater discharges (5) and historical contamination of the upper Hudson River (6). The New Jersey Atmospheric Deposition Network (NJADN) was established in late 1997 as a research and air monitoring network (i) to characterize the regional atmospheric levels of hazardous air pollutants, (ii) to estimate atmospheric loadings to aquatic and terrestrial ecosystems, (iii) to identify and quantify regional versus local sources and sinks, and (iii) to identify environmental variables controlling atmospheric concentrations of PCBs, polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides, trace metals, Hg, and nutrients. The first three sites were located within the Hudson River Estuary: New Brunswick, Jersey City, and Sandy Hook (Figure 1). The NJADN was gradually expanded during 1997–2000 to a total of nine sites representing a variety of land-use regimes.

The NJADN design is based on the well-developed experience in the Great Lakes and Chesapeake Bay. The Integrated Atmospheric Deposition Network (IADN) operating in the Great Lakes (3, 4) and the Chesapeake Bay Atmospheric Deposition Study (CBADS) (7) were designed to capture the *regional* atmospheric signal, and thus, sites were typically located in background areas away from local sources. On the basis of this experience, NJADN was designed to capture both the urban and regional signals of air pollution by locating monitoring sites (Figure 1) in urban (Jersey City and Camden), suburban (New Brunswick, Washington Crossing, Chester), forested (Pinelands), and coastal (Sandy Hook, Tuckerton, Delaware Bay) environments. The objective of this work is to summarize the NJADN PCB data from October 1997 through May 2001.

Methods

Details of sample collection, preparation, extraction, and analysis can be found elsewhere (8, 9) and will be summarized here. Air samples (24 h) were typically collected at 12 d frequencies using a modified high-volume air sampler (Tisch Environmental, Village of Cleves, OH) with a calibrated airflow of $\sim 0.5 \text{ m}^3 \text{ min}^{-1}$. Quartz fiber filters (QFFs; Whatman) were used to capture the particulate phase, and polyurethane foam plugs (PUFs) were used to capture the gaseous phase. QFFs were weighed before and after sampling to determine total suspended particles (TSPs). Wet-only integrating precipitation samplers were employed (Meteorological Instrument Center, MIC, Richmond Hill, ON, Canada) to collect integrated precipitation samples over 12–24 d in a 0.212 m^2 stainless steel funnel that drained through a glass column containing XAD-2 resin.

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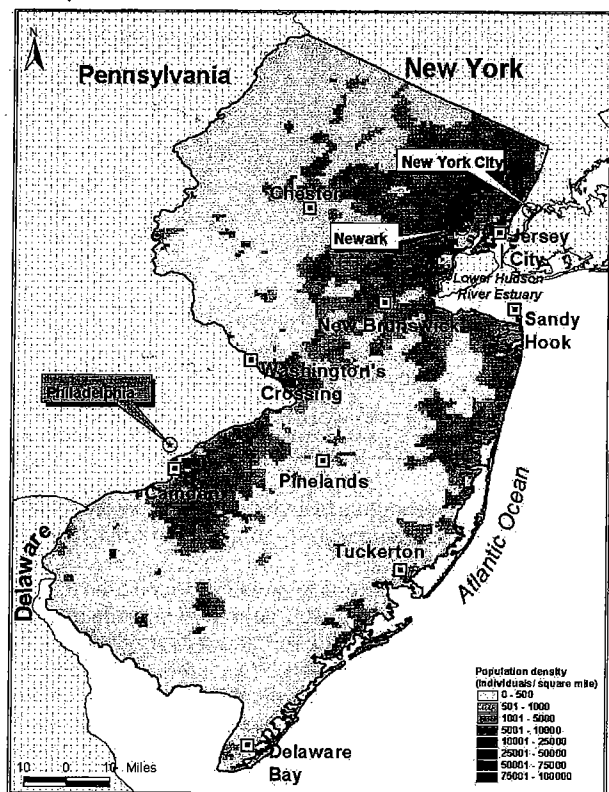


FIGURE 1. Map of New Jersey with population density, depicting sampling sites of the New Jersey Atmospheric Deposition Network (squares).

Analytical Procedures. Samples were injected with surrogate standards (PCBs 14, 23, 65, and 166) before extraction. Because an interference with PCB 14 was observed in most samples, PCB 23 was used as a surrogate after mid-2000. Each sample was extracted in a Soxhlet apparatus for 24 h in petroleum ether (PUFs), dichloromethane (QFFs), or 1:1 acetone/hexane (XAD). For XAD samples, the extracts were then liquid-liquid extracted in 60 mL of Milli-Q water. The aqueous fractions were back-extracted with 3×50 mL of hexane in separatory funnels with 1 g of sodium chloride. These and all other extracts were then reduced in volume by rotary evaporation and subsequently concentrated via N_2 evaporation. The samples were then fractionated on a column of 3% water-deactivated alumina. The PCB fraction was eluted with hexane, concentrated under a gentle stream of nitrogen gas, and injected with internal standard containing PCBs 30 and 204 prior to analysis. PCBs were analyzed on an HP 6890 gas chromatograph equipped with a ^{63}Ni electron capture detector using a 60 m, 0.25 mm i.d. DB-5 (5% diphenyl dimethyl polysiloxane) capillary column with a film thickness of 0.25 μm . A total of 60 peaks representing 93 congeners were quantified.

Quality Assurance. Field blanks and matrix spikes were used for quality control purposes. The method detection limit (MDL) for each congener was determined from field blanks by taking the mean of the mass detected in all field blanks plus 3 times the standard deviation about the mean. No significant differences were observed between masses of PCBs measured in field blanks collected at the different sampling sites. Thus, one detection limit was calculated which applies to all sites. ΣPCB method detection limits were 19, 18, and 1.5 ng for QFF, PUF, and XAD samples, respectively. These can be converted to concentration units by dividing by the exact sample volume. Typical sample volumes are 600 m^3 for QFF and PUF samples, and 30 L for XAD samples. The relative percent difference between two side-by-side samples for

$\Sigma PCBs$ was 2% for QFFs and 9% for PUFs. Surrogate recoveries averaged more than 78% for PCBs 23, 65, and 166 in all matrices and were used to correct individual compound concentrations for surrogate recoveries. PCB concentrations measured in precipitation and particle-phase samples were also corrected for laboratory blank masses as described by VanRy et al. (10). Gas-phase PCB concentrations were not corrected for laboratory blanks because masses in the blanks were in all cases less than 5% of the mass in the samples.

Several PUFs were cut in half before deployment in the field to quantify gas-phase breakthrough. The bottom half PUF contained on average ($n = 3$) 13% of the total mass of PCBs, and on average less than 10% of each individual congener ($n = 3$), except for the di- and trichloro-PCBs, for which a maximum of 31% was found in the bottom half PUF.

Framework for Deposition Calculations. The dry deposition flux (F_{dry}) consists of the product of the concentration of PCBs in each particle size fraction (C_i) times the deposition velocity of that size fraction ($V_{d,i}$), summed over all size fractions:

$$F = \sum_{i=1}^n C_i V_{d,i} \quad (1)$$

Because it is difficult and expensive to collect size-fractionated particle samples, high-volume air samplers were used to collect a bulk atmospheric particle sample. The dry deposition flux is calculated from the resulting data by applying a single deposition velocity (V_d) to the bulk particle phase:

$$F_{dry} = V_d C_{part} \quad (2)$$

where F_{dry} is the flux ($ng\ m^{-2}\ d^{-1}$) and C_{part} is the average particle concentration of the chemical ($ng\ m^{-3}$). Zufall et al. (11) provide convincing evidence that particle deposition is dominated by large particles. We selected a value for the V_d of $0.5\ cm\ s^{-1}$ that reflects the disproportionate influence that large particles have on atmospheric deposition, especially in urbanized and industrialized regions (12–14). Other studies have employed a deposition velocity of $0.2\ cm\ s^{-1}$ (4, 15). Thus, the choice of V_d represents by far the largest source of error in the calculation of dry deposition flux. Moreover, V_d may differ between sites due to changes in particle characteristics.

Wet deposition fluxes (F_{wet}) were estimated at each site as follows:

$$F_{wet} = C_{VWM} P \quad (3)$$

where C_{VWM} is the volume-weighted mean concentration of the chemical in precipitation and P is the precipitation intensity ($m\ yr^{-1}$). The standard error of the volume-weighted mean concentration ranged from 14% to 32% (10), and this error dominates the error in F_{wet} .

Calculations of absorptive gas fluxes ($F_{gas,abs}$) are described in refs 9 and 16–21 and will be summarized here. These fluxes represent absorption of PCBs into a real or hypothetical water body which, for the purposes of easy comparison between sites, is assumed to have zero salinity. In Raritan Bay, where salinity is typically about 0.35 M, the correction for salinity caused a 28% increase in the H values for PCBs (9). The modified two-layer model used assumes that the rate of gas transfer is controlled by the compound's ability to diffuse across the water and air layer on either side of the air-water interface. The net flux calculation is

$$F_{gas,net} = K_{OL} \left(C_d - \frac{C_a}{H} \right) \quad (4)$$

where $F_{gas,net}$ is the net flux ($ng\ m^{-2}\ d^{-1}$), K_{OL} ($m\ d^{-1}$) is the

overall mass transfer coefficient, $C_d - C_a/H$ describes the concentration gradient (ng m^{-3}), C_d (ng m^{-3}) is the dissolved-phase concentration of the compound in water, C_a (ng m^{-3}) is the gas-phase concentration of the compound in air which is divided by the dimensionless Henry law constant, $H' = H/RT$, R is the universal gas constant ($8.315 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$), H is the temperature-dependent Henry law constant ($\text{Pa m}^3 \text{ mol}^{-1}$), and T is the temperature at the air-water interface (K). For PCBs, values for H and its temperature dependence (ΔH_H) were taken from Bamford et al. (22, 23). The net flux is divided into volatilization ($F_{\text{gas,vol}}$) and absorption ($F_{\text{gas,abs}}$) terms as follows:

$$F_{\text{gas,vol}} = K_{\text{OL}} C_d \quad (5)$$

$$F_{\text{gas,abs}} = K_{\text{OL}} C_a / H \quad (6)$$

In this study, only the absorptive gas flux (eq 6) was calculated from gas-phase PCB concentrations measured at the land-based sites, because C_d was not available or not applicable. Calculation of $F_{\text{gas,abs}}$ requires knowledge of air and water temperature and wind speed. For this reason, $F_{\text{gas,abs}}$ was calculated separately for each day of sample collection, and the results were averaged to yield an annual estimate of $F_{\text{gas,abs}}$. Although salinity was assumed to be zero, an increase in H due to salinity will decrease the gas absorption flux directly due to the presence of H in eq 6 and indirectly as a result of a smaller increase in K_{OL} .

The error in $F_{\text{gas,abs}}$ (eq 6) depends on the uncertainty in K_{OL} , which has been found to be about 40% (18, 19, 24), and the uncertainty in C_a , which in this study is about 25%. The propagated error in $F_{\text{gas,abs}}$ is thus 47%. This figure does not encompass the error in H because it is assumed to be a systematic, not random, error (18, 19, 24).

Results and Discussion

Gas Phase. Gas-phase Σ PCB concentrations vary over more than 2 orders of magnitude from site to site in the region, with highest concentrations typically occurring in the urbanized areas of Camden and Jersey City (Figure 2). The strong association between urbanization and gas-phase PCB concentrations suggests that atmospheric PCBs in New Jersey arise primarily from highly localized, urban sources and that long-range transport is relatively unimportant. At Camden, Jersey City, New Brunswick, and Sandy Hook, gas-phase Σ PCB concentrations averaged 3250, 1260, 540, and 430 pg m^{-3} , respectively. At the five other sites (Pinelands, Chester, Delaware Bay, Washington Crossing, Tuckerton) encompassing forested, coastal, and suburban environments, Σ PCB concentrations were essentially the same (averaging 150–220 pg m^{-3}) and similar to concentrations observed from 1996 to 1998 at remote areas surrounding the Great Lakes, where concentration averages ranged from 63 to 260 pg m^{-3} (25). This level of contamination therefore appears to represent a regional (northeastern United States) background. Thus, the influence of high PCB concentrations appears to be localized within the urban zone. For example, the urban/industrial complex of New York City/Newark/northern New Jersey emits PCBs resulting in the high concentrations observed at Jersey City. These emissions, combined with PCBs volatilized from the Hudson River Estuary (9), result in concentrations of PCBs at the Sandy Hook and New Brunswick sites (30 and 40 km away from Jersey City, respectively) which are elevated over regional background. The urban/industrial area of Camden also emits PCBs resulting in gas-phase Σ PCB concentrations which are comparable to measurements in urban Chicago, IL (26). This local signal is, however, diminished by dilution and removal to regional background at Washington's Crossing and Pinelands, both about 45 km from Camden.

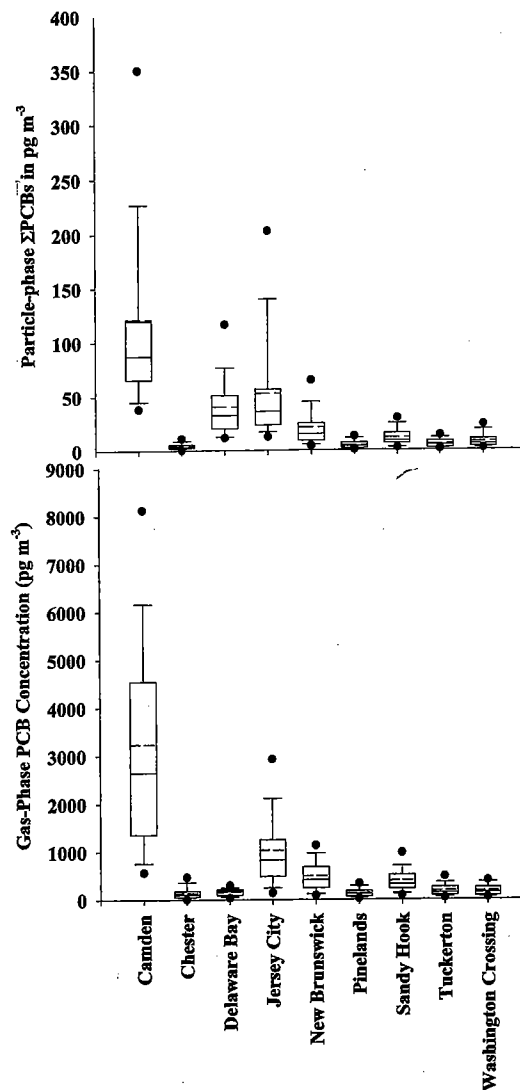


FIGURE 2. Box and whisker plot of particle-phase (upper panel) and gas-phase (lower panel) Σ PCB concentrations at all nine NJADN sites. The upper dot, upper error bar, upper edge of the box, lower edge of the box, lower error bar, and lower dot represent 95th, 90th, 75th, 25th, 10th, and 5th percentile concentrations, respectively. Within each box, mean and median concentrations are shown as dashed and solid lines, respectively.

The spatial pattern of concentrations observed near urban areas in New Jersey is similar to that observed around Chicago, IL, and Baltimore, MD. In Baltimore (27), Σ PCB concentrations ranged from 680 to 3360 pg m^{-3} (similar to those in Jersey City), while 18 km away, the range dropped to 210–740 pg m^{-3} (similar to those in Sandy Hook) and thence to 20–340 pg m^{-3} at a rural site 23 km downwind of Baltimore (similar to those at the five "less-impacted" sites in the present study). In Chicago, high concentrations of Σ PCBs in the urban area (14200–270 pg m^{-3}) are diluted to 780–230 pg m^{-3} at a rural site 125 km to the northwest (26). This site, South Haven, is thought to be impacted by sources of PCBs other than the Chicago urban/industrial complex (26). Thus, the range of PCB concentrations measured there is slightly higher than the range observed at the five less-impacted sites in this study.

Gas-phase PCBs are dominated by tri- and tetrachlorinated congeners, which comprise about 50–65% of the total measured PCBs at each site, with heavier homologue groups comprising decreasing percentages with MW. The dichloro congeners comprised from 8% to 18% of the total measured,

TABLE 1. Σ PCB Deposition Fluxes at the NJADN Sites

| site | gas absorption | | dry deposition (ng m ⁻² d ⁻¹) | wet deposition | |
|---------------------|--|---|---|---------------------------------------|--|
| | actual ^a (ng m ⁻² d ⁻¹) | modeled ^b (ng m ⁻² d ⁻¹) | | VWM \pm SE (ng L ⁻¹) | flux \pm SE (ng m ⁻² d ⁻¹) |
| Camden | 238 (4.0) | 310 | 53 ↑ | 13 \pm 2.8 | 44 \pm 9.3 |
| Chester | 4.1 (1.4) | 21 | 2.1 | 0.52 \pm 0.10 | 0.90 \pm 0.17 |
| Delaware Bay | 2.5 (1.1) | 18 | 6.5 | NM ^c | NM |
| Jersey City | 127 (4.9) | 119 | 23 | 3.9 \pm 0.72 | 11 \pm 2.0 |
| New Brunswick | 12 (1.8) | 59 | 9.4 | 1.3 \pm 0.18 | 3.0 \pm 0.44 |
| Pinelands | 6.2 (2.6) | 14 | 2.4 | 0.38 \pm 0.076 | 1.0 \pm 0.21 |
| Sandy Hook | 53 (5.4) | 43 | 5.1 | 0.80 \pm 0.23 | 2.1 \pm 0.60 |
| Tuckerton | 15 (5.0) | 18 | 2.9 | 0.35 \pm 0.11 | 0.85 \pm 0.27 |
| Washington Crossing | 19 (4.0) | 24 | 3.8 | NM | NM |

^a Gas absorption flux calculated using actual wind speeds (average wind speed (m s⁻¹) given in parentheses). ^b Gas absorption flux calculated assuming a constant wind speed of 5 m s⁻¹. ^c NM, not measured.

despite the fact that the analytical methods quantified a single dichloro chromatographic peak (consisting of PCBs 8 and 5).

PCB congener profiles were compared to assess whether sites are affected by similar PCB sources. The Delaware Bay site consistently demonstrated the lowest correlation coefficients with the other eight sites ($R^2 = 0.64-0.74$), suggesting that this site, geographically separated from the other eight, may be affected by different sources of PCBs. The next most dissimilar site was Camden; its correlation coefficients were the lowest in comparison with six of the seven remaining sites. This may again reflect different PCB sources in the Delaware River Basin. Correlation coefficients ranged from 0.79 to 0.98 at the other seven sites, suggesting that PCBs in the rest of the state arise from a single dominant source type or process.

Gas-phase concentrations of PCBs drive the gross gas absorption component of total atmospheric deposition, resulting in the highest gross gas absorption at Camden and Jersey City (Table 1). Wind speed is also a critical parameter in the calculation of gas absorption, evidenced by a higher gas absorption flux at Sandy Hook relative to New Brunswick, despite higher gas-phase PCB concentrations at New Brunswick. For the same reason, fluxes are higher at Tuckerton and Washington Crossing than at New Brunswick. It must be noted that the wind speeds were measured at a variety of land-based sites. Wind speeds over open waters such as Raritan Bay and Delaware Bay are likely to be higher than those measured over land (28), and the corresponding gas absorption fluxes are therefore likely to be higher. If the wind speed is assumed to be constant at 5 m s⁻¹, the gross gas absorption fluxes are a direct function of gas-phase PCB concentration: highest at the urbanized and impacted sites and lowest at the five less-impacted sites (Table 1). Given the 47% uncertainty in the gas absorption fluxes, it is not possible to state with certainty that gas absorption fluxes are different at the five regional background sites, but they are higher at the urban sites (Jersey City and Camden).

The homologue profile of the gas absorption fluxes is dominated by the low MW congeners to an even greater extent than the gas-phase concentrations, with congeners containing two to four chlorines contributing 60–95% of the overall gas absorption flux at all sites. No clear seasonal trend in gas absorption fluxes was observed.

Zhang et al. (20) calculated a gross gas absorption flux for southern Lake Michigan of approximately 27 ng m⁻² d⁻¹, about half that observed at Sandy Hook. Bamford (24) calculated gas absorption fluxes ranging from 6 to 120 ng m⁻² d⁻¹ in Baltimore Harbor and from 1 to 93 ng m⁻² d⁻¹ in northern Chesapeake Bay during 1997–1998. These are similar to the range in fluxes observed between Jersey City and New Brunswick.

Particle Phase. Typically, less than 10% of the total atmospheric Σ PCB burden is found in the particle phase. This percentage is higher during colder sampling periods due to the decrease in vapor pressure of PCB congeners at lower temperatures, increasing sorption onto airborne particles. The percentage is also higher, of course, for the higher MW PCBs. The homologue profile of particle-phase PCBs measured by NJADN is therefore different from the gas-phase profile. Dichloro congeners typically comprise less than 1% of Σ PCBs in the particle phase, while homologues containing three, four, five, or six chlorines each comprise about 20% of Σ PCBs in the particle phase. PCBs containing seven, eight, and nine chlorines make up about 10%, 5%, and 2% of the total particle-phase PCB burden, respectively.

Σ PCBs in the particle phase generally followed the same spatial trends as in the gas phase, with Camden and Jersey City exhibiting the highest concentrations and several sites (Chester, Delaware Bay, Pinelands, Sandy Hook, Tuckerton, Washington Crossing) displaying concentrations that rarely exceed 40 pg m⁻³ (Figure 2). Particle-phase Σ PCB concentrations at New Brunswick exceed this level in about 10% of the samples. These results are similar to observations at sites surrounding the Great Lakes (15), where particle-phase Σ PCB concentrations in remote regions are usually less than 40 pg m⁻³, but concentrations in Chicago frequently exceed 100 pg m⁻³. Particle-phase concentrations of Σ PCBs of less than 40 pg m⁻³ thus appear to represent a regional (northeastern United States) background. The spatial distribution of particle-phase PCBs observed in New Jersey demonstrates that, like gas-phase PCBs, particle-phase PCBs in this region arise from sources that are highly localized in urban areas. Dilution of the particle-phase PCB signal appears to occur more rapidly than dilution of the gas-phase PCB signal, with particle-phase concentrations approaching regional background even at New Brunswick and Sandy Hook.

By the algorithm chosen to calculate dry deposition fluxes, higher particle-phase Σ PCB concentrations translate directly into higher dry deposition fluxes (Table 1). However, because of the large uncertainty in the deposition velocity, the differences in dry deposition fluxes between sites may not be significant. Despite this uncertainty, it seems clear that dry deposition fluxes are generally higher in urban areas, due to higher particle-phase PCB concentrations. The calculated dry deposition fluxes are similar to those estimated for Lake Michigan (15), which average 3.3 ng m⁻² d⁻¹ in remote regions and 15 ng m⁻² d⁻¹ in Chicago. Hillery et al. (4) estimate Σ PCB dry deposition fluxes to Lakes Superior, Michigan, and Erie to be about 2 ng m⁻² d⁻¹ on the basis of particle-phase measurements at remote locations. Both these studies used a deposition velocity of 0.2 cm s⁻¹ (versus 0.5 cm s⁻¹ in the present study).

Precipitation Phase. A detailed analysis of VWM (\pm standard error) precipitation concentrations and wet deposition of PCBs has been conducted by VanRy et al. (10), and will be summarized here (Table 1). VWM concentrations of Σ PCBs at the seven sites at which precipitation was collected varied over 2 orders of magnitude. The spatial variations in concentrations mirrored those of the gas phase, with the highest concentrations occurring at Camden and Jersey City, followed by New Brunswick and Sandy Hook. The three less-impacted sites display the lowest VWM concentrations of all (rain samples were not collected at Delaware Bay and Washington Crossing). Offenber and Baker (2) observed a similar spatial pattern, with VWM concentrations of Σ PCBs in precipitation collected in Chicago, over Lake Michigan near Chicago, and at South Haven being 29.3, 5.8, and 0.1 ng L^{-1} , respectively.

Wet depositional flux is a function of both the VWM concentration and the precipitation intensity, but because precipitation is largely constant across the state, the wet deposition fluxes follow the same spatial trend as the VWM concentrations. Due to the lower uncertainty associated with the calculation of wet deposition fluxes, differences between the sites are clearly discernible, with the spatial trend once again suggesting that highly localized, urban sources of PCBs exert an influence over atmospheric concentrations and deposition fluxes over a distance of a few tens of kilometers. Hillery et al. (4) calculated wet deposition fluxes of Σ PCBs to the Great Lakes from observations at remote sites; the resulting averages ranged from 4 to 9 $\text{ng m}^{-2} \text{d}^{-1}$, slightly higher than the fluxes calculated for the three less-impacted sites in New Jersey. Offenber and Baker (2) calculated wet deposition fluxes on an event basis, but by applying a 30 yr average precipitation flux for Chicago of 85 cm yr^{-1} , their VWM concentrations may be converted to fluxes of 68, 14, and 0.2 $\text{ng m}^{-2} \text{d}^{-1}$ at Chicago, over Lake Michigan near Chicago, and at South Haven. Their results thus display a similar spatial pattern driven by urbanization, again suggesting that concentrations and fluxes of PCBs are diluted to background levels 30–50 km from the source.

At all sites except Camden, the homologue distribution of PCBs in precipitation was dominated by PCBs containing three to six chlorines (about 70–80% of the total), with dichloro congeners typically comprising less than 4% of Σ PCBs, and PCBs containing seven, eight, and nine chlorines comprising about 8%, 8%, and 1% of the total PCB burden, respectively. At Camden, high MW congeners (octa- and nonachloros) make up a much larger proportion of the total (45%).

Summary of Deposition by Land Use Type and Deposition Mode. Assuming a constant wind speed of 5 m s^{-1} , gas absorption represents 75–85% of the total atmospheric deposition of Σ PCBs at all sites except Delaware Bay, where gas deposition is estimated to contribute about 60% of the total. Because precipitation was not sampled at Delaware Bay, wet deposition flux there was estimated on the basis of the ratio between dry particle deposition and wet deposition at the other sites. Dry deposition comprises 10–17% of the total atmospheric deposition, and wet deposition is typically 4–8%, except at Camden, where it contributes 12% of the total deposition. The relatively high wet deposition flux at Camden is partly a result of the predominance of octa- and nonachlorinated congeners there, as seen in Figure 3 and discussed by VanRy et al. (10). Examining the deposition fluxes by homologue group (Figure 3) demonstrates that congeners containing two to five chlorines are primarily deposited by gas absorption. Congeners with six or more chlorines are primarily deposited via wet + dry deposition. These deposition patterns apply generally to all the land-use types investigated in this study. While the magnitude of the fluxes may increase with urbanization, the relative propor-

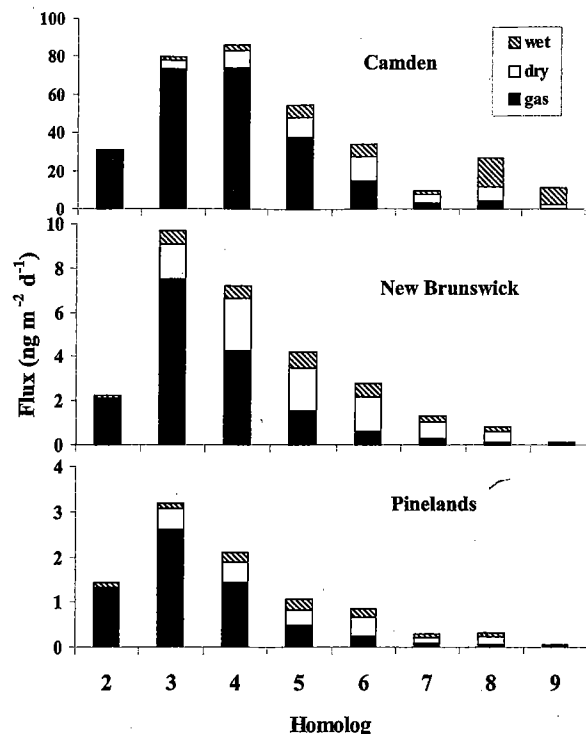


FIGURE 3. Gas absorption (black), dry particle deposition (white), and wet deposition (striped) fluxes of PCB homologues at three sites: Camden (top), New Brunswick (middle), and Pinelands (bottom). Note differences in the y-axis scales.

tions of wet, dry, and gaseous deposition remain largely constant, as demonstrated in Figure 3 for three sites: Camden (urban), New Brunswick (suburban), and Pinelands (forested). Delaware Bay represents an exception to this generalization. The gaseous, dry, and wet deposition fluxes at Delaware Bay are predicted to comprise about 60%, 25%, and 8–18% of the total, respectively. Thus, gas absorption is less important at Delaware Bay, even assuming a wind speed of 5 m s^{-1} .

Importance of Atmospheric Deposition of PCBs to the Hudson River Estuary. The estimated fluxes of Σ PCBs measured at Sandy Hook and Jersey City are assumed to represent the fluxes to the Hudson River Estuary, and may therefore be compared with those estimated for other aquatic systems. The sum of wet and dry particle deposition of Σ PCBs to the Chesapeake Bay estimated from CBADS data (1) and for the Great Lakes from IADN data (3, 4) are 4.9–9.0 and 2.7–6.8 $\text{ng m}^{-2} \text{d}^{-1}$, respectively. Comparing only wet and dry particle deposition, the Hudson River Estuary is loaded at a rate approximately 2–10 times the rate at which these other aquatic systems are loaded. At Jersey City and Sandy Hook, gaseous deposition of Σ PCBs dominates the overall depositional flux. Lower air concentrations of Σ PCBs in the Great Lakes and Chesapeake Bay areas suggest that gas deposition fluxes to these waters are not likely to exceed those to the Hudson River Estuary (3, 18, 26, 29). Thus, it is likely that the overall atmospheric deposition fluxes of PCBs to the Hudson River Estuary are at least 2–10 times those experienced in the Great Lakes and Chesapeake Bay.

Compared with other inputs of PCBs to the Hudson River Estuary, atmospheric deposition is small. It is estimated that, in 1998, water pollution control plants discharged about 88 kg of PCBs into the estuary (5). In addition, Farley et al. (30) estimate that the annual input of PCBs from the upper Hudson River at the Federal Dam in Troy, NY, was about 250 kg in 1997. Assuming that the plume of atmospheric contamination extends throughout the Raritan Bay and the New York/New Jersey Harbor area (surface area \sim 4700 km^2),

the current estimates of atmospheric deposition result in about 10 kg yr⁻¹ of ΣPCBs being deposited into the estuary.

The high concentrations of PCBs in the water column of the Hudson River Estuary contribute to a large volatilization flux (9, 31). Yan (31) reports that air-water exchange in Raritan Bay results in a gas absorption flux of 160 ng m⁻² d⁻¹, similar to that estimated at Jersey City. Yan (31) reports a volatilization flux of 330 ng m⁻² d⁻¹, however, resulting in a net loss of PCBs from the water column. Tri- and tetrachlorinated PCBs constitute about 85% of the volatilization signal. In contrast, congeners containing six to nine chlorines were near equilibrium with respect to air-water exchange. Thus, the total interaction of Raritan Bay with the atmosphere, encompassing gas exchange and dry and wet deposition, probably results in a net loss of low MW PCBs (congeners containing two to five chlorines) from the water column, but a net input of PCBs containing six to nine chlorines.

Acknowledgments

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Supporting Information Available

Four tables detailing annual average concentrations and depositional fluxes at all nine sites listed by congener and homologue group. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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