Environ. Sci. Technol. **2000**, *34,* 2410−2417

Atmospheric Seasonal Trends and Environmental Fate of Alkylphenols in the Lower Hudson River Estuary

DARYL A. VAN RY, JORDI DACHS, CARI L. GIGLIOTTI, PAUL A. BRUNCIAK, ERIC D. NELSON, AND STEVEN J. EISENREICH*

Department of Environmental Science, Rutgers University, 14 College Farm Road, New Brunswick, New Jersey 08901-8551

The atmospheric occurrence of nonylphenols and *tert*-octylphenol has been assessed at three sites in the lower Hudson River Estuary (LHRE). The samples ($n = 186$) were taken from June to December of 1998. Gas-phase nonylphenol (NP) concentrations at a coastal site (Sandy Hook) ranged from below the detection limit (DL) to 56.3 ng m^{-3}, while concentrations at a suburban site (New Brunswick) ranged from 0.13 to 81 ng m^{-3}. Gas-phase concentrations of *tert*-octylphenol (tOP) ranged from <DL to 1.0 ng m^{-3} at Sandy Hook and from 0.01 to 2.5 ng m^{-3} at New Brunswick. NPs and tOP exhibited seasonal dependence with higher gas-phase concentrations during summer than during fall and early winter. Temperature explained 40−62% of the variability in the log (gas phase) NP and tOP concentrations. Assessment of the influence of local wind direction on atmospheric NP concentrations provided evidence for the predominance of local sources rather than long-range transport. Based on simultaneous water and over-water gas-phase samples and subsequent estimation of air−water exchange fluxes, volatilization and advection to the Atlantic Ocean accounted for 40 and 26% of the removal of NPs from the water column of the LHRE, respectively. The estimated half-life of NPs in the water column of the LHRE was 9 days.

Introduction

Alkylphenol polyethoxylates (APEOs) are widely used as nonionic surfactants in industrial, commercial, and household detergent formulations (*1, 2*). They are also used as bulking agents in some paints and pesticides (*1, 3*). Worldwide, about 500 000 tons of APEOs are produced annually, with nonylphenol polyethoxylates (NPEOs) being the primary constituents (80%) of this class of surfactants (*1*). Biological transformations by progressive shortening of the APEO ethoxylate chain under aerobic and anaerobic conditions results in the formation of alkylphenol mono- and diethoxylates (*2, 4, 5*). However, it has been suggested that the final transformation to alkylphenols (APs) occurs primarily under anaerobic conditions (*2−4, 6−9*). Though most degradation studies have been performed in wastewater treatment systems (*2−4*), similar in situ transformations in natural aquatic environments are also feasible (*6, 10*). Nonylphenols (NPs) and *tert*-octylphenol (tOP), the main alkylphenols produced by this process, are persistent in the environment with half-lives of NPs and NPEOs in marine sediments on the order of 30−60 years (*11−13*). Due to their persistence and hydrophobicity, these APs bioaccumulate in aquatic food chains with bioaccumulation factors of $\sim 10^4$ (*14−17*). Furthermore, alkylphenols are toxic to aquatic organisms (*12, 16, 18−23*) and to vascular plants (*24, 25*). NPs and tOP have been shown to disrupt estrogen function at the receptor site (*26−28*) and to effect sex determination in populations of aquatic fauna (*19, 29*). For example, NPs have been reported to be three times more estrogenic than DDT (*26*).

The ubiquitous occurrence of APs in industrial and urban wastewaters has suggested that discharges from wastewater treatment plants may be an important source of NP and tOP to the environment (*2−4, 9, 30−32*). Research on the environmental fate of APEOs and their metabolites has mainly focused on rivers (*3, 33−37*), estuaries (*33, 34, 37−41*), groundwater (*31, 42*), marine systems (*43*), and the Laurentian Great Lakes (*36*). High concentrations of NP and tOP have been reported for estuaries located in urban and industrial areas. For example, NP concentrations range from 5 to 42 ug g^{-1} in sediments from the Venice Lagoon (Italy) (*41*) and from 3 to 30 μg L^{-1} in the water column of the Aire Estuary (U.K.). Water column concentrations are significantly lower in other estuaries such as the Krka River Estuary (20−1200 ng L^{-1}, Croatia) (*39*), the Tee estuary (ca. 130 ng L^{-1}, U.K.) (*44*), and the Lower Hudson River Estuary (15−120 ng L^{-1}, U.S.A.) (*38*). Recently, the occurrence of NPs in the atmosphere was reported for the first time in the New Jersey urban and coastal atmosphere (*38*). Volatilization of NPs from the lower Hudson River Estuary (LHRE) was found to be a source of NPs to the regional atmosphere. However, there is insufficient knowledge about the primary mechanisms that drive the environmental fate of APs. For example, the seasonal dependence of atmospheric AP concentrations and the relative importance of depositional processes and air−water exchange to the fate and transport of APs are unknown.

The results reported are a research component within the framework of the New Jersey Atmospheric Deposition Network (NJADN). NJADN is a research and monitoring network created to study the local, regional, and long-range transport of persistent organic pollutants (POPs) in the New York/New Jersey urban and coastal area and to evaluate the role of the LHRE in these processes. The specific objectives of the present paper are the following: (i) to assess the occurrence of tOP and NPs in the atmosphere, (ii) to study the seasonal trends of NPs and tOP in the atmosphere of the LHRE, (iii) to determine the influence of meteorological conditions such as temperature and wind direction on atmospheric NP and tOP concentrations, and (iv) to assess the relative importance of volatilization as a removal mechanism of NPs from the water column of the lower Hudson River Estuary.

Experimental Section

Site Characterization and Sampling Strategy. The lower Hudson River Estuary is a tidal estuary surrounded by the New York/New Jersey metropolitan area, one of the most densely populated regions in North America with a heavy concentration of industry and wastewater treatment facilities. However, the impact of the urban and industrial activities on the occurrence of NP in the LHRE has not been thoroughly assessed (*38*). Atmospheric research and monitoring stations were established at three locations surrounding the LHRE (Figure 1). Sandy Hook (SH, 40.46°N,74.00°W) is a coastal site located on a peninsula that extends into the LHRE region and is bordered on the east by the Atlantic Ocean. Liberty

* Corresponding author phone: (732)932-9588; fax: (732)932-3562; e-mail: eisenreich@envsci.rutgers.edu.

10.1021/es9910715 CCC: $19.00 © 2000 American Chemical Society
Published on Web 05/12/2000

TABLE 1. Atmospheric Alkylphenol Concentrations (ng m^{-3}) at NJADN Sampling Sites[a]

	Sandy Hook		Liberty Science Center		New Brunswick	
AP (r.t.)[b]	gas	aerosol	gas	aerosol	gas	aerosol
tOP (12.20)	0.21 (nd−1.0)	0.038 (nd−0.63)	0.19 (0.012−0.74)	0.034 (0.0−0.073)	0.40 (0.0091−2.5)	0.022 (0.0011−0.18)
n[c]	22	21	10	10	26	26
NP1 (15.03)	1.0 (nd−9.2)	0.78 (0.012−2.9)	0.41 (nd−2.7)	0.50 (0.043−3.0)	0.81 (0.018−3.5)	0.15 (0.0047−0.94)
NP2 (15.29)	1.5 (nd−13)	1.1 (0.0012−1.5)	0.55 (nd−3.6)	0.79 (0.067−5.3)	2.4 (0.026−11.8)	0.11 (nd−1.3)
NP3 (15.45)	0.63 (nd−5.1)	0.39 (nd−0.62)	0.26 (nd−1.5)	0.28 (nd−2.0)	1.1 (0.011−5.1)	0.044 (nd−0.45)
NP4 (15.53)	0.56 (nd−5.3)	0.41 (0.0047−1.3)	0.18 (nd−1.2)	0.30 (0.011−2.2)	0.4 (0.0082−1.8)	0.041 (nd−0.51)
NP5 (15.64)	0.63 (nd−5.1)	0.38 (nd−0.58)	0.249 (nd−1.5)	0.28 (0.017−2.2)	1.1 (0.011−5.4)	0.040 (nd−0.46)
NP6 (15.94)	0.31 (nd−3.0)	0.24 (nd−0.79)	0.12 (nd−0.77)	0.17 (0.0080−1.2)	0.34 (0.0067−1.4)	0.026 (nd−0.38)
NP7 (16.23)	0.57 (nd−4.2)	0.39 (nd−0.59)	0.27 (nd−1.4)	0.32 (0.017−1.5)	1.1 (0.014−4.5)	0.049 (nd−0.53)
NP8 (16.34)	0.13 (nd−1.1)	0.30 (nd−0.32)	0.086 (nd−0.84)	0.16 (nd−0.81)	0.78 (nd−10)	0.022 (nd−0.33)
NP9 (16.52)	0.72 (nd−6.7)	0.59 (0.0062−1.7)	0.20 (nd−1.3)	0.41 (0.020−2.7)	0.53 (0.013−2.5)	0.064 (0.0023−0.74)
NP10+11 (16.72, 16.82)	0.85 (nd−5.9)	0.79 (nd−0.53)	0.35 (nd−1.8)	0.57 (0.014−2.4)	4.7 (0.014−48)	0.053 (nd−0.70)
ΣNPs	6.9 (nd−56)	5.4 (0.067−51)	2.6 (nd−17)	3.8 (0.23−23)	13 (0.13−81)	0.55 (0.020−6.4)
n[c]	38	38	23	23	27	27

[a] Given are the average concentrations and (range). nd, not detectable. [b] Retention time (min), r.t. [c] *n* is the number of samples analyzed for the respective alkylphenol.

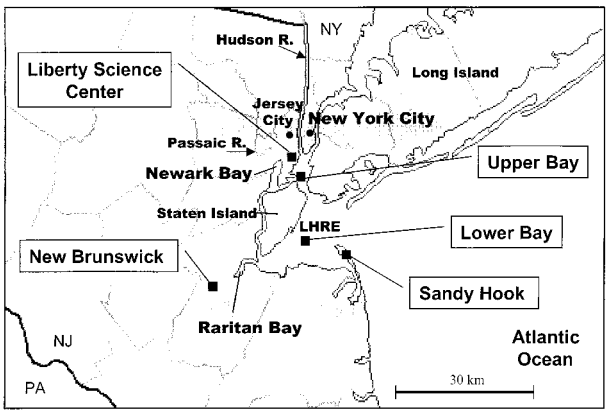

FIGURE 1. Map of the lower Hudson River Estuary region showing NJ Atmospheric Deposition Network sampling stations. Shaded areas indicate the location of urban and suburban areas. Map adapted from the USGS web atlas.

Science Center (LSC, Jersey City, NJ, 40.71°N,74.05°W) is an urban/industrial site located about 0.5 km west of the Hudson River across from New York City and about 4 km east of Newark Bay and the mouths of the Passiac and Hackensack Rivers. These two water bodies receive effluents from municipal waste treatment facilities and are contaminated with persistent organic pollutants (*45*). New Brunswick (NB, 40.48°N,74.43°W), a suburban site located in an agricultural/botanical research area maintained by Rutgers University, is located about 1 km from the Upper Raritan River Estuary, which is also known to receive municipal wastewater treatment effluents.

This paper presents data from two complimentary sampling efforts. To study the seasonal behavior of NPs and tOP, 24 h integrated air samples were taken every 6 (June−August, 1998) or 9 days (September−December, 1998) at the three sites. Analysis of APs at the LSC site began in October 1998, and tOP analysis began at Sandy Hook in July 1998. Additional samples were taken during an intensive sampling campaign that took place from July 5−11, 1998, wherein, consecutive 12-h air samples (8:00 to 20:00 and 20:00 to 08:00 EST) were obtained at LSC and Sandy Hook. Furthermore, simultaneous air and water samples were taken onboard the R/V *Walford* in the LHRE during four of these sampling days. On July 5−7, the samples were taken at locations in Raritan Bay (lower bay), 2−4 km off Staten Island, while two samples (A, morning and B, afternoon) were collected on July 10, 1998 in the upper bay (see Figure 1). The samples from the LSC site during the intensive sampling campaign were taken from the top of a 40-m building, whereas the 24-h integrated samples, taken on a 9-day schedule, were collected from a 1-m high platform.

Air and Water Sampling. Atmospheric particulate and gas-phase samples were obtained with modified high volume air samplers (calibrated flow rate of ~0.3−0.5 m^3 min^{-1}) using quartz fiber filters (QFFs, Whatman) and polyurethane foam (PUFs), respectively. Water particulate and dissolved samples (23−49 L) were obtained using an "Infiltrex 100" in-situ sampler (Axys Environmental Systems, Canada) fitted with glass fiber filters (GFFs, Whatman) and XAD-2 adsorbent (Suppelco), respectively, as generally described elsewhere (*46*). PUFs were precleaned in a Soxhlet apparatus for two periods of 24 h with acetone and petroleum ether, respectively. XAD-2 was precleaned in a Soxhlet apparatus by systematic 24-h extractions using hexane, acetone, and methanol and then rinsed with Milli-Q water. QFFs and GFFs were preweighed in a laboratory with controlled humidity and temperature after being baked at 450 °C for 4 h.

Analytical Procedure. PUFs and QFFs were extracted in a Soxhlet apparatus with petroleum ether and dichloromethane (DCM), respectively. XAD-2 and GFFs were extracted with 1:1 acetone:hexane, followed by liquid−liquid extractions with Milli-Q water (3 × 60 mL) and treatment with an excess of anhydrous sodium sulfate. All extracts were concentrated to ~0.5 mL by rotoevaporation and reduction under a gentle stream of N_2. Samples were fractionated on a 3% H_2O-deactivated alumina (4 g) column prerinsed with 5 mL of 2:1 DCM:hexane and 15 mL of hexane. The first fraction, eluted with 13 mL of hexane, contained PCBs and chlorinated pesticides (CPs). The second fraction, eluted with 15 mL of 2:1 DCM:hexane, contained PAHs and CPs. The third fraction containing the APs was obtained by eluting with 15 mL of dichloromethane:methanol (2:1).

Alkylphenols were identified and quantified by gas chromatography mass spectrometry with electron impact (HP 5890 GC-HP5972 MSD-EI) in selective ion monitoring mode using the ions 135 and 149, as reported by Kannan et al. (*43*), and employing a DB-5 GC column (J&W Scientific; 0.25 mm ID × ~30 m; 0.25 μm film thickness). The oven temperature program, starting with an initial temperature of 70 °C, was as follows: 25 °C min^{-1} to 150 °C; 2 °C min^{-1} to 175 °C; 10 °C min^{-1} to 315 °C. The retention times for the 11 most abundant NP isomers in the technical mixture (Fluka, Germany) were from 14.20 to 15.92 min for this temperature program as shown in Table 1 and were used to calculate the sum of NPs (ΣNPs) (*38*). Isomeric NP concentrations were

calculated by accounting for the relative contribution of ions 135 and 149 to the total spectra for each individual isomer. Separation between the peaks of isomers NP10 and NP11 during gas chromatography was poor for some samples. Therefore, the concentrations of these isomers are reported as the sum of the two (NP10+11). *tert*-Octylphenol (Aldrich) was quantified using the 135 ion and had a retention time of 11.40 min. NPs were derivatized in the water particulate samples using bis(trimethylsilyl)trifluoroacetamide (TMS, Sigma) to improve resolution during chromatographic analysis of a polar fraction with high organic matter content (*47*). Quantification was performed using the internal standard 1-phenyldodecane (Aldrich), whereas 2,4,6-trimethylphenol (Aldrich) or 4-*n*-heptylphenol (Avocado) were used as surrogate compounds.

Matrix spikes for all the matrices, where known amounts of APs were spiked onto sample media, were processed together with the field samples. Matrix spike recoveries were from 45 to 98% for NPs and 47 to 71% for tOP. Sample concentrations were not corrected for surrogate recovery. Method detection limits (MDL) for both NPs and tOP were 4 and 1 ng for aerosol and PUF samples, respectively. Nonylphenol concentrations were detectable in all except one of the air samples analyzed ($n = 186$) and all of the water samples ($n = 9$). Concentrations of tOP were above detection limits in all but five air samples analyzed ($n = 115$). Procedural blanks ($n = 19$) and field blanks ($n = 10$) were processed for all of the sampling sites and all of the matrixes. The mass of ΣNPs measured in field blanks ranged from <MDL to 84 ng, while the mass measured in samples ranged from <MDL to 94 900 ng. The mass of tOP measured in field blanks ranged from <MDL to 1.6 ng, while the mass in samples ranged from < MDL to 2900 ng. The mass of APs in blanks was always below 5% of corresponding field values, and, therefore, no correction of samples was made.

Meteorological Data. Meteorological data for LSC and Sandy Hook sites was obtained from the National Oceanographic and Atmospheric Administration (NOAA) observation stations located at nearby Newark and John F. Kennedy airports, respectively. Meteorological data used for New Brunswick was collected onsite on a 10-m tower. All temperature measurements were arithmetically averaged using weighted hourly observations taken during the sampling period. Predominant local wind directions for each sampling period were estimated by vector addition of hourly observations with wind speed as the vector's magnitude as described by Zhang et al. (*48*).

Results and Discussion

Atmospheric Spatial Variability and Seasonal Trends. Occurrence of NPs and tOP in the NJ Coastal Atmosphere. Averages and ranges of gas- and aerosol-phase concentrations of the NP isomers and ΣNPs at each of the sampling sites are reported in Table 1. The occurrence of tOP in the atmosphere is shown for the first time. At the coastal Sandy Hook site, gas-phase concentrations of ΣNPs averaged 6.9 ng m^{-3} and ranged from <MDL in one sample to 56 ng m^{-3}. The aerosol-phase concentration of ΣNPs averaged 5.4 ng m^{-3} and ranged from 0.067 to 51 ng m^{-3}. The average tOP gas-phase concentration was 0.21 ng m^{-3} and ranged <MDL in one sample to 1.0 ng m^{-3}. Aerosol tOP ranged from <MDL to 0.63 ng m^{-3} and had a mean of 0.038 ng m^{-3}. Since both NPs and tOP were usually enriched in the gas phase, and since the Sandy Hook site is surrounded by the LHRE and the Atlantic Ocean, volatilization from proximate waters is likely an important source of NPs and tOP to the local atmosphere (*38*). However, for samples enriched in the particle phase, regional advective transport may also be important.

The LSC site is located amidst an urban-industrial area about 0.5 km from the Hudson River. The mean gas-phase concentration of ΣNPs was 2.6 ng m^{-3} and ranged from <MDL in one sample to 17 ng m^{-3}, while the aerosol phase had an average concentration of 3.8 ng m^{-3} and ranged from 0.23 to 23 ng m^{-3}. The mean tOP gas-phase concentration was 0.19 ng m^{-3} and ranged from 0.012 to 0.74 ng m^{-3}. Aerosol tOP concentrations ranged from <MDL in one sample to 0.073 ng m^{-3} and had a mean of 0.034 ng m^{-3}.

New Brunswick is a suburban site situated within a small agricultural and botanical research area and is located less than a kilometer from the Upper Raritan River Estuary. The average ΣNPs concentration in the gas phase was 13 ng m^{-3} and ranged from 0.13 to 81 ng m^{-3}, while the aerosol-phase ΣNPs concentrations ranged from 0.020 to 6.4 ng m^{-3} and had a mean of 0.55 ng m^{-3}. The average gas-phase tOP concentration was 0.4 ng m^{-3} and ranged from 0.0091 to 2.5 ng m^{-3}, while aerosol bound tOP concentrations ranged from 0.0011 to 0.18 ng m^{-3} and averaged 0.024 ng m^{-3}. Concentrations of APs at New Brunswick were *highly* enriched in the gas phase in comparison to the other sites, which suggests local evaporative sources (*38*).

The mean gas-phase concentrations of ΣNPs at New Brunswick, Sandy Hook, and LSC were not statistically different from each other. However, aerosol-phase ΣNP concentrations at Sandy Hook and LSC were statistically higher than at New Brunswick ($p < 0.05$). The similar gas-phase NP concentrations at each of the sampling sites suggest that sources of NPs may be ubiquitous in the region surrounding the LHRE. This result was surprising for the New Brunswick site, which is not near water. APs and APEOs have been used in agricultural products (*22, 25, 28, 49, 50*), suggesting that land applied sources may also contribute to the atmospheric occurrence of APs. No other data for atmospheric NPs/tOP have been reported so comparisons to other fields studies was not possible. ΣNP concentrations in the gas phase, however, often exceed phenanthrene and pyrene concentrations for the same samples (*51*). Furthermore, ΣNP concentrations exceeded total PCB concentrations for the same samples by 2 orders of magnitude (*51*).

Temporal trends of gas- and aerosol-phase concentrations of ΣNPs and tOP at the three sampling sites are shown in Figure 2. At both the Sandy Hook and New Brunswick sites, gas-phase NPs and tOP concentrations were significantly higher ($p < 0.05$) during the summer (June−September) than during the fall and early winter (October−December). At the New Brunswick site, gas-phase tOP concentrations showed a trend similar to NP concentrations. For example, the four highest gas-phase concentrations of tOP and NPs at the New Brunswick site occurred on the same sampling days. At LSC, gas-phase NPs and tOP concentrations followed similar seasonal trends with significantly lower concentrations during late autumn and early winter ($p < 0.05$), while the aerosol-phase NP and tOP concentrations showed less variability throughout the entire sampling period. The observation of higher gas-phase AP concentrations during the summer than during the fall/early winter at all the sampling sites is consistent with the notion that temperature is a driving factor of the atmospheric occurrence of APs.

Influence of Temperature. The effect of temperature on atmospheric concentrations of persistent organic pollutants has been reported (*48, 52−57*). These studies have shown that a large fraction of the seasonal variability of gas-phase concentrations of semivolatile organic compounds can be explained by temperature using a Clausius−Clapeyron equation of the type

$$\log C_g = b + m/T \qquad (1)$$

where C_g is the gas-phase concentration (ng m^{-3}), T is the average temperature (K) during the sampling period, m is the slope, and b is a constant. Air temperatures ranged from

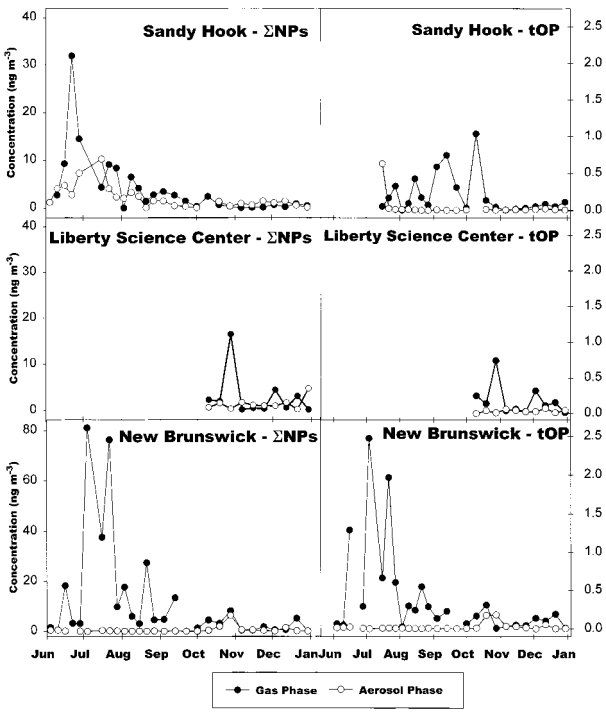

FIGURE 2. Atmospheric concentrations of ΣNPs and tOP (ng m^{-3}) obtained from June 4 to Dec 30, 1998 in 6- or 9-day intervals. Given separately are the gas-phase (filled circles) and aerosol-phase (open circles) concentrations.

TABLE 2. Temperature Regression Parameters for tOP, NP Isomers, and ΣNPs at the New Brunswick Site[a]

	slope	SE[b]	r^2	p
tOP	−4100	940	0.45	<0.001
NP1	−5100	960	0.53	<0.001
NP2	−5400	840	0.63	<0.001
NP3	−5500	900	0.60	<0.001
NP4	−5700	870	0.63	<0.001
NP5	−5700	820	0.66	<0.001
NP6	−5600	870	0.62	<0.001
NP7	−5500	870	0.61	<0.001
NP9	−5700	890	0.62	<0.001
ENPs	−5500	900	0.60	<0.001

[a] Isomers NP8 and NP10+11 were excluded because concentrations were frequently below the limit of detection. [b] Standard error.

−7 to 31 °C during the sampling period (June to Dec 1998). Table 2 reports the values of m, the standard error of m, the regression coefficients (r^2), and p-values obtained from the regressions for gas-phase concentrations of tOP and the individual NP isomers at the New Brunswick site. All regressions were statistically significant ($p < 0.001$). Although, there were slight differences between the slopes (−5700 to −5100) for the individual NP isomers, the differences were not statistically significant ($p > 0.05$). Thus, the temperature dependence of NP concentrations was investigated using the sum of NP isomers.

Figure 3 shows the results obtained from applying eq 1 to gas-phase NP and tOP concentrations at each of the sampling sites. Statistically significant correlations (95% confidence level) between log C_g and $1/T$ were obtained at each of the sampling sites for both ΣNPs and tOP. Temperature explains about 62% of the variability of the log of gas-phase NP concentrations at Sandy Hook ($r^2 = 0.62$, $p < 0.001$, extreme outlier removed). ΣNP gas-phase concentrations at Liberty Science Center ($r^2 = 0.56$, $p < 0.001$) and New Brunswick ($r^2 = 0.60$, $p < 0.001$) showed slightly lower

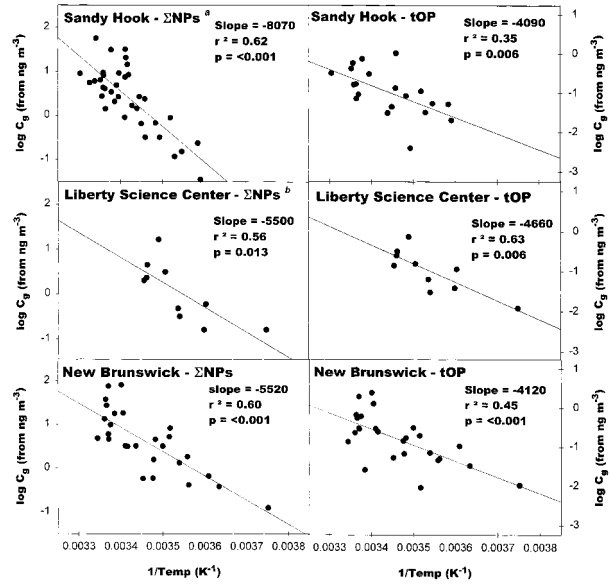

FIGURE 3. Regressions of the log gas-phase concentrations (C_g) of NPs and tOP verses reciprocal temperature (T) at each of the sampling sites (log $C_g = m/T + b$). [a]Extreme outlier removed. [b]Plot contains samples taken in 9-day intervals.

correlations with temperature. For tOP, the log gas-phase concentrations showed significant correlations with $1/T$ for all the sampling sites ($p < 0.01$, see Figure 3) with regression coefficients of 0.35 and 0.63 for the Sandy Hook and LSC sites, respectively.

Slopes of smaller absolute magnitude should correspond to compounds with lower heats of air-surface exchange and thus with higher vapor pressures at a given temperature (*58*). This is consistent with the slopes obtained for tOP and ΣNPs. Indeed, at all the sampling sites, the slopes m for tOP (−4090 to −4660) were shallow compared to the slopes for ΣNPs (−5500 to −8070). Equation 1 describes an air-surface partitioning process. Therefore, a high correlation between the log C_g and $1/T$ indicates that atmospheric NP and tOP concentrations are driven by air-surface exchange. Wania et al. (*54*) concluded that steep slopes can be associated with local sources. Therefore, the very steep slope obtained from Sandy Hook data (−8070) is consistent with the proximate waters being the source of NPs to the local atmosphere. Dachs et al. (*38*) suggest that concentrations of atmospheric NPs at Sandy Hook and LSC are likely the result of volatilization from the LHRE and its composite water bodies such as Newark Bay. The dependence of NP concentrations on temperature demonstrated here gives further evidence for this scenario.

Gas-phase NP concentrations at New Brunswick were not only temperature dependent but also higher than Sandy Hook and LSC for some sampling periods in July 1998. These high concentrations at New Brunswick must not be exclusively the result of volatilization from the nearby Upper Raritan River Estuary (RRE). Given its size, concentrations in the RRE would need to be several orders of magnitude higher than the in the LHRE (*38*) to support such high gas-phase concentrations. Therefore, it is reasonable to suspect that volatilization of APs from sources other than RRE may be important. Since APs have been used as adjuvants in agricultural products (*22, 25, 28, 49, 50*), terrestrial sources could explain a portion of the occurrence of NPs and tOP at the New Brunswick site. Higher temperatures during the summer could lead to enhanced volatilization of applied APs from these terrestrial surfaces. However, further research on these mechanisms is needed.

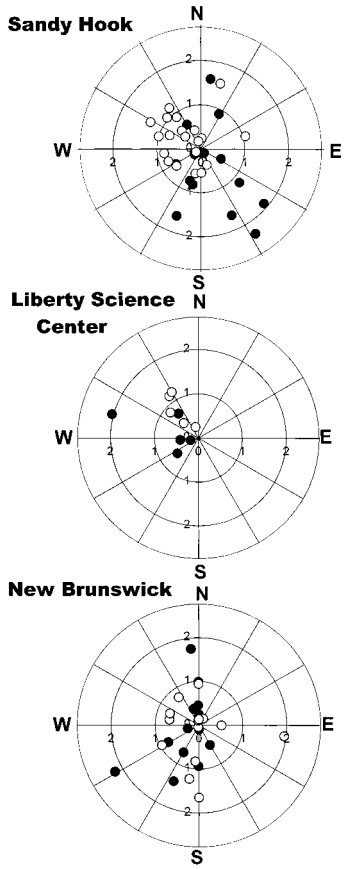

FIGURE 4. Polar plots of wind direction (angular data) vs the absolute magnitude of positive (filled circles) and negative (open circles) standardized residuals (radial data) from the temperature regressions for ΣNPs at each site presented in Figure 3.

Influence of Wind Direction. A systematic analysis of the effects of local wind direction was carried out to further evaluate the influence of meteorological variables and potential sources on the atmospheric occurrence of NPs and tOP. Removing the influence of temperature is useful when trying to determine the effects of wind direction (*59*). Standardized residuals were obtained from the application of eq 1 to gas-phase ΣNP concentrations at the three sampling sites (Figure 3). Standardized residuals are the residuals (*predicted* − *observed* log C_g) normalized by the standard error of the linear regression. These values represent the relative distance a particular data point lies from the value predicted by the log C_g-$1/T$ regression line (eq 1 and Figure 3) and provide the fraction of the variability of gas-phase NP concentrations not explained by temperature. Positive standard residuals correspond to NP concentrations that fall above the prediction line (i.e., uncharacteristically high concentrations for a given temperature), while negative standard residuals refer to gas-phase NP concentrations that fall below the regression line (low concentrations). Figure 4 shows polar plots of each sample data point using predominant wind direction and standardized residuals as the angles and radii, respectively.

At the Sandy Hook site, larger positive residuals occurred when local winds were from the south, while a greater proportion of negative residuals occurred when winds were from the NW. However, all residuals from the NW were below or close to unity, indicating that temperature is a good predictor of NP concentrations when winds are derived from over the estuary. Larger positive residuals associated with air masses coming from the south are consistent with local advective transport of NPs, presumably from sources along the NJ coastline or coastal terrestrial sources. At the New Brunswick site, the polar plot of standardized residuals (Figure 4) suggests that no particular wind direction was more important than another for determining the effects of temperature. The Raritan River is located to the north of the New Brunswick site. If it was a significant source of NP to the local atmosphere, local winds from that direction should give high positive residuals; this trend was not observed. This provides further evidence for the occurrence of surface related sources other than volatilization from the Raritan River. At the LSC site, winds were almost always from the NW corridor. Therefore, the influence of wind direction could not be elucidated. Nevertheless, air masses coming from this direction may be influenced by volatilization from Newark Bay and the Passaic and Hackensack River watersheds as well as other terrestrial sources. In fact, the relatively aerosol-enriched concentrations of NPs at LSC are consistent with regional transport.

A complementary analytical tool to evaluate the influence of wind direction is multiple linear regression (*48, 53*) of the gas-phase ΣNP concentrations against temperature and wind direction

$$\log C_g = a_0 + a_1/T + a_2\sin(\mathrm{wd}) + a_3\cos(\mathrm{wd}) \quad (2)$$

where a_0, a_1, a_2, and a_3 are fitting parameters and wd is the predominant wind direction for the sampling period (degrees). The results of applying eq 2 to gas-phase NP concentrations for the Sandy Hook site were

$$\log C_g = 19.5 - 6993/T + 0.33\sin(\mathrm{wd}) - 0.18\cos(\mathrm{wd}) \quad (3)$$

The regression coefficient was 0.74, where temperature explained 62% of the variability and wind direction explained the remaining 12%. All the fitting coefficients were statistically significant at the 95% confidence level ($p < 0.001$ to < 0.05). These results confirm that wind direction is important at Sandy Hook, and air masses approaching from the south are generally associated with higher concentrations of NPs. At the New Brunswick site, temperature was the only statistically significant parameter. Wind direction did not correlate with the log of gas-phase concentrations, confirming that sources of AP are probably local. Since winds at LSC were almost always from the NW corridor, no significant correlation between the wind direction parameters and concentration could be attained.

The study of the influence of temperature and wind direction has shown that surface-air exchange processes drive air concentrations of NPs and tOP and explained the importance of local sources versus long-range atmospheric transport. This is consistent with short atmospheric half-lives (<1 day) of NP and tOP as suggested by the behavior of other phenols in the atmosphere (*60*). Therefore, inputs from aquatic and, perhaps, terrestrial environments are important in supporting the atmospheric occurrence of NPs and tOP. However, it remains unclear how important volatilization is as a removal process of NPs from aquatic environments.

Fate of Alkylphenols in the Lower Hudson River Estuary. Mass Balance Approach. To assess the relative importance of volatilization as a removal process of NP from the water column, a budget of input and removal processes was constructed. A box-model was devised to estimate the input and removal fluxes of NPs from the water column of the lower Bay of the Hudson River estuary during the July 1998 sampling campaign. The input boundary for the box model was assumed to be the mouth of the Hudson River, close to the sampling position corresponding to the upper bay site. The output boundary to the Atlantic Ocean was an imaginary

TABLE 3. Aquatic Concentrations, Over-Water Atmospheric Concentrations, and Air–Water Exchange Fluxes of ENPs in the Lower Hudson River Estuary 1998

	Lower Bay				Upper Bay		
sample date	7/5/98	7/6/98	7/7/98	av	07/10/98 A	07/10/98 B	av
dissolved (ng L^{-1})	12	24	49	28	61	94	78
water particulate (ng L^{-1})	3.9	2.6	3.4	3.3	22	na	22
TSM (mg L^{-1})[a]	5.4	5.7	4.2	5.1	5.5	na	5.5
f_{oc} (%)[b]	34	35	32	34	12	na	12
gas phase (ng m^{-3})	2.6	1.5	69	24	21	2.2	12
aerosol phase (ng m^{-3})	6.9	14	6.3	9.0	3.6	0.50	2.0
wind speed (m s^{-1})	1.7	3.3	2.3	2.4	4.1	5.6	4.8
k_{ol} (m day^{-1})[c]	0.22	0.42	0.29	0.31	0.52	0.72	0.62
air–water flux (ng m^{-2} day^{-1})[d]	2100	9500	1200	4300	25000	66700	46000

[a] Total suspended matter. [b] Fraction of organic carbon on suspended aquatic particles. [c] Air–water mass transfer coeffecient. [d] Positive values indicate volatilization.

line between Sandy Hook and Long Island (Figure 1). The total control volume (2.5×10^9 m^3), total surface area (A_S, 3.8×10^8 m^2), and the net dry season river flow rate of water (Q) through the entire bay for a typical year (7.1×10^7 m^3 day^{-1}, 1987) were obtained from Farley et al. (*45*). Loadings of NPs to the NY/NJ bay are advection in, diffusive absorption, and dry and wet atmospheric deposition, whereas removal processes are advection out, volatilization, sedimentation, and degradation.

Advection Inputs and Outputs. The Hudson River accounts for about 50% of the advective water flow into the control volume (*45*). Since concentrations were not available for the other rivers entering the study area (mainly the Passiac, Hackensack, Raritan, and East Rivers), the total concentrations of NPs in the upper bay ($C_{T,up}$, July 10, see Figure 1), near the mouth of the Hudson River, were assumed to be typical of all water entering by advection. Furthermore, the lower bay was assumed to be a completely mixed system, and concentrations obtained at the lower bay sampling site ($C_{T,low}$, July 5–7, see Figure 1) were assumed to be those transferred by advection to the Atlantic Ocean.

Table 3 reports the dissolved and particulate phase concentrations of ΣNPs in the upper and lower bay water samples (see Figure 1). The average water (dissolved + particulate) ΣNPs concentration in the lower bay was 31 ng L^{-1} and ranged from 15 to 53 ng L^{-1}. In the upper bay, the average water concentration of ΣNPs was 100 ng L^{-1}. The higher concentrations at the upper bay sampling site are consistent with proximity to the location of wastewater treatment facilities that discharge to the Hudson and Passaic Rivers and Newark Bay. Therefore, inputs (I) and outputs (O) of NPs by advection (g day^{-1}) are estimated by

$$I = QC_{T,\,up} \times 10^{-9} \tag{4}$$

and

$$O = QC_{T,\,low} \times 10^{-9} \tag{5}$$

where $C_{T,up}$ and $C_{T,\,low}$ are the water total NP concentrations (ng m^{-3}) in the upper and lower bay, respectively.

Air–Water Exchange. Air–water diffusive fluxes of NPs in the lower bay were calculated using a modified two-layer resistance model (*46, 61–63*). Volatilization and absorption fluxes were treated separately in the mass balance model and are given by

$$\text{volatilization} = k_{ol}(C_d) \tag{6}$$

$$\text{absorption} = k_{ol}(C_g/H') \tag{7}$$

where C_d and C_g (ng m^{-3}) are the dissolved and gas-phase concentrations, respectively, H' is the dimensionless Henry's Law constant for ΣNPs, and k_{ol} is the mass transfer coefficient (m day^{-1}). H' (1.5×10^{-3} at 25 °C) was not corrected for temperature since water temperatures ranged from 20 to 23 °C during sampling and exerted negligible influence on the flux calculations (*64*). Details on methods to estimate k_{ol} are described elsewhere (*48, 61*). The estimated values of k_{ol} and air–water fluxes are given in Table 3. All *net* air–water fluxes calculated (volatilization − absorption) were positive, indicating net volatilization. Net fluxes in the upper bay ranged from 25 to 67 μg m^{-2} day^{-1} (average = 46 μg m^{-2} day^{-1}) and were nearly an order of magnitude greater than the average net flux in the lower bay (4.3, range 1.2–9.5 μg m^{-2} day^{-1}). The difference in net fluxes between the two sampling areas was not only the result of a shift in the air–water concentration gradient but also because higher wind speeds during the sampling periods in the upper bay enhanced k_{ol} (*46*). Volatilization and absorption fluxes used in the box model correspond to those calculated for the lower bay.

Dry and Wet Deposition. The dry deposition flux of NPs to the lower bay was estimated by (*65, 66*)

$$\text{dry deposition} = C_{a,p}v_dA_S \times 10^{-9} \tag{8}$$

where $C_{a,p}$ (ng m^{-3}) is the concentration of NPs in the aerosol phase and v_d is the particle deposition velocity. The average concentration of NPs on aerosols above the water column of the lower bay was 2 ng m^{-3} (Table 3). A range for v_d of 0.2–0.5 cm s^{-1} was chosen as representative of over water areas with urban influence (*65*). Concentrations of NPs in rainwater were not available so the wet deposition flux of NPs was estimated by (*67, 68*)

$$\text{wet deposition} = (PA_s) \times (W_gC_g + W_{a,p}C_{a,p}) \times 10^{-9} \tag{9}$$

where P is the seasonal average precipitation rate (2.44×10^{-3} m day^{-1}), and W_g and $W_{a,p}$ are washout coefficients for the gas and aerosol phases, respectively. W_g is defined as the reciprocal of the dimensionless Henry's Law constant ($1/H'$, 645), whereas $W_{a,p}$ was assumed to be 10^4 based on literature values (*67*).

Sedimentation. The average particle sedimentation rate (w_s) for the estuary, calculated from Adams et al. (*69*), is 3.6 g m^{-2} day^{-1}. Sediment resuspension is a common process in the LHRE (*69*), and, therefore, the water column particles were likely to have similar NP concentrations to the surficial sediments. Assuming that water column particulate concentrations are representative of those in the sediments, the sedimentation rate for NPs can be estimated as

$$\text{sedimentation rate of NP} = w_sA_SC_{w,p} \times 10^{-9} \tag{10}$$

where $C_{w,p}$ (ng m^{-3}) is the average aquatic particle concentration of NPs in the lower bay.

Relative Contributions of Loadings and Removal Processes. Degradation of nonylphenol polyethoxylates to NPs in the sediments with subsequent resuspension is a potential input of NP to the water column. On the other hand, in situ degradation of NPs may also be an important removal mechanism (*70*). The *net* degradation rate (*formation − degradation*) of NPs (D, g day^{-1}) can be estimated by closing the mass balance as given by

$$[(QC_{T,up}) + (C_{a,p}v_dA_S) + (A_SK_{ol}C_g/H')] \times 10^{-9} = [(QC_{T,low}) + (w_sA_SC_{wp,low}) + (A_SK_{ol}C_d)] \times 10^{-9} + D \quad (11)$$

and is assumed to be all the NP mass not accountable by the summation of the other removal processes. Since concentrations of NPs to the atmosphere are temperature dependent, and samples were taken only for a 1-week period, the results obtained should be viewed as a preliminary approach to assessing the predominant mechanisms driving the fate of NPs in the shallow aquatic environment of the LHRE during the summer.

The total loading of NPs to the lower bay was 9100 g day^{-1}. Advection accounted for 69% of this input (6300 g day^{-1}), while gaseous absorption and dry deposition accounted for 19% (1700 g day^{-1}) and 11% (1000 g day^{-1}), respectively. The estimated wet deposition accounted for less than 1% of the total loading. Removal from the estuary was dominated by volatilization (37%, 3400 g day^{-1}). In fact, actual volatilization fluxes may be significantly higher than those estimated with the available data set since the average wind speed during the summer season (4.5 m s^{-1}) is significantly higher than the wind speeds during the sampling periods (2.4 m s^{-1}) in the lower bay. Advection (2200 g day^{-1}) and degradation (2600 g day^{-1}) accounted for 24 and 29% of the total removal of NPs from the water column. Some processes have not been taken into account, therefore adding to the uncertainty of the mass balance. For example, removal of NPs from the water column to the atmosphere due to formation of marine aerosol could not be estimated with the data available and was omitted in the present budget for the lower bay.

The total inventory of NPs in the control volume was approximately 78 kg. Therefore, the overall residence time (R_t) of NPs in the water column of the lower bay can be estimated as

$$R_t = (\text{total inventory})/\text{loadings} = (\text{total inventory})/\text{removal} \quad (12)$$

The calculated R_t is approximately 9 days, which was significantly lower than the residence time of the water in the bay (35 days) (*45*). Short residence times (0.9−2.7 days) have also been observed for NPs in the shallow Krka River estuary in Croatia (*40*).

The results obtained from the budget of NP in the lower bay shows that the biogeochemical cycling of NP is a very dynamic process where inputs are dominated by advection and outputs by volatilization to the local atmosphere. Degradation may also be an important loss mechanism, but its relative importance is difficult to assess due to the fact that the values obtained were estimated indirectly by closing the mass balance for NPs in the lower bay.

The present study demonstrates the necessity to study the environmental fate of semivolatile persistent organic pollutants using a multicompartment approach. This is not only because the atmospheric occurrence and fate of POPs is influenced by the adjacent aquatic and terrestrial environments but also because the atmosphere may be an important sink for POPs in shallow aquatic environments.

Acknowledgments

T. R. Glenn, R. Pelleriti, and R. Lohmann are kindly acknowledged for their field and laboratory assistance. J. Dachs acknowledges a postdoctoral fellowship from the Spanish Ministry of Education and Culture. This research was funded in part by the Hudson River Foundation (Project Officer, D. Suszkowski), NJ Sea Grant College (NOAA) (Grant No. NA76-R60091: Project No. R/E 9704; Publ. No. NJSG-00-437), and the NJ Agricultural Experiment Station.

Literature Cited

(1) Renner, R. *Environ. Sci. Technol.* **1997**, *31*, 316A−320A.
(2) Giger, W.; Brunner, P. H.; Schaffner, C. *Science* **1984**, *225*, 623−625.
(3) Field, J. A.; Reed, R. L. *Environ. Sci. Technol.* **1996**, *30*, 3544−3550.
(4) Ahel, M.; Giger, W.; Koch, M. *Water Res.* **1994**, *28*, 1131−1142.
(5) Ahel, M.; Giger, W.; Schaffner, C. *Water Res.* **1994**, *28*, 1141−1152.
(6) Maki, H.; Fujita, M.; Fujiwara, Y. *Bull. Environ. Contam. Toxicol.* **1996**, *57*, 881−887.
(7) Ball, H. A.; Reinhard, M.; McCarty, P. L. *Environ. Sci. Technol.* **1989**, *23*, 3, 951−961.
(8) Ahel, M.; Hršak, D.; Giger, W. *Arch. Environ. Contam. Toxicol.* **1994**, *26*, 540−548.
(9) Ejlertsson, J.; Nilsson, M. L.; Kylin, H.; Bergman, A.; Karlson, L.; Oquist, M.; Svensson, B. H. *Environ. Sci. Technol.* **1999**, *33*, 301−306.
(10) Kveštak, R.; Ahel, M. *Arch. Environ. Contam. Toxicol.* **1995**, *29*, 551−556.
(11) Shang, D. Y.; MacDonald, R. W.; Ikonomou, M. G. *Environ. Sci. Technol.* **1999**, *33*, 1366−1372.
(12) Liber, K.; Knuth, M. L.; Stay, F. S. *Environ. Toxicol. Chem.* **1999**, *18*, 357−362.
(13) Heinis, L. J.; Knuth, M. L.; Liber, K.; Sheedy, B. R.; Tunell, R. L.; Ankly, G. T. *Environ. Toxicol. Chem.* **1999**, *18*, 363−375.
(14) Ahel, M.; McEvoy, J.; Giger, W. *Environ. Pollut.* **1993**, *79*, 243−248.
(15) Lewis, S. K.; Lech, J. J. *Xenobiotica* **1996**, *26*, 813−819.
(16) Liber, K.; Gangl, J. A.; Corry, T. D.; Heinis, L. J.; Stay, F. S. *Environ. Toxicol. Chem.* **1999**, *18*, 394−400.
(17) Ekelund, R.; Bergman, Å.; Granmo, Å.; Berggren, M. *Environ. Pollut.* **1990**, *64*, 107−120.
(18) Comber, M. H. I.; Williams, T. D.; Stewart, K. M. *Water Res.* **1993**, *27*, 273−276.
(19) Shurin, J. B.; Stanley, D. I. *Environ. Toxicol. Chem.* **1997**, *16*, 1269−1276.
(20) O'Halloran, S. L.; Liber, K.; Gangl, J. A.; Knuth, M. L. *Environ. Toxicol. Chem.* **1999**, *18*, 376−385.
(21) Schmude, K. L.; Liber, K.; Corry, T. D.; Stay, F. S. *Environ. Toxicol. Chem.* **1999**, *18*, 386-393.
(22) McLeese, D. W.; Zitko, V.; Sergeant, D. B.; Burridge, L.; Metcalf, C. D. *Chemosphere* **1981**, *10*, 723−730.
(23) Agrese, E.; Marcomini, A.; Miana, P.; Bettiol, C.; Perin, G. *Environ. Toxicol. Chem.* **1994**, *13*, 737−742.
(24) Bokern, M.; Harms, H. H. *Environ. Sci. Technol.* **1997**, *31*, 1849−1854.
(25) Caux, P. Y.; Weinberger, P.; Carlisle, D. B. *Environ. Toxicol. Chem.* **1988**, *7*, 671−676.
(26) Soto, A. M.; Justicia, H.; Wray, J. W.; Sonnenschein, C. *Environ. Health Perspect.* **1991**, *92*, 167−173.
(27) White, R.; Jobling, S.; Hoare, S. A.; Sumpter, J. P.; Parker, M. G. *Endocrinology* **1994**, *135*, 175−182.
(28) Fairchild, W. L.; Swansburg, E. O.; Arenault, J. T.; Brown, S. B. *Environ. Health Perspect.* **1999**, *107*, 349−357.
(29) Purdom, C. E.; Hardiman, P. A.; Bye, V. J.; Eno, N. C.; Tyler, C. R.; Sumpter, J. P. *Chem. Ecol.* **1994**, *8*, 275−285.
(30) Brunner, P. H.; Capri, S.; Marcomini, A.; Giger, W. *Water Res.* **1988**, *22*, 1465−1472.
(31) Rudel, R. A.; Melly, S. J.; Geno, P. W.; Sun, G.; Brody, J. G. *Environ. Sci. Technol.* **1998**, *32*, 861−869.
(32) Castillo, M.; Alonso, M. C.; Riu, J.; Barceló, D. *Environ. Sci. Technol.* **1999**, *33*, 1300−1306.
(33) Blackburn, M. A.; Waldock, M. J. *Water Res.* **1995**, *29*, 1623−1629.
(34) Blackburn, M. A.; Kirby, S. J.; Waldock, M. J. *Mar. Pollut. Bull.* **1999**, *38*, 109−118.
(35) Espadler, I.; Caixach, J.; Om, J.; Ventura, F.; Cortina, M.; Pauné, F. *Water Res.* **1997**, *31*, 1996−2004.
(36) Bennie, D. T.; Sullivan, C. A.; Lee, H. B.; Peart, T. E.; Maguire, R. J. *Sci. Total Environ.* **1997**, *193*, 263−275.
(37) Maruyama, K.; Yuan, M.; Otsuki, A. *Environ. Sci. Technol.* **2000**, *34*, 343−348.

(38) Dachs, J.; Van Ry, D. A.; Eisenreich, S. J. *Environ. Sci. Technol.* **1999**, *33*, 2676−2679.
(39) Kveštak, R.; Ahel, M. *Ectotoxicol. Environ. Safety* **1994**, *28*, 25−34.
(40) Kveštak, R.; Terzic, S.; Ahel, M. *Mar. Chem.* **1994**, *46*, 89−100.
(41) Marcomini, A.; Pavoni, B.; Sfriso, A.; Orio, A. A. *Mar. Chem.* **1990**, *29*, 307−323.
(42) Ahel, M.; Schaffner, C.; Giger, W. *Water Res.* **1996**, *30*, 37−46.
(43) Kannan, N.; Yamashita, N.; Petrick, G.; Duinker, J. C. *Environ. Sci. Technol.* **1998**, *32*, 1747−1753.
(44) Lye, C. M.; Frid, C. L. J.; Gill, M. E.; Cooper, D. W.; Jones, D. M. *Environ. Sci. Technol.* **1999**, *33*, 1009−1014.
(45) Farley, K. J.; Thomann, R. V.; Cooney, T. F. I.; Damiani, D. R.; Wands, J. R. *An Integrated Model of Organic Chemical Fate and Bioaccumulation in the Hudson River Estuary;* Hudson River Foundation: 1999.
(46) Achman, D. R.; Hornbuckle, K. C.; Eisenreich, S. J. *Environ. Sci. Technol.* **1993**, *27*, 75−86.
(47) Maldonado, C. A.; Dachs, J.; Bayona, J. M. *Environ. Sci. Technol.* **1999**, *33*, 3290−3296.
(48) Zhang, H.; Eisenreich, S. J.; Franz, T. R.; Baker, J. E.; Offenburg, J. H. *Environ. Sci. Technol.* **1999**, *33*, 2129−2137.
(49) McLeese, D. W.; Sergeant, D. B.; Metcalfe, C. D.; Zitko, V.; Burridge, L. E. *Bull. Environ. Contam. Toxicol.* **1980**, *24*, 575−581.
(50) McLeese, D. W.; Zitko, V.; Metcalfe, C. D.; Sergeant, D. B. *Chemosphere* **1980**, *9*, 79−82.
(51) Eisenreich, S. J.; Brunciak, P. A.; Dachs, J.; Glenn, T.; Lavorgna, C.; Nelson, E. D.; Totten, L. A.; Van Ry, D. A. In *Persistent Bioaccumulative Toxic Chemicals*; Lipnick, R., Ed.; Washington, DC, 1999.
(52) Hoff, R. M.; Muir, D. C. G.; Grift, N. P. *Environ. Sci. Technol.* **1992**, *26*, 276−283.
(53) Hillery, B. R.; Basu, I.; Sweet, C. W.; Hites, R. A. *Environ. Sci. Technol.* **1997**, *31*, 1811−1816.
(54) Wania, F.; Haugen, J. E.; Lei, Y. D.; Mackay, D. *Environ. Sci. Technol.* **1998**, *32*, 1013−1021.
(55) Hoff, R. M.; Brice, K. A.; Halsall, C. J. *Environ. Sci. Technol.* **1998**, *32*, 1793−1798.
(56) Haugen, J.-E.; Wania, F.; Ritter, N.; Schlabach, M. *Environ. Sci. Technol.* **1998**, *32*, 217−224.
(57) Hornbuckle, K. C.; Eisenreich, S. J. *Atmos. Environ.* **1996**, *30*, 3935−3945.
(58) Goss, K.-U.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1999**, *33*, 3390−3393.
(59) Subhash, S.; Honrath, R. E.; Kahl, J. D. W. *Environ. Sci. Technol.* **1999**, *33*, 1509−1515.
(60) Howard, P. H.; Boethling, R. S.; Jarvis, W. F.; Meylan, W. M.; Michalenko, E. D. *Handbook of Environmental Degradation Rates*; Lewis Pubishers: Chelsea, MI, 1991.
(61) Nelson, E. D.; McConnell, L. L.; Baker, J. E. *Environ. Sci. Technol.* **1998**, *32*, 912−919.
(62) Hornbuckle, K. C.; Jeremiason, J. D.; Sweet, C. W.; Eisenreich, S. J. *Environ. Sci. Technol.* **1994**, *28*, 1491−1501.
(63) Bamford, H. A.; Offenberg, J. H.; Larsen, R. K.; Ko, F. C.; Baker, J. E. *Environ. Sci. Technol.* **1999**, *33*, 2138−2144.
(64) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 1st ed.; John Wiley & Sons: New York, NY, 1993.
(65) Franz, T. P.; Eisenreich, S. J.; Holsen, T. M. *Environ. Sci. Technol.* **1998**, *32*, 3681−3688.
(66) Swackhamer, D. L.; McVeety, B. D.; Hites, R. A. *Environ. Sci. Technol.* **1988**, *22*, 664−672.
(67) Eisenreich, S. J.; Strachan, W. M. J. *Mass Balancing of Toxic Chemicals in the Great Lakes: The Role of Atmospheric Deposition;* Canada Centra for Inland Waters: 1992.
(68) Dickhut, R. M.; Gustafson, K. E. *Environ. Sci. Technol.* **1995**, *29*, 1518−1525.
(69) Adams, D. A.; O'Connor, J. S.; Weisberg, S. B. *Final Report: Sediment Quality of the NY/NJ Harbor System;* EPA: 1998.
(70) Ekelund, R.; Granmo, Å.; Magnusson, K.; Berggren, M.; Bergman, Å. *Environ. Pollut.* **1993**, *79*, 59−61.

Received for review September 20, 1999. Revised manuscript received February 28, 2000. Accepted March 24, 2000.

ES9910715