

Distribution and Fate of Neutral Alkylphenol Ethoxylate Metabolites in a Sewage-Impacted Urban Estuary

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The distribution and fate of neutral metabolites of the alkylphenol ethoxylate (APEO) surfactants in an urbanized estuarine environment were examined utilizing a recently developed, highly sensitive LC–MS method. Results indicated that short ethoxyl-chain APEOs and alkylphenols (APs) were present in surficial sediments throughout the estuary at concentrations roughly correlated to the organic carbon content of the sediment and that the APEO mixture was dominated by nonylphenol ethoxylate (NPEOs) metabolites (0.05–30 $\mu\text{g/g}$), with lesser amounts of octylphenol ethoxylate metabolites (OPEOs) (<0.005–0.09 $\mu\text{g/g}$) and halogenated nonylphenols (<0.001–0.03 $\mu\text{g/g}$). NPEO metabolites in surface water (0.22–1.05 $\mu\text{g/L}$) were also present at higher concentrations than OPEO metabolites (0.007–0.040 $\mu\text{g/L}$). APEO metabolite concentrations in both sediment and water showed a strong correlation with conventional sewage tracers, affirming a wastewater source of these contaminants. APEO distributions in surface waters within the estuary could be explained by a combination of post-discharge degradation and mixing with a seawater end-member enriched in OPEO metabolites. Measured *in situ* K_{oc} values of APEO metabolites were comparable to previously reported values derived from field experiments but higher than K_{ow} and K_{oc} values derived from laboratory experiments. Results from the present work indicate that the fate of APEO metabolites entering the estuarine environment through discharge of wastewater is directed primarily by scavenging onto particles and subsequent burial in sediments, degradation during residence in the water column, and transport out of the estuary through advective and dispersive processes.

Introduction

Alkylphenol ethoxylates (APEOs) are commercially important surfactants used in both industrial and domestic detergent and emulsifier formulations. This class of compounds has a use-history dating from the mid-twentieth century. They are synthesized commercially by base-catalyzed addition of ethylene oxide to an alkylphenol hydrophobe. The most common hydrophobe used in this process is nonylphenol

(NP), formed from the reaction of refinery-grade nonene (tripropylene) with phenol. NP is actually a complex mix of branched nonyl-chain and ring-substituted isomers. The only other major alkylphenol used in the synthesis of APEOs commercially is octylphenol (OP), which is prepared from 2,2,4-trimethylpentane and phenol, resulting in only a single OP isomer product. Octylphenol ethoxylates (OPEOs) typically make up less than 10% of the APEO market (1) and are typically used in specialized applications, including the Triton-X series of laboratory detergents.

Interest in the environmental fate of APEO surfactants has steadily increased since the 1980s, when Giger and co-workers found that these compounds and/or their myriad metabolites may survive wastewater treatment and persist in the aquatic environment (2–5). Subsequent research has shown the metabolites of APEOs to be more toxic than the APEOs themselves (6), and several of these biodegradation products have recently been shown to cause endocrine disruption in aquatic organisms (7). The biodegradation mechanisms of APEOs during wastewater treatment and after discharge to the environment have been the subject of sometimes heated debate in the literature. Generally, however, it is believed that aerobic degradation processes result in the shortening and/or oxidation of the APEO ethoxyl chain [leading to alkylphenol ethoxy carboxylates (APEC) (8) and short EO chain APEOs] (9) as well as the oxidation of the branched alkyl chain (10, 11). Anaerobic degradation of APEOs may also result in shortening of the ethoxyl chain (9), with the eventual formation and accumulation of AP (4).

Studies to date have largely focused on the occurrence of APEO metabolites in wastewater (9, 12, 13) and fresh receiving waters (14–18). Fewer reports have been made of APEO metabolites in coastal marine and estuarine environments (19–22). Despite the interest in the occurrence of APEO metabolites in the aquatic environment, there is relatively little known about the environmental fate of these compounds. In a freshwater study, dissipation of NP from the water column of a spiked littoral enclosure was found to be rapid (6–22 days); however, no degradation of sediment-associated NP could be detected (23). Shang et al. (22) also found that NPEOs and their metabolites persisted in field-collected sediments from the coastal marine environment, with a reported half-life of 60 yr. A recent study in the Hudson–Raritan Estuary system in New York found that volatilization may play a significant role in determining the fate of some APEO metabolites once released into the nearshore marine environment (24, 25). It is clear from the work done so far in aquatic systems that the environmental fates of APs and APEOs may differ due to their differing physicochemical properties.

In the present work, we utilize newly developed HPLC–MS methods (26) to report on the distribution of neutral NPEO and OPEO metabolites (including APs, APEOs with 3 ethoxyl units, and halogenated APs, presumably derived from wastewater chlorination treatment) in sediment, water, and suspended particulates in Jamaica Bay, a highly urbanized and sewage-impacted estuary on the south shore of Long Island, NY (Figure 1). Trends in the concentration and composition of measured APEO metabolites provide evidence that *in situ* microbially mediated transformation and sediment sorption and burial are important processes controlling the fate of APEO metabolites.

Experimental Section

Study Site. Jamaica Bay, on the Southwestern shore of Long Island, NY (Figure 1), provides a nearly ideal site for study

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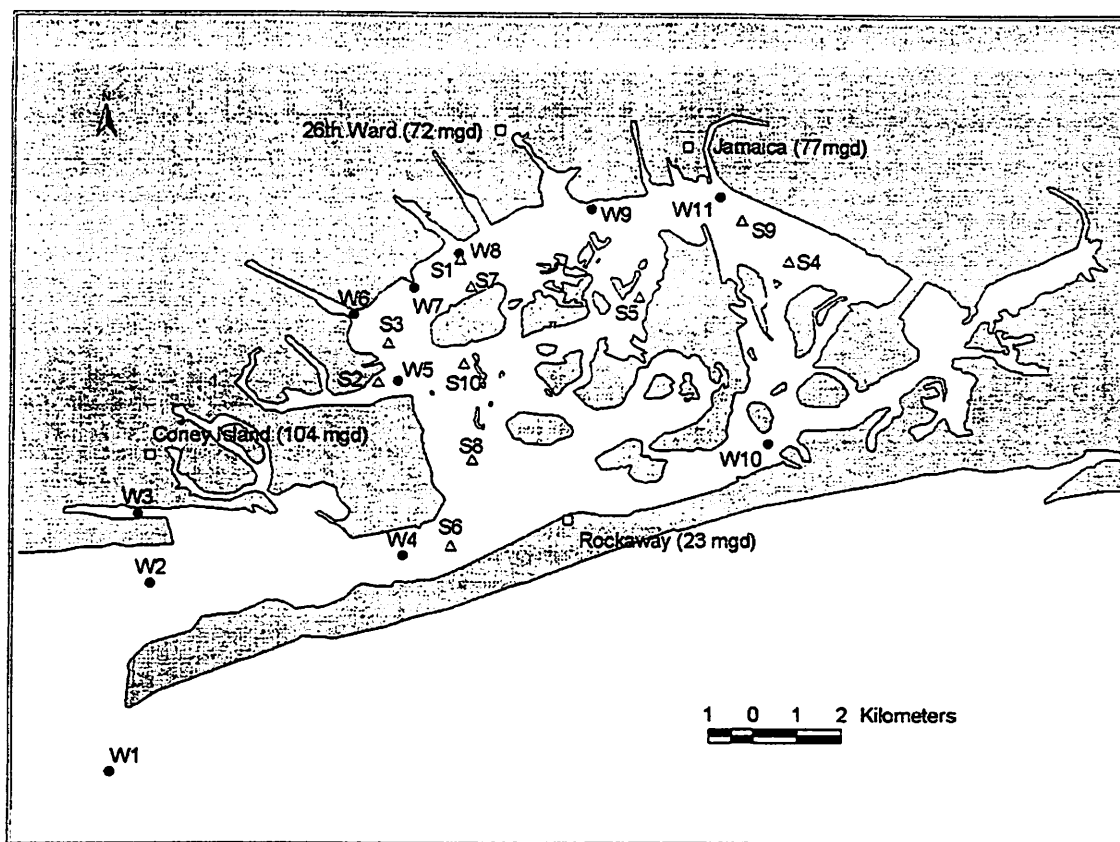


FIGURE 1. Map of Jamaica Bay, Long Island, NY (latitude 40.6, longitude -73.8) showing sediment (Δ) and water ($\bullet$) sampling stations as well as locations and capacities (millions of gallons per day, MGD) of the four largest wastewater treatment plants discharging into the estuary ($\square$).

of the fate of sewage-derived contaminants such as APEO metabolites in a coastal marine environment. It is an enclosed embayment approximately 6.5 km in diameter (27), with a single inlet for communication with the open Atlantic Ocean. Over the years, the bay has been heavily modified by anthropogenic activities. Extensive dredging over 80 yr has increased the average water depth from 1 to 5 m currently, thus increasing the volume in the bay by 70% relative to its pristine state (28). Consequently, the residence time has increased from 11 d in 1900 to up to 35 d presently (28). The effect of dredging has also been to modify the bathymetry and hydrography of the bay such that some areas are now highly depositional (28, 29). The tidal range of the bay is between 1 (neap) and 2 (spring) m, and the period is predominantly semidiurnal (27). Strong tidal currents (up to 0.6 m/s) exist along the north and south perimeter channels, causing the shallow waters of the bay to be generally well-mixed (27). The deeper, depositional areas of the bay experience much weaker currents, and this may lead to vertical stratification of the water column (27). Six wastewater treatment plants discharge roughly $1.1 \times 10^9 \text{ L d}^{-1}$ biologically treated sewage (the locations and capacities of the four largest plants are shown in Figure 1), constituting by far the largest input of freshwater to the bay (28). This is useful as the measurement of salinity within the bay may be used as a reliable tracer of wastewater.

Sample Collection. Sediment samples were collected in the summer 1998 from sites within Jamaica Bay (see Figure 1 for locations) by the U.S. EPA, Region 3, as part of the Regional Environmental Monitoring and Assessment Program (R-EMAP). Composite grab samples from each site were taken using a 0.1-m² stainless steel Van Veen grab. The top 2 cm of each grab was sampled using a stainless steel spoon,

and the collective samples from each site were homogenized in a glass bowl, subsampled to glass jars, and stored on ice until returning to the laboratory. The sediments were air-dried to avoid microbial degradation and stored in glass jars at 4 °C until analysis. Independent analyses carried out on spiked sediment indicated no loss of analytes during air-drying of sediment.

Water and suspended particulates were collected from Jamaica Bay on September 8 and 28, 1999, in coordination with the New York City's Department of Environmental Protection Harbor Water Quality Survey Program. Water samples were collected just below the air/water interface at each station using a 1.2-L Kemmerer bottle (Wildco Instruments, Saginaw, MI) constructed entirely of stainless steel and Teflon. Subsamples (100 mL) were taken from each cast for particulate organic carbon (POC) measurements. The 1-L aliquots from each sample were vacuum filtered (47 mm, Gelman A/E filters, 1 μm nominal pore size) on site using an all-glass apparatus. Filters (which had been baked overnight at 450 °C) were stored in aluminum foil-capped glass test tubes (which had also been baked at 450 °C). Independent experiments with spiked filtered seawater showed that no appreciable loss of APEOs to filter adsorption was detected. Filtered water was immediately spiked with a $^{13}\text{C}_6$ -*n*-NP-(0-3)EO surrogate standard cocktail (obtained from Cambridge Isotope Laboratories, Andover, MA) (100 ng added to 1 L), and the samples were acidified to pH < 2 with concentrated sulfuric acid. All water samples were stored in glass-stoppered Erlenmeyer flasks. Upon returning to the laboratory, POC samples were preserved with HgCl_2 and refrigerated; filters were frozen at -80 °C and subsequently freeze-dried.

TABLE 1. Neutral APEO Metabolites in Jamaica Bay Sediment, Water, and Suspended Particulates

	TOC (%)	NP	NP1EO	NP2EO	Sediment Concentrations (ng/g) (SD)			OP	OP1EO	OP2EO	OP3EO
					NP3EO	Cl-NP	Br-NP				
S1 ^a	0.344	29.9 (1.2)	119 (4)	62.9 (4.0)	4.23 (2.16)	nd ^a	0.41 (0.09)	nd	nd	nd	nd
S2 ^b	4.90	846 (106)	2120 (104)	1020 (19)	110 (4)	4.38 (0.45)	9.38 (0.31)	8.11 (0.42)	60.7 (3.2)	13.0 (0.4)	5.96 (0.45)
S3	4.52	326	860	389	98.0	1.64	6.50	3.23	21.0	5.60	2.16
S4	7.05	13700	13300	2650	328	1.51	4.90	nd	nd	nd	nd
S5	1.86	276	517	326	72.8	1.68	5.87	nd	nd	nd	nd
S6	0.189	6.99	26.4	16.1	nd	nd	nd	nd	nd	nd	nd
S7	0.470	64.6	134	92.4	9.22	0.91	1.55	nd	nd	nd	nd
S8	3.53	444	914	844	201	2.46	6.80	3.40	25.5	8.85	4.06
S9	6.35	5330	8050	3580	876	18.7	26.9	45.0	184	46.6	14.1
S10	0.57	52.7	132	93.3	15.0	0.49	nd	2.43	3.66	1.56	0.19
Water Concentrations (ng/L) (SD)											
	salinity	TSS (mg/L)	NP	NP1EO	NP2EO	NP3EO	OP	OP1EO	OP2EO	OP3EO	
W1	30.92	2.6	330	71.2	82.3	98.9	2.90	7.75	9.43	10.3	
W2	30.38	8.0	240	77.5	94.4	128	1.61	4.22	6.70	6.66	
W3	29.39	3.8	246	59.5	130	138	2.10	3.05	7.52	5.75	
W4	29.13	6.2	176	125	108	112	1.85	2.96	3.88	2.09	
W5	28.24	6.2	193	145	197	153	2.66	5.51	4.53	2.94	
W6	27.86	6.0	208	125	176	156	2.84	5.94	3.59	2.55	
W7	27.42	6.0	229	168	285	222	2.77	5.01	3.65	1.00	
W8	27.05	6.8	249	194	358	246	3.50	4.48	7.34	2.61	
W9	27.27	7.6	206	217	381	246	2.76	4.50	6.60	1.96	
W10	28.40	6.8	152	144	103	66.8	1.76	2.27	1.73	1.48	
W11 ^b	26.62	7.8	416 (50)	141 (10)	473 (26)	328 (34)	8.34 (2.19)	3.11 (1.05)	11.3 (1.9)	2.83 (0.30)	
9/28/99											
W1	30.21	8.2	99.2	56.8	38.6	26.2	1.66	17.2	5.95	1.66	
W2	29.55	4.2	77.4	61.0	62.9	33.8	1.56	18.5	3.93	1.44	
W2 part. ^c	12.8 ^d		3.57	2.03	1.09	0.52	0.05	nd	nd	nd	
W3	27.13	4.4	134	74.6	341	164	3.21	8.66	3.69	1.67	
W4	28.65	9.8	80.5	118	116	67.2	1.86	12.4	2.58	0.94	
W5	27.31	8.0	106	168	144	81.1	2.83	8.69	1.70	0.89	
W6	27.12	6.4	85.2	202	171	87.6	2.12	15.0	3.35	0.58	
W8	26.45	6.0	187	326	398	200	7.03	15.8	15.6	2.75	
W8 part. ^c	11.1 ^d		5.80	18.3	18.2	4.99	0.05	nd	nd	nd	
W9	25.77	9.4	180	172	308	187	3.88	10.8	7.88	1.44	
W10	24.94	5.8	84.8	160	131	65.2	1.74	8.89	2.63	0.31	
W11 ^b	25.03	7.0	201 (7)	157 (6)	320 (9)	202 (8)	3.27 (0.09)	26.0 (3.2)	4.89 (0.38)	1.04 (0.32)	
W11 part. ^{b,c}	19.7 (1.2) ^{b,d}		8.39 (1.76)	7.55 (0.18)	7.11 (0.61)	1.80 (0.51)	0.11 (0.04)	nd	nd	nd	

^a nd, not detected. ^b Mean and standard deviation of $n = 3$ samples. ^c Suspended particle concentrations, units of ng/mg. ^d Organic carbon content of particulate samples (POC %).

Chemical Analysis. APEO degradation products were analyzed in environmental samples using LC-MS, as described by Ferguson et al. (26). Briefly, APEO metabolites were isolated from water samples using solid-phase extraction (SPE) on C₁₈-silica. Dried sediment was extracted with methanol using a novel continuous-flow sonication procedure. Sediment extracts were then purified using normal-phase SPE followed by semi-preparative reverse-phase HPLC. Glass fiber filters were ultrasonically extracted for APEO degradation products with methanol using a high power (600 W) ultrasonic probe. APEO metabolites (including NP-(0-3)EO and OP(0-3)EO) were quantitatively determined in all extracts by reverse-phase HPLC with electrospray mass spectrometry detection. APEOs, APs, and halogenated NPs were separated chromatographically according to their alkyl-chain length (octyl elutes before nonyl) and halogen substitution (Cl-NP elutes after the APs and APEOs and before Br-NP) and were detected by the mass spectrometer in selected ion monitoring mode as (M + Na)⁺ ions in positive ion mode (AP(1-3)EO) or as (M - H)⁻ ions in negative ion mode (APs, halogenated NPs) (26). Field blanks for water sampling consisted of Milli-Q water that was carried through the entire sampling and extraction procedure prior to analysis. Sediment blank extractions were carried out using an appropriate mass of sea sand that had been baked at 450 °C

overnight (26). Recoveries of ¹³C₆-*n*-NP(0-3)EO surrogate standards using this method were 78-90% for water and 80-94% for sediment. Method detection limits (corrected for field blank measurements) ranged from 1 to 30 pg and were analyte-dependent (26).

Water quality parameters (including salinity and total suspended solids) were measured by the NYC DEP. Salinity was measured by conductivity using a CTD (conductivity, temperature, and depth) device. Total suspended solids (TSS) were determined gravimetrically. TOC and POC of sediments and suspended solids, respectively, were measured in acidified samples using a CHN combustion analyzer.

Results and Discussion

Sediment. Measured concentrations of APEO metabolites in Jamaica Bay sediments varied considerably among sampling sites (Table 1). Total NP(0-3)EO were found at concentrations ranging from 0.05 to 30.0 µg/g, while OPEO metabolites were much less concentrated, ranging from 4.5 to 289 ng/g. The higher measured concentrations of NPEO metabolites are consistent with greater consumption and use of NPEO surfactant products relative to OPEOs (1), and this trend is similar to results reported for other sediment environments (30). After normalization of sediment con-

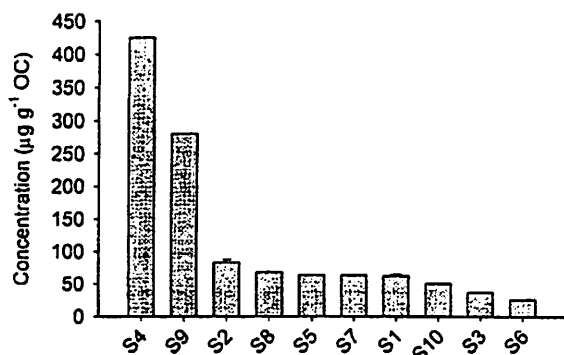


FIGURE 2. Organic carbon-normalized concentrations of Σ NP(0–3)EO in Jamaica Bay sediments. Values are single determinations except S2 and S1, which are means of triplicate sample analysis, with error bars corresponding to ± 1 SD.

centrations to sediment TOC (Table 1), the variability of NPEO metabolite levels within most Jamaica Bay sediments was reduced (Figure 2), suggesting that these contaminants are primarily associated with organic-rich, fine-grained sediment fractions and that they are actually relatively well-mixed in the fine-grained sediment fractions throughout the basin. The two sediments having anomalously high TOC-normalized NPEO metabolite concentrations (S4 and S9) are highly enriched in organic carbon, and the sites are located within a depositional basin (29) in the bay proximal to the discharge of a large wastewater treatment plant (Figure 1). The higher normalized concentrations at these sites may result either from rapid settling of NPEO-rich sewage particles close to the source or from enhanced NPEO concentrations in the Jamaica WWTP effluent relative to the other WWTPs around the Bay. It should be noted that the concentration of NP(0–3)EO in S4 sediment (30 $\mu\text{g/g}$) is one of the highest values ever reported for these contaminants in coastal marine sediments. Concentrations of NPEO metabolites in freshwater sediments have been reported to range from less than 2 ng/g in U.S. rivers to in excess of 70 $\mu\text{g/g}$ in heavily impacted sites within Canada (31), while reports in coastal marine sediments range from less than 6 ng/g offshore Barcelona, Spain, to nearly 14 $\mu\text{g/g}$ in the Venice Lagoon, Italy (31).

Distribution of APEO ethoxymers in the sediments was remarkably constant among sites (Figure 3a). NPEO metabolites were dominated by NP1EO with lesser, but significant, amounts of NP and NP2EO. NP3EO was present at less than 10% of the total measured concentration. In some environments, quantifying only APEOs with 0–3 ethoxyl units in sediments may result in underestimation of the total APEO pool due to the presence of significant amounts of the higher numbered ethoxylates, as was recently shown by Shang et al. (22). To verify that selective analysis of NP(0–3)EO in sediments did not significantly impact reporting of NPEO ethoxymer distributions in sediment samples, a selected sample (S4) was analyzed for NP(0–15)EO using a newly developed method based on quantitative high-performance size-exclusion chromatography with electrospray mass spectrometry detection (32). Results indicated that NP(4–15)EO collectively made up only 8.5% of the total measured NPEO concentration in S4 sediment; therefore, the NPEO ethoxymer distribution was dominated by the more hydrophobic metabolites [i.e., NP(0–3)EO]. The sample (S4) analyzed for NP(0–15)EO was taken from a depositional basin very close to one of the major wastewater sources to Jamaica Bay. Therefore, this site was probably more likely to contain significant amounts of NP(4–15)EO than any other sampled sediment in our study. The fact that it did not contain significant concentrations of these ethoxymers, coupled with the fact that all wastewater treatment plants discharging to

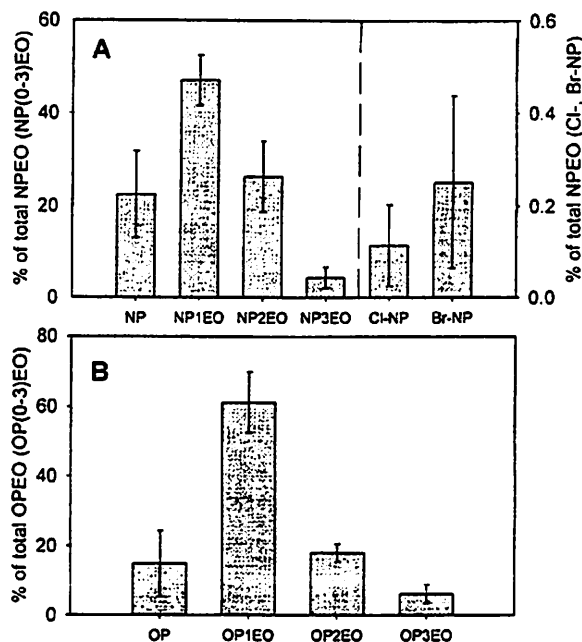


FIGURE 3. Mean (± 1 SD) ethoxymer distributions of NPEO metabolites (A) and OPEO metabolites (B) in Jamaica Bay sediments.

Jamaica Bay currently operate with full secondary biological treatment, is strong evidence that the bay's sediments are characterized by a dominance of short ethoxy-chain APEO metabolites. OPEO metabolite ethoxymers in Jamaica Bay sediments showed a similar profile to that of the NPEOs (Figure 3b), i.e., the distribution was dominated by short ethoxy-chain OPEOs, especially OP1EO.

The ethoxymer distributions of APEO metabolites in Jamaica Bay surface sediments are reflective of a highly degraded APEO mixture (9) and are similar to distributions that have been reported for other aquatic environments receiving biologically treated wastewater (15, 16, 19, 30). This result is in contrast to data reported by Shang et al. (22), where substantial levels of highly ethoxylated NPEOs occurred in sediments, presumably due to the lack of biological treatment in wastewater treatment plants adjacent to the sampling area. This profile was found to persist throughout sediment cores (22), providing evidence for the relative recalcitrance of NPEOs toward degradation in anoxic sediment. The apparent resistance to anaerobic degradation of APEOs in bedded sediment indicates that the profile of APEO metabolites measured in sediments in the present work (which are likely predominately anoxic, with the exception of the top couple of millimeters, due to their relatively high organic carbon content) may have been the result of degradation processes that occurred prior to deposition during both secondary wastewater treatment and in the water column of Jamaica Bay.

Chlorinated and brominated nonylphenol (Cl-NP, Br-NP) were found in many Jamaica Bay sediments, although they accounted for less than 1% of the total measured NPEO metabolite pool (Figure 3a, concentrations in Table 1). No halogenated OPEO metabolites were detected in any of the samples analyzed. Halogenated derivatives of APEOs and their degradation products have been reported as byproducts of wastewater chlorination processes (33–35). The very low relative abundance of these contaminants in Jamaica Bay sediments indicates that they are likely not of major toxicological concern; however, they may prove useful as tracers of APEO sources that have experienced chlorination (e.g., during disinfection of wastewater or pulp and paper mill bleaching processes).

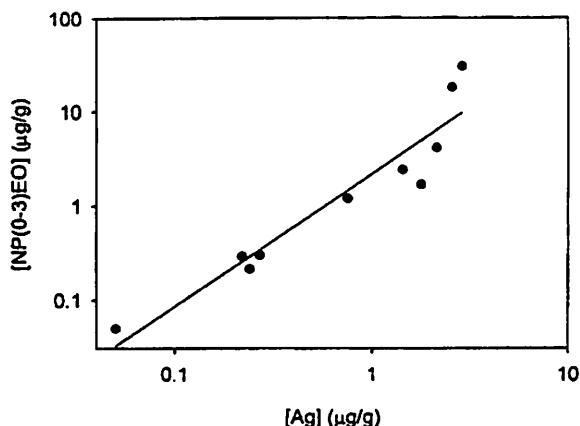


FIGURE 4. Correlation of Σ NP(0-3)EO concentrations with silver (a sewage tracer) in Jamaica Bay sediments ($r^2 = 0.898$).

The primary source of APEOs and their metabolites to the nearshore marine environment is the discharge of treated and untreated wastewater. These compounds may, therefore, be useful tracers of sewage in nearshore sediments. To test this hypothesis, concentrations of NP(0-3)EO in Jamaica Bay sediments were examined for correlation with concentrations of sediment bound silver (measured by U.S. EPA contractors in the course of the 1998 R-EMAP program). Silver has been used as a reliable wastewater tracer in sediments (36) due to its particle reactivity and principal use in photographic film development. Summed NP(0-3)EO concentrations showed a strong correlation with silver in Jamaica Bay sediments (Figure 4, $r^2 = 0.874$). It can be concluded therefore that NPEO metabolites in Jamaica Bay sediments do provide a reliable marker of sewage impact. In addition, data presented here along with that of Shang et al. (22) indicate that the distribution of NPEO ethoxymers in sediments may be a valuable indicator of the treatment level of wastewater impacting coastal marine sediments.

Water. Individual neutral NPEO degradation products in Jamaica Bay surface water were detected at concentrations from <100 to nearly 500 ng/L (Table 1) on two separate sampling dates (Table 1), which were separated by 20 days. Interestingly, there was a very large tropical storm (Floyd) that occurred on September 15-16 (between the two sampling dates) and deposited 9.0 cm of precipitation at nearby Kennedy Airport. The reported concentrations are consistent with recent measurements of these compounds in other similar aquatic systems. Average concentrations of NP(0-2)EO in Swiss rivers during 1997-1998 reportedly ranged between 100 and 300 $\mu\text{g/L}$ (18). Dissolved NP was found at an average concentration of 78 ng/L in Upper New York Harbor during summer 1998 (25). The dissolved concentrations of NPEO metabolites measured in these recent studies and in the present work are much lower than those measured in impacted aquatic systems during the 1980s [up to 70 $\mu\text{g/L}$ (15, 37)] and likely represent improvements in sewage treatment processes and, in the case of Swiss waters, risk reduction measures implemented as part of the Swiss ordinance for environmental pollutants. As in sediments, OPEO metabolites in Jamaica Bay waters were much less concentrated than NPEO metabolites. The few previous studies that have examined both OPEO and NPEO metabolites in water (16, 30) reported similar trends for these compound classes. Although they were not quantified, APECs, which are acidic metabolites of APEOs formed by terminal oxidation of the ethoxyl-chain under aerobic conditions (9), were detected in Jamaica Bay waters using the LC-MS approach in both positive and negative ion modes (26). These compounds are highly water-soluble due to their ionic nature

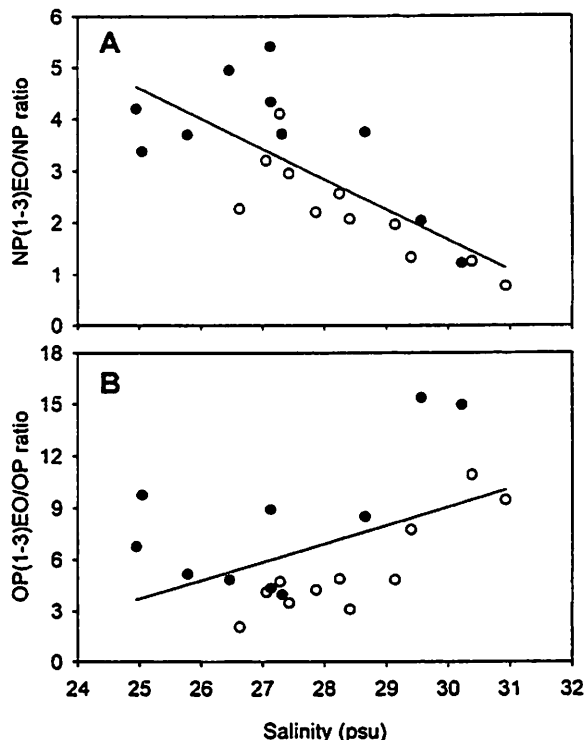


FIGURE 5. Ratios of dissolved Σ NP(1-3)EO to NP (A) and Σ OP(1-3)EO to OP (B) versus salinity in Jamaica Bay surface waters collected on 9/8/99 (○) and 9/28/99 (●).

and have been found to be important constituents of the APEO metabolite pool in some aquatic systems (18, 38). Distributions of APEC ethoxymers in Jamaica Bay waters (based on mass spectral profiles) were dominated by short (1-3) ethoxy-chain oligomers, indicative of a degraded mixture of APEOs and APEO metabolites.

Since one mechanism of APEO biodegradation proceeds via shortening of the ethoxy chain, the ratio of AP(1-3)EO to the completely de-ethoxylated metabolite AP should be an indicator of extent of APEO mixture biodegradation. This ratio was found to decrease with increasing salinity within Jamaica Bay for NPEO metabolites at both sampling times (Figure 5a). As increasing salinity corresponds to increased mixing of wastewater with seawater (and generally longer times), these data suggest that post-discharge degradation of the NPEO mixture did occur within the water column at a rate faster than volatilization (which selectively removes nonylphenol relative to the ethoxy-substituted forms; thereby increasing the ratio) or hydraulic residence time in Jamaica Bay [2-5 weeks (27, 28)]. The ratio of OP(1-3)EO to OP, however, showed a more complicated trend than that of the NPEO metabolites with respect to salinity (Figure 5b). In general, the extent of OPEO degradation decreased with increasing salinity. This suggests that the distribution of OPEO metabolites was decoupled from that of the NPEO metabolites, perhaps due to differences in the sources of the two classes of APEOs. Further evidence for this hypothesis is provided below. It should be noted that, although the method for determining total NPEO ethoxymers distributions [including NP(0-15)EO] mentioned above for sediments (32) was not applied to water samples, qualitative examination of full-scan electrospray MS spectra of NPEOs in water extracts indicated that highly ethoxylated APEOs did not make up a large fraction of the dissolved APEO pool. This is consistent with the level of wastewater treatment in area WWTPs, which discharge to Jamaica Bay, and indicates that transformation of highly ethoxylated APEOs in the water column would not

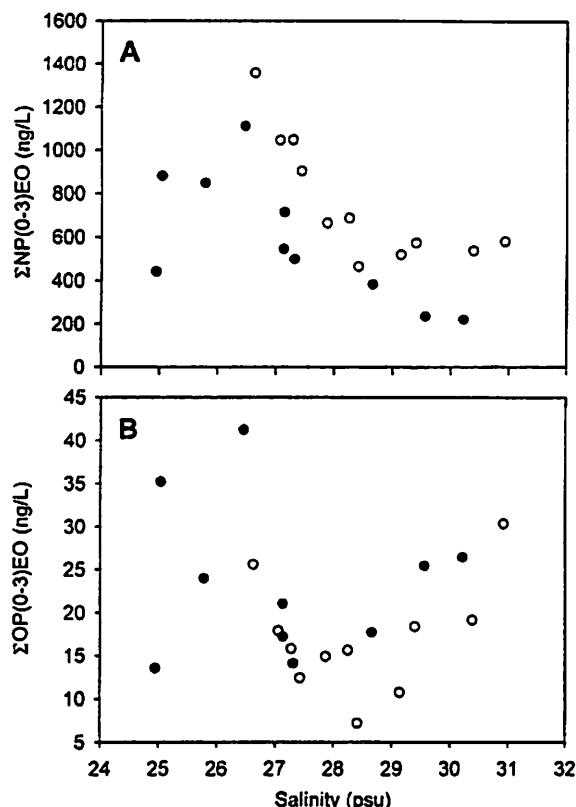


FIGURE 6. Σ NP(0-3)EO (A) and Σ OP(0-3)EO (B) dissolved concentrations versus salinity in Jamaica Bay surface waters collected on 9/8/99 (○) and 9/28/99 (●).

have significantly complicated the interpretation of AP/AP-(1-3)EO ratios.

A plot of dissolved analyte concentrations vs salinity in an estuary can be thought of as a "mixing diagram" where distribution of concentrations along a straight line represents conservative mixing between two end-members. Deviations from a straight line indicate (i) nonconservative behavior caused by degradation, sorption, or volatilization of the analytes; (ii) additional analyte sources at intermediate salinities; or (iii) temporal and spatial variability in the sources of APEOs. The mixing diagram of total neutral NPEO metabolite concentrations within the estuary (Figure 6a) was nonlinear, suggesting that these compounds behave non-conservatively, possibly due to biodegradation or removal by sorption onto settling particles, as evidenced above. Nevertheless, it is clear from the diagram that high concentrations were associated with lower salinities, consistent with a "fresh" wastewater source of these compounds. Further evidence for a wastewater source of NPEO metabolites to the bay is provided by the strong correlation ($r^2 = 0.919$) obtained between the measured dissolved NPEO metabolite concentrations and fecal coliform counts in the water samples (measured by NYC DEP as part of their water quality monitoring program). Fecal coliform is generally used as a water quality indicator of sewage impact, although the extent of wastewater treatment will greatly affect the input of coliform bacteria to receiving waters.

An examination of the mixing diagram of total neutral OPEO metabolites in Jamaica Bay (Figure 6b) reveals a "V" shape, providing further evidence (in addition to that described above for Figure 5b) that there was a significant source of OPEO at high salinity, in addition to the source from fresh wastewater. An indication of decoupled sources of NPEO and OPEO within Jamaica Bay is seen in Figure 7.

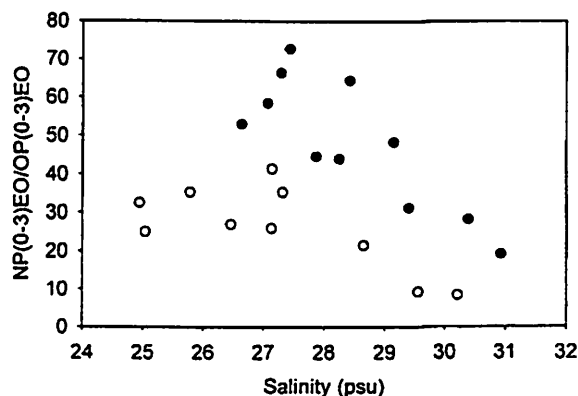


FIGURE 7. Ratios of Σ NP(0-3)EO to Σ OP(0-3)EO dissolved concentrations in Jamaica Bay surface waters collected on 9/8/99 (○) and 9/28/99 (●).

where the ratio of NPEO metabolites to OPEO metabolites decreased with increasing salinity for the two independent sampling dates. The trend is most obvious for the samples taken on September 8, 1999. It is possible that OPEOs may be delivered to the estuary from the coastal ocean through the inlet to the bay. OPEOs find diverse uses and may be more commonly employed in industrial processes than the NPEOs. The inlet to Jamaica Bay is adjacent to the mouth of New York Harbor, and OPEO-rich water from the more industrialized Harbor may be mixed into Jamaica Bay through estuarine transport.

Partitioning of APEO Metabolites to Suspended Solids. Short ethoxyl-chain APEOs are moderately hydrophobic contaminants (see $\log K_{ow}$ values in Table 2) that have been found to associate strongly with organic-rich particulate matter in aqueous systems (39, 40). In the present work, NP and NP(1-3)EO concentrations of <1 to nearly 20 ng/mg were found on suspended particulate samples from three sites within Jamaica Bay on September 28, 1999 (Table 1). OPEO metabolites adsorbed to suspended particles were generally below detection limits, except in the case of OP, which was found at concentrations approximately 1.0% that of NP (Table 1).

The organic carbon normalized distribution coefficients (K_{oc}) derived from our data are seen in Table 2. Also included in Table 2 are measured K_{ow} values and available estimates of K_{oc} from both laboratory and field experiments reported by others. In the present work, $\log K_{oc}$ does not vary greatly among the different neutral metabolites, and the measured average $\log K_{oc}$ for NP is very similar to that measured in five samples by Sekela et al. (41) and in four samples by Van Ry et al. (25). Most significantly, the values of K_{oc} are higher (typically by a factor of 10) than either the measured K_{ow} values or the laboratory measurements reported for NP3EO (40) or OP (39). The sorbent properties and mechanisms controlling sorption of APEOs and their metabolites onto particles are not fully understood. In a comparison between the sorption of APEOs on an organic-rich sediment before and after organic matter removal, John et al. (40) provided data indicating that interactions with organic matter were important in controlling sorption of APs and short ethoxyl-chain APEOs. However, as the level of APEO ethoxylation increased, association with mineral surfaces became the dominant contributor to APEO sorption, consistent with other observations in the literature for structurally related alcohol ethoxylates (42).

The higher K_{oc} values measured in the field relative to those predicted by K_{ow} and by short-term laboratory studies could be the result of several factors. First, higher energy sorption to a limited number of sorption sites may lead to

TABLE 2. Partition Coefficients for APEO Metabolites Determined in This and Other Freshwater Lab and Field Studies

	NP	NP1EO	NP2EO	NP3EO	OP
log K_{ow} ^a	4.48 (0.12)	4.17 (0.15)	4.21 (0.18)	4.20 (0.11)	4.12 (0.10)
log K_{oc} (measd) ^b	5.39 (0.12)	5.46 (0.12)	5.18 (0.25)	4.87 (0.35)	5.18 (0.28)
log K_{oc} (lit)	5.28 (0.43) ^c			4.16 ^d	3.91 (0.24) ^e
	5.10 (0.48) ^f				

^a From ref 43. ^b Mean of $n = 5$ total determinations at three stations: W11 (triplicate), W8, and W2. ^c From ref 41. ^d From ref 40. ^e Calculated from ref 39. ^f Calculated from ref 25.

increased K_{oc} measurements at low sorbate levels (due to isotherm nonlinearity at low sorbate loadings). Most laboratory sorption experiments are conducted at high nanomolar to micromolar solute concentrations due to analytical limitations and, consequently, may underpredict sorption at more realistic field concentrations in the picomolar to low nanomolar range. Interestingly, there was a clear inverse relationship between measured K_{oc} values of NP and dissolved aqueous concentrations in the study of Sekela et al. (41), as log K_{oc} decreased from 5.6 when NP concentration was 6.6 and 7.6 ng/L down to a log K_{oc} of 4.7 when NP was 130–2900 ng/L. A second possibility for the higher K_{oc} values measured for APEO metabolites in the field may be “aging” of these compounds on suspended particles, such that the APEOs may have become associated with more resistant (to desorption) phases on sediments or detritus. This process may not be easily reproduced in spiked laboratory sorption experiments. A final possibility is that partitioning of APEO metabolites in the field may not accurately mimic “equilibrium” distributions if dissolved metabolites are removed by volatilization or microbial degradation at rates faster than desorption from waterborne particles can occur. It should be noted that the organic carbon-normalized concentrations of APEO metabolites in bedded sediments in the present study were similar to those for suspended particulates, which were described by the reported K_{oc} values. Thus, prediction of sediment APEO concentrations using K_{ow} values or laboratory-derived K_{oc} values coupled with dissolved APEO concentrations would substantially underpredict actual levels of these compounds in the bedded sediments.

APEO Metabolite Fate in Jamaica Bay. Data reported here for the distribution of APEO metabolites within the waters and sediments of Jamaica Bay indicate that degradation and sorption processes strongly influence the fate of these compounds following their release into this estuary. Comparison of estimates of characteristic times for removal of APEO metabolites due to burial, volatilization, and hydraulic residence time may be used to place limits on the rate of in situ microbial transformation. Characteristic times for volatilization of NP are estimated to be on the order of 9–17 days, based on the mean depth (5 m) of Jamaica Bay and on a range of mass-transfer coefficients for volatilization of NP (25) (1.2–2.4 cm h⁻¹). Volatilization rates of NP(1–3)EOs must be lower than those of NP due to their lower Henry’s law constants and molecular diffusion coefficients. Thus, volatilization in the absence of other processes would lead to an increase in the NP(1–3)EO/NP ratio in the water column. A characteristic time for removal of APEO metabolites from the water column through sediment burial is more difficult to estimate, as sediment budgets for the entire bay have not been determined. However, in the broad depositional zone in the northeast portion of the bay, the characteristic time for APEO metabolite burial has been estimated at ~9 days based upon water column inventory, sediment burial rate (1.4 cm yr⁻¹) (29), and a mean sediment concentration of 20 µg/cm³. Thus, for Jamaica Bay, the time scales of APEO metabolite volatilization and removal by sediment burial are both comparable to the hydraulic residence time of the bay (= 35 days) (28). We suggest that

microbial transformations in the water column must be faster than volatilization and therefore other removal mechanisms to explain the trend found in the present work [i.e., decreasing ratios of NP(1–3)EO/NP with increasing salinity or mixing time]. In contrast, Van Ry et al. (25), using a simple one-box model for lower New York Harbor, estimated that volatilization accounted for a larger fraction of the total loss of NP (37%) than did sediment burial (10%) or biodegradation (29%). The differences in these estimates could be either due to the modeling assumptions used by the authors or due to differences between the highly sewage impacted Jamaica Bay and the less eutrophic lower New York Harbor. Microbial transformation of APEO metabolites in Jamaica Bay may be faster than in New York Harbor because it contains a much higher percentage of sewage effluent and, hence, a microbial community potentially more acclimated to utilizing APEOs. Given the likely importance of microbial transformations of APEO mixtures, more work should be performed to elucidate the relative magnitude of this process in various environments.

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