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Biogeochemistry of Nonylphenol Ethoxylates in Urban Estuarine Sediments

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We have examined the concentrations and distributions of nonylphenol ethoxylate (NPEO) surfactants and their primary neutral metabolites in two dated sediment cores collected in 1988 and 1996 from a depositional area proximal to a wastewater treatment plant within Jamaica Bay, NY. Total NPEO concentrations ranged from >50 μg/g near the surface (4−6 cm, deposited ca. 1990) to below detection limits (<0.1 μg/g) at 50 cm depth (deposited ca. 1940). The general decrease in NPEO concentrations with increasing depth in sediment reflected increased commercial use of these compounds over the last 50 yr. NPEO ethoxymer distributions in recent sediments were dominated by NP-(0−3)EO, consistent with the increased relative input of these particular ethoxymers to the estuary following the upgrade of local biological sewage treatment processes to full activated sludge in the late 1970s. NPEO ethoxymer profiles in deeper sediments were characterized by relatively higher proportions of unmetabolized, highly ethoxylated NPEOs. Depth profiles of NP1EO and NP in the upper portion of the sediment core showed evidence for in situ diagenetic conversion of NP1EO to NP. However, comparison of NPEO concentrations in selected strata from the core collected in 1996 with those in matched strata from a core collected from the same location in 1988 provided no evidence for in situ degradation of total NPEOs during the elapsed 8 yr between collection dates.

Introduction

Nonylphenol ethoxylates (NPEOs) are high production volume surfactants used as detergents, wetting agents, and emulsifiers in various commercial and industrial products worldwide. In the United States, they have experienced rapid growth since their introduction in the mid-1950s, with total U.S. sales reaching 225 t in 1995 (Figure 1) (*1*). Due to their primary route of disposal through wastewater treatment, they may occur as pollutants in coastal marine environments that receive significant quantities of treated or untreated sewage (*2*−*5*).

The issue of NPEO persistence and biodegradability in wastewater treatment and in the aquatic environment has been controversial and has sparked considerable research on the environmental fate and behavior of these compounds (*6*−*10*). Numerous degradation pathways have been proposed for NPEOs (see refs *11* and *12* for reviews), but it has been generally observed that biodegradation of NPEO mixtures in the environment results in a decrease in the relative abundance of NPEOs with long ethoxy (EO) chains and a concomitant increase in the relative abundances of the shorter ethoxy chain NPEOs, including nonylphenol (NP), which for the present purposes will be considered as part of the NPEO series (i.e., NP0EO). In laboratory experiments, it has been shown that short ethoxy chain NPEOs (e.g., NP-(0−3)EO) may be formed as metabolites of highly ethoxylated NPEOs by successive elimination of EO units during aerobic (*13*, *14*) and anaerobic (*10*, *15*) degradation. Accumulation of hydrophobic, short ethoxy chain NPEOs and NP in the aquatic environment is of toxicological interest because of their potential acute and chronic toxicity in sediments (*16*) and because several of these compounds have been reported to act as environmental endocrine disruptors (*17*). The apparent persistence of NPEO metabolites in the aquatic environment has led to the initiation of regulatory action in Europe (*18*) and North America (*19*, *20*) and has apparently driven much of the research on the environmental fate and occurrence of these compounds to date.

Much of the environmental fate research on NPEOs has focused on surface waters and surficial sediments in freshwater and marine systems (*2*, *5*, *7*, *21*). Work in aquatic environments has shown that NPEOs and their neutral metabolites accumulate and persist in sediments, where they may be bioaccumulated by sediment-ingesting benthic organisms (*16*). Sequestration of surface-active NPEOs and their hydrophobic metabolites into sediment is not surprising as these compounds have been shown to be relatively particle reactive (*5*, *22*). To date, only a few authors have reported on the occurrence, distribution, and post-depositional behavior of NPEOs and their metabolites in bedded sediments (*4*, *23*−*26*).

In previous work, we have found locally high surficial sediment concentrations of NPEO metabolites (up to 30 μg/g) within Jamaica Bay (Figure 2), a highly urbanized and sewage impacted estuary located within the New York City metropolitan area (*5*). These findings led us to hypothesize that the elevated sediment concentrations in some areas of the estuary could be due to high loadings of NPEOs from wastewater discharge coupled with a biogeochemical sediment regime favoring preservation of organic contaminants such as NPEOs. In the present work, we have utilized chemical analysis of sediment cores to study the geochronology, preservation, and diagenetic behavior of NPEOs in sediments within a highly NPEO-contaminated and depositional area of Jamaica Bay. Our objectives were to examine the persistence and compositional changes of NPEOs in a well-dated estuarine sediment core, to compare NPEO concentrations and distribution in selected date-matched horizons from a core taken previously at the same site, and to interpret the data using a diagenetic model to describe the post-depositional behavior of NPEOs in estuarine sediment.

Experimental Section

Description of Study Site. The site chosen for the present work was located within Jamaica Bay, NY (Figure 2). This bay is an extensively urbanized estuary within the boroughs of Queens and Brooklyn in New York City. It is located on the

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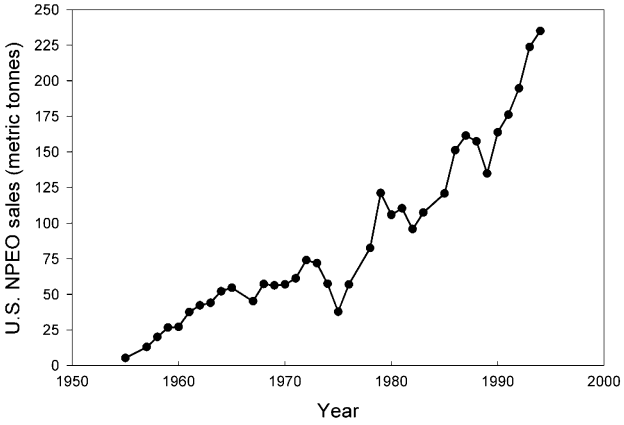

FIGURE 1. Annual sales of NPEO surfactants in the United States from 1955 to 1995.

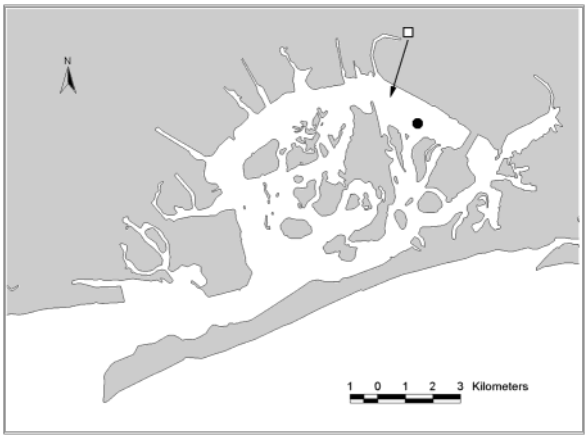

FIGURE 2. Map of Jamaica Bay, on the South shore of Long Island, NY, showing the locations of the JB13/JB16 core site within Grassy Bay (●, latitude 40.6322, longitude −73.8032) and the Jamaica WWTP (□). The outfall of the Jamaica WWTP into Grassy Bay is shown as an arrow on the map.

southwestern shore of Long Island and has a single channel (Rockaway inlet) for exchange with the Atlantic Ocean. The hydrography of the bay has been significantly altered over the last century by dredging of ship channels and landfilling of the fringing marshland to allow commercial and residential development (*27*). Our coring site is within an area of the bay known as Grassy Bay. This deep basin was formed in 1939 when a large area in the northeastern portion of the bay was dredged to provide fill for the construction of what is now John F. Kennedy International Airport (*27*). Grassy Bay now acts essentially as a catchment basin for the adjacent Jamaica Wastewater Treatment Plant (WWTP) (Figure 2), which discharges approximately 360×10^6 L of biologically treated effluent/day directly into the basin (*27*).

The Jamaica WWTP was built in 1943 with modified aeration secondary treatment. In 1963, plant capacity was increased from 60 million gal/day (MGD) to 100 MGD. During this upgrade, the plant's total flow dropped sharply as untreated wastewater was bypassed directly to the bay (Diane Hammerman, New York City Department of Environmental Protection, personal communication). The plant has operated with full activated-sludge step aeration since an upgrade in 1978. As of the 1990 census, the Jamaica WWTP served 644 100 people in the boroughs of Queens and Brooklyn. Several other WWTPs discharge an additional 200 MGD of effluent into Jamaica Bay, but the northern sections of the bay and in particular Grassy Bay are impacted most significantly by the Jamaica WWTP (*27*) (Figure 2). Grassy Bay is the deepest (up to 15 m as compared to ~1 m average depth prior to dredging), most heavily polluted region of the bay (*27*). It is highly depositional (*28*, *29*) and poorly flushed by tidal currents with seasonal water-column stratification and bottom water anoxia (*29*). In addition, a recent survey of NPEO metabolites in surface (0−3 cm) sediments of Jamaica Bay found that concentrations of NP(0−3)EO were highest in sediments collected from Grassy Bay (up to 30 μg g^{-1}; *5*). The particular site chosen for core collection within Grassy Bay was the subject of a previous, detailed study on geochronology of sediment-associated pollutant metals and chlorinated organic contaminants (*28*) that provided data on sediment characteristics and particle accumulation rates.

Sample Collection and Analysis. Gravity cores were collected from the same location within Grassy Bay on October 1, 1988 (JB13), and October 4, 1996 (JB16). Cores were prepared for radioisotope, metal, and organic contaminant analysis as previously described (*28*). Briefly, cores were sectioned at 2−4-cm intervals, dried in an oven at 35 °C, and stored at room-temperature pending analysis. Radioisotopes (^{7}Be and ^{137}Cs) used for sediment dating were analyzed in sediment section aliquots by γ-spectrometry using lithium-drifted germanium or intrinsic germanium detectors. Trace metals (including Cu, Pb, Zn, Fe, Ag, Cd, Sb, and Sn) were determined in core sections by a combination of atomic absorption spectrometry and ICP-MS (*28*).

NPEOs, including NP, were analyzed in 13 sections (with one section analyzed in triplicate) of core JB16 (collected 1996) and 3 sections of core JB13 (collected 1988) using a mixed-mode HPLC separation with electrospray mass spectrometry detection, as described previously (*30*). This method is suitable for the quantitative determination of multiple NPEO ethoxymers (NPEOs with ethoxy chain lengths ranging from 0 to 15; i.e., NP to NP15EO) in estuarine sediment. It eliminates interferences among NPEO ethoxymers that could otherwise complicate mass spectrometric detection (*31*, *32*) by separating the NPEOs chromatographically, by ethoxy chain length, prior to the mass spectrometer. In addition, the method incorporates custom synthesized $^{13}C_6$-NPEO surrogate standards, thereby improving the precision and quantitative reliability of electrospray mass spectrometric detection of NPEOs in complex mixtures such as sediment extracts (*30*). Briefly, dried sediments (0.2−1.0 g dry wt) were spiked with surrogate standards (described above), and NPEOs were extracted with methanol using high-temperature flow sonication (*32*). NPEOs were purified from crude extracts by semi-preparative HPLC, and the purified extracts were spiked with internal standards (*n*-NP, *n*-NP3EO) prior to HPLC−MS analysis (*30*). Analytical variability was estimated by triplicate extraction and analysis of NPEOs in a single sediment horizon from core JB16 (28−32 cm). Relative standard deviations (RSDs) for individual NPEO ethoxymer concentrations ranged from 0.8 to 9.1 (average 3.7) (*30*).

Results and Discussion

Sediment Dating. The sediment core samples collected from Grassy Bay were visibly anoxic at all depths and were predominately composed of silt/clay materials, with relatively high organic carbon content (~6−7% organic carbon) (*28*), consistent with a highly depositional, eutrophic estuarine environment. In core JB16 (collected in 1996), a single sandy layer of sediment was found at 48−52 cm depth. Trace metal analysis of this layer showed significantly lower concentrations of Fe and other metals than in sections above and below this depth (unpublished data). The anomaly at 48−52 cm may be related to the dredging of Grassy Bay in 1939 to provide fill for the adjacent airport runway (described above).

Depth profiles of ^{137}Cs and ^{7}Be in core JB16 are shown in Figure 3. The ^{137}Cs profile is dominated by a maximum at 30 cm. The major historical source of this predominantly anthropogenic isotope to the environment has been fallout

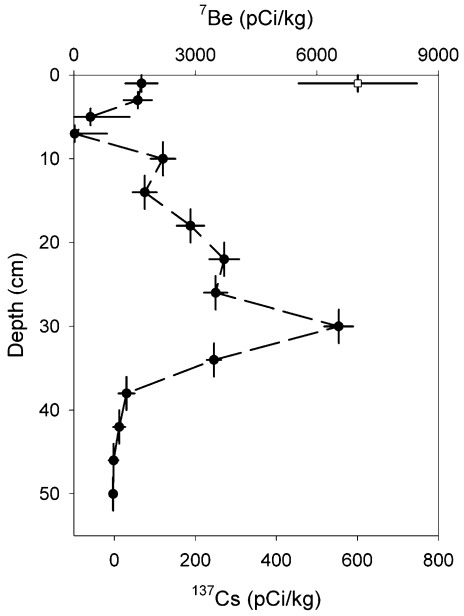

FIGURE 3. Depth profiles of radionuclides in core JB16. Vertical error bars represent the depth interval of sampling, while horizontal error bars represent counting error (two times standard deviation). ^{7}Be (□) was detected significantly above background only in the top 2 cm of the core. Peak ^{137}Cs (●) activity was detected in the 28−32-cm section, consistent with deposition of this sediment layer during the peak of atmospheric atomic weapons testing in ca. 1963.

from atmospheric nuclear weapons testing and nuclear reactor effluent (*33*) as well as accidents such as Chernobyl in the Ukraine. The peak activity observed for ^{137}Cs in the 28−32 cm depth section in the present core is interpreted to indicate deposition of this layer in approximately 1963, corresponding to the peak in atmospheric nuclear weapons testing in the Northern Hemisphere. The first measurable activity of ^{137}Cs, defined as the deepest depth section in which the measured activity is greater than its 2σ counting error, in the 36−40 cm depth section is interpreted to correspond to beginning of large-scale atmospheric tests in the early-1950s. A net burial velocity of 0.92 cm yr^{-1} places both of these ^{137}Cs horizon layers at their proper time periods and is also consistent with the anomalously low metal concentrations of the 48−52 cm depth section, mentioned previously, being an artifact of the dredging of Grassy Bay in 1939. ^{7}Be is a cosmogenic isotope with a half-life of 53 day. Counts of this isotope were detected significantly above background only in the upper 2 cm of core JB16 (Figure 3). This is consistent with recent deposition and limited vertical mixing (physical or biogenic) of sediment in the upper few centimeters of the core (*28*).

Detailed interpretations of radionuclide depth profiles in core JB13 (collected in 1988 from the same location as core JB16, described above) have been previously reported (*28*). In this core, ^{7}Be was confined to the upper 2 cm, and the collection date and ^{137}Cs maximum indicated a net burial velocity of 1.4 cm yr^{-1} for the period between the mid-1960s and the late-1980s. The estimated burial rates for the two cores were used to assign deposition dates to individual core sections, providing matched-time horizon samples. Additional confidence in the dating assignments was provided by the trace metal data (unpublished data). When plotted against date of deposition, trace metal levels in the two cores superimposed nearly perfectly. For example, silver concentrations peaked at 12 μg g^{-1} in sediments deposited in the late 1960s in both cores and decreased sharply to 5 μg g^{-1} in sections deposited ca. 1980.

Vertical Distributions of NPEOs in Sediment Cores. Total NPEO concentrations in Jamaica Bay sediments were found to decrease with depth (Figure 4a) from a maximum of ∼50 μg g^{-1} at 5 cm to undetectable levels in sediments deposited prior to 1950, consistent with the steady increase in use of these compounds from that date until the approximate date of the JB16 core collection (Figure 1; complete data for total NPEO and individual NPEO ethoxymers are given in table S2 in the Supporting Information). The local maximum observed for the total NPEO profile in JB16 in the early−mid-1960s (Figure 4a) may be related to the flow capacity upgrade at the Jamaica WWTP in 1963 (discussed above), during which untreated wastewater was shunted to the bay. Only a single report exists in the literature for comparison of vertical sediment profiles of total NPEOs. In contrast to our results, Shang et al. (*4*) found that total NPEO concentrations (NP(0−19)EO) in cores collected offshore of Vancouver, BC, Canada, decreased only very slightly over a depth interval of 50 cm, reported to represent approximately 30 yr of deposition. However, interpretation of these profiles may have been significantly complicated by vertical sediment mixing as the geochronologies were based on ^{210}Pb profiles, which can be dominated by deep biogenic mixing processes in coastal marine sediments (*34*).

A particularly powerful method for studying the biogeochemical behavior of organic contaminants in sediments is the concept of "matched cores" (*28*). In this technique, cores are taken periodically from a single highly depositional (burial rate ideally ≥ 1 cm yr^{-1}) site of interest over an interval of several years. Contaminants of interest are analyzed in selected horizons from the cores, and estimates of geochronology are made for each core based on radioisotope measurement, date of collection, and known parameters from the site of interest (such as dredging history). Deposition date-matched sediment core horizons obtained from a single core site represent endpoints of an in situ incubation. Observed differences in organic contaminant concentrations in matched horizons from different cores should reflect any modification of the contaminant within the sediment over the time between core collections. This approach has been applied to the study of depositional chronology of pollutant metals and selected chlorinated organic contaminants in sediments of our study area (*28*) and the Hudson River in New York (*33*, *35*). In the present work, the matched core approach was utilized to study the post-depositional behavior of NPEOs in sediments from Jamaica Bay. Examination of total NPEO concentrations in matched sections from cores JB13 and JB16 (Figure 4a) revealed that there was no appreciable in situ removal of total NPEOs at depths corresponding to deposition between ∼1960 and ∼1985 during the 8 yr that elapsed between the core collections. Total NPEO concentrations were remarkably similar between the matched core sections. This observation is consistent with the reported persistence of NPEO mixtures in anoxic sediments (*4*).

NPEO mixtures were quantitatively dominated by NP and NP1EO throughout the sediment cores, with lesser amounts of NP2EO and NP3EO (shown for JB16 in Figure 4b). NPEOs having ethoxy chain lengths between 4 and 15 were detected in all core sections, although usually at lower concentrations than NP2EO and NP3EO. The observed NPEO mixture depth profile, dominated by NP(0−3)EO, is consistent with the fact that Grassy Bay has received biologically treated wastewater effluent from the Jamaica WWTP since 1943 (Diane Hammerman, New York City Department of Environmental Protection, personal communication).

The relative concentrations of NP and NP1EO changed considerably over the upper 20 cm of core JB16 (Figure 4b). The concentration of NP1EO attenuated rapidly with increasing depth over this interval, perhaps indicative of in

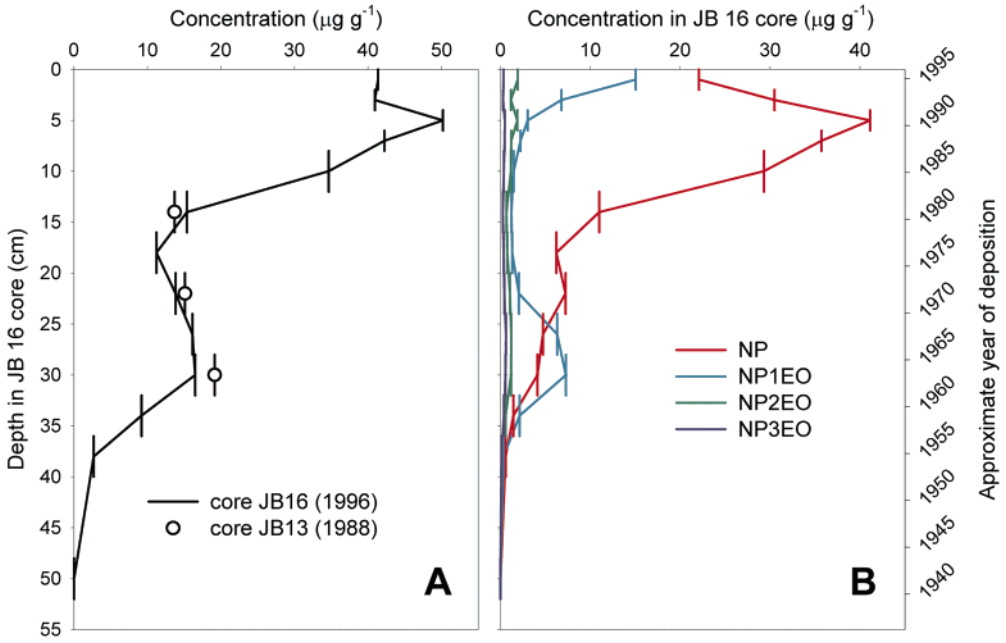

FIGURE 4. Depth profiles of total NPEOs (A) and short ethoxy chain NPEOs (B) in core JB16 collected in 1996. Total NPEO concentrations in selected sections of core JB13 (collected 1988) are plotted according to deposition date (A) for comparison with core JB16. Vertical error bars represent sampling depth interval.

situ diagenetic transformation of this ethoxymer in the upper region of the core. This was accompanied by a corresponding increase in NP, leading to a subsurface maximum at 4−6 cm, followed by a steady decrease with depth to ~38 cm (~1955) that may be reflective of both changing loadings of NPEOs to the bay over time (Figure 1) and slow degradation of this compound. A diagenetic model describing NP and NP1EO behavior in the upper region of the core is presented below. Between ~20 and 30 cm, NP1EO concentrations increased again before declining to nearly undetectable levels at ~38 cm. This subsurface peak in NP1EO may have been related to the less efficient wastewater treatment regime in place at the Jamaica WWTP prior to 1978, resulting in less efficient in-plant degradation of NP1EO. Alternatively, it may have been caused by the release of untreated or poorly treated wastewater to the bay during the aforementioned flow capacity upgrade at the Jamaica WWTP in 1963.

The maximum concentrations of NPEOs observed in previous sediment core studies ranged from 0.2 μg g^{-1} to approximately 6 μg g^{-1} (*4*, *23*−*26*), while the maximum concentration of total NPEOs reported for core JB16 reached 50 μg g^{-1} (Figure 4a). It should be noted that, of the previously cited sediment core studies, only Shang et al. (*4*) measured NPEOs with ethoxy chain lengths greater than 3. The elevated NPEO concentrations found in the sediment cores studied in the present work likely reflect the proximity of the study site to a major WWTP outfall within Jamaica Bay, the lack of regulatory restrictions on the use and disposal of NPEOs in the United States, and the local sedimentological conditions. It has been noted previously that organic matter preservation in sediments increases as the average particle residence time in the oxic surface layer decreases (*36*). In the present case, the high burial rate and reducing environment of the sediment likely contribute to a very short particle residence time in the oxic surface layer and, hence, increased preservation of sediment-associated organic compounds such as NPEOs.

NPEO Compositional Changes with Depth: Markers of Wastewater Treatment Efficiency. NPEOs are extensively biotransformed during wastewater treatment, and one observable effect of this biotransformation is a change in the ethoxymer distribution of the total NPEO mixture. More specifically, a relative decrease of highly ethoxylated NPEOs and a corresponding increase in NP(0−3)EO has been observed (*30*, *37*). NP(0−3)EO have been reported to be formed from NPEOs during biodegradation (*10*, *13*−*15*) and are present at only very low levels in commercial NPEO formulations. They can therefore be considered predominantly as metabolites. Since NPEO ethoxymer distributions have been observed to persist in bedded sediments (discussed below and in ref *4*), these distributions and the observed ratio of NP(4−15)EO (parents) to NP(0−3)EO (metabolites) in dated sections of sediment cores may be useful historical markers of the extent of wastewater treatment in adjacent sewage treatment plants.

Throughout the history of the Jamaica WWTP, modifications and upgrades caused changes in the biological oxygen demand (BOD) and total suspended solids (TSS) load in the plant effluent (Figure 5a). These parameters are a measure of the efficiency of the wastewater treatment process. Prior to 1963, the Jamaica WWTP was operating at or near its flow capacity under relatively inefficient modified aeration biological treatment, and the BOD and TSS were highly variable (D. Hammerman New York City Department of Environmental Protection, New York, personal communication, 2001). Both BOD and TSS peaked in 1963 during the plant flow capacity upgrade, during which raw wastewater bypassed the plant and was released untreated to Jamaica Bay.

In sediment core sections of JB16 deposited prior to ~1963, NPEO ethoxymer distributions were characterized by relatively higher amounts of highly ethoxylated NPEOs. For example, in the 32−36-cm section, NP(4−15)EO accounted for 50% of the total NPEO mixture (Figure 6). NP1EO was the most abundant single ethoxymer (> 20% of total NPEO), while NP made up less than 20% of the total NPEO. This NPEO ethoxymer distribution was very similar to those reported previously for marine sediments impacted by non-biologically-treated wastewaters (*4*). The average NPEO ethoxymer number (EO number, effectively the center of mass of the NPEO ethoxymer distrubution) in the 32−36-cm section of core JB16 was 3.36. Corresponding NPEO parent to metabolite ratios in sediment core sections deposited prior to ~1963 were consistent with release of untreated or poorly treated sewage to Jamaica Bay, as may have occurred during

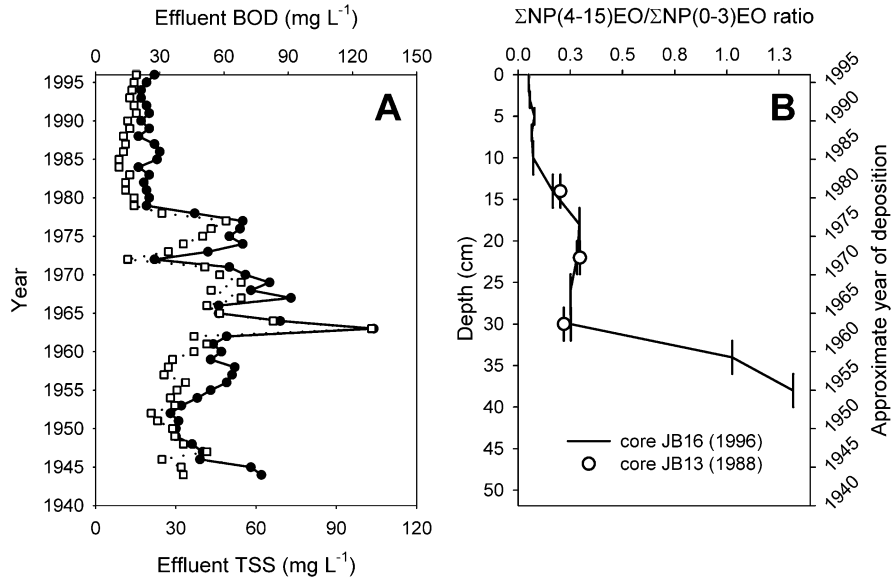

FIGURE 5. Biological oxygen demand (BOD) (□) and total suspended solids (TSS) (●) loadings in Jamaica WWTP effluent from1943 to 1996 (A). Changes in these parameters over time reflect modifications of the wastewater treatment regime at the plant (see text for details). These temporal changes are reflected in depth profiles of NPEO parent compound to metabolite ratios in sediment core JB16 and deposition date-matched sections of core JB13 (B). Vertical error bars represent sampling depth interval.

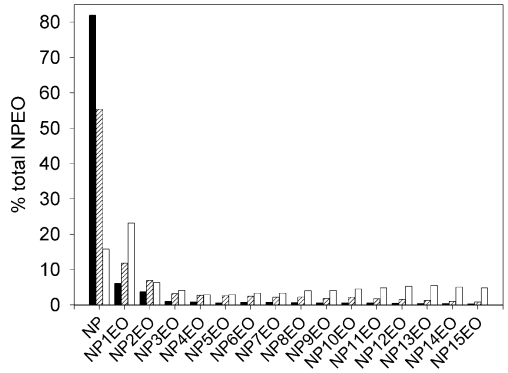

FIGURE 6. Normalized NPEO ethoxymer distributions in selected depth sections of sediment core JB16. Shaded bars: 4−6 cm horizon; cross hatched bars: 16−20 cm horizon; unshaded bars: 32−36 cm horizon.

the Jamaica WWTP flow capacity upgrade or during the period prior to the upgrade when the plant was operating near its capacity. Specifically, NP(4−15)EO/NP(0−3)EO ratios were observed to increase with increasing depth from 30 to 38 cm, below which depth NPEOs were not detected (Figure 5b).

The ratio of NP(4−15)EO to NP(0−3)EO was observed to plateau at an intermediate level in core sediments deposited between ∼1965 and ∼1978, consistent with the relatively high but variable effluent BOD and TSS values observed in the effluent of the Jamaica WWTP during this period after the flow capacity upgrade and before the change to full-step aeration biological treatment (Figure 5). A typical NPEO ethoxymer distribution in sediments deposited within Grassy Bay during this period is represented by the 16−20 cm depth section of core JB16 (Figure 6). The NPEO mixture in this section was dominated by NP (>50% of total NPEO), and there was significant contribution of NP(1−2)EO (19% of total NPEO). The more highly ethoxylated NPEOs were less prominent components of the total NPEO mixture at intermediate depths of core JB16 than in deeper sediments. At this depth horizon of core JB16, the average EO number of the NPEO distribution was 1.16.

After the upgrade in 1978 to batch aeration activated sludge treatment, the Jamaica WWTP effluent BOD and TSS decreased sharply to relatively low levels, at which they remained until the time of the JB16 core collection in 1996 (Figure 5a). This increased efficiency of biological wastewater treatment at the Jamaica plant was reflected in the decrease of NPEO parent to metabolite ratios in JB16 sediments deposited between ∼1978 and ∼1982, followed by stabilization of the ratio at a low level from ∼1982 until the core collection date of 1996 (Figure 5b). Accordingly, the more recently deposited sediments (e.g., 4−6-cm section of core JB16, Figure 6) were characterized by NPEO ethoxymer distributions dominated by NP (>80%) and with very little (<8%) quantitative contribution from highly ethoxylated NPEOs (average EO number 0.37). This ethoxymer profile was consistent with a highly degraded NPEO mixture (*37*) and was similar to ethoxymer profiles previously reported for NPEOs in surface sediments throughout Jamaica Bay (*5*). The presence of an NP-rich NPEO mixture in recent, near-surface sediments from JB16 was likely reflective of both biotransformation of NPEOs during activated sludge secondary wastewater treatment (*30, 37*) and in situ transformation of the NPEO mixture in the upper reaches of the sediment core (discussed below).

In general, the depth profile of NPEO parent to metabolite ratios in sediment core JB16 tracked the historical wastewater treatment upgrades at the Jamaica WWTP. The ratio decreased toward the sediment surface in a stepwise fashion corresponding temporally with the plant's effluent BOD and TSS loadings (Figure 5). The decrease in this ratio from deep to shallow sediments in core JB16 was consistent with an increased relative loading of NPEO metabolites to the Jamaica Bay estuary over time as a result of enhancements in biological treatment processes (and corresponding NPEO biotransformation efficiency) at the Jamaica WWTP. It is unlikely that in situ biodegradation processes appreciably altered the NP(4−15)EO/NP(0−3)EO ratios observed in our sediment core sections. Any slow degradation processes occurring within the sediments would most likely have decreased this ratio in the deepest (oldest) layers, relative to more recently deposited sediments. This trend was not observed in core JB16 (Figure 5b). Furthermore, no difference in NP(4−15)EO/NP(0−3)EO ratio (or NPEO ethoxymer distribution pattern) was observed between date-matched sediment core sections from cores JB13 and JB16 (Figure

5b), indicating that no appreciable NPEO parent to metabolite biotransformation occurred in deep sediments over the 8-yr interval between the collection of these cores. Indeed, average EO numbers for NPEO distributions were very similar between the matched core horizons (0.69 in JB16 12−16 cm vs 0.90 in JB13 8−12 cm; 1.20 in JB16 20−24 cm vs 1.28 in JB13 24−28 cm; 1.52 in JB16 28−32 cm vs 1.40 in JB13 32−36 cm). This indicates that NPEO ethoxymer distributions in dated sediment cores may provide valuable tracers for the wastewater treatment regime in adjacent "sewersheds". In addition, these distributions may prove useful as markers of sediment sources where horizontal advective transport of sediment occurs within and between regions impacted by different sewage treatment regimes.

In Situ Diagenetic Transformation of NP1EO and NP. As discussed above, the NPEO mixture seems to have persisted relatively unaltered in deeper regions of the sediment cores. There is, however, some evidence for conversion of NP1EO to NP as well as loss of NP in the upper sections of core JB16 (Figure 4b). Specifically, NP1EO concentrations decayed rapidly with depth over the top ∼7 cm of the core, while NP levels increased. The concentration of NP then decreased sharply with depth to ∼18 cm. This decrease in NP (5-fold from 7 to 18 cm, Figure 4b) was more rapid than could be explained by the change in NPEO loading to Jamaica Bay over the corresponding time period (approximated by the 2-fold increase in NPEO sales figures from 1978 to 1990, Figure 1). The conversion of NPEOs to NP under anaerobic conditions, such as those found in the sediment environments studied here, has been previously reported (*6*, *10*, *15*).

A non-steady-state diagenetic model was developed in order to quantitatively describe the biotransformation of NP1EO and NP in the upper region of core JB16. The model was limited to the upper ∼16 cm of the core, as this region corresponded approximately to sediment deposited since the upgrade of the Jamaica WWTP to batch aeration activated sludge treatment (1978). As shown in Figure 5a, the BOD and TSS in the Jamaica WWTP effluent remained relatively constant from the time of this upgrade until the collection of core JB16 in 1996, indicating that the wastewater treatment regime (and thus, NPEO degradation processes during wastewater treatment) did not change dramatically over this time period. Consequently, the model uses a constant average NPEO mixture ethoxymer distribution in the plant effluent. Annual loadings of total NPEOs from the Jamaica WWTP effluent during this time should have been a function primarily of the change in usage of these compounds over the corresponding time period, approximated by the change in U.S. NPEO sales (Figure 1). Essentially, the input of NPEOs to the sediment at the JB16 core site from the Jamaica WWTP was constrained as steady-state over the period ∼1978 to 1996 with regard to the NPEO ethoxymer distribution and non-steady-state but defined over the same period with regard to NPEO loading.

Initial assumptions made in the development of the diagenetic model have been described in detail elsewhere (*38*). Briefly, it was assumed that sediment porosity was constant over the depth interval modeled, that NP and NP1EO transport and reaction within the sediment occurred solely in association with particles (pore-water diffusion was neglected), and that biogenic sediment mixing was insignificant. A fourth assumption made when formulating the diagenetic model was that NP and NP1EO biotransformation kinetics in the sediments were first order with respect to the reactants (NP and NP1EO) and that NP1EO was converted quantitatively to NP, which was then further metabolized and/or mineralized. This is likely an oversimplification since it is possible that NP1EO may have been mineralized or otherwise transformed via a pathway not including NP as a metabolite. NP was assumed to have no significant in situ source in the sediments other than NP1EO since the concentrations of NPEOs with ethoxyl chain lengths >1 (which have been shown to degrade to NP under anaerobic conditions; *10*) were quantitatively insignificant in the upper 16 cm of core JB16 (Figure 4b).

Solid-phase NP and NP1EO diagenesis in the upper 16 cm of core JB16 was described by a simple advection-reaction model:

$$\frac{\partial C_{\mathrm{NP1EO}}}{\partial t} = -\frac{\omega \partial C_{\mathrm{NP1EO}}}{\partial x} - k_{\mathrm{NP1EO}} C_{\mathrm{NP1EO}}$$

$$\frac{\partial C_{\mathrm{NP}}}{\partial t} = -\frac{\omega \partial C_{\mathrm{NP}}}{\partial x} + k_{\mathrm{NP1EO}} C_{\mathrm{NP1EO}} - k_{\mathrm{NP}} C_{\mathrm{NP}}$$

where ω is the burial velocity derived from the radionuclide profiles (0.92 cm yr^{-1}); x is the sediment depth (cm); t is time (yr); and C_{NP} and C_{NP1EO} are the reactive sediment concentrations of NP and NP1EO, respectively. The two reactions considered in the present model were

$$\mathrm{NP1EO} \xrightarrow{k_{\mathrm{NP1EO}}} \mathrm{NP}$$

$$\mathrm{NP} \xrightarrow{k_{\mathrm{NP}}} \mathrm{metabolites}$$

with corresponding first-order rate constants, k_{NP1EO} and k_{NP}. Quadratic functions derived from a least-squares fit of the U.S. NPEO sales data in Table S1 were used to provide an estimate of the non-steady-state input of NP and NP1EO to the sediment over the sediment deposition time interval (ca. 1978−1996) for which the model was evaluated. These functions were anchored to the measured concentrations of NP and NP1EO at the surface (0−2 cm) section of core JB16. The non-steady-state model was then solved numerically (fully explicit, upstream finite difference method) using Mathcad 2000 software (MathSoft, Inc.). An analytical solution was also evaluated assuming steady-state input boundary conditions in order to confirm both the validity of the numerical model and the estimated range of degradation rates. Values of first-order rate constants for the loss of NP1EO and NP were adjusted iteratively to give the best model fit to the experimentally measured NP and NP1EO concentrations.

The steady- and non-steady-state model outputs are shown in Figure 7 along with measured NP and NP1EO concentrations. The exponential decay of NP1EO predicted by both models appears to describe the main features of the data, suggesting that this compound's depth profile over the model interval could be described solely by advection and first-order decay. There appears to have been a residual, "degradation resistant" NP1EO pool present in the sediment as the observed profile of this compound decayed to a constant, nonzero value at the bottom of the modeled depth interval. Further evidence for this resistant pool was provided by the good agreement between NP1EO concentrations in matched sections of cores JB16 and JB13 deposited ca. 1982 (12−16 cm in JB16), at the bottom of the exponential profile shown in Figure 7. This indicates that no appreciable NP1EO degradation occurred within sediments deposited in ∼1982 during the 8 yr between the collection of cores JB13 and JB16. The resistant pool may reflect NP1EO that was unavailable for microbial biotransformation due to strong association with desorption resistant phases in the sediment. This behavior has been reported previously for other hydrophobic organic contaminants in sediments (*39*). In the determination of a best-fit reaction rate constant, only the reactive NP1EO pool (the analytical concentration at any

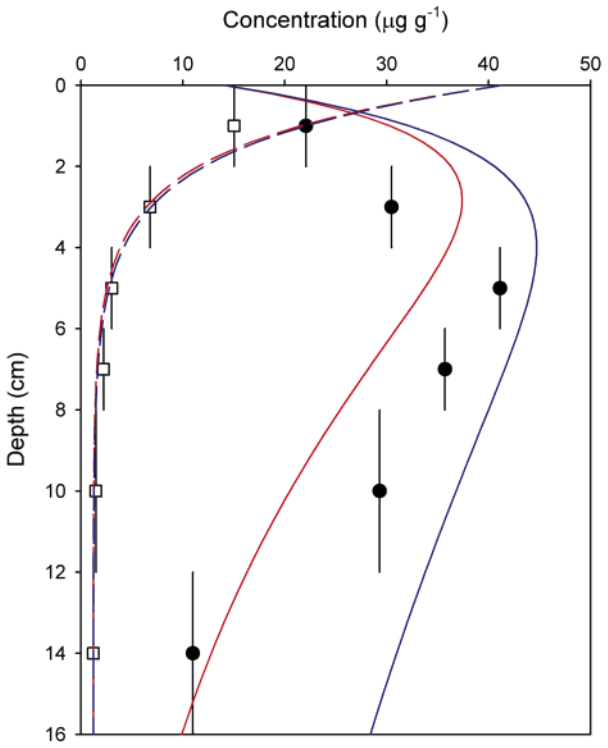

FIGURE 7. Measured depth profiles of NP (●) and NP1EO (□) in the upper 16 cm of core JB16. Vertical error bars represent sampling depth interval. The results of the steady-state (blue) and non-steady-state (red) diagenetic models described in the text are shown for NP (solid line) and NP1EO (dashed line).

depth minus the resistant concentration, 2.3 μg g^{-1} measured in the 12−16 cm depth interval) was considered.

The first-order rate constant for transformation of NP1EO to NP (k_{NP1EO}) was estimated at 0.60 yr^{-1} on the basis of the above model, corresponding to a 1.2 yr NP1EO half-life in the upper 16 cm of core JB16. Half-lives determined in laboratory experiments for conversion of NP1EO to NP under anaerobic conditions have previously been reported to range from 15 day in slurried municipal solid waste to much greater than 150 day in diluted anaerobic digestor sludge with incubation temperatures of 30 °C (*15*). It is clear that many factors including temperature, level of microbial community acclimation, and substrate concentration will affect the rate at which NP1EO is converted to NP under anaerobic conditions in sediment or other matrixes; therefore, the half-life reported here for NP1EO should be viewed as approximate and reflective of the environmental conditions characteristic of core site JB16.

The NP1EO half-life of 1.2 yr in the upper 16 cm of core JB16 would seem to be inconsistent with the observation of significant NP1EO levels in deeper sections (Figure 4b). It must be noted, however, that sediment in these deeper layers was deposited during a time period corresponding to less efficient wastewater treatment at the Jamaica WWTP (Figure 5a). Consequently, the NPEO loading to the sediment during this time was likely to have been different from the time period modeled above. It is conceivable that NP1EO loadings may have been greater prior to the 1978 treatment upgrade and that the corresponding resistant pool of sediment-bound NP1EO may have also been greater in depths below 16 cm than that observed at, for example, 12−16 cm. It is also likely that the microbial communities were very different in the near surface and deeper sediment horizons. This may have caused the NPEO degradation pathways and rates to differ substantially between the near surface and deeper regions of the sediment. It is thus possible that NPEOs that escape an "active" degradation regime near the sediment surface through rapid burial (or initially high concentrations) may persist unaltered for long time periods in metabolically "inactive" sediments in deeper horizons.

The modeled behavior of NP in the upper 16 cm of core JB16, based on non-steady-state input, first-order production from NP1EO degradation and subsequent first-order decay, reproduces the general features of the observed vertical profile of NP (Figure 7, solid red line). Deviations from the model may have been due to non-diagenetic processes (e.g., inaccuracies in the non-steady-state input function) or in situ processes such as small-scale vertical sediment mixing. The steady-state model of NP degradation produces reasonable agreement with upper part of the profile but provides a poor fit to the measured data from the deepest sections (Figure 7, solid blue line). The non-steady-state model yields an estimated first-order rate constant for NP degradation of 0.04 yr^{-1}, corresponding to a half-life on the order of 20 yr. In most short-term anaerobic laboratory experiments, degradation of NP has not been observed (*10*, *12*, *15*), although Ekelund et al. (*40*) reported 20% mineralization of ^{14}C-NP after 58 day in anoxic sediment/water slurries at 11 °C. In general, NP degradation rates have been reported to be strongly influenced by oxygen concentration (*41*) and temperature (*42*). The NP half-life reported here was considerably longer than that of NP1EO, suggesting that NP was more recalcitrant in anoxic sediments than its NPEO parents. This is likely due to the fact that mineralization of NP must begin either with ring cleavage or oxidative attack on the branched alkyl chain, whereas NPEOs may be degraded via sequential cleavage or oxidation of the more easily attacked linear ethoxy chain. No evidence for a resistant sediment bound pool of NP was found during the model development, although it is likely that if such a pool did exist, it would not have been observable over the depth interval studied in the present work given the relatively slow kinetics of NP degradation.

It is clear from the present work that under biogeochemical sediment regimes, such as are found in Grassy Bay (high burial rate, reducing environment, high organic carbon loads), NPEOs can persist and accumulate in sediments, leading to locally elevated concentrations. Under such conditions, NPEO ethoxymer distributions in sediment are heavily influenced by the extent of wastewater treatment prior to release of NPEOs into surface water and subsequent deposition and burial. Indeed, ethoxymer distributions in sediment cores may represent a valuable tracer for extent of wastewater treatment in the sewersheds surrounding an appropriate collection site. While diagenetic alteration of NPEO mixtures in near surface sediments appears to have been an important process on year-to-decade time scales in Grassy Bay, this was clearly not the case for NPEOs deeper within the sediment. More work will be needed to describe the biogeochemical behavior and persistance of NPEOs in more biologically and physically disturbed sedimentary environments.

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Supporting Information Available

Data for historical production and sales of NPEOs in the United States and the complete table of NPEO concentrations in sections of the two sediment cores. This material is available free of charge via the Internet at http://pubs.acs.org.

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