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Persistence of Nonylphenol Ethoxylate Surfactants and Their Primary Degradation Products in Sediments from near a Municipal Outfall in the Strait of Georgia, British Columbia, Canada

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Marine sediment cores and surface grabs were collected from the Strait of Georgia, British Columbia, Canada, near the Iona municipal outfall and were analyzed for nonylphenol (NP) and its ethoxylate compounds (NP*n*EOs). We used normal-phase liquid chromatography with electrospray mass spectrometric detection to determine concentrations of ethoxylates from $n = 1$ to $n = 19$. Over half the NP*n*EO inventory in marine sediments resides in ethoxylates of chain length greater than $n = 2$, suggesting that analyses limited to short-chain ethoxylates ($n = 2$) are under-reporting total NP*n*EO by a factor of 2. The NP*n*EO vertical profiles and oligomer distributions in dated sediment cores suggest that little degradation occurs once these compounds enter the sediments: the half-life for these compounds is estimated to be greater than 60 yr. The lack of change in NP*n*EO oligomer distribution with age suggests that degradation by chain shortening does not occur significantly. A rough inventory shows that over 30 t of NP*n*EO resides in Fraser River Delta sediments near the Iona municipal outfall and that the entire Strait of Georgia sediments contain over 170 t of NP*n*EO.

Introduction

Alkylphenol polyethoxylates (APEOs) are the second largest class of nonionic surfactants in commercial production in North America (*1, 2*). In use for over 40 yr, APEO production has been estimated at >0.3 Mt yr^{-1} worldwide (*2*) and about 0.2 Mt in the United States (*1, 3*). In Canada, about 6.0 kt of nonylphenol polyethoxylates were used in 1989 with this figure expected to rise to 7.0 kt by 1993 (*4*). APEOs are contained in cleaning products, paints, herbicides, and pesticides and are used to facilitate processes in pulp and paper production and textile manufacturing (*4*−*6*). Commercial nonylphenol ethoxylates (NPEOs) are complex mixtures of a series of homologues, usually maximizing at nine ethoxy groups, each made up of a large number of isomers (*7*). In the following, we use the abbreviation NP*n*EO, where N refers to nonyl- and *n* is the number of ethoxylate groups.

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Naylor et al. (*1*) estimated that about 0.1 Mt yr^{-1} of APEOs enter the North American aquatic environment via wastewater systems—or about half the production. Some of these surfactants biodegrade before reaching the environment (*4, 8*−*11*): primary degradation (chain oxidation) may be 90% complete within a few hours to 1 month under favorable laboratory conditions, and treatment plants often remove more than 95% of the higher ethoxylates through secondary treatment (*6*). Initial degradation proceeds as an attack on the ethoxy chain to produce shorter-chain NP*n*EOs or carboxylic acids. These APEO metabolic intermediates are more toxic than their parent compounds (*8, 9*) and more bioaccumulative in aquatic organisms (*12, 13*). Degradation is highly variable with the result that treatment plant effluent concentrations of NPEOs and metabolites are also highly variable (*4*). Adsorption onto solids and removal of sludge in treatment plants confounds estimates of total degradation based on a comparison of influent/effluent concentration. Clearly, a portion of NPEOs passes through treatment plants to enter the environment (*1, 5, 9, 14, 15*). However, insufficient data have been generated for North America to provide confident estimates of environmental inventories for these compounds. The degradation of NPEOs in the environment has been the subject of disagreement, contradiction, and controversy for many years (*3, 8, 9, 11, 16*).

Recent concern has focused on APEOs as potential endocrine disrupters (*2, 17, 18*). Considering toxicity, the large production volumes and likely persistence, APEOs—especially NPEOs—have emerged as a leading issue in Europe where a phased withdrawal for many uses will occur for a number of countries by the end of the century (*19*). Similar action has not been planned for North America where, it is argued, lower environmental concentrations of NPEOs are found (*1, 20*).

Although APEO data have been produced for many years (*8*), there remains a need to improve and standardize analytical methods for their determination in complex environmental matrixes and to produce better environmental inventories. Commonly used chromatographic methods lack the sensitivity and specificity required for accurate identification and quantitation of NP*n*EOs beyond about $n = 2$ in environmental samples (*21*). Accurate determination of the complete range of individual NPEO oligomers is as crucial to the determination of the fate of these compounds in the environment as it is to the correct assessment of risk because aquatic toxicity and estrogenicity vary with ethoxy chain length and branching (cf. White (*2*)).

Here, we apply a new, highly specific and sensitive analytical method (*21*) to determine individual oligomers ($n = 1$−19) of NPEO in marine sediment from the Strait of Georgia (Figure 1). We focused our analytical efforts on sediments because NPEOs with log (K_{OW}) values > 10^4 (*22*) partition onto solids, and therefore, we predicted sediments to be an important environmental sink for these contaminants. For this investigation, we examine surface sediment samples and dated sediment cores from a region known to have been impacted by municipal wastewater disposal (*23*).

Methods

Sampling. Marine sediment samples were collected on a series of transects in April 1996 from the Strait of Georgia, BC, off the Fraser River Delta (Figure 1). Sites were chosen by referring to a sediment survey using Ag and other tracers to reveal the region most heavily impacted by the Iona municipal outfall (*23*). Five box cores (20 cm × 30 cm × 50 cm) were collected and sectioned immediately on board for

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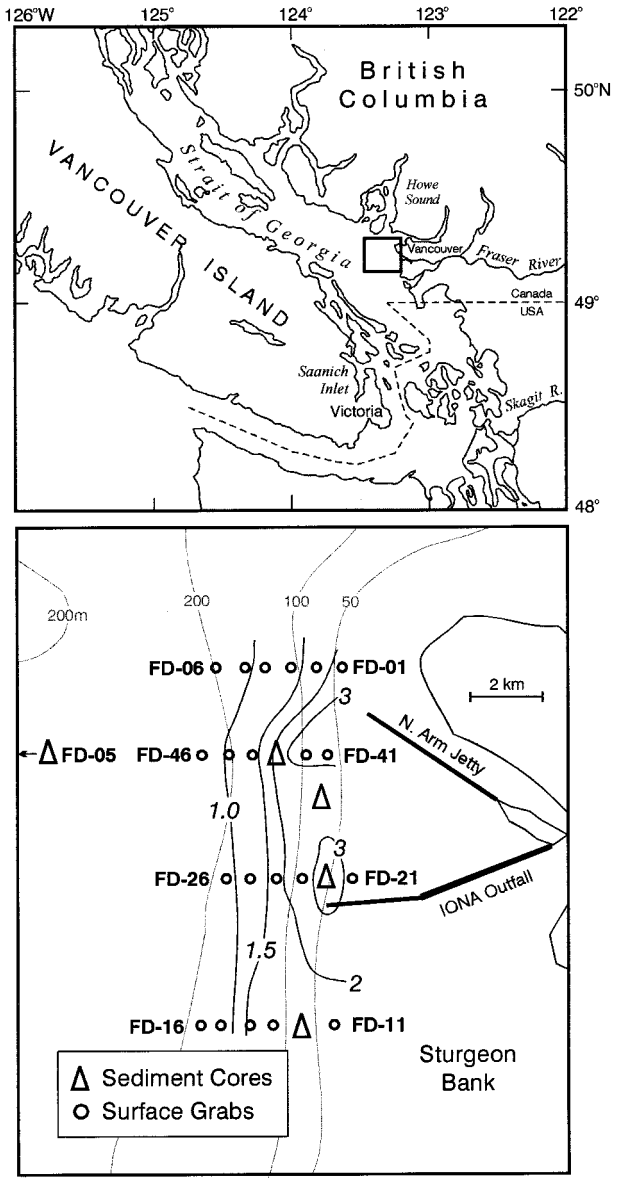

FIGURE 1. Chart showing the sampling sites for sediment cores (△) and surface grabs (○). Also shown is the location of the Iona municipal outfall and City of Vancouver (population of about 1.8 million). Contours of NPEO concentration for surface sediment are given in μg g^{-1}.

^{210}Pb and NPEO determination. Subsampling was carried out in such a way as to avoid surface smear from the walls of stainless steel box using cleaned, stainless steel instruments, which were rinsed with acetone between samples. One core, FD-5, was collected at a baseline site in the center of the Ballenas Basin well away (~20 km) from municipal or industrial outfalls (*24, 25*). Surface samples (top 2 cm) were collected using a Smith-McIntyre grab (0.12 m^2). Sediment samples for NPEO determination were stored in precleaned amber glass jars with aluminum foil lined cap and frozen at −15 to −20 °C in the dark before being freeze-dried. Samples for ^{210}Pb determination were stored frozen in Zip-Lok bags.

Reagents and Chemicals. Acetone, *n*-hexane, toluene, dichloromethane (DCM), and methanol (MeOH) were HPLC grade from Mallinckrodt used without further purification. Sodium sulfate (analytical reagent grade, Mallinckrodt) was baked at 450 °C overnight and stored at 110 °C before use. Double Milli-Q purified water was used (Millipore, Bedford, MA). Large reservoir capacity (LRC) cyanopropyl (CN) SPE cartridges (500 mg stationary phase, Varian) were used to clean up samples. Copper metal (AR grade, fine granular, Mallinckrodt) was activated by rinsing 1 M HCl, deionized water, acetone, and hexane consecutively before use. All materials and glassware were repeatedly cleaned with deionized water without using detergent, rinsed with HPLC grade acetone and hexane, baked at 450 °C overnight, and stored at 110 °C before use. All chemicals were tested for background concentrations of the compounds of interest. NPEO (N-100) standards were obtained from Huntsman Co. (Houston, TX). Nonylphenol (~85% technical grade) was obtained from Aldrich (Milwaukee, WI) and purified by column chromatography.

NPEOs Determination. Sediment samples were processed in batches of 12 that contained three procedural blanks, one spiked sediment sample, and 8 real samples. NPEOs were extracted from marine sediment using an accelerated solvent extraction (ASE) system from Dionex. A total of 15−25 g of freeze-dried sediment was ground to a free-flowing powder and then packed into an ASE extraction cell (33 mL). Hexane/acetone solvent (v:v 1:1) was passed through the heated (100 °C) and pressurized (1500 psi) cell to extract NPEO (repeated three times). To prevent cross-contamination, a similar extraction was carried out on prebaked sodium sulfate between each sample run.

The extract preparation and cleanup, liquid chromatography, and electrospray−mass spectrometry detection have been described elsewhere in a detailed protocol (*21*). Briefly, the extract was reduced to dryness under N_2 at 40 °C; the residue was reconstituted to 6 mL with hexane/DCM (90:10, v:v) and subjected to SPE CN sample cleanup. The reconstituted extract together with two 5-mL hexane rinses of the beaker that contained the extract were added to a preconditioned SPE CN cartridge. Desorption was accomplished with three 6-mL aliquots of acetone, the extract was reduced to dryness under flowing N_2 at 40 °C, and the residue was reconstituted with toluene/DCM/MeOH (60:20:20, v:v:v) containing 0.5 mM sodium acetate and 4-fluoro-4′-hydroxybenzophenone, which was used as an internal standard to monitor fluctuations of the analytical instrumentation and correct the data accordingly. The reconstituted volume was 1.0 mL, except where high concentrations of NPEOs were encountered. Sample vials were shaken for 3−5 min and then stored at 4 °C in dark for at least 12 h before analysis.

The final extracts were analyzed by normal-phase liquid chromatography/electrospray−mass spectrometry (LC/ESI-MS). Quantitation of NP and NPEO oligomers was based on five-point calibration curves, of response (peak area) vs known amount of injected compound, covering the range 836 ng mL^{-1} to 836 μg mL^{-1} of total NP plus all the NPEOs. Peak areas realized from the analyses of standards and real samples were integrated and normalized to 4-fluoro-4′-hydroxybenzophenone, which was present at the 20 μg mL^{-1} level in both the calibration standards and the sample extracts. Detection limits were in the low nanogram per gram range depending on individual NPEO oligomers using selected ion mode acquisition. The final real sample concentrations were procedural blank corrected by using the average concentration measured for the procedural blanks and the recovery obtained from the spiked sample. The performance of the ASE was evaluated using spiked samples of all oligomers; recoveries of 65−93% with relative standard deviation of 3.5−15.9% were obtained.

^{210}Pb Determination and Sediment Dating. ^{210}Pb was determined by measuring ^{210}Pb using a 300-mm silicon surface barrier detector with a Canberra 8180 MCA (*26*). Counting errors were generally less than 10%. Replicate, unlabeled sediment samples verified this error. ^{210}Pb was used to develop the time sequence and mixing history for the five box cores. For each core, supported ^{210}Pb was determined by measuring ^{226}Ra (as ^{222}Rn) in three sections

TABLE 1. Sediment Core Parameters Derived from the ^{210}Pb Model[a]

core	location	water depth (m)	mixed layer depth (cm)	mixing coeff ($cm^2\ yr^{-1}$)	supported ^{210}Pb ($dpm\ g^{-1}$)	^{210}Pb flux ($dpm\ cm^{-2}\ yr^{-1}$)	sediment velocity ($cm\ yr^{-1}$)	porosity	sediment rate ($g\ cm^{-2}\ yr^{-1}$)	time resolution (yr)
FD-3	49°14.1′ N 123°18.15′ W	120	10	30	0.88 ± 0.22	6.9 ± 1.0 (6.7)	1.34 ± 0.15	0.747 ± 0.015	0.90 ± 0.11	7.5
FD-5	49°13.0′ N 123°35.0′ W	360	12	100	1.20 ± 0.18	6.4 ± 1.6 (6.9)	0.74 ± 0.21	0.837 ± 0.008	0.32 ± 0.09	16
FD-12	49°10.4′ N 123°18.7′ W	110	10	10	0.83 ± 0.30	9.6 ± 2.2 (9.3)	1.95 ± 0.40	0.737 ± 0.20	1.36 ± 0.30	5
FD-22	49°12.7′ N 123°18.0′ W	90	20	10	0.70 ± 0.19	(3.6)		0.663 ± 0.011		
FD-43	49°14.7′ N 123°19.2′ W	170	15	30	0.92 ± 0.17	8.3 ± 1.3 (7.9)	1.20 ± 0.29	0.762 ± 0.017	0.76 ± 0.19	13

[a] A plus/minus sign (±) refers to 95% confidence intervals. For sedimentation rate ($g\ cm^{-2}\ yr^{-1}$) 95% CI was estimated by propagation of error formula. Value in parentheses under ^{210}Pb flux is estimated from sediment inventory using decay constant of $0.0311\ yr^{-1}$.

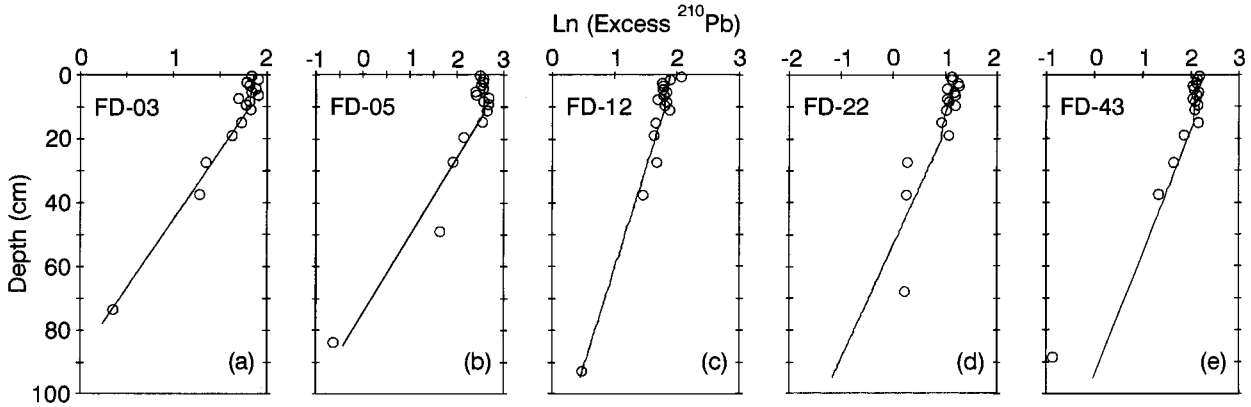

FIGURE 2. Data and advection−diffusion model fit for the sediment cores used in this study. Surface mixed layers were selected by eye, and model parameters (sedimentation rate, ^{210}Pb flux to surface and diffusion coefficient) were chosen to give the best fit to the data.

using the method of Mathieu et al. (*27*). Surface mixing is probably the most important impediment to a simple interpretation of time versus depth in the sediments. To address this problem, we have used analytical solutions to the advective−diffusive equation as provided by ref *28*. The depth of the surface mixed layer (SML) was chosen by eye, and the model was fitted by varying surface flux and sedimentation rate to minimize least mean square difference between the model and data. Assumptions and model results are summarized in Table 1.

Results and Discussion

Sediment Mixed Layers and Accumulation Rates. All five of the sediment cores show evidence of an SML (Figure 2). The simple assumption of a surface mixed layer together with an advective−diffusive model gave good fits to all of the cores with the exception of FD-22 (Table 1). The model fit is not particularly sensitive to the choice of mixing coefficient (*28*) with the result that this parameter is only poorly constrained and must be considered approximate. Sedimentation rates and ^{210}Pb fluxes to the sediment surfaces fall in the ranges found in other studies for this region (*24*, *25*). In the case of the core collected at FD-22, the profile (Figure 2d) and the total inventory of ^{210}Pb in the core suggest that a loss of surface material may have occurred, perhaps a decade or so ago, followed by renewed sedimentation to rebuild the surface mixed layer but leaving deeper sediments impoverished in ^{210}Pb.

Concentration and Distribution of NPEO in Sediments. The average concentration of total NPEO in surface samples collected from the Fraser foreslope in the Strait of Georgia was determined to be $1500\ ng\ g^{-1}$ ($\pm 130\ ng\ g^{-1}$ (SE); $n = 25$). We found only two published reports of NPEO concentrations in marine sediments with which to compare these numbers. Using LC−UVF, Marcomini (*29*) found average concentrations of NP, NP*1*EO, and NP*2*EO to be 500−6700 ng g^{-1} for resuspended surface sediment from a Venice lagoon depending on season and collecting device. Using GC/MS, Valls et al. (*30*) reported NP to NP*3*EO concentrations of 100−6600 ng g^{-1} in marine sediment collected near a Barcelona municipal outfall. Neither of these studies reported values for oligomers higher than NP*3*EO. The GC/MS technique used by Valls et al. (*30*) precludes determination of higher oligomer of NPEOs. However, the LC−UVF method used by Marcomini (*29*) might have found higher NPEO oligomers if a polar solvent had been used for the extraction. A more abundant data set is available for river sediments: based on a variety of analytical techniques and including varied ranges of oligomers, NPEO concentrations have been found in the range of 100−5000 ng g^{-1} (see, for example, refs *1*, *4*, and *31*).

In view of the SML as indicated by ^{210}Pb profiles, our surface sediment concentrations can be taken to represent at least the top 10 cm or so of the sediment for this region. Although NP, NP*1*EO, and NP*2*EO are important contributors to the observed NPEO profiles, they actually comprise less than half the total NPEO inventory for the Strait of Georgia sediments (Figure 3; top panel). The histogram and the cumulative sum of NPEOs show clearly that the sediments contain degraded NPEO, evident as enriched amounts of NP and the first two ethoxylates in sediments as compared to NP-100, plus relatively undegraded NPEO, evident as a distribution centered around NP*9*EO that looks very similar to common commercial formulations (Figure 3; bottom panel). These two components contribute approximately

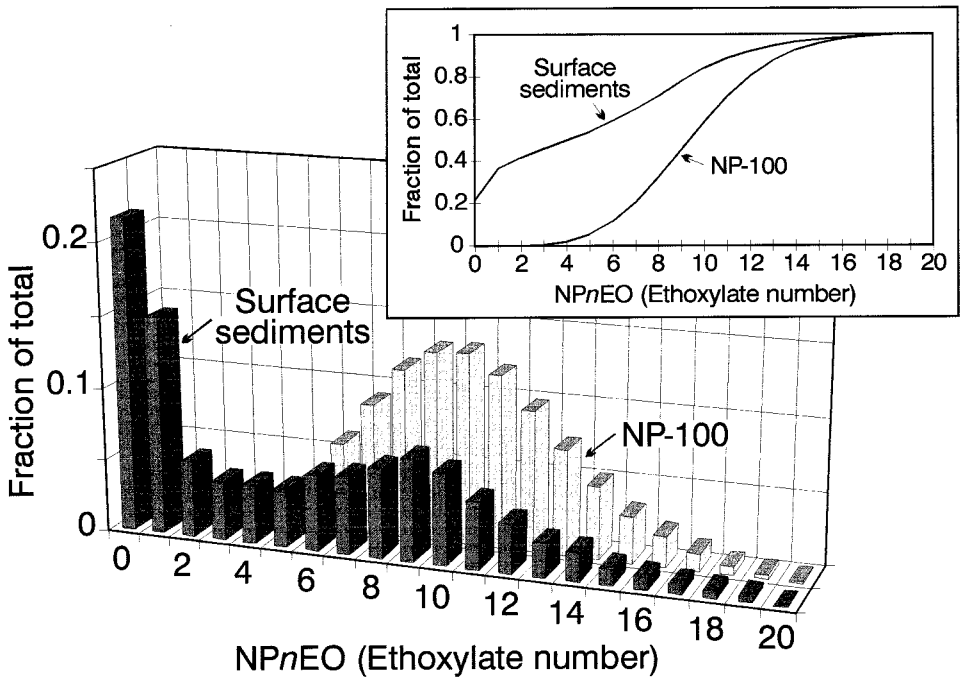

FIGURE 3. Bottom panel shows histograms of average composition of NPEO in surface sediments (n = 25) and the composition of a commonly used commercial product, NP-100. The top inset panel shows cumulative contribution for the two histograms presented in the bottom panel.

equally to the total NPEO sediment burden, suggesting that analyses which have neglected the higher oligomers (n = 3−19) are probably under-reporting the total concentration by a factor of 2.

The contours of surface concentrations of total NPEO (n = 1−19; Figure 1) mimic the sewage tracer Ag as measured by Gordon (*23*), providing conclusive evidence that the dominant source of these compounds is the Iona municipal outfall. From these data, it is clear that the NPEOs have become strongly attached to particles, either within the wastewater treatment plant or shortly afterward, and have sedimented in close proximity to the outfall (Figure 1). The highest NPEO concentrations are observed at FD-22, close to the end of the diffuser.

The Iona municipal discharge began in 1963 before which time a disorganized system of trunk and intercepting sewers disposed of crude sewage through numerous outfalls into various points including the Fraser River. Until 1988, primary-treated sewage was released from Iona into a 1−3-m ditch cut across the intertidal zone. A deep outfall was constructed in 1988 with an underwater diffuser pipe at the 70−105-m water depth. Although the discharge from Iona (540×10^6 L day^{-1}) is the largest point source to the Fraser Estuary, there are two other Greater Vancouver outfalls that discharge primary-treated municipal effluent to the Fraser River upstream (Annacis Island, 440×10^6 L day^{-1}; Lulu Island, 60×10^6 L day^{-1}). The influent to Iona derives primarily from domestic and storm sewers, with industry contributing only 7% of the volume (*15*). Primary treatment is used to reduce the average suspended solid load in the influent (143 mg L^{-1}) to about 77 mg L^{-1} in the effluent (*23*). Digested sludge is discharged to open-air storage lagoons where it is stored for about 8 yr when it is excavated and allowed to dry in land storage on site.

The asymmetry in the horizontal distribution around the outfall diffuser pipe shows transport primarily to the north and secondarily to the south along isobaths in agreement with water motions determined from dye studies at this site and from current meter moorings. The surface sediment concentration of total NPEO at the background station, FD-5, approximately 20 km from the nearest outfall at Iona is much lower (300 ng g^{-1}), but nevertheless, these sediments still contain significant amounts of these compounds.

Biodegradation of NPEOs in Marine Sediment. Surprisingly, the sediment core profiles (Figure 4) show no obvious decreasing trends with depth in the sediment that could be interpreted as *rapid* degradation. For example, cores FD-3 and FD-43 (Figure 4) show very slight decreases in the total concentration at depth whereas stations FD-12 and FD-22 show no decrease with depth. Station FD-5 similarly shows no consistent decrease with depth, taking into account limits of detection for NPnEOs with n greater than about 11. Furthermore, for all cores shown in Figure 4 there is little evidence of a shift from higher NPnEOs to lower NPnEOs on going from the surface to deep in the core that would indicate sequential breakdown of the ethoxy groups with time. The deep sediment layers show a bimodal NPnEO distribution almost identical to that observed in the surface sediments, with peak concentrations at NP and NP9EO−NP*11*EO. These results can be explained partly, but not entirely, by sediment mixing. Long intrinsic time resolutions (Table 1) indicate that the two uppermost samples for all cores contain mixed material of about the same vintage. However, for the slower sedimentation rate sites, the median age for the bottom NPEO sample would be equivalent to about 30 yr or longer—sufficient time to produce detectable changes if degradation were rapid. For comparison, our steady-state advection−diffusion model very easily fits ^{210}Pb profiles, which show a clear radiodecay loss of ^{210}Pb in the lower sections of all cores. This observation alone suggests that, provided NPEOs have been entering the sediments at steady-state or even at a rate increasing with time since the Iona plant began operations in 1963, the rate of NPEO degradation must be slower than the rate of radiodecay for ^{210}Pb with a half-life of 22 yr. Furthermore, because the use of NPnEOs has generally been increasing since their introduction, we cannot explain the profiles, for example, as loadings decreasing with time balanced by degradation to produce almost constant sediment concentrations with depth.

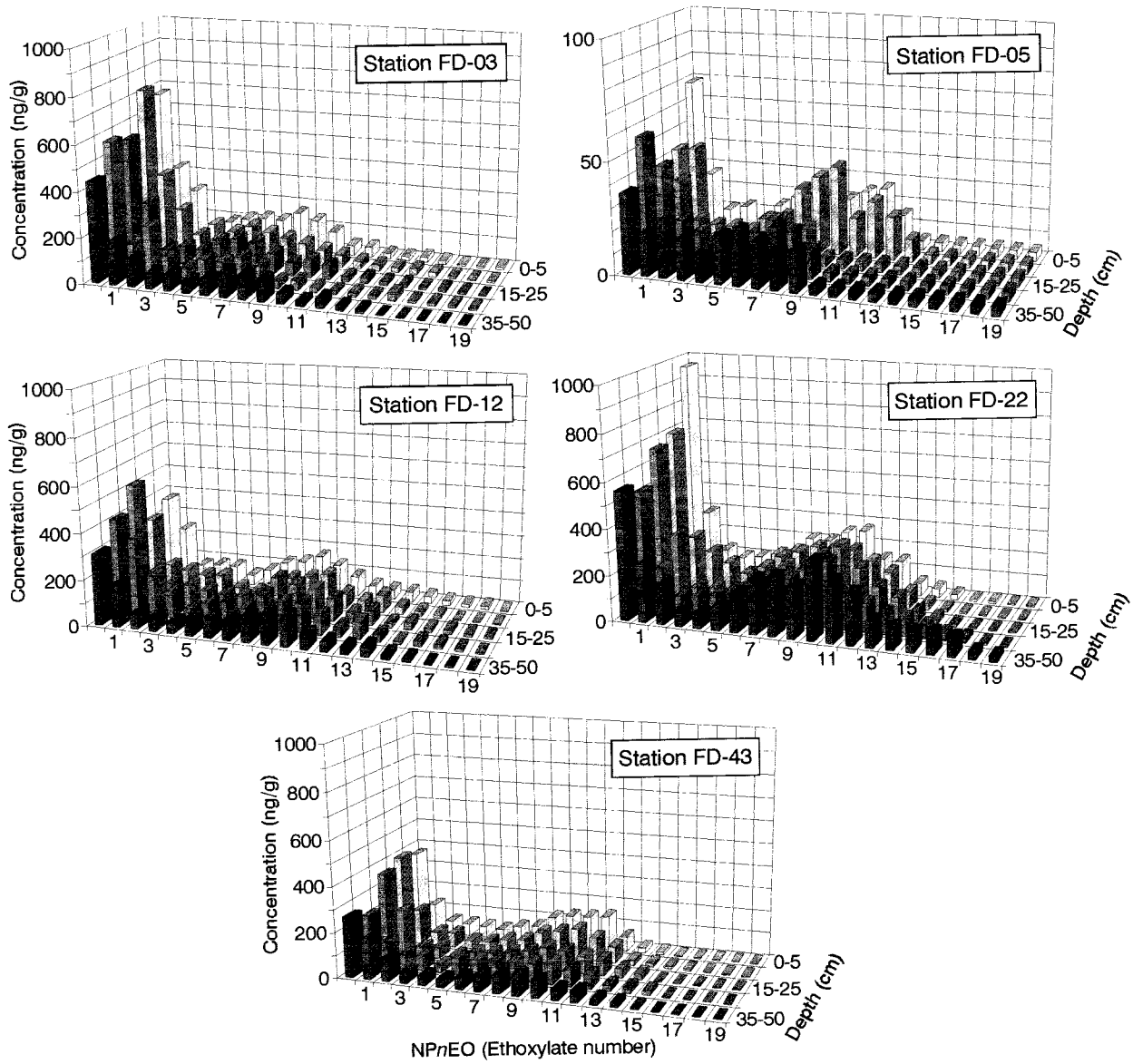

FIGURE 4. NP*n*EO profile as a function of depth for (a) core FD-3, (b) core FD-5, (c) core FD-12, (d) core FD-22, and (e) core FD-43. Note change of scale for the FD-5 sediment core.

The resistance to degradation apparent in individual sediment profiles, both in total amount of NP*n*EO and in cascade from higher to lower *n*, is strong evidence that the NP*n*EO composition observed in sediments must have developed through biodegradation before adsorption onto the sediments rather than in situ degradation. That is, the degradation evident in the bimodal composition (NP, NP*1*EO, and NP*2*EO enrichment) has not been produced within the sediments but in a more favorable location, probably the wastewater treatment plant, and then delivered to the sediments where the composition then remains unchanged for periods measured in decades or longer. Degradation is enhanced in the wastewater/delivery system due to high organic carbon content, high oxygen supply, relatively warm temperatures, and acclimated microbial populations. In contrast, conditions in marine sediments must provide a better environment to preserve NP*n*EOs. Efficient preservation may occur due to low temperature (~8 °C), due to low concentration (ng g^{-1} to μg g^{-1} range—i.e., they comprise a minute (~0.01%) and relatively refractory portion of the organic carbon in sediments), and because NP*n*EO compounds are protected from microbial attack by adsorption as organic coatings on inorganic solids (cf. Kvestak (*32*)). This latter mechanism has been proposed as an important control on the ultimate preservation of organic carbon in marine sediments (*33*).

An alternate explanation for the NPEO distribution observed in sediments might be preferential adsorption of the low-mass oligomers onto particles. Hydrophilic ethoxylates are more likely to remain in the water column longer than the more hydrophobic NP, NP*1*EO, and NP*2*EO as observed by Valls (*30*), who found that seawater and wastewater contained higher concentrations of long-chain ethoxylates. Nevertheless, our sediment data show that long-chain ethoxylates ($n = 3-20$) are incorporated in sediments in a way that apparently preserves the original distribution of commercial mixtures (Figure 3; NP-100 composition), suggesting that preferential adsorption/diffusion does not play a role.

To estimate the degradation rate of NP*n*EOs in sediments, we have plotted the total concentration normalized to the surface concentration as a function of median time for the four cores that had interpretable ^{210}Pb profiles (Figure 5). If we assume that the slight apparent decrease in total NP*n*EO with sediment depth to be derived entirely from degradation and that none of it derives from increasing loadings with

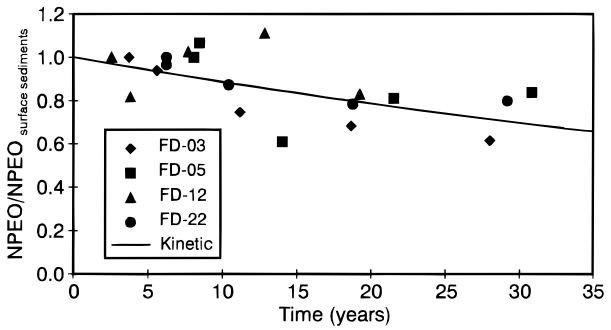

FIGURE 5. NPEO concentration in sediment cores plotted as a fraction of the surface concentration. Time axis has been constructed using the ^{210}Pb model to estimate the median age of sediment for each sample. The line through the data shows the degradation that would occur with first-order kinetics and a half-life of 60 yr.

time, then the calculated half-life would conservatively be about 60 yr.

The general subject of biodegradation of APEOs in the environment has given rise to more disagreement, contradiction, and controversy than any other aspect of surfactant biodegradation (*6*, *8*, *9*, *11*). The consensus is that the primary biodegradation of APEOs (i.e., ethoxy chain shortening) can be completed substantially with suitable acclimation, but the ultimate biodegradation (mineralization) is slow and uncertain. Our data suggest that although degradation clearly takes place in the delivery system (municipal plant/outfall) as evidenced by higher amounts of NP and the 1- and 2-ethoxylates, once these compounds become incorporated as minor components of marine sediments, neither primary degradation nor mineralization proceed very rapidly, if at all.

Estimates of Total NP*n*EO Loadings in the Strait of Georgia. The distribution of NP*n*EOs in surface sediments and sediment cores provides an approximate estimate of the present inventory in Strait of Georgia sediments. The standing stock of NP*n*EO in the top 50 cm of sediment at the five core sites is as follows: 66 μg cm^{-2} (FD-3); 6 μg cm^{-2} (FD-5); 63 μg cm^{-2} (FD-12); 140 μg cm^{-2} (F-22); and 42 μg cm^{-2} (FD-43). Using 60 μg cm^{-2} as the standing stock together with the area in Figure 1 where total NPEO surface concentrations exceed 1 μg g^{-1} (40 km^2), there resides in the sediments surrounding the Iona outfall at least 30 t of NP*n*EO. The background sediment concentration of 5 μg cm^{-2} measured at FD-5 suggests that the entire sedimentary basin of the Strait of Georgia (2700 km^2) contains at least a further 140 t of total NPEO and probably more considering that there are other likely sources, for example, pulp mills, with adjacent enriched sediment loadings. A survey of alkylphenol polyethoxylates by Bennie et al. (*4*) for 16 wastewater treatment plants across Canada gave a mean NPEO (NP + NP*1*EO + NP2EO) effluent concentration of 7.8 μg L^{-1} with a wide range of individual values (0.19−60 μg L^{-1}). Selecting the mean given by Bennie et al. (*4*) and doubling it to account for higher ethoxylates, the 540 × 10^6 L day^{-1} of effluent from IONA would supply about 1.5 t yr^{-1} of NPEO. The 30 t inventory in sediments near Iona could, therefore, account for about 20 yr of effluent discharge at present levels. For the greater Strait of Georgia, total discharges from 16 municipal outfalls (1270 × 10^6 L day^{-1} at 7.8 μg L^{-1}) would supply about 4 t yr^{-1} of NP*n*EOs, which could account for the estimated inventory for Strait of Georgia sediments in about 40 yr (or less, depending on the importance of pulpmill loadings). Annual usage of NP*n*EOs in Canada for 1993 was estimated at 7 kt (*4*, *34*). Use in the United States (250−300 kt yr^{-1}) prorated for population suggests that Canadian use may actually be somewhat higher and closer to 25−30 kt yr^{-1} (Naylor; personal communication). Prorating this range of estimates for the population surrounding the Strait of Georgia (presently about 2.8 million) suggests annual usage to be in the range of 0.7−3 kt yr^{-1}. The NPEOs preserved in the Strait of Georgia sediments can be accounted for by a small percentage of the use (<1%), which is consistent with substantial removal in treatment plants either by degradation or into sludge that is stored on land.

The vertical distribution of NP*n*EOs in sediments, the distribution among oligomers, and the sediment inventories all strongly suggest that NPEOs are preserved indefinitely once they become entrained in marine sediments. Although the evident lack of breakdown of these compounds is of concern, one must still question their environmental significance in sediments. If preservation is accomplished, as we suggest, by irreversibly sequestering into organic coatings on solids, NP*n*EOs may not be bioavailable and may not have the estrogenic activity of the unbound compounds.

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