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BEHAVIOR OF ANIONIC AND NONIONIC SURFACTANTS AND THEIR PERSISTENT METABOLITES IN THE VENICE LAGOON, ITALY

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Abstract—The occurrence and behavior of the aromatic surfactants linear alkylbenzene sulphonates (LAS) and nonylphenol polyethoxylates (NPE) as well as their biotransformation products in the central lagoon of Venice, Italy, were investigated by monitoring deep- and shallow-water lagoon stations, two riverine sites, and one sea station. Additional samplings were conducted at the three inlets connecting the lagoon with the open sea under both ebb and low-tide conditions, and a radiometrically dated sediment core spanning the last century was examined. The spatial distributions of LAS, NPE, and their carboxylic metabolites sulphophenyl carboxylates and nonylphenol carboxylates, respectively, appeared to be rather homogeneous over the entire central lagoon. Remarkable seasonal differences were found, however, primarily because of the increased biodegradation at temperatures greater than 20°C. The estimated primary and ultimate biodegradations of LAS in the lagoon waters were approximately 90 and 72%, respectively. Analysis of the dated sediment core showed similar annual fluxes of both LAS and NPE (48 ng/cm^2 year), which were between previously reported values of polychlorinated biphenyls (4.7 ng/cm^2 year) and polycyclic aromatic hydrocarbons (167 ng/cm^2 year).

Keywords—Surfactants Linear alkylbenzene sulphonates Nonylphenol polyethoxylates Nonylphenol Surfactant metabolites

INTRODUCTION

Surfactants, which are largely used by both households and industry, and surfactant-derived chemicals (i.e., precursors, side products, and metabolites) can contribute significantly to the formation of dissolved organic carbon and particulate organic carbon. Because of their widespread use, source specificity, and environmental persistence, surfactants can be effectively used as molecular markers for the contamination of waters and sediments by human activities [1].

Aromatic surfactants mainly consist of linear alkylbenzene sulphonates (LAS) and nonylphenol polyethoxylates (NPE), which in Europe have completely different markets. Alkylbenzene sulphonates, which has been extensively used since the mid-1960s, when they replaced the recalcitrant branched LAS (tetrapropylenebenzene sulphonates [TPS]), are the most widely used surfactants in household detergents, with a worldwide production during 1995 of approximately 1.5×10^6 tons [2]. Nonylphenol polyethoxylates, which were employed in household products until the mid-1980s, are now used only by industry, with an annual worldwide production of approximately 370,000 tons [3].

Alkylbenzene sulphonates consist of homologues with 10 to 13 carbon atoms in the linear alkyl chain as well as isomers resulting from the different attachment positions of the phenyl group along the alkyl chain, with the exclusion of the first carbon atom (Fig. 1A). Nonylphenol polyethoxylates are mixtures of ethoxymers (with 1 to 20 ethoxy units) and isomers depending on the branching of the nonyl alkyl chain (Fig 1b).

Both LAS and NPE exhibit relatively high acute toxicities, with 48-h LC50 values typically in the range of 5 to 10 and 0.1 to 2.0 mg/L range, respectively [4,5]. The NPE and their biointermediates also have some estrogenic effects on fish [6].

Aerobic biodegradation of LAS and NPE leads to the formation of carboxylated biointermediates, namely sulphophenyl carboxylates (Fig. 1c) and nonylphenol polyethoxylate carboxylates (NPEC; Fig. 1d), respectively [7]. The NPE can also biodegrade by nonoxidative cleavage of the polyethoxylic chain, leading to the formation of shorter NPE (mainly NPE ethoxymers with one or two polyethoxylic groups in the molecule [NP1E and NP2E, respectively]) and nonylphenol (NP).

The hydrophobic moieties of LAS and NPE interact with particulate matter contained in the water column, which lowers their bioavailability. The overall removal from natural waters of these compounds results from both biodegradation and transfer to the sediment. The LAS interact preferentially with organic surfaces through longer homologues and outermost positional isomers, exhibiting an increased adsorption capability by more than two orders of magnitude from the 5-C_{10} isomer to the 2-C_{14} isomer [8]. The NPE interact with organic surfaces mainly through the shorter ethoxymers, especially NP1E and NP2E, as well as through the completely de-ethoxylated NP because of their relatively high octanol-water partition (log K_{ow}) coefficients (4.5, 4.2, and 4.2 for NP, NP1E, and NP2E, respectively) [9]. These ethoxymers are minor components (<10%) in the commercial mixtures, but their relative abundance compared with the total NPE concentration increases remarkably in sediment because of the nonoxidative biodegradation of the longer NPE ethoxymers [10]. Moreover, NP transfers from the water phase to the gas phase by volatilization and aerosol formation [11].

Environmental monitoring of LAS has been performed in many industrialized countries, but fewer data are available regarding the neutral NPE metabolites, partly because of the progressive decline in the domestic use of NPE triggered by their unsatisfactory environmental profile [12]. The open literature reports wide concentration ranges for LAS, ranging

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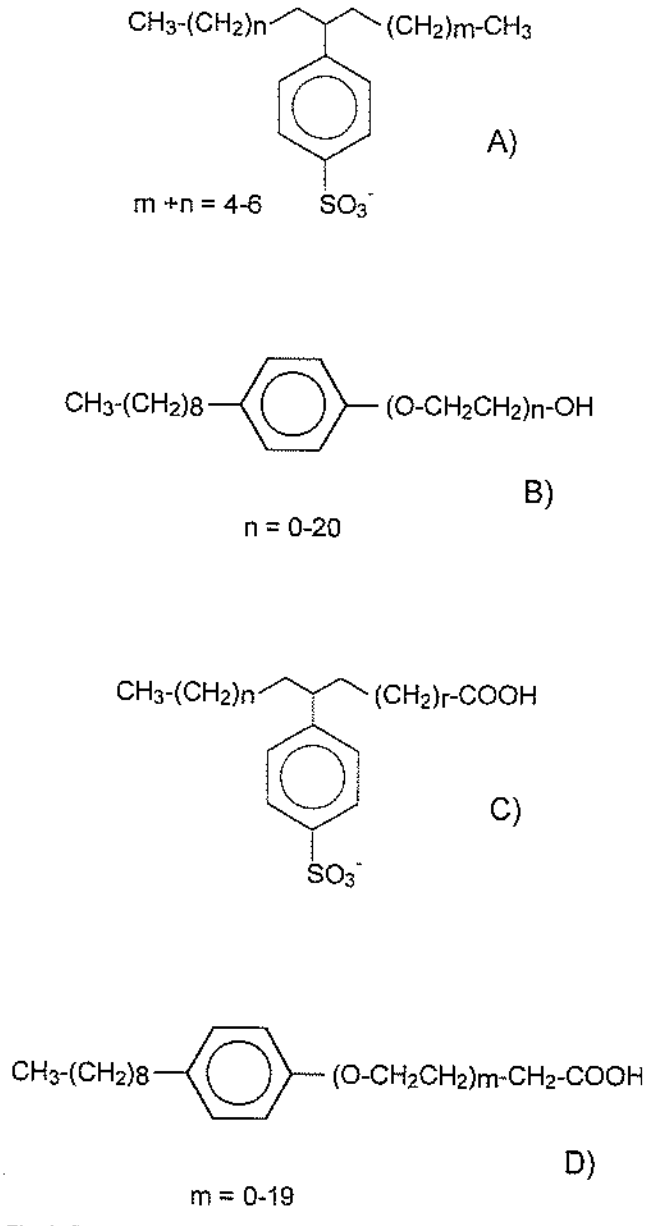

Fig. 1. Structures of linear alkylbenzene sulphonates (A), nonylphenol polyethoxylates (B), and their aerobic biointermediates, sulphophenyl carboxylates (C) and carboxylated nonylphenol polyethoxylates (D).

from 0.8 to 500 μg/L in coastal marine waters and from 0.01 to 600 μg/g in sediments [13–19]. The recorded NPE concentrations for such locations are in the ranges of 0.5 to 76 μg/L and 20 to 1500 ng/g, respectively [20–24]. To our knowledge, no data are available regarding their aerobic biointermediates, SPC and NPEC, in the marine environment. These cited concentrations were obtained by applying specific analytical procedures based on high-performance liquid chromatography or gas chromatography. Concentration values resulting from semispecific methods, such as methylene blue active substances for LAS or bismuth iodine active substances and cobalt thiocyanate active substances for NPE, have been not included because of the inaccuracy of these methods [25]. The determined values in waters and surface sediments strongly depend on the distance of the sampling site from sources of treated or untreated sewage [17].

In coastal waters, and especially those with low renewal rates and relatively low temperatures, the local adverse effects from the discharge of LAS and NPE can be considerable. This is because of the harmful effect of such compounds on the larvae and fry among many species of commercial interest [26].

We present here the results of a field study on LAS and NPE behavior in the Venice lagoon, Italy. This lagoon receives untreated sewage from the historical center of the town (≈120,000 inhabitants), treated municipal and industrial effluents from mechanical-biological sewage treatment plants (STPs), and contaminated freshwater from rivers such as the Lusore, Osellino, and Naviglio Brenta [27]. The aerobic biointermediates of LAS and NPE (SPC and NPEC, respectively) were also studied to infer the contribution of both primary and ultimate biodegradation to the removal of LAS and NPE from the lagoon waters. Removal of LAS and neutral NPE metabolites by sedimentation was assessed by analyzing a dated sediment core that was collected near the Porto Marghera industrial area and spanned a time period of 100 years.

MATERIALS AND METHODS

Chemicals

The LAS and TPS used as reference standards (active material, >98%) were supplied by Hüls (Marl, Germany). The mono- (NP1E) and diethoxylated (NP2E) NP ethoxymers were obtained from A.G. Kolb as a 75:25 (w/w) NP1E-NP2E mixture. Nonylphenol (active material, >95%) and sodium perchlorate ($NaClO_4$; active material, >99%) were supplied by Fluka (Buchs, Switzerland). The carboxylated NP1E, carboxylated NP2E, and sulphophenyl-4-butyric acid (C_4-SPC) employed as reference standards were synthesized according to methods described in the literature [28].

All the organic solvents employed were high-performance liquid chromatographic grade and were supplied by Baker (Deventer, The Netherlands). Water for chromatographic purposes was purified by a Milli-Q system (Millipore; Milli-Q, Bedford, MA, USA).

The cellulose thimbles (80 × 22 mm; Schleicher & Schuell, Feldbach, Switzerland) were Soxhlet extracted for 2 h in methanol or hexane (depending on the analysis) before use.

Sampling

This study included sampling of water at 13 sites: one in the Adriatic Sea (Station S, ≈ 2 km from Lido Island), two along the terminal branch of the Osellino River, upstream and downstream of the mechanical-biological Campalto STP (stations 8 and 7, respectively), and 10 inside the Venice lagoon (Fig. 2).

Lagoon stations 9 through 12 and river stations 7 and 8 were located in shallow areas (depth, <1 m). Stations 1 through 6 were in 1.4 to 4.5 m of water. Station S, in the Adriatic Sea, was in 11 m of water. Sampling sites were monitored twice monthly from January to September 1994.

In each sampling campaign, the 13 sites were monitored following the itinerary illustrated in Figure 2, starting from station 1 at the Malamocco mouth. Sampling began at rising tide and ended at ebb tide, and it spanned more than one tidal hemicycle (6 h). The sampling campaigns at the three harbor mouths—Lido, Malamocco, and Chioggia (the latter, though not reported in Fig. 2, is the southern mouth of Venice lagoon, 11 km from the Malamocco mouth)—were performed during both flood and ebb tide. Flood tide was first sampled at the

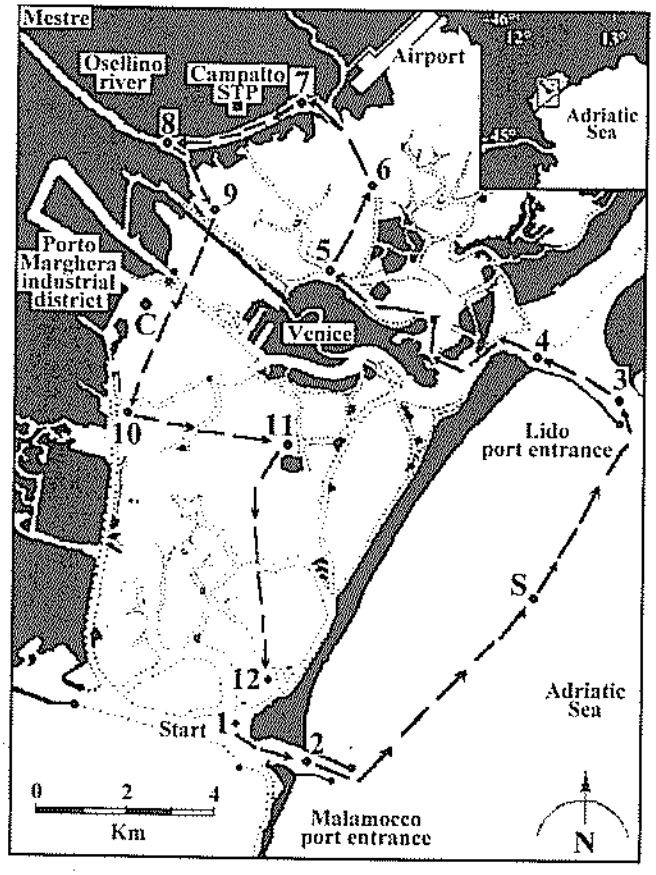

Fig. 2. Map of the central Venice lagoon, Italy, with the location of water sampling stations and the sequence of sampling. Station E is the location of the sedimentary core sampling site.

Lido mouth, then at the Malamocco mouth, and finally, at the Chioggia mouth. At ebb tide, these stations were sampled in the reverse order. For these stations, water samples (1,000 ml) were collected at three different sites and depths and then mixed together before filtering.

At the deep stations (stations 1–6 and S), water-sample aliquots (1,000 ml) were collected with a homemade bottle-sampler at three different depths (i.e., surface, bottom, and half depth), then mixed to obtain an average sample before analysis. At the shallow stations (stations 7–12), the water sample (1,000 ml) was collected at half depth. All the collected water samples were immediately filtered by a Swinnex Millipore (Milli-Q) apparatus using a Whatman (Whatman, Clifton, NJ, USA) glass-microfiber filter (0.7 μm), added to formaldehyde (5% v/v), and then stored in the dark at 4°C.

Water transparency was obtained using a Secchi disk (radius, 20 cm). Oxygen saturation and chlorinity were determined by Winkler and Mohr-Knudsen titrimetric methods, respectively. During the six sampling campaigns, the average temperature of the lagoon water was 7°C in January, 8°C in February, 20°C in May, 26°C in June, 29°C in August, and 25°C in September.

The sediment core was collected from the Venice lagoon near the Porto Marghera industrial area on July 1, 1982 (station C; Fig. 2) using a Plexiglas® cylindrical corer (100 × 10 cm) equipped with a steel handling apparatus. The values for redox potential, which were recorded immediately after sampling, ranged +16 mV at the surface to −74 mV at the bottom [29]. The core was sectioned and frozen at −20°C within 3 h of sampling, and the sections were successively freeze-dried, homogenized, sieved with a stainless-steel sieve (2 mm), and then stored at 4°C.

Determination of the analytes was performed in 1994 on subsamples from the core. The storing temperature (4°C) and lack of moisture in the sediment permit the assumption that no biodegradation occurred during storage.

The total organic carbon (TOC) in the sediment core sections was determined with a Perkin-Elmer CHN Analyzer (Model 240B; Perkin-Elmer, Norwalk, CT, USA) after carbonate removal with 1 M H_3PO_4. The granular-size fractions of 63 to 125 μm and of less than 63 μm were determined by sieving the sediment with 125- and 63-μm, American Society for Testing and Materials (Philadelphia, PA, USA) sieves, respectively. The sediment core was homogeneous in grain size, with the TOC ranging from 1.1% in the lower levels to 1.6% in the upper layers.

Radiodating of the core, which has been previously reported [30], was performed by measuring the total ^{210}Pb activity and then subtracting the supported ^{210}Pb activity from that value. A constant supply rate of unsupported ^{210}Pb to the sediment was assumed. An independent check was made by measuring the ^{137}Cs activity from nuclear fallout.

Extraction from water samples

Determination of LAS, SPC, NPE, and NPEC was performed on every water sample within 24 h of sampling using solid-phase extraction of 200-ml aliquots according to methods described in the literature [31].

Extraction from sediment samples

For every core fraction, 10 to 20 g of dry sediment were Soxhlet extracted for 20 h with 80 ml of methanol for the reversed-phase, high-performance liquid chromatographic determination and with 80 ml of hexane for the normal-phase, high-performance liquid chromatographic determination [32,33]. The methanolic solution, after rotoevaporation to approximately 10 ml, was passed over a strong anion-exchange cartridge column from Supelco (Bellefonte, PA, USA) that was previously conditioned with 10 ml of methanol and 5 ml of 2:1 (v/v) methanol-HCl 1 M water solution. After sample dilution to 30 ml with water and pH adjustment to 7 with sodium hydroxide, the solution was passed through a C18–solid phase extraction cartridge (Supelco). The retained LAS and TPS were eluted in a test tube with 5 ml of methanol and the eluate dried on a sand bath under a gentle nitrogen stream. The residue was then redissolved in 500 μl of a 1:1 (v/v) water-acetonitrile solution, ultrasonicated for 5 min, and centrifuged at 5000 rpm for 5 min before injection.

The hexane extract containing NPE was concentrated to approximately 5 ml and then percolated through an NH_2–solid phase extraction cartridge (Supelco) previously conditioned with 5 ml of hexane. Desorption of NPE was performed with 5 ml of a 3:1 (v/v) hexane:acetone solution, and the eluate was dried on a sand bath under a gentle nitrogen stream. The residue was then redissolved in 500 μl of hexane, ultrasonicated for 5 min, and centrifuged at 5000 rpm for 5 min before injection.

Chromatographic separation and detection

The chromatographic apparatus consisted of a 1050 series liquid chromatograph (Hewlett Packard, Avondale, PA, USA) equipped with a model 1046A fluorescence detector (flow cell

Table 1. Concentrations (μg/L) of linear alkylbenzene sulphonates (LAS), sulphophenyl carboxylates (SPC), nonylphenol polyethoxylates (NPE), and nonylphenol carboxylates (NPEC) during the six sampling campaigns

	Station												
	1	2	S	3	4	5	6	7	8	9	10	11	12
January													
LAS	3.1	5.2	2.4	4.0	3.6	11.3	13.2	205	188	4.6	2.3	4.2	2.6
SPC	5.2	7.3	4.0	7.0	8.3	26.1	21.5	397	492	6.3	3.5	7.3	3.8
NPE	2.3	1.6	1.6	1.4	1.9	4.4	4.9	62	56	2.9	2.3	2.7	2.0
NPEC	1.0	0.8	0.5	0.5	1.1	2.0	3.3	212	225	1.5	6.2	1.5	0.9
February													
LAS	2.5	4.3	1.9	4.5	3.2	14.4	12.9	234	256	4.2	2.5	3.9	3.0
SPC	5.7	9.3	3.2	8.2	5.9	24.3	29.1	607	535	8.3	4.3	8.0	5.4
NPE	2.8	2.1	1.3	1.8	1.5	5.1	3.9	51	55	2.8	6.8	2.3	2.4
NPEC	1.8	1.5	0.7	0.7	1.0	3.4	2.0	142	166	1.8	4.0	1.3	0.9
May													
LAS	3.6	3.2	2.4	11.1	4.2	5.2	6.7	245	152	5.3	4.5	3.2	2.4
SPC	2.9	3.4	1.8	6.4	3.7	3.4	26.5	543	246	5.6	3.8	6.0	4.8
NPE	2.8	2.5	1.2	1.9	1.3	2.5	2.4	30	14	2.4	6.8	1.7	1.8
NPEC	1.6	1.1	0.9	0.7	0.5	1.7	1.9	48	7.3	1.9	2.9	0.8	1.0
June													
LAS	4.0	7.1	1.9	3.6	2.7	4.0	3.9	135	157	4.8	2.5	2.4	2.7
SPC	2.8	3.9	1.6	4.1	1.9	2.3	7.0	177	143	6.0	2.3	5.2	5.0
NPE	1.9	1.6	0.8	1.1	1.4	2.8	1.8	23	7.9	2.0	4.5	2.0	1.4
NPEC	0.9	0.4	0.4	0.5	0.7	2.1	1.1	33	9.1	1.4	4.1	1.1	0.7
August													
LAS	1.8	3.0	1.3	2.3	1.3	5.6	6.9	138	153	3.3	1.7	1.4	2.0
SPC	4.0	4.9	2.3	4.8	3.3	12.4	18.2	361	403	5.4	2.3	3.7	4.6
NPE	1.4	1.6	0.6	0.8	0.6	2.6	2.5	28	26	1.9	3.3	1.7	1.2
NPEC	0.8	0.8	0.3	0.3	0.4	1.7	1.5	86	78	1.3	1.6	0.9	0.6
September													
LAS	2.5	3.6	1.4	2.9	1.3	6.3	6.6	166	155	4.6	1.5	2.0	3.2
SPC	3.6	6.0	2.8	5.6	4.7	10.8	16.0	433	388	6.9	3.9	3.9	6.8
NPE	1.7	1.8	1.1	1.4	1.3	2.3	2.8	37	29	3.0	4.0	2.0	2.1
NPEC	1.0	1.3	0.3	0.8	1.0	1.6	1.8	91	86	2.1	4.0	1.0	0.9

volume, 5 μl; Hewlett Packard) set at a λ_{ex} of 228 nm and λ_{em} of 295 nm. The environmental samples and reference standard solutions were injected in a manual 7125 injector (Rheodyne, Rohnert Park, CA, USA) equipped with a 200-μl loop. The LAS and SPC were separated on a reversed-phase octylsilica (C-8), 5 μm, with 250- × 4.6-mm column (Supelco) at a flow rate of 1.5 ml/min using a linear gradient elution by methanol and a 0.2% (v/v) trifluoroacetic acid solution in water. The mobile phase was 10% methanol, which was increased to 80% in 50 min. The NPE were separated on a reversed-phase C-8, 5 μm, with a 250- × 4.6-mm column (Supelco) at a flow rate of 1.5 ml/min using an isocratic elution by methanol (77%) and a 1 mM phosphate buffer (pH, 6.5) water solution (23%). The NPEC were separated on a reversed-phase C-8, 5 μm, with a 250- × 4.6-mm column (Supelco) at a flow rate of 1.5 ml/min using an isocratic elution by methanol (65%) and a 1 mM phosphate buffer (pH, 6.5) water solution (35%) [32]. The NP, NP1E, and NP2E from the core samples were separated on a normal-phase amminopropylsilica, 3 μm, with a 100- × 4-mm column (Knauer, Berlin, Germany) at a flow rate of 1 ml/min using an isocratic elution by hexane (98.5%) and isopropanol (1.5%) [33]. The LAS and TPS in the sediment core were separated on a reversed-phase octylsilica (C-18), 5 μm, with a 250- × 4.6-mm column (Supelco) using methods described in the literature [32].

Quantitation, accuracy, and precision

Quantitation of target compounds in both water and sediment samples was performed by external calibration curves that were obtained using reference standard solutions. The extraction/enrichment/detection procedure employed for water samples included triplicate analysis of selected water samples spiked with reference standards at approximately 5 μg/L. Recovery values obtained were 96 ± 4% for LAS, 98 ± 6% for NPE, 94 ± 8% for SPC, and 95 ± 5% for NPEC. No correction was made for recovery. The limit of detection (LOD; s/n ratio, 5) was 0.1 μg/L for LAS and 0.2 μg/L for SPC, NPE, and NPEC. Procedure blanks (200 ml of Milli-Q water), which were performed for every set of six samples, were always less than the LOD. The NP was analyzed in all water samples. Concentration values were always less than the LOD.

The extraction/enrichment/detection procedure employed for the core samples included triplicate analysis of selected samples spiked with LAS, NP, NP1E, and NP2E, each at a concentration of 50 ng/g. The obtained recovery values were 92 ± 6% for LAS, 88 ± 5% for NP, 90 ± 7% for NP1E, and 89 ± 8% for NP2E. No correction was made for recovery. The LOD (s/n ratio, 5) was 4 ng/g for all the target compounds.

RESULTS AND DISCUSSION

Monitoring of lagoon water

The values of LAS, SPC, NPE, and NPEC determined during the six sampling campaigns at all stations are reported in Table 1. The average values of the physicochemical parameters and the contaminant concentrations are reported in Table 2.

The spatial trend for the average concentration values revealed a homogeneous distribution of the examined com-

Table 2. Average values of physicochemical parameters and concentrations (μg/L) of linear alkylbenzene sulphonates (LAS), sulphophenyl carboxylates (SPC), nonylphenol polyethoxylates (NPE), and nonylphenol carboxylates (NPEC) determined during the six sampling campaigns

Station	Water temperature (°C)	Secchi disk (m)	Oxygen (sat.)	Chlorinity (g/L)	Average concentration (μg/L)			
					LAS	SPC	NPE	NPEC
1	15.6	4.5	118	18.6	2.9	4.0	2.2	1.2
2	15.6	4.3	120	18.8	4.4	5.8	1.9	1.0
S	15.6	3.8	119	18.2	1.9	2.6	1.1	0.5
3	16.0	3.4	119	18.4	4.7	6.0	1.4	0.6
4	16.0	3.1	122	18.2	2.7	4.6	1.3	0.8
5	16.3	1.7	124	16.1	7.8	13.2	3.3	2.1
6	16.2	1.4	139	14.5	8.4	19.7	3.1	1.9
7	17.2	0.9	94	0.5	187	420	38.5	102
8	16.1	1.1	85	0.4	177	368	31.3	95
9	17.2	0.6	143	14.4	4.5	6.4	2.5	1.7
10	18.7	0.6	156	16.4	2.5	3.4	4.6	3.8
11	17.1	Bottom	150	17.2	2.9	5.7	2.1	1.1
12	16.9	Bottom	130	17.7	2.7	5.1	1.8	0.8

pounds at both shallow-water stations (stations 9–12) and lagoon stations (stations 1–6). Much higher values were observed at stations 7 and 8, over the terminal part of the Osellino River. Moreover, the LAS and SPC concentrations determined at the Lido and Malamocco mouths (stations 2 and 3, respectively) were similar to those found inside the lagoon itself (e.g., stations 9 and 11).

The recorded values were within the range of values as reported in literature [14,15,18] but showed a much narrower distribution, especially for LAS. The average NPE concentration at station 10 (4.6 μg/L) was higher than that recorded in that area during 1990 (3.3 μg/L) [20], indicating a possible increased input of NPE into the lagoon waters.

Both LAS and NPE showed a marked seasonality, suggesting a strong dependence of their biodegradation on temperature, as has been previously reported [34]. Other factors, such as biogenic uptake or dilution by river water inflow, cannot quantitatively influence the observed behavior. The effects of temperature generally were more marked for SPC than for LAS, as shown by Figure 3, which presents the concentrations of LAS, SPC, NPE, and NPEC at station 5, near the city of Venice (presently discharging raw sewage into the lagoon). Higher values of the concentration ratio SPC:LAS were observed when the temperature rose from between 7 and 8°C (January–February) to between 26 and 29°C (June–August).

The SPC concentrations at all stations were generally higher than the corresponding LAS concentrations, except during

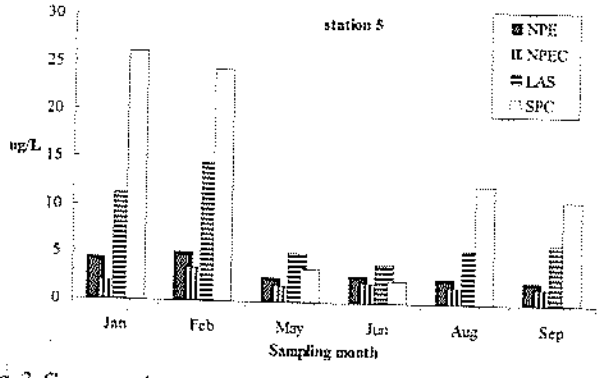

Fig. 3. Concentrations (μg/L) of linear alkylbenzene sulfonates (LAS), sulphophenyl carboxylates (SPC), nonylphenol polyethoxylates (NPE), and nonylphenol carboxylates (NPEC) as determined at station 5.

May and June at the open sea (station S), the Lido and Malamocco mouths (stations 1–4), and stations 5 and 10 (Table 1). The NPEC concentrations were two- to threefold greater than the NPE concentration in the Osellino River but one- to twofold lower in the lagoon waters. Considering the different NPE:NPEC concentration ratios observed, the hydrolytic biodegradation mechanism, which leads to shortening of the NPE polyethoxylic chain, is thought to prevail over the hydrolytic-oxidative mechanism, leading to a faster disappearance of the carboxylated NPE biointermediates [35]. The carboxylated NPE metabolites usually dominate over the neutral metabolites in freshwater and during aerobic biological treatments of sewage [36].

Station 10 (near the Porto Marghera industrial area) exhibited the highest average concentrations of NPE and NPEC (excluding stations 7 and 8), with values of 4.6 and 3.8 μg/L, respectively. This indicates the dominant influence of industrial effluents on this area. The relatively high concentrations of NPE and NPEC found at station 5 (near the historical center of Venice), with average values of 3.3 and 2.1 μg/L, respectively, can be ascribed to the presence of craftsman activities (e.g., small boat yards) that use industrial detergents.

The SPC concentrations downstream (station 7) of the Campalto STP were higher than those upstream (station 8), whereas little difference was found for NPE and NPEC (Table 1). Given the mean annual flow of the Osellino river (5.4×10^7 m³/year [37]) and the average concentrations of LAS, SPC, NPE, and NPEC at station 7 (187, 420, 39, and 102 μg/L, respectively), the annual loading of surfactants and their metabolites in the lagoon waters by this river can be estimated to be 10 tons/year for LAS, 23 tons/year for SPC, 2.1 tons/year for NPE, and 5.5 tons/year for NPEC.

The annual loading of LAS into the central part of the lagoon from the historical center of Venice can be estimated from the average individual consumption of LAS in northern Italy (1.75 kg/year; Assocasa-Federchimica, personal communication) and the number of equivalent inhabitants discharging untreated sewage into the central lagoon (≈ 120,000 people, including the tourist and commuter flow). The resulting loading of 220 tons/year is much more significant than the contribution by the Osellino River and accounts for more than 95% of the total loading (230 tons/year).

Because of the dominant use of LAS in household detergents, their average concentration in the Venice lagoon (under

Table 3. Concentrations (μg/L) of linear alkylbenzene sulphonates (LAS), sulphophenyl carboxylates (SPC), nonylphenol polyethoxylates (NPE), and nonylphenol carboxylates (NPEC) determined during the three sampling campaigns at the Lido, Malamocco, and Chioggia mouths

Sampling month	Entrance mouth	Concentration (μg/L)			
		LAS	SPC	NPE	NPEC
February	Lido				
	Ebb tide	3.9	5.2	3.1	1.3
	Flood tide	5.0	6.3	3.9	1.5
	Malamocco				
	Ebb tide	7.1	7.0	4.0	2.2
	Flood tide	6.1	5.7	2.6	1.4
	Chioggia				
	Ebb tide	5.6	4.7	2.4	1.1
	Flood tide	2.4	2.7	1.8	0.7
April	Lido				
	Ebb tide	3.5	4.7	1.9	0.6
	Flood tide	3.2	3.3	1.2	0.4
	Malamocco				
	Ebb tide	4.3	7.8	2.9	1.3
	Flood tide	2.3	4.5	1.5	0.3
	Chioggia				
	Ebb tide	2.5	4.1	1.3	0.4
	Flood tide	1.5	2.8	0.8	0.3
September	Lido				
	Ebb tide	3.7	5.7	2.6	0.9
	Flood tide	2.6	4.3	2.0	0.8
	Malamocco				
	Ebb tide	5.0	9.2	5.0	1.9
	Flood tide	3.2	4.9	2.8	1.3
	Chioggia				
	Ebb tide	3.6	5.2	3.0	1.1
	Flood tide	2.8	3.9	1.8	0.7

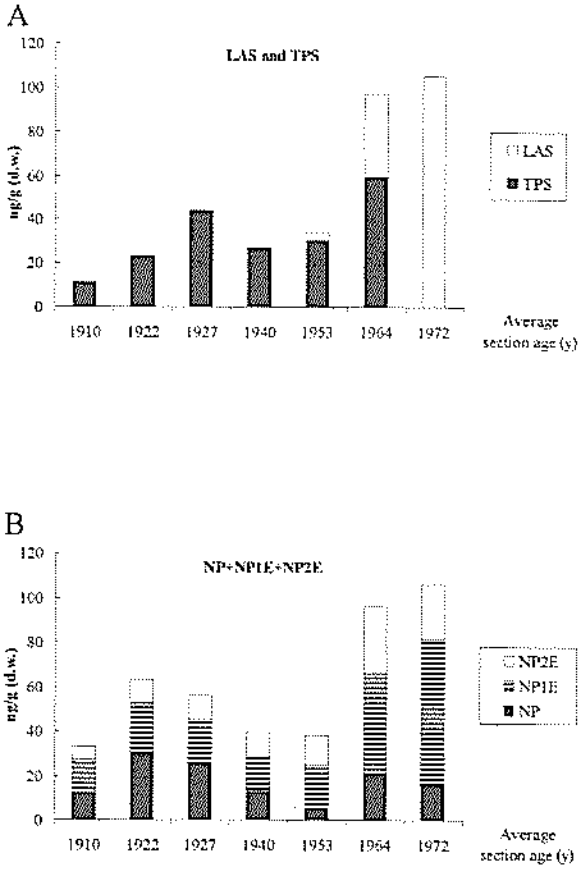

Fig. 4. Concentrations of linear alkylbenzene sulfonates (LAS; A) tetrapropylenebenzene sulphonates (TPS; A), nonylphenol (NP; B), monoethoxylated nonylphenol ethoxymers (NP1E; B), and diethoxylated nonylphenol ethoxymers (NP2E; B) as determined in sections of the examined sediment core (μg/g dry wt).

conservative conditions) can be estimated with reasonable accuracy by considering the daily input (I) of LAS in the central part of the Venice lagoon, or 630 kg/d; the water volume (V) of the central lagoon, or 132 km^2 with an average depth of 1 m; and the mean residence time (T) of water inside the central part of lagoon, or 10 d [38]. The average concentration of LAS can then be calculated as

$$\text{LAS} = (I \times T)/V$$

The estimated LAS concentration, assuming conservative behavior (i.e., no removal by biodegradation or sorption/sedimentation), is 48 μg/L. Compared with the average LAS concentration in the central lagoon (4.3 μg/L), this value suggests that approximately 90% of the LAS was lost through biodegradation and sedimentation. Such a result is similar to other values reported by literature [39]. Thus, total loss (i.e., mineralization of SPC) is approximately 72%.

Consumption of NPE by industrial activities (NPE have not been used in household detergents since the mid 1980s) in the central Venice lagoon can be estimated using the equation and assuming the same primary biodegradation rate as that estimated for LAS. Such an assumption is in good agreement with data reported in the literature [7]. The average concentration measured (2.6 μg/L) gives an estimated value of 380 kg/d (139 tons/year) for NPE input, of which only 5.8 kg/d come from the Osellino River.

The sampling campaigns performed at the Lido, Malamocco, and Chioggia mouths allowed quantification of the sea's influence on the distributions of the target compounds inside the Venice lagoon. The outflowing waters from the Venice lagoon always exhibited concentrations higher than those of the inflowing waters, except for the Lido mouth in February (Table 3). Moreover, concentrations at the entrance mouths were always greater than those recorded in the open sea (station S), confirming that some of the lagoon waters flowing out during ebb tide re-enter the lagoon during flood tide, as has been previously inferred from hydrodynamic data [40].

Sediment core

To examine the adsorption of LAS and NPE in the Venice lagoon sediments, a radiodated sediment core, collected during 1982 near the Porto Marghera industrial area, was examined (station C; Fig. 2). The concentrations determined in the core allowed verification through the sedimentary record of the transition from TPS to LAS during the 1960s and preliminary assessment of the role played by sedimentation as a nonbiodegradative removal mechanism for the aromatic surfactants. The concentrations of LAS and TPS determined in the seven analyzed sections of the core are shown in Figure 4a, whereas the concentrations of NP, NP1E, and NP2E are shown in Figure 4b.

The LAS concentrations in the core sections were lower than those previously reported for Venice lagoon sediments

collected near the historical center of Venice [19]. The cumulative concentrations of NP, NP1E, and NP2E recorded at the surface layer, however, confirm the values previously determined in that area during 1987 [21].

Available literature regarding the effects of sorbed LAS on Venice lagoon benthic organisms indicate that LAS concentrations in the investigated sediment core are at least 10-fold lower than those causing adverse effects on marine organisms [41].

The concentrations of NP1E and NP2E decrease four- and threefold, respectively, whereas the concentration of NP decreases twofold, from the core surface moving downward to deeper layers dating to the 1950s. This behavior can be ascribed to nonoxidative anaerobic biodegradation of NP2E to NP1E and, then, to NP, as has already been observed during previous studies regarding anaerobic digestion of STP sludges [42]. Both NP2E and NP1E were biotransformed into NP without significantly reducing the total concentrations of these metabolites.

An increase of the NP concentration moving downward in older layers, dating to 1920s, also was observed. The presence of NP as well as of NP1E, NP2E, and TPS, also in sediment layers dating to before the World War II, can be ascribed to a postdepositional, vertical transport through the sediment layers caused by pore water diffusion, as has been observed for LAS in river sediments [43], or to a partial biomixing of the sediment, as inferred by the ^{210}Pb and ^{137}Cs profiles [29].

The concentration ratio LAS:(NP + NP1E + NP2E) was approximately 1 in the top sediment. At that time (1970–1980), the LAS:NPE ratio in domestic detergents was approximately 2 [44]. Therefore, such evidence indicates the prevailing influence of industrial inputs over the municipal ones, as would be expected from the location of the core sampling site.

The vertical profiles of the selected compounds also were used to estimate the average sedimentation flux. The LAS and the combined NP/NP1E/NP2E annual fluxes on the surface sediment were calculated (in situ density value, 0.77 g/cm^3; sedimentation rate computed by core radiodating, 0.59 cm/year [29]) using the average determined concentrations reported in Figure 4. For each type of aromatic surfactant, the sedimentary annual fluxes were very similar: 48 ng/cm^2 year for the period 1972–1982, and 30 ng/cm^2 year for the period 1954–1972. By comparison, the concentrations and yearly fluxes previously determined in the sediment core for polychlorinated biphenyls and polycyclic aromatic hydrocarbons were 19 ng/g and 4.7 ng/cm^2 year and 510 ng/g and 167 ng/cm^2 year, respectively [29].

The fraction of LAS and NPE removed by sedimentation can be estimated through combining the reported fluxes (48 ng/cm^2 year for both LAS and NPE) with the annual loading (calculated for LAS and estimated for NPE) in the lagoon (230 and 139 tons/year, respectively) and in the extension of the lagoon (132 km^2). The values obtained for the period 1972–1982, without considering NP volatilization [11], were negligible (<0.1%) compared with the total annual loading, clearly indicating that biodegradation of LAS and NPE in the Venice lagoon is much more effective than removal by sedimentation.

CONCLUSIONS

Anionic and nonionic surfactants of the LAS and NPE types can be effectively employed as molecular markers for municipal and industrial sewage contamination in lagoonal and coastal waters and sediments. Their homogeneous spatial distribution in the Venice lagoon allowed good estimation of their field biodegradation. No significant differences were observed for canal waters (depth, >1.5 m) and shallow areas (depth, <1 m). The influence of the examined STP final effluent on the receiving lagoon waters was significant only for SPC.

The self-purifying capability of the Venice lagoonal environment was clearly demonstrated by the efficient biotransformation of LAS to SPC and of NPE to NPEC, particularly at temperatures greater than 20°C (late spring and summer). The overall results allowed the first, reliable evaluation of both primary and total biodegradation of LAS in the central lagoon, which was 90 and 72%, respectively.

Biodegradation of the surfactants in the lagoonal waters significantly reduces the transfer of LAS and NPE to the lagoonal sediment. When in the sediment, the subsequent degradation is much lower, with anaerobic transformation of NP2E and NP1E in the subsurface layers to NP, which does not significantly alter their total concentration.

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REFERENCES

1. Takada H, Eganhouse RP. 1998. Molecular markers of anthropogenic waste. In Meyers RA, ed, *Encyclopedia of Environmental Analysis and Remediation*. John Wiley & Sons, New York, NY, USA. pp 2883–2940.
2. Granados J. 1996. Surfactant raw materials. Constant evolution and solid future. *Proceedings*, 4th World Surfactants Congress, Barcelona, Spain, June 3–7, pp 100–123.
3. Raymond A. 1996. The global outlook for surfactant from a U.S. perspective. *Proceedings*, 4th World Surfactants Congress, Barcelona, Spain, June 3–7, pp 21–36.
4. Holfman WF, Macek KJ. 1980. An aquatic safety assessment of linear alkylbenzene sulfonate (LAS): Chronic effects on *Fathead minnows*. *Trans Am Fish Soc* 109:122–131.
5. Hall WS, Patoczka JB, Mirenda RJ, Porter BA, Miller E. 1989. Acute toxicity of industrial surfactants to *Mysidopsis bahia*. *Arch Environ Contam Toxicol* 18:765–772.
6. Purdom CE, Hardiman PA, Bye VY, Eno NC, Tyler CR, Sumpter JP. 1994. Estrogenic effects of effluents from sewage treatment works. *Chem Ecol* 8:275–285.
7. Swisher RD. 1987. *Surfactant Biodegradation*. Marcel Dekker, New York, NY, USA.
8. Hand VC, Williams GK. 1987. Structure-activity relationship for sorption of linear alkylbenzene sulphonates. *Environ Sci Technol* 21:370–373.
9. Giger W, Brunner PH, Schaffner C. 1984. 4-Nonylphenol in sewage sludge: Accumulation of toxic metabolites from nonionic surfactants. *Science* 225:623–625.
10. Schröder HF. 1993. Surfactants: Nonbiodegradable, significant pollutants in sewage treatment plant effluents. Separation, identification and quantitation by liquid chromatography, flow-injection analysis-mass spectrometry and tandem mass spectrometry. *J Chromatogr* 647:219–234.
11. Dachs J, Van Ry DA, Eisenreich SJ. 1999. Occurrence of estrogenic nonylphenols in the urban and coastal atmosphere of the lower Hudson River estuary. *Environ Sci Technol* 33:2676–2679.
12. Naylor CG. 1995. Environmental fate and safety on nonylphenol ethoxylate. *Text Chem Color* 27:29–33.
13. Takada H, Ishiwatari R, Ogura N. 1992. Distribution of linear alkylbenzenes (LABs) and linear alkylbenzene sulphonates (LAS) in Tokyo bay sediments. *Estuar Coast Shelf Sci* 35:141–156.
14. Takada H, Ogura N. 1992. Removal of linear alkylbenzene sulphonates (LAS) in the Tamagawa estuary. *Mar Chem* 37:257–273.
15. Kikuchi M, Tokai A, Yoshida T. 1986. Determination of trace levels of linear alkylbenzene sulphonates in the marine environment by high-performance liquid chromatography. *Water Res* 20: 643–650.
16. Takada H, Ishiwatari R. 1987. Linear alkylbenzenes in urban

riverine environments in Tokyo: Distribution, source, and behaviour. *Environ Sci Technol* 21:875–883.
17. Hon-nami H, Hanya T. 1980. Linear alkylbenzene sulphonates in river, estuary and bay water. *Water Res* 14:1251–1256.
18. González-Mazo E, Maria Forja J, Gómez-Parra A. 1998. Fate and distribution of linear alkylbenzene sulfonates in the littoral environment. *Environ Sci Technol* 32:1636–1641.
19. Marcomini A, Pavoni A, Sfriso A, Orio AA. 1988. Aromatic surfactants in the marine environment: Analysis and occurrence of LAS, NPEO and NP. *Proceedings*, 3rd International Conference on Environmental Contamination, Venice, Italy, October 26–29, pp 94–98.
20. Marcomini A, Stelluto S, Pavoni B. 1989. Determination of linear alkylbenzene sulphonates and alkylphenol polyethoxylates in commercial products and marine waters by reversed- and normal-phase HPLC. *Int J Environ Anal Chem* 35:207–218.
21. Marcomini A, Pavoni B, Sfriso A, Orio AA. 1990. Persistent metabolites of alkylphenol polyethoxylates in the marine environment. *Mar Chem* 29:307–323.
22. Blackburn MA, Kirby SJ, Waldock MJ. 1999. Concentrations of alkylphenol polyethoxylates entering UK estuaries. *Mar Pollut Bull* 38:109–118.
23. Kveštak R, Terzic S, Ahel M. 1994. Input and distribution of alkylphenol polyethoxylates in a stratified estuary. *Mar Chem* 46: 89–100.
24. Shang DY, MacDonald RW, Ikonomou MG. 1999. 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. *Environ Sci Technol* 33: 1366–1372.
25. Zanette M, Marcomini A, Capri S, Liberatori A. 1995. Revision of the regulatory semispecific methods for the determination of surfactants in aqueous samples. Part I: Nonionic surfactants. *Ann Chim* 85:201–220.
26. Lewis M. 1991. Chronic and sublethal toxicities of surfactants to aquatic animals: A review and risk assessment. *Water Res* 25: 101–113.
27. Vazzoler S, Costa F, Bernardi S. 1987. *Lagoon of Venice and Transfer of Fresh Water and Pollutants*. Istituto Veneto di Scienze ed Arti, Venice, Italy.
28. Marcomini A, Tortato C, Capri S, Liberatori A. 1993. Preparation, characterization and RP-HPLC determination of sulphophenyl and nonylphenoxy carboxylates. *Ann Chim* 83:461–484.
29. Pavoni B, Sfriso A, Marcomini A. 1987. Concentration and flux profiles of PCBs, DDTs and PAHs in a dated sediment core from the lagoon of Venice. *Mar Chem* 21:25–35.
30. Battiston GA, Degetto S, Gerbasi R, Sbrignadello G. 1989. Determination of sediment composition and chronology as a tool for environmental impact investigations. *Mar Chem* 26:91–100.
31. Di Corcia A, Samperi R, Marcomini A. 1994. Monitoring aromatic surfactants and their biodegradation intermediates in raw and treated sewages by solid-phase extraction and liquid chromatography. *Environ Sci Technol* 28:850–858.
32. Marcomini A, Giger W. 1987. Simultaneous determination of linear alkylbenzene sulphonates, alkylphenol polyethoxylates and nonylphenol by high-performance liquid chromatography. *Anal Chem* 57:1709–1715.
33. Marcomini A, Cecchi F, Sfriso A. 1991. Analytical extraction and environmental removal of alkylbenzene sulphonates, nonylphenol and nonylphenol monoethoxylate from dated sludge-only landfills. *Environ Technol* 12:1–8.
34. Quiroga JM, Sales D. 1989. Effect of temperature kinetics on anionic surfactant detergents in seawater. *J Dispers Sci Technol* 10:773–784.
35. Ahel M, Giger W, Koch M. 1994. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment—I. Occurrence and transformation in sewage treatment. *Water Res* 28: 1131–1142.
36. Ahel M, Schaffner C, Giger W. 1996. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment—III. Occurrence and elimination of their persistent metabolites during infiltration of river water to groundwater. *Water Res* 30:37–46.
37. Bernardi S, Cecchi R, Costa F, Ghermandi G, Vazzoler S. 1986. Freshwater and pollutants inputs in the Venice lagoon. *Inquinamento* 2:46–64.
38. Magistrato alle Acque di Venezia. 1992. Concessioni allo Scarico di Reflui da Unità Produttive (CRUP) Model. Venice, Italy.
39. Sales D, Quiroga JM, Gomez-Parra A. 1987. Primary kinetics of anionic surfactants in marine environment. *Bull Environ Contam Toxicol* 39:385–392.
40. Ente per le Nuove Tecnologie, l'Energia e l'Ambiente. 1990. Rapporto sullo stato attuale dell'ecosistema lagunare. Rapporto Finale 1.3.9, Consorzio Venezia Nuova, Venice, Italy.
41. Marin MG, Pivotti L, Campesan G, Turchetto M, Tallandini L. 1994. Effects and fate of sediment-sorbed linear alkylbenzene sulphonates (LAS) on the bivalve mollusc *Mytilus Galloprovincialis Lmk*. *Water Res* 28:85–90.
42. Brunner PH, Capri S, Marcomini A, Giger W. 1988. Occurrence and behaviour of linear alkylbenzene sulphonates, nonylphenol, nonylphenol mono- and nonylphenol diethoxylates in sewage and sewage sludge treatment. *Water Res* 22:1465–1472.
43. Reiser R. 1997. Occurrence and fate of detergent-derived alkylbenzene sulphonates in recent sediments. PhD thesis. Swiss Federal Institute of Technology, Zurich, Switzerland.
44. Marcomini A, Filipuzzi F, Giger W. 1988. Aromatic surfactants in laundry detergents and hard-surface cleaners: Linear alkylbenzene sulfonates and alkylphenol polyethoxylates. *Chemosphere* 17:853–863.