SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 21, No. 1, pp. 37–46, 2002
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Printed in the USA
0730-7268/02 $9.00 + .00

OCCURRENCE AND DISTRIBUTION OF NONIONIC SURFACTANTS, THEIR DEGRADATION PRODUCTS, AND LINEAR ALKYLBENZENE SULFONATES IN COASTAL WATERS AND SEDIMENTS IN SPAIN

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(*Received* 19 *March* 2001; *Accepted* 29 *June* 2001)

Abstract—Spain is one of the European countries that still discharges untreated wastewaters and sewage sludge to the sea. A total of 35 samples of coastal waters and 39 samples of harbor sediments was analyzed. Samples were collected from several hot spots on the Spanish coast, such as the harbors of Tarragona, Almería, and Barcelona, the mouths of the Besos and Llobregat rivers, the Bay of Cadiz, and various yacht harbors at the Mediterranean coast. A generic analytical procedure based on solid-phase extraction-liquid chromatography-atmospheric pressure chemical ionization/electrospray ionization mass spectrometry (SPE-LC-APCI/ESI-MS) was employed for determining the concentrations of alcohol ethoxylates (AEO), nonylphenol ethoxylates (NPEO), coconut diethanol amides (CDEA), nonylphenoxy-monocarboxylates (NPEC), nonylphenol (NP), octylphenol (OP), and linear alkylbenzene sulfonates (LAS) in sediment and water samples. The analysis revealed the presence of considerably high concentrations of NPEOs and NP near the points of discharge of industrial and urban wastewaters. Nonylphenol was found in 47% of water samples and in 77% of all sediment samples analyzed. Values for NP ranged from <0.15 to 4.1 μg/L in seawater and from <8 to 1,050 μg/kg in sediments. Levels of AEOs and CDEAs in seawater and marine sediments are reported for the first time. Concentrations of CDEAs in sediment, which were predominated by C_{11} through C_{15} homologues, ranged from 30 to 2,700 μg/kg, while in seawater, concentrations found were up to 24 μg/L. The AEOs were found to accumulate in a bottom sediment and they were detected in all analyzed sediment samples in concentrations from 37 to 1,300 μg/kg.

Keywords—Surfactants   Degradation products   Coastal waters   Marine sediments

INTRODUCTION

Surface-active compounds, used in industrial processes as well as in households, have one of the highest production rates of all organic chemicals. The total quantity of surfactants produced all over the world in 1996 was more than 10 million metric tons with a predicted upward trend for the year 2005 of 3.6% [1]. Approximately one half of the production is emitted via wastewater treatment plants (WWTPs) into surface waters. Some of these surfactants biodegrade to nontoxic compounds before reaching the environment, but recent concern has focused on alkylphenol ethoxylates (APEO) and their degradation products as potential endocrine disrupters. Ahel and coworkers [2] estimated that approximately 60 to 65% of nonylphenol ethoxylates (NPEOs) introduced to WWTPs are discharged into the environment, with 19% in the form of carboxylated derivatives, 11% in the form of lipophilic NP_1EO and NP_2EO, 25% in the form of nonylphenol (NP) and 8% as untransformed NPEO. The main environmental concern is not the toxicity of these compounds but rather their estrogenic potential, confirmed by numerous in vitro and in vivo studies [3,4]. Because of this finding, APEOs are banned or restricted in Europe. Throughout northern Europe (Scandinavian countries, England, Germany), a voluntary ban on APEO use in household cleaning products began in 1995 and restrictions on industrial cleaning applications began in 2000 [5].

In our previous studies, we found significant concentrations of NPEOs and their degradation products in effluents of several WWTPs in the Catalonian region in Spain [6,7]. Concentrations ranged from 8 to 50 μg/L of NPEO, from 6 to 144 μg/L of NP, and from 13 to 113 μg/L of NP_1EC. In receiving waters, i.e., in the Anoia and Cardener rivers and in tributaries of the Llobregat River, which ends in the Mediterranean sea, concentrations found downstream of WWTPs ranged from 2 to 40 μg/L of NPEO, from 2 to 15 μg/L of NP, and from 0.1 to 35 μg/L of NP_1EC [6]. Furthermore, very high concentrations were found in digested sewage sludges from the same WWTPs, specifically 20 to 135 mg/kg of NPEOs, 170 to 600 mg/kg of NP, and up to 14 mg/kg of NP_1EC [8].

Directive 91/271/European Economic Community (EEC) [9] indicates that all wastewater in the territories of the European Union have to be properly collected and subjected to secondary (biological treatment with secondary settlement) or equivalent treatment before being discharged into estuaries or coastal waters. However, in Spain, a significant portion of wastewater from highly populated cities and industrial complex zones is still discharged into surface waters without proper treatment. Moreover, during the past decades, a significant portion of WWTP sludge was discharged directly into surface waters. Directive 91/271/EEC sets the end of 1998 as a deadline for phasing out the disposal of sludge to surface waters.

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However, Spain continued this type of discharge, and in 1998, 57,000 tons of sludge (dry matter) was disposed of in surface water.

With respect to this, one of the priority tasks is to determine the environmental distribution of synthetic organic compounds in coastal areas and to assess the environmental hazards of these compounds to aquatic organisms.

There have been numerous studies on the occurrence of nonionic surfactants, mainly APEOs and their degradation products, in rivers and lakes [10–15], estuaries, and coastal areas [16–23]. However, very little data on the occurrence of nonionic surfactants and their refractory metabolites in the marine environment have been generated in Spain and, to our knowledge, this article offers the first reported data for the coastal area. Numerous studies have dealt with the fate of linear alkylbenzene sulfonates (LAS) in the aquatic environment and several of them reported the levels of LAS and their carboxylic degradation products in coastal waters in Spain [24–28].

The objectives of this study were to optimize the solid-phase extraction-liquid chromatography-atmospheric pressure chemical ionization/electrospray ionization mass spectrometry (SPE-LC-APCI/ESI-MS) method and to apply it as a generic approach for the analysis of seawater and marine sediment, to identify nonionic surfactants and their degradation products in harbor and coastal areas in Spain, and to characterize their spatial and temporal distributions in water and sediment.

The studied area includes different hot spots on the Spanish coast, such as the mouths of the Besos and Llobregat rivers, sites near outflows of municipal and industrial wastewaters in harbor areas of Barcelona, Tarragona, and Almería, and various sport harbors with intensive yacht transit. We have focused our attention on nonionic polyethoxylene surfactants (alcohol ethoxylates [AEOs] and APEOs), their degradation products alkylphenoxycarboxylates and alkylphenols, nonionic surfactants containing an amide group (coconut diethanol amides [CDEAs]), and LAS. The structures of target compounds are shown in Figure 1.

MATERIALS AND METHODS

Standards and chemicals

Commercial LAS with a low dialkyltetralinsulfonates content (<0.5%) was supplied by Petroquimica Española S.A. (San Roque, Spain) in a single standard mixture with the proportional composition of the different homologues as follows: C_{10}, 3.9%; C_{11}, 37.4%; C_{12}, 35.4%; and C_{13}, 23.1%.

The individual polyethoxylated surfactants, corresponding to a mixture with an average number of ethoxy groups, were from KAO (Barcelona, Spain). The standards of AEO were individual pure C_{10} through C_{16} ethoxylates with an even number of carbon atoms and an average of four ethoxy units. The standard of NPEO contained chain isomers and oligomers with an average of four ethoxy units. High-purity (98%) 4-*tert*-octylphenol and technical-grade 4-nonylphenol were obtained from Aldrich (Milwaukee, WI, USA). The NP_1EC was synthesized according to the method described by Marcomini et al. [29]. A commercial mixture of CDEA was kindly supplied by H.Fr. Schröder. The proportional composition of the different homologues is C_7 (7%), C_9 (7.5%), C_{11} (60.9%), C_{13} (18%), and C_{15} (6.6%).

High-performance liquid chromatography (HPLC) grade water, acetonitrile, methanol, and dichloromethane were obtained from Merck (Darmstadt, Germany). Analytical-grade acetic acid (HOAc) was from Panreac (Barcelona, Spain). The ion-pair reagent used was triethylamine, purchased from Sigma (St. Louis, MO, USA).

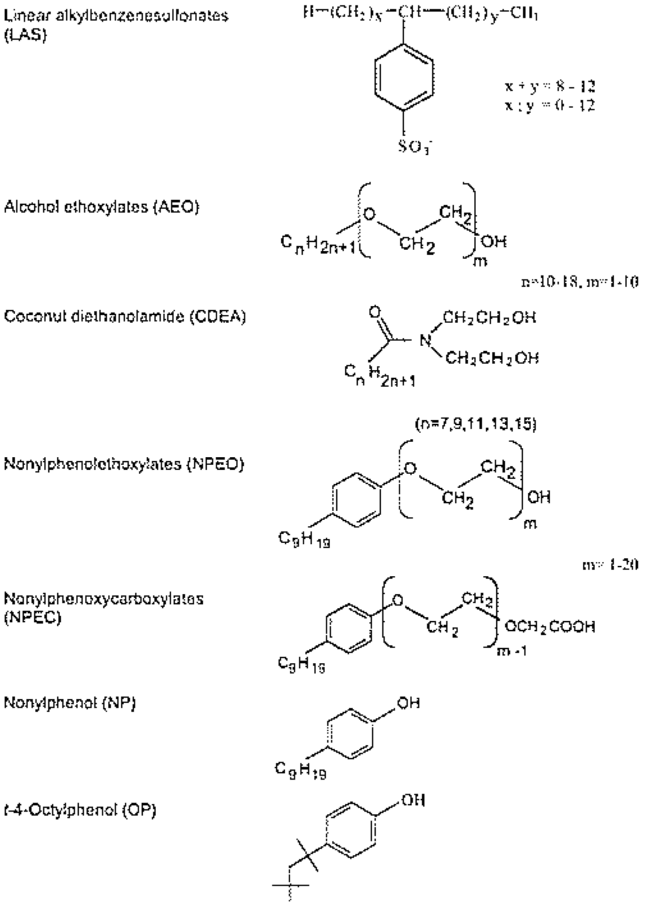

Fig. 1. Structures of studied compounds.

Study sites

Sediment samples were collected from 23 sites along the Mediterranean coast and from 3 sites on the Atlantic coast. Water samples were taken at 14 locations on the Mediterranean coast. Locations of sampling sites are shown in Figure 2. A global positioning system (GPS) was employed to identify each location precisely. The description of the sampling sites is given in Table 1. Sediment samples from Barcelona and Tarragona harbors (B3, T1–T4) were taken on two occasions (March 1999 and March 2000), while water samples (B1–B3, T3, T4) were collected every two months from July 1999 to July 2000. Water samples from the Harbor of Almería (A1) were collected in January 2000. Sediments from this location and from the vicinity (A1–A4, AD, AM) were analyzed on two occasions, in June 1999 and in December 1999. Eleven samples of sediments from the Andalusian Mediterranean and the Atlantic coast were collected in February 2000.

Sample collection

Sediments were collected using a Van Veen grab. The samples were transferred to the laboratory at a temperature of 4°C, then frozen at −20°C before being freeze dried. The lyophilized sediment samples were ground and homogenized by sieving through a stainless steel 2-mm sieve. The samples were wrapped in aluminum foil and stored at −20°C until extraction.

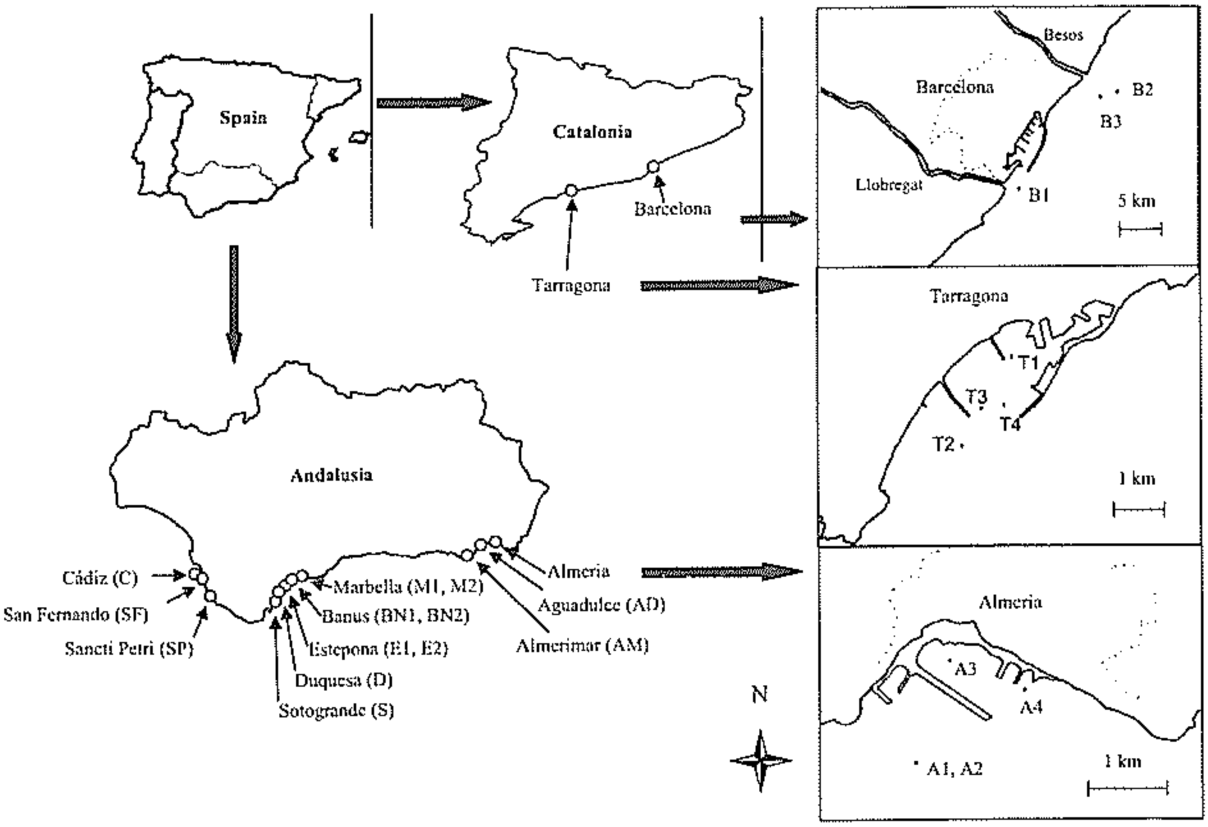

Fig. 2. Map of the studied areas showing the locations of the sampling sites.

Seawater was collected in Pyrex borosilicate amber glass containers by means of a bottle sampler. Sample preservation was accomplished by storing the bottles at 4°C immediately after sampling.

Sample preparation

All aqueous samples were filtered through 0.45-μm membrane filters and preconcentrated on LiChrolut C18 SPE cartridges (Merck, Darmstadt, Germany) within 24 h in order to avoid any degradation of target compounds and loss of sample integrity [30]. The complete SPE procedure is described elsewhere [7]. After preconcentration, SPE cartridges were wrapped in aluminum foil and kept at −20°C until analysis (maximum of one month). Cartridges were eluted with 2 × 5 ml of methanol-dichloromethane (9:1, v/v). The eluates were evaporated to dryness with a gentle stream of nitrogen and reconstituted with methanol to a final volume of 1 ml.

Target compounds were extracted from sediment samples by ultrasonic solvent extraction using a mixture of methanol dichloromethane (7:3, v/v). Subsequent clean-up of extracts was performed by SPE. A more detailed description of the method can be found elsewhere [31].

Liquid chromatography conditions

The HPLC system consisted of a HP 1100 autosampler having a 100-μl loop and a HP 1090 LC pump, both from Hewlett-Packard (Palo Alto, CA, USA). The flow rate was 1 ml/min. The HPLC separation was achieved on a 5-μm, 250 × 4-mm i.d. C_{18} reversed phase column (LiChrospher 100 RP-18, Merck). The injection volume was 20 μl.

Nonionic surfactants (AEO, NPEO, and CDEA) were separated using a mobile phase of solvent A, methanol:acetonitrile (50:50), and solvent B, water, both acidified with 0.5% HOAc. The solvent programming used was that initial conditions were held linear at 30% A for 3 min, then linearly increased to 90% A over 10 min, then linearly increased to 100% A over 10 min, and then kept isocratic for 10 min.

For successful separation of LAS, NPEC, NP, and OP, ion pair chromatography with HOAc/triethylamine was performed. The eluent A consisted of acetonitrile:water (80:20) and eluent B was water, both containing 5 mM HOAc and 5 mM triethylamine. The gradient was held linear at 50% A for 5 min, then increased to 100% A over 15 min, and then held constant for an additional 10 min.

Mass spectroscopy detection

Detection was carried out using a HP 1040 M diode array ultraviolet-Vis detector coupled in series with a HP 1100 mass selective detector equipped with an atmospheric-pressure ionization source that can use either an atmospheric-pressure chemical ionization (APCI) or electrospray (ESI) interface. Two analyses were performed for each sample, one using ESI in negative ion mode for the determination of LAS, NPEC, NP, and OP and one using APCI in positive ion mode for the determination of all polyethoxylates and CDEA.

Using the APCI interface, characteristic peaks checked in positive ion mode were 271 and 291 *m/z* units for NPEOs and 151 and 195 *m/z* for AEOs. In addition, polyethoxylated surfactants were identified by checking the characteristic pattern showing the $[M+H]^+$ ion for each compound and equidistant signals with mass differences of ±44 *m/z* relative to the various ethoxylated oligomers. Different CDEA homologues were

Table 1. Description of sampling sites

Sample code	Location (Spain)	Description of location	Samples analyzed	Type of sediment	Total organic carbon (%)
B1	Barcelona	River Besos mouth	Water	—	NA[a]
B2	Barcelona	River Llobregat mouth	Water	—	NA
B3	Barcelona	Outflow of sludge and municipal wastewater	Water/sediment	Clay	NA
B3-N	Barcelona	1 km north of B3	Water/sediment	Clay	NA
B3-S	Barcelona	1 km south of B3	Water/sediment	Clay	NA
B3-E	Barcelona	1 km east of B3	Water/sediment	Clay	NA
B3-W	Barcelona	1 km west of B3	Water/sediment	Clay	NA
T1	Tarragona	Outflow of industrial plant	Sediment	Clay	NA
T2	Tarragona	Outflow of industrial plant	Sediment	Clay	NA
T3	Tarragona	Outflow of industrial plant	Water/sediment	Clay/sand	NA
T4	Tarragona	Outflow of industrial plant	Water/sediment	Clay	NA
A1	Almería	Outflow of municipal wastewater	Water/sediment	Clay/sand	2.77
A1-N	Almería	North of A1	Water	—	NA
A1-S	Almería	South of A1	Water	—	NA
A1-E	Almería	East of A1	Water	—	NA
A1-W	Almería	West of A1	Water	—	NA
A2	Almería	5 m from A1	Sediment	Sand	NA
A3	Almería	Harbor	Sediment	Clay/sand	1.51
A4	Almería	Sport harbor	Sediment	Clay/sand	NA
AM	Almerimar	Sport harbor	Sediment	Clay/sand	0.87
AD	Aguadulce	Harbor	Sediment	Clay	8.72
C	Cadiz	Nautic club, sport harbor	Sediment	Clay	NA
SF	San Fernando	Close to an untreated urban waste water effluent	Sediment	Clay/sand	NA
SP	Sancti Petri	Nautic club, sport harbor	Sediment	Clay	NA
SG	Sotogrande	Nautic club, sport harbor	Sediment	Clay/sand	1.50
D	Duquesa	Nautic club, sport harbor	Sediment	Clay	1.03
E1	Estepona 1	Nautic club, sport harbor	Sediment	Clay	2.46
E2	Estepona 2	Nautic club, sport harbor	Sediment	Clay	1.56
BN1	Banus 1	Nautic club, sport harbor	Sediment	Clay/sand	1.44
BN2	Banus 2	Nautic club, sport harbor	Sediment	Clay/sand	0.38
M1	Marbella 1	Nautic club, sport harbor	Sediment	Clay	1.31
M2	Marbella 2	Nautic club, sport harbor	Sediment	Clay/sand	0.47

[a] NA = not analyzed.

identified by their characteristic ion of 106 *m/z* and by molecular ions of 232 to 344 *m/z* corresponding to the homologues with odd numbers of carbon atoms from C_7 to C_{15}.

In negative ion mode, using ESI, C_{10} through C_{13} LAS were quantified by their $[M-H]^-$ ions with *m/z* values of 297, 311, 325, and 339, respectively. The nonylphenol (NP) and nonylphenoxycarboxylate (NP_1EC) were quantified by monitoring *m/z* values corresponding to $[M-H]^-$ ions (219 *m/z* for NP and 277 *m/z* for NP_1EC).

Quantitation

Target compounds were identified in full-scan mode (100–1,000 *m/z*) by matching the retention time and mass spectrum with authenticated standards. Final quantification was performed in selected ion monitoring mode using external calibration. Initially, a series of injections of target compounds in the concentration range of 0.05 to 50 mg/L was used to obtain the calibration equations. Afterward, five-point calibrations were performed daily over the established concentration range. Linear regression of peak area versus concentration gave a good fit (typically, $R^2 > 0.990$) for all compounds. The possible fluctuation in signal intensity was checked by injecting standard solutions at two concentration levels after each six to eight injections. Quantification of AEOs with an odd number of C atoms (standards were not available) was made assuming that they gave the same response as the adjacent even-number homologue. The sediment sample concentrations were expressed on a freeze-dried weight basis.

Method validation

The recoveries (percent of standard added to sample recovered during extraction and clean-up) and reproducibility (relative standard deviation for triplicate analysis) of the extraction–preconcentration–detection procedure were determined by means of a spiking experiment. The marine sediment spiked with 100 μg/kg of standard mixture of nonionic surfactants was analyzed in triplicate by applying the method described above together with a nonamended sample. The recoveries from seawater were determined by the preconcentration of 200 ml of water spiked with a final concentration of 50 μg/L of each compound. Procedure blanks (200 ml of Milli-Q water, Bedford, MA, USA) were performed for each set of samples.

The limits of detection (LODs) of target compounds in sediment and in seawater were calculated by a signal-to-noise ratio (the ratio between intensity of signal of each compound obtained under selected ion monitoring conditions and intensity of noise) of three. The recoveries and limits of detection are reported in Table 2.

RESULTS AND DISCUSSION

Concentrations of nonionic surfactants and their degradation products in water and sediment samples

The concentrations of target compounds in water and sediment samples collected in industrialized and urbanized areas with point sources of industrial and municipal wastewater effluents are listed in Tables 3 and 4.

Table 2. Mean recoveries, standard deviations (SD), and limits of detection (LOD) of linear alkylbenzene sulfoantes (LAS), alcohol ethoxylates (AEO), coconut diethanol amides (CDEA), noylphenol ethoxylates (NPEO), nonylphenoxy carboxylate (NP_1EC), nonylphenol (NP), and octylphenol (OP) obtained for water samples and sediments

Compound	Recovery ± SD (n = 3) (water sample)[a]	LOD (water) (µg/L)	Recovery ± SD (n = 3) (sediment)[b]	LOD (sediment) (µg/kg)
LAS				
C_{10}LAS	97 ± 8	0.05	90 ± 12	2.5
C_{11}LAS	96 ± 5	0.10	94 ± 9	5
C_{12}LAS	94 ± 6	0.10	91 ± 8	5
C_{13}LAS	90 ± 10	0.10	86 ± 15	5
AEO				
C_{10}EO	101 ± 8	0.10	95 ± 8	5
C_{12}EO	98 ± 6	0.10	92 ± 12	5
C_{14}EO	84 ± 11	0.10	86 ± 10	5
CDEA	90 ± 12 (mixture)		92 ± 7 (mixture)	
C_7DEA		0.02		1
C_9DEA		0.01		0.5
C_{11}DEA		0.01		0.5
C_{13}DEA		0.01		0.5
C_{15}DEA		0.01		0.5
NPEO[c]	102 ± 5	0.20	95 ± 9	10
NPE_1C	88 ± 7	0.10	83 ± 12	5
NP	91 ± 9	0.15	81 ± 10	10
OP	81 ± 6	0.15	75 ± 8	10

[a] Concentration factor 200.

[b] Concentration factor 10.

[c] NPEO with an average of four ethoxy units.

Nonylphenol ethoxylates were found in more than 70% of water samples in concentrations up to 11 µg/L. Average concentrations ranged from 0.3 to 5 µg/L, with several incidental values found in Tarragona Bay (T3 and T4), which receives wastewaters from several industrial plants mixed with domestic wastewaters. At site B3 (outflow of wastewater), NPEOs were found in concentrations ranging from 0.8 to 1.8 µg/L, while at sites B3-W, B3-E, B3-S, and B3-N, located 1 km from outflows, only NP was detected, which may indicate in situ degradation of NPEOs. Nonylphenol was found in water samples at 7 of 15 locations. The average values were from <0.15 µg/L (LOD) to 1.0 µg/L, with incidental values of 3.8 and 4.1 µg/L for the mouths of the Besos and the Llobregat River. These values are indicative of the contamination produced by several WWTPs that discharge treated effluents into these rivers or their tributaries. These WWTPs, especially the WWTPs at Igualada and Manresa, receive 30 to 60% of their wastewater from the tannery industry, and high concentrations of NPEOs, NP, and NPECs were repeatedly [6,7] observed in secondary effluents (NPEO up to 49 µg/L, NP up to 144 µg/L, NPEC up to 115 µg/L).

The highest concentrations of NP found in seawater are about five times lower than the lowest concentration of NP (20 µg/L) required to induce a significant elevation of the plasma vitellogenin concentration in mature male fish (experiments were done with rainbow trout) in a three-week exposure [32]. However, it is possible that estrogenic effects can be induced with lower concentrations and long-term exposures. Measurable levels of OP (0.3 µg/L) were found only at one site (T3), near the outflow of a chemical plant in Tarragona Harbor. The NP_1EC was analyzed in all water samples, and concentration values were always less than the LOD. However,

Table 3. Concentrations of linear alkylbenzene sulfoantes (LAS), alcohol ethoxylates (AEO), coconut diethanol amides (CDEA), noylphenol ethoxylates (NPEO), and nonylphenol (NP) in seawater (µg/L)

Sample	Number of samples	LAS_{total}	AEO_{total}	$CDEA_{total}$	NPEO	NP
B1	4	5.4–92 (51)[a]	<0.1–3.9 (1.9)	0.3–4.2 (2.0)	0.8–4.8 (2.0)	<0.15–4.1 (2.0)
B2	4	2.5–84 (49)	<0.1–0.8 (0.2)	<0.05–1.7 (0.6)	<0.2–3.9 (1.0)	<0.15–3.8 (1.3)
B3	4	3.8–67 (40)	<0.1–1.4 (0.7)	<0.5–1.5 (0.5)	0.8–1.8 (0.9)	<0.15–1.1 (0.7)
B3-N	1	3.4	<0.1	<0.05	<0.2	0.5
B3-S	1	4.1	<0.1	<0.05	<0.2	0.3
B3-E	1	2.8	<0.1	<0.05	<0.2	0.3
B3-W	1	3.0	<0.1	<0.05	<0.2	0.5
T3	7	4.2–64 (22)	<0.1–11 (4.8)	<0.05–19 (11)	1.4–11 (6.3)	<0.15
T4	7	2.4–70 (25)	<0.1–15 (5.3)	<0.05–24 (12)	<0.2–8.7 (3.6)	<0.15
A1	1	19	<0.1	<0.05	0.4	<0.15
A1-N	1	4.3	<0.1	<0.05	<0.2	<0.15
A1-S	1	4.9	<0.1	<0.05	<0.2	<0.15
A1-E	1	5.1	<0.1	<0.05	<0.2	<0.15
A1-W	1	4.1	<0.1	<0.05	<0.2	<0.15

[a] Average.

Table 4. Concentration of linear alkylbenzene sulfonates (LAS), alcohol ethoxylates (AEO), coconut diethanol amides (CDEA), nonylphenol ethoxylates (NPEO), and nonylphenol (NP) in marine sediment

Sample	Date of sampling	LAS_{total} (mg/kg)	AEO_{total} (μg/kg)	$CDEA_{total}$ (μg/kg)	NPEO (μg/kg)	NP (μg/kg)
B3	March 1999	105	530	390	270	190
	March 2000	60	450	310	330	450
B3-N	March 1999	100	360	790	320	210
	March 2000	78	1,000	90	280	130
B3-S	March 1999	167	230	830	94	<10
	March 2000	67	670	750	130	150
B3-E	March 1999	8.3	480	570	165	<10
	March 2000	17	95	150	200	80
B3-W	March 1999	17	450	150	120	90
	March 2000	18	140	320	290	190
T1	March 1999	0.10	265	65	140	<10
	March 2000	0.49	400	150	160	
T2	March 1999	9.7	180	50	90	<10
	March 2000	5.6	140	34	130	
T3	March 1999	3.2	150	66	190	<10
	March 2000	4.0	300	70	200	15
T4	March 1999	0.21	150	30	50	<10
	March 2000	1.9	190	50	90	
A1	June 1999	65	890	400	100	590
	December 1999	42	510	275	530	450
A2	June 1999	7.2	1,300	720	620	480
A3	December 1999	28	530	280	45	<10
A4	June 1999	0.5	1,000	650	52	<10
	December 1999	27	530	630	45	
AM	June 1999	1.6	360	750	44	270
	December 1999	70	380	250	29	60
AD	June 1999	0.47	440	820	60	<10
	December 1999	8.1	460	85	40	
C	February 2000	1.23	63	230	89	23
SF	February 2000	238	810	2,710	410	1,050
SP	February 2000	1.12	280	380	240	27
SG	February 2000	2.02	37	120	10	40
D	February 2000	2.85	250	310	170	22
E1	February 2000	1.17	240	440	28	32
E2	February 2000	2.63	44	220	36	31
BN1	February 2000	0.90	160	120	60	20
BN2	February 2000	1.41	74	140	48	18
M1	February 2000	3.72	70	190	95	23
M2	February 2000	0.76	99	110	35	23

polyethoxylated oligomers (NPEC, $n_{EO} > 1$) and carboxylated alkylphenoxy carboxylates were not covered in this study.

In sediment samples (Table 4) collected along the Mediterranean coast and at three points on the Atlantic coast, the concentrations of NPEOs and NP ranged from 35 to 620 μg/kg for NPEOs and from undetectable (LOD = 5 μg/kg) to 1,000 μg/kg for NP. Several samples were found to be heavily contaminated with NP. The highest values were found in sediments collected in the Bay of San Fernando (SF), in Almería (A1 and A2), and in Barcelona (B3). All these points are situated in close proximity to the outflows of untreated or partially treated wastewaters. Certain differences obtained from repeated analyses on the same sampling point cannot be explained in terms of fast degradation but probably indicate that the analytes are not distributed homogeneously within the sediment.

Octylphenol was found only in three samples, in sediment from the Bay of San Fernando (145 μg/kg), in Tarragona Harbor (21 μg/kg), and in sediment collected near the outflow of wastewaters in the Harbor of Barcelona (17 μg/L), indicating that octylphenol polyethoxylates were probably being used for industrial applications in these areas. However, the presence of NP and OP cannot only be attributed to the metabolism of APEOs, but also their occurrence, resulting from application in other fields, has to be taken into account. For example, NP is also used as an ingredient in pesticide formulations and 4-*t*-OP is a chemical used in various industrial applications.

Several extensive studies reported similar levels of NPEOs and NP in sea or estuary waters and sediments. Blackburn [18] reported concentrations from <0.2 to 5.8 μg/L of NP and from <0.6 to 76 μg/L of $NP_1EO + NP_2EO$ in estuaries and offshore areas of England and Wales. The concentrations of NP in sediments in northeast England ranged from 30 to 80 μg/kg in the industrialized and urbanized Tyne estuary to 1,600 to 9,050 μg/kg in the highly industrialized Tees estuary. The concentrations of NPEOs were from 125 to 3,970 μg/kg. Marcomini et al. [23] found 500 to 6,700 μg/kg of NP, NP_1EO, and NP_2EO in surface sediment from a Venice lagoon, whereas the average concentration of NP_1EO and NP_2EO in water samples ranged from 1.1 to 38.5 μg/L [16].

Alcohol ethoxylates are widely accepted as environmentally safe surfactants, and today they are often used as an alternative to APEOs. Their concentrations in Spanish coastal waters ranged from undetectable to 15 μg/L. The highest concentrations were found in samples collected near the outflows of industrial plants in Tarragona and from the mouths of the Besos and Llobregat rivers in Barcelona, which may indicate that the main source of these compounds is industry situated

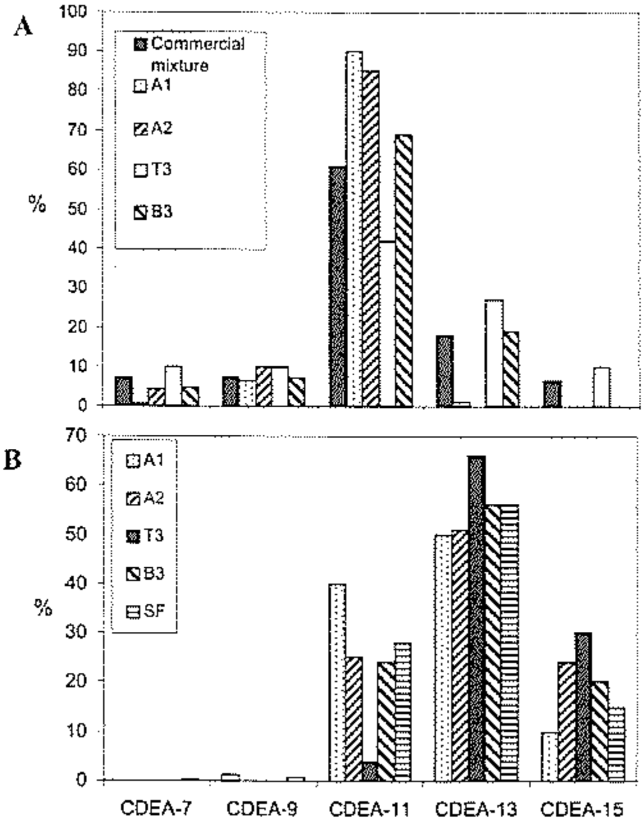

Fig. 3. Distribution of coconut diethanol amide (CDEA) homologues in water and sediment samples: (A) seawater; (B) sediment.

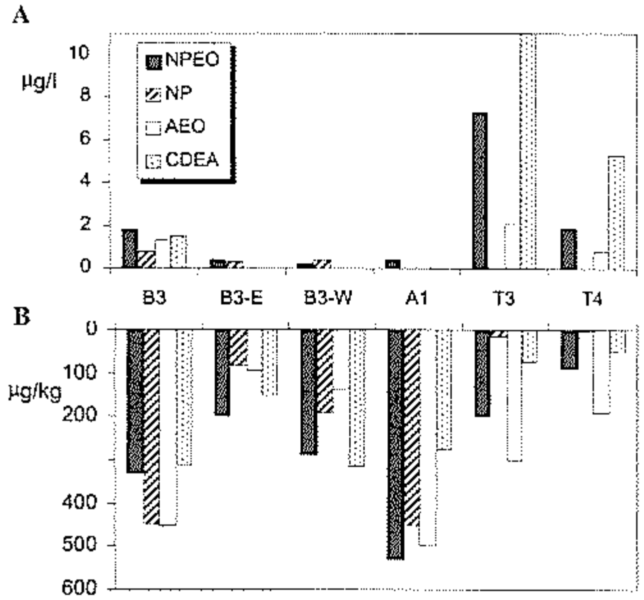

Fig. 4. Distributions of nonylphenol ethoxylates (NPEO), nonylphenol (NP), alcohol ethoxylates (AEO), and coconut diethanol amides (CDEA) between aqueous and solid phase: (A) seawater; (B) sediment.

upstream. In sediments, AEOs were detected in all analyzed samples in concentrations from 37 to 1,300 µg/kg. In view of the distribution of individual AEO homologues, two distribution profiles are distinguished. In samples from Barcelona and Tarragona harbors and in samples C, SF, SG, and M, homologues C_{12} and C_{13} were found to be the most abundant, while in other samples, homologues with an even number of carbon atoms in an alkyl chain (C_{10}, C_{12}, and C_{14}) were predominant.

Nonionic surfactants containing an amide group represent a relatively small part of the total volume of nonionic surfactants, but their production and application are growing because of good chemical stability combined with fast biodegradation and somewhat simple manufacturing processes mainly based on renewable raw materials [33]. Coconut diethanolamides are mainly used in households in textile-washing and hand-dish-washing formulations. In three WWTPs from Catalonia, the concentrations of CDEAs in influents varied from 270 to 475 µg/L, while in effluents, concentrations rarely exceeded 10 µg/L, indicating elimination rates higher than 97% [7]. The concentrations found in coastal water samples were generally lower than 0.05 µg/L, with the exception of a few values ranging from 0.3 to 24 µg/L found in samples from Tarragona and Barcelona. However, they were found in all sediments tested in concentrations ranging from 30 to 2,700 µg/kg (average value, 410 µg/kg). The distributions of different homologues in water and sediment are shown in Figure 3. The results show significant differences between distributions of CDEA homologues in water and sediment as compared with the original distribution in detergent formulations, yielding a higher average molecular weight in sediment samples. In sediments, the shift in the alkyl chain length toward increased hydrophobicity was observed. In commercial mixtures, the most abundant homologue is C_{11}, while in sediment samples, the profiles differed, and the most abundant homologue groups were C_{13} and C_{15}. However, there is little information on toxicology and ecotoxicology of these compounds and there is not sufficient data to conclude whether this change in average molecular weight influences their biodegradability and toxicity.

Distributions of the nonionic surfactants among water and sediment are shown in Figure 4. The ratios of concentration in sediment and concentration in water ranged from 30 to 1,450 for NPEO, 475 to 2,250 for NP, 150 to 5,000 for AEOs, and 10 to 3,150 for CDEAs. For all compounds, the lowest values, resulting mainly from high water concentrations, were measured in samples from Tarragona Bay, which indicates the dominant influence of industrial effluents on this area. In order to test a potential relationship between the total organic carbon content in sediment and the corresponding concentrations of target compounds, pairwise correlation coefficients were calculated. However, poor correlation was obtained, probably due to the specificity of the samples studied. Organic matter in the sediments provides matrices for sorbing hydrophobic compounds and releasing them slowly and incompletely, but the proximity of wastewater outflows appears to be a more important determinant than the organic content of the sediment. This is in accordance with findings of Bennet and Metcalfe [14] and Khim et al. [20]. Similarly, Cano and Dorn [34] and Brownawell et al. [35] found that the sorption of alcohol ethoxylate surfactant is better correlated with the clay content of the sediment than to the organic carbon content.

Concentration of linear alkylbenzene sulfonates

Linear alkylbenzene sulfonates (LAS) are found in relatively high concentrations in all samples analyzed. The highest reported values in water samples were obtained from the mouth of the Besos and Llobregat rivers in Barcelona (up to 92 µg/

L) and in samples from the industrial area in Tarragona (up to 70 μg/L). These values are comparable with levels cited in the literature for densely populated zones, which discharge urban wastewaters directly into the sea. Considerably higher concentrations were found in sediments. Linear alkylbenzene sulfonate sorption on marine sediment was found to be an irreversible process [36], and the degradation rate under anoxic conditions was found to be extremely low. In sediment samples, LAS concentrations ranged from values of several 10s of μg/kg to more than 200 mg/kg. The highest concentrations were found in sediments collected at sampling points in Barcelona (B3) and in San Fernando (SF), in proximity to the outflow of untreated urban wastewaters. Linear alkylbenzene sulfonates are the major surfactant class used in detergents throughout the world because of their effectiveness and environmental safety. Laboratory and field studies indicate that LASs are biodegraded at high rates under aerobic conditions during wastewater treatment. A significant proportion of the LAS is removed by adsorption onto sewage solids during primary settlement, and sewage sludge, as a final product, contains high concentrations of LAS, usually on the order of 2 to 10 g/kg. High values found in coastal waters and sediments are indicative of the contamination produced by discharges of untreated urban wastewaters and by direct disposal of sewage sludge into the sea.

The relative concentrations of the lower homologues C_{10} LAS and C_{11} LAS in water samples were found to be higher than in a typical laundry detergent, mainly due to partial removal or/and enrichment of these species during transportation of the wastewater in the sewage system because of the higher degradation rate and adsorption tendency of the longer alkyl chain homologues. The average chain length of LAS in water ranged from 10.6 to 11.6, whereas in sediment, it ranged from 12.0 to 12.8. The longer alkyl chain homologues are preferentially sorbed to particulate matter because of the higher lipophilicity of these compounds, and consequently, an increase in relative concentration of C_{12} and C_{13} homologues in sediment samples is observed. Appreciable quantities of the C_{14} homologue have also been found despite its proportion in commercial LAS being very low (0.2%) and despite its greater biodegradability. A relationship between the molecular weight (alkyl chain) of LAS and toxicity to an aquatic organism (*Daphnia*) has been studied by Prats et al. [37]. They reported that the change in homologue distribution of LAS implies an increase in the toxicity to *Daphnia* because higher average molecular weights of LAS are more toxic. However, exposure of benthic invertebrates from marine and freshwater environments in systems in which the LAS were sorbed on sediment did not result in alterations in the treated organisms (over 96 h) in spite of LAS concentrations, which were 3 to 10 times higher than 50% lethal concentrations for LAS in water [38].

Seasonal variations

The monitoring surveys at stations T3 and T4 (Tarragona Harbor) were undertaken from July 1999 to July 2000. During this period, all target compounds showed a marked seasonal fluctuation. The seasonal dependence is clearly illustrated in Figure 5. Concentrations were significantly lower in warmer periods (from May to September) than during months with lower temperatures. This can be attributed either to lower inputs of wastewater or, which is more probable, to the more efficient biodegradation of studied compounds in seawater during warmer months. Marcomini et al. [16] reported remarkable seasonal differences in concentrations of LAS and NPEOs in the Venice lagoon, primarily due to the increased biodegradation at temperatures greater than 20°C (late spring and summer). Ahel and coworkers [15] observed similar seasonal fluctuation of NP, NP_1EO, and NP_2EO in the Glatt River (Switzerland).

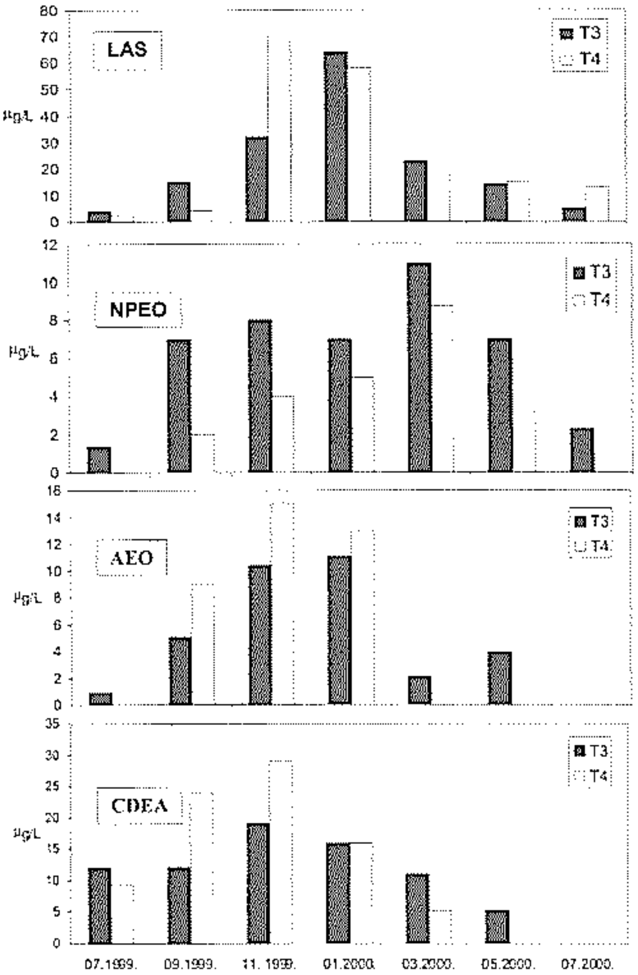

Fig. 5. Seasonal variation of concentrations of nonylphenol ethoxylates (NPEO), alcohol ethoxylates (AEO), coconut diethanol amides (CDEA), and linear alkylbenzene sulfonates (LAS) in seawater from Tarragona.

CONCLUSIONS

Although the sites chosen are hot spots with point sources of municipal and industrial discharges, it can be concluded that nonionic surfactants and their degradation products are wide-spread contaminants in the marine environment. The high concentrations of these compounds have been shown to accumulate in sediments, which appear to act as a sink for nonionic surfactants and LAS in studied areas. Overall, the data obtained in this study show that nonylphenol polyethoxylate surfactants and their persistent metabolites exist in concentrations up to 620 μg/kg of NPEOs and more than 1,000 μg/kg of NP in sediments collected near discharges of domestic or industrial wastewaters in Spanish harbor areas.

The levels of AEOs and CDEAs are reported for the first time. It was found that these compounds accumulate in surface sediment, and the concentrations found in coastal areas studied were up to 1,300 μg/kg (AEO) and 2,700 μg/kg (CDEA).

Levels found in seawater are generally lower than the no-observed-effect concentration for the induction of vitellogenesis in caged fish (10 μg/L). However, this threshold concentration is determined in the short-term studies, and it is suggested that long-term exposure may exert an effect on reproductive health of fish populations [32].

This survey demonstrates that there is a concern that discharge of the wastewater effluents with high concentrations of APEOs and their degradation products (especially NP) into marine environments can cause contamination that can induce estrogen-like activity and exert cumulative action with other endocrine-disrupting compounds. Therefore, these substances should be monitored and further studies conducted in order to determine the effects on the life cycle of fish and other marine organisms.

Acknowledgement—This work has been supported by the European Union Environment and Climate Program through the Waste Water Cluster project SANDRINE (ENV4-CT98-0801) and by CICYT (AMB98-0913-CO3). We thank Merck for supplying the SPE cartridges and LC column. M. Petrovic acknowledges the grant from the Spanish Ministry of Education and Culture (SB97-B09092411).

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