

# Simultaneous extraction and fate of linear alkylbenzene sulfonates, coconut diethanol amides, nonylphenol ethoxylates and their degradation products in wastewater treatment plants, receiving coastal waters and sediments in the Catalonian area (NE Spain)<sup>☆</sup>

Susana González, Mira Petrovic\*, Damiá Barceló

*Department of Environmental Chemistry, IIQAB-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain*

Received 8 March 2004; received in revised form 24 July 2004; accepted 16 August 2004

## Abstract

The efficiency of six wastewater treatment plants (WWTPs) in the Catalonian region to remove several classes of ionic and non-ionic surfactants was investigated, using solid-phase extraction (SPE) followed by liquid chromatography–mass spectrometry (LC–MS). Occurrence and distribution of linear alkylbenzene sulfonates (LASs), coconut diethanol amides (CDEAs), nonylphenol ethoxylates (NPEOs) and their degradation products were studied in coastal areas receiving WWTP effluents. For the analysis of sediment samples pressurized liquid extraction (PLE) followed by SPE extract clean-up and LC–MS detection was used for simultaneous extraction of all target compounds. Concentrations of parent long ethoxy chain NPEOs in raw water entering WWTPs ranged from 60 to 190  $\mu\text{g/L}$ . In effluents concentrations ranged from 2.8 to 6.6  $\mu\text{g/L}$ , which corresponded to an average primary elimination of 93–96%. Nonylphenol (NP) was found in concentrations from 0.2 to 18  $\mu\text{g/L}$  in WWTP influents and up to 5  $\mu\text{g/L}$  in the treated water, showing a clear declining trend with respect to concentrations reported in the last 5 years. The elimination of LASs and CDEAs varied depending on the WWTP and was higher than 85% in well operated WWTPs with secondary treatment and only 56% (for CDEAs) and 30% (for LAS) in WWTPs with primary treatment. Levels up to 86 mg/kg of LAS, 1.7 mg/kg of NP, 400–760  $\mu\text{g/L}$  for NPEOs and NPECs were detected in sediments at sampling points near the discharge of WWTP effluents, clearly showing that in coastal area receiving WWTP effluents surfactants and their degradation products are widespread contaminants. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Wastewater treatment plants; Degradation products; Coastal waters and sediments

## 1. Introduction

Surfactants have one of the highest production rates of all organic chemicals. They have been used for a long time as detergents, emulsifiers, antifoamers, pesticide adjuvants, wetting agents and dispersing agents for domestic and industrial use [1]. They are used as household detergents,

in personal care products such as cosmetics and pharmaceuticals and in different industrial formulations used in textile and fibres processing; mining, flotation and petroleum production; paint, plastics and lacquers production; food industry; pulp and paper industry; leather and fur industry and agriculture.

Their widespread use, primarily in aqueous solutions, leads to later introduction into the environment via wastewater discharges. After use, consumer detergents are usually discharged down the drain into municipal sewer systems and afterward treated in wastewater treatment plants (WWTPs), where they are completely or partially removed by a combination of sorption and biodegradation. After wastewater

<sup>☆</sup> Presented at the 3rd Meeting of the Spanish Association of Chromatography and Related Techniques and the European Workshop: 3rd Waste Water Cluster, Aguadulce (Almeria), 19–21 November 2003.

\* Corresponding author. Tel.: +34 93 400 6172; fax: +34 93 204 59 04.  
E-mail address: [mpeqam@cid.csic.es](mailto:mpeqam@cid.csic.es) (M. Petrovic).

treatment, non-degraded surfactants together with their biodegradation products (metabolites) are discharged by WWTP effluents into surface waters.

In the Catalonian region (NE Spain), several extensive studies have been conducted with objective to determine the concentrations of surfactants and their degradation products in raw and treated wastewaters and in the receiving aquatic environment. However, non-ionic surfactants nonylphenol ethoxylates (NPEOs) received most attention as precursors of weakly estrogenic metabolic products generated during wastewater treatment. Removal of NPEOs during wastewater treatment in WWTPs receiving mixed urban and industrial wastewaters (mainly from tanneries and textile industry) was studied, as well as their impact in the aquatic environment receiving WWTP effluents [2–4]. Concentrations of NPEOs and of their degradation products, nonylphenol (NP) and nonylphenol carboxylates (NPECs), in WWTP effluents often exceeded 200 µg/L, which corresponded to an overall elimination of less than 50%. In two rivers (Anoia and Cardener) receiving WWTP effluents, the occurrence of NP has been related to biological effects, measured as alterations of plasma vitellogenin concentration in natural fish populations [5,6]. Another study [7] demonstrated that there is a concern that discharge of the wastewater effluents into coastal area can cause contamination of the marine environment and induce estrogen-like activity due to presence of high concentrations of nonylphenolic compounds.

Because of formation of undesirable recalcitrant metabolites that gave rise to environmental concern APEOs are banned or restricted in Europe [8]. Restriction of the use of APEOs in household detergents and voluntary replacement in industrial formulations resulted in a substantial drop of APEOs concentrations throughout northern Europe. However, in Spain, mainly because of lower production costs, APEOs are still being used in substantial amounts in institutional and industrial applications and it is important to continue to monitor their occurrence and distribution in the environment in order to determine the concentration trends, and therefore, predict their long-term fate.

Other surfactants received less attention. Several studies dealt with the fate of linear alkylbenzene sulfonates (LASs), alcohol ethoxylates (AEs) and coconut diethanol amides (CDEAs) and reported levels in WWTP effluents [4,7,9] and in coastal waters [7] in Catalonia, however this kind of contamination still need to be evaluated.

Thus, the objectives of the work presented here were: (i) method development for the simultaneous determination of LASs, CDEAs, NPEOs and their degradation products in water and solid samples (ii) to study the efficiency of different WWTPs in the Catalonian region to remove several classes of ionic and non-ionic surfactants and (iii) to study their occurrence and distribution in coastal waters receiving WWTP effluents. One of the specific objectives was to determine whether the general European trend of declining APEOs concentrations is also observable in Spanish aquatic environment. Another specific objective was to adapt previously

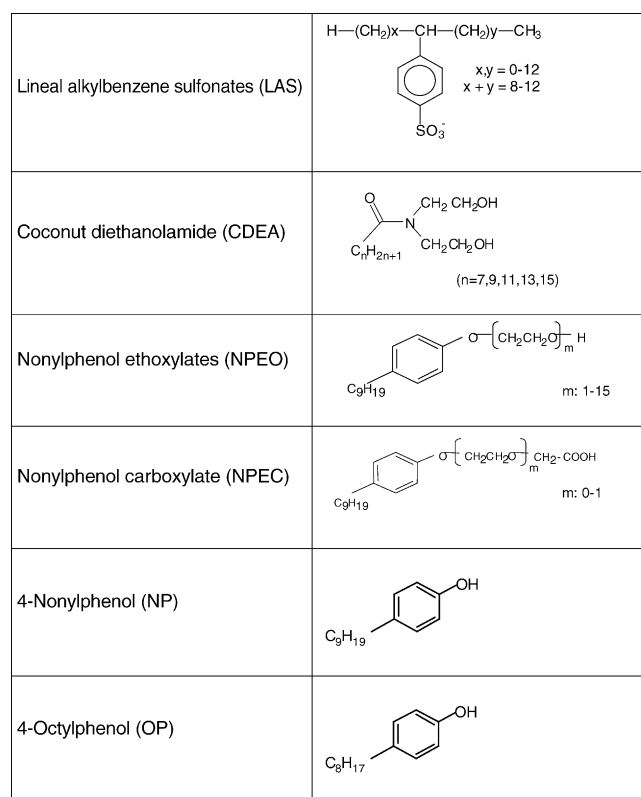


Fig. 1. Structures of studied compounds.

developed LC–electrospray ionization (ESI) MS methodology and to apply it as a generic protocol for the analysis of surfactants in wastewaters, surface waters and sediments.

The target compounds studied in this work included three classes of surfactants; LASs, anionic surfactants used in household detergents, NPEOs and their degradation products (NP and NPECs) and coconut diethanol amides (CDEAs) another class of non-ionic surfactants which are used in certain household textile washing and hand dish-washing formulations. The structures of target compounds are shown in Fig. 1.

## 2. Experimental

### 2.1. Materials and standards

All solvents (water, acetonitrile and methanol) were HPLC grade and were purchased from Merck (Darmstadt, Germany).

The standards used in this study were of the highest purity available. High-purity (98%) 4-*tert.*-OP and 4-NP were obtained from Aldrich (Milwaukee, WI, USA). NP<sub>1</sub>EO, NP<sub>2</sub>EO and NP<sub>1</sub>EC were synthesized according to the method described elsewhere [10]. Additionally, technical mixture of NPEOs containing chain isomers and oligomers with an average of 10 ethoxy units (Findet 9Q/22) was from Kao Corporation (Barcelona, Spain).

Commercial LASs with a low dialkyltetralinsulfonate content (<0.5%) were supplied by Petroquímica Española in a single standard mixture with the proportional composition of the four homologues of: C<sub>10</sub>: 3.9%, C<sub>11</sub>: 37.4%, C<sub>12</sub>: 35.4%, C<sub>13</sub>: 23.1%.

The mixture of CDEAs was kindly supplied by H.Fr. Schröder. The proportional composition of the five homologues is: C<sub>7</sub>: 7%, C<sub>9</sub>: 7.5%, C<sub>11</sub>: 60.9%, C<sub>13</sub>: 18%, C<sub>15</sub>: 6.6%.

High-purity (98%) 4-heptylphenol (which was used as the internal standard) was obtained from Panreac (Barcelona, Spain).

Stock solutions (1 mg/mL) of individual standards and standard mixtures were prepared by dissolving accurate amounts of pure standards in methanol. Working standard solutions were obtained by further dilution of stock solutions with methanol.

## 2.2. Study area

Six WWTPs from the Catalonian area were included in this study ranging from small WWTPs treating around 1000 m<sup>3</sup>/day to very big WWTPs with the capacity to treat more than 500 000 m<sup>3</sup>/day. Among them WWTP Besòs that has only physico-chemical treatment, while the other five WWTPs have secondary biological treatment. However, during the period of this study (July 2002–July 2003) WWTP Depurbaix, which was recently inaugurated as the biggest biological WWTP in Spain (2 000 000 inhabitant equivalents and capacity for 420 000 m<sup>3</sup>/day) was under probe regime and not fully functioning so only influent samples were collected and analyzed. The type of wastewater treated in the selected WWTPs varies from urban wastes to mixed urban/industrial influents (mainly from tanneries and textile industry). Main characteristics of the studied WWTPs are summarized in Table 1.

To study the impact of WWTP effluents to receiving waters, sea water near the points discharge of effluents from WWTP Depurbaix (sampling points B2, B3 and B4 along the tube for disperse discharge of treated water; distance from the coast 3–5 km, depth 50 m) and sludges and effluents from WWTP Besòs (sampling point B5; distance from the coast 5 km, depth 50 m) was collected.

Additionally, the studied area included several “hot spots” on Catalonian Spanish coast, such as the mouths of the rivers Llobregat (B1) and Besòs (B6) (province of Barcelona; Spain) and the harbor of Tarragona (sites T1–T4), where samples were collected near outflows of several industrial plants (Fig. 2).

## 2.3. Sample collection

Influent and effluent samples of WWTP1, WWTP2 were taken bimonthly from July 2002 to July 2003 (total of six sampling at each WWTP). Influent and effluents of WWTPs 3–6 were collected twice, in October and December 2003

Table 1  
Characteristics of WWTP studied

WWTP characteristics	Depurbaix (WWTP1)	Besòs (WWTP2)	Piera (WWTP3)	Igualada (WWTP4)	Tarragona (WWTP5)	Reus (WWTP6)
Type of treatment	Primary and secondary*	Primary	Primary and secondary	Primary and secondary	Primary and secondary	Primary and secondary
Type of influent	Urban	Urban	Urban	Mixed urban/industrial (tanneries, textile industry)	Mixed (mostly urban)	Mixed (mostly urban)
Inflow (m <sup>3</sup> /day)	420000	500000	1100	20000	30000	16000
Inhabitants equivalents	2000000	2800000	14000	223000	140000	125000
BOD <sub>5</sub> Influent (mg/L)			146	875	400	400

\* During the period of this study only primary treatment.

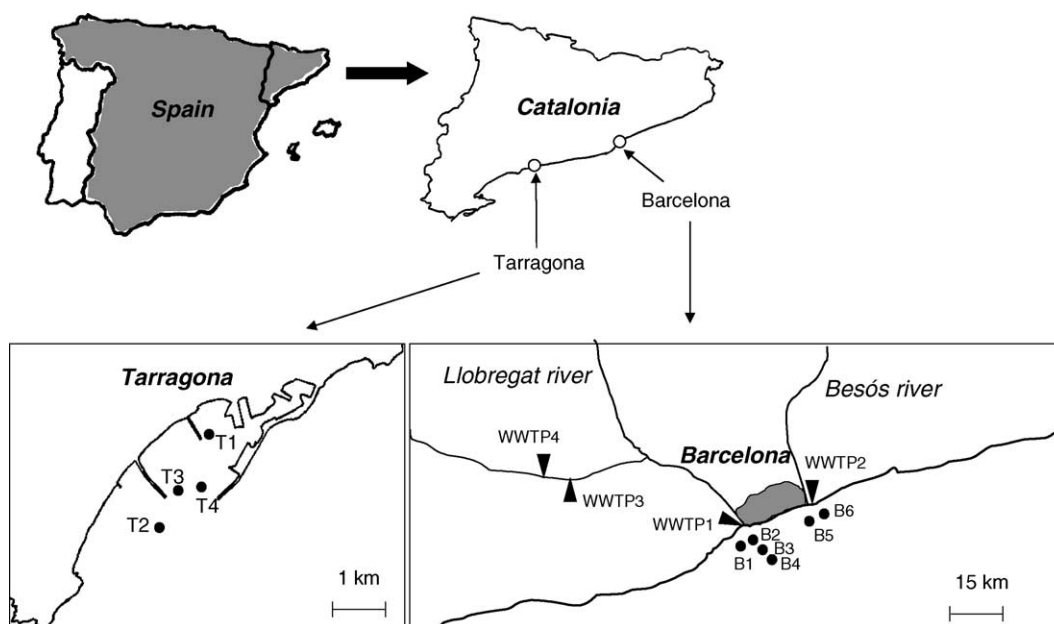


Fig. 2. Map of the studied areas showing the locations of the sampling sites.

for WWTP 5–6 and in February and May 2003 for WWTPs 3–4. Sediments and water samples (sampling points B1–B6) were sampled twice, in July 2002 and July 2003. At sampling points T1–T4, sediment sample was taken once, in October 2002.

WWTP samples were collected in precleaned glass bottles as 24-h composite samples. All samples were stored at 4 °C immediately after sampling.

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.

Sediment samples were collected using a Van Veen grab; placed in stainless steel containers and transferred to the laboratory at 4 °C where they were frozen at –20 °C and freeze-dried. Lyophilized samples were ground and homogenized with a mortar and pestle, sieved through a 125 µm sieve and kept at –20 °C until analysis in glass containers.

#### 2.4. Water sample extraction: solid-phase extraction

All aqueous samples were filtered through 0.45 µm membrane filter and preconcentrated on Isolute C<sub>18</sub> SPE cartridges (IST, UK) within 48 h, in order to avoid any degradation of target compounds and loss of sample integrity. Different volumes were taken depending on the type of the sample: 500 mL for surface waters, 200 mL of effluent of the WWTP and 100 mL of the influent. The complete SPE procedure is described elsewhere [11]. After preconcentration SPE cartridges were wrapped in aluminum foil and kept at –20 °C until analysis (maximum 1 month). Cartridges were eluted with 2 × 4 mL of methanol. The eluents were evaporated to

dryness with a gentle stream of nitrogen and reconstituted with methanol to a final volume of 1 mL.

#### 2.5. Sediments: pressurized liquid extraction

Target compounds were extracted from sediment samples using a Dionex ASE 200 (Dionex, Idstein, Germany). A detailed description of the method is described elsewhere [12]. Briefly, 5 g of sediment were placed in the 11 mL stainless steel extraction cell; the empty space was filled with Hydromatrix (an inert material) and extracted with acetone–methanol (1:1, v/v). Two cycles of extraction in static mode (flush 60%, purge 60 s) of 5 min, with 5-min of heat, were carried out. The extracts were concentrated to an approximate volume of 1 mL using a rotary vacuum evaporator at 30 °C and redissolved in 100 mL of HPLC water. Subsequent clean-up of extracts was performed by SPE as described above for water samples.

#### 2.6. Liquid chromatography–mass spectrometry

The HPLC system consisted of an HP 1100 autosampler with a 100-µL loop and HP 1090 A LC binary pump, both from Hewlett-Packard (Palo Alto, CA, USA). HPLC separation was achieved on a 5-µm, 125 mm × 2 mm i.d., C<sub>18</sub> reversed-phase column (Purospher STAR RP-18), preceded by a guard column (4 µm × 4, 5 µm) of the same packing material from Merck. The injection volume was set at 15 µL and the flow-rate was 0.5 mL/min.

The separation was performed under gradient elution conditions, using methanol (A) and water (B). LASs, NPECs, NP and OP were detected under negative ionization (NI) conditions, while CDEAs and NP<sub>(1,2)</sub>EOs were analyzed under

positive ionisation (PI) conditions. In both modes the compounds are separated using the following solvent programming: initial conditions were 30% A, in 10 min it is linearly increased to 80%, then increased linearly in 5 min to 90% and finally increased again to 95% in 5 min more.

Detection was carried out, using an HP 1040M diode-array UV–vis detector coupled in series with an LC-MSD HP 1100 mass-selective detector, equipped with an atmospheric-pressure ionization source and ESI interface. The operating parameters of ESI–MS were as follows (NI/PI): drying gas flow: 12/11 L/min, drying gas temperature: 375/325 °C, nebulizer pressure: 55/50 psi (1 psi = 6894.76 Pa); capillary voltage: 4500/4000 V; fragmentation voltage: 90/60 V. The ions monitored in a selected ion monitoring (SIM) mode are shown in Table 2.

### 2.7. Quantitation and method validation

Quantitative analysis was performed in SIM mode, using external calibration (internal standard 4-heptylphenol was used to check the extent of ion suppression on MS detection). A series of injections of target compounds in the concentration range from 50 ng/mL to 50 µg/mL was used to determine the linear concentration range. Calibration curves were generated using linear regression analysis and over the established concentration range (0.05–10 µg/mL) gave good fits ( $r^2 > 0.990$ ). Five-point calibration was performed daily and the possible fluctuation in signal intensity was checked by injecting a standard solution at two concentration levels after each 6–8 injections. The confirmation of compound identity in environmental samples was done in a full scan mode.

The recoveries (percent of standard added to sample recovered during extraction and clean-up) and reproducibil-

ity (relative standard deviation for triplicate analysis) of the extraction–preconcentration–detection procedure for aqueous and solid samples were determined by the analysis of spiked samples. Sediment samples, spiked with 200 µg/kg of standard mixture of target analytes were analyzed by applying the method described above, together with a blank sample (no spiked sample). Water was spiked with a standard mixture of analytes to a final concentration of 100 µg/L.

The limits of detection (LODs) of target compounds in sediment and in seawater were calculated by a signal-to-noise ratio of 3 (the ratio between intensity of signal of each compound obtained under SIM conditions and intensity of noise in a spiked sample).

LODs, recoveries and the precision of the method, expressed by the relative standard deviation for triplicate analysis, are shown in Table 2.

## 3. Results and discussion

### 3.1. LC–MS analysis of surfactants in aqueous and sediment samples

Fig. 3 shows the extracted ion chromatograms for compounds detected under NI (Fig. 3a) and PI conditions (Fig. 3b), respectively. In order to quantify all target compounds, it was necessary to perform two injections for each sample. Four LAS homologues (C<sub>10</sub>–C<sub>13</sub>), NPECs and alkylphenols (NP and OP) were detected as deprotonated molecules in NI mode, while CDEA homologues (odd C<sub>7</sub> to C<sub>15</sub>) and NPEOs were detected as sodium adducts [M + Na]<sup>+</sup> in PI mode achieving a baseline separation of all target compounds.

Table 2  
Performances of LC–MS method: ions monitored, limits of detection (LODs), recoveries and relative standard deviations (R.S.D.s)

Compound	<i>m/z</i>	Water			Sediment		
		LOD (ng/L) <sup>a</sup>	Recovery (%)	RSD (%)	LOD (µg/kg) <sup>b</sup>	Recovery (%)	R.S.D. (%)
NPEO ( <i>n</i> <sub>EO</sub> = 3–15)	375 + Δ44 [M + Na] <sup>+</sup>	5	98	4	1	97	5.9
NP <sub>1</sub> EO	287 [M + Na] <sup>+</sup>	50	86	3.8	7	92	14
NP <sub>2</sub> EO	331 [M + Na] <sup>+</sup>	50	81	2.4	4	94	6.9
NP <sub>1</sub> EC	277 [M – H] <sup>–</sup>	100	83	1.6	4	74	5.4
NP	219 [M – H] <sup>–</sup>	50	88	7	2	89	11
OP	205 [M – H] <sup>–</sup>	50	85	4.7	5	77	6.7
CDEA							
C <sub>7</sub> DEA	254 [M + Na] <sup>+</sup>	30	87	2	2	95	2.8
C <sub>9</sub> DEA	282 [M + Na] <sup>+</sup>	10	91	4.4	1	84	2.4
C <sub>11</sub> DEA	310 [M + Na] <sup>+</sup>	10	89	8.2	1	102	6.0
C <sub>13</sub> DEA	338 [M + Na] <sup>+</sup>	10	72	9.2	1	104	11
C <sub>15</sub> DEA	366 [M + Na] <sup>+</sup>	10	53	4.1	1	61	10
LAS							
C <sub>10</sub> LAS	297 [M – H] <sup>–</sup>	50	90	3.1	3	72	10
C <sub>11</sub> LAS	311 [M – H] <sup>–</sup>	50	87	2.4	7	86	6.9
C <sub>12</sub> LAS	325 [M – H] <sup>–</sup>	50	84	3.1	6	65	9.0
C <sub>13</sub> LAS	339 [M – H] <sup>–</sup>	50	73	3.2	8	56	2.9

<sup>a</sup> SPE preconcentration factor 500.

<sup>b</sup> PLE–SPE preconcentration factor 5.

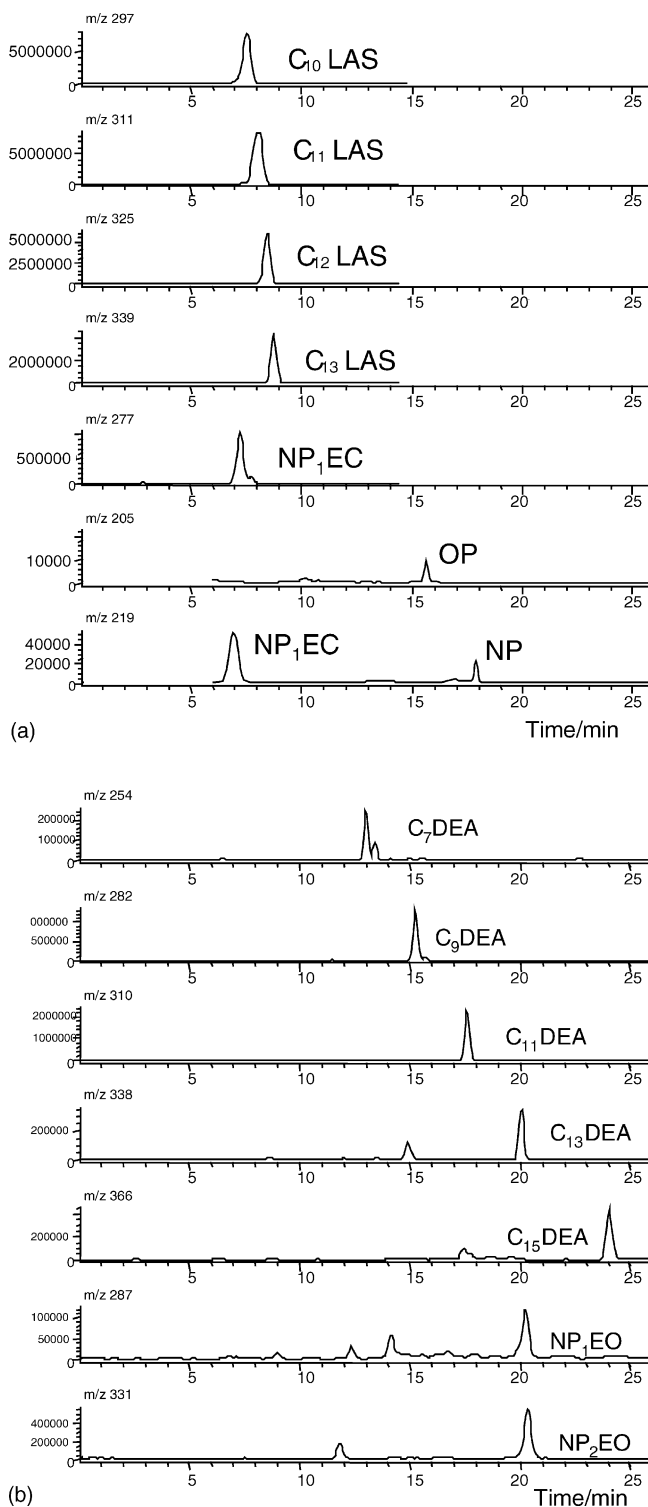


Fig. 3. Reconstructed ion chromatograms obtained by ESI–MS in NI mode (a) and PI mode (b) for effluent of WWTP Besòs (sampling July 2003).

The protocol used in this study (PLE followed by SPE extract clean-up and LC–MS detection) was previously developed and validated for the extraction of alkylphenolic compounds from river sediment [12]. In this work the method was adapted and used for simultaneous extraction of LASs

and CDEAs. Recoveries obtained ranged from 53 to 104% (Table 2). SPE of target analytes from water samples combined with LC–MS detection yielded recoveries from 56 to 98%. The relative standard deviation ( $n=3$ ) for water analysis was below 9% and for sediment below 14%.

This procedure yielded rather clean extracts that produced low background MS noise, as described in details elsewhere [12]. The extent of ion suppression was checked by adding an internal standard (4-heptylphenol) to all extracts and monitoring the ion  $m/z$  191 (NI mode) (retention time  $t_R = 14.8$  min). When the comparison of the signal intensity obtained in a standard solution (methanol) and in sample extracts showed ion suppression higher than 20% the extracts were diluted with methanol (typically 1:1 or 1:2, v/v) and re-analyzed. Generally, ion suppression was observed in some WWTP influent and sediment extracts, while less complicated matrices (sea water and WWTP effluent) showed negligible loss of sensitivity.

### 3.2. Occurrence and removal of surfactants in WWTPs

The concentrations of target compounds in WWTPs are showed in Table 3. Catalonia (NE Spain) is a heavily industrialized area and in many cases industrial effluents (i.e. from tannery, textile, pulp and paper industries that use surfactants in high amounts) are discharged into the municipal sewer systems and afterwards treated in municipal WWTPs together with urban wastewaters. This is reflected in the occurrence of NPEOs used in industrial formulations in influent samples. Concentrations of parent long ethoxy chain NPEOs ranged from 60 to 190  $\mu\text{g/L}$ . In effluents concentrations ranged from 2.8 to 6.6  $\mu\text{g/L}$ , which corresponded to an average primary elimination of 93–96%. However, the ultimate elimination was significantly lower due to formation of recalcitrant degradation products. Concentrations of estrogenic short chain NPEOs formed during wastewater treatment were up to 50  $\mu\text{g/L}$ , with exception of WWTP Depurbaix and WWTP Tarragona where higher values for NP<sub>1</sub>EO were found (124 and 156  $\mu\text{g/L}$ , respectively).

Acidic metabolites NPECs were found in influents of WWTP Depurbaix and WWTP Besòs in concentrations (mean value of 295  $\mu\text{g/L}$ ) that significantly exceed levels reported for other WWTPs. It should be mentioned that the presence of these compounds not only can be attributed to the degradation of alkylphenolic compounds but also to the use of in other applications (e.g. NPECs are used as corrosion inhibitor). Thus, more research will be needed to explain these values in WWTPs mainly receiving urban wastewaters.

NP was found in concentrations from 0.2 to 18  $\mu\text{g/L}$  in influents and up to 5  $\mu\text{g/L}$  in the treated water, with the highest values found in the two WWTPs operating in Barcelona (WWTP Depurbaix and Besòs).

Generally, levels of nonylphenolic compounds found in raw water are significantly lower than those measured several years ago, which suggest a gradual withdraw and replacement of NPEOs by Spanish tanneries and textile industry. As

Table 3  
Range of concentration of target compounds in WWTP influents and effluents ( $\mu\text{g/L}$ )

Compound	Depurbaix (WWP 1)	Besós (WWTP 2)		Piera (WWTP 3)		Igalada (WWTP 4)		Tarragona (WWTP 5)		Reus (WWTP 6)	
	Influent ( $n = 6$ )	Influent ( $n = 6$ )	Effluent ( $n = 6$ )	Effluent ( $n = 2$ )	Effluent ( $n = 2$ )	Influent ( $n = 2$ )	Effluent ( $n = 2$ )	Influent ( $n = 2$ )	Effluent ( $n = 2$ )	Influent ( $n = 2$ )	Effluent ( $n = 2$ )
NPEOs ( $n_{\text{EO}} = 3-15$ )	NA <sup>a</sup>	NA	NA	60 71	2.8 3.6	123 190	5.8 6.6	NA	NA	NA	NA
NP <sub>1</sub> EO	<lod-125 (26) <sup>b</sup>	4.4–54 (18)	<lod-10 (4.4)	0.54 7.4	0.73 3.4	<lod 2.5	1.4 1.4	<lod 50	<lod 156	<lod	<lod
NP <sub>2</sub> EO	2.2–33 (9.3)	2.8–16 (6.9)	0.12–4.1 (1.9)	1.4 5.1	0.32 1.3	<lod 5.3	1.6 1.8	<lod 16	1.8 4.7	0.71 2.7	0.80 4.4
NP <sub>1</sub> EC	182–450 (295)	108–478 (294)	129–307 (251)	<lod 0.42	0.65 16	<lod 0.16	1.2 1.3	7.5 56	20 26	143 256	8.4 15
NP	<lod–18 (4.5)	<lod–11 (2.6)	0.79–5.0 (2.4)	0.24 3.8	0.43 1.1	NA	0.31 0.83	<lod 3.7	<lod 0.4	<lod 1.4	<lod 0.22
OP	<lod–14 (3.4)	<lod–11 (2.8)	0.14–13 (3.6)	NA	NA	0.89 2.6	NA	<lod 1.4	<lod 0.80	<lod 0.91	<lod 0.90
CDEAs	86–260 (158)	78–203 (142)	0.32–100 (62)	NA	NA	NA	NA	4.9 3.0	<lod 1.9	28 23	<lod 1.3
LASs	307–1920 (910)	532–1635 (837)	126–872 (590)	NA	NA	NA	NA	525 595	17 73	104 205	11 33

<sup>a</sup> NA: not analyzed.

<sup>b</sup> Expressed as maximum–minimum (mean value).

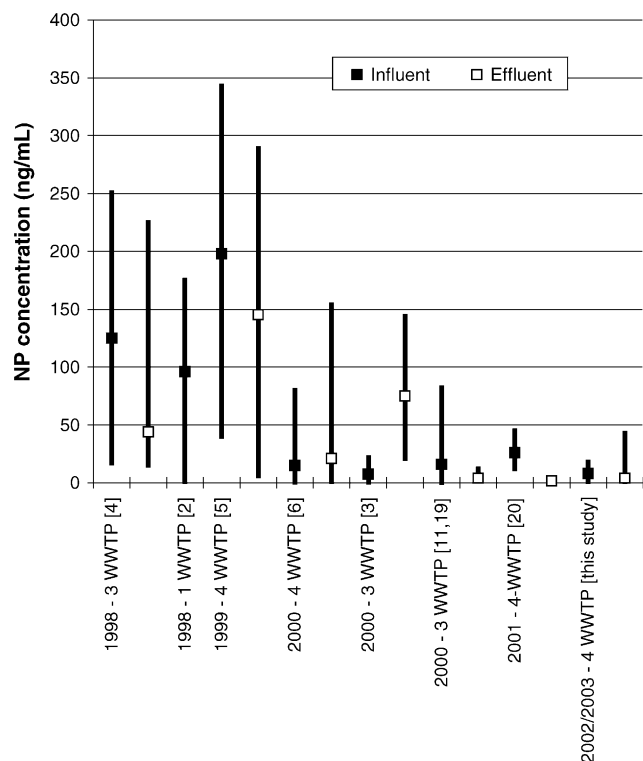


Fig. 4. Concentration of NP in influents and effluents of WWTP in Catalonia in the period from 1998 to present.

shown in Fig. 4, typical levels of NP measured in the Catalonian WWTPs in 1998 and 1999 ranged from 100 to 200  $\mu\text{g/L}$  in influents and from 50 to 150  $\mu\text{g/L}$  in effluents, while more recent data, including this study, show almost a 10-fold decrease. As mentioned above, throughout northern Europe and especially in the Scandinavian countries, UK, Germany and Switzerland the general trend of declining of NPEOs concentrations started almost 10 years ago. However, until now, in Spain such trend was not reported.

LASs were found in all samples in concentrations between 25 and 1920  $\mu\text{g/L}$ . The highest values were found in WWTP Depurbaix and Besòs that treat wastewater from areas with high density of population. The same happens with CDEAs, mainly used in households in detergents and personal care products, which were found at maximum concentrations of 260  $\mu\text{g/L}$ . The elimination of these compounds varied depending on the WWTP; in the WWTPs Reus and Tarragona the elimination of LASs and CDEAs was higher than 85% while in WWTP Besòs (applying only physico-chemical treatment) only 56% of CDEAs and 30% of LASs were removed and treated water, discharged into aquatic environment, contained substantial concentrations of these compounds (mean value of 62  $\mu\text{g/L}$  of CDEAs and 590  $\mu\text{g/L}$  of LASs in effluents). LAS are regarded as non-toxic compounds [13], however, increased concentrations discharged into aquatic environment may cause relevant environmental problem due to excessive foam generation. From the other hand, very little is known about the ecotoxicology of CDEAs

and it is difficult to conclude whether the concentrations found may induce long-term negative effects in the receiving aquatic environment.

### 3.3. Occurrence of surfactants in receiving waters and sediments

Concentrations found in sea waters and sediments are shown in Tables 4 and 5, respectively. In sea water collected near the points of discharge of WWTP effluents and sludges (B2–B5 and T1–T4) all target compounds were found in approximately 100-fold lower concentrations in comparison to the values found in the effluents of the WWTP, due to dilution and further in-situ their degradation. Concentrations of nonylphenolic compounds were generally below the limit of detection and only two surfactant classes mainly used in households, LASs and CDEAs, were found in measurable levels, ranging from 0.67 to 26  $\mu\text{g/L}$  for LASs and 0.13 to 2.8  $\mu\text{g/L}$  for CDEAs.

Similarly at sampling points B1 and B6 (mouths of the Llobregat river and the Besòs river) low concentrations of all target compounds were detected; typically less than 1  $\mu\text{g/L}$  of nonylphenolic compounds and CDEAs and less than 8  $\mu\text{g/L}$  of LASs. These two rivers (both in the province of Barcelona) receive, directly or via their tributaries, effluents from more than 40 WWTPs and the quality of water is strongly influenced by the hydrological regime of the river.

As expected surfactants were found to accumulate in sediment and several samples were found to be heavily contaminated. LASs were found in sediments at all sampling points in concentrations ranging from 160  $\mu\text{g/kg}$  to more than 86  $\text{mg/kg}$ . Generally, for all the compounds studied, the highest concentrations were found at site B5, the point of discharge of primary sludge and effluent from WWTP Besòs (86  $\text{mg/kg}$  of LASs). Second highest concentrations were found at sites B2, B3 and B4 (up to 9.4  $\text{mg/kg}$  of LASs), along the tube for dispersing of effluents from recently inaugurated WWTP Depurbaix, that during the period of this study worked under probe regime (only primary settlement). Lower concentrations were found at sites B1 and B6 where water from the mouths of the Llobregat and Besòs rivers, respectively, were collected. Certain differences obtained for repeated analysis 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.

CDEA were found at maximum values of 324  $\mu\text{g/kg}$  at sampling point B5, whereas at other sampling points concentrations were much lower. The highest values for NP were also found in sediments collected at sampling points B5 (980–1730  $\mu\text{g/kg}$ ) and B4 (270–450  $\mu\text{g/kg}$ ). Both sites are situated in the close proximity to the outflows of WWTP effluents and concentrations found are in the upper range of concentrations found in other studies determining NP in estuary and coastal sediments. Petrovic et al. [6,7,11,12] reported NP sediment concentrations of <10–450  $\text{ng/g}$  at the coast



Table 4  
Concentrations of target compounds in seawater ( $\mu\text{g/L}$ )

Compound	B1	B2	B3	B4	B5	B6	T1	T2	T3	T4
NP <sub>1</sub> EO	<lod 0.52	<lod 0.20	<lod 0.25	<lod 0.34	<lod 0.11	<lod 0.21	9.2	<lod	<lod	7.4
NP <sub>2</sub> EO	<lod 0.16	0.086 0.060	<lod 0.076	<lod 0.14	<lod	<lod 0.069	0.086	<lod	0.058	0.058
NP <sub>1</sub> EC	<lod	<lod	<lod	<lod	<lod	<lod	<lod	0.22	<lod	<lod
NP	<lod 0.16	<lod 0.21	<lod 0.12	0.10	<lod	<lod	<lod	<lod	<lod	<lod
OP	<lod 0.071	<lod	<lod 0.070	<lod 0.046	<lod 0.053	<lod 0.056	<lod	<lod	<lod	<lod
CDEAs (total)	0.13 0.73	0.25 0.41	0.54 1.9	0.36 0.55	0.18 0.85	0.34 0.68	1.9	0.73	2.8	2.3
LASs (total)	0.93 8.0	1.2 1.2	1.3 5.4	0.85 2.0	1.94 26	0.67 2.0	3.8	1.7	12	4.6

Sampling points B1–B6: July 2002 and July 2003; T1–T4: October 2002.

Table 5  
Concentrations of target compounds in marine sediments ( $\mu\text{g/kg}$ )

Compound	B1	B2	B3	B4	B5	B6	T1	T2	T3	T4
NP <sub>1</sub> EO	21 22	186 227	112	192 240	562 629	<lod	<lod	<lod	<lod	56
NP <sub>2</sub> EO	9.4 12	50 99	65	93 106	254 404	<lod	<lod	<lod	<lod	22
NP <sub>1</sub> EC	8.1 35	<lod 9.7	202	213 227	498 766	<lod 4.2	63	38	5.2	17
NP	25 42	90 232	127	272 449	982 1731	4.9 122	33	18	40	68
OP	<lod 11	7.1 11	14	13 25	<lod	3.6 6.4	3.3	2.8	18	19
CDEAs	21 28	21 227	199	<lod 36	136 323	<lod 3.4	28	31	33	11
LASs	164 481	1570 2700	2800	2190 9390	86810 86940	493 1140	202	174	718	763

Sampling points B1–B6: July 2002 and July 2003; T1–T4: October 2002.

of Barcelona, whereas other sites along the Spanish coast showed a maximum NP concentration of 1050 ng/g at a site in the proximity of the outflow of partially untreated waste water. In Venice lagoon Marcomini et al. [14] reported NP levels of 5–42  $\mu\text{g/kg}$ . In estuaries concentrations ranged from 0.3–1080  $\mu\text{g/kg}$  in the Scheldt estuary (The Netherlands) [15] and from 360 to 480 in the Elbe estuary (Germany) [16]. The concentrations of NP in sediments of two estuaries in north-east England ranged from 30 to 80  $\mu\text{g/kg}$ , in industrialized and urbanized Tyne estuary, to 1600–9050  $\mu\text{g/kg}$  in highly industrialized Tees estuary [17,18].

In sediments from Tarragona harbour (sampling points T1–T4) LAS were at highest concentrations ranging from 174 to 763  $\mu\text{g/kg}$ , while CDEAs were found in concentrations ranging from 11 to 33  $\mu\text{g/kg}$ . Short ethoxy chain NPEOs were found at only one of four locations, while NP were found at all the locations, at maximum concentrations of 68  $\mu\text{g/kg}$ .

#### 4. Conclusions

Elimination of surfactants in selected Catalanian WWTPs was found to be incomplete, which resulted in effluent concentrations that exceeded in many cases 20  $\mu\text{g/L}$  for estrogenic nonylphenolic compounds and 200  $\mu\text{g/L}$  for LASs. However, clear declining trends in concentrations of nonylphenolic compounds was observed, comparing the present levels and those found in previous studies. However, in spite of this, nonylphenolic compounds are still present in the marine environment receiving WWTPs and industrial effluents.

Levels up to 86 mg/kg of LASs; 1.7 mg/kg of NP, 400–760  $\mu\text{g/L}$  for NPEOs and NPECs were detected in sediments at sampling points near the discharge of WWTP effluents, clearly showing that in coastal area receiving WWTP effluents surfactants and their degradation products

are widespread contaminants. These levels are similar or in some cases higher than previously observed showing that these contaminants, accumulates in sediments and suggesting that biodegradation of compounds accumulated in bottom sediments is a slow process.

### Acknowledgements

The work described in this article was supported by the EU Project P-THREE (EVK1-CT-2002-00116) and by the Spanish Ministerio de Ciencia y Tecnología (PPQ2002-10945-E). S.G. acknowledges the grant from the Spanish MCyT (PPQ2001-1805-CO3-01). M.P. acknowledges the “Ramon y Cajal” contract from the Spanish MCyT. We thank Merck for the gift of LC columns and IST for the SPE cartridges.

### References

- [1] D.R. Karsa, *Chem. Ind.* 9 (1998) 685.
- [2] M. Castillo, D. Barceló, *Anal. Chem.* 71 (1999) 3769.
- [3] P. Eichhorn, M. Petrovic, D. Barceló, T.P. Knepper, *Wasser* 95 (2000) 245.
- [4] M. Castillo, E. Martínez, A. Ginebreda, L. Tirapu, D. Barceló, *Analyst* 125 (2000) 1733.
- [5] M. Solé, M.J. López de Alda, M. Castillo, C. Porte, K. Ladegaard-Pedersen, D. Barceló, *Environ. Sci. Technol.* 34 (2000) 5076.
- [6] M. Petrovic, M. Solé, M.J. López de Alda, D. Barceló, *Environ. Toxicol. Chem.* 21 (2002) 2146.
- [7] M. Petrovic, A. Rodríguez Fernández-Alba, F. Borrell, R.M. Marce, E. González Mazo, D. Barceló, *Environ. Toxicol. Chem.* 21 (2002) 37.
- [8] R. Renner, *Environ. Sci. Technol.* 31 (1997) 316.
- [9] J. Riu, E. Gonzalez-Mazo, A. Gomez-Parra, D. Barceló, *Chromatographia* 50 (1999) 275.
- [10] A. Díaz, F. Ventura, M.T. Galcerán, *Anal. Chem.* 74 (2002) 3869.
- [11] M. Petrovic, A. Díaz, F. Ventura, D. Barceló, *Anal. Chem.* 73 (2001) 5886.
- [12] M. Petrovic, S. Lacorte, P. Viana, D. Barceló, *J. Chromatogr. A* 959 (2002) 15.
- [13] HERA, Human and Environmental Risk Assessment, Report of Linear Alkylbenzene Sulphonates, CEFIC, Brussels, 2002.
- [14] A. Marcomini, B. Pavoni, A. Sfriso, A. Orio, *Mar. Chem.* 29 (1990) 307.
- [15] N. Jonkers, P. de Voogt, in: T.P. Knepper, D. Barceló, P. de Voogt (Eds.), *Analysis and Fate of Surfactants in the Aquatic Environment*, Elsevier, Amsterdam, 2003.
- [16] O.P. Heemken, H. Reincke, B. Stachel, N. Theobald, *Chemosphere* 45 (2001) 245.
- [17] M.A. Blackburn, S.J. Kirby, M.J. Waldock, *Mar. Pollut. Bull.* 38 (1999) 109.
- [18] C.M. Lye, C.L.J. Frid, M.E. Gill, D.W. Cooper, D.M. Jones, *Environ. Sci. Technol.* 33 (1999) 1009.
- [19] M. Farré, G. Kloeter, M. Petrovic, M.C. Alonso, M.J. Lopez de Alda, D. Barceló, *Anal. Chim. Acta* 456 (2002) 19.
- [20] R. Céspedes, D. Raldua, B. Piña, S. Lacorte, D. Barceló, Report on Determination of EDCs in Rivers and WWTP Effluents in Catalonia, 2003.