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Presence of surfactants and their degradation intermediates in sediment cores and grabs from the Cadiz Bay area

P.A. Lara-Martín [a,1], M. Petrovic [b,1], A. Gómez-Parra [a,1],
D. Barceló [b,1], E. González-Mazo [a,1,*]

[a] *Departamento de Química Física, Facultad de Ciencias del Mar y Ambientales, Universidad de Cádiz, Campus Río San Pedro, s/n 11510 Puerto Real, Cádiz, Spain*
[b] *Departamento de Química Ambiental, IIQAB-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain*

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The presence of vertical and longitudinal distribution of the major surfactants and their intermediates in sediments and pore water is reported for the first time.

Abstract

The occurrence and distribution of the major surfactants – LAS, AES, APEOs and AEOs – and their degradation intermediates – SPCs, AP and APECs – in a marine–estuarine environment at Spain are presented. Results show that their concentration in surface sediments is clearly correlated with their usage and the existence of wastewater discharges. The degradation processes appear to lead to the formation of SPCs in the case of LAS, and to the shortening of the average ethoxylated chain length in the case of NPEOs, AEOs and AES. Vertical profiles for AEOs and AES are reported for the first time and present the highest values nearest the surface, followed by a sharp decrease with depth for all surfactants, as well as the appearance of degradation intermediates in deeper sedimentary layers. Shorter LAS homologues and SPCs tend to be present in pore water while strongly non-polar intermediates like NP are firmly attached to the sediments.

Keywords: Anionic surfactants; Non-ionic surfactants; Estuaries; Sediments; Vertical profiles

1. Introduction

The shallow part of the continental shelf is the portion of the ocean most studied in respect to human activities since it is the part most significantly impacted by anthropogenic factors, and is the most sensitive due to its smaller volume of water and proximity to sources of wastewater discharge. Surfactants are key components of detergent formulations due to their surface activity; they are among the most widely used chemicals in the world (around 10 millions of tons are produced per year); and coastal ecosystems receive large quantities of these compounds. After a relatively rapid degradation in water, the fate of the remaining quantities is to be incorporated in the sediments due to the high affinity of surfactants for the organic carbon in the particulate phase. We therefore focused our studies on sediments because they ought to play an important environmental role acting as sink for these contaminants. Moreover, because of their widespread use, source specificity and low degradation rate under anaerobic conditions, surfactants can usefully be employed as molecular indicators in sediments for the contamination caused by human activities (Reiser et al., 1997).

The two major groups of surfactants, classified according to the charge on the hydrophilic moiety, are the anionics and non-ionics. Their main components are linear alkylbenzene sulfonates (LAS) (Fig. 1a) for the anionics and alkylphenol polyethoxylates (APEOs) (Fig. 1b) for the non-ionics, with

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* Corresponding author. Tel.: +34 956 016159; fax: +34 956 016040.
E-mail address: eduardo.gonzalez@uca.es (E. González-Mazo).
[1] Oceanography and Littoral Contamination – CSIC Associated Unit.

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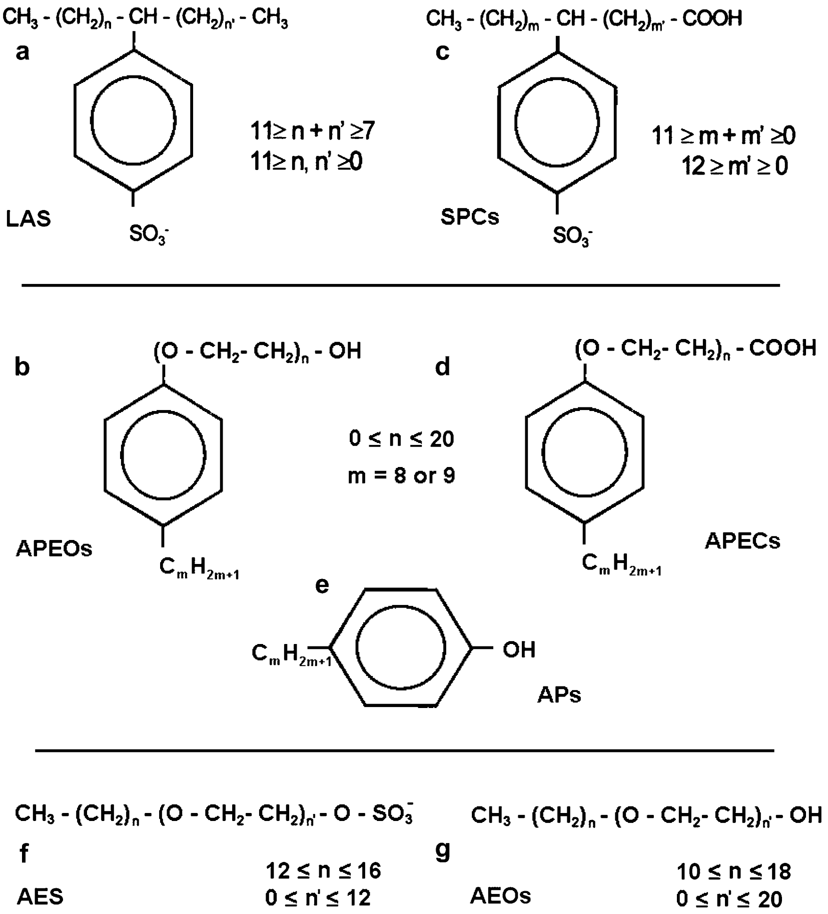

Fig. 1. Chemical structures for the target compounds: (a) LAS, (b) APEOs, (c) SPCs, (d) APECs, (e) APs, (f) AES and (g) AEOs.

annual worldwide production volumes of around 2.5 and 0.5 millions tons, respectively. LAS are used mainly in the formulation of detergents and other cleaning products, while APEO applications also include pesticide formulations and industrial products, mainly as nonylphenol polyethoxylates (NPEOs). However, the use of APEOs is being banned or restricted in Europe because their degradation products are toxic and estrogenic to aquatic organisms (Jobling et al., 1996). The occurrence of LAS and APEOs has been extensively researched in a variety of different freshwater–estuarine (Naylor et al., 1992; Bennett and Metcalfe, 1998; Krueger et al., 1998; Ding et al., 1999; Blackburn et al., 1999; Eichhorn et al., 2001; Lee Ferguson et al., 2001; Isobe and Takada, 2004) and marine environmental compartments (Takada and Ogura, 1992; González-Mazo et al., 1998; Shang et al., 1999; Zoller and Hushan, 2000; Marcomini et al., 2000a; Petrovic et al., 2002; León et al., 2002; Folke et al., 2003). Their aerobic biodegradation in these aquatic environments takes place by the formation of sulphophenyl carboxylic acids (SPCs) (Fig. 1c) in the case of LAS and by progressive shortening of the APEO ethoxylated chain and/or formation of alkylphenol polyethoxycarboxylates (APECs) (Fig. 1d) in the case of APEOs. Several studies have confirmed the occurrence of these pathways (Trehy et al., 1996; González-Mazo et al., 1997; Ejlertsson et al., 1999; Maruyama et al., 2000; Jonkers et al., 2001; Lee Ferguson and Brownawell, 2003; León et al., 2004), but anaerobic degradation is still under consideration: some papers report that LAS is not degraded anaerobically (Sarracin et al., 1999) or that only primary biodegradation occurs (Krueger et al., 1998; León et al., 2001; Sanz et al., 2003), while it has also been suggested that the final transformation of APEOs to alkylphenols (APs) occurs primarily under anaerobic conditions (Fig. 1e), so a high percentage of the original APEOs is converted into these very persistent and non-polar metabolites and remains buried in the sediments.

Alkyl ethoxysulfates (AES) (Fig. 1f) and alcohol polyethoxylates (AEOs) (Fig. 1g) are two surfactants, anionic and non-ionic, respectively, the annual production of which has been increasing recently (around 0.8 millions of tons are produced every year). In fact, AEOs are currently the most important non-ionic surfactant in Europe in economic terms (accounting for 75% of the total production of non-ionic surfactants in Europe) due to the recent restrictions on the production of APEOs. These four major surfactants – LAS, APEOs, AES and AEOs – are the most important and constitute about 90% of the total volume of surfactants on the markets of countries like the Netherlands (Van de Plassche et al., 1999). However, unlike the case of LAS and APEOs, there are very few published papers about the environmental behaviour of AEOs and AES, and of those that do exist, most are studies in river waters (Pojana et al., 2004), wastewaters (Popenoe et al., 1994) and sludges (Bruno et al., 2002). Only two recent papers (Petrovic et al., 2002; Lara Martín et al., 2005a) deal with the occurrence and distribution of these compounds in the marine environment. Laboratory tests of their aerobic (Marcomini et al., 2000b) and anaerobic biodegradation (Nuck and Federle, 1996) have suggested that rapid degradation takes place by the shortening of the ethoxylated chain and formation of polyethylene glycols (PEGs), but the lack of field studies makes it difficult to reach further conclusions about their environmental behaviour.

Most of this research on the environmental fate of surfactants has focused on surface waters and surface sediments in freshwater and marine systems. In the present work we have also sampled sediment cores to study the vertical distribution of surfactants in sediments. These types of study are useful to evaluate the effectiveness of legislative actions on the inputs of contaminants because depositional histories of contaminants like PCBs and PAHs are often preserved in the sediment bed. Also their biogeochemistry and post-depositional fate can be observed in order to obtain environmentally relevant data about their persistence and/or their degradation pathways in situ and to compare them with the results obtained in laboratory tests. However, vertical profiles for surfactants, which are contaminants of increasing concern in many cases, are meagre and only refer to LAS and APEOs (Reiser et al., 1997; Shang et al., 1999; Marcomini et al., 2000a; Yamashita et al., 2000; Isobe et al., 2001; León et al., 2001; Lee Ferguson et al., 2003), with no studies of this type for AEOs and AES carried out to date to our knowledge.

Thus, the present work investigates recent sediment cores in the littoral environment of the Bay of Cadiz (SW of Spain) in order to document the record of LAS, APEOs, AES and AEOs and some of their biodegradation intermediates, as well as surface grabs to determine the present levels of surfactants in the area. The partition between sediment and pore water for LAS and SPCs and the differential sorption for each surfactant homologue have been studied. The presence of degradation intermediates like NP and SPCs at anoxic depths in the sediment cores, reported in previous papers, also has been confirmed, suggesting a possible degradation pathway for NPEOs and LAS, respectively, by means of the formation of these metabolites.

2. Material and methods

2.1. Chemicals

Methanol, triethylamine and acetonitrile were of chromatography quality, purchased from Scharlau (Barcelona, Spain); acetic acid, sodium acetate and sodium sulfate were purchased from Panreac (Barcelona, Spain); and water was Milli-Q quality. The solid-phase extraction (SPE) mini-columns used (500 mg) were supplied by Varian (Bond Elut C_{18}).

The 99% pure C_{16} LAS internal standard and the commercial LAS mixture were supplied by Petroquímica Española (PETRESA), with the following homologue distribution for the commercial mixture: C_{10} (10.9%), C_{11} (35.3%), C_{12} (30.4%), C_{13} (21.2%) and C_{14} (1.1%). The commercial AES mixtures were supplied by KAO Corporation and Procter and Gamble. Their proportional compositions of the various homologues are C_{12} (68.5%), C_{14} (29.8%) and C_{16} (1.7%) for the KAO standard and C_{12} (17.5%), C_{13} (28.2%), C_{14} (32.1%) and C_{15} (22.2%) for the P&G standard. Their average numbers of EO units are 3.4 and 4.2, respectively. The commercial AEOs mixture was supplied by KAO, with an average number of EO units of 11.5. The AEOs homologue distribution is: C_{12} (53.4%), C_{14} (32.6%) and C_{16} (14.0%). The 99% pure $2\Phi C_2$ to $13\Phi C_{13}$ SPCs, NP, OP, NP_1EO, NP_2EO, OP_1EO, OP_2EO, NP_1EC, NP_2EC, OP_1EC and OP_2EC standards were kindly supplied by F. Ventura (AGBAR, Spain) and J.A. Field (Oregon State University, USA).

2.2. Study area and sampling

The study was carried out at five different sampling stations (Fig. 2) in a salt-marsh environment in the Bay of Cadiz (in southwest Spain). The station SP1 was located at 20 m distance from the discharge outlet for the untreated urban effluents from San Fernando, a town of about 100 000 inhabitants, located in a tidal channel (Sancti Petri channel) in the south of the bay which connects the inner part of the bay with the Atlantic Ocean. Several sediment cores and grabs were taken from this station where these urban wastewater discharges had a considerable effect on the study area due to its shallow waters and hence low volume. The sediment samples were taken four months before a nearby WWTP, which now treats these discharges, was put into operation (summer of 2002). An additional sampling point was selected at SP2, at 1 km distance from SP1.

The other three stations were located in an estuary (river Guadalete) discharging into the north of the bay. The first of these stations (G1) was located at the mouth of this river, where El Puerto de Santa Maria, a town of about 150 000 inhabitants, is situated; here there are only occasional untreated discharges into the river since a WWTP which treats the wastewater of this population and discharges into the ocean has existed for several years. The third station (G3) was located several hundred meters away from the effluent discharge point of the WWTP of Jerez (a city of about 200 000 inhabitants, located up stream). Also station (G2) in an intermediate location was sampled. Sediment grab samples were taken from three stations in the spring of 2002.

All these stations were sampled from an inflatable launch on an ebbing tide by means of a Van Veen grab, taking the topmost 10 cm layer of the sediments,

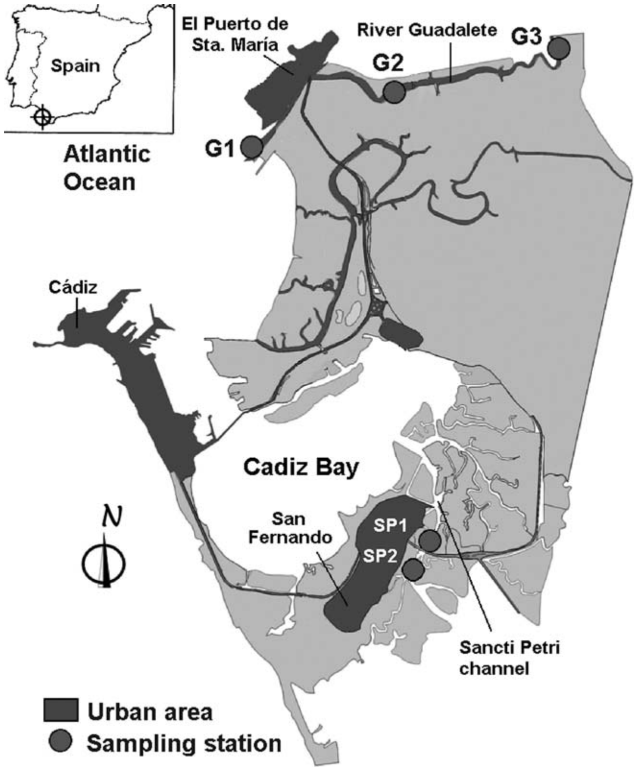

Fig. 2. Map of the Bay of Cadiz showing the location of the sampling stations.

and several PVC cores of 50 cm length obtained with a scuba diver's help. The cores were maintained in a vertical position and at a temperature of 4 °C, as were the grab samples, during transfer to the laboratory, where they were frozen and stored until the time of analysis. Later, the frozen cores were sectioned taking slices of 1 cm from a length of 40 cm. These slices were centrifuged at 10 000 g for 30 min to extract pore water from sediment which was frozen until analysis. All sediment samples were dried in a heater at 75 °C until a constant weight was reached. The dried samples of sediment were milled using a zirconium oxide ball mill (Fritsch) and passed through a 0.063 mm sieve.

2.3. Analytical methods

The complete analytical procedures are described elsewhere (González et al., 2004; Lara Martín et al., 2005b). Briefly, surfactants were extracted from the sediment samples using an ASE 200 pressurized liquid extraction (PLE) unit from Dionex. Duplicates were performed for each sample, taking 5 g of dried and sieved sediment which was packed into the ASE 200 extraction cells. Methanol was passed through them at 50–100 °C and 1500 psi during three cycles of 5 min each. Subsequently, the methanolic extracts were evaporated to 1 mL in a rotavapor and re-dissolved in 50 mL of water in an ultrasonic bath. These extracts, as well as the pore water samples, were purified and preconcentrated by solid-phase extraction (SPE) using mini-columns of the hydrophobic C_{18} type in an automated SPE unit (ASPEC XL) with methanol and water as solvents. The elution was evaporated until dry and re-dissolved in 1 mL of a methanol/water (80:20) solution containing 1 μg mL^{-1} of C_{16} LAS as internal standard and 50 μM of sodium acetate.

The HPLC system consisted of a Spectrasystem liquid chromatograph with autosampler, with the injection volume set to 100 μL. The chromatographic separation was performed using a reversed-phase C-18 analytical column (LiChrospher 100 RP-18) of 250 × 2 mm and 3 μm particle diameter, from Merck. The detection was carried out using an LCQ ion-trap mass spectrometer (Finnigan), equipped with an atmospheric pressure ionization source with electrospray interface (ESI). All extracts were analyzed using ESI full-scan positive ion mode in order to identify APEOs and AEOs and full-scan negative ion mode in order to identify LAS, AES, SPCs, APs and APECs. Quantification was performed using selected ion monitoring (SIM) mode to achieve better sensitivity and lower limits of detection (between 1 and 5 μg L^{-1} per compound) and monitoring the quasimolecular ion $[M-H]^-$ for each homologue of LAS, AES, APs, APECs and SPCs. In the case of APEOs and AEOs each ethoxymer was quantified by monitoring its adduct ion $[M+Na]^+$. Concentrations of surfactants and their metabolites were determined by measuring the peak areas of the quasimolecular ions for the anionics and adduct ions for the non-ionics, using external standard solutions (0.1–10 mg L^{-1}) prepared in methanol/water 1:1 and C_{16} LAS as internal standard (1 mg L^{-1}). Recoveries per homologue were in the following ranges for each target compound: 62–109% for LAS, 54–61% for AES, 66–109% for AEOs, 92–94% for APEOs, 77–89% for APs, 40–68% for SPCs and 74% for APECs.

3. Results and discussion

3.1. Surface sediments

Table 1 shows concentration values for surfactants and their metabolites in the sediment grabs taken at the selected sampling stations. It can be observed that these values are much higher at station SP1, in the Sancti Petri channel, than at the rest of the stations. The explanation is the presence of an untreated wastewater discharge outlet from the town of San Fernando adjacent to SP1 and the restricted hydrodynamic conditions of this tidal channel (width and depth are very limited, so surface water has a long residence time). LAS concentrations at every station are higher than those of the rest of the surfactants due to its greater production and domestic usage, with values at station SP1 higher than those determined in similar polluted marine environments like Tokyo Bay (Takada and Ogura, 1992), Venice Lagoon (Marcomini et al., 2000a) or Barcelona Harbour (Petrovic et al., 2002). Values reported in these cited articles are more similar to those found in other parts of the tidal channel (SP2) and along the river Guadalete (G1–G3), where a WWTP prevents the continuous discharge of untreated wastewater, unlike at SP1. LAS concentrations at this last station are very similar to those found in previous studies in the same location (González-Mazo et al., 1998; León et al., 2001, 2002), which confirms the heavy contamination levels to which this ecosystem is exposed. These previous studies also reported a sharp decrease of LAS the farther the sampling station is from the effluent discharge point: values of 1.5–2.0 ppm were found at the two entrances to the channel. This pattern has been confirmed in the present work, in which much lower surfactant levels are found at SP2, compared with SP1. Degradation of surfactants like LAS and NPEOs takes place in sediments from both zones, confirmed by the presence of high concentrations of metabolites (see Table 1) like SPCs, short ethoxylated chain nonylphenols and NP, as previous papers have described in other marine and estuarine areas (Marcomini et al., 2000a; Lee Ferguson et al., 2001; Isobe et al., 2001; Jonkers et al., 2003; Isobe and Takada, 2004). As in the case of LAS, AEOs and AES, concentrations reported along the Spanish coast (Petrovic et al., 2002; Lara Martín et al., 2005a) are much lower than at SP1 and about the same order of magnitude as those found at the rest of the sampling stations. Values for AES are about one order of magnitude lower than those for LAS at these other stations, which reflect the lower usage of AES. However, AEO concentrations in the same sediment samples are similar when compared with LAS values, in spite of the lower usage of AEOs, probably due to their very strong hydrophobic character (octanol–water partition coefficients of 1.96 and 5.91 have been calculated for C_{12} LAS and $C_{14}EO_5$, respectively) which leads to a highest affinity for the particulate phase.

Table 1
Concentration values for surfactants and their degradation intermediates in the sampled sediment grabs

	SP1	SP2	G1	G2	G3
LAS[a]	67.6	3.2	3.6	1.2	1.9
AEOs[a]	9.9	1.6	1.6	0.8	0.9
AES[b]	1728	161	365	257	147
SPCs[b]	1867	379	63	67	388
NP_2EO[b]	399	n.a.	22	59	45
NP_1EO[b]	597	n.a.	n.d.	45	77
NP[b]	168	n.a.	28	13	225

n.d. = not detected, n.a. = not analyzed.
[a] μg g^{-1}.
[b] ng g^{-1}.

Surfactant values along the river Guadalete show a decrease moving upstream, from sampling stations G1 to G3. This trend reflects the known fact that, although there is a WWTP in operation, occasional untreated wastewater discharges, from an old part of the sewage system not integrated into the main system, take place near G1, where the town of El Puerto de Santa Maria is located. However, an opposite trend can be found in the case of the degradation intermediates of LAS and NPEOs, with higher concentrations for SPCs, NP_1EO, NP_2EO and NP found at sampling station G3. Their presence could be explained by the location of the discharge outlet of the WWTP of the city of Jerez only several hundred meters distant from this station and confirmed by the fact that SPCs/LAS and NP/NPEOs ratios are one order of magnitude higher at G3 than at the rest of the sampling stations. The extent of the degradation and sorption processes which are taking place at stations like G3 can also be studied by comparing the ratios between the short and long chain homologues and/or ethoxymers for each surfactant. At this station, the relative proportions for shorter alkyl chain homologues like C_{10} LAS are much higher compared with longer ones like C_{13} LAS, which are more easily biodegraded and show higher values of sorption onto solids. Illustrating this, the C_{10} LAS:C_{13} LAS ratio increases from 0.2 at G1 to 0.6 at G3. Fig. 3A and B shows the distribution of C_{12}-AEOs and C_{12}-AES ethoxymers. A reduced average number of EO units for the sediment samples, compared with the standard (5.3 for AEOs and 5.1 for AES) is observed, particularly for those collected at G3 (4.3 for AEOs and 2.5 for AES). In the case of AEOs, this trend can be explained by a degradation mechanism which involves the shortening of the ethoxylate chain, as has previously been described for these and other related compounds like NPEOs (Lee Ferguson et al., 2003). Similar degradation mechanisms may explain the AES ethoxymers distribution, but the much higher level of the alkyl sulfates (AS) percentage with respect to the AES standards suggests that their occurrence in sediments cannot be explained as being solely the result of the degradation of AES and impurities in AES manufacture, because AS are also manufactured apart from AES and used in other applications (Lara Martín et al., 2005a).

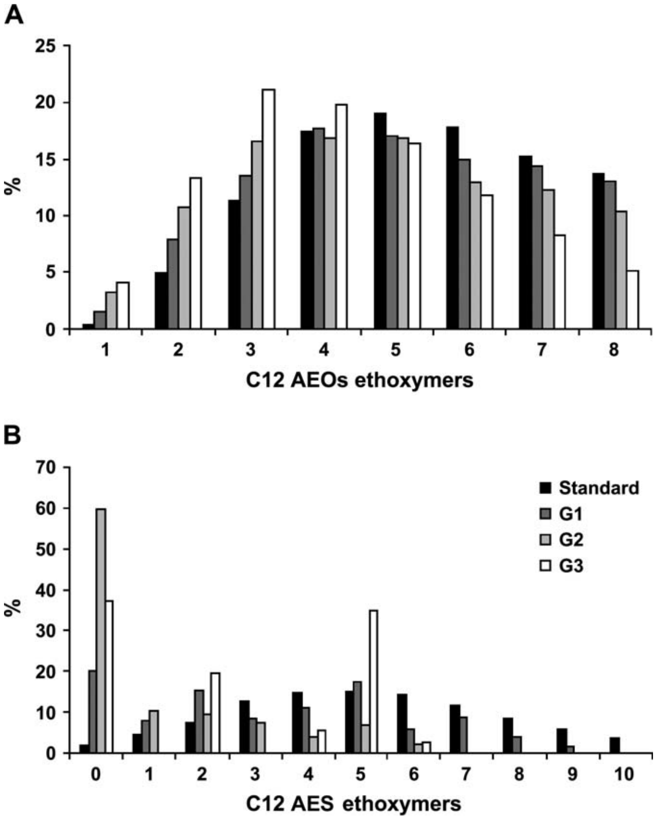

Fig. 3. Ethoxymers distributions for (A) C_{12} AEOs and (B) C_{12} AES in the sediments from the sampling stations located at river Guadalete.

3.2. Vertical profiles

Several sediment cores were taken at station SP1 to study the evolution of the surfactant levels by means of their vertical profiles, because this area has been subjected to heavy urban contamination during recent decades. Fig. 4A and B shows the vertical profiles for C/N ratio and porosity along the sedimentary column in SP1. Fig. 4C shows the vertical variations for redox potential (E_h), between −300 and −400 mV, and this clearly shows the anoxic conditions of the sediments. The usual trend is a decrease in the porosity with depth due to the sediment being more compact, as well as an increase in the C/N ratio because the organic matter becomes more refractory. However, at a depth of 10–15 cm, an alteration in these trends is observed, where the porosity value increases and the C/N ratio decreases. The cause of this perturbation was the building in 1996 of a highway bridge near the sampling station SP1, which introduced an amount of new material into the natural sedimentation regime in the zone.

Fig. 5A and B shows the vertical profiles for LAS in sediment and pore water, respectively. The concentration of LAS in the sediment is up to 1000 times greater than the LAS concentration in the pore water, whereas the concentration of SPC in both (Fig. 5C), sediment and pore water, is of the same order of magnitude. These results are similar to those obtained for sorption tests in the laboratory (Rubio et al., 1996) and in previous field studies (León et al., 2001), in which it was concluded that the interaction between LAS and the sediment is predominantly of the hydrophobic type, while SPCs have little affinity for the sediment due to their low hydrophobicity. Also the influence of the length of the alkyl chain on the process of sorption is demonstrated by the distribution of homologues presented by the LAS incorporated into the sediments, as González-Mazo et al. (1998) have described, where, unlike the process occurring in the pore water, the proportion of each homologue between C_{10} and C_{13} LAS increases in line with the number of carbon atoms in the chain.

A maximum for LAS is found in the first centimetres followed by a clear decrease with depth. This pattern is more prominent in the sediment than in the pore water. The decline is steeper in the first few centimetres, which may be related to greater discharges of effluent into the zone during the last decade as well as to the elimination of LAS due to degradation processes. However, a secondary maximum for LAS can be observed between 10 and 15 cm depth. Other papers considering the distribution of surfactants in sediment cores (Marcomini et al., 2000a; León et al., 2001; Lee Ferguson et al., 2003) only report the existence of the first maximum in the topmost layer, even the previous study by León et al. (2001) carried out in the same area. The explanation for this

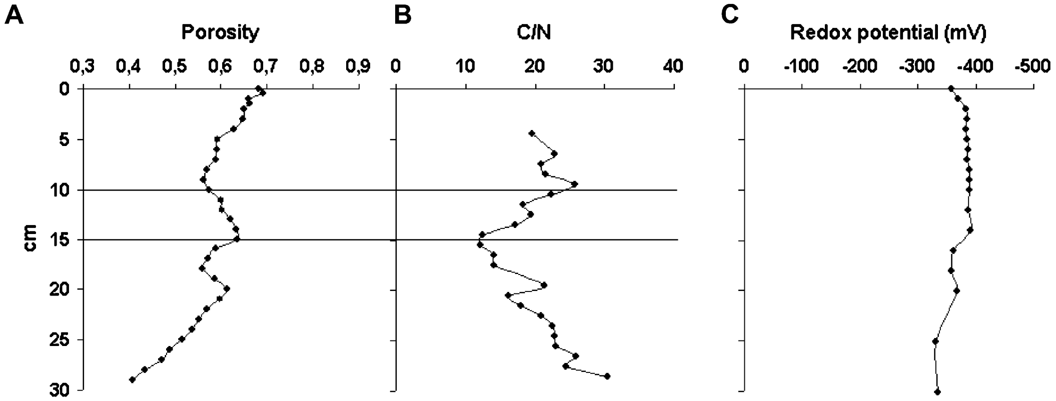

Fig. 4. Vertical profiles showing the variations in the sedimentary column from SP1 sampling station for (A) porosity, (B) C/N index and (C) redox potential.

phenomenon is the same as that for the C/N ratio and porosity anomalies at the same depth, namely an alteration in the sedimentation due to the construction of a highway bridge, which took place after the sampling done by León et al. (2001) in 1995. This alteration trapped the former maximum in the topmost layer, which later diffused to the new material to take its present Gauss bell shaped distribution. After the building work finished, sedimentation in the zone returned to its normal regimen and the present maximum in the topmost layer was formed again.

The vertical profile obtained for the SPCs in pore water (between 6 and 13 carbon atoms) was greatest at depths of around 10 and 25 cm, where LAS concentrations show a minimum after the two maxima between 0–5 and 10–15 cm depth. Considering that the predominant mechanism of transport in pore water is diffusion, this type of distribution implies that the SPCs may actually be produced by LAS degradation at these depths, where the conditions are anoxic (see Fig. 4C), as León et al. (2001) have suggested in a previous study where a maximum for SPCs was also found below the LAS maximum in the same area. At these two depths, the C_{10}-LAS:C_{13}-LAS ratio in sediment reaches its maximum value, probably due to the faster degradation of longer homologues, which raises the percentage of the shorter homologues. At depths of more than 25 cm, this ratio increases due to the higher diffusion of C_{10}-LAS with respect to C_{13}-LAS, as has previously been described by Reiser et al. (1997). Recent studies have also confirmed the occurrence of NPECs as intermediates in the anaerobic degradation of NPEOs in the marine environment (Lee Ferguson and Brownawell, 2003), so it would be reasonable to think that the reported occurrence of SPCs in anoxic sediments could take place through an anaerobic mechanism for the primary biodegradation of LAS, although anaerobic degradation tests need to be performed with these sediments in the laboratory to confirm this hypothesis.

Fig. 6A and B shows the vertical profiles for AES and AEOs, respectively, in sediments from the sampling station SP1. The profiles for these two surfactants are very similar when compared with that for LAS, due to their tensioactive nature; these also show the presence of two maxima, although the maximum corresponding to AES is slightly deeper than those for LAS and AEOs. The AES and AEO concentrations reflect their relative production and usage levels in comparison with LAS, with top values of 3.6 and 17.5 mg kg^{-1}, respectively, in sediments. However, the lower solubility of AEOs compared with AES may have played a significant role in their greater incorporation into sediments, which would explain the sixfold higher concentrations found for AEOs, while the production and usage quantities of AEOs and AES are of about

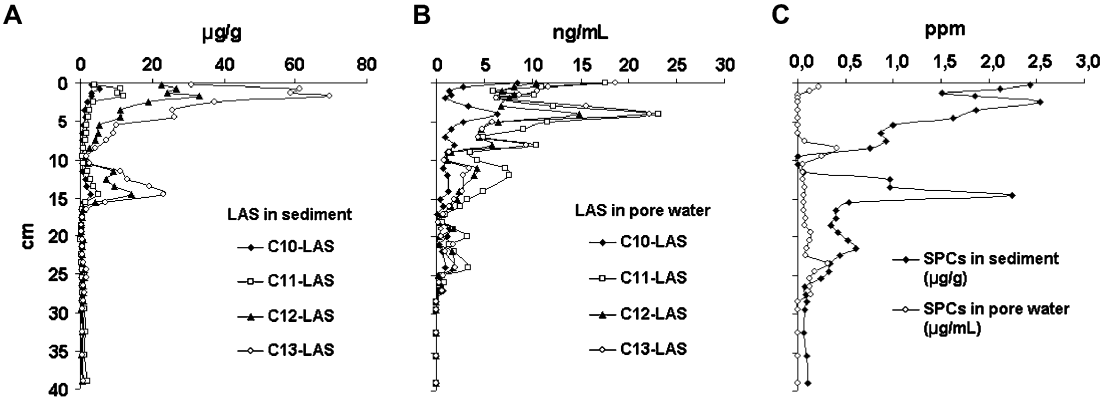

Fig. 5. Vertical profiles showing the concentration values in sediments and pore water from SP1 sampling station for (A, B) LAS and (C) SPCs.

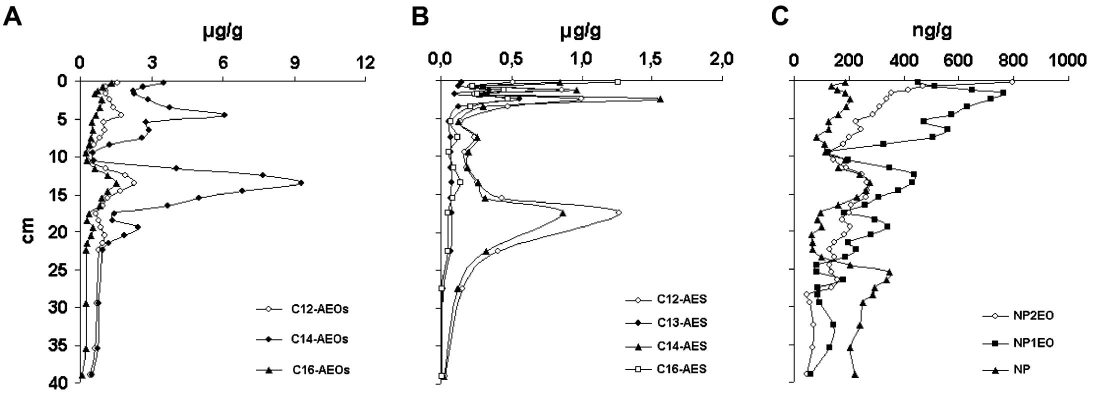

Fig. 6. Vertical profiles showing the concentration values in sediments from the SP1 sampling station for (A) AEOs, (B) AES and (C) NP, NP_1EO and NP_2EO.

the same order. As in the case of LAS homologues previously described, the relative proportions of the longer alkyl chain homologues of AEOs and AES in sediment are higher in comparison with those in commercial standards due to their greater hydrophobicity and affinity for the particulate phase. In the case of AEOs, only homologues with an alkyl chain with an even number of carbon atoms have been analyzed (C_{12}, C_{14} and C_{16} AEOs), and the C_{14} AEOs are found to be the most abundant homologue in the sediment as well as in pore water, where the highest level of concentration of 1.7 mg kg^{-1} has been found in the topmost few centimetres. Even and odd homologues from C_{12} to C_{16} AES were analyzed and the distribution of AES homologues (Fig. 6b) shows that homologues with an even number of carbon atoms in their alkyl chain (primarily C_{12} and C_{14} homologues, but also C_{16}) are predominant over homologues with an odd number (like C_{13}). As previously reported (Lara Martín et al., 2005a), the explanation for this distribution is that, in Europe, coconut-type alcohol polyethoxylates (the type of AEOs that we have determined, with an even number of carbon atoms in their alkyl chains) are the primary source for the synthesis of AES instead of using AEOs of petrochemical origin (which also includes odd-numbered homologues).

Vertical profiles for the degradation intermediates of NPEOs in sediments are shown in Fig. 6C. Although degradation of NPEOs in anoxic sediments in Canadian and Japanese marine zones has been questioned by some authors (Shang et al., 1999; Isobe et al., 2001), others have found a decrease in short ethoxylate ethoxymer concentrations due to their degradation into NP, in sediments from lagoons in Venice (Marcomini et al., 2000a) and New York (Lee Ferguson et al., 2003) as well as in anaerobic tests at the laboratory using estuarine sediments (Lee Ferguson and Brownawell, 2003). This latter situation is our case, where degradation is taking place by progressive shortening of the NPEOs ethoxylated chain, as can be observed by the presence of a maximum of NP_2EO which decreases through the formation of NP_1EO and finally of NP at greater depths. In this respect, the $NP_2EO > NP_1EO > NP$ trend is reversed along the sedimentary column to $NP > NP_1EO > NP_2EO$. Anaerobic degradation of NPEOs may be taking place in these sediments, and this is confirmed not only by the E_h vertical profile (Fig. 4c) but also by the major presence of short ethoxylate chain NPEOs as degradation intermediates: these are produced mainly by anaerobic degradation (Lee Ferguson and Brownawell, 2003). NPECs, more relevant in aerobic degradation of NPEOs, were below limits of detection. Furthermore, a previous study (Lara Martín et al., 2005c) at the same sampling station has confirmed reductive dechlorination as the main mechanism for the degradation of DDT along the sedimentary column, with a high presence of DDD as the main degradation intermediate. No OPEOs, OP or OPECs were found in any sediment sample, probably due to the low usage of the parent compound in comparison with NPEOs (between 10 and 20%) and their more specific usage associated with industrial processes (Jonkers et al., 2003).

4. Conclusions

The occurrence and distribution of the major surfactants (LAS, AES, APEOs and AEOs) and some of their degradation intermediates (SPCs, AP, APECs and AP_1EO and AP_2EO) in a marine–estuarine environment have been reported in this paper. The presence of these compounds in the sediments is clearly correlated with the presence of both treated and untreated wastewater discharges, while the occurrence of their degradation intermediates is associated with the proximity of wastewater treatment plants and the degradation processes taking place in the sediments. These processes appear to lead to the formation of SPCs, in the case of LAS, and to NP, NP_1EO and NP_2EO in the case of NPEOs. The use of ratios between longer and shorter homologues and/or ethoxymers for these surfactants is another useful tool for studying the extent of their degradation processes as well as their distribution. Partition for the surfactants and their degradation intermediates between sediments and pore water depends mainly on the hydrophobic character of their molecules: in the case of LAS, the shorter homologues and their degradation products (SPCs) are more polar than longer homologues and these tend to be present in pore water; in the case of NPEOs, the strongly non-polar intermediates like NP are found attached firmly to the sediments.

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