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Sources, transport and reactivity of anionic and non-ionic surfactants in several aquatic ecosystems in SW Spain: A comparative study

Pablo A. Lara-Martín*, Abelardo Gómez-Parra, Eduardo González-Mazo

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

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Occurrence and reactivity of the main synthetic surfactants in freshwater and marine systems are discussed.

Abstract

Presence, distribution and transport mechanisms of the four major synthetic surfactants -linear alkylbenzene sulfonates (LAS), alkyl ethoxysulfates (AES), nonylphenol ethoxylates (NPEOs) and alcohol ethoxylates (AEOs)- have been simultaneously studied in different aquatic ecosystems. Urban wastewater discharges and industrial activities were identified as the main sources for these compounds and their metabolites. LAS, AES and carboxylic metabolites remained in the dissolved form (87–99%). However, NPEOs and AEOs were mostly associated with particulate matter (65–86%), so their degradation in the water column was limited due to their lower bioavailability. It was also observed that sorption to the particulate phase was more intense for longer homologs/ethoxymers for all surfactants. With respect to surface sediments, AES levels were considerably below (<0.25 mg/kg) the values detected for LAS and NPEOs. Concentrations of AEOs, however, were occasionally higher (several tens of ppm) than those found for the rest of the target compounds in several sampling stations.

Keywords: Surfactants; Sediments; Waters; Sorption; Biodegradation; Estuaries

1. Introduction

Surfactants comprise a broad group of chemical compounds synthesized to exhibit tensioactive properties that make them useful for employment as a key ingredient of household and industrial detergents, but also in personal care products and pesticide formulations, among other applications. These compounds can be classified, according to their charge, into several types, where those of the anionic and non-ionic classes show the highest volumes of production. According to the data reported by CESIO (Comité Européen des Agents de Surface et de leurs Intermediaries Organiques), 998 ktons of anionics and 1231 ktons of non-ionics were manufactured during the year 2000 in the EU, these together account for about 90% of the total production of synthetic surfactants. Linear alkylbenzene sulfonates (LAS) are the most representative anionic surfactants (434 ktons), closely followed by alkyl ethoxysulfates (AES) and the non-ethoxylated alkyl sulfates (404 ktons both together). Alcohol polyethoxylates (AEOs) are the main non-ionic surfactants produced in Europe (747 ktons). The recent restrictions in the use of alkylphenol polyethoxylates (APEOs) in household detergents mainly due to the estrogenic properties shown by their metabolites (Jobling et al., 1996) have reduced their production to 116 ktons.

Once used, surfactants are discharged via wastewater treatment plants (WWTPs) into aquatic environments. Thus, a considerable number of studies have reported the presence of LAS

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* Corresponding author. Tel.: +34 956 016 159; fax: +34 956 016 040.
E-mail address: pablo.lara@uca.es (P.A. Lara-Martín).

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in many parts of the world, in both water (Bester et al., 2001; Eichhorn et al., 2002; Ding et al., 1999; González-Mazo et al., 1997, 1998; León et al., 2002; Marcomini et al., 2000; Takada and Ogura, 1992; Terzic and Ahel, 1994; Trehy et al., 1996; Ying, 2006) and sediment phases (Bester et al., 2001; Folke et al., 2003; González-Mazo et al., 1998; León et al., 2002; Marcomini et al., 2000; Trehy et al., 1996), with values typically ranging from less than 50 to more than 1000 $\mu g\ L^{-1}$ and from less than 0.1 to several tens of mg kg^{-1} respectively, depending on the distance from urban wastewater discharge sources and type of wastewater treatment. Several papers also consider LAS intermediates, the sulfophenylcarboxylic acids (SPCs), which appear mostly in the water column at concentrations up to 100 $\mu g\ L^{-1}$ due to their low hydrophobicity (Ding et al., 1999; Eichhorn et al., 2002; González-Mazo et al., 1997; León et al., 2002; Marcomini et al., 2000; Trehy et al., 1996). With respect to the non-ionics, the potential estrogenicity of the metabolites of NPEOs (nonylphenol polyethoxylates, which are the major class of APEOs) has resulted in these intermediates being studied even more than the parent compound, which shows levels from 0.01 to 50 mg kg^{-1} in sediments (Bester et al., 2001; Jonkers et al., 2003, 2005; Marcomini et al., 2000; Maruyama et al., 2000; Naylor et al., 1992). Thus, the presence of nonylphenol (NP) and NPEOs with one and two ethoxylated units (EO) -which are hydrophobic degradation intermediates- has been widely detected in sediments from rivers (Ahel et al., 1994; Isobe and Takada, 2004; Jonkers et al., 2003; Lee Ferguson et al., 2001; Naylor et al., 1992), lakes (Bennett and Metcalfe, 1998) and the sea bed (Bester et al., 2001; Lee Ferguson et al., 2001; Marcomini et al., 2000), ranging from 0.1 to 72 mg kg^{-1}. Concentrations of up to 100 $\mu g\ L^{-1}$ have been found in surface waters (Ahel et al., 1994, 2000; Isobe and Takada, 2004; Jonkers et al., 2003, 2005) for the more polar nonylphenol ethoxycarboxylates (NPECs). On the other hand, data concerning the presence of aliphatic surfactants such AES and AEOs are rather limited. One of the main reasons for this could be that conventional high performance liquid chromatography coupled to ultraviolet or fluorescence detectors (HPLC-UV-FLD) and gas chromatography coupled to mass spectrometry (GC-MS) cannot be used, as these compounds lack volatilization capability and fluorescence. However, by developing specific protocols, some authors have found concentrations between 0.1 and 2 $\mu g\ L^{-1}$ for AES (Neubecker, 1985; Pojana et al., 2004; Popenoe et al., 1994) and AEOs (Dunphy et al., 2001; Eadsforth et al., 2006; Fendinger et al., 1995) in surface waters. The presence of AES in sediment, showing concentration values ranging from 0.02 to 0.40 mg kg^{-1}, has recently been reported for the first time by our group in a previous study (Lara-Martín et al., 2005) and confirmed later by Sanderson et al. (2006) in other areas. The few papers dealing with the occurrence of AEOs in sediments (Lara-Martín et al., 2006a; Petrovic et al., 2002) have shown levels ranging from 0.04 to 9.9 mg kg^{-1}, although these data may underestimate the true values because in these studies the analysis was conducted on a limited set of homologs and ethoxymers.

With respect to the environmental behavior of surfactants, sorption and degradation have been described as two of the main processes affecting these compounds in aquatic ecosystems (Ying, 2006). Thus, a non-conservative behavior has been described for LAS (Eichhorn et al., 2002; León et al., 2002; Takada and Ogura, 1992; Terzic and Ahel, 1994) and NPEOs (Ahel et al., 1994; Isobe and Takada, 2004; Jonkers et al., 2003; Lee Ferguson et al., 2001; Maruyama et al., 2000) in rivers and estuaries. The percentage of LAS sorption onto particulate matter is commonly below 20% although it appears to be higher at higher salinities (González-Mazo et al., 1998), while a relatively fast degradation into SPCs (most of them found in the dissolved form) has been confirmed in Spanish (León et al., 2002) and Brazilian rivers (Eichhorn et al., 2002). NPEOs have shown a higher affinity for suspended solids (more than 25% is adsorbed according to Jonkers et al., 2005) while their polar metabolites (NPECs) are only present in the aqueous phase (Isobe and Takada, 2004; Jonkers et al., 2003). In-situ degradation by progressive shortening of the ethoxylated chain has been also detected (Maruyama et al., 2000) and the highly hydrophobic compounds generated by this process are often preserved in sediments (Bennett and Metcalfe, 1998). It is especially remarkable that this kind of study has never been carried out for AES and AEOs in spite of their production volumes being comparable to those for aromatic surfactants (LAS and NPEOs). Given this situation our main object in the present work is to perform a comparative study for the first time concerning the distribution and environmental behavior of these four main surfactants in three different Spanish aquatic ecosystems by: a) determining their occurrence in water, suspended solids and sediments; b) identifying their distribution and sources in each area; and c) characterizing their reactivity attending to their sorption capacities onto the particulate phase, changes in their homolog/ethoxymer patterns and the generation of carboxylated metabolites in the water column due to degradation processes.

2. Experimental

2.1. Sampling areas

Sediment and water samples were collected using an inflated boat, at several sampling stations located in three different aquatic ecosystems in the region of Cadiz, in the southwest of Spain (Fig. 1). Zone A is a tidal marine channel (named the Sancti Petri channel) which is located in the south of the Bay of Cadiz, a salt marsh environment. This channel connects the inner part of the bay with the Atlantic Ocean and is 18 km in length. It has a reduced depth (between 3 and 6 m) and the tidal influx which enters from both ends of the channel, meets at a point 5 km from the bay (near station S10). It is at exactly this point where the untreated urban wastewater from the adjacent town of San Fernando (100 000 inhabitants) used to be discharged, until summer 2002. A military naval station is located at the north end of the channel. Fourteen sampling stations (from S1 to S14) were established over the length of the Sancti Petri channel, where sediment grabs were taken by means of a Van Veen grab, during the spring season in 2002 and 2004. Zone B comprises the estuary of the Guadalete river. This river is 157 km long and flows across the province of Cadiz. Another fourteen sampling stations (G1–G14) were selected at different parts of this estuary, and in addition to sediment grabs, water samples were collected during an ebbing tide

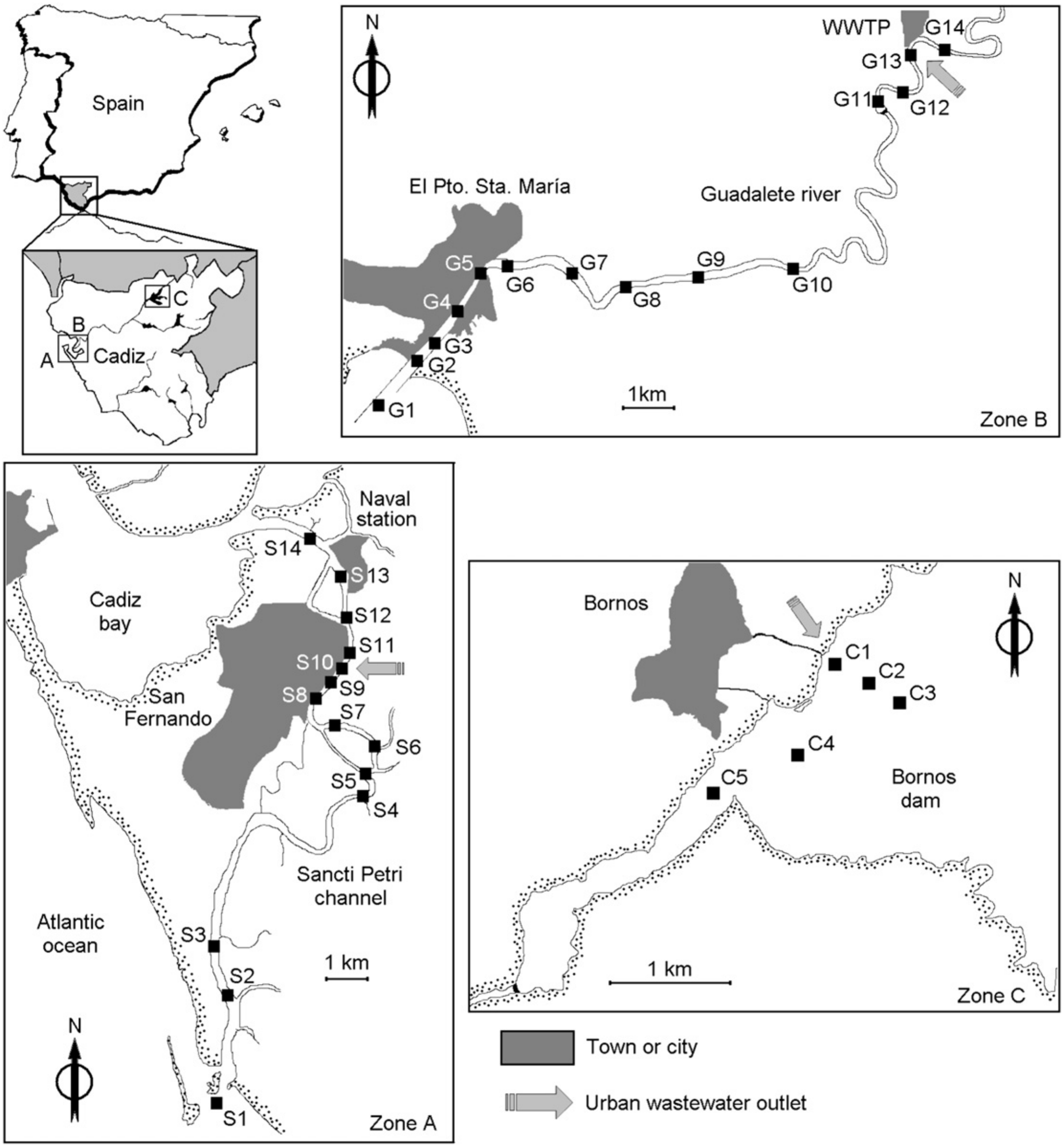

Fig. 1. Map showing the location of the zones studied and their sampling stations.

in spring of 2004 using 2.5 L amber glass bottles. Station G13 is located a few meters from the discharge outlet of a WWTP which serves a town of 200 000 inhabitants (Jerez de la Frontera) situated to the north of the estuary. Another town (El Puerto de Santa Maria, 80 000 inhabitants) is located at the mouth of the Guadalete river, where there is a fishing port and related industries. Finally, zone C is situated at the Bornos reservoir, which has a water capacity of 200 hm^3 and is surrounded by a protected area employed only for recreational activities. This dam receives water from the Guadalete river. A town of 8000 inhabitants (Bornos) is located near this reservoir and discharges wastewater to this aquatic ecosystem after a primary treatment. Water and sediment samples were taken at five different stations (C1–C5) during spring of 2004.

2.2. Materials, standards and analytical methodology

This aspect of the study has been optimized and described in a previous analytical paper (Lara-Martín et al., 2006b). All solvents were of chromatography quality, purchased from Scharlau (Barcelona, Spain) or Panreac (Barcelona, Spain) and water was Milli-Q quality. Surfactant standards were supplied by Petroquímica Española (PETRESA) and KAO Corporation, whereas their metabolites were kindly supplied by F. Ventura (AGBAR, Spain) and J.A. Field (Oregon State University, USA).

First, 4% of formaldehyde was added to aqueous samples, these, together with the sediment grabs, were kept at 4 °C during their transport to the laboratory, and later frozen until their analysis. In the laboratory the sediment was dried in a heater at 65 °C, then milled and sieved. Water samples were filtered through glass fiber filters (AP 40 Millipore) to separate the suspended solids. Target compounds were extracted from the sediment and suspended solid samples in triplicate using pressurized liquid extraction (PLE) by means of an accelerated solvent extraction ASE 200 unit from Dionex. Methanol was passed through the heated (120 °C) and pressurized (1500 psi) PLE cells for three cycles of 5 min each. The extracts were evaporated and redissolved in 100 mL of water. Later, these extracts and the water samples (250 mL), also in triplicate, were purified and preconcentrated by solid-phase extraction (SPE) using mini-columns of the hydrophobic C18 type (Bond Elut, Varian) in an automated SPE AutoTrace unit (Zymark). The mini-columns were rinsed with 10 mL of methanol and 5 mL of water prior to passing the samples, previously acidified to pH 2.5. They were then washed with 5 mL of water and eluted with 5 mL of methanol/acetone 1:1 and 5 mL of dichloromethane/ethyl acetate 1:1. Finally, the eluate was evaporated to dryness and redissolved in 1 mL of a methanol/water 8:2 solution containing 1 mg L^{-1} of C_{16}LAS as internal standard and 50 μM of sodium acetate. Recoveries were in the range from 70 to 107% for most homologs.

Identification and quantification of target compounds were carried out by HPLC-MS. The HPLC system consisted of a Spectrasystem liquid chromatograph with autosampler, with the injection volume set to 100 μL. The chromatographic separation was done using a reversed-phase C-18 analytical column (LiChrospher 100 RP-18, Merck) of 250 mm × 2 mm and 3 μm particle diameter. The following gradient was used (A = methanol, B = water with 5 mM acetic acid and 5 mM triethylamine, flow rate = 0.15 mL min^{-1}): 0% A during the first 5 min, then increased linearly to 70% A over 15 min, then increased linearly to 100% A over another 15 min, and kept isocratic for yet another 15 min. The detection was carried out using a LCQ ion-trap mass spectrometer (Thermo), equipped with an atmospheric pressure ionization source with electrospray interface (ESI). From 0 to 38 min ESI was used in full-scan negative ion mode in order to detect SPCs, NPECs, LAS, AS and AES, and then switched to positive ion mode to allow the detection of NPEOs and AEOs. Identification of each homolog of LAS and SPCs was carried out by monitoring their quasimolecular ions $[M-H]^-$ and their specific fragment ion at *m/z* 183. In the cases of AS and AES their specific fragment ion was *m/z* 97, and *m/z* 219 for NPECs, respectively. Monitoring of their sodium adduct ions $[M+Na]^+$ was performed in the case of NPEOs and AEOs. Concentrations of the analytes were determined by measuring the peak areas of the quasimolecular or adduct ions using external standard solutions (0.5–25 mg L^{-1}) and C_{16}LAS as internal standard (1 mg L^{-1}). The limits of detection were calculated using a signal-to-noise ratio of 3:1, and were found to be 0.05 μg L^{-1} in water and from 1 to 10 μg kg^{-1} in sediment.

3. Results and discussion

3.1. Identification of contamination sources

Concentrations of target compounds in sediments from the selected areas spanned a wide range of values, from less (<0.1 mg kg^{-1}) to more (several tens of mg kg^{-1}) contaminated points. In general terms, similar values for LAS and NPEOs have been detected previously in other aquatic environments in Europe (Bester et al., 2001; Folke et al., 2003; González-Mazo et al., 1998; León et al., 2002; Marcomini et al., 2000; Trehy et al., 1996) and America (Ahel et al., 1994; Jonkers et al., 2003; Lee Ferguson et al., 2001; Marcomini et al., 2000; Naylor et al., 1992). Our data are also in agreement with the few recent studies about levels of AES in sediment (Lara-Martín et al., 2005; Sanderson et al., 2006) but concentrations were significantly higher than those previously reported for AEOs along the Spanish littoral (Lara-Martín et al., 2006a; Petrovic et al., 2002).

Fig. 2 shows the distribution of each surfactant in surface sediments over the length of the Sancti Petri channel (zone A) during the years 2002 and 2004. A complete transect between the two ends of the channel was carried out during the first sampling (spring 2002), showing that concentration of anionic surfactants was generally less than 1 mg kg^{-1} for LAS and 0.25 mg kg^{-1} for AES along this channel. These differences between AES and LAS levels could be explained by a combination of the lower use and hydrophobicity of the aliphatic surfactant. However, a sharp increase could be observed for both compounds near sampling station S10, reaching the highest values of 67.6 mg kg^{-1} for LAS and 1.7 mg kg^{-1} for AES. This is a shallow point where the two waves of the flow tide entering the channel meet, and where untreated wastewater from the adjacent town of San Fernando was discharged until summer of 2002, so urban contamination is especially severe here, as confirmed by previous studies (González-Mazo et al., 1998; Lara-Martín et al., 2005, 2006a; León et al., 2002; Petrovic et al., 2002) monitoring LAS levels in the area. The steep decrease in the concentration of anionics as one moves from S10 towards the ends of the channel could be explained by the effects of biodegradation (in fact, values of 1.9 mg kg^{-1} for SPCs were determined at station S10), sorption and precipitation once the surfactants entered the water column (González-Mazo et al., 1998). Although maximum values for non-ionics (14.8 mg kg^{-1} for NPEOs and 23.3 mg kg^{-1} for AEOs) were also reached where the untreated wastewater discharges used to take place, it was

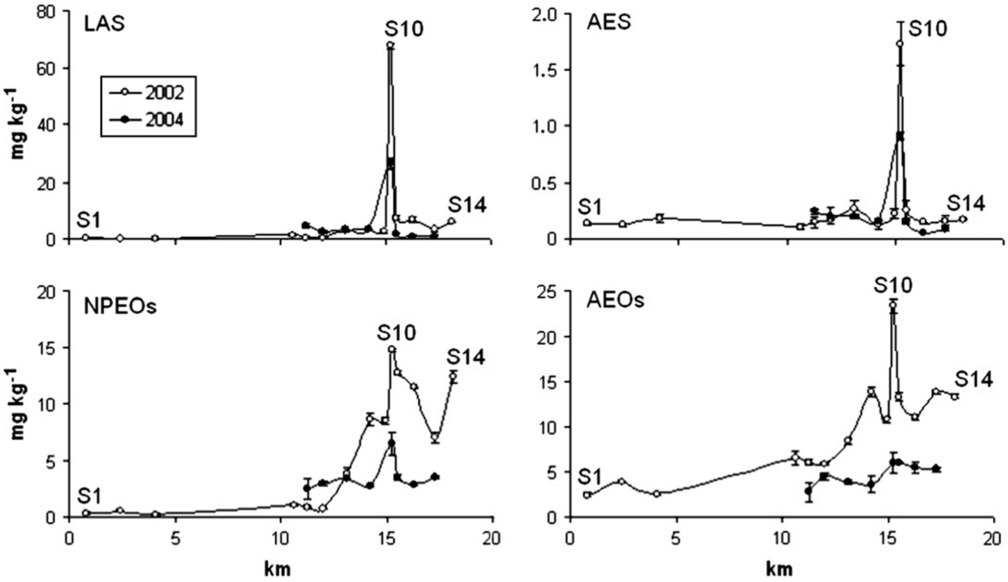

Fig. 2. Distribution of surfactants in surface sediments (mg kg^{-1}) in zone A (over the length of the Sancti Petri channel) during the years 2002 and 2004.

noticeable that these compounds exhibited a different distribution pattern along the channel. Thus, while a progressive decrease was confirmed toward the southern end, similar concentrations to those found at S10 were detected at the northern end, where the military naval station is located. This suggests that NPEOs and AEOs may originate from another source different from that for LAS and AES at the northern end. The explanation for this is that the two types of compound are employed for different uses and applications. Thus, LAS is mostly used in household detergents and AES is a component of shampoos and other personal care products, so their presence is typically associated to urban wastewater discharges. On the other hand, NPEOs, and their alternative, the AEOs, are surfactants also employed in industrial processes as well as for the cleaning of ships (Jonkers et al., 2003). It is also noticeable that the highest concentrations of AEOs in the zone (between 0.8 and 9.9 mg kg^{-1}) that were reported in two previous articles (Lara-Martín et al., 2006a; Petrovic et al., 2002), were far below those detected in the present study. Moreover, although AEOs have shown a high and fast biodegradability under laboratory tests (Huber et al., 2000), their levels along the channel were generally higher than those found for the rest of the surfactants. As commented in the Introduction, a limited set of homologs (only those with an even number of carbon atoms in their alkylic chains) and ethoxymers (from 1 to 8 EO units) were taken into account in those studies, whereas now we have considered the whole range for the first time. A second sampling was carried out during spring of 2004 in the central part of the channel and we detected a significant decrease in the concentration of all the surfactants, especially at the most contaminated point (station S10). This reduction (of between 47 and 74%) could be the consequence both of the halting of wastewater discharges and of the progressive sedimentation of non-contaminated particles after that, although anaerobic degradation processes occurring in the sedimentary column could not be discounted, because these compounds have been demonstrated to disappear in the absence of oxygen (Huber et al., 2000; Lara-Martín et al., 2007; Lee Ferguson and Brownawell, 2003; Nuck and Federle, 1996). This trend was also observed in dated sediment cores from the same area (data not shown). Lower values were

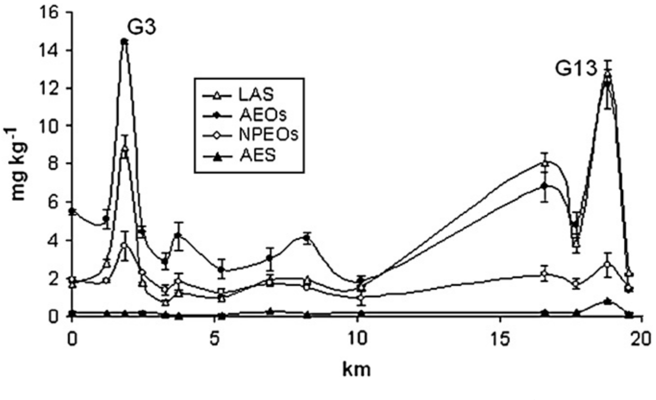

Fig. 3. Distribution of surfactants in surface sediments (mg kg^{-1}) in the zone B (Guadalete estuary).

Table 1
Total concentration of surfactants in sediment (μg kg^{-1}), water and suspended solids (μg L^{-1}) ($n = 3$) in zone C (Bornos reservoir)

Surfactant	Sediment				Water				Suspended solids			
	C1	C2	C3	C4	C1	C3	C4	C5	C1	C3	C4	C5
LAS	293 ± 39	682 ± 121	1938 ± 338	1713 ± 80	17.4 ± 0.8	16.1 ± 0.1	11.7 ± 0.8	10.7 ± 1.6	1.2 ± 0.2	1.3 ± 0.2	1.8 ± 0.5	2.6 ± 0.3
AES	47 ± 10	43 ± 12	132 ± 35	164 ± 28	n.d.	0.1 ± 0.1	0.1 ± 0.0	0.1 ± 0.0	n.d.	n.d.	n.d.	n.d.
NPEOs	260 ± 9	2388 ± 200	2664 ± 295	2700 ± 287	0.9 ± 0.3	1.0 ± 0.2	1.2 ± 0.1	1.2 ± 0.0	0.3 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	0.4 ± 0.2
AEOs	114 ± 41	1645 ± 25	2666 ± 146	2157 ± 320	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = non-detected (limits of detection: 1−10 μg kg^{-1} in sediment and 0.05 μg L^{-1} in water).

also found at the northern end, which was dredged during the year 2003 to facilitate navigation.

Fig. 3 shows the distribution of surfactants in sediments from zone B (estuary of the river Guadalete). Levels of these compounds were comparable with those found in zone A in 2004, once the untreated wastewater discharges ceased in this area. Two main sources could be detected: the first corresponding to the effluent of the WWTP located upstream (station G13) and the second near the town of El Puerto de Santa Maria, at the mouth of the river (not only at this location but centred on station G3). Levels of AEOs and LAS were very similar (12.2 and 12.8 mg kg^{-1}) in sediments at the discharge outlet of the WWTP, and considerably higher than those for NPEOs (2.7 mg kg^{-1}) and AES (0.8 mg kg^{-1}). These concentrations were relatively high in spite of urban wastewater being treated and the efficiency of this process in eliminating surfactants (McAvoy et al., 1998). As at sampling stations in zone A, differences in surfactant values could be explained by considering differences in the use of LAS and AEOs, the lower hydrophobic nature of AES and the restrictions imposed on NPEOs consumption. The concentration values were found to get lower moving downstream, especially for anionics, excepting at station G11, where the presence of a small dam reduces the flow velocity and, hence, facilitates sedimentation. Contamination by surfactants was again higher near the mouth of the river, reaching its highest value at station G3. There was a different relative distribution of surfactants at this point when compared with the previous station located upstream. Here, concentration of non-ionics (3.7 and 14.4 mg kg^{-1} for NPEOs and AEOs respectively) was higher in comparison with anionics (8.9 mg kg^{-1} for LAS and 0.2 mg kg^{-1} for AES) probably due to industrial and seaport activity on both banks of the river. Occasional urban wastewater discharges may also originate from the old sewage disposal network of the adjacent town (which is not connected to the WWTP).

Finally, the data on surfactant levels in zone C (Bornos reservoir) are given in Table 1. Concentrations in sediments were much lower than in zones A and B, almost certainly due to the much lower population in the area. Non-ionics (almost 2.7 mg kg^{-1} for NPEOs and AEOs) were predominant over anionics (up to 1.9 mg kg^{-1} for LAS and 0.2 mg kg^{-1} for AES) in sediments from this area. As in the other two cases, the presence of urban wastewater discharges, local industries and the existence of a small dock for recreational boats seemed to be the causes of this pollution. The lowest levels (<0.3 mg kg^{-1}) were detected at station C1, located near the WWTP outlet but also at reduced depth (<5 m) which makes it reasonable to think that during dry periods (such as summer months) this point is not covered by water and becomes oxic, so degradation processes are accelerated.

3.2. Transport and reactivity of surfactants

Fig. 4 shows the concentrations of each surfactant in suspended solids and in total water (water + suspended solids) over the length of the Guadalete river estuary (zone B). Their levels for aromatics ranged from 17.7 to 80.7 μg L^{-1} for LAS and from 1.6 to 8.9 μg L^{-1} for NPEOs. This agrees with previous studies, where similar concentrations were found in European (Jonkers et al., 2003; Terzic and Ahel, 1994), Japanese (Maruyama et al., 2000; Takada and Ogura, 1992) and USA (Naylor et al., 1992; Trehy et al., 1996) rivers. These data also represent some of the first known levels of aliphatic surfactants in European rivers, showing concentrations of up to 13.2 and 5.5 μg L^{-1} for AES and AEOs respectively, which were of the same order of magnitude as those reported in USA rivers (Dunphy et al., 2001; Fendinger et al., 1995; Neubecker, 1985; Popenoe et al., 1994; Sanderson et al., 2006). Values for AEOs in seawater are often below the limits of detection (Petrovic et al., 2002). Lower concentration values for

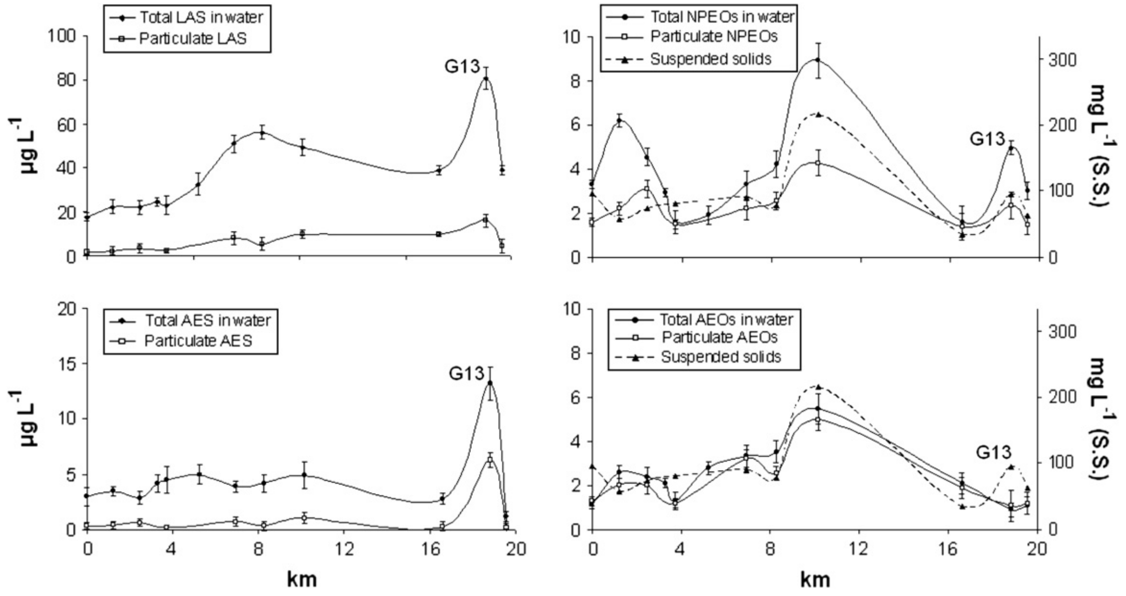

Fig. 4. Concentration of each surfactant in water and suspended solids (μg L^{-1}) over the length of zone B (Guadalete estuary). Concentration of suspended solids (mg L^{-1}) is also plotted.

these four surfactants ($<10\ \mu g\ L^{-1}$) were found in water at zone C (Table 1) due to the lower population living near this protected area. With respect to the estuary, a maximum was detected upstream, adjacent to the effluent discharge outlet of the WWTP (station G13), especially for LAS and AES, while higher concentrations for non-ionics were observed in the middle part of the estuary. This suggests that different transport mechanisms are taking place for each compound. In fact, a reactive behavior has been observed for these compounds along this estuary, by plotting salinity vs. dissolved concentration (Fig. 5a). Sorption is one of the main processes involved due to the relative hydrophobic nature of these compounds. In this respect, different partitioning could be observed depending on the hydrophobicity and sorption capacity of each compound: more polar anionic surfactants were predominant in the dissolved form (average values of only 13% ± 10 for LAS and 12% ± 7 for AES were found in the particulate phase) while non-ionics tended to be attached to the particulate phase (65% ± 23 for NPEOs and 86% ± 21 for AEOs), so these were transported associated with suspended solids (both compounds showing similar profiles, which can be observed in Fig. 4, where concentration of suspended solids is also plotted). Average coefficient sorption values (K_d) have been calculated in order to illustrate these differences and they seem to be directly proportional to their respective average K_{ow} (Fig. 5b), which confirms the existence of hydrophobic mechanisms that control sorption.

Sorption capacity was also reduced for those homologs with shorter alkyl chains, so their relative percentages in water were higher in comparison with those containing longer chains (Fig. 5c). Fig. 6a shows the differences in the homolog distributions in water and suspended solids from zone B. A standard commercial mixture is also represented. The same trend that was previously observed for LAS homologs (González-Mazo et al., 1998; León et al., 2002; Terzic and Ahel, 1994) was found for the aliphatic surfactants AES and AEOs, showing higher percentages of short-chain homologs such as C_{10}LAS, C_{12}AES or C_{12}AEOs in the dissolved form, whereas longer homologs exhibited higher affinity for the particulate phase. Once surfactants are attached to suspended solids they tend to be deposited on the bottom, where their bioavailability is lower and conditions are often anoxic. In this case sediments act as a sink for these compounds and concentrations can be several orders of magnitude higher than in water (as can be observed by comparing data in Figs. 3 and 4). Homolog distributions were different between these two phases, too. Fig. 6a also shows average homolog distributions for the target surfactants in sediments from zone B, which were similar to those found at zones A and C. It can be observed that relative percentages of those homologs with longer alkyl chains were higher in comparison with those found in commercial mixtures and surface waters. These distributions in sediments were also similar to those corresponding to suspended solids, although the concentrations of the most hydrophobic homologs such as C_{13}LAS, C_{16}AES and C_{18}AEOs, were somewhat higher in the first case.

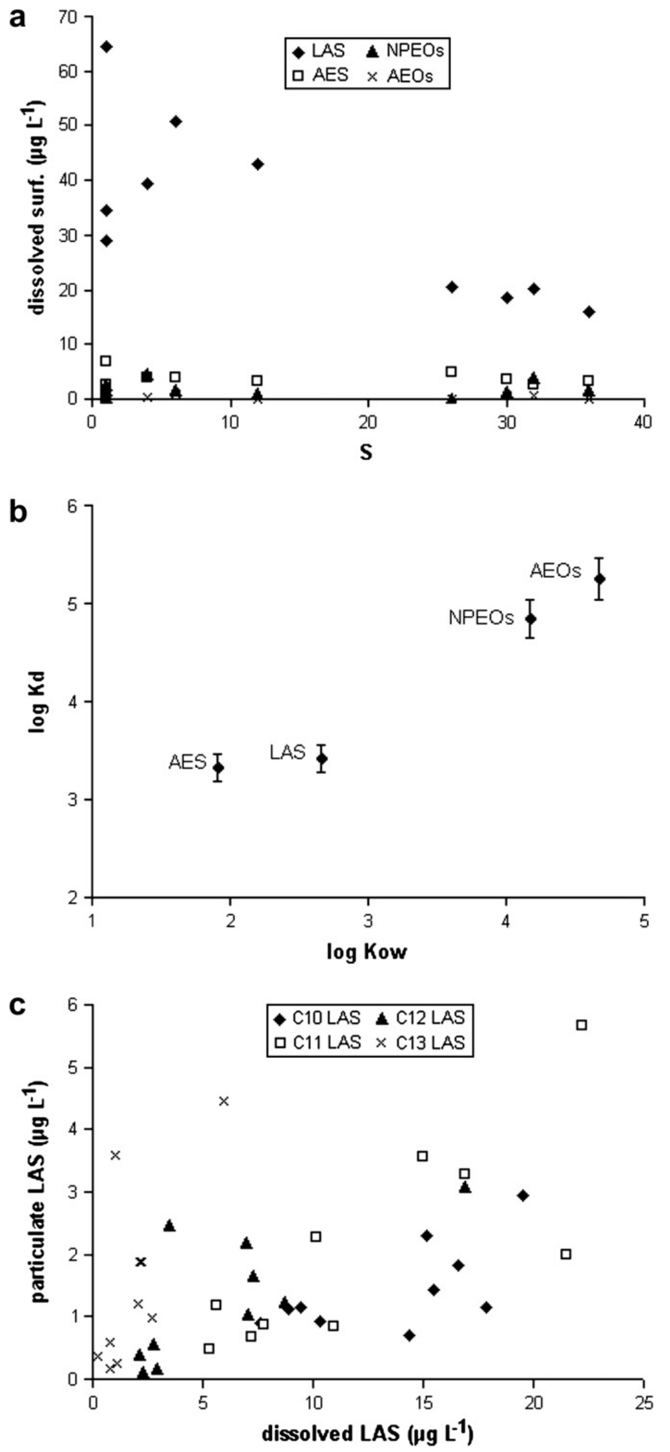

Fig. 5. a) Dissolved concentration for each surfactant studied vs. salinity at zone B (Guadalete estuary), b) calculated log K_d vs. average log K_{ow} for each surfactant, and c) particulate LAS concentration vs. dissolved LAS concentration in the same area.

Aliphatic surfactants can be derived from vegetable or animal fatty acids (so even-carbon numbered linear homologs are produced) or petroleum (resulting in odd- and even-carbon numbered linear alcohols which contain a certain proportion of mono-branched 2-alkyl isomers). Thus, it is noticeable (Fig. 6a) that AES detected came from the first type of source

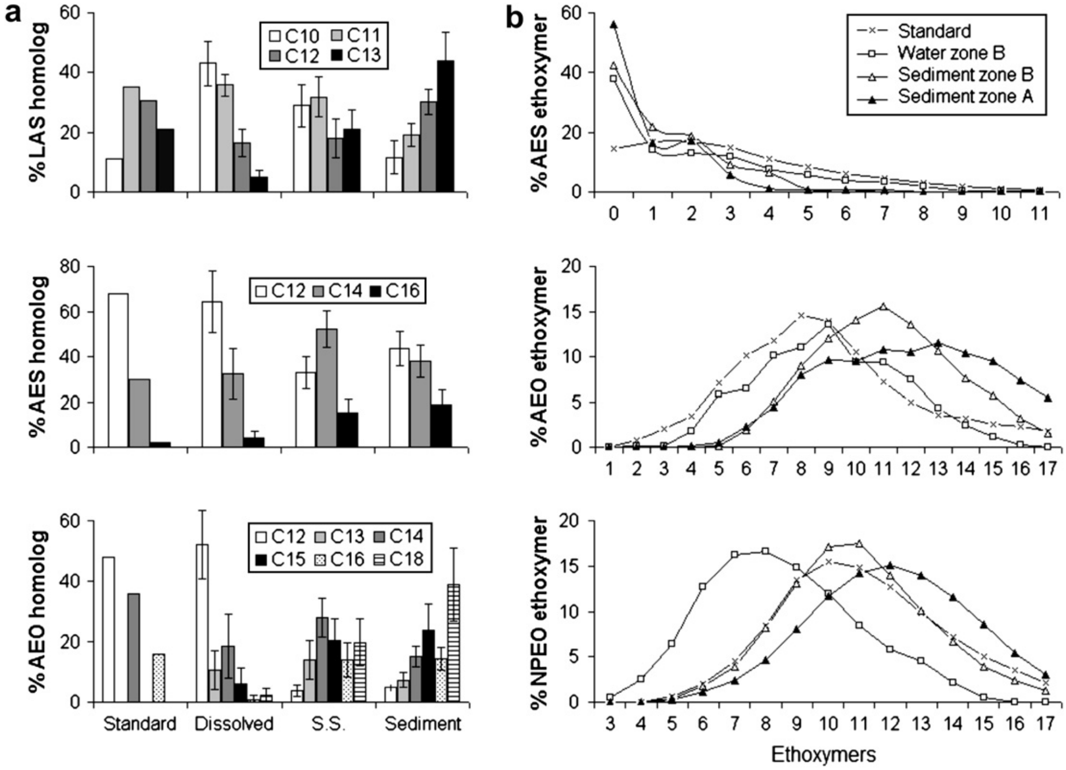

Fig. 6. Average homolog (a) and ethoxymer (b) distributions of surfactants in water, suspended solids and sediments from zones A and B. A commercial mixture is also represented.

because of their higher use in EU countries (71% of the total), although some traces of C_{13}AES and C_{15}AES (petrochemical homologs represent the remaining 29%) have been found occasionally (Lara-Martín et al., 2005). On the other hand, greater volumes of petrochemical AEOs are produced (60%) and these showed higher affinity for the particulate phase than AES, so every homolog was found at all the sampling stations. These homolog distribution patterns could found to differ significantly from one region to another, reflecting the use of different alcohol feedstocks (Petrovic et al., 2002). Moreover, further differences could be observed between AES and AEOs if we consider their respective ethoxymer distributions (Fig. 6b). Thus, the commercial mixture of AES has an average EO number of 3.1 but this value fell to 2.0 in water, and to 1.0 and 1.2 in sediments from zones A and B respectively. The main reason is the contribution of alkyl sulfates (with zero EO units) which account for 40% of the total, because they are also manufactured and used separately from AES, although the influence of degradation processes on the longer ethoxymers should not be discounted. With respect to AEOs, a similar average EO number could be observed for the commercial mixture and the water (8.8 and 9.0 respectively) whereas this value rose to 11.8 and 11.1 in sediments from zones A and B respectively. This was in accordance with previous laboratory assays which have demonstrated that the longer the alkyl and polyethoxylated chains, the higher the sorption capacity for non-ionic surfactants (Brownawell et al., 1997; John et al., 2000). NPEOs represent an intermediate situation: a decrease in the average EO number with respect to the standard (11.0) could be observed in water, whereas the value was slightly higher in sediment (up to 12.0).

Degradation, another of the main processes involved in the reactive behavior of surfactants in the aquatic environment, should be also considered for a fully understood of the homolog and ethoxymer distributions reported above. Fig. 7a shows the concentrations in water of SPCs and $NPE_{1-2}C$s, carboxylated metabolites from LAS and NPEOs respectively, along the Guadalete estuary (zone B). Almost the entire amount (>99%) of these degradation intermediates were found in the aqueous phase, which is not surprising considering their much higher polarity compared with their parent compounds (Isobe and Takada, 2004). Concentrations (up to 150 $\mu g\,L^{-1}$ for SPCs and less than 10 $\mu g\,L^{-1}$ for $NPE_{1-2}C$s) were of the same order of magnitude as those previously reported by other authors for different parts of the world (Ahel et al., 1994; Ding et al., 1999; Eichhorn et al., 2002; González-Mazo et al., 1997; Isobe and Takada, 2004; Jonkers et al., 2003, 2005; Lee Ferguson et al., 2001; León et al., 2002; Marcomini et al., 2000; Trehy et al., 1996). The highest values were found at station G13, which indicates that probably most of them were generated by degradation processes occurring at the WWTP, although the contribution of the biodegradation of surfactants along the estuary has to be considered too, in order to identify the different sources for these metabolites. Progressive shortening in the alkyl chain of SPC homologs could be observed over the length of the estuary (Fig. 7b), changing from long-chain (C_{10}–C_{13}SPCs) at G13 to short-chain homologs (C_5, C_6SPCs) at the mouth of the river. On the other hand,

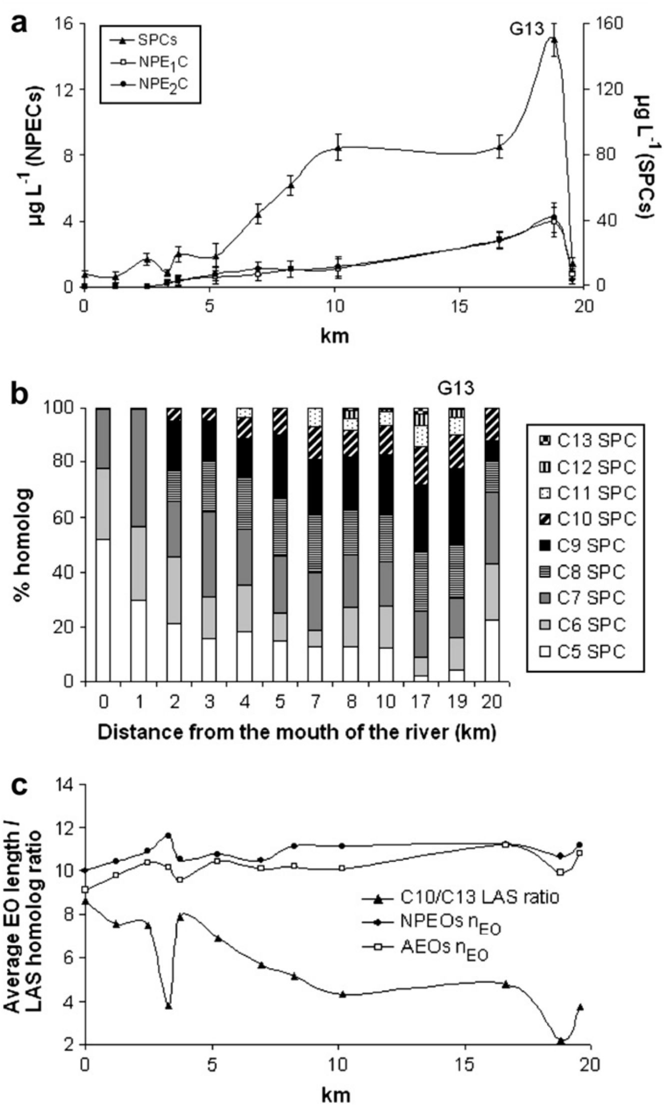

Fig. 7. a) Concentration of carboxylated metabolites from degradation of LAS (SPCs) and NPEOs (NPECs) (µg L^{-1}), b) distribution of SPC homologs in water samples and c) C_{10}/C_{13}LAS ratio and average EO numbers for NPEOs and AEOs from zone B (Guadalete estuary).

values of C_{10}/C_{13}LAS ratio (Fig. 6c) increased with the distance from the WWTP outlet, which implies that LAS was also being degraded during transport along the river (this process was preferential over long-chain homologs in aqueous phases according to the distance-principle by Swisher, 1987). Two exceptions to this trend could be found precisely at the sampling stations where LAS discharges were taking place, so homolog distribution was closer to that commonly found in commercial mixtures (the C_{10}/C_{13} LAS ratio decreases). Therefore it could be assumed that occurrence of SPCs at this zone was due to the existence of two origins, WWTP and in-situ biodegradation of LAS. The same could be stated for NPECs, but with reservations because there was only a very gradual decrease in the average EO number for NPEOs along the river (Fig. 7c). Most of this surfactant was found to be associated with suspended solids instead of being transported in dissolved form like anionics, so probably biodegradation was limited in that case. A similar conclusion could be inferred from Fig. 7c for AEOs, which showed even lower bioavailability and no metabolites were detected. Moreover, previous studies carried out at different European rivers (Ahel et al., 1994, 2000) and estuaries (Jonkers et al., 2003, 2005) polluted by wastewater have reported higher levels of NPECs than those for NPEOs and significantly higher values for the relative percentages of these metabolites nearer the sea, which are not found in our case, so probably most quantities of NPECs found in this area are generated at the WWTP rather than in-situ.

4. Conclusions

The present study provides several new insights into the distribution and environmental fate of surfactants in different aquatic systems, especially in the case of AES and AEOs, where there are almost no data. Surfactants are ubiquitous in sediments from both freshwater and coastal marine environments, acting as a sink for most hydrophobic organic compounds. Higher values have been detected next to urban wastewater discharge points and industrial/naval activities. However, significant decreases in their concentration have been observed towards farther sampling stations and after the halting of wastewater discharges. It has been reported for the first time that AEOs levels in these sediments are generally higher (up to several tens of ppm) than those found for the rest of the surfactants, most probably due to their strong hydrophobic character and high consumption rate. In respect to the water column, partitioning between water and suspended solids depends on the hydrophobicity and sorption capacity of each compound, so anionic surfactants and carboxylated metabolites are predominant in the dissolved form (87–99%) while non-ionics tend to be attached to the particulate matter (65–86%). Sorption capacity is reduced for those LAS, AES and AEO homologs with shorter alkyl chains, so their relative percentages in water are higher in comparison with those containing longer chains, which exhibit higher affinity for suspended solids and sediments. This process appears to play a major role in the reactive behavior of surfactants along the sampled estuary, especially in the case of the most hydrophobic non-ionics (NPEOs and AEOs), whereas biodegradation processes are favoured for anionics (LAS and AES) due to their higher bioavailability.

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References

Ahel, M., Giger, W., Schaffner, C., 1994. Behaviour of alkylphenol polyethoxylates surfactants in the aquatic environment – II. Occurrence and transformation in rivers. Wat. Res. 28, 1143–1152.

Ahel, M., Molnar, E., Ibric, S., Giger, W., 2000. Estrogenic metabolites of alkylphenol polyethoxylates in secondary effluents and rivers. Wat. Sci. Technol. 42, 15–22.

Bennett, E.R., Metcalfe, C.D., 1998. Distribution of alkylphenol compounds in Great Lakes sediments, United States and Canada. Environ. Toxicol. Chem. 17, 1230–1235.

Bester, K., Theobald, N., Schröder, H.Fr., 2001. Nonylphenol, nonylphenolethoxylates, linear alkylbenzenesulfonates (LAS) and bis (4-chlorophenyl)-sulfone in the German Bight of the North Sea. Chemosphere 45, 817–826.

Brownawell, B.J., Chen, H., Zhang, W., Westall, J.C., 1997. Sorption of nonionic surfactants on sediment materials. Environ. Sci. Technol. 31, 1735–1741.

Ding, W.H., Tzing, S.H., Lo, J.H., 1999. Occurrence and concentrations of aromatic surfactants and their degradation products in river waters of Taiwan. Chemosphere 38, 2597–2606.

Dunphy, J.C., Pessler, D.G., Morrall, S.W., Evans, K.A., Robaugh, D.A., Fujimoto, G., Negahban, A., 2001. Derivatization LC/MS for the simultaneous determination of fatty alcohol and alcohol ethoxylated surfactants in water and wastewater samples. Environ. Sci. Technol. 35, 1223–1230.

Eadsforth, C.V., Sherren, A.J., Selby, M.A., Toy, R., Eckhoff, W.S., McAvoy, D.C., Matthijs, E., 2006. Monitoring of environmental fingerprints of alcohol ethoxylates in Europe and Canada. Ecotoxicol. Environ. Saf. 64, 14–29.

Eichhorn, P., Rodrigues, S.V., Baumann, W., Knepper, T.P., 2002. Incomplete degradation of linear alkylbenzene sulfonate surfactants in Brazilian surface waters and pursuit of their polar metabolites in drinking waters. Sci. Total Environ. 284, 123–134.

Fendinger, N.J., Begley, W.M., McAvoy, D.C., Eckhoff, W.S., 1995. Measurement of alkyl ethoxylated surfactants in natural waters. Environ. Sci. Technol. 29, 856–863.

Folke, J., Cassani, G., Ferrer, J., López, I., Karlsson, M.O., Willumsen, B., 2003. Linear alkylbenzene sulphonates, branched dodecylbenzene sulphonates and soap analysed in marine sediments from the Baltic Proper and Little Belt. Tenside Surf. Det. 40, 17–24.

González-Mazo, E., Honing, M., Barceló, D., Gómez-Parra, A., 1997. Monitoring long-chain intermediate products from the degradation of linear alkylbenzene sulfonates in the marine environment by solid-phase extraction followed by liquid chromatography/ionspray mass spectrometry. Environ. Sci. Technol. 31, 504–510.

González-Mazo, E., Forja, J.M., Gómez-Parra, A., 1998. Fate and distribution of linear alkylbenzene sulfonates in the littoral environment. Environ. Sci. Technol. 32, 1636–1641.

Huber, M., Meyer, U., Rys, P., 2000. Biodegradation mechanisms of linear alcohol ethoxylates under anaerobic conditions. Environ. Sci. Technol. 34, 1737–1741.

Isobe, T., Takada, H., 2004. Determination of degradation products of alkylphenol polyethoxylates in municipal wastewaters and rivers in Tokyo. Japan. Environ. Toxicol. Chem. 23, 599–605.

Jobling, S., Sheahan, D., Osborne, J.A., Matthiessen, P., Sumpter, J.P., 1996. Inhibition of testicular growth in Rainbow trout (*Oncorhynchus mykiss*) exposed to estrogenic alkylphenolic chemicals. Environ. Toxicol. Chem. 15, 194–202.

John, D.M., House, W.A., White, G.F., 2000. Environmental fate of nonylphenol ethoxylates: differential adsorption of homologs to components of river sediment. Environ. Toxicol. Chem. 19, 293–300.

Jonkers, N., Laane, R.W.P.M., de Voogt, P., 2003. Fate of nonylphenol ethoxylates and their metabolites in two Dutch estuaries: evidence of biodegradation in the field. Environ. Sci. Technol. 37, 321–327.

Jonkers, N., Laane, R.W.P.M., de Voogt, P., 2005. Sources and fate of nonylphenol ethoxylates and their metabolites in the Dutch coastal zone of the North Sea. Mar. Chem. 96, 115–135.

Lara-Martín, P.A., Gómez-Parra, A., González-Mazo, E., 2005. Determination and distribution of alkyl ethoxysulfates and linear alkylbenzene sulfonates in coastal marine sediments from the Bay of Cadiz (southwest of Spain). Environ. Toxicol. Chem. 24, 2196–2202.

Lara-Martín, P.A., Petrovic, M., Gómez-Parra, A., Barceló, D., González-Mazo, E., 2006a. Presence of surfactants and their degradation intermediates in sediment cores and grabs from the Cadiz Bay area. Environ. Poll. 144, 483–491.

Lara-Martín, P.A., Gómez-Parra, A., González-Mazo, E., 2006b. Development of a method for the simultaneous analysis of anionic and non-ionic surfactants and their carboxylated metabolites in environmental samples by mixed-mode liquid chromatography – mass spectrometry. J. Chromatogr. A. 1137, 188–197.

Lara-Martín, P.A., Gómez-Parra, A., Köchling, T., Sanz, J.L., González-Mazo, E., 2007. Anaerobic biodegradation of linear alkylbenzene sulfonates in coastal marine sediments. Environ. Sci. Technol. 41, 3573–3579.

Lee Ferguson, P., Brownawell, B.J., 2003. Degradation of nonylphenol ethoxylates in estuarine sediment under aerobic and anaerobic conditions. Environ. Toxicol. Chem. 22, 1189–1199.

Lee Ferguson, P., Iden, C.R., Brownawell, B.J., 2001. Distribution and fate of neutral alkylphenol ethoxylate metabolites in a sewage-impacted urban estuary. Environ. Sci. Technol. 35, 2428–2435.

León, V.M., Sáez, M., González-Mazo, E., Gómez-Parra, A., 2002. Occurrence and distribution of linear alkylbenzene sulfonates and sulfophenylcarboxylic acids in several Iberian littoral ecosystems. Sci. Total Environ. 288, 215–226.

Marcomini, A., Pojana, G., Sfriso, A., Quiroga Alonso, J.M., 2000. Behavior of anionic and nonionic surfactants and their persistent metabolites in the Venice Lagoon, Italy. Environ. Toxicol. Chem. 19, 2000–2007.

Maruyama, K., Yuan, M., Otsuki, A., 2000. Seasonal changes in ethylene oxide chain length of poly(oxyethylene)alkylphenyl ether nonionic surfactants in three main rivers in Tokyo. Environ. Sci. Technol. 34, 343–348.

McAvoy, D.C., Dyer, S.D., Fendinger, N.J., Eckhoff, W.S., Lawrence, D.L., Begley, W.M., 1998. Removal of alcohol ethoxylates, alkyl ethoxylate sulfates, and linear alkylbenzene sulfonates in wastewater treatment. Environ. Toxicol. Chem. 17, 1705–1711.

Naylor, C.G., Mieure, J.P., Adams, W.J., Weeks, J.A., Castaldi, F.J., Ogle, L.D., Romano, R.R., 1992. Alkylphenol ethoxylates in the environment. JAOCS 69, 695–703.

Neubecker, T.A., 1985. Determination of alkylethoxylated sulfates in wastewaters and surface waters. Environ. Sci. Technol. 19, 1232–1236.

Nuck, B.A., Federle, T.W., 1996. Batch test for assessing the mineralization of ^{14}C-radiolabeled compounds under realistic anaerobic conditions. Environ. Sci. Technol. 30, 3597–3603.

Petrovic, M., Rodriguez Fernández-Alba, A., Borrull, F., Marce, R.M., González-Mazo, E., Barceló, D., 2002. Occurrence and distribution of nonionic surfactants, their degradation products, and linear alkylbenzene sulfonates in coastal waters and sediments in Spain. Environ. Toxicol. Chem. 21, 37–46.

Pojana, G., Cassani, G., Marcomini, A., 2004. Determination, aerobic biodegradation and environmental occurrence of aliphatic alcohol polyethoxylate sulfates (AES). Int. J. Environ. Anal. Chem. 84, 729–738.

Popenoe, D.D., Morris III, S.J., Horn, P.S., Norwood, K.T., 1994. Determination of alkyl sulfates and alkyl ethoxysulfates in wastewater treatment plant influents and effluents and in river water using liquid chromatography/ion spray mass spectrometry. Anal. Chem. 66, 1620–1629.

Sanderson, H., Dyer, S.D., Price, B.B., Nielsen, A.M., van Compernolle, R., Selby, M., Stanton, K., Evans, A., Ciarlo, M., Sedlak, R., 2006. Occurrence and weight-of-evidence risk assessment of alkyl sulfates, alkyl ethoxysulfates, and linear alkylbenzene sulfonates (LAS) in river water and sediments. Sci. Total Environ. 368, 695–712.

Swisher, R.D., 1987. Chemical Structure and Primary Biodegradation. Surfactant Biodegradation. In: Surfactant Science Series 18. Marcel Dekker, New York.

Takada, H., Ogura, N., 1992. Removal of linear alkylbenzenesulfonates (LAS) in the Tamagawa estuary. Mar. Chem. 37, 257–273.

Terzic, S., Ahel, M., 1994. Input and behaviour of linear alkylbenzenesulphonates (LAS) in a stratified estuary. Mar. Poll. Bull. 28, 735–740.

Trehy, M.L., Gledhill, W.E., Mieure, J.P., Adamove, J.E., 1996. Environmental monitoring for linear alkylbenzene sulfonates, dialkyltetralin sulfonates and their biodegradation intermediates. Environ. Toxicol. Chem. 15, 233–240.

Ying, G.G., 2006. Fate, behavior and effects of surfactants and their degradation products in the environment. Environ. Int. 32, 417–431.