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DETERMINATION AND DISTRIBUTION OF ALKYL ETHOXYSULFATES AND LINEAR ALKYLBENZENE SULFONATES IN COASTAL MARINE SEDIMENTS FROM THE BAY OF CADIZ (SOUTHWEST OF SPAIN)

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Abstract—The distribution of the two main anionic surfactants manufactured and used in the world, alkyl ethoxysulfates (AES) and linear alkylbenzene sulfonates (LAS), has been studied in sediments from a salt marsh and an estuary of the Bay of Cadiz (southwest of Spain). The identification and quantification of AES and LAS was carried out after automated Soxhlet extraction with methanol, followed by solid-phase extraction and liquid chromatography coupled to electrospray mass spectrometry. The latter procedure permitted the unequivocal identification of every LAS homologue as well as the AES homologues of up to 16 carbon atoms in their alkyl chain and of up to 12 ethylene oxide groups. Recoveries were in the range of 51% to 84% and limits of detection from 1 to 5 μg/kg. We have focused our attention particularly on AES because, in spite of their great use, these compounds have received less attention than LAS and their occurrence has not been described in marine environmental samples. Alkyl ethoxysulfates concentration values range between 100 and 400 μg/kg in the topmost layer of sediments at the sampling areas. The relative distribution of AES homologues shows higher percentages for the longer alkyl chain homologues in sediments as well as for the shorter ethoxymers. A decrease in LAS concentrations has been found relative to past studies in one of the sampling areas as a consequence of the reduction of urban wastewater discharges.

Keywords—Anionic surfactants Alkyl ethoxysulfates Alkyl sulfates Linear alkylbenzene sulfonates Marine sediments

INTRODUCTION

Surfactants are the primary cleaning agents used in laundry and cleaning products. Approximately 65% of the worldwide production of these chemicals are anionic surfactants. Alkyl ethoxysulfates (AES) and linear alkylbenzene sulfonates (LAS) comprise the largest volume of anionic surfactants currently in commercial use in Europe, where 400,000 tons of LAS ([1]; http://www.heraproject.com/files/04%20-HERA%20LAS%20Full%20web%20wd%20version%202%20may1.pdf) and 276,000 tons of AES ([2]; http://www.heraproject.com/files/1-E-04-HERA%20AES%20ENV%20%20web%20wd.pdf) are consumed yearly. Commercial surfactants are most often mixtures with variable compositions. In the case of AES (Fig. 1a), their chemical structure in commercial formulations comprises an alkyl chain length of 12 to 16 carbon units joined to an ethylene oxide (EO) chain of between 1 and 12 EO units with a terminal sulfate group. Also, AES mixtures typically contain various proportions of alkyl sulfates (AS), but with no EO units. These compounds, AES and AS, are produced via sulfation of alcohol polyethoxylates (AEOs) or fatty alcohols, respectively, and both are in common use in shampoos, hand dishwashing liquids, and laundry detergents. The commercial formulation of LAS (Fig. 1b) is a mixture of homologues, most with alkyl chain lengths of between 10 and 14 carbon atoms. Each of these homologues consists of various positional isomers. Linear alkylbenzene sulfonates are commonly used in household detergents and surface cleaners.

The environmental behavior of LAS, as one of the most widely used xenobiotic organic compounds, has generated considerable interest and study. A large number of articles have appeared dealing with determination methods for LAS during the last decade, as reviewed by Reemtsma [3], as well as for the biodegradation intermediates of LAS, the sulfophenyl carboxylic acids [4–7]. Linear alkylbenzene sulfonates distribution in continental and marine areas [8–11] and their aerobic and anaerobic biodegradation [12–15] have been studied among other processes in the environment, as well as their sorption in marine sediments [16,17]. In contrast, with respect to the AES, there is very little information about them. Analytical methods for AES are reported only in a few articles on their nonspecific determination by the methylene blue active substance method [18] or identification and quantification in wastewaters and surface waters by gas chromatography/mass spectrometry [19]. High-performance-liquid chromatography/mass spectrometry (HPLC/MS) also has been used for the determination of AES in wastewater and river waters [20] and sewage sludge [21]. Several biodegradation test studies have been carried out, showing rapid AES biodegradation under aerobic conditions [22–24], as in the case of LAS, as well as the efficient elimination of both surfactants in wastewater treatment plants (WWTPs) [25–27]. Alkyl ethoxysulfates biodegradation in anaerobic conditions has also been reported [14,28–30]. However, there is a significant lack of environmental data for this surfactant and its environmental behavior, especially in the marine environment, where no studies have been carried out.

This article presents a new and highly specific method for the simultaneous determination of these major anionic surfactants, AES and LAS, in marine environmental matrices such

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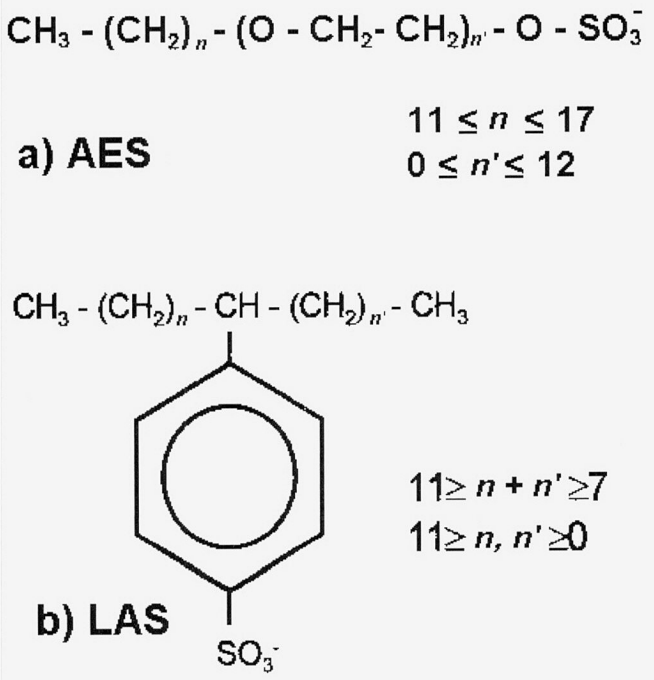

Fig. 1. General chemical structures of (**a**) alkyl ethoxysulfates (AES) and (**b**) linear alkylbenzene sulfonates (LAS) compounds.

as sediments, based on automated hot Soxhlet extraction followed by purification and preconcentration by using solid-phase extraction (SPE) cartridges and identification and quantification by means of HPLC/MS. To our knowledge, this is the first time that AES levels have been reported in the marine environment and, in view of this, relevant information about their distribution and environmental behavior is shown. Therefore, the aims of the research presented in this article are: first, the isolation, identification, and quantification of the major anionic surfactants (AES and LAS) in marine sediments, by means of a new method that combines automated hot Soxhlet extraction, SPE, and HPLC/MS, and second, to demonstrate for the first time the presence of AES in the marine environment, as well as their distribution in sediment samples from a coastal marine area (Bay of Cadiz) compared with that of LAS in the same zone.

MATERIAL AND METHODS

Chemicals

All solvents used as the chromatographic eluents in the experiments (water, acetonitrile, and methanol) were of chromatography quality and purchased from Scharlau (Barcelona, Spain). Triethylamine and acetic acid were purchased from Scharlau and Panreac (Barcelona, Spain), respectively. Commercial mixtures of AES were kindly supplied by KAO Corporation (Barcelona, Spain) and The Procter and Gamble Company (P&G Cincinnati, OH, USA). 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. Commercial LAS and a C_{16} LAS pure standard were supplied by Petroquímica Española S. A. (PETRESA, Cadiz, Spain). The proportional composition of the different homologues for LAS is as follows: C_{10} (10.9%), C_{11} (35.3%), C_{12} (30.4%), C_{13} (21.2%), and C_{14} (1.1%).

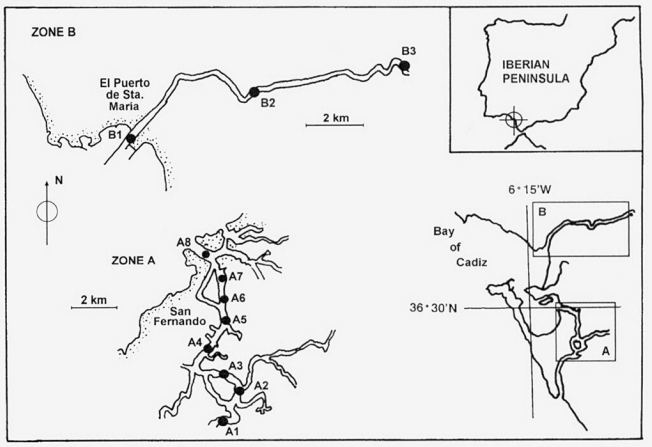

Fig. 2. Map of the Bay of Cadiz (southwest Spain), showing its location and the positions of the sampling stations (A1–A8 and B1–B3).

Study area

The study was carried out in two different areas (Fig. 2) in a salt-marsh environment in the Bay of Cadiz (southwest of Spain). The first area (indicated as zone A in Fig. 2) is an 18-km-long tidal channel (Sancti Petri channel) in the south of the bay that connects the inner part of the bay with the Atlantic Ocean. Sediment grab samples were taken from eight stations (A1–A8) along the length of this channel. The discharge outlet for the untreated urban effluents from San Fernando, a town of about 100,000 inhabitants, was formerly situated on this channel (20 m away from A5). These urban wastewater discharges had a considerable effect on the study area due to its shallow waters and, hence, low volume. The grab samples were taken in December 2002 after the construction in summer of 2002 of a nearby WWTP that now treats this urban wastewater and discharges it into the open sea, not into the channel.

The second area (indicated as zone B in Fig. 2) is the final stage of an estuary (river Guadalete) in the north of the bay. Sediment grab samples were taken from three stations in May and November 2002. The first of these stations (B1) is located at the mouth of this river, where El Puerto de Santa Maria, a town of about 150,000 inhabitants, is situated; a WWTP has been in operation here for several years, so there are only occasional untreated discharges from the city into the river. The third station (B3) is located adjacent to the effluent discharge point of the WWTP of Jerez (a city of about 250,000 inhabitants upstream). Also an intermediate station (B2) was sampled.

Sampling and pretreatment of the samples

The stations were sampled from a pneumatic launch on an ebbing tide by means of a Van Veen grab (Hydro-Bios, Kiel, Germany), taking the topmost 10-cm layer of the sediments. The sediment samples were maintained at a temperature of 4°C during transfer to the laboratory, where they were frozen and stored until the time of analysis. Later, the sediments were dried in a heater until constant weight. The dried samples of sediment were milled using a zirconium oxide ball mill (Fritsch, Idar-Oberstein, Germany) and passed through a 0.063-mm sieve.

Five grams of these sediments were extracted with methanol in an automated Soxhlet unit (Büchi, Flawil, Switzerland) for

Table 1. Recovery percentages (SD = standard deviation and $n = 9$) obtained for sediment spiked with linear alkylbenzene sulfonates (LAS) and alkyl ethoxysulfates (AES); SD = standard deviation

LAS homologue	Recovery (% ± SD)	AES homologue	Recovery (% ± SD)
C_{10} LAS	76 ± 10	C_{12} AES	84 ± 13
C_{11} LAS	78 ± 13	C_{13} AES	67 ± 14
C_{12} LAS	73 ± 13	C_{14} AES	55 ± 10
C_{13} LAS	76 ± 12	C_{15} AES	51 ± 7

5 h in hot Soxhlet mode. The methanolic extract was then evaporated until completely dry in a rotary evaporator, and the residue was redissolved in 100 ml of water in an ultrasonic bath. These extracts were purified and preconcentrated by solid-phase extraction using minicolumns of the hydrophobic C_{18} type (500 mg, Bond Elut; Varian, Harbor City, CA, USA) in an automated SPE AutoTrace unit (Zymark, Hopkinton, MA, USA). These C_{18} cartridges were rinsed with 10 ml of methanol and 5 ml of water before passing the 100 ml of sediment extracts. Then they were washed with 5 ml of water and eluted with 10 ml of methanol. Finally, the elution was evaporated until dryness and redissolved in 1 ml of methanol:water 1:1, where 1 μg/ml of C_{16} LAS was added as an internal standard.

Spiked sediments

Recovery studies were performed by spiking nonpolluted sediments with 1, 5, and 10 mg/kg of commercial standards of AES (supplied by P&G) and LAS (supplied by PETRESA). For this purpose, 100 g of wet sediment were mixed by means of a mechanical arm during 24 h with 100 ml of seawater containing AES and LAS. The entire mixture was poisoned with 1 g of $HgCl_2$ and kept in darkness to avoid surfactant degradation. Finally, these spiked sediments were treated in triplicate ($n = 9$) in the same way as the sediment grab samples to calculate the method recovery values.

Recoveries around 80% were found for LAS and AES, except for the longer AES homologues. The lower values of these latter are probably due to their more hydrophobic character and, consequently, their retention in the sediment and in the SPE cartridge. No significant differences were found for the three spiked concentrations. Results are shown in Table 1.

AES and LAS determination

Alkyl ethoxysulfates (AES) and LAS were analyzed using a Spectrasystem liquid chromatograph (Thermo Spectrasystem, San Jose, CA, USA) with autosampler coupled to a LCQ ion-trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA). The homologues were separated using a Luna C-18 column of 125 mm length and 2 mm internal diameter, with a particle size of 3 μm (Phenomenex, Torrance, CA, USA). Water (with 5 mM of acetic acid and triethylamine added) and a mixture of acetonitrile and water in relation 80:20 were used as solvents in the following gradient (flow = 0.15 ml/min): initial conditions 47% A, linearly increased to 100% A in 40 min and kept isocratic for 10 min. The injection volume into the LC/MS system was 100 μl. For routine analysis, electrospray ionization was used in the mass spectrometer, scanning the mass/charge (m/z) range between 75 and 800 in full-scan negative-ion mode. Other MS parameters values were ion fragmentation energy, −40 V; needle tip voltage, 4.5 kV; gas stealth flow, 60 ml/min; and ion source temperature 220°C.

Identification of each LAS homologue and AES ethoxymer was carried out by monitoring their main fragment ions and their specific fragment ion with m/z 183 and 97, respectively (Table 2). Concentrations of LAS homologues were determined by measuring the peak areas of the main fragment ions by using external standards followed by normalization by means of a C_{16} LAS used as the internal standard. Alkyl ethoxysulfates homologues were determined using their main fragment ions by the sum of their ethoxymers areas from 0 to 12 EO units. The system was linear for all the homologues ($r^2 > 0.999$) between 0.5 and 20 mg/L (0.5, 1, 2, 5, 10, and 20 mg/L). Under the experimental conditions used, the observed minimum detectable concentration for each homologue (three times the standard deviation of the blank) was between 1 and 5 μg/kg in sample. Also, clean sediment extracts and a methanol:water 1:1 solution were spiked with 1 mg/L of LAS and AES standards to check the influence of ion suppression (suppression of the analytes signals caused by high concentrations of matrix components) on the MS detection of target compounds. The influence of ion suppression was determined to be a reduction of less than 5% on the signal intensity for each analyte.

Table 2. Mass/charge (m/z) relations scanned for the identification of linear alkylbenzene sulfonates (LAS), alkyl ethoxysulfates (AES), and alkyl sulfates (AS). EO is the number of ethoxy units (arrows indicate that it is needed to add 44 m/z units consecutively in order to get the m/z relations for the AES ethoxymers existing between 1 and 10–12)

Compound	m/z	Compound	m/z
C_{10} LAS	297, 183	C_{14} AS	293, 97
C_{11} LAS	311, 183	C_{14} AES $n_{EO} = 1$	337, 97
C_{12} LAS	325, 183	↓	+44
C_{13} LAS	339, 183	C_{14} AES $n_{EO} = 11$	777, 97
C_{12} AS	265, 97	C_{15} AS	307, 97
C_{12} AES $n_{EO} = 1$	309, 97	C_{15} AES $n_{EO} = 1$	351, 97
↓	+44	↓	+44
C_{12} AES $n_{EO} = 12$	793, 97	C_{15} AES $n_{EO} = 11$	791, 97
C_{13} AS	279, 97	C_{16} AS	321, 97
C_{13} AES $n_{EO} = 1$	323, 97	C_{16} AES $n_{EO} = 1$	365, 97
↓	+44	↓	+44
C_{13} AES $n_{EO} = 11$	763, 97	C_{16} AES $n_{EO} = 10$	761, 97

RESULTS AND DISCUSSION

AES identification in the marine environment

The upper part of Figure 3 shows two LC/MS chromatograms obtained from a standard solution (Fig. 3a) and from a sample taken at a station in the Sancti Petri channel (Fig. 3b), by applying the procedure described in the preceding section, *AES and LAS determination*. An increase in the retention time for homologues with higher length of the alkyl chain can be observed for both surfactants in the total ion current chromatogram, but it is not possible in a first approach to achieve a complete separation among them with the HPLC conditions employed. In this case, LAS homologues show higher signal intensity and overlap to the AES signal.

According to Jewett et al. [31] and to Gonzalez-Mazo et al. [5], under the HPLC/MS conditions used (electrospray ionization and negative ion mode), these surfactants should show a specific fragment ion with m/z 97 for AES, corresponding to their sulfate group ($[HSO_4]^-$), and with m/z 183 for LAS. Really, as shown in the middle part of Figure 3, these specific fragment ions allow us to distinguish between the different LAS and AES homologues, just by scanning them (m/z 183 and 97, respectively) within the total ion current chromato-

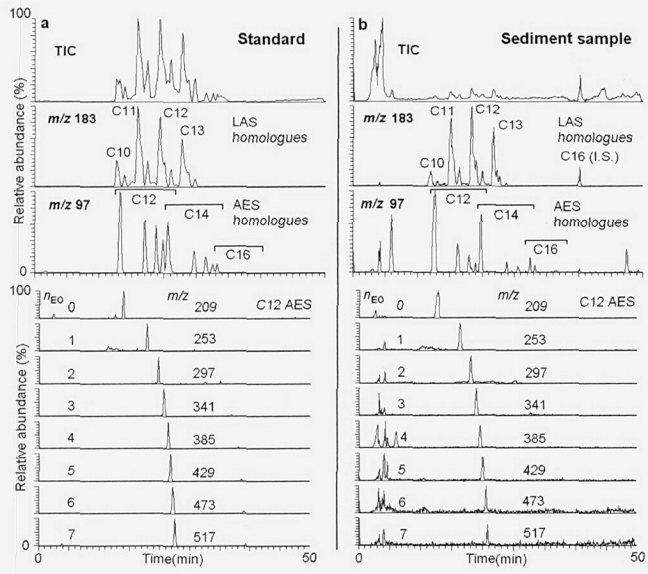

Fig. 3. Liquid chromatography/mass spectrometry (LC/MS) electrospray ionization negative ion chromatograms from (**a**) a standard solution and (**b**) a sediment sample. Total ion current (TIC) and specific fragment ions with mass/charge 183 for linear alkylbenzene sulfonates (LAS) and 97 for alkyl ethoxysulfates (AES) are shown, as well as C_{12} AES homologues from n_{EO} = 1 to n_{EO} = 7 and C_{12} AS (n_{EO} = 0) (EO is the number of ethoxy units).

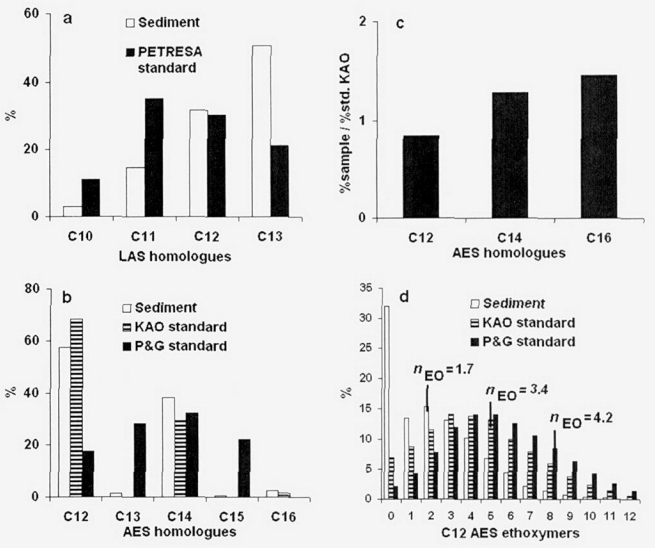

Fig. 5. Typical homologues distribution in percentages for (**a**) linear alkylbenzene sulfonates (LAS) and (**b**) alkyl ethoxysulfates (AES) in sediments and commercial standards from KAO (Barcelona, Spain), Procter and Gamble Company (P&G Cincinnati, OH, USA) and Petroquímica Española (PETRESA, Cadiz, Spain). Two additional distributions are shown for AES: (**c**) an average normalized distribution indicating % of each homologue in sample/% of each homologue in KAO standard (std. KAO) and (**d**) an average distribution of ethoxymers for C_{12} AES in sediments and commercial standards (EO is the number of ethoxy units).

gram. Hence, we can search for all the ethoxymers and ASs, with n_{EO} = 0, in the AES standard as well as in sediment samples by scanning their main fragment ions. The lower part of Figure 3 shows C_{12} AES ethoxymers from 0 to 7 in a standard (Fig. 3a) and in a sediment sample (Fig. 3b), as an example, where the separation of ethoxymers with 0, 1, 2, and 3 ethoxylated groups, the most abundant in environmental samples, is achieved, while the rest of ethoxymers are eluted into the same chromatographic peak.

Full-scan mass spectra shown on the left part of Figure 4 for C_{13} LAS and C_{13} AES with n_{EO} = 2 confirm the identification of LAS and AES in standards (Fig. 4a) and sediment samples (Fig. 4b), where 339 and 367 correspond to their main fragment ions and 183 and 97 to their specific fragment ions, respectively. Also using the LCQ MS/MS capabilities, final confirmation of the presence of AES in sediments was achieved by means of studying the generation of the *m/z* 97-specific fragment ion from the main fragment of one of the AES ethoxymers: *m/z* 381 for the C_{14} AES with n_{EO} = 2 (right part of Fig. 4). That demonstrates that the procedure developed produces chromatograms showing an efficient separation of each LAS homologue and AES ethoxymer without interference and with sufficient intensity to permit an accurate quantification by LC/MS.

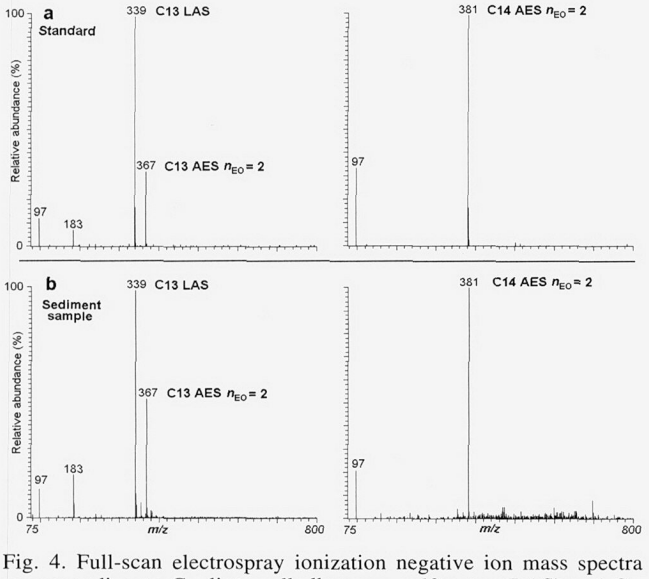

Fig. 4. Full-scan electrospray ionization negative ion mass spectra corresponding to C_{13} linear alkylbenzene sulfonates (LAS) and C_{13} AES and MS/MS spectra corresponding to C_{14} alkyl ethoxysulfates (AES) with n_{EO} = 2 in (**a**) a standard solution and (**b**) in a sediment sample (EO is the number of ethoxy units).

AES and LAS homologues distribution in sediments

Analyzing the sediment samples taken in the Bay of Cadiz, we have found C_{10} to C_{13} LAS homologues and traces of C_{14} LAS, as well as C_{12} to C_{16} AES homologues with n_{EO} from 0 to 12 in all samples. A typical homologues distribution of each surfactant in sediments is shown in Figure 5a and b, where differences between sediments and commercial standards can be observed. Linear alkylbenzene sulfonates and AES homologues distributions have been found to show very little variation among all the sampling stations. The LAS homologues distribution presents a typical distribution that has been described in past articles [9,16], where the concentration of homologues in sediment increases with their alkyl chain length due to their greater hydrophobicity and, consequently, greater affinity for the particulate phase.

In contrast, in the AES homologues distribution, it can be observed (Fig. 5b) that homologues with an alkyl chain with an even number of carbon atoms (primarily C_{12} and C_{14} homologues, but also C_{16}) are predominant over homologues with an odd number (like C_{13} and C_{15}). The explanation for this distribution is that, in Europe, coconut-type alcohol polyethoxylates (AEOs, with an even number of carbon atoms in

their alkyl chains) are the primary source for the synthesis of AES [2] and most commercial AES mixtures (~71%), like the KAO standard, are manufactured with only even-numbered homologues. However, traces of odd-numbered homologues are also detected due to the less frequent use (31% in Europe) of commercial AES mixtures similar to P&G standard. It is this latter kind of AES that is most often used in the United States, where they are produced using AEOs feed stocks, which have alkyl chains between 12 and 15 carbon units [20]. For this reason, different homologues distributions of AES can be expected in sediments of different regions depending on the type of AEOs homologues employed in their production. Also, as we can see in Figure 5c, the relative proportions of longer alkyl chain homologues in sediment are higher in comparison with commercial standards proportions, because these longer homologues show a greater hydrophobicity and affinity for the particulate phase, as in the case of LAS previously described.

Comparing ethoxymer distribution for an AES homologue like C_{12} AES in commercial standards and in sediments (Fig. 5d), it can be observed that the average number of EO units in this surfactant decreases from 4.2 or 3.4 in the standards (for P&G and KAO standards, respectively) to 1.7 in sediments, with the proportion of AS increasing from less than 5% in the AES standards to more than 30% in sediments. These differences may be explained due to the existence of other sources of AS apart from their presence as impurities in AES mixtures because AS compounds are also manufactured and used separately. In fact, AS even alkyl chain homologues from C_{12} to C_{18} AS were found, while no levels of AS with odd homologues were detected in most of the sampling stations due to their low usage (less than 10% in Europe ([32]; http://www.heraproject.com/files/3-E-04-HERA%20AS%20Env%20web%20wd.pdf). Another factor that explains the abundance of lower AES ethoxymers in sediment is the increasing hydrophobicity of AES in line with the lower number of EO units, which enhances their affinity for the organic carbon present in the sediments. Also, AES degradation as a result of the shortening of their ethoxylated chain, as has been described previously in laboratory tests in other studies on these surfactants [22] and on other similar surfactants, like AEOs [33] and alkylphenol polyethoxylates (APEOs) [34], should be considered.

Spatial distribution of AES and LAS

Figure 6a and 6b shows the variation for LAS and AES concentrations, respectively, at the different sampling stations along the Sancti Petri channel. Distances are shown from the sampling station A1 (10 km away from the Atlantic Ocean entrance) to A8 (at the inner bay exit). It can be observed that the LAS values found near the old effluent discharge point of the city of San Fernando (sampling station A5) are high, close to 10 mg/kg, higher even than those reported for highly contaminated parts of the lagoon of Venice, Italy [10], or the bay of Tokyo, Japan [35]. However, a notable decrease has been detected when these results are compared with the data published by Gonzalez-Mazo et al. [9] some years ago, around 50 mg/kg. This finding is explained mainly by the construction and entry into service of a WWTP six months before the time of the sampling, which has contributed to a considerable reduction of the wastewater discharges into the channel. The LAS concentration decreases sharply the further the sampling station is from the effluent discharge point, due to dilution and degradation processes that take place in the marine environment, with values lower than 1 mg/kg being found between the stations A1 and A2. An exception can be found in the last station, A8, at the beginning of the inner part of the bay, a consequence of the fact that discharges in that point from a wastewater outlet belong to a small settlement not connected to the WWTP. In respect of the AES concentration levels (shown in Fig. 6b as the sum of all homologues and ethoxymers found), it can be observed that their values are notably lower than for LAS, especially near the effluent outlet, mainly due to their lower production and usage. Also, fast anaerobic biodegradation for AES has been reported [28–30] and must be considered. Their longitudinal profile is very similar to that of LAS, although the trend observed is less clear, with lower differences between stations. However, lack of environmental

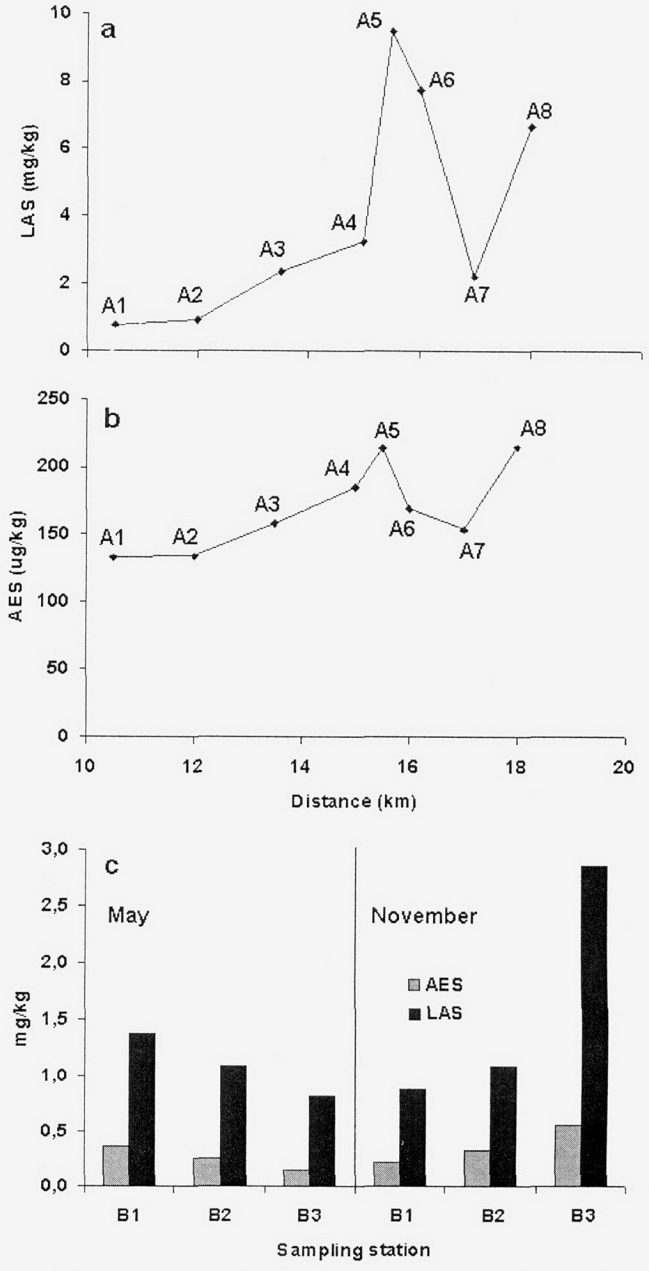

Fig. 6. Longitudinal profiles showing concentrations of linear alkylbenzene sulfonate (LAS) and alkyl ethoxysulfates (AES) in sediments at sampling stations (A1–A8) along (**a**) and (**b**), the Sancti Petri channel (zone A) and (**c**) the river Guadalete (zone B), both zones located in the southwest of Spain.

data about these compounds does not allow us to compare these values with other zones and to establish further discussions.

Figure 6c shows the variation in the LAS and AES concentrations in the three sampling stations along the estuary of river Guadalete: B1, at the river mouth, near the town of El Puerto de Santa Maria; B3, near the effluent outlet of the WWTP of the city of Jerez; and B2, an intermediate station. In this estuary, LAS concentration values are around 1 mg/kg, notably lower than those in the Sancti Petri channel. During the sampling realized in May, there are no significant differences in LAS concentration along the estuary, although higher LAS values are found at sampling station B1, probably due to occasional urban wastewater discharges from the town. Lower LAS concentrations are found at the other two stations, B2 and B3, although LAS is still present because of its discharge in the effluent of the WWTP of Jerez. However, in November, high LAS concentrations are detected at the B3 station, up to 3 mg/kg, a consequence of the high precipitations that happened during this season (autumn), which forced the WWTP of Jerez to discharge wastewater without previous depuration. As in Sancti Petri channel, AES presents a similar distribution in comparison with that of LAS, with concentration values ranging between 150 and 400 μg/kg (except the month of November at B3 station, when more than 500 μg/kg were detected); therefore, these two surfactants may originate from the same sources along the entire length of this estuary as well as the tidal channel and can be considered effective indicators for urban wastewater discharges.

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