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Occurrence and distribution of linear alkylbenzene sulfonates and sulfophenylcarboxylic acids in several Iberian littoral ecosystems

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Abstract

The distribution of linear alkylbenzene sulfonates (LAS) and sulfophenylcarboxylic acids (SPC) has been characterized in water and sediment of five Iberian estuaries and a saltmarsh channel. The highest concentrations of LAS and SPC were detected in shallow zones close to discharge points of untreated urban effluent, and decreased sharply with increasing distance from these. SPC homologues of between 3 and 12 carbon atoms were detected, although their concentrations were several orders of magnitude lower than the corresponding LAS. The highest SPC concentrations found were of medium carboxylic chain lengths (C6–C8) in water, and of longer chain lengths (C9–C11) in particulate material. LAS homologues were associated preferentially with the particulate material. The vertical distribution of LAS in the water column was not homogeneous, in contrast to that presented by the SPC homologues. In the case of the Sancti Petri Channel, there was a net flow of LAS exportation into the Bay of Cádiz, of -38.6 kg day^{-1}, and a net flow for SPC of -6.0 kg day^{-1}. The daily mass input of LAS and their biodegradation intermediates from the Sancti Petri Channel to Cadiz Bay was 44.6 kg. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Linear alkylbenzene sulfonates; Sulfophenylcarboxylic acids; Water; Sediment; Suspended solids; Estuarine and marine environment

1. Introduction

Coastal ecosystems receive large quantities of surfactants from urban wastewater which is discharged either treated or untreated, directly into the sea or estuary, or indirectly via rivers, groundwater, etc. Linear alkylbenzene sulfonate (LAS) is the most commonly used anionic surfactant worldwide, and in many countries the rate of consumption is relatively high (e.g. 5 g inhab.$^{-1}$ day^{-1} in Spain) (Berna and Cavalli, 1999).

The behavior of LAS has been researched in a variety of different estuarine and marine environmental compartments (Takada et al., 1992; Terzic and Ahel, 1994; González-Mazo and Gómez-Parra, 1996; González-Mazo et al., 1998). The transport processes of LAS in the aquatic envi-

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ronment (e.g. LAS removal by biodegradation and/or adsorption), including the flux of LAS from freshwater to a coastal environment, have been studied (Takada et al., 1992). However, a complete study of LAS behavior requires knowledge of their primary biodegradation intermediates, sulfophenylcarboxylic acids (SPC). These intermediates are generated by successive oxidations (ω,β) of the alkylic chain of the parent compound (Swisher, 1987; Schöberl, 1989). SPC have been detected in different laboratory tests (Gledhill et al., 1991; Di Corcia et al., 1999; Knepper and Kruse, 2000) and their existence in fresh water (Field et al., 1992; Ding et al., 1999) and marine water (González-Mazo et al., 1997) has been demonstrated recently.

LAS and SPC behavior depends largely on their molecular properties and on the physicochemical properties of the medium into which the effluent containing them is discharged. As a result of the surfactant nature of LAS, it tends to accumulate first on the surface of the aqueous medium (Terzic and Ahel, 1994; González-Mazo et al., 1998). This compound also shows a notable capacity for adsorption by sediments and suspended solids, both in continental ecosystems (Amano et al., 1989, 1992) and in the marine medium (Rubio et al., 1996), and by the biota (Tolls et al., 1997). These characteristics affect the transport mechanisms involved in the dispersion of LAS. However, SPC are not surfactant in character, being more polar compounds, and must show lower affinities with particulate matter. Therefore the differences in the behavior of LAS and SPC (transport, distribution, degradation,...) reflect differences in their physicochemical properties.

Moreover, there are many physicochemical variables of the medium that can affect the distribution of these compounds (temperature, salinity, suspended solids concentration, hydrodynamic regime of the ecosystem, . . .). It has been argued that surfactant concentrations in the aquatic environment could be relatively higher during the colder periods of the year, due to the reduced activity by the microbial organisms responsible for biodegradation (Amano et al., 1991). However, several long-term monitoring studies (González-Mazo et al., 1998; Schröder, 1995) have not demonstrated a seasonal effect on LAS concentration. It has also been observed that LAS sorption is closely correlated with the ionic strength (Amano et al., 1992; Rubio et al., 1996), therefore this parameter must be taken into account in determining the fate of LAS in estuaries.

Recently León et al. (2000) have proposed a method that permits the simultaneous quantitative determination of LAS (C10–C13) and SPC (C4–C13) in samples (water, interstitial water and sediment) with wide variability in the expected concentrations of these compounds and with different salinities. In this paper, we present the levels of LAS and SPC homologue concentrations detected in water and sediment from a variety of Iberian littoral ecosystems (bays and estuaries). The concentrations of these compounds have also been determined in suspended solids in a shallow narrow channel subjected to strong tidal currents (Santi Petri Channel, Bay of Cádiz, south-west Spain), into which untreated urban wastewater is discharged. In this latter case, the concentrations have been determined during complete tidal cycles.

The specific objectives of this research are:

1. To determine the behavior of LAS and SPC homologues in various Iberian littoral ecosystems subjected to different physicochemical variables and to the discharge of either untreated or treated urban wastewater.
2. To establish the distribution of SPC homologues in water, suspended solids and sediments taken from these littoral ecosystems.
3. To determine the flux of LAS and SPC homologues from the Sancti Petri Channel to the Bay of Cadiz.

2. Material and methods

2.1. Chemicals

The methanol was of chromatography quality, purchased from Scharlau (Barcelona, Spain), and water was Milli-Q quality. Tetraethylammonium hydrogen sulfate (TEAHS) was purchased from

Sigma-Aldrich (Steinheim, Germany). Sodium chloride was purchased from Scharlau (Barcelona, Spain) and potassium di-hydrogen phosphate from Panreac (Barcelona, Spain). The commercial LAS was supplied by Petroquímica Española S.A, with the following homologue distribution: C10 (3.9%), C11 (37.4%), C12 (35.4%), C13 (23.1%) and C14 (0.2%). Our research group has collected a complete set of monocarboxylic SPC standards (C3 to C13-SPC) with the exception of C7-SPC. The solid phase extraction minicolumns used were supplied by Varian (Bond Elut C18) and Supelco (SAX).

2.2. Study area

The study was carried out in five different estuaries, three located in the north of the Iberian Peninsula: Besaya, Asón and Oka (Fig. 1a–c, respectively) and two in the south-west: Guadalquivir and Palmones (Fig. 1d,f). These ecosystems are of considerable ecological value and are subjected to different forms of official protection (the Natural Park of the Liencres Dunes, the Natural Reserve of the Santoña and Noja saltmarshes, the Biosphere Reserve of Urdaibai, the National Park of Doñana and Palmones saltmarshes, respectively). All the areas studied are in general shallow and almost all are affected by a strong semidiurnal tidal regime (tidal amplitude = 3.0 m), sometimes reaching a tidal amplitude of 4.0 m in the Cantabrian Sea; the exception is the Bay of Algeciras (Fig. 1f), where the tidal amplitude is 0.8 m. The Guadalquivir River (Fig. 1d) is one of the largest of the entire Iberian peninsular in terms of flow volume (typical flow = 60 m^3/s), while the rest of the rivers studied are shallow (< 3 m) and have low flows. In each of these estuaries two zones were differentiated according to the tidal effect: one zone nearer to the seaward limit, with a higher renewal and dilution rate, and the other zone comprising the more continental and fluvial part of the estuary, where the water is shallower and the rate of renewal lower. The predominant sediment grain size changes from one zone to the other, consisting more of sand in the seaward part and more of clay in the fluvial part. The sediments (upper 8–10 cm) of the different areas studied present very similar concentrations of organic carbon (2–2.5%), with the exception of the Asón (Fig. 1b) sediments where this value was higher (3.5–4.0%). Urban centers of different sizes are located on the various estuaries: the most important towns (with numbers of inhabitants) are: Santoña (11 700), Torrelavega (57 000), Guernica-Lumo (15 500) and Sanlúcar de Barrameda (50 000) situated on the Asón, Besaya, Oka and Guadalquivir estuaries, respectively. Up until the time of sampling, the urban wastewaters discharged from all these towns were untreated.

The LAS and SPC fluxes from the Sancti Petri Channel to the Bay of Cádiz were evaluated and the distribution of SPC homologues in water, suspended solids and sediments were determined in the zone indicated in Fig. 1e. This is a branch of the sea linking the southern part of the Bay of Cádiz with the Atlantic Ocean, which provides sea water to an area of salt-ponds of approximately 6000 Ha. It is a channel of 18 km length and very shallow — between 3 and 6 m in depth. It is subjected to a semi-diurnal tidal regime, with an average amplitude of 2.56 m. The tidal wave enters from both ends of the channel, with a delay of 0.5 h at the north. The Channel receives untreated urban wastewater discharged from San Fernando, a town with a population of 90 000 (see Fig. 1e).

2.3. Estimation of LAS and SPC fluxes from Sancti Petri Channel to Bay of Cadiz

During the samplings made in the Sancti Petri Channel, continuous records of current velocity and tidal amplitudes were obtained. These data have been used in the calculations of the fluxes (input–output). The fluxes for a determined compound C are calculated using the following expression:

$$\text{Flux}_{\text{C}}(\text{kg s}^{-1}) = V(\text{m s}^{-1}) \times S(\text{m}^2)\cdot[C](\text{kg m}^{-3})$$

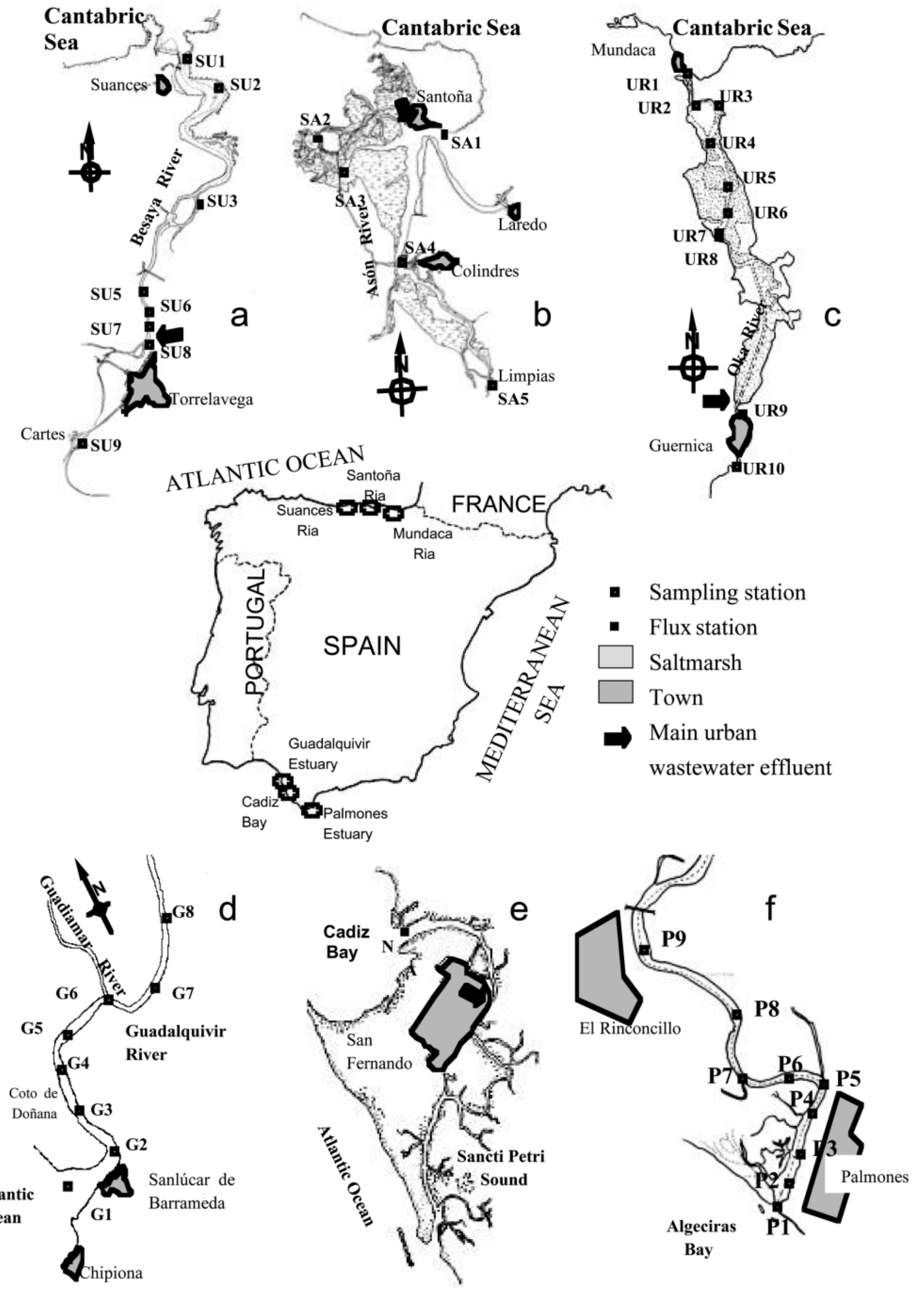

Fig. 1. Map of the studied areas showing the corresponding sampling points. The arrows indicate positions of the main effluent discharge points.

where V is the current velocity, S is the channel section and $[C]$ the concentration of the compound under study. The channel section is variable, and depends on the tidal height. The flux for each sample is calculated and is plotted vs. time. The curve is integrated obtaining the total mass of the compound that is imported or exported in every sampling campaign.

2.4. Sampling

The sampling in the five estuaries was conducted using longitudinal transects, samples being taken at different depths (surface and at 1, 2 and 3 m depth) using either a Ruttner oceanographic bottle or, from the surface microlayer (0–3.5 mm), a surface microlayer sampler (Hydrobios, Kiel). Sampling stations were established at the locations shown in Fig. 1. Table 1 shows the main characteristics of areas studied, during the sampling campaigns.

The Sancti Petri Channel sampling campaigns were conducted over complete tidal cycles (12 h), with different tidal amplitudes (samplings S1 and S2, Table 1) at the northern mouth of the channel (Fig. 1e). The water samples were taken every hour at different depths (surface microlayer, upper, middle and bottom layers) and the samples of solids in suspension every 2 h. The average suspended solids content was 22.6 ± 4.9 and 20.6 ± 12.7 mg l^{-1} for the sampling campaigns S1 and S2, respectively.

Each sample of water (250 ml) and solids in suspension (5 l) was fixed with formaldehyde (2%) and conserved at 4°C until subsequent analysis. Suspended solids samples were passed through glass fiber filters with a average pore diameter of 0.45 μm (AP40), previously cleaned (Milli-Q). LAS and SPC homologues were extracted by Soxhlet extraction with 60 ml of MeOH over 12 h. The methanolic extract was evaporated until dry in a rotary evaporator and the residue obtained was re-dissolved in 150 ml of water in an ultrasonic bath. This procedure provides a good recovery (> 90%) of the compounds studied (León et al., 2000).

In addition, sediment samples were taken from the more contaminated parts of the different areas studied. The sediment samples (0–8 cm depth) were taken with a Van Veen drag and then transferred to the laboratory at 4°C. The dry and milled sediment (10 g) were placed in Soxhlet extraction cartridges and the LAS and SPC were extracted over 12 h with methanol.

The samples (water or the dried extract from suspended solids or sediments, re-dissolved in water), were isolated and pre-concentrated in Bond Elut C_{18} and SAX solid phase extraction minicolumns using an Adsortex Solid Phase Unit. LAS (C10–C14) and SPC (C4–C13) homologues were analyzed simultaneously in a high-performance liquid chromatograph (HP 1050) equipped with a fluorescence detector (HP 1046A, λ_{em} = 225 nm and λ_{em} = 295 nm) and an automatic injector (HP 1100). The different homologues were separated using a Lichrosorb RP-8 column (250 × 4.6 mm with a particle size of 10 μm) and a non-linear gradient regime (A: H_2O and B: $MeOH/H_2O$ 80:20 with 1.25 mM of tetraethylammonium hydrogen sulfate) according to León et al. (2000). The quantification was performed using external standards treated in the same way as samples. The detection limit is similar for LAS and SPC homologues, ranging from 0.2 to 0.4 μg l^{-1} for water samples and from 5 to 10 μg kg^{-1} for sediment ones. The identification of the ho-

Table 1
Main characteristics of the different studied areas

Estuary	Tidal amplitude (m)	Salinity range	Sampling points	Sampling date
Besaya	2.33	0.23–35.02	8	6/6/1998
Asón	2.60	18.34–34.46	7	16/6/1998
Oka	2.75	0.19–34.5	11	15/6/1998
Guadalquivir	3.02	0.95–34.64	8	25/5/1998
Palmones	0.70	5.81–35.89	9	3/3/1997
Sancti Petri S1	1.87	37.27–38.25	1	7/6/1999
Sancti Petri S2	3.09	36.62–38.24	1	13/6/1999

mologues whose standards were not available (C7-SPC) had been performed using liquid chromatography with mass detector (HPLC/MS) according to González-Mazo et al. (1997).

3. Results and discussion

3.1. LAS and SPC levels in different zones

In general LAS and SPC concentrations are low for the various estuaries and phases studied, although high levels of these compounds were detected in specific zones. The high levels of LAS (> 500 μg l^{-1}) found in water from Besaya and Asón estuaries and in the Sancti Petri Channel must be the consequence of the presence of untreated urban wastewater effluent from the nearby population centers: Torrelavega (57 000 inhab.), Guernica-Lumo (15 500 inhab.) and San Fernando (90 000 inhab.), respectively. The shallow waters and the low rate of renewal of the receiving watercourses close to the wastewater discharge outlets reduce the degree of dilution of the effluent. These factors explain the observation of higher values than those obtained in other highly contaminated areas (Takada et al., 1992; Terzic and Ahel, 1994). The lower concentrations (< 50 μg l^{-1}) of LAS in water from the Asón, Palmones and Guadalquivir estuaries were due to the higher renewal rate characterizing these zones and to a lower impact of wastewater discharges. Total SPC concentrations in water were low (< 50 μg l^{-1}) and at some stations SPC were not detected, probably due to the rapid LAS biodegradation kinetic. The LAS and SPC concentrations detected for the sediments from those areas closest to the wastewater discharge outlets were generally high, reaching between 1–5 μg g^{-1} for LAS and 0.05–0.25 μg g^{-1} for SPC. SPC and LAS levels in the studied Iberian estuaries are in general of the same magnitude order than the obtained at Venize Lagoon (Marcomini et al., 2000), but in these area the detected LAS concentrations were lower than SPC concentrations.

In the water samples, the LAS homologues usually detected were those of between 10 and 13 carbon atoms, with C11 and C12 being the most abundant. The SPC homologues with 3–12 carbon atoms in their carboxylic chain were detected too, and the highest concentrations in water corresponded to those of medium chain length (6–8 carbon atoms), particularly C6-SPC (18.1 μg l^{-1}). In all the cases studied, the combined amount of these three homologues detected constituted more than 70% of the total SPC detected. These results are in agreement with those obtained previously by other authors (Field et al., 1992; Knepper and Kruse, 2000) who have designated these homologues as 'key intermediates' since they are the most persistent in the LAS biodegradation

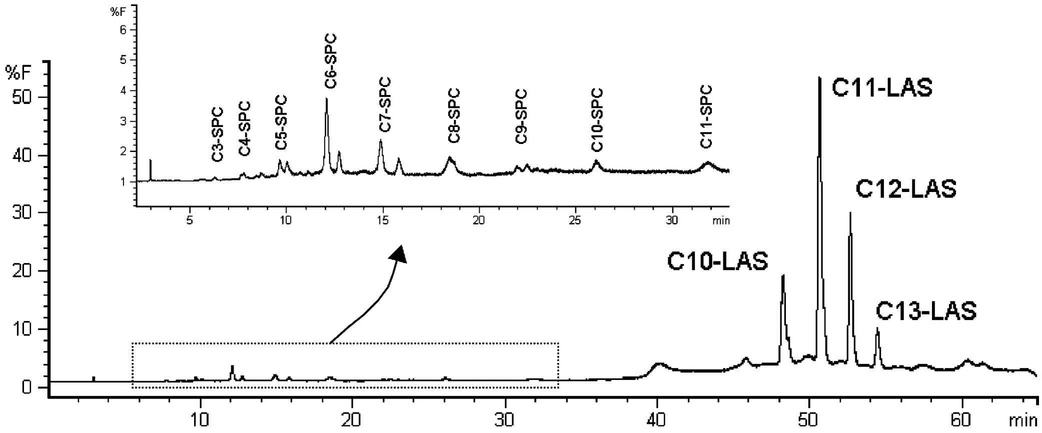

Fig. 2. HPLC chromatograms obtained for a water sample treated using the simultaneous LAS and SPC determination method (León et al., 2000).

process. In the more highly contaminated areas (Besaya Estuary), the long-chain SPC (e.g. C11-SPC) were detected at significant concentrations as a consequence of continuous LAS input to these zones. But in general these intermediates were present at relatively low levels ($< 5\ \mu g\ l^{-1}$) in the medium. Fig. 2 shows, as an example, a HPLC chromatogram obtained for a water sample from the Besaya Estuary, treated by the method proposed by León et al. (2000).

All the homologues of LAS (C10–C14) were detected in sediment, with those of longer alkylic chain being preferentially adsorbed onto the particulate matter. For example, C14-LAS constitutes more than 1% of total LAS in all the samples, reaching 14% in Asón (the area with the highest organic carbon content), despite constituting only 0.2% in the commercial product. SPC of 4–13 carbon atoms were detected in the sediment. The highest concentrations of SPC homologues (47.1–119.3 $\mu g\ kg^{-1}$) corresponded to those of longer carboxylic chain (C9–C11), which present the greatest affinity for the solid phase. The heavier SPC have been previously detected in sediments of the same area by González-Mazo et al. (1997), suggesting their higher tendency to sorption than the rest of SPC homologues.

The partition coefficient between sediment and supernatant water normalized by organic carbon content (O.C.) for the LAS homologues presents mean values of the order of 10^3, 6×10^3, 2×10^4 years 10^5 L kg^{-1}, for C10–C13 homologues, respectively. The results show a great affinity of LAS for the solid phase, as well as an increase in the adsorption in line with increased chain length, this being evidence of a hydrophobic-type interaction. This behavior has been previously described for different estuarine and marine ecosystems (Terzic and Ahel, 1994; González-Mazo et al., 1998), and also for laboratory experiments for the same media (Rubio et al., 1996). However, a wide variability between the different zones was observed. Although the organic carbon content is similar, this is not the only parameter to be taken into account in considering the process of adsorption in the medium (Westall et al., 1999). On the other hand, the adsorption of SPC homologues is less intense than that of LAS, and their distribution is function of the length of the carboxylic chain (e.g. partition coefficient of 22 for C6-SPC and 45 for C7-SPC).

3.2. Spatial and vertical distribution of LAS and SPC homologues

Fig. 3 shows the variation in the total LAS (C10–C13) and SPC (C4–C13) concentrations for water in the Besaya and Oka estuaries (Fig. 3). The maximum LAS concentrations were detected close to each population nucleus; they then decrease sharply with the distance from the wastewater discharge outlet, due to the existence of different processes that simultaneously operate to reduce the LAS concentration in the water: biodegradation, adsorption–precipitation and dilution, as previously described by Takada and Ogura (1992) and González-Mazo et al. (1998). In the Oka Estuary (Fig. 1c), the concentration of SPC observed increases in proportion to the distance from the discharge outlet, reaching a maximum a few kilometers downstream, and then decreases progressively. This disphase, previously described for other zones, may be explained by the increase of the residence time of the LAS in the medium at greater distances from the discharge outlet (González-Mazo et al., 1997). However, in more stagnant zones (Besaya Estuary), the maximum SPC concentrations coincided with those of the precursor molecules.

The average chain length found for LAS in water does not present significant variation over the length of the Asón, Besaya or Palmones estuaries (Table 2). The average values in these zones are similar to those of LAS in the commercial product (11.7). However, significant variation was found in the Oka estuary, where this parameter varied between the typical value for the commercial product, close to the main wastewater discharge outlet, and 12.54 at the estuary mouth. In the sediments of the various ecosystems studied, the average length of chain reached 12.2 (Table 2) and the variations were not very significant.

According to the LAS biodegradation pathways (Swisher, 1987), SPC are generated by successive ω- and β-oxidations. This sequence can be appre-

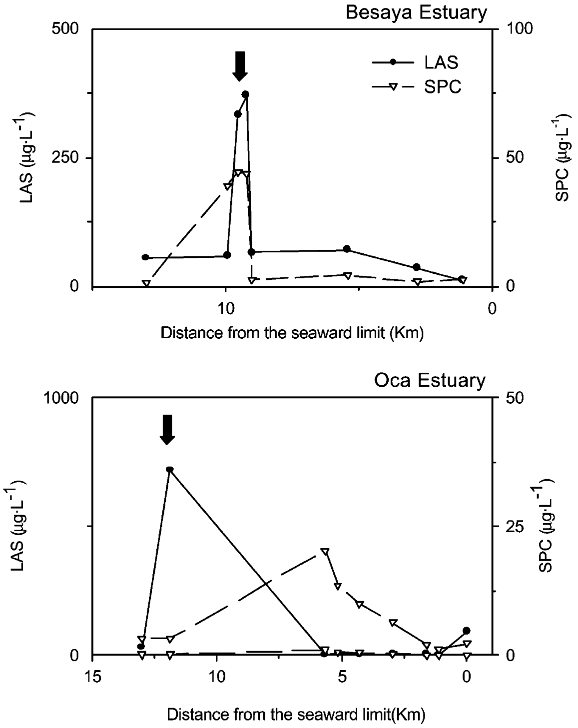

Fig. 3. Spatial distribution of the total concentrations of LAS (C10–C13) and SPC (C4–C13) in Besaya and Oka estuaries. The starting point for the distances is the seaward limit of the estuary (distance = 0). The arrows indicate positions of the main effluent discharge points.

ciated in the results from the Oka Estuary (Table 3); at a relatively short distance from the discharge outlet (UR7) all the monocarboxylic SPC were found, but at increasing distances, as the biodegradation process continues, the proportion of SPC of intermediate chain length (C6–C8) increases until, at the estuary mouth (UR1), these constitute 100% of the SPC detected.

Table 2
Average chain length (A.C.L.) for LAS in water and sediment

Estuary	A.C.L. in water	A.C.L in sediment
Besaya	11.68 ± 0.19	12.05 ± 0.20
Asón	11.84 ± 0.12	12.27 ± 0.06
Oka	12.13 ± 0.43	12.23 ± 0.23
Palmones	11.43 ± 0.06	12.05 ± 0.35
Guadalquivir	11.45 ± 0.28	–

LAS vertical distribution is not homogeneous, as previously other authors have detected (Terzic and Ahel, 1994; González-Mazo et al., 1998), and depends on the physical mixture of the water column and on the existence of wastewater discharged either onto the surface or at depth. In Fig. 4a the highest levels are found at 2.5 m depth (station SU6), due to wastewater being discharged at depth in this estuary. A short distance away from this outlet (station SU4, Fig. 4b), LAS was found to be distributed more homogeneously, and the distribution is now inverse in the more stagnant zone (station SU3, Fig. 4c). At this latter point, the concentrations detected in the surface microlayer were up to one order of magnitude higher than the corresponding samples from 10 cm depth in the water column; this is due to the surfactant character of LAS (Fig. 4c). The behavior of SPC homologues is different (Fig. 4a–c): they are usually distributed more homogeneously due to their higher polarity.

3.3. LAS and SPC fluxes from the Sancti Petri Channel to the Bay of Cadiz

LAS concentrations in water and suspended solids (dry wt.) varied with the tidal amplitude.

Table 3
Spatial distribution (%) of SPC homologues in water from the Oka Estuary

Station	Distance from seaward limit (km)	SPC homologue (%)					
		< C5	C5	C6	C7	C8	> C8
UR7	5.7	16.8	7.2	37.7	18.3	15.1	4.9
UR4	4.3	24.9	6.5	36.3	25.2	7.1	0
UR1	0.0	0	0	65.8	25.7	8.5	0

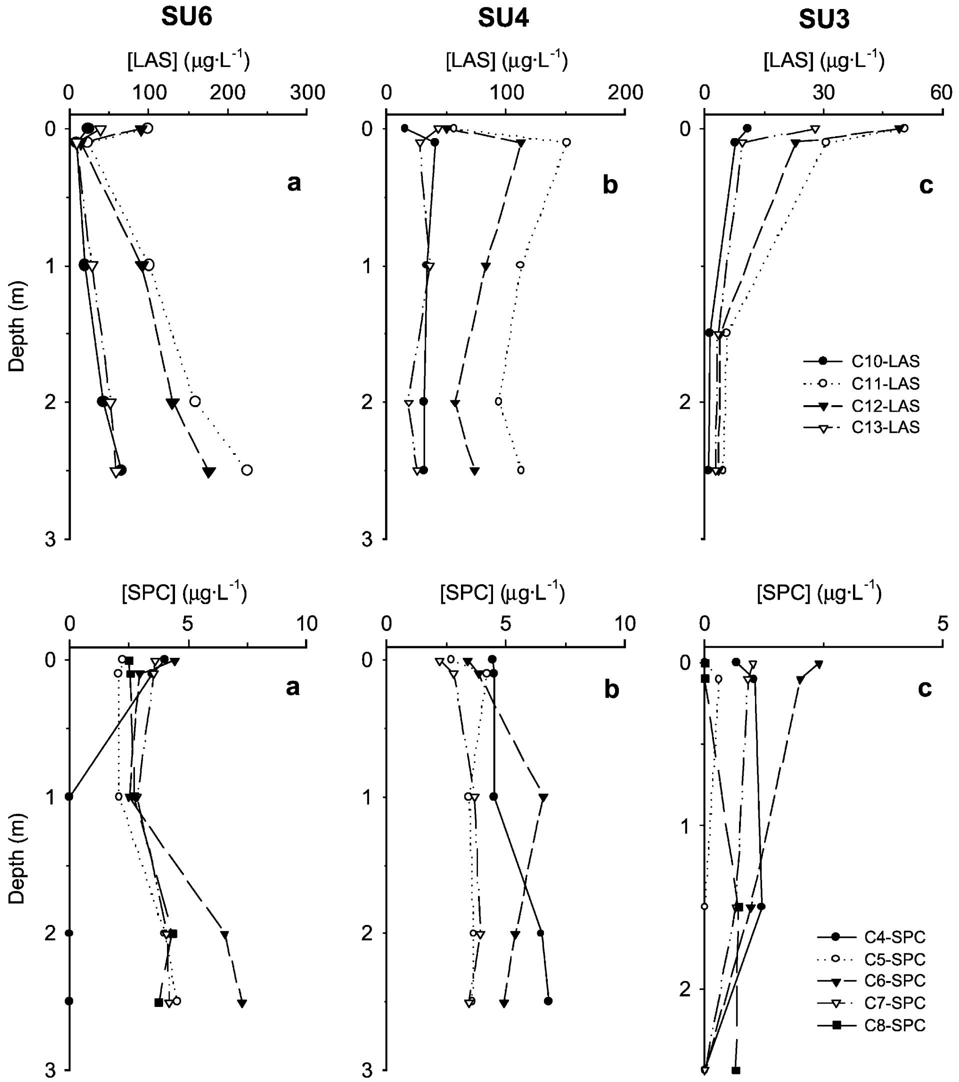

Fig. 4. Vertical profiles obtained for LAS and SPC homologue concentrations in several sampling points from the Besaya Estuary.

The average values detected were 8.7 ± 2.3 μg l^{-1} and 17.6 ± 13.5 μg l^{-1} in water, and 56.8 ± 14.2 μg g^{-1} and 114.8 ± 48.8 μg g^{-1} in suspended solids, for the sampling periods S1 and S2, respectively. This difference is due to the greater influence of the wastewaters discharged from the town of San Fernando (Fig. 1e) for high tidal amplitudes (S2). The percentage of LAS adsorbed onto the solids in suspension is less than 20% in all the samples, with average values of 12.2 ± 2.3% and 12.2 ± 4.1% for the two sampling periods, S1 and S2, respectively. These values are within the range (2.6–38%) obtained for other systems (Takada et al., 1992; Terzic and Ahel, 1994). This percentage depends on suspended solids concentration, and low suspended solids concentration implies a lower proportion of LAS associate to this fraction. Specifically, the average partition coefficients obtained are 3450 ± 830, 4751 ± 1231, 6575 ± 1896 and 12254 ± 3803 l kg^{-1}, for the LAS homologues C10, C11, C12 and C13, respectively, similar to the coefficients detected previously by Terzic and Ahel (1994).

In both samplings, it can be observed that the

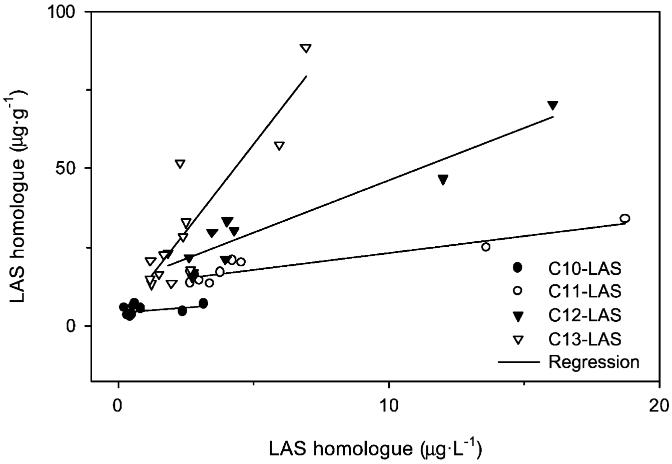

Fig. 5. Representation of the concentration of LAS in suspended solids against the concentration of LAS in water.

evolution of the concentration of the various homologues of LAS in solids in suspension is similar to that found in water (Fig. 5). An increase is seen in the process of adsorption onto the suspended solids, in line with the chain length: for each additional carbon atom in the alkylic chain, the adsorption is between 2.5 and 3.2 times greater.

The average concentrations of SPC were 11.0 ± 6.3 g l^{-1} and 18.9 ± 11.8 g l^{-1} in the water, and 0.1 ± 0.2 µg g^{-1} and 1.0 ± 1.1 µg g^{-1} in the solids in suspension, for the two sampling periods, S1 and S2, respectively. In the solids in suspension, SPC homologues of between C5 and C13-SPC were detected, with longer carboxylic chain predominating. Although variable, the percentages associated with the suspended solids were always less than 1%.

Fig. 6 shows the fluxes of LAS and SPC from the Sancti Petri Channel to Cadiz Bay for the three depths studied (surface, middle and bottom), in the two samplings conducted. The largest flux of LAS occurs when there is a high tidal amplitude (S2). There is an exportation of LAS originating from the wastewater discharge, from the Sancti Petri Channel to the Bay (Fig. 1e) when the tide is ebbing (negative flux). The input of LAS into the channel is much lower with the inflowing tide (positive direction of flux), therefore, a net export flux of −65.2 kg day^{-1} take place towards the Bay. The exportation is less (−12.0 kg day^{-1}) for a low tidal amplitude (S1). The average net flux of SPC (−6.0 kg day^{-1}) is lower than the LAS one (Fig. 6). Considering the average values for net flux of LAS (−38.6 kg day^{-1}) and SPC (−6.0 kg day^{-1}) found in this system, it has been calculated that there is an average daily supply of some 38.6 kg of LAS and 6.0 kg of SPC into the interior part of the Bay. Taking into account the approximate population of San Fernando (90 000 inhab.) and the estimated LAS average consume (5 g inhab^{-1} d^{-1}), the LAS mass that access to the Cadiz Bay via Sancti Petri Channel represents only the 10% of the total consumed. The rest has been previously degraded or sorbed to the sediments in the nearest area to the effluent discharge point.

4. Conclusions

LAS and SPC concentrations in Iberian littoral waters are, in general, lower than 50 µg l^{-1}, except for areas close to urban waste water effluents, where there has been detected concentrations for LAS higher than 500 µg l^{-1} and for SPC higher than 200 µg l^{-1}. LAS and SPC concentrations are higher in sediments, especially for LAS homologues, that have shown partition coefficients between 10^3 and 10^5 l kg^{-1} for C10 and

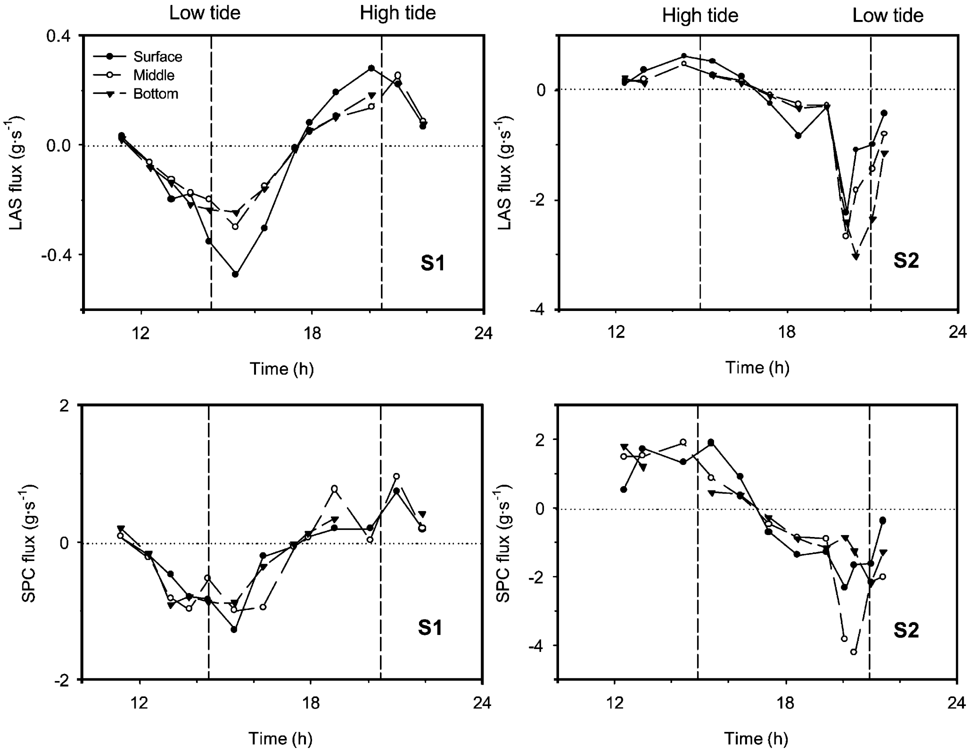

Fig. 6. LAS fluxes obtained for the three water depths studied (upper, middle and bottom), between the Sancti Petri Channel and Cadiz Bay, during the periods of the two sampling campaigns S1 and S2.

C13-LAS, respectively (values normalized by organic carbon content). The highest SPC concentrations have been detected for homologues with medium carboxylic chain length (C6–C8) in water and with longer chain lengths (C9–C11) in particulate material.

LAS homologues are heterogeneously distributed in the estuarine waters due to accurate tendency to accumulate in the interfaces, however, SPC do not show surfactant character and their distribution is more homogeneous.

LAS and SPC fluxes between Sancti Petri Sound and Cadiz Bay has been determined and a clear tidal effect has been observed. The higher concentrations have been detected during the sampling with higher tidal amplitude. The higher contribution to the average net flux corresponds to LAS homologues (86.5%) and the rest to SPCs. The input of LAS/SPC to Cadiz Bay represents 10% of the total LAS than is discharged by San Fernando town, and the rest has been retired from the water column by biodegradation or sorption/sedimentation.

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