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VERTICAL DISTRIBUTION PROFILES OF LINEAR ALKYLBENZENE SULFONATES AND THEIR LONG-CHAIN INTERMEDIATE DEGRADATION PRODUCTS IN COASTAL MARINE SEDIMENTS

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Abstract—The variation with depth of the concentration of linear alkylbenzene sulfonates (LASs) and of the long-chain sulfophenyl carboxylic acids (SPCs) resulting from LAS biodegradation was determined in coastal sediments. We analyzed samples of sediment cores taken from three locations in a littoral zone subjected to the discharge of untreated urban effluents in the Bay of Cádiz in the southwestern part of the Iberian Peninsula. The vertical profile of LAS concentrations showed a sharp reduction with depth, whereas the concentration of long-chain SPCs (6–13 carbon atoms) was greatest at 10 to 14 cm depth. At this depth, the conditions in the interstitial water are strictly anoxic (Eh = −380 mV). The partition coefficients between the solid phase of the sediment versus the interstitial water are very different for LAS and for its degradation intermediates. For LAS, the organic carbon-based partition coefficient values were between 2.4×10^3 and 6.6×10^5 L/kg for the C10 and C13 homologues, respectively; these values are similar to those obtained from laboratory tests for the sorption of LAS onto marine sediments. For the long-chain SPCs, the partition coefficients are several orders of magnitude less as a consequence of their lower hydrophobicity.

Keywords—Linear alkylbenzene sulfonates Sulfophenyl carboxylic acids Coastal marine sediments Vertical profiles Distribution

INTRODUCTION

Coastal ecosystems that are exposed to discharges of untreated urban wastewater receive large quantities of surfactants, which are the principal constituents of commercial detergents. Among these is linear alkylbenzene sulfonate (LAS), the anionic surfactant most used in the formulation of detergents and other cleaning products. The global production of LAS is 2 million tonnes per year [1]. The commercial formulation of LAS (Fig. 1a) is a mixture of homologues, most with chain lengths between 10 and 14 carbon atoms. Each of these homologues consists of various positional isomers.

The distribution of LAS in continental sediments has been studied [2], and the vertical profiles of LAS concentrations with depth in several lake sediments have been established [3,4]. However, there is little information available on LAS concentrations in littoral sediments. In Tokyo Bay (Japan), the LAS content in sediments is reported to be extremely low (<0.01 μg/g) [5]. However, in other coastal zones, such as Cádiz Bay (Spain), concentrations of LAS as great as 10s of ppm have been reported [6]. The differences between these two bays in regard to LAS levels detected in sediments are thought to be due mainly to the different routes of entry of LAS into the marine medium, i.e., removal of much of the LAS in the estuary before it reaches the Bay of Tokyo, compared with the direct influx of LAS to the Bay of Cádiz without prior treatment, and differences in the characteristics of each zone, mainly with respect to the grain size of the sediment and the salinity of the water. Despite this variability, laboratory tests with marine sediment provide experimental confirmation for the importance of the process of sorption of LAS at environmental concentrations [7]. These results agree with previous experiments conducted with continental sediments [8,9] and have shown that LAS sorption is a hydrophobic process that takes place predominantly onto organic matter [8,10,11]. For this reason, the partition coefficient (K_d) is usually normalized by the fractional organic carbon content (FOC) [11]. The organic carbon-based partition coefficient (K_{OC}) is expressed as $K_{OC} = K_d/\text{FOC}$, as Karickhoff et al. [12] have proposed for hydrophobic organic compounds.

Many studies have demonstrated that LAS can biodegrade under aerobic conditions in continental waters [13,14], estuaries [15,16], and seawater [17,18]. The generally accepted LAS biodegradation pathway begins with ω-oxidation of the terminal methyl of the alkylic chain and continues with the shortening of the chain by successive β-oxidations (two carbon atoms) generating various sulfophenyl carboxylic acids (SPCs) (see Fig. 1b) [14]. Some authors consider ω-oxidation to be the phase that controls the rate of the entire LAS biodegradation process [19,20], particularly in systems with low oxygen [13]. Sulfophenyl carboxylic acids with longer carboxylic chain are rapidly degraded to shorter chain SPCs (first β-oxidations). However, the degradation of short carboxylic chain SPCs requires the opening of the ring, which is the other limiting step in the complete LAS biodegradation pathway [21]. This explains why the long-chain SPCs usually are not detected in field studies. However, LAS intermediates have been detected in ground waters [22] and in coastal waters that receive discharges of untreated urban sewage effluent that contains LAS [23].

Under anaerobic conditions, LAS does not biodegrade [24] or biodegrades very slowly [16,25,26]. Some investigators suggest that biodegradation of LAS can take place in purely anaerobic conditions only after the compound has resided in

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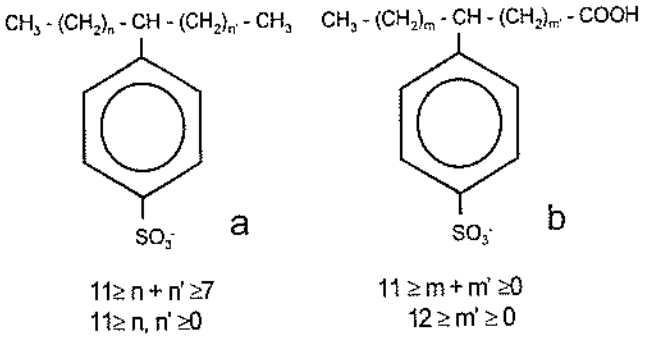

Fig. 1. General chemical structures of linear alkylbenzene sulfonates (a) and the sulfophenyl carboxylate (b) compounds.

the medium under aerobic conditions [13]. As far as we know, to date, no study has been published on the possible biodegradation of LAS under anaerobic conditions in marine sediments. Nor are there data on levels of SPCs in marine sediments, although these have recently been identified for the first time in the water column [23].

The three objectives of this study are to determine the levels of LAS in coastal sediments in areas receiving discharges of untreated urban effluents; to determine the distribution of LAS between the solid phase and the interstitial water; and to determine, in turn, the presence of SPCs in the sediment column at depths between that at which an aerobic oxidation of the organic material takes place and that at which conditions are very reductive.

MATERIAL AND METHODS

Description of the study area

The study was carried out in a salt marsh in the south part of the Bay of Cádiz in the southwest of Spain. Samples were taken from three stations along the Sancti Petri channel, which receives untreated urban effluents from San Fernando, a town of about 100,000 inhabitants (Fig. 2). The width and depth of this channel are very limited, so the levels of LAS in the medium are very high, especially near the effluent discharge points (i.e., 2 μg/ml) [6].

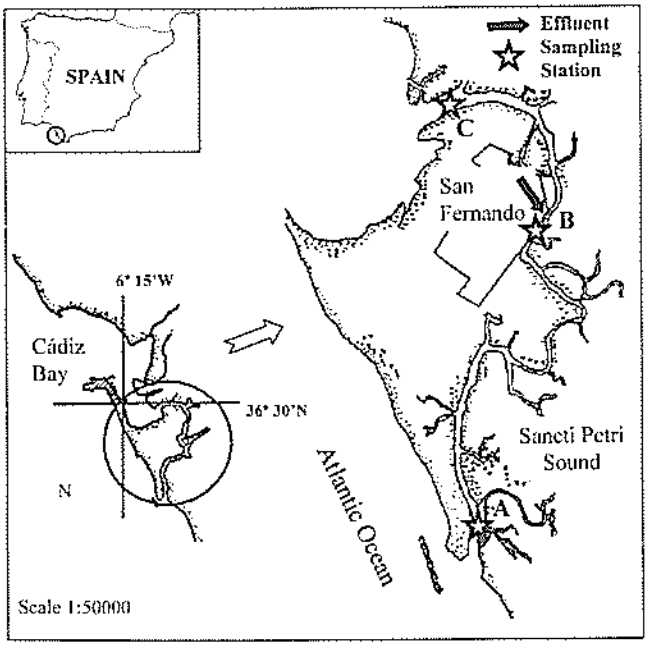

Fig. 2. Map of the Bay of Cádiz, Spain, showing the positions of the sampling stations A, B, and C.

Table 1. Sediment characteristics at the sampling stations

	Station		
	A	B	C
DPD (km)[a]	13.0	0.1	3.0
Porosity[b]	0.55 ± 0.06[c]	0.63 ± 0.08	0.67 ± 0.05
Sand (%)	48.5	14.0	22.0
Silt (%)	17.5	30.0	19.0
Clay (%)	34.0	56.0	59.0
Organic carbon (%)	1.61	2.96	2.85

[a] Distance from source of wastewater effluent/discharge point.
[b] Mass of interstitial water per unit of wet sediment mass.
[c] Standard deviation.

Table 1 shows the location and sediment characteristics of the three sampling stations selected. The sediment at station A is sandy and subjected to intense bioturbation. Station B is the closest to the urban effluent discharge point, and Station C is typified by a strong tidal current regime. The sediments at stations B and C have a high proportion of clay and are severely contaminated. As a consequence, benthic organisms are very scarce [27]. Station B constitutes an extreme case; based on 10 samplings there with a Van Veen drag (each ~0–10 cm depth and 250 cm^2 area), we found only two organisms with a size greater than 900 μm. The capacity for irrigation of the sediment also is very low. This conclusion was drawn from studies conducted in the same zone to measure nutrient fluxes across the water–sediment interface [28]. Because bioturbation is essentially absent, diffusion is the primary mechanism controlling the vertical transport of the chemical species dissolved in the interstitial water in this littoral zone.

Sampling and sample pretreatment methods

At each station, 10 cores of sediment were collected using a gravity corer with an internal diameter of 40 mm and a length of 40 cm. The cores were maintained in a vertical position and at a temperature of 4°C during transfer to the laboratory, where they were frozen and stored until the time of analysis. Later, they were cut into 1-cm-thick sections; then 12 of these sections were selected from between 0- and 31-cm depth. The interstitial water of each section was obtained by centrifugation at 39,200 *g* for 30 min. The aqueous phase was separated by decanting, obtaining a recovery of total interstitial water of between 75 and 85%, and the solid phase was dried in a heater at 85°C until constant weight. Hereafter, sediment should be understood to refer only to the solid phase. Then the sections of cores of each station were pooled by depth in order to get sufficient volumes for analysis.

The dried samples of sediment were milled using a zirconium oxide ball mill (Fritsch) and passed through a 63-μm sieve. Six to 10 g of sediment were extracted with methanol in a Soxhlet extraction cartridge for 11 h. The methanolic extract was then evaporated until dry in a rotavapor, and the residue was redissolved in 200 ml of hot water in an ultrasonic bath.

Both the interstitial water (25 ml) and the sediment extract samples (200 ml) were acidified to pH 3 with HCl, and the analytes were purified and concentrated by solid-phase extraction using minicolumns of the hydrophobic (C_{18}) and strong anionic exchange types consecutively [23]. The recoveries us-

Table 2. Recovery percentage, standard deviations (SD) (n = 3), calibration curves, and detection limit obtained for seawater (100 ml) spiked with linear alkylbenzene sulfonate (LAS) and sulfophenyl carboxylic acid (SPC) standards in the solid-phase extraction;[a] calibration was performed by plotting the peak area (y) versus the mass injected (x, µg)

Compound	Recovery (%) ± SD	Calibration curve	r^2	Detection limit (µg/L)
C6-SPC	43.9 ± 4.4	$y = 7.897x + 7.672$	0.999	1.5
C8-SPC	68.3 ± 3.8	$y = 4.948x + 3.578$	0.998	0.8
C10-SPC	72.9 ± 4.4	$y = 6.073x + 7.020$	0.999	0.7
C11-SPC	72.3 ± 6.4	$y = 5.757x + 8.785$	0.999	0.7
C10-LAS	92.1 ± 1.9	$y = 5.666x + 9.036$	0.998	0.6
C11-LAS	94.2 ± 1.6	$y = 6.133x + 15.770$	0.999	0.5
C12-LAS	96.1 ± 2.3	$y = 3.784x + 16.772$	0.999	0.5
C13-LAS	94.6 ± 1.8	$y = 3.228x + 9.046$	0.998	0.5
C14-LAS	67.8 ± 3.0	$y = 4.512x + 4.895$	0.997	0.7

[a] Spiked level, 10–600 ppb.

ing this procedure were calculated using seawater and sediment samples spiked with C6-, C8-, and C10-SPC and LAS homologues at environmental concentrations.

Linear alkylbenzene sulfonates and SPC analysis methods

Concentrations of LAS and SPC were determined using a HP 1050 high-performance liquid chromatograph (HPLC) equipped with a fluorescence detector (λ_{ex} = 225 nm, λ_{em} = 295 nm). Homologues were separated using a Lichrosorb RP-8 column of 250-mm length and 4.6-mm i.d., with a particle size of 10 µm (Teknokroma). Eluents used were (A) 100% water and (B) 80% methanol/20% water. Eluent B also contained 1.25 mM of tetraethylammonium hydrogen sulfate. The chromatographic separation gradient was from 90% solvent A and 10% solvent B to 100% solvent B over a 40-min period. Isocratic conditions (solvent B) were maintained until elution of all the compounds was complete. Quantities injected were 100 µl of sample. Both LAS and SPC concentrations were determined by measuring the peak areas using external standards. These standards were treated in the same way as the samples. The SPCs of 7, 9, 12, and 13 carbon atoms, for which standards were not available, were identified by HPLC mass spectrometry according to the procedure described by González-Mazo et al. [23] and were quantified by measuring their peak areas by means of C8-, C10-, and C11-SPC (for C12 and C13-SPC), respectively.

Quality assurance/quality control considerations

The recovery efficiencies for LAS and SPC using the Soxhlet extraction procedure for sediment samples spiked with LAS (from 0.05 to 25.0 µg/g) and SPC (from 0.05 to 0.5 µg/g) homologues were >90% in all cases except for C6-SPC (72%). The recovery efficiencies obtained for the LAS and SPC in the solid-phase extraction stage are shown in Table 2. Recovery decreased as polarity of the compounds increased. The recovery efficiency for the shorter chain (C < 5) SPCs was <20% (data not shown). As the nonpolar character of these molecules diminishes, they interact less with the C_{18} minicolumn. The more polar homologues are lost during the treatment, as previously indicated by other authors [29]. When the nonpolar interaction is very intense, the compounds tend to be retained and not fully eluted. This seems to be the case with C14-LAS.

Figure 3 shows the chromatogram corresponding to a sediment sample spiked with commercial LAS and SPC homologues, applying the described analytical treatment. The chromatogram shows an efficient separation of each homologue of LAS and SPC in one single peak, under which all the positional isomers are eluted without interference and with sufficient intensity to permit accurate quantification.

The calibration curves obtained for SPE in 100 ml seawater spiked with 10, 30, 50, 100, 300, and 600 µg/L of each homologue of LAS and SPC are shown in Table 2, which also

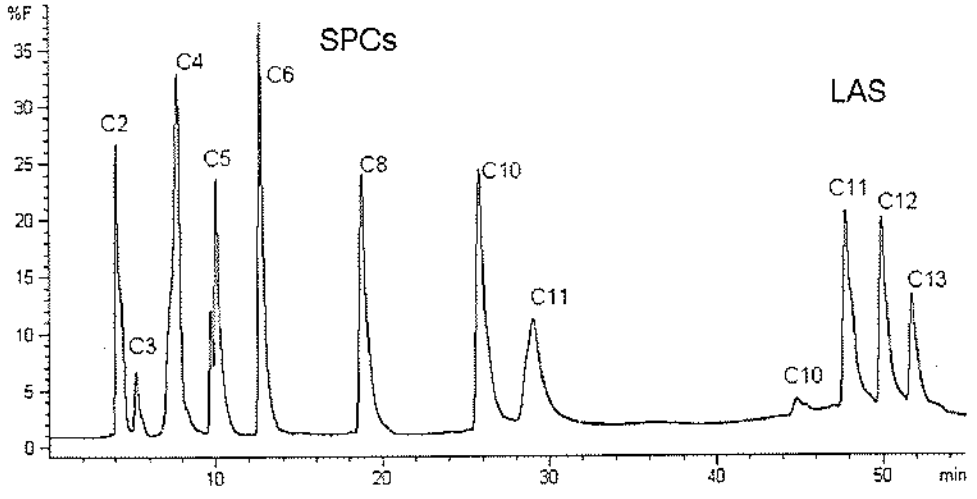

Fig. 3. High-performing liquid chromatography/fluorescent detection (HPLC/FL) chromatogram corresponding to a sediment sample (10 g) spiked with linear alkybenzene sulfonate (LAS) and sulfophenyl carboxylate (SPC) homologues (100 µg/homologue). The units of fluorescence are expressed as percentage full scale.

Table 3. Average surface layer concentrations (0–8 cm depth) of total linear alkylbenzene sulfonates (LASs) and total sulfophenyl carboxylates (SPCs) in sediment (sed), expressed as dry weight, and in interstitial water (iw) at the three sampling stations

Station	ΣLAS_{sed}[a] (10^{-3} μg/kg)	ΣLAS_{iw}[a] (μg/L)	ΣSPC_{sed}[b] (μg/kg)	ΣSPC_{iw}[b] (μg/L)
B	138.6 ± 14.2	44.8 ± 13.3	924.6 ± 316.7	232.6 ± 114.1
C	16.4 ± 8.0	35.9 ± 10.9	224.2 ± 169.0	128.7 ± 60.7
A	0.8 ± 0.2	22.8 ± 8.9	70.6 ± 12.1	28.4 ± 3.2

[a] $\Sigma LAS = \Sigma_{i=10-14} (C_i - LAS)$.
[b] $\Sigma SPC = \Sigma_{i=6,8,11} (C_i - SPC)$.

includes their detection limits for this treatment based on a signal-to-noise ratio of 3:1. The behavior of all the compounds was linear over the range of concentrations studied.

The solvents used as the chromatographic eluents in the chromatographic measurement experiments were water and methanol, both of chromatography quality, purchased from Scharlau (Barcelona, Spain). Tetraethylammonium hydrogen sulfate was purchased from Sigma-Aldrich (St. Louis, MO, USA). The LAS standards, of composition similar to the commercial product used in Spain and with low dialkyltetralinsulfonates content (<0.5%), were supplied by PETRESA (Algeciras, Spain). The proportional composition of the different homologues was C10, 3.9%; C11, 37.4%; C12, 35.4%; C13, 23.1%; and C14, 0.2% (PETRESA, J.L. Berna, personal communication). Due to the very low proportion at which C14-LAS occurs in this mixture, a specific standard for this homologue was used. The standards of C6-, C8-, and C10-SPC were provided by Jennifer Field (Oregon State University, Corvallis, OR, USA). The C11-SPC was prepared in our laboratory by sulfonation of the corresponding acid according to the procedure described by Marcomini et al. [30] for short-chain SPCs. The solid-phase extraction minicolumns used (C_{18} and strong anionic exchange) were purchased from Supelco (Bellefonte, PA, USA).

Other analyses

We used the method described by El Rayis [31] to determine the organic carbon content in sediment samples that had been previously dried and pulverized. Redox potential was determined directly in the sediment cores using a redox electrode (Metrohm, Herisau, Switzerland). The nitrate concentration was determined spectrophotometrically with a segmented continuous flow autoanalyzer (Technicon, TRAACS 800, Bran Luebbe, Buffalo Grove, IL, USA). The analytical method employed is a modification of that described by Grasshoff et al. [32]. Sulfate was determined gravimetrically [32].

RESULTS AND DISCUSSION

Spatial distribution of LAS and long-chain SPCs in marine interstitial water and sediments

Table 3 shows the average upper-layer concentrations (top 8 cm) of the total LAS (the sum of all the homologues, from C10 to C14) and of the SPC (the sum of homologues analyzed). The LAS concentration in this sediment layer (0–8 cm) decreased with distance from the point of effluent discharge, presumably due to the removal of the surfactant from the water column by biodegradation and sorption onto the particulate matter. These results are similar to those obtained in previous studies in zones with similar characteristics [2,6].

The concentration of LAS in the sediment was up to 1,000 times greater than the LAS concentration in the interstitial water, whereas the concentration of SPC in interstitial water was similar to the concentration of SPC in sediment. These results are similar to those obtained for sorption tests in the laboratory [7,9,10] and for samples taken from a sewage-contaminated aquifer [33], in which it was concluded that the interaction between the LAS and the sediment is predominantly of the hydrophobic type. The behavior of SPC may be explained in these terms since these compounds have little affinity for the sediment due to their low hydrophobicity.

The highest concentration of LAS in sediment occurred at station B. In this zone, the surface water presents a long residence time [6], permitting a higher rate of deposition of particulate matter onto which LAS has been sorbed. The low solubility product of LAS calcium salts [34] could also contribute to this increased LAS concentration in sediment by precipitation, particularly given the high concentration of LAS in water detected near the effluent discharge point [6]. This phenomenon is less intense at stations A and C due to the lower amounts of particulate matter reaching these areas. Therefore, the differences found between stations C and A may be explained by another two factors, i.e., the sediment at station C has a greater specific surface area due to its higher content of clay, which correlates positively with LAS sorption [9], and the sediment at station C has a higher content of organic carbon, which also favors LAS sorption [8,10,11]. This latter factor is a consequence of the hydrodynamics of the zone that lead to a much greater incidence of the urban effluent discharge than at station A [6]. Also, it can be observed in Table 4 that, the further the station is located from the point of effluent discharge, the lower is the concentration in the sediment of the long-chain homologues (those more easily degradable in the aqueous phase and having greater tendency for sorption onto the sediment) [7]. Hence, at station A, which is furthest from the point of discharge, shorter-chain homologues of LAS predominate (Table 4). The presence of C14-LAS in the sediment is also notable, even though it comprised a very small percentage (<0.5%) of the commercial LAS used in this region. However, this homologue was not detected in interstitial water since its more hydrophobic character leads to its preferential sorption to sediment. In this context, we note that the organic carbon-based partition coefficient (K_{OC}) of LAS homologues (Table 4) tends to increase in line with the increase in the chain length for the three stations sampled. This increase is higher for station B than the others, probably because of the fresh LAS received in wastewater discharged nearby, which contains a higher proportion of long-chain homologues than that in other areas studied, and the low solubility product of LAS_2Ca, which decreases for homologues

Table 4. Distribution, expressed as percentage of total linear alkylbenzene sulfonates (LASs), and average partition coefficient normalized by the organic carbon content (K_{OC}) of the LAS homologues in the surface layer sediments (0–8 cm depth) at the three sampling stations

	Station	LAS-C10	LAS-C11	LAS-C12	LAS-C13	LAS-C14
Sediment (%)	B	0.9 ± 0.1	12.7 ± 0.7	34.6 ± 0.6	50.5 ± 1.1	1.2 ± 0.1
	C	1.6 ± 0.6	14.7 ± 3.5	30.7 ± 0.3	50.8 ± 5.7	2.2 ± 1.5
	A	5.9 ± 0.2	33.1 ± 1.2	34.5 ± 1.0	25.5 ± 2.1	1.0 ± 0.6
Interstitial water (%)	B	11.6 ± 1.8	41.7 ± 4.9	37.4 ± 5.7	9.2 ± 2.1	ND[a]
	C	6.9 ± 1.5	31.1 ± 3.4	52.2 ± 4.1	9.7 ± 4.2	ND
	A	6.1 ± 1.0	26.9 ± 5.6	51.9 ± 7.6	15.1 ± 9.3	ND
$K_{OC} \times 10^{-3}$ (L/kg)	B	8.7 ± 2.7	35.0 ± 10.9	103.6 ± 18.1	660.2 ± 173.5	—
	C	3.5 ± 1.5	7.4 ± 3.4	9.8 ± 4.6	11.3 ± 43.3	—
	A	2.4 ± 0.8	2.8 ± 1.2	3.4 ± 1.0	4.3 ± 2.3	—

[a] ND = not detected.

with longer alkylic chains [34], favoring their preferential precipitation.

Long-chain SPCs (C8- to C10-SPC) predominate in the sediment, particularly at station B. The SPCs of 12 and 13 carbon atoms were detected at this station, which confirms that the LAS biodegradation process starts with ω-oxidation of the terminal methyl of the alkylic chain. For the interstitial water, the SPCs of 8 and 9 carbon atoms constituted the greatest proportions.

Vertical profiles of LAS and SPC

The vertical profiles of the concentrations of the LAS homologues in the sediment and interstitial water found at the three stations are shown in Figure 4. Except for station A, where LAS concentrations were very low in both phases, a clear decrease in concentration with depth was observed. This pattern was more prominent in the sediment than in the interstitial water. The decline was steeper in the first few centimeters, which may be related to greater discharges of effluent into the zone in recent years. At station B, the maximum surfactant concentration found in the sediment was deeper than surface layer (Fig. 4). This condition may be due to the process of physical mixing of the surface sediment [4].

For stations B and C, where the LAS concentrations were higher than for A, the variation in total LAS concentration with sediment depth was determined by the homologues with

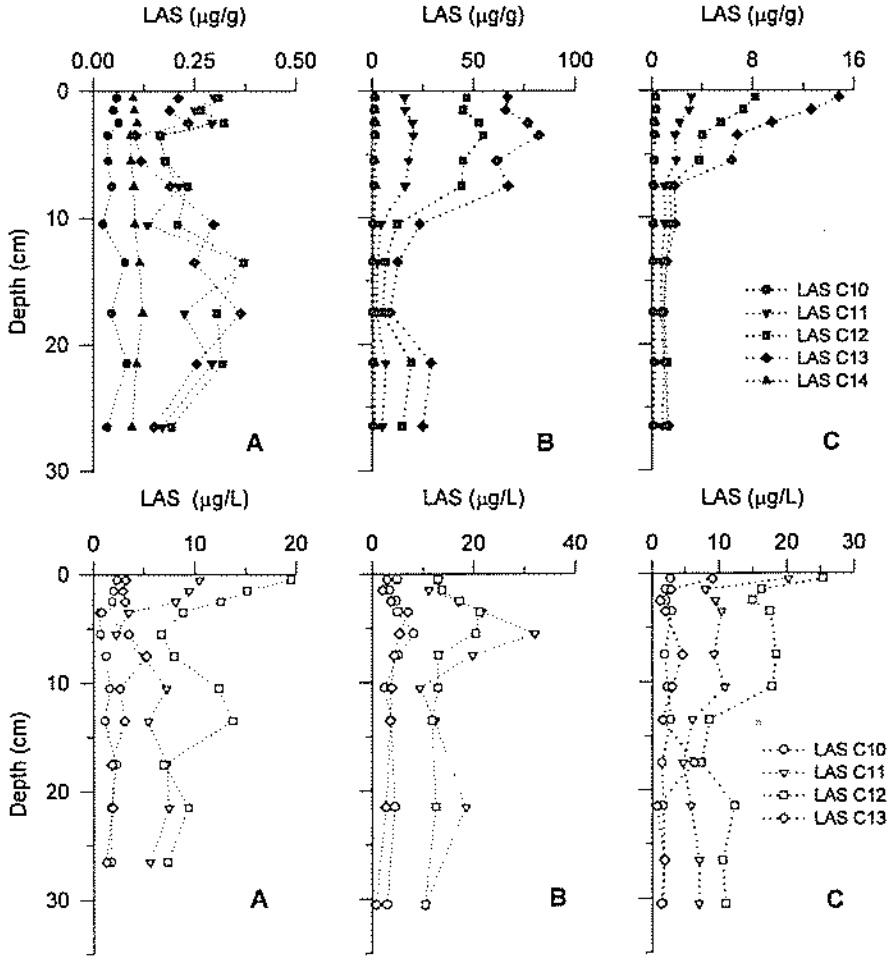

Fig 4. Vertical profiles showing concentrations of linear alkylbenzene sulfonate (LAS) homologues (C10–C13) measured in sediment (upper graphs) and interstitial water (lower graphs) for sampling stations A, B, and C.

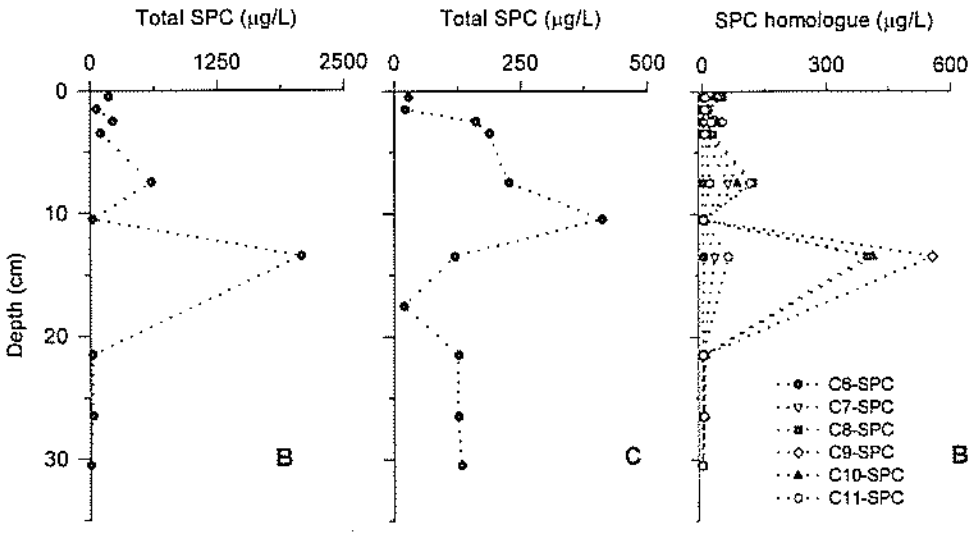

Fig. 5. Vertical profiles of total sulfophenyl carboxylates (SPCs) for stations B and C and vertical profile of SPC homologues in interstitial water for station B.

12 and 13 carbon atoms (Fig. 4). These homologues have a large sorption tendency and are readily biodegradable. The vertical profile of the LAS concentration in interstitial water is similar to that observed for the sediment, particularly at stations B and C. Considered in this manner, the homologue-specific partition coefficient did not vary much with depth. The reason for this was that there is no appreciable variation in the composition of the sediment with depth, as evidenced by the vertical profiles of porosity and organic matter content.

A pronounced decrease in LAS concentration with depth was noted at the stations closest to the point of effluent discharges, which may be due to increases both in population and per capita consumption, hence in the amounts of LAS discharged, in recent decades and LAS degradation occurring in the sediment. The first of these two hypotheses is certainly true—the population of the city of San Fernando has increased by 40% in the last 20 years (1975–1995), but LAS consumption per inhabitant had not varied significantly in Spain during this period. However, it is necessary to verify the second possibility, too.

To that end, the interstitial water at different depths between 0 and 30 cm was analyzed. The results obtained for stations B and C (closer than A to the effluent discharge point) are shown in Figure 5. The vertical profile obtained for the ΣSPC (between 6 and 13 carbon atoms) was greatest at depths between 10 and 14 cm, with values as great as 2,100 µg/L at station B. Considering that the predominant mechanism of transport in the interstitial water is diffusion [28], this type of distribution implies that the SPCs are actually produced at this depth, where the conditions are anoxic (Eh = −380mV). The distribution of SPCs measured is determined mainly by the C8 to C11 homologues (station B, Fig. 6). Although the presence of short-chain SPCs has not been determined, it is probable that these intermediates could also be a relevant fraction of LAS metabolites. The SPCs of 5 to 8 carbon atoms have been described in several studies as the key intermediates [19,35], but other mono- and dicarboxylic SPCs could also be present at lower concentrations [36]. The reduction in SPC homologue concentration found at sediment depths above and below this depth (10–14 cm) suggests that, after their initial production, the SPCs are transformed into others SPCs of shorter chain length, probably by successive β-oxidations [14,37]. The SPCs with carboxylated chains <6 carbon atoms in length have been detected both in sediment and in interstitial water, but these have not been quantified due to the low recoveries obtained for these compounds with the methods used in this study.

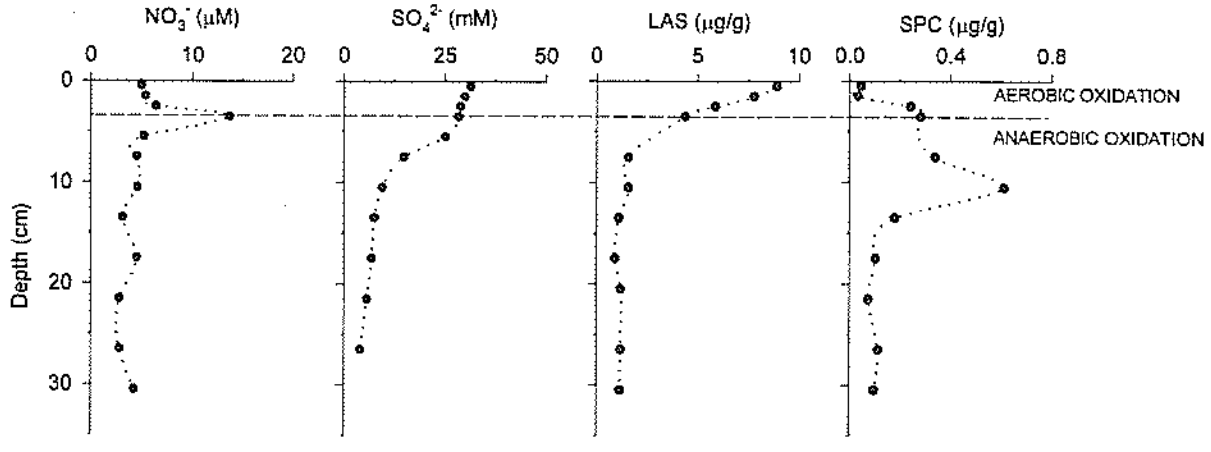

Fig. 6. Vertical profiles of nitrate and sulfate concentrations in interstitial water and total linear alkybenzene sulfonate (LAS) and sulfophenyl carboxylate (SPC) concentrations, in sediment wet weight, for station C.

We suggest that the long-chain SPCs are produced in the initial stages of the degradation of LAS, which accounts for their appearance at a considerable depth (10–14 cm). But this result also suggests that the rate of degradation of SPCs under anoxic conditions must be very slow. Unfortunately, the cores used in this study were not dated, although data are available on the rate of sedimentation in other parts of the zone of study (<5 km distant), which permits the calculation of the time of deposition of the material at a depth of 10 to 14 cm as being approximately 15 to 22 years ago.

In Figure 6, for station C, we show concentrations of the total LAS and long-chain SPCs (sediment + interstitial water) compared with the variation of NO_3^- and SO_4^{2-} in the interstitial water. In the oxic zone, the lower limit (≅3 cm) of which could be estimated from the maximum concentration of NO_3^- [38], we observed an abrupt decrease with depth in the concentration of LAS. Aerobic oxidation of LAS should contribute to this pattern. The low concentrations of SPCs in this zone indicate that the successive β-oxidations occur relatively rapidly in oxic conditions [14].

At greater depths, where an increase in the vertical gradient of SO_4^{2-} concentration occurs, sulfate serves as the terminal electron acceptor in the degradation of organic matter [39]. Nevertheless, at this depth (4–8 cm), the vertical gradients of the concentration of LAS and long-chain SPCs are not as steep. This observation is coincident with the opinion expressed by Klump and Martens [40] that sulfate reduction is not an efficient metabolic route for the degradation of complex organic molecules. The maximum concentration of long-chain SPCs occurred at a depth of 10 to 14 cm, where sulfate concentrations were low (<10 mM), and decreased smoothly. Another anaerobic mechanisms of organic matter decomposition could be involved in the LAS degradation process.

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