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

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The distribution of linear alkylbenzene sulfonates (LAS) and their biodegradation intermediates (SPC) has been studied at a salt marsh of the Bay of Cadiz. The identification and quantification of LAS and SPC was carried out after solid-phase extraction of 250 mL of water samples followed by liquid chromatography with fluorescence, diode array, and ionspray mass spectrometry. The latter procedure permitted the unequivocal confirmation of long-chain SPC, of up to 11 carbon atoms in seawater, and of up to 13 carbon atoms in interstitial water. Some of these compounds have not been described until now in environmental samples. The relative abundance of the SPC found at some of the sampling stations agrees with what would be expected after the occurrence of the first and second β-oxidations of the alkyl chain of the various homologues of commercial LAS. Furthermore, the existence of SPC-C13 in interstitial water proves unequivocally that ω-oxidation occurs in the environment. In general terms, the persistence of long-chain SPC is evidence that the biodegradation of LAS is a slow process in a marine environment that is deficient in oxygen and highly contaminated with other organic substrates.

Introduction

Linear alkylbenzene sulfonates (LAS) are synthetic surfactants used mainly in the formulation of detergents and other cleaning products. Some 2.4×10^6 per year of LAS are produced globally (*1*). The commercial product, whose formula is shown in Figure 1a, is a mixture of homologues, most with chain lengths between 10 and 13 carbon atoms. Each of these homologues consists of a varying number of positional isomers.

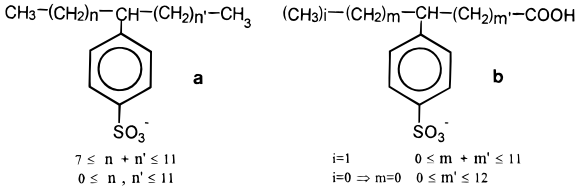

FIGURE 1. General chemical structures of the linear alkylbenzene sulfonates (a) and the sulfophenyl carboxylate (b) compounds.

The environmental behavior of LAS, as one of the most widely-used xenobiotic organic compounds, has aroused considerable interest and study. As a result, it has been determined that, under certain conditions, LAS compounds are completely biodegradable products. It is known that they have a limited persistence in continental waters [half- life of 3 days (*2*)] and that their degradation in waste water treatment plants is very rapid (*3*). In the marine environment, their degradation is slower (*4*, *5*) and depends to a considerable extent on the specific environmental conditions (*6*, *7*). In this regard, Vives-Rego *et al*. (*8*) have reported that the half-life of LAS in seawater is two or three times longer than in freshwater. Two factors may explain this difference: (i) the microbial communities present in the marine environment are less active in degrading xenobiotic organic chemicals than those in freshwater (*6*, *4*) and (ii) the association of the LAS with Ca^{2+} and Mg^{2+} may cause a reduction in their bioavailability, as happens with other organic compounds (*9*).

Although the knowledge of the LAS biodegradation pathways is still somewhat incomplete (*10*), the scheme generally accepted (*11*) begins with the oxidation of a methyl group at the end of the alkyl chain, giving rise to an acid [ω-oxidation (*12*)]. Later the alkyl chain undergoes further oxidations that generate new sulfophenylcarboxylic acids (SPC), whose chain length shortens each time by two carbon atoms (β-oxidation) or by one carbon atom (α-oxidation). Figure 1b gives the structures of the SPC resulting from these successive oxidations.

From the environmental point of view, the determination of the levels of these degradation intermediates is a very relevant question. Although the toxicity of SPC is not known with any certainty, Kimerle and Swisher (*13*) found that SPC give LC_{50} values that are 120−240% higher than that of LAS. The problem of analyzing the different homologues of LAS in environmental samples has now been resolved, using techniques based on gas chromatography (*14*, *15*) and liquid chromatography (*16*−*20*), coupled to various detection systems. Due to their low volatility and anionic form, derivatization of these compounds is necessary when GC-based analytical methods are used. This drawback is not encountered when LC-based methods are used. Furthermore, with LC, the even more polar carboxylated transformation products (SPC) of the linear alkylbenzene sulfonates (LAS) compounds can be analyzed (*16*). However, the complex SPC mixtures and a lack of reference standards currently limit the applicability of high-perfomance liquid chromatography (HPLC) with UV fluorescence detection methods (*21*). For confirmation purposes, mass spectrometry utilizing various ionization techniques has been applied.

The development of LC−MS techniques has enabled the identification and quantification of pollutants in environmental samples (*22*−*26*). In earlier reports, the thermospray interface was mainly used (*22*, *23*), whereas in the recent

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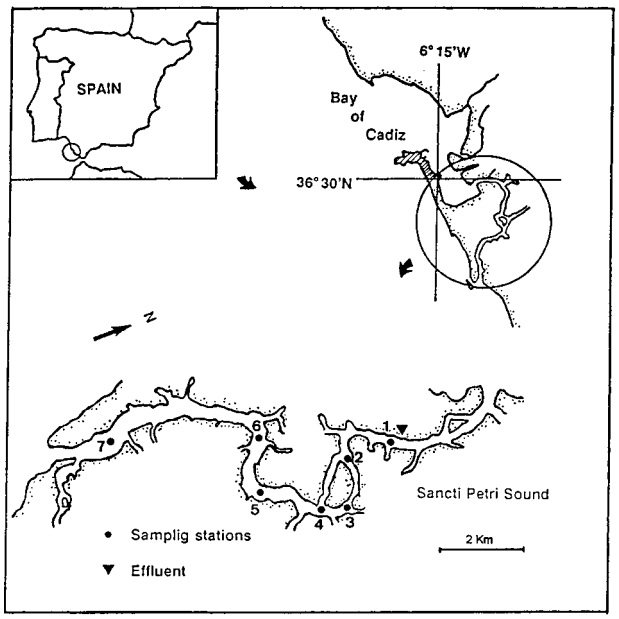

FIGURE 2. Map of the Bay of Cadiz showing positions of sampling stations.

past, a considerable number of new analytical methods have been published using the atmospheric pressure ionization (API) interfacing techniques (*24*, *25*). With these techniques better limits of detection, by approximately 2 orders of magnitude, were obtained. Also, more fragment ions can be generated with the API interfaces [atmospheric pressure chemical ionization (APCI) and electrospray (ESP)], making the confirmation of the "unknowns" possible (*25*).

The electrospray (ESP) interface in particular has been shown to be very valuable when ionic compounds, e.g., quaternary ammonium compounds, need to be analyzed. However, the major drawback of this interfacing system is the limited eluent flow rates (<10 μL/min). Modifications of the interface have been made in order to solve this problem. The so-called pneumatically assisted electrospray or ionspray interface is a relevant example, although optimum flow rates are still below 100 μL/min. Results have recently been reported with a newer version of this latter interface (*25*), utilizing flow rates up to 300 μL/min. In this paper, the main objective was the determination of carbamate and organophosphorus pesticides and their more polar transformation products.

The determination of azo dyes and other detergents and surfactants in environmental samples has also received serious attention from various groups. Various LC−MS methods have been developed for these compounds. The recently developed ionspray (ISP) interface has proved its capabilities for the determination of ionic compounds, such as azo dyes (*27*). For the linear alkylbenzene sulfonates and their carboxylated transformation products, only one paper describing the application of LC−MS with the thermospray interface has been published (*17*). In particular, the ISP technique for the determination of the LAS compounds and the identification of the transformation products in water samples is of interest from both the analytical and the environmental points of view. Therefore, the aim of the research presented in this paper has been to identify the so-called long-chain intermediate transformation products of LAS compounds in a number of actual samples from a marine environment.

Experimental Section

Chemicals. The solvents used as the chromatographic eluents in the experiments were water, acetonitrile, and methanol, all of chromatography quality and purchased from Merck

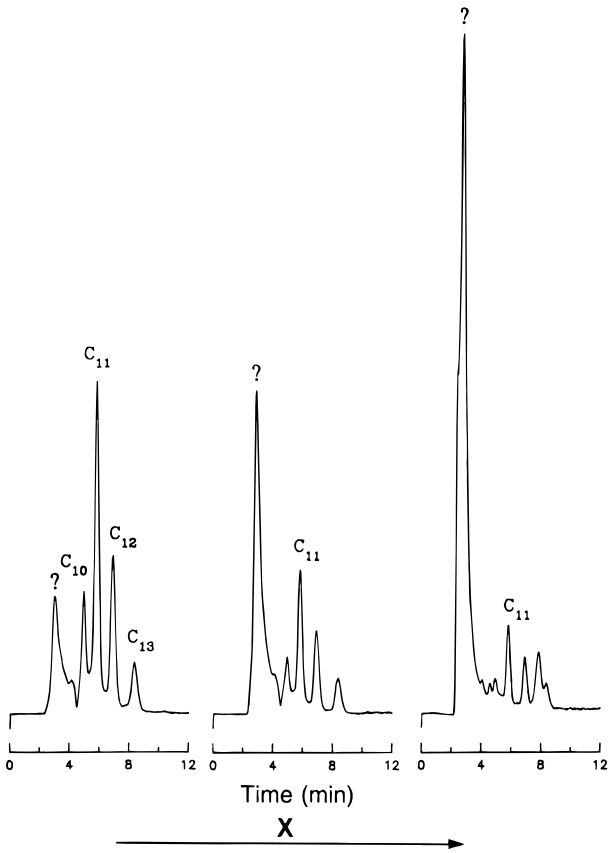

FIGURE 3. Chromatograms corresponding to three sampling stations in the zone studied. The stations have been listed in increasing order of distance (X) from the LAS discharge point. The chromatograms shown were obtained from a sampling exercise undertaken prior to those discussed in this paper. The analytical conditions are described in section LAS Analysis (Lichrosorb RP-8 column 250 × 4.6 mm, 10 μm, isocratic regimen).

(Darmstadt, Germany). Tetraethylammonium hydrogen sulfate (TEAHS) was purchased from Sigma-Aldrich (USA). Triethylamine and acetic acid were purchased from Merck (Darmstadt, Germany). The commercial LAS with a low dialkyltetralinsulfonates (DATS) content (<0.5%) was supplied by Petroquímica Española S.A. The proportional composition of the different homologues is as follows: C_{10} (3.9%), C_{11} (37.4%), C_{12} (35.4%), C_{13} (23.1%), and C_{14} (0.2%). The SPC standards ($2C_2$SPC, C_3SP2C, $3C_3$SPC, $2C_4$SPC, $3C_4$SPC, $4C_4$-SPC, and $5C_5$SPC) were supplied by A. Marcomini (University of Venice).

Study Area. The study was carried out in a salt-marsh area to the south of the Bay of Cadiz in the southwest of Spain. Samples were taken from stations along the length of a 18-km channel, as per the map shown in Figure 2. Tidal flows from the Atlantic Ocean and from within the bay enter by both mouths of the channel and meet close to the position of station 1. On this channel is situated the discharge outlet for the untreated urban effluents from San Fernando, a town of about 100 000 inhabitants. The seven sampling stations were selected so that they should represent locations decreasingly subjected to the effects of these urban wastes. These urban waste discharges have a considerable effect on the study area, due to its shallow waters and hence low volume. The dissolved organic carbon content varies from 35.5 ± 18.2 mg L^{-1} at station 1 to 4.6 ± 3.1 mg L^{-1} at station 7. The percentage of oxygen saturation varies from 32 ± 27% at station 1 to 92.5 ± 6.1% at station 7. These values are subject to wide seasonal variation and depend in great measure on the tidal condition (*28*).

Sampling and Pretreatment of the Samples. The stations were sampled during the autumn, on an ebbing tide, when

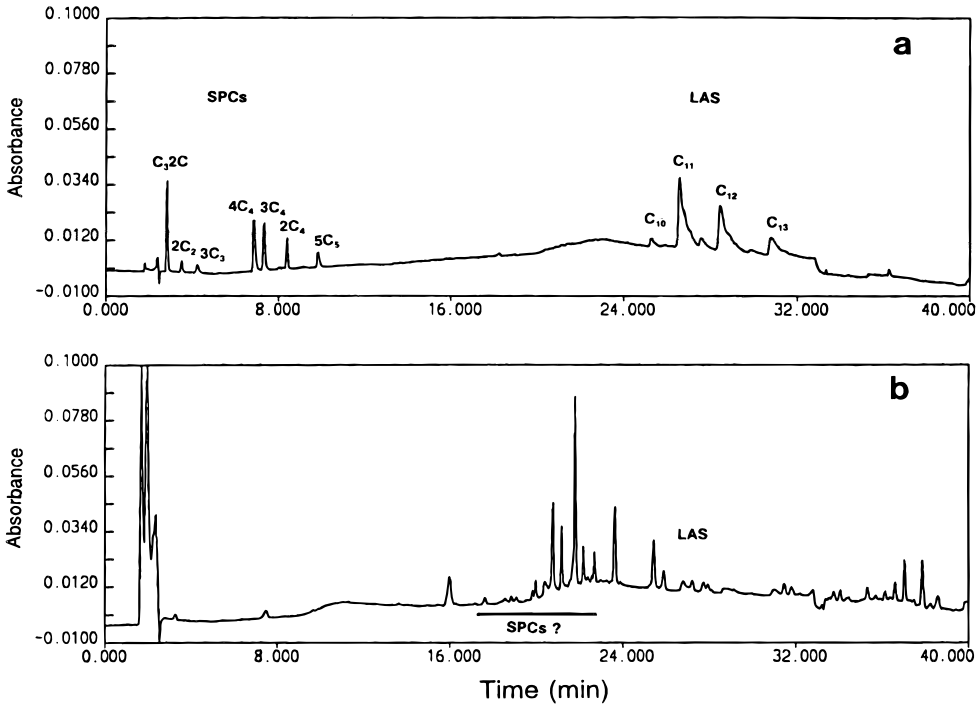

FIGURE 4. LC−DAD chromatograms of (a) standard of LAS + SPC ($2 < n < 5$) and (b) sample of interstitial water. (C_{18} column, ODS Hypersil, 5 μm, 200 × 4.6 mm, using elution gradient, and a water−acetonitrile mixture shown in Table 1).

the tidal range was relatively low (tidal coefficient of 0.57). The water temperature was 14.2 ± 0.8 °C, and the salinity was 34.3 ± 2.6. Water samples were taken with Ruttner bottles prewashed with acid. Later, these samples were transferred to polyethylene jars and a quantity of formaldehyde was added to obtain a concentration of 0.3 M (approximately 1% w/w of HCHO). The samples were stored in the dark at 4 °C until they were analyzed. Sediments were sampled by means of a Van Veen grab. Interstitial water was obtained after centrifugation at 39200*g* and stored in the same way as the seawater. In accordance with previously described procedures (*29*), water samples (250 mL) and interstitial water (100 mL) were acidified to pH 3, then purified, and concentrated by solid-phase extraction in a C_{18} hydrophobic-type minicolumn and subsequently in a SAX strong anionic exchanger. The elution was carried out with 3 mL of 2 N HCl in methanol. The eluate was evaporated until dry and was redissolved in 1mL of the same mobile phase used in the liquid chromatography analysis. Recovery of the LAS in the solid-phase extraction stage was 96.5 ± 1.5%.

LAS Analysis. The LAS was analyzed in a HP 1050 high-perfomance liquid chromatograph equipped with a fluorescence detector (λ_{exc} = 225 nm and λ_{em} = 295 nm). Homologues were separated using a Lichrosorb RP-8 column of 250 mm length and 4.6 mm internal diameter, with a particle size of 10 μm (Teknokroma), and precolumns of the same stationary phase. Sodium perchlorate (10 g × L^{-1}) in methanol−water (80:20), at a flow rate of 1.0 mL × min^{-1}, was used as eluent.

Identification of SPC. Prior to the identification of SPC, LAS and SPC were separated by HPLC (HP 1050) equipped with a diode array detector. The HPLC system incorporated an analytical C_{18} column (ODS Hypersil, 5 μm, 200 × 4.6 mm, HP), and an elution gradient as shown in Table 1 was used.

The identification of the SPC was performed by LC/ISP−MS analysis.The HPLC analytical conditions are given in Table 2. The LC/ISP−MS analyses were performed on a VG Platform (VG Biotech, Manchester, U.K.) equipped with a quadrupole mass spectrometer. The interface technique and its optimization are extensively discussed elsewhere (*25*). A voltage of 3.5 kV was applied to the needle tip, meanwhile the extraction lens was operated at potentials of −20, −60, or −80 V. A gas flow of 25 L/h was used for the additional pneumatic nebulization, whereas a drying gas flow of 400 L/h was applied. The ion source temperature was held at 150 °C. Full-scan mass spectra over a scan range of *m/z* 75−500 at 425 amu/s were obtained. A solvent flow rate of 0.15 mL/min was maintained with a Waters 616 pump, coupled to a Waters 600S pump controller (Waters, Cincinnati, PA.

TABLE 1. Elution Gradient Used for Separation of LAS and SPC[a]

time (min)	*A* (%)	*B* (%)	flow rate
0	10	90	1.0
15	36	64	1.0
19	60	40	1.0
33	85	15	1.0
36	100	0	1.8
40	100	0	1.8
42	10	90	1.0

[a] A, AcN/H_2O 80/20 + 5 mM tetraethylammonium hydrogen sulfate, TEAHS; B, H_2O + 5 mM TEAHS.

Quantitation. LAS concentrations were determined by measuring the peak areas, using external standards. These standards were treated in the same way as the samples. The system was linear for all of the homologues, using six points between 1 and 200 μg L^{-1} (1, 10, 30, 50, 100, and 200 μg L^{-1}). The long-chain SPC, for which standards were not available, were quantified by measuring their peak areas by means of C_{10}-LAS homologue. The SPC data were expressed as equivalent C_{10}-LAS. From 1 mL of the sample extract, 50−100 μL was injected into the LC−ISP−MS system. Under the experimental conditions used, the observed minimum detectable concentration for each homologue was approximately 0.1 μg L^{-1}.

Results and Discussion

Evidence of the Presence of SPC. Figure 3 shows the chromatograms obtained from samples taken at the first three stations, by applying the techniques described in the above section LAS Analysis. The procedure followed, which has

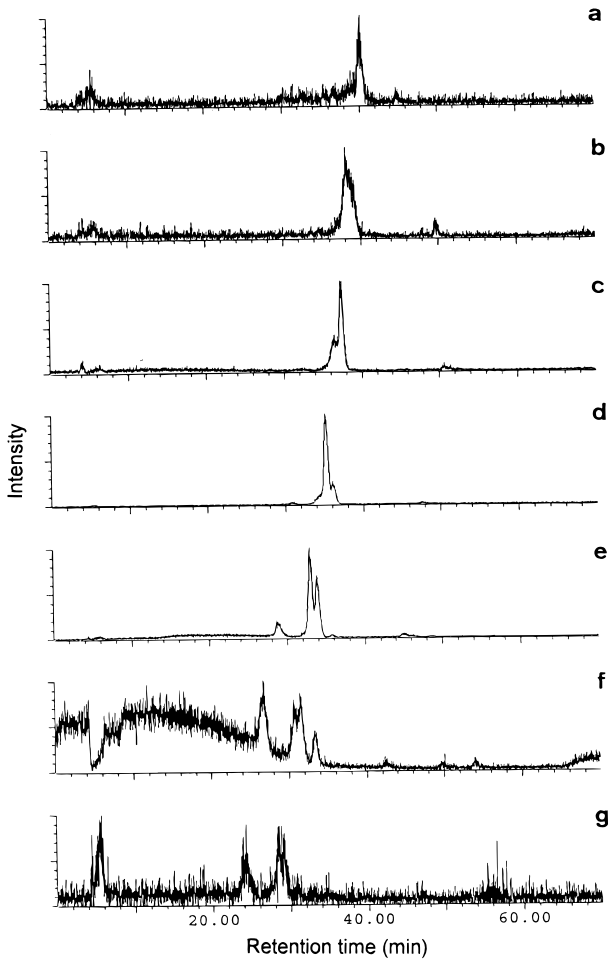

FIGURE 5. LC/ISP (negative ions)−MS selected ion monitoring (SIM) traces from the total ion current (TIC) chromatogram corresponding to the ions with (a) *m/z* 369, (b) *m/z* 355, (c) *m/z* 341, (d) *m/z* 327, (e) *m/z* 313, (f) *m/z* 299, and (g) *m/z* 285, corresponding to the sulfophenyl carboxylates with alkyl chain of C_{13-7}. Analytical column, 250 × 2.0 mm packed with C_{18}, using an elution gradient shown in Table 2.

TABLE 2. HPLC Analytical Conditions for SPC Analysis

columns	analytical column 250 × 2 mm i.d. Hypersil 5 μm, Shandon		
solvents	A, 80% AcN, 20% water B, 100% water additives to A and B 5 mM triethylamine + 5 mM CH_3COOH		
flow	0.15 mL/min		
vol. injection	50−100 μL		
mobile phase	**time (min)**	***A* (%)**	***B* (%)**
	0	5	95
	25	60	40
	40	100	0
	50	100	0
	60	5	95

been used in previous work (*29*), produces chromatograms showing an efficient separation of each LAS homologue as a unique peak, under which all the positional isomers are eluted without interference and with sufficient intensity to permit an accurate quantification.

However, the results obtained in this study showed the presence of one peak of an unknown compound, with a retention time less than that of C_{10}-LAS. The intensity of this peak was observed to increase in line with the decrease in LAS concentration for sampling stations at increasing distances from the effluent discharge point. Because the technique used is specific for sulfonated benzene ring-type compounds and because the signal retention time is less than that of LAS, this peak must be produced by the intermediate products from the degradation of LAS (sulfophenyl carboxylic acids). This possibility had previously been suggested by Taylor and Nickless (*30*) during laboratory biodegradation tests on LAS and, subsequently, by Marcomini *et al.* (*31*) and Di Corcia *et al.* (*20*) in biologically treated wastewater.

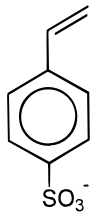

FIGURE 6. Chemical structure of the specific fragment ion with *m/z* 183.

The addition of a mixture of available SPC standards (C_2-C_5) after the pretreatment stage increased the peak intensity proportionally to the quantity of SPC added (data not shown). This confirmed the presence of SPC, although the co-elution of all of them in a single peak did not permit their individual identification. Using the gradient scheme according to the analytical conditions described for the separation of LAS and SPC, it was possible to achieve the separation of the different SPC and the different LAS homologues. Figure 4 shows a comparison between the chromatograms obtained from a mixture of LAS and available SPC standards and from a sample of interstitial water (Figure 4, panels a and b, respectively). For the interstitial water sample, various peaks with intermediate retention times between those of the short-chain SPC standards and those of the LAS were seen; those peaks with UV spectra denoting the existence of sulfonated benzene ring-type compounds are marked on Figure 4b. For the seawater samples, similar results were obtained, although the peak intensities are less. These compounds may be long-chain SPC, which to date had only previously been described in groundwater samples and in water from waste treatment plants by means of the negative chemical ionization gas chromatography−mass spectrometry (NCI GC−MS) technique (*21*). In that study, the SPC found were of chain lengths of up to 10 carbon atoms.

Identification of SPC by Mass Spectrometry. LAS and SPC are anionic compounds. The ISP interface technique generates mass spectra from compounds that are ionic in the eluent. Therefore, the ISP interface operating in the negative ion mode is an obvious choice for the identification of these compounds.

In the negative ion mode and applying a low extraction voltage of 20 V, mainly the deprotonated molecules [M − H] were observed. That is, corresponding to the four C_{10-13} LAS compounds present in the commercial mixture, the ions with *m/z* 297, *m/z* 311, *m/z* 325, and *m/z* 339 were found. The primary transformation products of these compounds are formed after carboxylation of the aliphatic chain (ω-oxidation). The ions of these compounds are thus expected to be found at *m/z* values that are 30 amu higher. In fact, in our samples from a marine environment, ions with *m/z* values of 327, 341, 355, and 369 from compounds with longer chain lengths (C_{10-13}), together with ions with *m/z* 313, 299, and 285 from compounds with shorter chain lengths (C_{9-7}) were found. This is clearly illustrated in Figure 5, where the ion chromatograms of these transformation products are depicted. Various isomers of these compounds can be present. These observations are very interesting because, to our knowledge, no reports are available describing the presence of transformation products from LAS in water samples of marine origin.

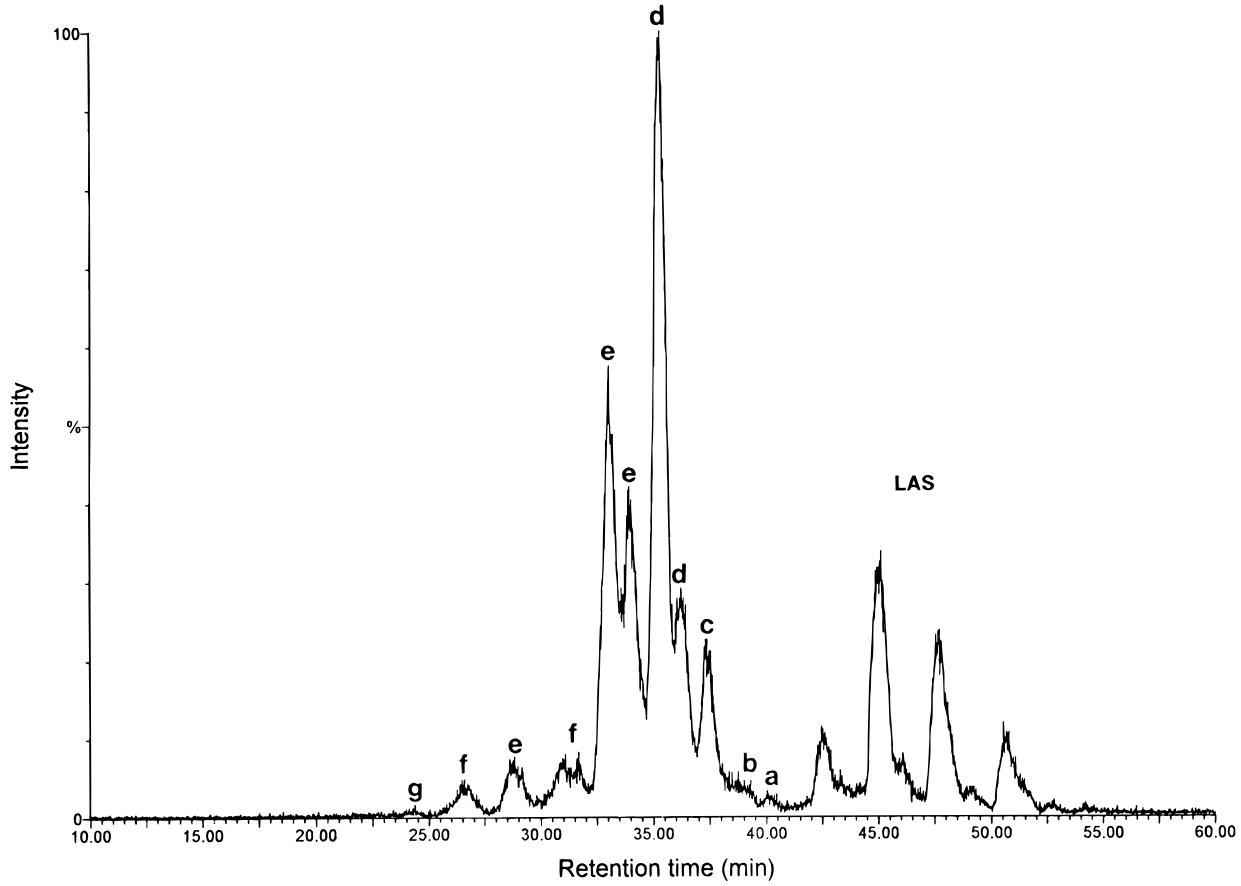

FIGURE 7. LC/ISP (negative ion)−MS ion chromatogram of *m/z* 183 of a water sample (Figure 4b). Analytical column, 250 × 2.0 mm packed with C_{18}, using an elution gradient shown in Table 2: (a) C_{13} SPC, (b) C_{12} SPC, (c) C_{11} SPC, (d) C_{10} SPC, (e) C_9 SPC, (f) C_8 SPC, (g) C_7 SPC.

Furthermore, an increase of the extraction cone voltage enhances the formation of fragment ions and thus enables the unambiguous identification of these compounds. An extraction cone voltage of 60 V resulted in the formation of the specific fragment ion with *m/z* 183 (Figure 6) for all SPC and LAS compounds. This ion had previously been detected for LAS with collision-induced dissociate mass spectra from MS/MS experiments in combination with soft ionization techniques such as field desorption (FD) and fast atom bombardment (FAB) (*32*, *33*, *16*).

Selected ion monitoring (SIM) of this ion at higher extraction voltages can be used for the identification of these compounds. The potential of this system is illustrated in Figure 7, which depicts the LC/ISP(negative ions)−MS ion chromatogram of *m/z* 183, with a extraction cone voltage of 60 V, of the same sample as shown in Figure 4b.

In Figure 8a−e, the ionspray mass spectra of the more abundant SPC transformation products are displayed. The intensities of the C_7 and C_{13} analytes, in particular, were very low (see Figure 5), making the formation of a good mass spectrum rather difficult.

The further increase of the extraction cone voltage to 80 V enhances the formation of fragment ions. In Figure 9a−c, the ionspray mass spectra of C_9 SPC at extraction voltages of 20, 60, and 80 V are depicted.

Spatial Distribution of LAS and SPC. Figure 10 shows the variation in the concentration of LAS and approximate concentrations of long-chain SPC (C_7−C_{11}) for the different sampling stations, according to the distance from the urban effluent discharge point. The concentrations of LAS found near the effluent source are high, similar to those reported for highly contaminated zones [e.g., Tokyo Bay (*34*)]. But in this case, the fundamental cause must be the relatively low volume of the area of water into which the LAS is discharged.

The LAS concentration decreases exponentially with the distance from the discharge point, but to a greater extent than would normally be expected as a result of the dilution of wastewater with seawater. There are two processes by which LAS may tend to be eliminated from the water: (a) through its adsorption by matter in suspension and by the sediments and (b) by biodegradation. In estuarine waters, Takada and Ogura (*34*) found that biodegradation was the more efficient of these mechanisms.

In a previous study (*35*), it was demonstrated that the process of adsorption of LAS by the sediments in the Bay of Cadiz is significantly encouraged by increasing the ionic strength (*I*) of the medium. It was also demonstrated that, for normal values of *I* in seawater, the adsorption process is practically irreversible. The results obtained in this study showed the presence of SPC (C_7−C_{11}) in the medium at a high concentration (Figure 10); therefore, both processes, adsorption and biodegradation, should be considered relevant to explain the elimination of LAS from the water column in the study zone.

The observed approximate concentration of SPC (between C_7 and C_{11}) increases in proportion to the distance from the discharge point, as far as the proximities of station 3, and then decreases progressively. Bearing in mind that the residence time of the LAS in the seawater medium is related to the distance from the discharge point, the variation observed in the concentrations of LAS and the SPC between C_7 and C_{11} (Figure 10) calls to mind the idea of two consecutive chemical reactions of the A → B → C type, in which both reactions have a first-order kinetic. In this simplified idea, A would represent the LAS, B would represent the longer chain SPC, and C would represent the shorter chain SPC. Theoretically, these last compounds should progressively increase their concentration, reaching a maximum at the point

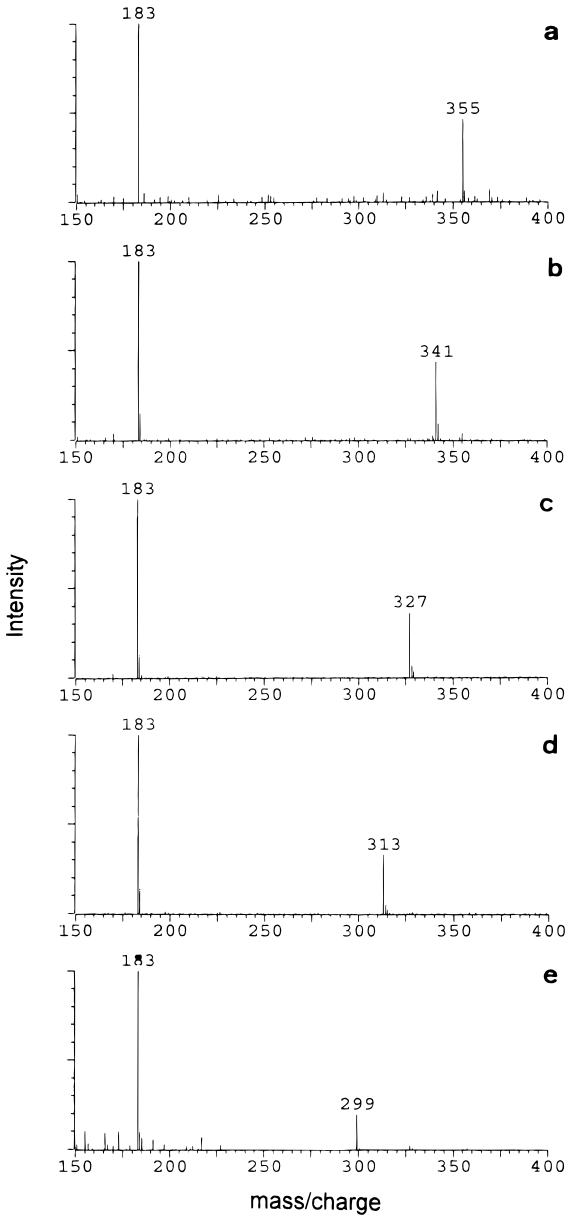

FIGURE 8. Full-scan ISP negative ion mass spectra of the (a) C_{12}, (b) C_{11}, (c) C_{10}, (d) C_9, and (e) C_8 alkyl chains of the SPC compounds most abundant in water samples, at an extraction voltage of 60 V.

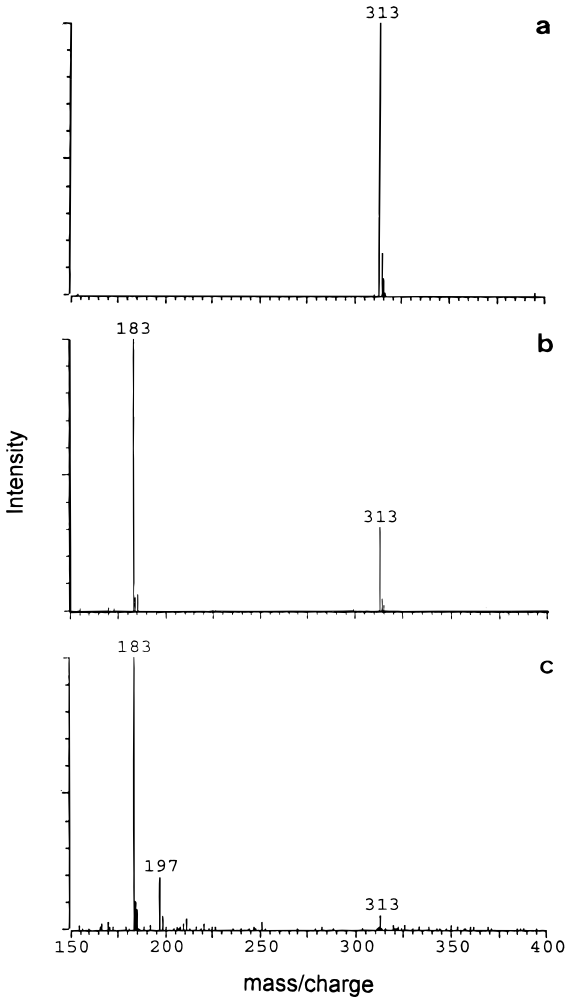

FIGURE 9. ISP full-scan mass spectrum of the C_9 SPC compound at extraction cone voltages of (a) 20, (b) 60, and (c) 80 V.

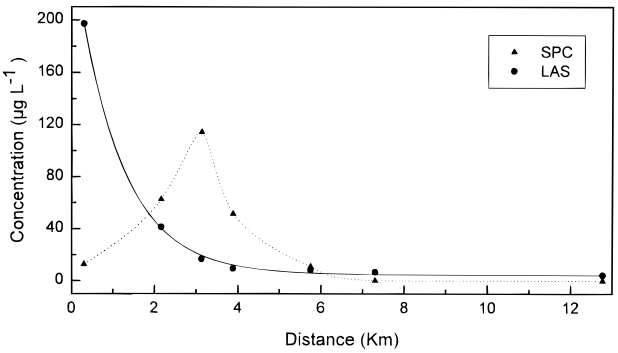

FIGURE 10. Variation of the concentrations of LAS and approximate concentrations of SPC (C_7−C_{11}) in the sampling stations, with their distance from the urban effluent discharge point.

furthest from where the maximum concentration of longer chain SPC occurs. Subsequently, they should steadily decrease until the LAS biodegradation reaches the benzene ring.

In this study, the SPC of chain lengths less than 7 carbon atoms were only found at trace levels (<0.2 ppb) in samples from stations furthest from the urban effluent source. This does not agree with the results obtained by Field *et al.* (*21*), who found that the SPC of between 5 and 8 carbon atoms chain length were the most persistent. Before that, Taylor and Nickless (*30*) had referred to the C_4−C_8 SPC as the "key intermediates" in the biodegradation of LAS. The procedure used in this study for the concentration of sulfonated benzene ring-type compounds encourages the more hydrophobic compounds to interact with and to be retained by the C_{18} minicolumn. For this reason, the absence of the shorter chain SPC from the chromatograms could be the result of their being lost during the treatment received by the environmental samples prior to their analysis (*36*). Tests carried out with the standards of SPC between C_2 and C_5 confirmed this idea . Another possibility that was raised by Schöberl (*11*) is that when the alkyl chain length of the SPC is equal to or less than 5 carbon atoms, the benzene ring may open and/or desulfonation may take place. At this moment, the resulting compound would cease to be a SPC.

Figure 11 gives the percentage distribution of the SPC found at sampling stations 1−5. Only SPC of chain lengths C_9, C_{10}, and C_{11} were found at station 1. These are precisely the compounds that would be produced after the first β-oxidation of the alkyl chain. The proportions in which they were found also coincide with those expected, given the particular proportions of the different homologues in the commercial LAS. The further the sampling station's position

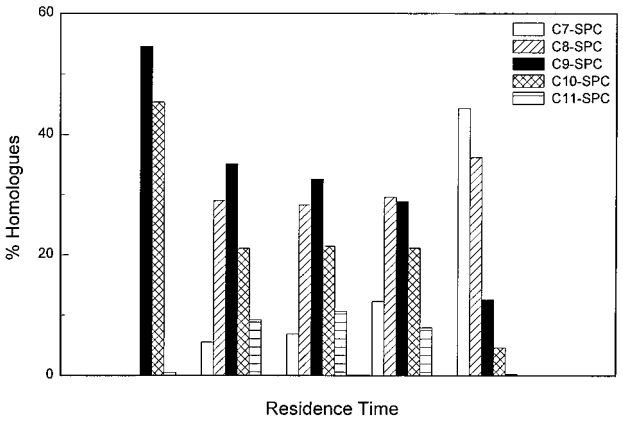

FIGURE 11. Percentage distribution of the different SPC found at sampling stations 1−5 against residence time of the LAS.

TABLE 3. Comparison between Theoretical Order of Abundance of SPC Resulting from Successive β-Oxidations of Alkyl Chain and Actual Order Observed from Analysis

commercial LAS	distribution of homologues
	$C_{11} > C_{12} > C_{13}$
(%)	37.4 35.4 23.1
SPC according to	**theoretical order of abundance**
1st β-oxidation	$C_9 > C_{10} > C_{11}$
2nd β-oxidation	$C_7 > C_8 > C_9$
3rd β-oxidation	$C_5 > C_6 > C_7$
SPC station	**experimental order of abundance**
no. 1	$C_9 > C_{10} \gg C_{11}$
no. 2	$C_9 > C_8 > C_{10}$
no. 3	$C_9 \geq C_8 > C_{10}$
no. 4	$C_8 \geq C_9 > C_{10}$
no. 5	$C_7 \geq C_8 > C_9$

from the urban effluent source, progressively, the lower is the proportion of SPC of 9 and 10 carbon atoms and the higher the proportion of those with 7 carbon atoms. At station 5, the sequence of abundance becomes $C_7 > C_8 > C_9$, which coincides with the theoretical sequence that would exist after a second β-oxidation of the commercial LAS, assuming that all homologues degrade at same rate.

Unfortunately, the complex hydrodynamics of the zone do not allow an estimate to be made of the residence time of the LAS along the length of the channel. Consequently, these explanations of the kinetics must be considered only a qualitative approximation. Nevertheless, it may be inferred from these observations that the first stages of the biodegradation of the LAS are not notably rapid in the marine environment. These conclusions are summarized in Table 3.

It is also noteworthy that, in the sample of interstitial water analyzed, SPC of chain lengths of 12 and 13 carbon atoms were found among others (Figure 7); the first of these SPC may be produced by means of a β-oxidation of the C_{14} homologue of the LAS, although its very low proportion in the commercial LAS (0.2%) makes this hypothesis rather unlikely. In fact, the presence of SPC-C_{13} confirms unequivocally the existence of a ω-oxidation prior to the shortening of the alkyl chain. It can also be concluded that the persistent presence of these SPC of equal chain length to the LAS homologues should bear a relationship to the slow biodegradation of these products in the reducing conditions of the sediment ($E_h \approx -200$ mV).

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