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# Monitoring the Primary Biodegradation of Linear Alkylbenzene Sulfonates and Their Coproducts in Anoxic Sediments Using Liquid Chromatography−Mass Spectrometry

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An accompanying article has demonstrated the anaerobic degradation of the surfactant linear alkylbenzene sulfonate (LAS) in microcosms filled with marine sediments through the generation of sulfophenylcarboxylic acids (SPCs). A detailed study shows that this process was uniform in the blanks (non-spiked natural sediments) for every LAS homologue during the complete course of the experiment. However, when sediments were spiked with commercial LAS and, therefore, enriched with short-chain homologues, degradation was enhanced for these homologues until their percentages were close to those for non-spiked sediments. The reason is that short-chain homologues are more bioavailable due to their higher solubility and lower sorption capacity. Thus, sorption on sediments was found to be increased with the length of the alkyl chain for LAS homologues, following a linear Freundlich isotherm, whereas the metabolites generated were predominant in solution due to their much higher polarity. Intermediate-chain SPC homologues ($C_7$−$C_9$ SPCs) were the most abundant during the experiment, but a significant increase in the concentration of shorter-chain SPC homologues ($C_4$−$C_6$ SPCs) was detected toward the end. In the case of isomers, the steric effect of the aromatic group implies that LAS primary degradation took place preferentially over external isomers. Therefore, the generation of external isomers of SPCs was predominant during the complete experiment although internal isomers of SPCs became more evident when the degradation process had advanced and external isomers of LAS became scarce. The identity of both types of SPC isomer was confirmed by tandem mass spectrometry. With respect to LAS coproducts, the relative percentage of iso-LAS increased during the complete experiment and removal percentages for dialkyl tetralinsulfonates (<30%) were typically lower that those for LAS (66−79%), although a similar behavior was observed for their homologues in both cases.

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## Introduction

This work discusses in detail the primary biodegradation of linear alkylbenzene sulfonates (LAS) under anaerobic conditions, which had previously been suggested (*1*) and later demonstrated to occur (*2*) in anoxic coastal marine sediments through the generation of sulfophenylcarboxylic acids (SPCs). The characterization of this process is a useful tool for establishing the persistence and risk assessment of this anionic surfactant, as well as for a full understanding of its fate in the environment. Commercial LAS consists of a mixture of homologues, termed $C_{10}$- to $C_{14}$-LAS in function of the length of the alkyl chain, although longer homologues are also employed outside the EU. Each homologue contains several isomers which can be considered as external or internal if the position of the sulfophenyl group link with the alkyl chain is toward the ends or the middle of the chain respectively. Commonly the isomers of LAS are expressed as $m\Phi C_n$-LAS, where $m$ and $n$ denote the site of the sulfophenyl group link with the alkyl chain ($m = 1$ indicates the C atom at the end of the alkyl chain which is the nearest to the sulfophenyl group) and the length of the alkyl chain respectively (e.g., $5\Phi C_{10}$-LAS should be considered as an internal isomer of a short-chain homologue whereas $2\Phi C_{13}$-LAS corresponds to an external isomer of a long-chain homologue) (see Figure S1a, Supporting Information).

The mechanism for the aerobic degradation of LAS has been widely studied. Although initial studies soon demonstrated the biodegradability of LAS by applying nonspecific methodologies, i.e., MBAS (methylene blue active substance) or DOC (dissolved organic carbon) removal, the use of specific analytical techniques such as HPLC (high-performance liquid chromatography) coupled to ultraviolet and/or fluorescence detectors allowed for the monitoring of their main metabolites, the sulfophenylcarboxylic acids (SPCs), in laboratory tests performed with several types of water (*3*−*5*) and soil (*6*). The presence of these intermediates implies a degradation mechanism which starts with the $\omega$-oxidation of the LAS alkyl chain that generates SPC homologues of the same length. This is followed by consecutive $\alpha$ and $\beta$-oxidations (*7*, *8*) which decrease the alkyl chain length by shortening the chain by one and two carbon atoms, respectively. As in the case of LAS, different SPC homologues and isomers exist and they can be described by the same terminology ($m\Phi C_n$-SPC) but taking into account that, although $m$ still denotes the site of the sulfophenyl group link with the alkyl chain, $m = 1$ indicates the C atom at the carboxylic group, so the higher the value of $m$ the more external the isomer (e.g., $7\Phi C_{11}$-SPC should be considered an internal isomer of a long-chain homologue whereas $5\Phi C_6$-SPC corresponds to an external isomer of a short-chain homologue) (see Figure S1b, Supporting Information). Degradation is completed with desulfonation and the rupture of the aromatic ring, although the order in which these two processes occur is still under discussion. The entire aerobic degradation process commonly takes a few days to be completed, although it has been reported to be slower (*9*−*12*) in the case of internal isomers of LAS and its coproducts, iso-LAS (monobranched isomers of LAS) (see Figure S1c, Supporting Information) and dialkyl tetralinsulfonates (DATS, isomers of LAS containing an alicyclic moiety) (see Figure S1d, Supporting Information),


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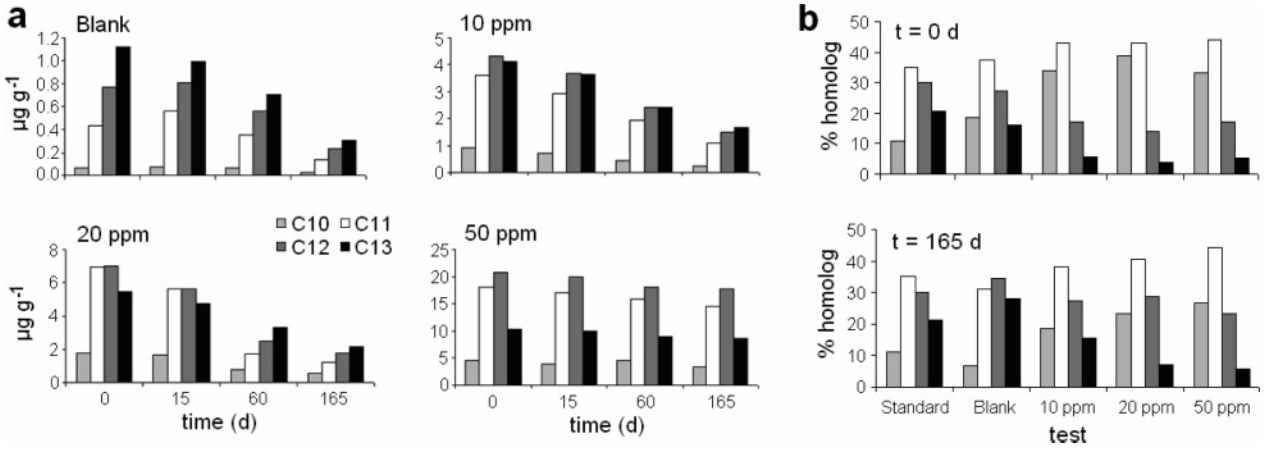


**FIGURE 1. (a) Evolution in the concentration of LAS homologues ($\mu$g g$^{-1}$) in sediment during the complete experiment. (b) Average distribution of LAS homologues in water at the beginning ($t$ = 0 d) and at the end ($t$ = 165 d) of the experiment.**

due to steric impediments that make the microbial attack on the alkyl chain difficult. The percentage of these coproducts ranges from <1 to 10% depending on the manufacturing process used.

The development of interfaces such as ESI (electrospray ionization) during the past decade has enabled a better understanding of the aerobic degradation pathway by using liquid chromatography−mass spectrometry (LC−MS). Not only have the identities of the different SPC homologues been confirmed (*13*−*15*) but also the presence of new metabolites have been recently detected in lower concentrations: sulfophenyldicarboxylic acids (*14*) and α,*β*-unsaturated SPCs (*15*). In contrast, there has been little advance regarding the anaerobic degradation of LAS since several studies in the 1980s claimed its non-biodegradability in the absence of oxygen (*16*−*18*). Anaerobic biodegradation of other major synthetic surfactants, not only of the anionic type such as alkyl ethoxysulfates (AES) and alkyl sulfates (AS), but also non-ionics, i.e., nonylphenol polyethoxylates (NPEOs) and alcohol polyethoxylates (AEOs), has been demonstrated in recent years (*19*−*21*). Their degradation pathways appear to be similar to those reported for the aerobic process and even carboxylated metabolites have been detected during degradation tests performed with NPEOs (*21*). This is our case, where the generation of SPCs associated with a sharp decrease in LAS concentrations have been both found at anoxic depths in coastal marine sediments during field samplings (*1*, *22*) and in laboratory assays (*2*). Hence, our main object in the present work is to perform for the first time an accurate characterization of the anaerobic primary degradation of LAS and its coproducts in marine sediments by the following: (a) monitoring the variations in their alkyl chain and isomer composition during the course of this process, (b) identifying their intermediates as well as their homologue and isomer distributions, and (c) comparing this case with the much better-known aerobic degradation.

## Experimental Section

**Materials and Standards.** See Supporting Information.

**Sample Collection and Microcosm Establishment.** The experimental setup has been previously described in ref *2*.

**Determination of LAS, Coproducts, and Metabolites.** The analytical procedure was the same as that reported in ref *2* with some modifications. See Supporting Information.

## Results and Discussion

**Monitoring LAS and SPC Homologue Distribution During the Anaerobic Degradation Process.** As reflected in the accompanying article (*2*), the major part of the added LAS was found to be attached (99.2% ± 0.5) to sediments. Data on the concentration of LAS homologues in water ($C_e$) and sediment ($X$) at the beginning of the experiment ($t$ = 0 d) for all cases were fitted to a linear Freundlich isotherm ($\log X = \log K + n \log C_e$). The resulting sorption coefficients ($K$) are very similar (see Table S1, Supporting Information) to those reported in a previous work (*23*) where sediments from the same area were employed in a sorption−desorption test conducted at lower LAS concentrations (0.03−1 ppm). In that paper it was observed that equilibrium was reached within 4 h so presumably it was also achieved in this case, because sample treatment was carried out after 12 h. The increase in $K$ with increasing alkyl chain length is indicative of a hydrophobic interaction controlling the adsorption of LAS on the sediment. Thus, longer alkyl chain homologues ($C_{12}$- and $C_{13}$-LAS) tend to show higher concentrations in accordance with their higher hydrophobicity and affinity for the organic carbon in the case of non-spiked sediments, as previous field samplings (*24*) corroborated.

Figure 1a shows the evolution in the concentration of LAS homologues in sediment during the experiment. It can be observed at day 0 that the larger the quantity of commercial LAS added in the microcosms, the higher the relative proportions of the shortest homologues ($C_{10}$- and $C_{11}$-LAS) found in sediment. The reason is that the homologue distribution in commercial LAS is enriched in $C_{10}$- and $C_{11}$-LAS with respect to the typical homologue distribution present in the blanks, which contain non-spiked natural sediments where sorption and degradation processes have already taken place. Once the anaerobic degradation of LAS had taken place during the following days, not only was the concentration of the different homologues considerably reduced in the blanks, the 10 and 20 ppm tests, but also a variation in their relative percentages was observed for the last two cases. Thus, while degradation seemed to be uniform for every homologue in the blanks, short-chain homologues showed higher relative percentages at $t$ = 0 d with respect to those found at $t$ = 165 d for the 10 and 20. The homologue distribution in spiked sediments gradually became adjusted to that present in non-spiked sediments toward the end of the experiment by preferential degradation over short-chain homologues. This finding indicates that the experimental design was satisfactory in reproducing the degradation process under realistic conditions. There is an exception for the 50 ppm case, as the LAS degradation was considerably inhibited. On the other hand, non-significant differences were observed in the LAS concentration in water during the experiment, showing average values of 6 ± 1, 66 ± 25, 166 ± 46, and 439 ± 168 ng mL$^{-1}$ for the blanks, 10, 20, and 50 ppm cases, respectively. Figure 1b shows the percentage of LAS homologues in this phase at the beginning ($t$ = 0 d) and

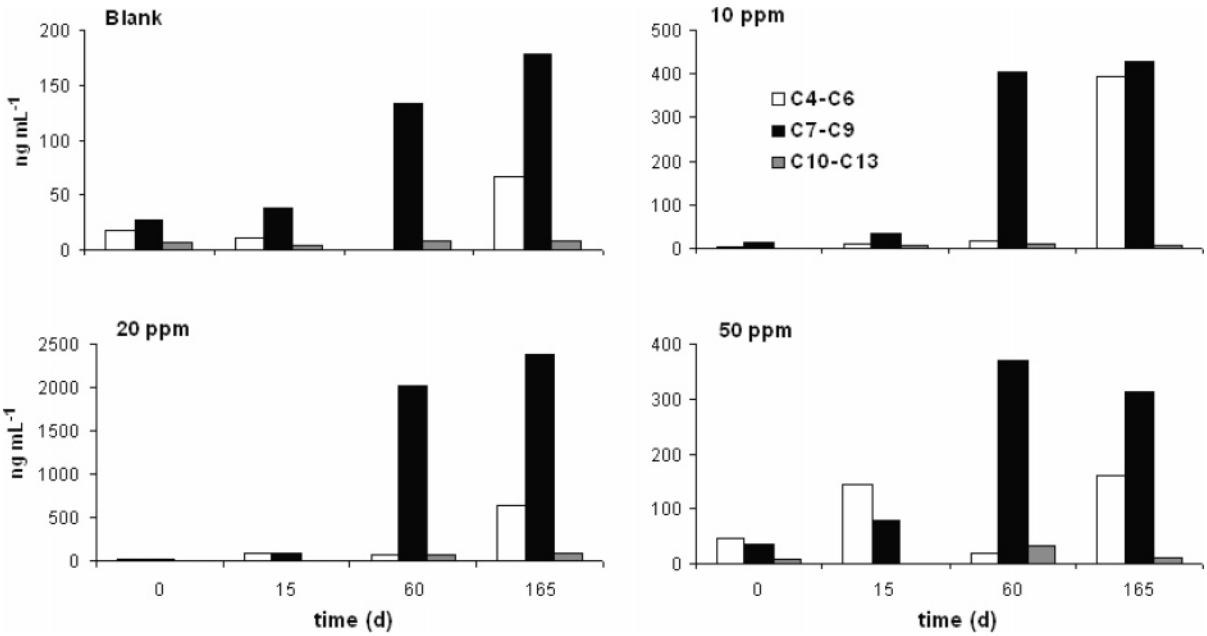


**FIGURE 2. Evolution in the concentration of SPC homologues (ng mL$^{-1}$) in water during the complete experiment.**

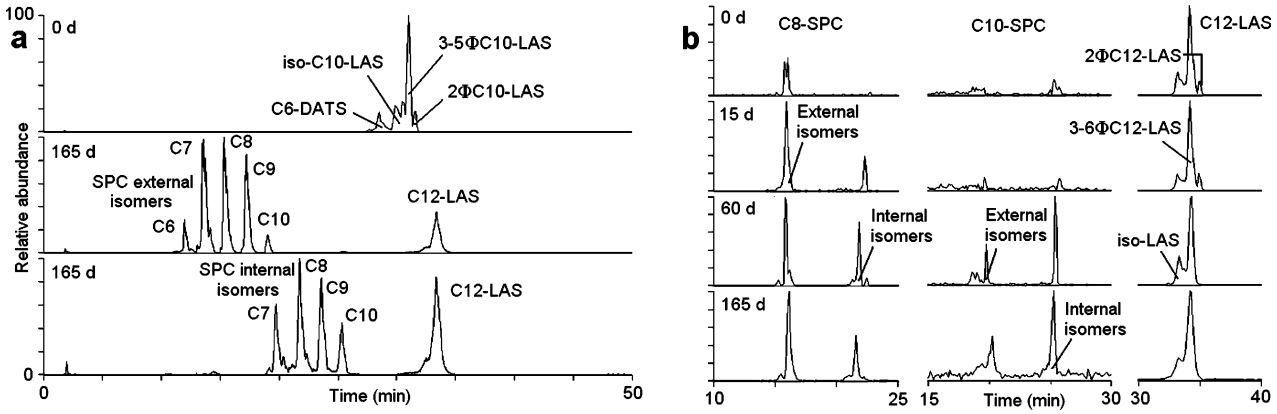


**FIGURE 3. (a) LC−ESI−MS extracted ion-chromatogram (*m/z* = 295−298) from a water sample showing peaks corresponding to $C_6$-DATS, iso-$C_{10}$-LAS, and $C_{10}$-LAS isomers at the beginning of the experiment (*t* = 0 d) and LC−ESI−MS/MS chromatograms from a water sample showing peaks corresponding to $C_6$−$C_{10}$-SPC isomers and $C_{12}$-LAS at the end of the experiment (*t* = 165 d), both for the 10 ppm case. (b) LC−ESI−MS extracted-ion chromatogram from a water sample showing the evolution of the relative intensity of the isomers of $C_8$-SPC (*m/z* = 299), $C_{10}$-SPC (*m/z* = 327), and $C_{12}$-LAS (*m/z* = 325) during the complete experiment for the 10 ppm case.**

at the end (*t* = 165 d) of the experiment for all the concentrations tested as well as for a commercial mixture. The presence of the shortest LAS homologues was predominant in water at the beginning with respect to this mixture and the particulate phase due to their higher solubility and lower sorption capacity, so their bioavailability was enhanced with respect to the longer homologues. After 165 days, however, the distribution for LAS homologues had changed (with the exception of the experiment conducted with 50 ppm of LAS, where degradation was minimal) so it was noticeable that there was a substantial decrease in the percentage of $C_{10}$-LAS for the 10 and 20 ppm cases. This finding implies not only a preferential degradation over short-chain homologues in the anoxic water of the microcosms, due to their higher bioavailability, but also that there was an increase in the relative percentages of long-chain homologues toward the end of the experiment probably due to a slower desorption from the sediment.

Overall, from data shown in Figure 1a and b, it is suggested that sorption−desorption and degradation are the two processes which were controlling the different homologue distributions in both aqueous and particulate phases. During the first days of the experiment, desorption and, therefore, degradation due to higher bioavailability, appeared to be extended for the relatively most abundant short-chain homologues for the 10 and 20 ppm tests. However, when their relative percentages decreased at the end of the experiment, degradation tended to be more uniform due to the much higher concentration of the less bioavailable longer homologues. Further, a previous study has pointed out that desorption takes place slowly and gradually in marine sediments due to the higher ionic strength of the medium (*23*). A more intense degradation of the short-chain LAS homologues at the beginning of the experiment, however, appears to be in contrast with previous studies of aerobic degradation of LAS in freshwater (*4*, *25*, *26*), seawater (*3*, *26*), and riverine sediments (*25*), which showed non-significant differences in the degradation percentages among the $C_{10}$- to $C_{13}$-LAS homologues (*3*, *25*) or preferential degradation over long-chain LAS homologues. This is probably because sorption−desorption processes were absent as only the aqueous phase was considered in performing those assays (*3*, *4*, *26*), or desorption was favored due to the scarce presence of sediments (1 g L$^{-1}$) and use of freshwater instead of seawater (*25*).

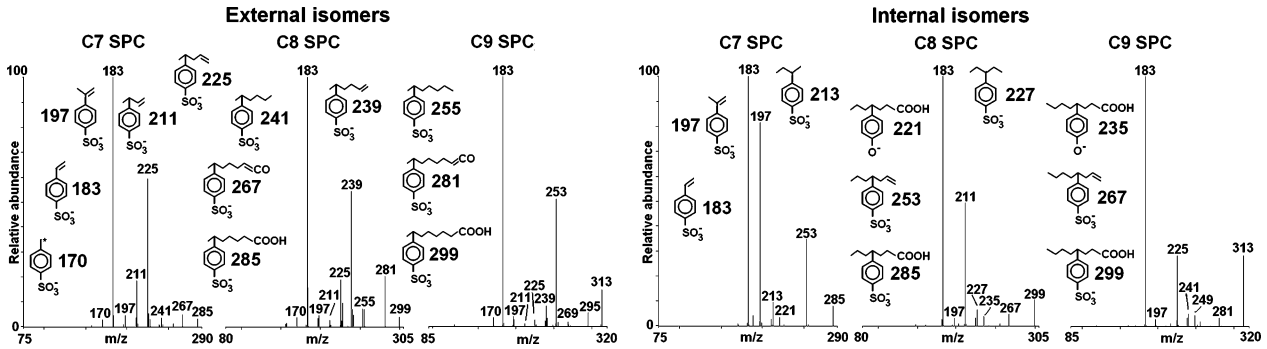


**FIGURE 4. LC−ESI−MS/MS spectra extracted from the chromatograms represented in Figure 3a (day 165) showing the fragmentation patterns for $C_7$−$C_9$-SPC isomers. Tentative structures of fragment ions are also shown.**

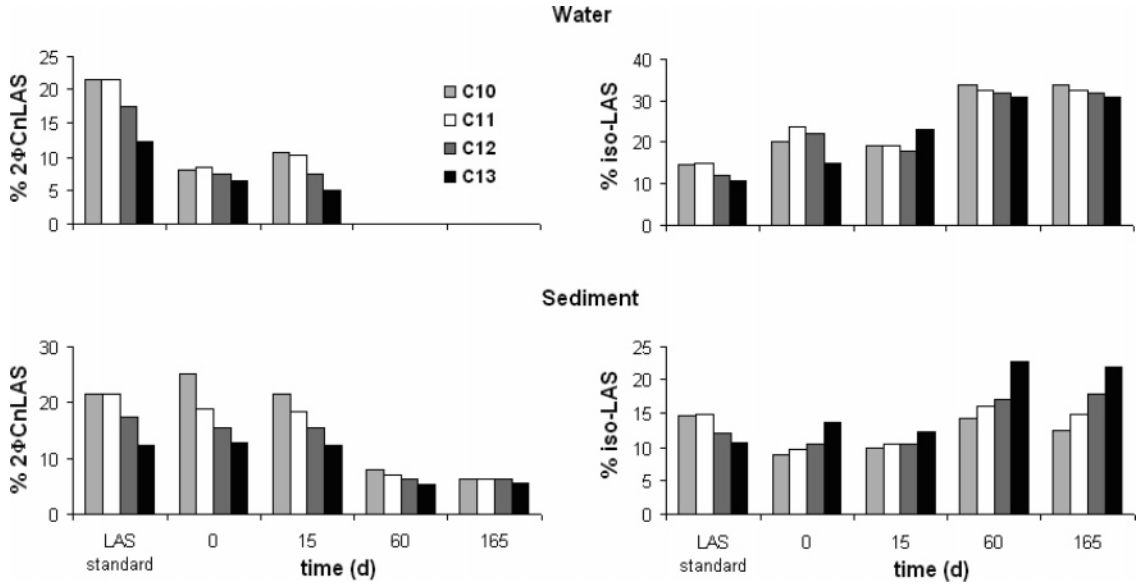


**FIGURE 5. Evolution in the average distribution of 2Φ$C_n$LAS and iso-LAS in water and sediment during the complete experiment for the 10 ppm case. LAS standard is referred to the percentage of 2Φ$C_n$LAS and iso-LAS commonly found in a commercial mixture.**

Figure 2 shows the evolution in the concentration of SPCs homologues in water during the complete experiment. After 15 days there was a sharp increase in their concentration in all microcosms, although it was smoother where 50 ppm of LAS were added, which is consistent with the lower disappearance detected for the surfactant in this case. Intermediate-chain SPCs ($C_7$−$C_9$) were predominant during the degradation process as the alkyl chain of longer SPCs ($C_{10}$−$C_{13}$) was rapidly shortened. These long-chain SPCs are not usually detected during the performance of degradation tests in presence of oxygen (*3*) due to the higher efficiency of the aerobic metabolism, but they have been previously detected in field samples close to untreated wastewater effluents points (*13*) and in pore water from sediments (*1*). Their presence and the fact that SPC concentrations still showed an increasing trend even at day 165 indicate that the anaerobic degradation process is relatively slow compared to the aerobic case, where both compounds are mineralized within a few days. Anyway, degradation continued toward the end of the experiment as can be observed in Figure 2, where values of short-chain SPCs ($C_4$−$C_6$) increased. Thus, from the data available, it appears that the anaerobic pathway for LAS degradation occurs in a very similar way to that reported for the aerobic case, starting with a $\omega$-oxidation of the LAS alkyl chain followed by consecutive $\beta$-oxidations and, probably, α-oxidations, although the presence of other metabolites should not be discounted.

**Evolution of the Isomeric Composition in the Biodegradation Process.** During the analysis of LAS and SPCs by liquid chromatography−mass spectrometry (LC−MS), it was evident that changes in the isomeric composition of both target compounds were taking place during the experiment. It is important to clarify that there are differences in retention time and elution order of isomers depending on whether they are internal or external and whether they are taking part of LAS or SPC homologues. The interaction of the molecule of a LAS isomer with the HPLC column takes place preferentially by the longer side of the alkyl chain with respect to the sulfophenyl group (see Figure S1a, Supporting Information), with the result that external isomers such as 2Φ$C_{10}$-LAS elute later than the rest (Figure 3a, day 0) (*4*, *27*). Iso-LAS is the first to elute because of the presence of a methyl branching (*27*). However, elution of the SPC isomers is performed in opposite order because the presence of a carboxylic group in one side of the alkyl chain (see Figure S1b, Supporting Information) enhances the interaction between the opposite side, which contains a higher number of carbon units in the case of internal isomers, and the HPLC column. Effectively, as is shown in Figure 3a at day 165, external isomers elute first and consecutively in function of the length of their alkyl chain, and they are followed by the internal isomers. The identities of all these peaks have been confirmed as belonging to SPCs by using tandem mass spectrometry (MS/MS). Figure 4 shows the MS/MS spectra of $C_7$-, $C_8$-, and $C_9$-SPCs isomers obtained after isolation and fragmentation in the LC−MS ion trap of their quasimolecular ions $[M - H]^-$ with *m/z* 285, 299, and 313 respectively. The specific fragment ion *m/z* 183, which has been previously

**TABLE 1. Changes in the Average Concentration of DATS (ng $g^{-1}$) ($n = 6$) during the Complete Course of the Experiment (0−165 Days) and Removal Percentage (%)**

| | | Blank | | | | | 10 ppm | | | | | 20 ppm | | | | | 50 ppm | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | time (d) | 0 | 15 | 60 | 165 | % | 0 | 15 | 60 | 165 | % | 0 | 15 | 60 | 165 | % | 0 | 15 | 60 | 165 | % |
| 1−10 cm | mean | 24 | 21 | 14 | 7 | 70 | 31 | 30 | 22 | 10 | 67 | 38 | 28 | 23 | 25 | 36 | 62 | 59 | 59 | 51 | 18 |
| | (SD) | (0) | (4) | (2) | (3) | | (2) | (7) | (6) | (2) | | (4) | (1) | (2) | (6) | | (2) | (5) | (4) | (11) | |
| 10−20 cm | mean | 27 | 26 | 10 | 8 | 72 | 33 | 35 | 31 | 23 | 31 | 47 | 37 | 36 | 35 | 25 | 62 | 59 | 60 | 54 | 12 |
| | (SD) | (1) | (2) | (2) | (3) | | (3) | (6) | (2) | (7) | | (7) | (12) | (12) | (5) | | (12) | (5) | (5) | (10) | |

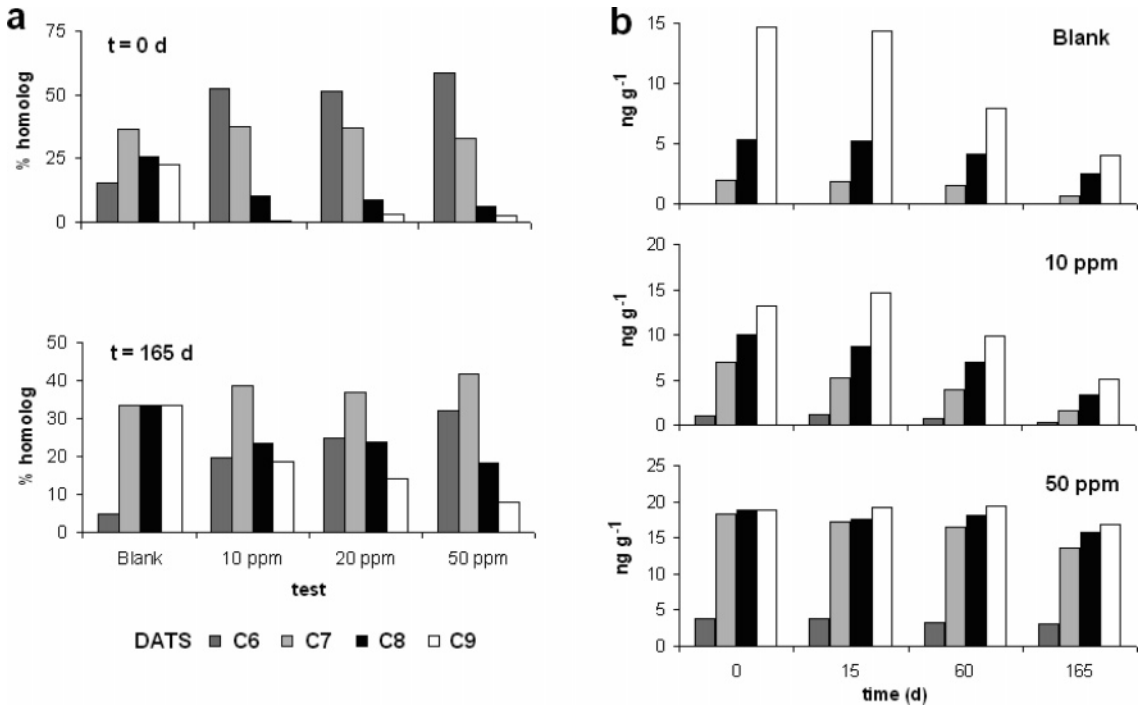


**FIGURE 6. (a) Average distribution of DATS homologues in water at the beginning ($t = 0$ d) and at the end ($t = 165$ d) of the experiment. (b) Changes in the concentration of DATS homologues in sediment during the complete experiment for the blank, 10 ppm, and 50 ppm cases. Blank is referred to a non-spiked natural sediment.**

described to be characteristic of SPCs and LAS isomers (*13*, *15*), is the most abundant in all cases under the same conditions (ESI ion fragmentation energy = −20 V, ion trap collision energy = 40%) but fragmentation patterns differ depending on whether the isomers are external or internal. A tentative elucidation of the remaining fragments was performed (Figure 4) in agreement with past studies (*13*, *15*, *28*).

Figure 3b displays several extracted-ion chromatograms showing two selected SPC homologues and one LAS homologue, in order to illustrate the variations in the isomeric composition during the complete experiment. Several authors (*4*, *7*, *29*) have reported that LAS internal isomers tend to show longer half-lives in aerobic degradation due to the steric effect that the aromatic group shows over the methyl terminal end of the alkyl chain where the process of biodegradation starts via $\omega$-oxidation (a phenomenon known as the "distance principle"), which makes the internal isomers less susceptible to microbial attack than the external isomers. This is reflected in Figure 3b, where the relative intensity of the $C_{12}$-LAS internal isomers increased throughout the duration of the experiment while the external isomers ($2\Phi C_{12}$-LAS) showed a faster degradation and disappeared. The percentage of iso-LAS was also increased because branched isomers are less biodegradable than the linear ones (*12*, *14*) due to the presence of a methyl branching that impedes microbial attack. As a consequence, SPC external isomers which result from the degradation of LAS external isomers were predominant over the SPCs internal isomers during the complete process. A noticeable increase of the internal SPC isomers was detected at the end of the experiment, as can be observed not only in Figure 3b but also in 3a when relative intensities of both types of SPC isomer are compared to that of $C_{12}$-LAS. This is particularly clear in the case of the longer chain SPCs, such as $C_{10}$-SPC, where the relative proportion of internal isomers surpassed that of the external ones at day 165 (Figure 3b). Thus, the degradation of LAS internal isomers increased the levels of SPC internal isomers toward the end of the experiment, when LAS external isomers had already been converted to SPC external isomers. Therefore, the biotransformation process was extended as the time passed, and the degradation pattern for LAS and SPCs was similar to that observed previously by Di Corcia et al. (*12*) and Eichhorn and Knepper (*15*) during aerobic degradation tests.

Figure 5 clearly illustrates that degradation was preferential for external isomers, as it shows the evolution of the average distribution of the LAS external isomers (2ΦCn-LAS) in water and sediment during the experiment for the 10 ppm case. The influence of the sorption process is also observed because the relative percentage of external isomers at the beginning (day 0) in the aqueous phase is lower than in the LAS standard due to their higher hydrophobicity. Thus, external isomers tend to be sorbed on the particulate phase, as their relative percentage in sediment increases slightly with respect to the standard. From day 60 to the end of the experiment, biotransformation of 2ΦCn-LAS isomers into external SPCs in the 10 ppm tests resulted in them no longer being detected in water samples, and their presence in

sediment became scarce. This trend could only be observed with difficulty in the case of the 50 ppm tests, because variations are minimal due to the more limited extent of the biodegradation process. A different behavior from that for 2ΦCn-LAS isomers is observed in the case of iso-LAS (Figure 5), the relative percentages of which show an increase in both water and sediment phases during the experiment due to higher persistence, which has been previously reported in aerobic degradation tests (*10*−*12*, *14*).

**DATS Removal in Marine Sediments.** In spite of their low percentage (from <1 to 8%) in commercial LAS standards, dialkyl tetralinsulfonates (DATS) can be detected in the marine sediments collected to perform this study. Their concentrations range from 22 to 27 ng $g^{-1}$. Table 1 shows the evolution in the concentrations in sediment of these coproducts during the complete experiment. As in the case of LAS, most of the DATS were found attached to sediments due to their affinity for the organic fraction, while concentrations in water remained below the ppb level. The LAS standard used to carry out the anaerobic degradation test contained less than 0.5% of DATS, which is reflected in the slight increases of these compounds in the sediment when 10, 20, and 50 ppm of LAS were added. Significant changes in their concentration were detected during the experiment, and removal percentages (Table 1) were estimated to be below 30% in most cases, with the exception of those found for the blanks (70−72%). It can be observed that added LAS is degraded preferentially over its coproduct when these results are compared with those obtained for LAS during the same test (*2*). The greater persistence of DATS has been previously studied in different aerobic environments: groundwater (*9*), laboratory tests (*11*, *12*), river water, and wastewater treatment plants (*14*). Their degradation pathway seems to be the same as that for LAS, via the generation of alkylcarboxylated metabolites, although longer half-lives have been reported for these intermediates than for LAS, iso-LAS, DATS, or SPCs. No intermediates were detected in our case, probably due to their low concentration, as the decrease in DATS concentrations was slight, and/or due to poor retention in the octadecylsilica cartridges because their polarities are even higher than those of SPCs. Therefore, we can only talk strictly about removal, although anaerobic degradation of DATS is suggested as an explanation of these data.

Figure 6a and b show the variations of DATS homologue distributions in water and sediment, respectively. A phenomenon similar to that observed for LAS in Figure 1a and b took place, although to a less extent. Thus, removal of the short-chain $C_6$-DATS homologue seems to be enhanced with respect to the rest of the homologues during the first days of the experiment, due to its higher bioavailability, but this process tended to be uniform for all homologues toward the end of the experiment, when the presence of $C_6$-DATS became scarce. Therefore, the changes of the DATS homologue distributions in both water and sediment phases are similar to those observed for LAS, including the final stage, where these distributions are close to those found in natural sediments.

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## Supporting Information Available

The analytical methodology followed for the identification and quantification of the different homologues and isomers of LAS and SPCs, the chemical structures of the target compounds (Figure S1), and the parameters corresponding to the Freundlich isotherms for LAS (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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