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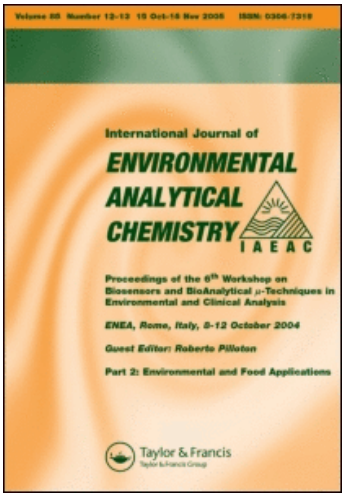

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Robert P. Eganhouse[a]
[a] Environmental Sciences Program, University of Massachusetts, Boston, Massachusetts, U.S.A.

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Long-Chain Alkylbenzenes: Their Analytical Chemistry, Environmental Occurrence and Fate†

ROBERT P. EGANHOUSE

Environmental Sciences Program, University of Massachusetts, Boston, Massachusetts 02125, U.S.A.

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Since ca. 1950 long-chain alkylbenzenes have been produced industrially for the synthesis of alkylbenzenesulfonates, the anionic surfactants most commonly used in commercial detergents. Prior to 1965 the alkylbenzenes were generated by Frieldel–Crafts alkylation of benzene with tetrapropylene. This reaction produces a complex assemblage of phenylalkanes (TABs) having highly branched side chains. Due to their stability, the TABs proved to be environmentally troublesome and were ultimately replaced (during the mid-1960s) by the linear alkylbenzenes (LABs). The LABs consist of a mixture of secondary phenylalkanes with linear alkyl side chains ranging in length from C_{10} to C_{14}. Because of their unique structures and composition, these compounds are easily identified and measured in complex environmental samples.

The linear alkylbenzenes are also found in municipal wastewaters where their presence is thought to result from the use of domestic and industrial detergents. Because they are synthetic and unlikely to occur in other significant inputs to coastal marine waters, long-chain alkylbenzenes have obvious potential as waste-specific molecular tracers. The presence of long-chain alkylbenzenes in sediment trap particulates and marine sediments collected near a major waste outfall system in southern California indicates that these hydrocarbons can survive exposure to an oxygenated water column during sedimentation. Whereas changes in the isomer composition of the LABs with depth in the sediments are suggestive of microbial alteration, the vertical distribution of the TABs and LABs can be used as a geochronological tool to reconstruct waste depositional histories.

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KEY WORDS: Long-chain alkylbenzenes, molecular tracers, sediment, waste depositional histories, alkylbenzenesulfonates (ABS), linear alkylbenzenesulfonates (LAS).

INTRODUCTION

Alkylated benzenes having side chains ranging in length from C_{10} to C_{15} are routinely used in the manufacture of synthetic anionic surfactants known as alkylbenzenesulfonates (ABS). First introduced to the detergent marketplace in the early 1950s, these surfactants rapidly assumed a position of dominance *vis à vis* natural product based soaps. Within a few years, however, it became apparent that the ABS were problematic. Their high surface activity and, in particular, their resistance to biodegradation resulted in formation of persistent foams in natural waters and waste streams. These difficulties were largely overcome during the mid-1960s with the introduction of a suite of analogs more susceptible to decomposition, the linear alkylbenzenesulfonates (LAS).

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Sulfonated alkylbenzenes of both types are synthesized in essentially three steps: (1) production of mono-olefins (or monochloroparaffins) having chain lengths from C_{10} to C_{20}, (2) Friedel–Crafts alkylation of benzene and (3) sulfonation of the alkylbenzene ring. A detailed discussion of the synthesis of ABS surfactants is beyond the scope of this paper, and the reader is referred to outside reviews on the subject.[1,2] For present purposes, it is important only to consider structural and compositional differences between the two types arising from the first reaction step. In TBS (tetrapropylene alkylbenzenesulfonate) production, the dominant method of olefin synthesis is polymerization of propylene (C_3H_6) in the presence of phosphoric acid. This reaction generates a complex assemblage of mono-olefins of varying chain lengths and a high degree of branching. The most commonly manufactured mixture consists mainly of C_{12} compounds and has, therefore, been generically termed "tetrapropylene". During catalytic alkylation of benzene with tetrapropylene, further rearrangements occur along the alkyl chain and also at the alkyl-aryl bond leading to the formation of several isomers for each reactant olefin. The resultant alkylbenzene mixture (TABs) is exceedingly complex as illustrated in Figure 1b. It has

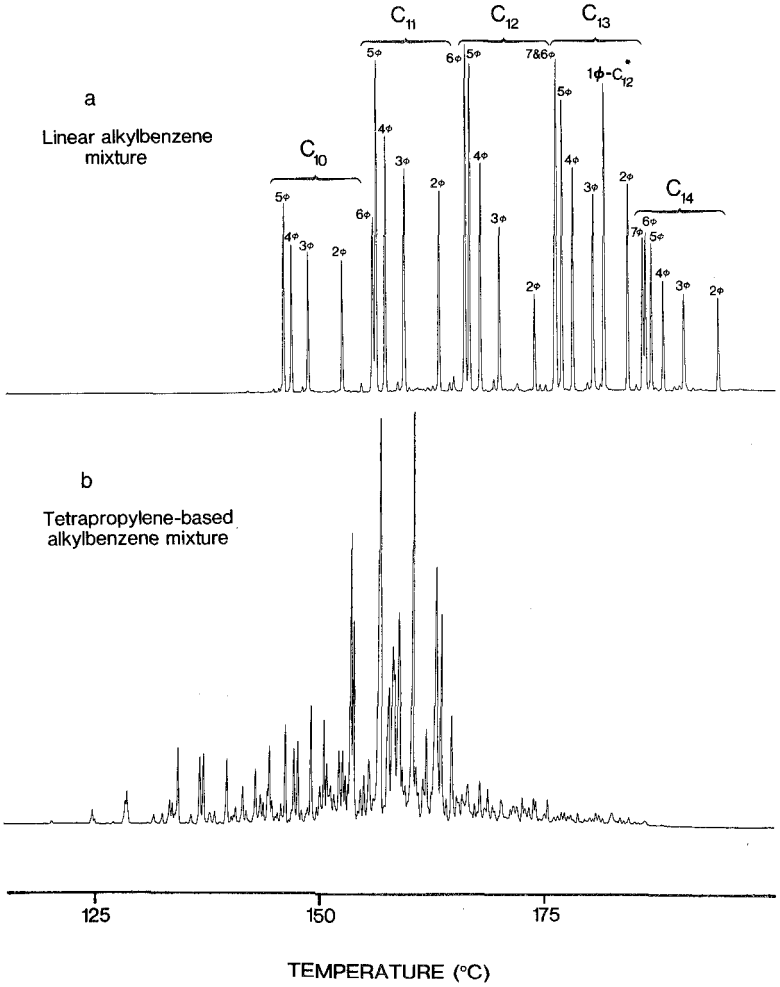

FIGURE 1 High resolution gas chromatogram of long-chain alkylbenzenes. (a) Linear alkylbenzenes (LAB); (b) Tetrapropylene-based alkylbenzenes (TAB) $n\emptyset$-C_m: n = position of phenyl attachment, m = number of carbon atoms in alkyl chain.

been estimated that if all C_{10-15} monoalkylbenzene isomers are considered, up to 80,000 individual compounds are possible.[3]

In contrast to the TABs, alkylbenzenes used for production of LAS (i.e. the linear alkylbenzenes; LABs) comprise a relatively simple mixture. In this synthesis benzene is alkylated using *linear* α-olefins

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(or monochloroparaffins) to form an assemblage consisting of all the possible secondary phenylalkanes. The absence of 1-phenylalkanes is attributed to the instability of the primary carbonium ion intermediate.[4] Figure 1a represents a high resolution gas chromatogram for a typical LAB formulation containing the C_{10}-C_{14} homologs. The structural and compositional differences between the tetrapropylene-based alkylbenzenes (TABs) and the linear analogs (LABs) have implications not only for their analytical chemistry, but also for their behavior and fate in the environment.

The purpose of this paper will be to present current approaches to the identification and quantitative determination of both alkylbenzene types in environmental samples. In addition, recent studies on the occurrence of these hydrocarbons and their transport and fate in the marine environment will be summarized.

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METHODS

The procedures used for sampling and analysis of waste effluents, detergents and marine sediments have been described in detail elsewhere.[5–7] Following is a brief summary of the methodology currently being used in our laboratory.

Isolation of the long-chain alkylbenzenes (LCABs) requires extraction using organic solvents of low to moderate polarity (e.g. dichloromethane, methanol or some mixture). In view of the volatility of the LCABs, every effort is made to avoid losses due to heating or cryogenic dehydration of the samples. Therefore, we employ ambient temperature extraction of wet sediments and liquid–liquid extraction for aqueous samples. Once concentrated by rotary evaporation, the total extract (in CH_2Cl_2) is dehydrated and treated for elemental sulfur removal by passage through a column of anhydrous Na_2SO_4/activated copper. After concentration under a stream of N_2, the purified extract is either chromatographed on thin layers of silica gel H using CH_2Cl_2 as mobile phase or on $AgNO_3$-impregnated silica gel (hexane development). The former provides a total hydrocarbon fraction, whereas the latter separation results in the isolation of a pure alkylbenzene fraction. Choice of separation procedures depends on the nature of the sample and the abundance and composition of the alkylbenzenes (discussed subsequently). Normally, we use high resolu-

tion gas chromatography/mass spectrometry (HRGC/MS) with electron impact ionization in full scan, limited mass scan or selected ion monitoring modes depending upon detection requirements and the need for spectral data. However, *if* sufficient amounts of only one of the two alkylbenzene types is present in the sample, direct analysis of the $AgNO_3$-silica gel alkylbenzene fraction can be achieved by HRGC. Throughout this paper LAB isomers will be symbolized as follows: $n\phi$-C_m, where n = position of phenyl attachment on the alkyl chain, and m = the number of carbon atoms in the alkyl chain.

RESULTS AND DISCUSSION

Analytical chemistry

In our experience, long-chain alkylbenzenes in waste effluents, detergent formulations and waste-impacted sediments are never present at greater than trace levels (e.g. ng-μg/g or ng-μg/liter). Thus, efficient procedures for their concentration, isolation and recovery preliminary to instrumental analysis are necessary. Figure 2 illustrates the

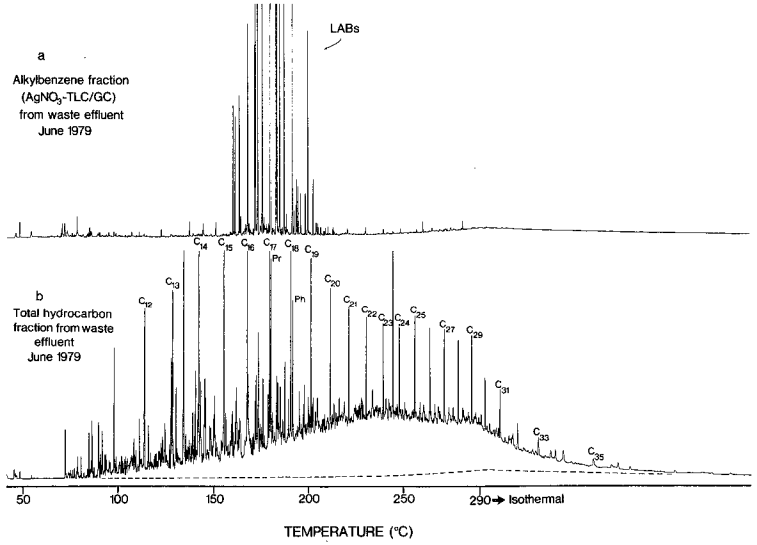

FIGURE 2 Alkylbenzene and total hydrocarbon fractions isolated from Los Angeles County primary waste effluent (a) $AgNO_3$-silica gel; (b) Silica gel H.

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types of separations possible for a waste effluent sample using the $AgNO_3$-silica gel and silica gel H procedures described above. The alkylbenzene fraction shown in Figure 2a was isolated in a single step from a sewage extract whose hydrocarbon content was 20%. Therefore, the effectiveness of the separation as depicted here is under-emphasized. The facile one-step separation of a pure alkylbenzene fraction from such a complex mixture is made possible because of the unusual structures of the LCABs. Complexation of Ag^+ ions and the π bonds of the benzene ring causes the alkylbenzenes to be retarded relative to aliphatic hydrocarbons during chromatogram development. Polynuclear aromatic hydrocarbons are retained even more effectively due to their multiple fused aromatic rings whereas all non-hydrocarbons are immobilized on the silica gel owing to the weak mobile phase used (hexane). The only conceivable interference to the LCAB fraction (as yet unobserved) would be from polyolefins whose retention characteristics might, in principle, be similar. Background contamination of sampling gear and glassware that has been prepared with cleansers containing LAS surfactants can, however, be a significant problem. In order to maintain acceptable procedural blank levels, these items must be scrupulously cleaned and, preferably, heated in a muffle furnace.

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If only one alkylbenzene type is known to be present in a sample (as in Figure 2a), the $AgNO_3$-silica gel procedure will yield a fraction amenable to direct analysis by HRGC. The LABs, with the exception of the 7-phenyl and 6-phenyl C_{13} isomers, can all be separated satisfactorily on conventional capillary columns wall-coated with a non-polar stationary phase such as SE-54 (number of effective theoretical plates $>$ca. 100,000). The TABs cannot be fully resolved (cf. Figure 1b), and it is clear from their mass spectra that many of the major peaks contain more than one compound. Nevertheless, the TABs can also be analyzed by HRGC. In this context, 1-phenylalkanes (C_{12-15}) prove to be suitable recovery surrogates and internal standards because of their similar physico-chemical properties and response to flame ionization detection, their absence from LAB and TAB mixtures and the fact that they do not co-elute with any of the LAB or TAB peaks. Secondary calibration standards can be developed from LAB and TAB reference mixtures using the 1-phenylalkanes for quantitation by the internal standard method.

The justification for using the silica gel H separation of a total

hydrocarbon fraction arises because other hydrocarbon analytes are often sought and/or qualitative examination of hydrocarbon (and other) non-hydrocarbon compound classes is required. As long as the alkylbenzenes are present at concentrations in the final fraction of >ca. 0.1 ng/μl, and the mass of total hydrocarbons transferred to the capillary column does not cause overloading or detector saturation, direct analysis by HRGC/MS in the full scan mode straightforward. Figure 3 illustrates the extreme selectivity that can be achieved. The fraction depicted in this diagram is the same one shown in Figure 2b, however, instead of GC/FID (FID-flame ionization detection) analysis, GC/MS in the full scan mode was performed with mass fragmentography at $m/z=91$, 105. These ions are characteristic of monoalkylbenzenes. Molecules other than the LCABs that produce $m/z=91$, 105 ions are rarely observed in the same retention range.[7,8] Consequently, interferences, even in a complex hydrocarbon fraction such as this, are minimal.

Instrumental detection limits can be substantially lowered (by factors of 10^2 to 10^3) through the use of selected ion monitoring, however, loss of significant structural information may be unacceptable, especially if more than one alkylbenzene type is present. In these instances, limited mass scanning over a mass range which includes salient diagnostic ions (e.g. $m/z=85$–135 and/or 216–278; see following discussion) can offer a practical compromise between detection/quantitation limits and the need for qualitative information. In order to attain the absolute minimum method detection limits and, at the same time, all but eliminate interferences, a combination of the $AgNO_3$-silica gel separation and HRGC/MS analysis is preferred. Table I summarizes the advantages and limitations of these various alternatives.

For reasons of detection and structural elucidation, HRGC/MS is clearly the instrumental technique of choice. Fortunately, the mass spectral characteristics of monoalkylbenzenes having minimal side chain branching have been investigated in some detail.[8] Ionization at 70 eV results in the generation of abundant molecular ions of formulae $C_nH_{2n-6}^+$ and a series of decomposition products corresponding to phenylalkyl ions ($C_nH_{2n-7}^+$). β-cleavage is clearly the most important fragmentation process. For all LAB isomers other than the 2-phenylalkanes, β-cleavage leads to formation of $(M\text{-}R)^+$ ions (where R is an alkyl substituent at the α-carbon). Upon further

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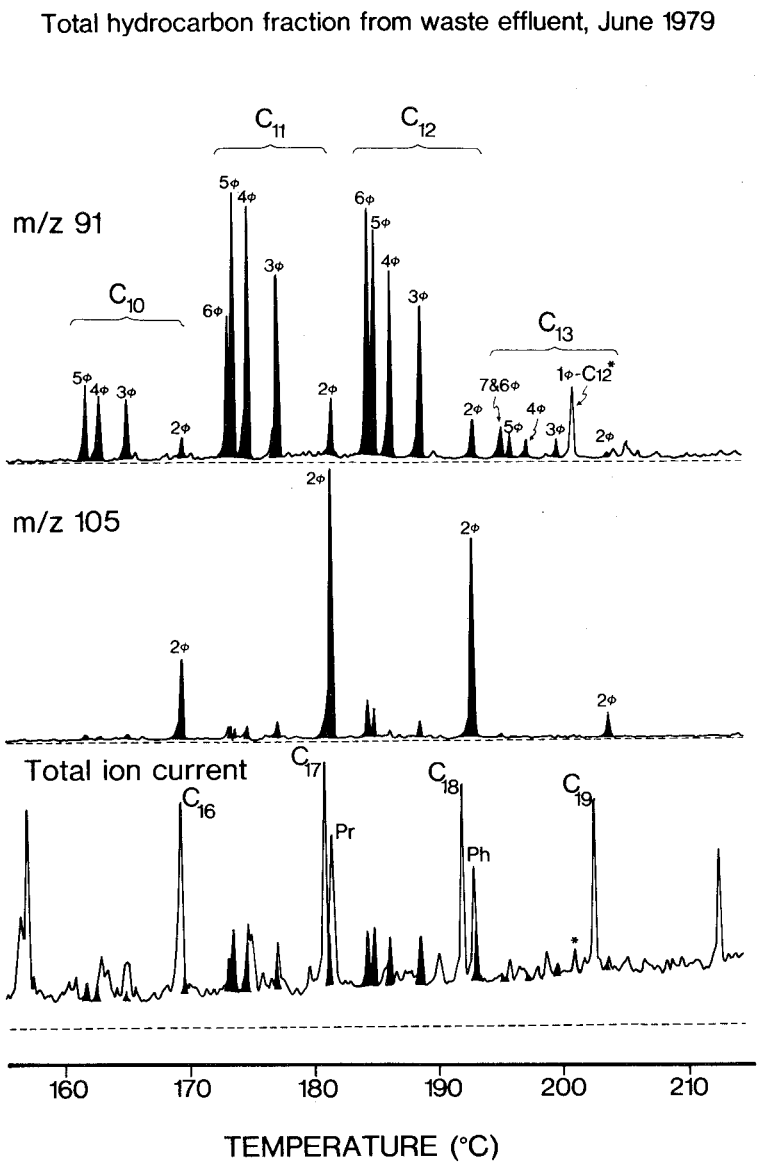

FIGURE 3 HRGC/MS analysis (full scan mode) of a total hydrocarbon fraction isolated from Los Angeles County primary effluent.

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TABLE I

Various approaches to the instrumental analysis of long-chain alkylbenzenes

Method of analysis[a]	Approximate ILD[b]	Advantages	Disadvantages
HRGC/FID	100 pg	1) low cost instrumentation	1) no structural information 2) largely restricted to samples with one alkylbenzene type 3) requires isolation of a "pure" alkylbenzene fraction
HRGC/MS-FS	100 pg	1) structural confirmation 2) generally does not require sample clean up 3) Useful for samples having more than one alkylbenzene type	1) expensive instrumentation 2) may be limited by [LCAB]/[total hydrocarbon] ratio
HRGC/MS-SIM	1 pg	1) extremely low detection limit 2) no sample cleanup	1) expensive instrumentation 2) limited structural information
HRGC/MS-LMS	20 pg	1) detection limits intermediate between full scan and SIM; lower than FID 2) no sample cleanup normally necessary 3) some structural information for isomer identification	1) expensive instrumentation

[a]HRGC/MS—high resolution gas chromatography/mass spectrometry; FID—flame ionization detection; FS—full scan; SIM—selected ion monitoring; LMS—limited mass scan.

[b]ILD—instrumental limit of detection.

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dissociation and hydrogen migration, these ions produce a base peak at $m/z=91$ ($C_7H_7^+$) corresponding to the stable tropylium (or benzylic) ion. The primary products of β-cleavage (i.e. the phenylalkyl ions) are, nevertheless, sufficiently abundant to provide a basis for differentiating the secondary phenylalkane isomers. In the specific case of the 2-phenyl isomers, cleavage of the large alkyl group is preferred, and a base peak at $m/z=105$ is characteristic (cf. Figure 3).

Individual long-chain alkylbenzenes of the TAB type have not as yet been successfully characterized because of the extreme complexity of the mixture, the lack of suitable reference materials and an inability to chromatographically resolve the many components.[9,10] Spectroscopic evidence suggests that on average there are 4-5 branches/molecule.[2] It is apparent from mass spectral analysis that many of the TABs have tertiary and quaternary α-carbons with monomethyl and dimethyl substituents, respectively. This assertion is based on the prevalence of base and near-base peaks at $m/z=105$ and 119 for most of the major components found in typical TAB mixtures (cf. Figure 4; cf. ref. 9). Thus, the phenylalkyl ions provide a direct means of discriminating between LABs and TABs present in the same sample. It is possible to quantitate both types of alkylbenzenes by simply using the appropriate phenylalkyl ions generated by β-cleavage. In the few cases where significant LAB and TAB components do co-elute, advantage can be taken of the mass spectral differences of the specific peaks involved by carefully selecting ions that minimize interference. They may not necessarily be the base peaks.

Mass spectrometry also reveals that 50–75% of the TABs have C_{12} chains, the remaining being $C_{10,11,13,14}$ (average chain length = 12.5; cf. refs. 2,9, Table II). LAB/TAB mixtures can easily be identified because of the fact that TABs of a given chain length elute before the corresponding LAB isomers (Figure 5). Thus, assuming alkylbenzenes are present in sufficient concentrations, the parent ions themselves could, in principle, be used for quantitation. In this regard, detection limits should be markedly lowered by using chemical rather rhan electron impact ionization.

Occurrence of long-chain alkylbenzenes in waste effluents

Among the earliest reports of long-chain alkylbenzenes in the

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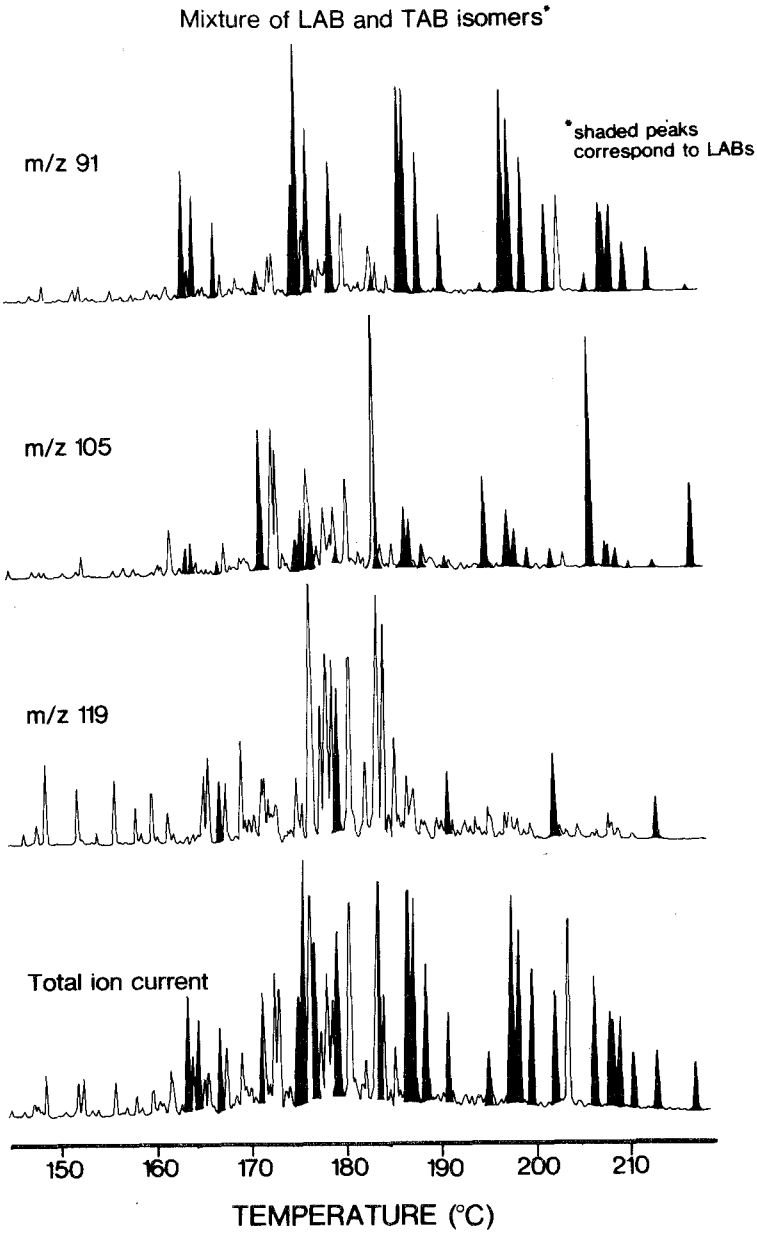

FIGURE 4 HRGC/MS analysis (full scan mode) of a LAB/TAB mixture.

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TABLE II

Chain length distribution of tetrapropylene-based alkylbenzenes (TABs)[a]

Chain length	Relative abundance (%)
C_9	6.4
C_{10}	12.8
C_{11}	18.9
C_{12}	46.1
C_{13}	12.5
C_{14}	2.6
C_{15}	0.7

[a]Material supplied by Monsanto Chemical Co. Chromatograms shown in Figures 1, 5. Relative abundance determined by integration of molecular ion currents.

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environment were those concerned with the analysis of extractable organic matter in municipal waste effluents.[11–13] These investigators failed to recognize the origin of the LCABs, and, therefore, attached no significance to their presence or potential uses. Several years later, Crisp *et al.*[14] observed a suite of secondary C_{10-13} alkylated benzenes in particulates trapped in San Pedro Basin, California. They correctly assessed the anthropogenic origin of the LABs and speculated that their probable source was a nearby waste outfall system. This supposition was later corroborated by direct examination of the effluent in question.[5]

Further study of other municipal effluents from California and the Boston area[15] have tended to confirm the early hypothesis[4] that LABs are, in fact, ubiquitous, if minor, components of municipal wastes. This is not unexpected insofar as they are associated with LAS surfactants, and these, in turn, are known to be abundant constituents of primary effluents and sewage sludge.[1,16] Figure 6 presents mass fragmentograms ($m/z=91$) for hydrocarbon fractions of five primary effluents from southern California along with a commercial laundry detergent. In addition to the variation in isomer and homolog distributions evident in this figure, there are substantial plant-to-plant and temporal fluctuations in total LAB concentration.[15] Whether these variations reflect changing inputs or the effects of treatment is unknown.

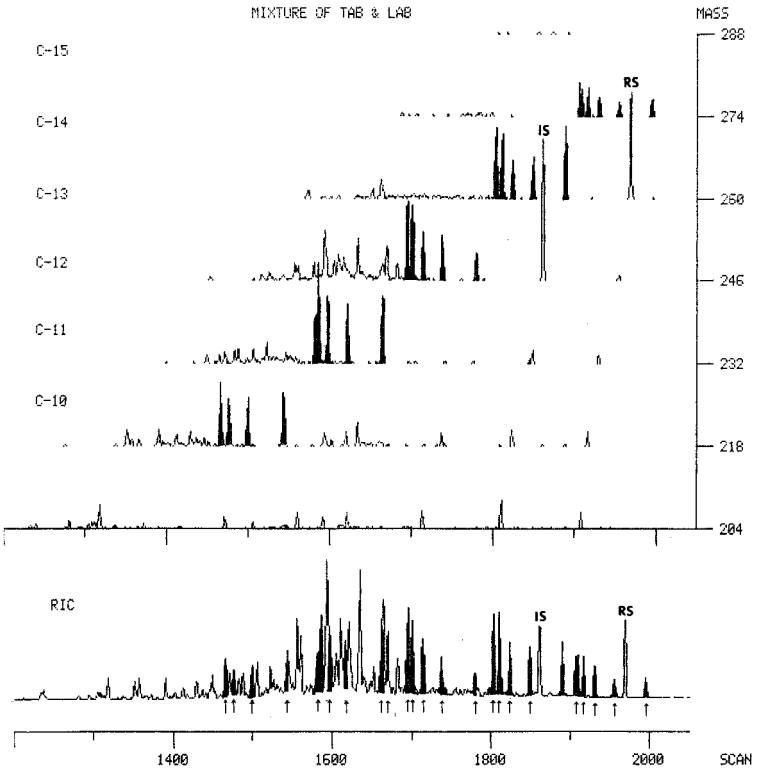

FIGURE 5 Mass fragmentograms at parent ion masses for C_{9-15} substituted benzenes in a LAB/TAB mixture. Shaded peaks (also indicated by arrows in the reconstructed ion chromatogram) are linear alkylbenzenes. IS = 10-C_{12} (internal standard), RS = 10-C_{13} (recovery surrogate). *Note:* late eluting TAB peaks correspond to "isotope" peaks of $(M\text{-}29)^+$ fragments.

The observation of LABs in detergents indicates that a major route for their introduction to waste streams is by carryover with LAS as the result of incomplete sulfonation. To test this hypothesis, an attempt was made to account for the LAB mass emissions from the Los Angeles County treatment facility through analyses of alkylbenzene residues in major household laundry detergents.[7] A number of assumptions were made in performing these calculations: (1) domestic laundering accounts for the total input of LAS (and therefore LABs), (2) washing requires 20 g/person-week and (3) no

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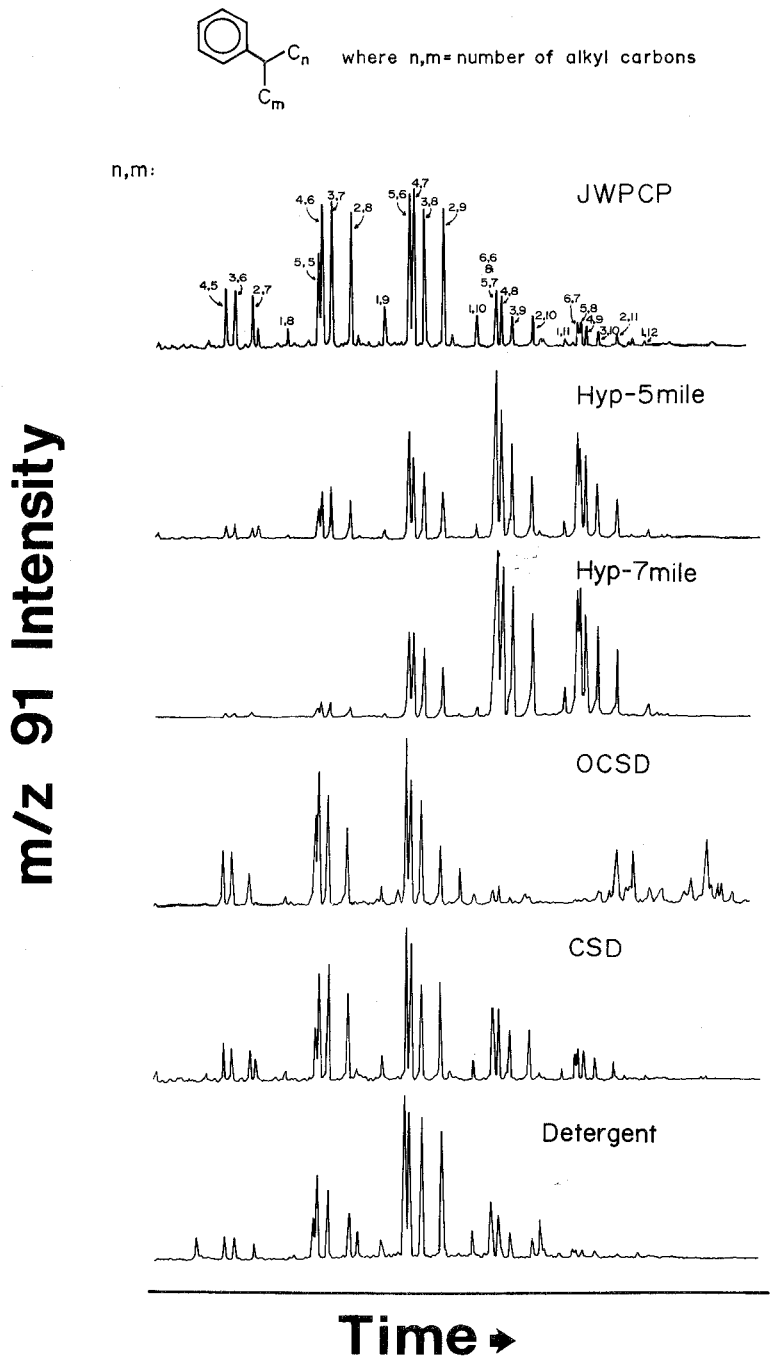

FIGURE 6 Mass fragmentograms (m/z-91) from total hydrocarbon fractions of five southern California municipal effluents and one commercial detergent. JWPCP—Los Angeles County; Hyp-5 mile, Hyp-7 mile—City of Los Angeles, primary effluent and sludge; OCSD—Orange County; CSD—San Diego.

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losses or production of the residual LABs during detergent use, disposal and waste treatment.

Only 13% of the LAB emissions could ultimately be attributed to direct introduction of detergent residues.[6] Thus, the lack of mass balance must be due to one or combinations of three factors: (1) industrial and non-laundry inputs are significant, (2) the detergent samples examined were not representative with respect to their LAB contents or (3) the LABs were generated during or after surfactant use by desulfonation of LAS. Data are not available to test the first two hypotheses, however, we will briefly examine the possibility of desulfonation.

Evidence in support of microbial desulfonation of LAS is lacking. A preponderance of data (cf. references in 1,2) indicates that LAS biodegradation is usually initiated by ω-oxidation of the alkyl side chain with beta cleavage yielding a series of sulfophenylcarboxylic acids as detectable, albeit transient, intermediates. Ultimate degradation (if it occurs) progresses through oxidation of the benzene ring (forming catechol) and subsequent cleavage (either *ortho* or *meta*) as well as desulfonation to yield inorganic sulfite or sulfate. Although reductive desulfonation has been observed in a pure culture of one species of fungus (*Cladosporium resinae*), oxidation of the alkyl side chain appears to have taken place concomitant with or prior to removal of the sufonate group as evidenced by the appearance of benzenecarboxylic acids, not hydrocarbons.[17] There is little justification for invoking a **chemical** desulfonation mechanism in view of the mild conditions of surfactant use and disposal. This hypothesis, however, has not been examined rigorously.

Residual unreacted alkylbenzenes are believed to constitute no more than a few percent of the sulfonated derivatives by weight, and the ecological impact of LCABs, if any, is unknown. Their environmental significance stems solely from the fact that they have a synthetic origin. These hydrocarbons do not occur naturally as either recent or ancient (e.g. fossil fuel) "biogenic" products. Hence, when found in the environment, they can be taken as unequivocal molecular evidence of (anthropogenic) waste contamination. In this context, the LABs differ from the LAS and other surfactants in an important way. They are hydrocarbons. Because sediments deposited near heavily populated coastal areas receive hydrocarbon inputs from a multitude of sources, it is extremely difficult to assess the

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impact of any one source reliably. The LABs may offer a molecular means of determining the contribution made by municipal wastes. The fact that they have physico-chemical properties intermediate between aliphatic and polynuclear aromatic hydrocarbons would suggest that they should be good model compounds for the transport and fate of these important classes of hydrocarbons in the environment. Consequently, it was of some interest to investigate the behavior of the LABs in a heavily waste-impacted coastal ecosystem. For this purpose, we selected the San Pedro Shelf and Basin, site of the Los Angeles County waste outfall system where Crisp, *et al.*[14] first observed LABs in trapped particulates.

Fate of long-chain alkylbenzenes in marine environment

Ishiwatari, *et al.*[18] presented data demonstrating the accumulation of LABs in Tokyo Bay sediments for periods exceeding 20 years (based on ^{210}Pb dating). The authors noted that the sedimentary LABs were present in roughly comparable amounts to their sulfonated analogs whereas in unaltered surfactants, the LABs represented only ca. 1.3% by weight. This led them to conclude that the sulfonates might be degraded preferentially due to their higher water solubility. In studies of sediments and trapped particulates on the San Pedro Shelf and Basin, we have found that the LAB isomer distributions exhibit a marked depletion of the external isomers (i.e. isomers whose phenyl group is attached near the end of the alkyl side chain) when compared with waste effluents and detergent formulations.[6] There is also evidence that the alteration is progressive with distance offshore and with depth in the sedimentary column. By analogy with similar patterns of LAS biodegradation,[1,2] we have interpreted these changes as reflecting structure-selective microbial degradation. (Another possibility, that is, physico-chemical fractionation, has not been examined to our knowledge.) Swisher[1] attempted to explain the isomer-specific degradation of the sulfonates on the basis of enzymatic geometric constraints. His proposed mechanism calls for preferential oxidation of external isomers because of the ability of their alkyl chains to span the distance (on the oxidizing enzyme) between the sites of sulfonate fixation and ω-oxidation. Because the LABs have no sulfonate group, such a mechanism cannot explain the alterations we observe.

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At a site 6 km downcurrent from the Los Angeles County outfall system we collected a sediment core to examine the depositional and diagenetic history of waste-derived organics. The distribution of long-chain alkylbenzenes in these sediments is shown in Figure 7. Both the LABs and TABs were found at depths in excess of 18 and 24 cm, respectively. The geochronology of these sediments has been reconstructed through the use of molecular markers such as the LCABs, elemental abundance (% organic carbon, % organic nitrogen), stable isotope composition ($\delta^{13}C$, $\delta^{15}N$) of the refractory organic matter, a knowledge of the historical discharge of wastes at this site (Figure 8a) and alkylbenzenesulfonate usage patterns in the U.S. (Figure 8b)). For an extensive discussion of the modeling effort in this reconstruction, the reader is referred elsewhere.[19]

To summarize, the TAB concentration profile shows a subsurface maximum at the 12–14 cm interval. This maximum correlates well with the approximate depths at which LAB concentrations begin to increase. Sediments deposited at 12–16 cm are, thus, presumed to correspond to the 1963–65 period when the changeover from ABS (i.e. TBS) to LAS surfactants took place in the U.S. (cf. Figure 8b). Such an assignment is consistent with other facts such as the maximum in % organic carbon, % organic nitrogen and total hydrocarbons (cf. Figure 7b) all of which occur at the 6–8 cm interval. Sediments at this depth were probably deposited at about the time (ca. 1970–71) when solids emissions from the outfalls reached a peak (Figure 8a). Similarly, a date of ca. 1950 is assigned to sediments at the 22–24 cm depth interval based on the fact that the TABs, total DDT, total hydrocarbons, % organic carbon, and % organic nitrogen all reach background levels at this depth. Perhaps fortuitously, surfactant usage, major DDT emissions and large scale waste discharges on the San Pedro Shelf began more or less simultaneously in the early 1950s/late 1940s. Collectively, these data provide a means for interpreting the TAB and LAB concentration profiles with respect to post-depositional alterations.

Assuming the surface sediments represent recently deposited material, the presence of TABs at the surface is clearly anomolous. Production of ABS of the TBS variety for domestic use in the U.S. was terminated abruptly in the mid-1960s, and TABs were not detected in the Los Angeles County waste effluent over the course of 12 months during 1979. The contradiction can be explained by

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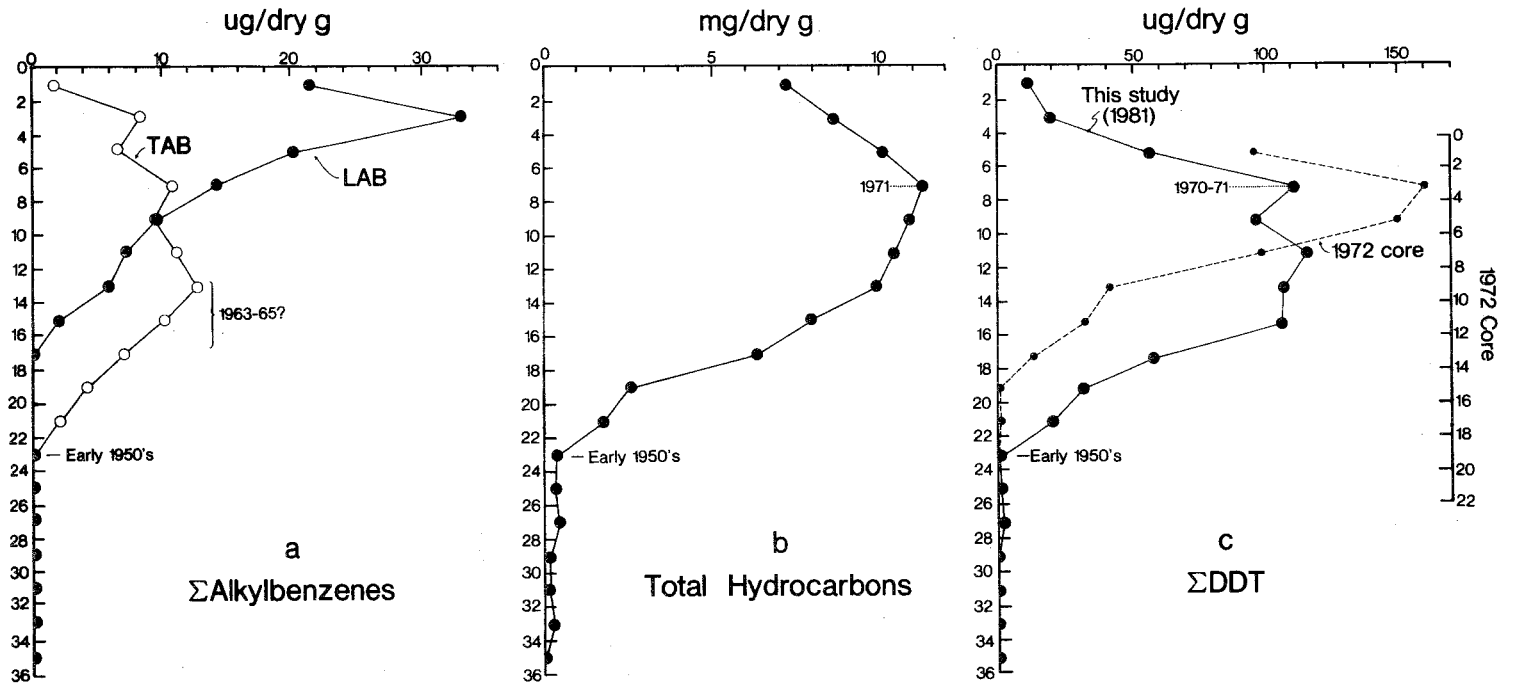

URE 7 Vertical concentration profiles of (a) Long-chain alkylbenzenes, (b) Total hydrocarbons and (c) Total DDT in sediments deposited near the Los
les County waste outfall system.

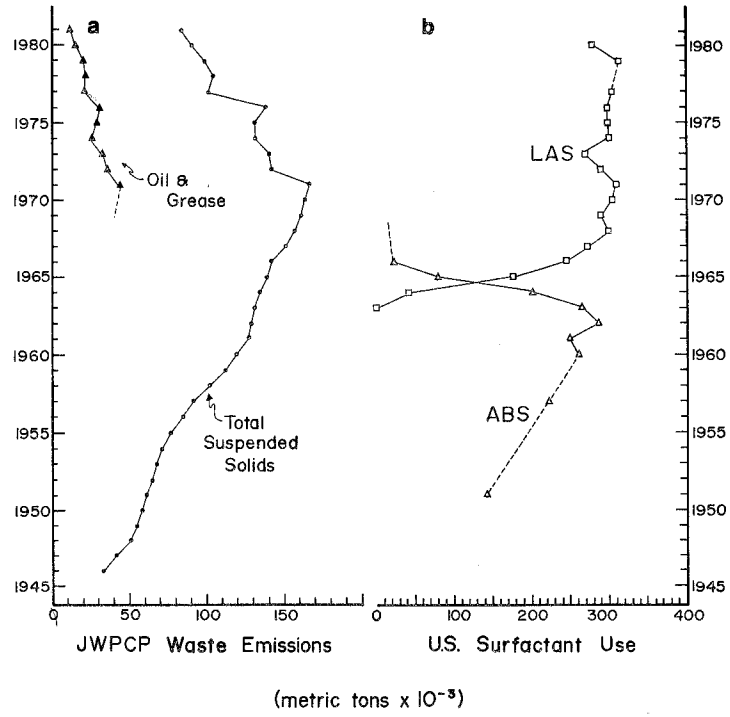

FIGURE 8 Historical data on (a) Solids emissions from the Los Angeles County waste outfall system and (b) U.S. alkylbenzenesulfonate surfactant usage.

vertical mixing of the sediments, either by storm events, biological activity or both. Mixing by storm resuspension alone seems unlikely in view of the relatively smooth and continuous concentration gradients we find in the sediment core. In addition, the concentration profiles contain inflection points which seem to correlate well with the historical facts, suggesting some degree of stratigraphic preservation. Bioturbation seems a more plausible explanation. These heavily impacted sediments are inhabited by large numbers of polychaetes of the sp. *Capitella.* The apparent homogenization of the sediments probably reflects the more or less continuous mixing that takes place due to the burrowing and feeding activities of the resident infauna. These questions require further study before definitive interpretations can be made. The remarkable similarity between

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the composition of a TAB reference mixture we obtained from Monsanto Chemical Company and the distribution of LCABs found at depth in the sediments (cf. Figure 9) suggests that relative to LABs, the TABs are resistant to degradation. It is, therefore, more likely that the shape of the TAB profile below 12–14 cm has resulted from mixing, than biodegradation.

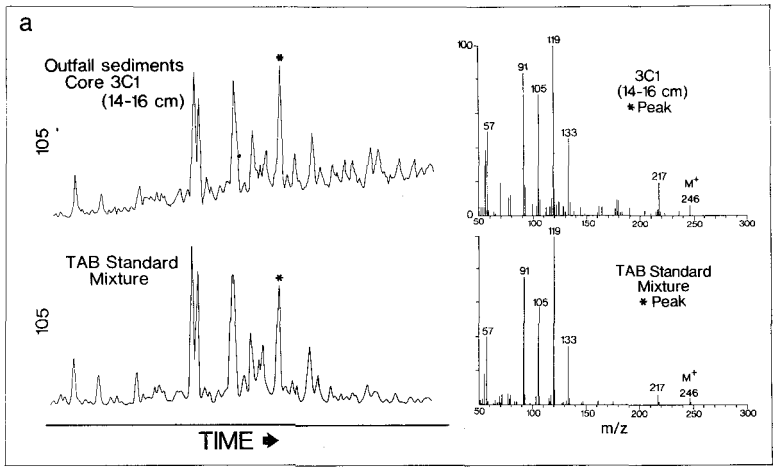

FIGURE 9 HRGC/MS analysis of sedimentary long-chain alkylbenzenes. Similarities between the TAB reference mixture and TABs in sediments taken at a location near the Los Angeles County outfall system.

Comparing the surfactant usage diagram (Figure 8b) with the geochronological assignments, the LAB profile also appears anomolous. Specifically, there is a subsurface maximum at the 2–4 cm interval (above the 1970–71 date) with a near exponential decline in concentration with increasing depth. Considering the aforementioned evidence for selective removal of the external isomers with depth, these changes may best be explained by microbial catabolism.

CONCLUSIONS

Although they are residual components of alkylbenzenesulfonate surfactants, the LCABs are easily detected in commercial detergent

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formulations. Their appearance in municipal waste effluents and sewage-impacted sediments suggests their potential as molecular tracers of waste-derived hydrocarbons in the environment. Evaluation of this potential will require further research in the following areas: (1) the partitioning of LCABs between particulate and dissolved phases, (2) the degradation kinetics of LCABs under varying environmental conditions and (3) the possibility of *in situ* formation of LCABs via microbial desulfonation of ABS.[6,19]

The analytical chemistry of the *linear* alkylbenzenes is relatively straightforward facilitated, as it is, by the characteristic LAB distribution pattern, the ease of separating alkylbenzenes from complex environmental matrices and a firm knowledge of LAB composition.[3,8,9,20–22] This enables one to detect LABs in waste effluents and sediments down to levels of ca. 50 pg/l and 5 pg/g, respectively using HRGC/MS in the selected ion monitoring mode.

The TABs present an altogether different situation. At this time, the identities, properties and relative abundance of individual TAB components are unknown. Furthermore, no methods are presently available for the complete chromatographic separation of all congeners. Consequently, if congener-specific alterations of TABs occur, there is no means of evaluating the nature of the alterations or the mechanisms involved. Due to their highly branched alkyl side chains, the TABs have mass spectral patterns different from their linear analogs. In addition, TABs of a given chain length elute before the corresponding LABs on conventional capillary columns wall-coated with a nonpolar stationary phase. This means that TABs and LABs present in the same sample can be differentiated by HRGC/MS using either characteristic β-cleavage phenylalkyl or molecular ions. Unfortunately, until the TABs can be separated chromatographically, their quantitation by HRGC/MS will require comparison with synthetic TAB reference mixtures. This approach can lead to inaccuracy whenever the composition of the reference mixture and that of the sample TABs differ. Our early observations indicated that the original composition of the TABs (at least, judging by the composition of the *major* peaks) is well preserved after incorporation in sediments. Although this seems to confirm their reported stability, more study is needed before analyses based on TAB reference mixtures are used routinely.

Early field work that we report here indicates that the LABs are

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more readily degradable than the TABs. This is consistent with the ω-oxidation, β-oxidation pathway of biodegradation and structural differences between the two LCAB types. In addition to their use as indicators of waste contamination, the LCABs may have some potential as geochronological tools. This application requires the preservation of historical inputs of LCABs to sediments in an intact stratigraphic record. Factors which favor the dating of sedimentary horizons by LCAB profiles include: (1) low E_h (i.e. limitation or elimination of biological mixing in the sediments), (2) quiescent depositional conditions in areas protected from the influence of storm/tidal resuspension and (3) proximity to a municipal waste discharge.

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