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Susceptibility of Synthetic Long-Chain Alkylbenzenes to Degradation in Reducing Marine Sediments

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Long-chain alkylbenzenes (LCABs) synthesized for production of alkylbenzene sulfonate surfactants have been used as molecular markers of anthropogenic waste for 25 years. Synthetic LCABs comprise two classes, the tetrapropylene-based alkylbenzenes (TABs) and the linear alkylbenzenes (LABs). LABs supplanted TABs in the mid-1960s because of improved biodegradability of their sulfonated analogs. Use of LCABs for molecular stratigraphy depends on their preservation in sediments over decadal time scales. Most laboratory and field studies suggest that LABs degrade rapidly under aerobic conditions but are resistant to degradation when oxygen is absent. However, recent work indicates that LABs may not be as persistent under reducing conditions as previously thought. To assess the potential for degradation of LCABs in reducing sediments, box cores collected in 1992 and 2003 near a submarine wastewater outfall system were analyzed using gas chromatography/mass spectrometry. The TABs were effectively preserved; differences between whole-core inventories were within analytical error. By contrast, whole-core inventories of the LABs decreased by about 50−60% during the same time interval. Based on direct comparison of chemical inventories in coeval core sections, LAB transformation rates are estimated at 0.07 $\pm$ 0.01 yr^{-1}. These results indicate that caution should be exercised when using synthetic LCABs for reconstruction of depositional records.

Introduction

Alkylbenzenes with 9−15 alkyl carbons have been synthesized industrially since the early 1950s. Although they are used in several applications (*1, 2*), their primary purpose (~98%) is as precursors to alkylbenzene sulfonate surfactants. The first long-chain alkylbenzenes (LCABs) produced on an industrial scale were synthesized by Friedel−Crafts alkylation of benzene using tetrapropylene, a complex mixture of branched monoalkenes produced by polymerization of propylene. The tetrapropylene-based alkylbenzenes (TABs) were sulfonated to form TBS (tetrapropylene benzene sulfonates). Unfortunately, the branched alkyl chains of TBS surfactants impeded their degradation in wastewater-treatment plants and receiving water bodies, resulting in undesirable foaming problems.

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In response, the surfactant industry switched to a structurally simpler, more degradable hydrocarbon intermediate, the linear alkylbenzenes (LABs). The changeover from TABs to LABs occurred in the early to mid-1960s in western Europe and the United States and somewhat later in Japan (*3*). LABs are produced by reaction of benzene with normal monochloroparaffins or monoalkenes in the presence of suitable catalysts. Upon sulfonation, LABs yield linear alkylbenzene sulfonates (LAS). As of 1995, global production of LAS was estimated at 2.6 million metric tons (*4*).

Although LCABs had been observed in municipal wastewater effluents and sediments during the mid-1970s, it was not until the early 1980s that their synthetic origin and potential uses as molecular markers were recognized (*5–7*). Because of their hydrophobicity (log octanol−water partition coefficient ~7−10 (*8*)), LCABs sorb strongly to the organic-rich particles in sewage and suspended matter (*9, 10*). Consequently, their transport to bottom sediments and uptake by aquatic organisms (e.g., refs *9, 11–13*,) is expected.

One of the principal criteria for a molecular marker is persistence (*14*). Unfortunately, our knowledge of the persistence of the LCABs (both LABs and TABs) is incomplete. Under aerobic conditions, LABs appear to undergo degradation through selective depletion of the "external" isomers (where benzene is attached near the end of the alkyl chain *15–18*). This led Takada and Ishiwatari (*18*) to propose an index of biodegradation, the I/E ratio, based on the relative abundance of phenyldodecane isomers. The I/E ratio is defined as $[6\text{-}C_{12} + 5\text{-}C_{12}]/[4\text{-}C_{12} + 3\text{-}C_{12} + 2\text{-}C_{12}]$, where $j\text{-}C_k$ indicates substitution of benzene at the j position of an alkyl chain having k carbon atoms (Supporting Information Figure S1a). LAB concentrations have sometimes been found to decrease and I/E ratios to increase in sediments collected at greater distance from a point source (*5, 9*), suggesting that significant LAB degradation may occur during transport through the oxygenated water column. However, this pattern is not always observed (*19–21*). Microcosm experiments in which untreated sewage or LAB-amended anaerobic sludge was incubated in the absence of oxygen showed little or no degradation of the LABs (*1, 17*). In general, this has been taken as evidence of the persistence of LABs in anoxic sediments (*5, 7, 17, 19, 22*). Conversely, it is sometimes tacitly assumed that little or no change in I/E ratio means that no biodegradation has occurred (*23, 24*). However, Lamoureux et al. (*25*) found that LABs were significantly depleted in sludge-contaminated sediments despite invariant I/E ratios. Recently, Johnson et al. (*2*) demonstrated that LABs could be degraded under nitrate-reducing conditions by microorganisms cultured from LAB-contaminated soil. In this case, isomer-selective degradation of the LABs, similar in character and extent to that reported for aerobic microcosm experiments (*17*), was observed. From the foregoing, it should be apparent that our understanding of the fate of LABs in reducing marine sediments is inadequate.

TABs have also been found in waste-contaminated sediments (*5, 19, 24, 26, 27*). Although limited, available evidence suggests that their composition closely matches that of the original synthetic product (*5, 28*). This has led to the general assumption that TABs, like their sulfonated analogs (TBS), are highly resistant to degradation, presumably due to branching of the alkyl side chain. However, no microcosm experiments or definitive field studies on TAB persistence have been reported.

LCABs have been used for purposes of molecular stratigraphy, whereby age-dating of sediments is accomplished by comparing vertical concentration profiles with historical

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usage and/or production data (*5, 24, 26, 29, 30*). This requires that marker compounds be preserved over decadal time scales (*3, 5*). In a previous report, we presented indirect evidence that the LABs may be susceptible to degradation in waste-impacted marine sediments (*28*). If this is the case, then use of LABs for reconstruction of sediment depositional records may be limited, and perhaps compromised. The present investigation was undertaken to test the hypothesis that degradation of LCABs can occur in reducing marine sediments under field conditions. Our principal objectives were to (1) assess the persistence of LABs and TABs in well-characterized waste-impacted sediments and (2) to estimate in situ transformation rates of LCABs in these sediments.

Materials and Methods

Sample Collection. Box cores were collected by the U.S. Geological Survey (USGS) in July 1992 and July 2003 (site C, Supporting Information Figure S3) approximately 7 km downcurrent from a submarine outfall system operated by the Los Angeles County Sanitation Districts (LACSD) on the Palos Verdes Shelf (PVS). Navigation, core collection, and core-handling procedures are described elsewhere (*28, 31*). Hereafter, the 1992 and 2003 subcores will be referred to as cores 124B1−92 and 124B1−03, respectively. Although the primary focus of this paper is a comparison of LCABs in these sediment cores, we also present data on the LAB composition of LACSD wastewater effluent (1979, 1990), near-bottom suspended particulate matter on the PVS (1992−93), and particles collected in sediment traps near the sea floor on the PVS (1989−90). These data are used to characterize the original composition of LABs discharged to waters of the PVS and processes occurring prior to and during their incorporation into bottom sediments.

Procedures used for collection of wastewater effluent in 1979 and 1990 have previously been described (*6, 32*). In 1979, wastewater received advanced primary treatment, whereas in 1990, treatment was partial secondary (60%). Samples of near-bottom suspended particles, hereafter called "bag samples", were collected at site B (Supporting Information Figure S3) using the GEOPROBE bottom tripod instrument system described separately (*33*). With this system, water samples (400−800 mL) were pumped into Teflon bags when suspended particle concentrations exceeded a specified threshold. Sample collection at ∼30 (or in one case ∼100) cm above the sea floor was completed within ∼40 s. Particles were also collected in sediment traps positioned 0.5, 2.0, and 5.0 m above the sea floor at site A (Supporting Information Figure S3) according to procedures reported elsewhere (*32*). The sediment traps were used to determine fluxes of solids and associated contaminants over 36 days.

Sample Preparation. Sediment cores were kept frozen until they had been sectioned at 2 cm intervals. Methods used for preparation of the 1992 and 2003 USGS subcores for determination of LCABs have previously been described (*28, 31*). Processing of wastewater effluent and sediment-trap samples was similar to that used in the preparation of sediment-core samples (*6, 32*) except that effluent samples were extracted by liquid−liquid partitioning. In the case of bag samples, particles were collected on precombusted Whatman GF/F glass-fiber filters and extracted by sonication using methanol and dichloromethane. From that point forward, processing of bag sample extracts was identical to that used for the sediment-core and sediment-trap samples.

Instrumental Analysis and Data. Procedures used in the instrumental analysis of wastewater effluent, sediment-core, bag, and sediment-trap samples were very similar. LCABs were isolated using adsorption chromatography and taken up in a solution containing known amounts of internal standard (see below). LAB concentrations were determined using gas chromatography/mass spectrometry (GC/MS) in full scan, electron impact mode (*28, 31, 32, 34*). Quantitation was by the internal standard method using ions chosen to avoid interference with coeluting TABs (*27, 28, 31, 34*). Targeted LABs included 26 secondary C_{10-14}-benzenes (Supporting Information Figure S1a). Total LAB concentrations, representing the sum of all 26 secondary alkylbenzenes, are given as ΣLAB_{26}.

Twelve major TAB peaks were targeted for quantitation by GC/MS (*5, 28*; Supporting Information Figure S1b). Single-point calibration was considered acceptable for the TABs because their physicochemical properties, behavior in the GC/MS, and concentrations in samples are essentially the same as the LABs. Quantitation ions for the TAB peaks were chosen to avoid interference with coeluting LABs (*31*). Summed concentrations of the 12 TAB peaks are given as ΣTAB_{12}. Average "total TAB" concentrations were estimated from measured abundances of each of the 12 targeted peaks relative to total TAB content in the calibration standard. Concentrations of the LCABs reported in this paper have not been corrected for recovery.

Materials. Secondary calibration standards for the LABs and TABs were developed from synthetic mixtures provided by Monsanto Company (*34*) amended with individual primary phenylalkanes, which were used as internal standards (1-C_9, 1-C_{15}) and recovery surrogates (1-C_{10}, 1-C_{11}, 1-C_{12}, 1-C_{13}, 1-C_{14}; Supporting Information Figure S1).

Quality Assurance/ Quality Control. In the case of USGS core analyses, stringent quality-assurance guidelines were developed as part of the Montrose investigations (United States of America, et al., vs Montrose Chemical Corporation of California, et al. (*35*)). Detailed information on method performance for wastewater-effluent, bag, sediment-trap, and sediment-core samples can be found elsewhere (*28, 31, 32, 34*). To our knowledge, no standard reference material has yet been developed for the LCABs. However, Hartmann et al. (*36*) reported concentrations of the LABs in National Institute of Standards and Technology SRM 1941a. In an effort to assess the accuracy of our measurements, we analyzed SRM 1941a for both classes of LCABs. As shown in Supporting Information Table S1, our results agree well with those published by Hartmann et al. (*36*). The TAB data given in Supporting Information Table S1 are the first such measurements in SRM 1941a to be reported. Based on our analyses, it appears that concentrations of ΣTAB_{12} and "total TABs" are approximately 11.6 and 4.4 times lower, respectively, than ΣLAB_{26}.

Calculations. Calculation of chemical inventories (ng/cm^2) and first-order transformation rates (yr^{-1}) for whole cores and discrete depth intervals are described elsewhere (*31*). Between-core transformation rates at coeval depths were computed following core alignment using a statistical optimization procedure (*30, 31*).

Results and Discussion

LCABs in LACSD Wastewater Effluent. Long-chain alkylbenzenes can be introduced to waste-treatment systems through the use and disposal of detergent−bearing products or via waste streams of alkylbenzene manufacturing or sulfonating operations. The LABs in detergents are thought to be unreacted residues that are carried over with LAS (*7, 18, 34*). Studies of wastewater effluents in southern California during 1979 and 1990 revealed significant quantities of LABs (*5, 6, 32, 34*), but no TABs were detected. This is reasonable because by the mid- to late 1960s, TABs were no longer used in the United States. In 1979, concentrations of LABs (ΣLAB_{26}) in the LACSD effluent ranged from 4.7 to 13.4×10^5 ng/g (Supporting Information Figure S4). Two effluent samples collected 11 years later had markedly lower concentrations ($1.7-3.9 \times 10^5$ ng/g). This decrease is most

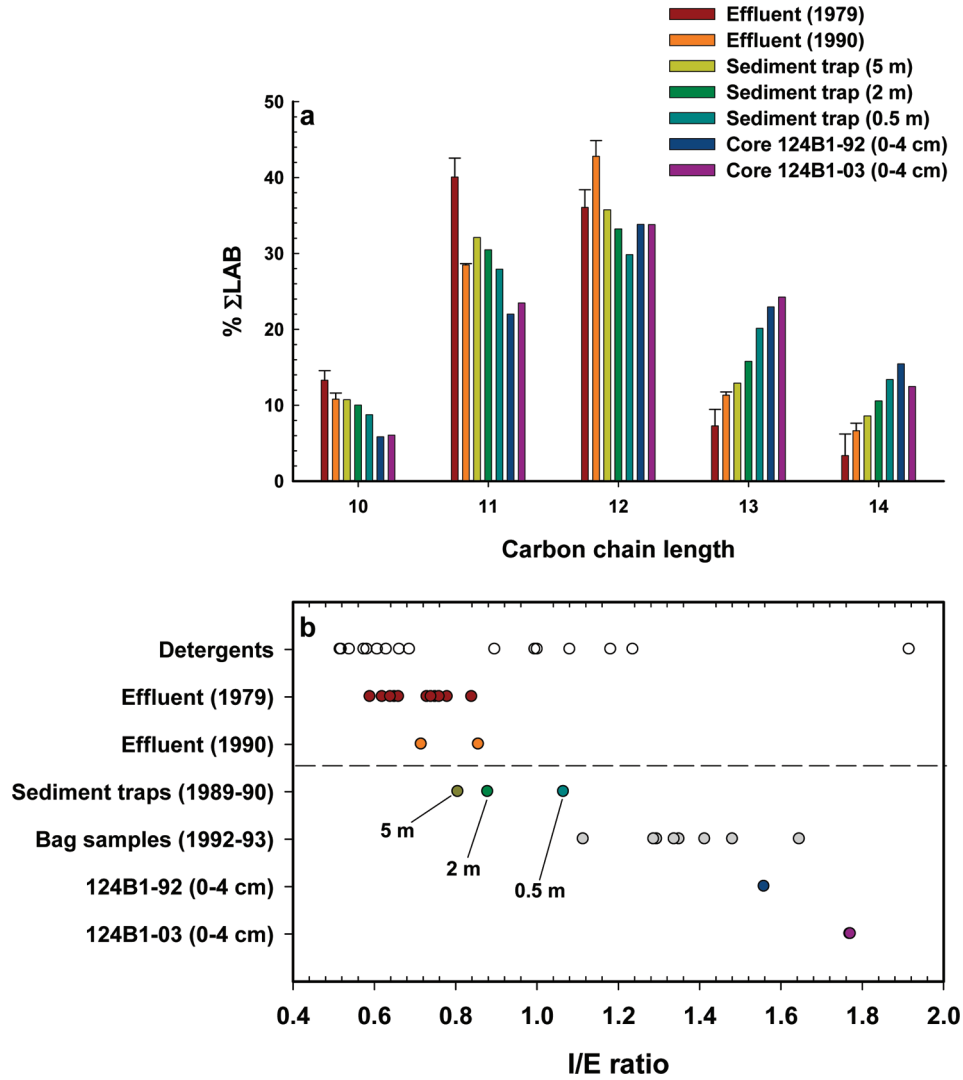

FIGURE 1. Composition of linear alkylbenzenes in commercial detergents, LACSD final effluent, sediment-trap particles, near-bottom suspended particles (bag samples), and surficial sediments: (a) alkyl chain-length distributions, and (b) I/E ratio (see text for explanation).

likely the result of source-control measures and improved waste treatment, which were both initiated in the early 1970s (*19, 37*).

Figure 1 provides information on the chain length (i.e., homologue) distributions and phenyldodecane isomer compositions (I/E ratio) of LABs in commercial detergents and LACSD effluent samples. The homologue distribution of LABs in LAS-bearing detergents (not shown) depends on the intended application, and striking variations in LAB homologue compositions have been reported (*18, 34*). Thus, little information can be gained by comparing LAB homologue distributions of specific detergent products with those observed in the LACSD effluent. In 1979, the LAB homologue distribution of LACSD effluent was dominated by C_{11}-benzenes, followed closely by C_{12}-benzenes, with significantly lesser amounts of C_{10}-, C_{13}- and C_{14}-benzenes, respectively (Figure 1a). Compositions were relatively invariant as indicated by the error bars for samples collected monthly throughout the year. Two effluent samples collected in 1990 showed a small but measurable shift in chain-length distribution with greater relative amounts of the C_{12}-benzenes compared with the C_{11}-benzenes; C_{13}- and C_{14}-benzenes appear to have increased and C_{10}-benzenes decreased in 1990. These differences probably reflect compositional changes in the dominant inputs during this time interval.

Synthetic LAB isomer compositions exhibit one of two patterns depending on the catalyst used in the alkylation reaction: (1) the so-called "flat" distribution characterized by roughly equivalent amounts of all isomers of a given chain length (HF catalyst) and (2) the "high 2-phenyl" distribution in which greater relative abundances of the external isomers are seen ($AlCl_3$ catalyst). Both distributions yield low I/E ratios in LAS-bearing detergents in the range ~0.6−1.1 (*3*). I/E ratios for commercial detergents purchased in Los Angeles cluster at 0.5−0.7 (Figure 1b), but ratios for some products are as high as 0.8−1.2 or more. LACSD effluent samples collected in 1979 had I/E ratios from 0.59 to 0.85, whereas those collected in 1990 generally fell in the upper part of that range (0.72, 0.86; Figure 1b). Because of the inherent variability in potential sources of LABs to the LACSD, it is not possible to ascertain whether the observed range in I/E ratios of effluent samples reflects time-varying inputs, differences in the extent of degradation during transport to and through the waste-treatment plant, or both.

Processes Affecting LABs during Sedimentation. LABs discharged from the LACSD outfall system could undergo transformation prior to incorporation into bottom sediments. Although LABs are very hydrophobic (*8*), homologue distributions might be altered as effluent particles mix with seawater. Because oxygen is available in the water column,

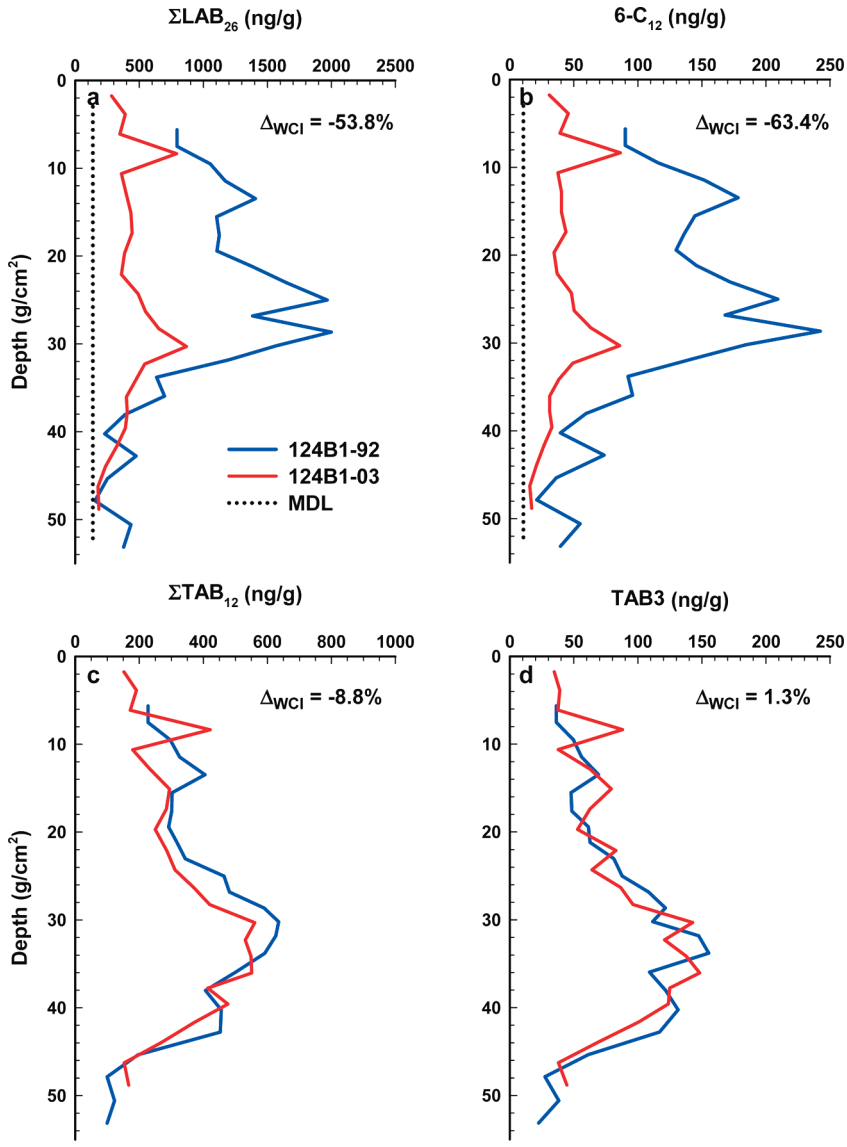

FIGURE 2. Vertical concentration profiles of long-chain alkylbenzenes in USGS cores: (a) total linear alkylbenzenes (ΣLAB_{26}), (b) 6-phenyldodecane (6-C_{12}), (c) summed concentrations of 12 major tetrapropylene-based alkylbenzenes (ΣTAB_{12}), and (d) a persistent tetrapropylene-based alkylbenzene (TAB3). MDL = method detection limit. Δ_{WCI} = percent difference between 1992 and 2003 whole-core inventories (Δ_{WCI} = ([inventory 1992 − inventory 2003]/inventory 1992) × 100).

isomer- or homologue-selective degradation could also occur. Comparing LACSD effluent and sediments collected on the PVS and in San Pedro Basin, Eganhouse et al. (*5*) noted a decrease in LAB concentration and progressive depletion of external phenyldodecane isomers with increasing distance from the outfalls. These differences were attributed to dilution and degradation during sedimentation and offshore transport. As illustrated in Supporting Information Figure S4, LAB concentrations decrease by nearly 3 orders of magnitude during transport of LACSD effluent (1990) to waste-impacted surficial sediments collected on the PVS in 1992 and 2003; intermediate LAB concentrations are found in particles collected near the sea floor using sediment traps and the GEOPROBE system (bag samples). A very similar progression was reported by Takada et al. (*10, 14*) for the 106-mile dumpsite. Because there was little or no difference in the I/E ratios of sewage sludge, sediment-trap and surficial-sediment samples, the authors concluded that dilution during and after sedimentation, not biodegradation, was primarily responsible for the 4 orders of magnitude range in LAB concentration. The apparent lack of degradation was attributed to rapid sinking of sludge particles (estimated transit time, ~1 month), possibly assisted by their incorporation into fecal matter of pelagic and mesopelagic organisms, and inhibition of microbial activity at the low temperatures and high pressures in the deep sea. In the following discussion, we consider evidence for the relative importance of dilution and biodegradation in explaining the large differences in LAB concentration between LACSD effluent particles and surficial sediments on the PVS.

Using a hydrographic mapping system, Jones et al. (*38*) characterized particles in the water column off Palos Verdes as belonging to four classes: wastewater effluent, phytoplankton, terrigenous material, and resuspended sediment. The latter was found at all times during the field investigations, primarily within 5 m of the sea floor. Elevated concentrations were observed near the sea floor during storm-induced wave events (*33*). Sediment traps positioned near the sediment−water interface collect particles sinking from the overlying water column and sediments resuspended from surficial layers of the sea floor. In terms of LABs, two sources can be postulated: (1) those associated with recently

TABLE 1. First-order Transformation Rates of Secondary Phenyldodecanes in Sediments of the Palos Verdes Shelf Based on Whole-Core Inventories and Direct Core-to-Core Comparison

	transformation rate (yr^{-1})		half-life (yr)	
compound[a]	WCI[b]	C−C_{mean}[c]	WCI	C−C_{mean}[d]
6-C_{12}	0.091 ± 0.003	0.089 ± 0.011	7.6 ± 0.2	7.8 ± 0.9
5-C_{12}	0.075 ± 0.003	0.072 ± 0.012	9.2 ± 0.4	9.6 ± 1.6
4-C_{12}	0.081 ± 0.003	0.078 ± 0.011	8.6 ± 0.3	8.9 ± 1.3
3-C_{12}	0.085 ± 0.004	0.087 ± 0.017[e]	8.2 ± 0.4	8.0 ± 1.5
2-C_{12}	0.075± 0.003	0.069 ± 0.011[e]	9.3 ± 0.4	10.1 ± 1.6
ΣC_{10}−LABs	0.061 ± 0.004	0.064 ± 0.016[e]	11.4 ± 0.8	10.8 ± 2.7
ΣC_{11}−LABs	0.063 ± 0.003	0.067 ± 0.012[e]	11.0 ± 0.6	10.4 ± 1.9
ΣC_{12}−LABs	0.083 ± 0.003	0.079 ± 0.012	8.4 ± 0.3	8.8 ± 1.3
ΣC_{13}−LABs	0.068 ± 0.004	0.070 ± 0.017[e]	10.2 ± 0.6	9.8 ± 2.4
ΣC_{14}−LABs	0.058 ± 0.007	0.079 ± 0.028[e]	11.9 ± 1.4	8.7 ± 3.0
ΣLAB_{26}	0.070 ± 0.003	0.071 ± 0.013[e]	9.9 ± 0.5	9.8 ± 1.8

[a] For nomenclature of individual LABs, see text. ΣC_n-LABs = summed concentration of LABs having *n* carbons in alkyl group. [b] WCI = whole-core inventories. [c] C−C_{mean} = mean rate for all intervals compared after alignment of 1992 and 2003 cores. [d] half-life for mean rate. [e] Mean rates and uncertainties were calculated excluding negative values (see text for explanation).

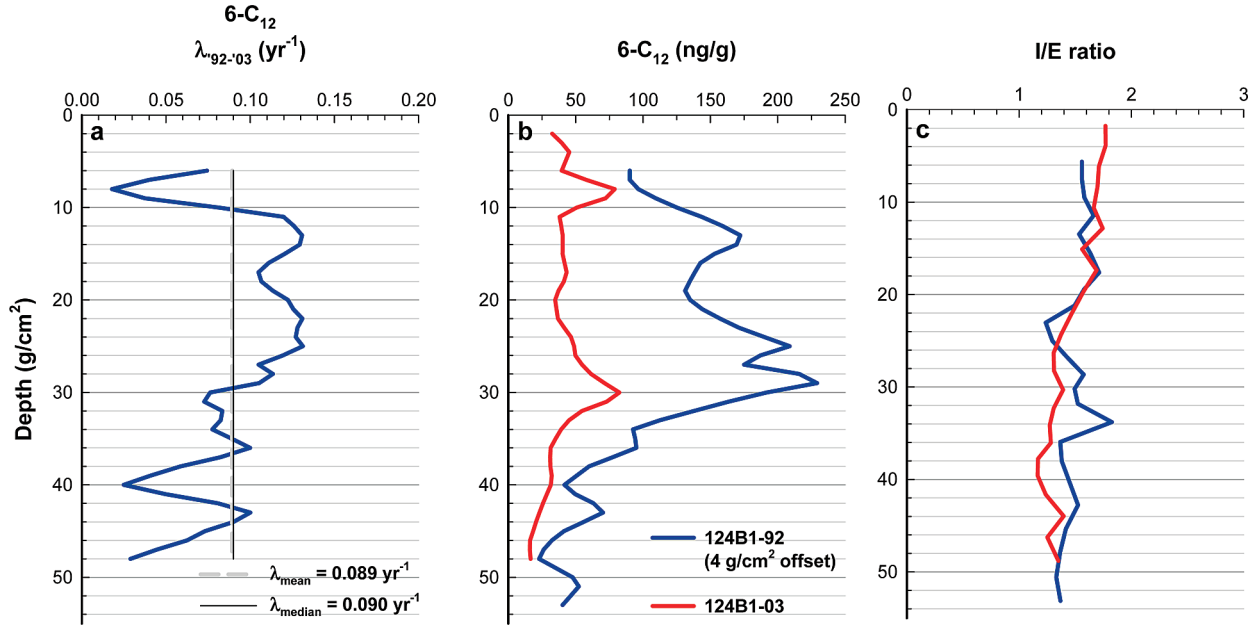

FIGURE 3. Vertical profiles of (a) first-order 6-C_{12} transformation rate constant, $\lambda_{'92-'03}$, computed from aligned core data, (b) concentration of 6-C_{12} in USGS cores, and (c) I/E ratio of phenyldodecanes in 1992, 2003 cores. Core profiles are aligned (4 g/cm² offset). Uncertainty in first-order 6-C_{12} transformation rate constant is estimated at 0.011 yr^{-1}.

discharged wastewater-effluent particles and (2) those in resuspended sediment. The relative contributions of these two sources can be expected to vary such that traps positioned at greater elevation above the sediment−water interface receive smaller contributions from resuspension of bottom sediments and greater contributions from the effluent plume. Fluxes of solids, total organic carbon (TOC), total nitrogen (TN), and ΣLAB_{26} decrease, whereas concentrations of TOC, TN, and ΣLAB_{26} increase with increasing trap elevation (Supporting Information Table S2). These trends strongly suggest that inputs from sediment resuspension were greatest in traps nearest the sea floor; with increasing elevation, the contribution of organic-rich effluent particles increased.

Figure 1a shows that LABs with longer alkyl chains (C_{13}−C_{14}) were less abundant and those with shorter alkyl chains (C_{10-12}) were more abundant in the effluent than they were in surficial sediments. This relation has been observed previously (*12, 39*). By comparison, homologue distributions for particles collected in sediment traps were intermediate between those in effluent and sediment samples. More importantly, as trap elevation decreased, the abundance of LABs with longer alkyl chains (C_{13}−C_{14}) increased, whereas the abundance of LABs with shorter alkyl chains (C_{10-12}) decreased. Together, these results suggest that the homologue distributions of LABs in the sediment traps varied according to the relative contributions of resuspended sediment and effluent particles. Causes for the progressive increase in abundance of homologues with longer alkyl chains on going from effluent to sediment traps to surficial sediments may include physical fractionation (*9, 40*) or preferential biodegradation of the lower homologues during transport and sedimentation. Sherblom et al. (*8*) found that octanol−water partition coefficients (K_{OW}) of the secondary C_{10-14}-benzenes vary over ~1.3−1.4 log units, whereas isomers within each homologue group span ~0.1 log units. Thus, if physical fractionation is primarily or solely responsible for the enrichment of longer-chain LABs in surficial sediments, one would expect little or no change in the I/E ratio (*17*). If aerobic biodegradation is partly responsible for the observed changes in LAB homologue distribution, one would expect the I/E ratio of effluent particles to increase following release to the environment.

Figure 1b shows I/E ratios for effluent, sediment-trap, bag, and surficial-sediment samples. Ratios generally increased in the following order: effluent < sediment traps < bag samples < surficial sediments and ranged from 0.6 to 1.8. With decreasing trap elevation, I/E ratios increased from 0.81 to 1.07. The ratio obtained at the 5.0 m elevation (0.81) is comparable with that of the LACSD effluent collected around the same time (i.e., 0.72−0.86). This indicates that the majority of the LABs collected in the 5.0 m sediment trap were derived from effluent particles that had experienced little, if any, degradation. This is reasonable because effluent particles traveling at or near current speeds typical of the PVS (20−30 cm/sec (*41*)) would take ∼4−6 h to reach site A (Supporting Information Figure S3). This is not long enough for significant biodegradation to occur (*17*). Comparison of the ΣLAB_{26} concentrations in effluent samples collected in 1990 with those in particles collected in the 5.0 m sediment trap (Supporting Information Figure S4) yields apparent dilutions of ∼7 to 16. This compares favorably with dilutions calculated from TOC concentration (6.8−10.6 (*32*)). We conclude that effluent particles containing LABs can reach the sea floor before any significant degradation takes place while experiencing dilutions of approximately 10:1. The similarity between the homologue distributions of effluent samples collected in 1990 and particles collected in the 5.0 m sediment traps (Figure 1a) precludes any firm conclusion concerning the effect of physical fractionation during transport of effluent particles to the sediments.

Particles collected in the sediment trap at 0.5 m have I/E ratios approaching those of the bag samples; the latter are expected to be dominated by sediments resuspended over relatively short periods of time (hours to days (*33*)), not by particles in the effluent plume. Concentrations of LABs in the bag samples span those of particles collected in the sediment traps, but most of the data cluster near the datum for the 0.5 m trap or at lower concentrations. The I/E ratios in the bag samples also span those of surficial sediments collected around the same time somewhat further downcurrent (124B1−92, 0−4 cm). Finally, TABs were found in all bag samples (data not shown). Because no TABs were detected in LACSD effluent as early as 1979; those in the bag samples must have originated from the sediments. Taken together, these results strongly support the supposition that particles in the bag samples were derived from resuspension of surficial layers of sediment. The foregoing discussion suggests that degradation of the LABs occurs following sedimentation. Examination of depth intervals in the 1992 core that are thought to correspond approximately to the late 1970s and early 1990s (*30*) showed that the sediments contain greater relative amounts of longer chain LABs than time-equivalent effluent samples (data not shown). This means that the homologue distributions of effluent samples are altered during and/or following sedimentation. Whether biodegradation, physical fractionation, or both are responsible for the difference in homologue distributions of effluent and sediment samples cannot be ascertained with confidence from the available data.

Post-depositional Fate of LCABs. Sediments on the PVS are oxic or suboxic in the upper 1−2 cm (*42*). Benthic chamber studies indicate that most of the organic matter decomposition in surficial sediments occurs with oxygen as terminal electron acceptor (*43*), but below this layer, conditions become reducing, and sulfate-reduction is the dominant terminal electron accepting process (*42*). Reductive dechlorination of *p,p′*-DDE to *p,p′*-DDMU, a process that requires anoxic conditions, has been shown to take place at all depths in the sediment column down to about 50 cm (*31, 44*).

Earlier we suggested that the LABs appeared to be degrading relative to the TABs in PVS sediments near site C (Supporting Information Figure S3 (*28*)). This was based on differences in whole-core inventory ratios for 6-C_{12}, TAB3 (a major persistent TAB peak; Supporting Information Figures S1b, S2a), and *p,p′*-DDE in cores obtained in 1981 and 1992. However, no definitive conclusions could be reached because the sediment cores were collected at slightly different water depths using different sampling devices. Because previous microcosm experiments have shown little or no degradation of LABs under anoxic conditions (*1, 17*), it has generally been assumed that these hydrocarbons are well preserved once buried below depths where conditions are reducing. For this reason, we decided to examine the geochemical fate of LCABs in two box cores collected 11 years apart at the same location. A key element of this comparison is the ability to demonstrate that inter-core differences reflect diagenetic processes.

As discussed elsewhere (*31*), concentrations of 84 polychlorinated biphenyls (PCBs) were determined in the 1992 and 2003 sediment cores. Our data show that PCB compositions in these cores were nearly uniform; there was no substantive evidence of reductive dechlorination. After alignment, vertical concentration profiles of the PCBs in these cores were virtually superimposable, and differences in whole-core inventories of individual or summed PCB congeners were within the estimated analytical uncertainty of about 9−11%. Together, these results indicate that the PCBs are conservative effluent markers. The constancy in whole-core inventories means that decreasing inventories of other hydrophobic organic contaminants having similar physicochemical properties (e.g., LCABs) must reflect post-depositional diagenetic transformations, not physical loss processes. In the following discussion we examine evidence for the fate of the LCABs in PVS sediments.

Figure 2 shows aligned vertical concentration profiles of ΣLAB_{26}, 6-C_{12}, ΣTAB_{12}, and TAB3 in the 1992 and 2003 cores. Data for 6-C_{12} and TAB3 are presented here because these analytes are the most abundant members of their respective LCAB classes. In the case of the TABs, aligned concentration profiles match well, and differences between the 1992 and 2003 whole-core inventories (Δ_{WCI}) of ΣTAB_{12}, and TAB3 were −8.8 and 1.3%, respectively. This can be compared with analytical uncertainties estimated from five replicate analyses of PVS sediments (9.5 and 11.5%). Thus, the TABs, like the PCBs, are largely recalcitrant and can serve as conservative markers of waste contamination. The persistence of the TABs may be attributable to the highly branched alkyl chains that are thought to be responsible for impeding degradation of the sulfonated analogs (i.e., TBS). Detailed examination of individual TAB peaks reveals decreases in the relative abundances of some of the targeted TABs between 1992 and 2003 (section 5, Supporting Information). This may explain the apparent decline in the whole-core inventory of ΣTAB_{12} between 1992 and 2003 cores and why the aligned core profiles of TAB3 are slightly more coherent than the ΣTAB_{12} profiles.

The aligned ΣLAB_{26} and 6-C_{12} concentration profiles in the 1992 and 2003 cores are quite different. Concentrations of 6-C_{12} in the 1992 core exceeded those at all coeval depths in the 2003 core. With the exception of one depth interval, the same is true for ΣLAB_{26}. Differences in whole-core inventories (2003−1992) for ΣLAB_{26} and 6-C_{12} were −53.8 and −63.4%, respectively, well beyond the range of analytical uncertainty (∼10%). Because the physicochemical properties of the TABs and LABs are very similar, the decline in LAB inventories from 1992 to 2003 must be due to diagenetic transformation processes. These processes are undoubtedly occurring under reducing conditions. Otherwise, reductive dechlorination of *p,p′*-DDE (*31*) would not be possible. It is most likely that, except for the upper few cm of the sediment column, LAB degradation is occurring under sulfidogenic

conditions (*42*). To our knowledge, this is the first unequivocal demonstration of the degradation of LABs in reducing marine sediments.

First-order transformation rates for the LABs were calculated in two ways (*31*): (1) using whole-core inventories and (2) by comparing inventories within coeval depth intervals in the 1992 and 2003 cores. Table 1 provides rates for the phenyldodecanes, C_{10-14} homologue groups, and ΣLAB_{26}. Uncertainties were estimated through propagation of error calculations (section 6, Supporting Information). Rates based on whole-core and interval-based ($C-C_{mean}$) calculations are generally in accord. Occasionally, as in the case of 2-C_{12}, inventories in a few intervals of the 2003 core exceeded that of the 1992 core, yielding negative rate coefficients (see Figure 2a, ~40 g/cm^2 depth interval). This was caused by the low concentrations encountered within these depth intervals and correspondingly higher uncertainties. For the phenyldodecane isomers, rates vary within a relatively narrow range (~0.07−0.09 yr^{-1}); the highest rate is observed for 6-C_{12}. Among homologues, the C_{12}-benzenes appear to degrade most rapidly (~0.08 yr^{-1}); other chain lengths exhibit rates around 0.06−0.7 yr^{-1}.

Figure 3 presents the vertical profile of the first-order transformation rate for 6-C_{12} along with aligned concentration profiles that form the basis for the rate calculation. Rates for this compound vary considerably (0.017−0.107 yr^{-1}), with highest values at depths where LAB concentrations were greatest in 1992. This pattern is quite different from the rate-concentration relation observed for *p,p′*-DDE in these same cores (*31*). This indicates that the factors controlling *p,p′*-DDE dechlorination and LAB degradation rates are not the same. The aligned I/E ratio profiles are also plotted in Figure 3. Despite significant attenuation in the inventory of LABs between 1992 and 2003, there has been little, if any, change in the I/E ratio. The slight decline in I/E ratio with sub-bottom depth probably reflects the somewhat greater transformation rate of 6-C_{12} (as compared with other phenyldodecanes; Table 1). Zeng and Venkatesan (*29*) published an I/E ratio profile for a sediment core collected at the same approximate water depth but closer to the outfall system. I/E ratios were near constant (~2) in the upper 18 cm but increased dramatically to almost 9 at greater depth (18−30 cm). The cause of this difference is unknown.

This study shows that effluent particles released from the LACSD outfall are diluted by a factor of 10 during sedimentation, but little or no degradation of the LABs occurs. Following deposition, further dilution occurs and LABs are lost through degradation. Most degradation occurs in the sediment column at depths where conditions are reducing (probably sulfidogenic (*42*)), and there is no apparent change in the I/E ratio, at least over the time scale of a decade. Degradation of the LABs is consistent with the well-established metabolism of short-chain alkylbenzenes by a variety of anaerobic bacteria (*45*). Further research would be needed to determine whether LABs are susceptible to degradation in other environments (*26*) and, if so, under what conditions. In the meantime, our results suggest that caution should be exercised when using LABs for molecular stratigraphy and LAB isomer composition (e.g., the I/E ratio) as an indicator of biodegradation in reducing environments.

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Supporting Information Available

Information concerning LCAB structures and synthesis, sampling locations, SRM 1941a results, concentrations in environmental samples, TAB compositions, and an example propagation-of-error calculation are provided in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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