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

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Supporting Information

1. Long-chain alkylbenzenes (LCABs): structure and synthesis

Two classes of long-chain alkylbenzenes were investigated in this study, the tetrapropylene-based alkylbenzenes (TABs) and the linear alkylbenzenes (LABs). The TABs have structures that contain highly branched alkyl side chains, whereas the LABs have linear alkyl side chains. Figure S1 shows high resolution gas chromatograms of the calibration standards that were prepared from commercially synthesized mixtures of the TABs and LABs along with identities of chromatographic peaks and model structures. The nomenclature used for the LABs is: j-C_k, where j = position of substitution on the alkyl chain and k = number of carbons in the chain.

The TABs were produced in two steps: 1) polymerization of propylene in the presence of phosphoric acid to produce 'tetrapropylene,' and 2) reaction of benzene with tetrapropylene using a Lewis acid catalyst such as $AlCl_3$, HF or BF_3 (*1*). Conditions of tetrapropylene production were drastic, resulting in cracking and recombination of polymer molecules (*2*). Formation of carbonium ions in the presence of acid lead to rearrangement, fragmentation, and cracking of polymers, resulting in a highly branched mixture of isomers and homologs having alkyl chain lengths from 9-15, with the double bond usually internal. Further rearrangement occurred during the benzene alkylation step, resulting in a mixture of compounds that was even more complex. Ötvös *et al.* (*3*) suggested that there were about 80,000 possible isomers within the C_{10} to C_{15} alkyl carbon range.

The LABs are produced by Friedel-Crafts alkylation of benzene using either chloroparaffins or monoolefins in the presence of $AlCl_3$ (olefin or chloroparaffins) or HF (olefin). The resultant product includes all secondary phenylalkanes of a given chain length with minor side products (dialkyltetralins and isoalkylbenzenes), the abundance of which depend on the alkylation reactants, catalyst, and reaction conditions (*4*). LABs quantitated in this study include alkyl chain lengths from 10 to 14.

Figure S2 shows representative chromatograms of the TAB and LAB calibration standards (using identical x-axis scaling) along with mass fragmentograms for a sample from the 2003 USGS core (124B1-03). Because of their branched alkyl chains, the TABs are more volatile and elute earlier than LABs of the same chain length. LAB isomers in which benzene is substituted at any position except the 2-carbon on the alkyl chain yield a base peak of m/z = 91 (Figure S2c), whereas 2-phenylalkanes have a base peak at m/z = 105. Because 2-phenylalkanes are degraded more rapidly under aerobic conditions than other LAB isomers, their abundance is often greatly reduced in environmental samples (Figure S2d). The mass spectra of most TABs exhibit base peaks at m/z = 119 due to α,α-dimethyl substitution (Figure S2e). However, some α -methyl isomers (base peak m/z = 105) and isomers with base peaks at m/z = 91 are also present. In the latter case (m/z = 91), two types of structures are known (*5*): 1) with benzene attached to a tertiary carbon, one substituent having 1 or more carbons and the other two having two or more carbons, and 2) with benzene attached to a secondary carbon with both alkyl substituents having 2 or more carbons. Examination of Figure S2 shows that in the environmental samples (panels c-e), the TABs appear in the early portion of all three mass fragmentograms. Their prominence in these chromatograms is due to the fact that at this depth in the sediment column, the TABs are more abundant than the LABs (see Figure 2, main paper).

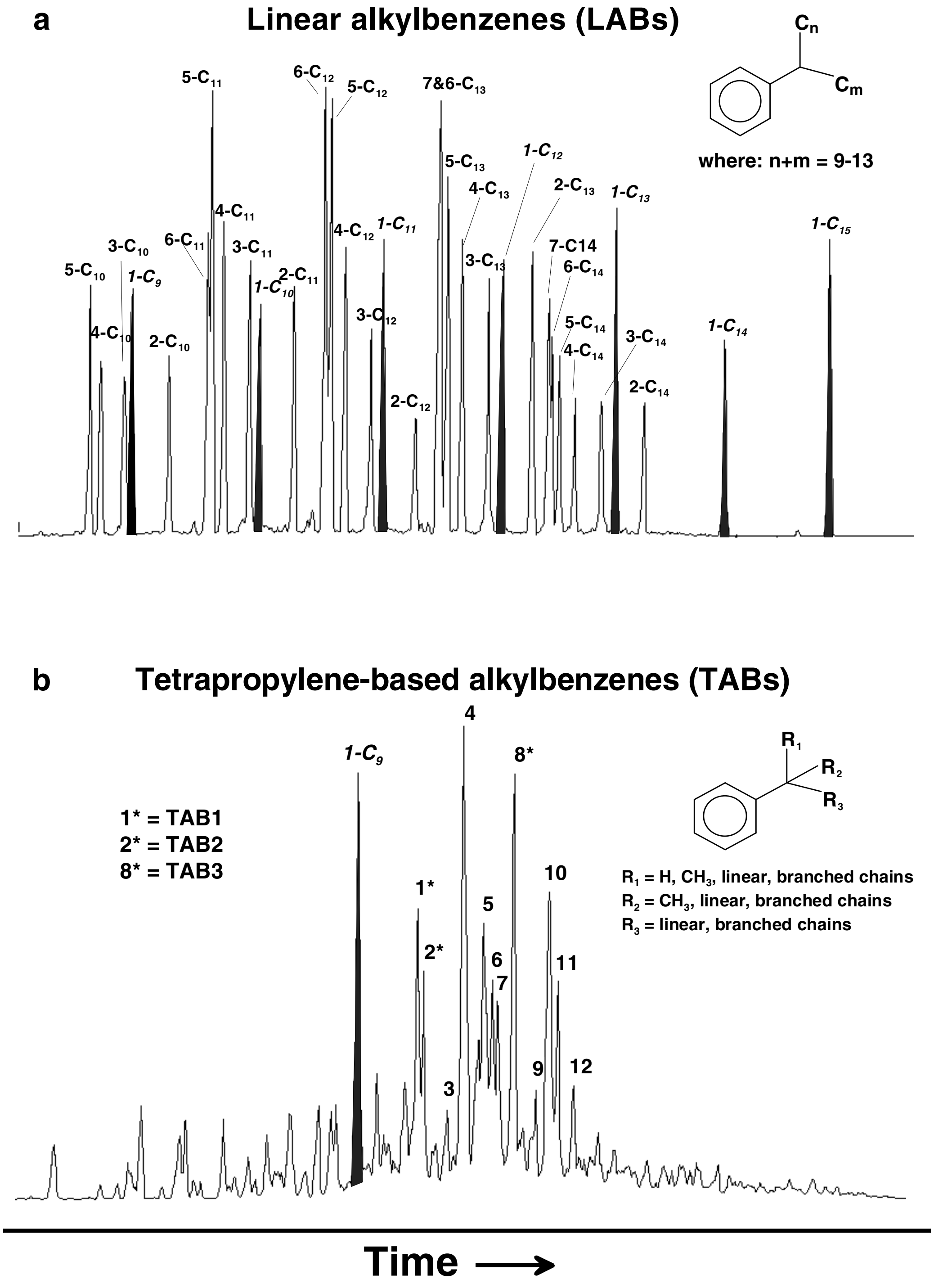

Figure S1. Gas chromatograms and structures of (a) linear alkylbenzenes (LABs), and (b) tetrapropylene-based alkylbenzenes (TABs). Numbers above TAB peaks indicate TABs quantitated in this study. TAB1, TAB2, and TAB3 are designations as given in Eganhouse *et al.* (*6*). Shaded peaks are internal quantitation standards or surrogates (see main text for explanation).

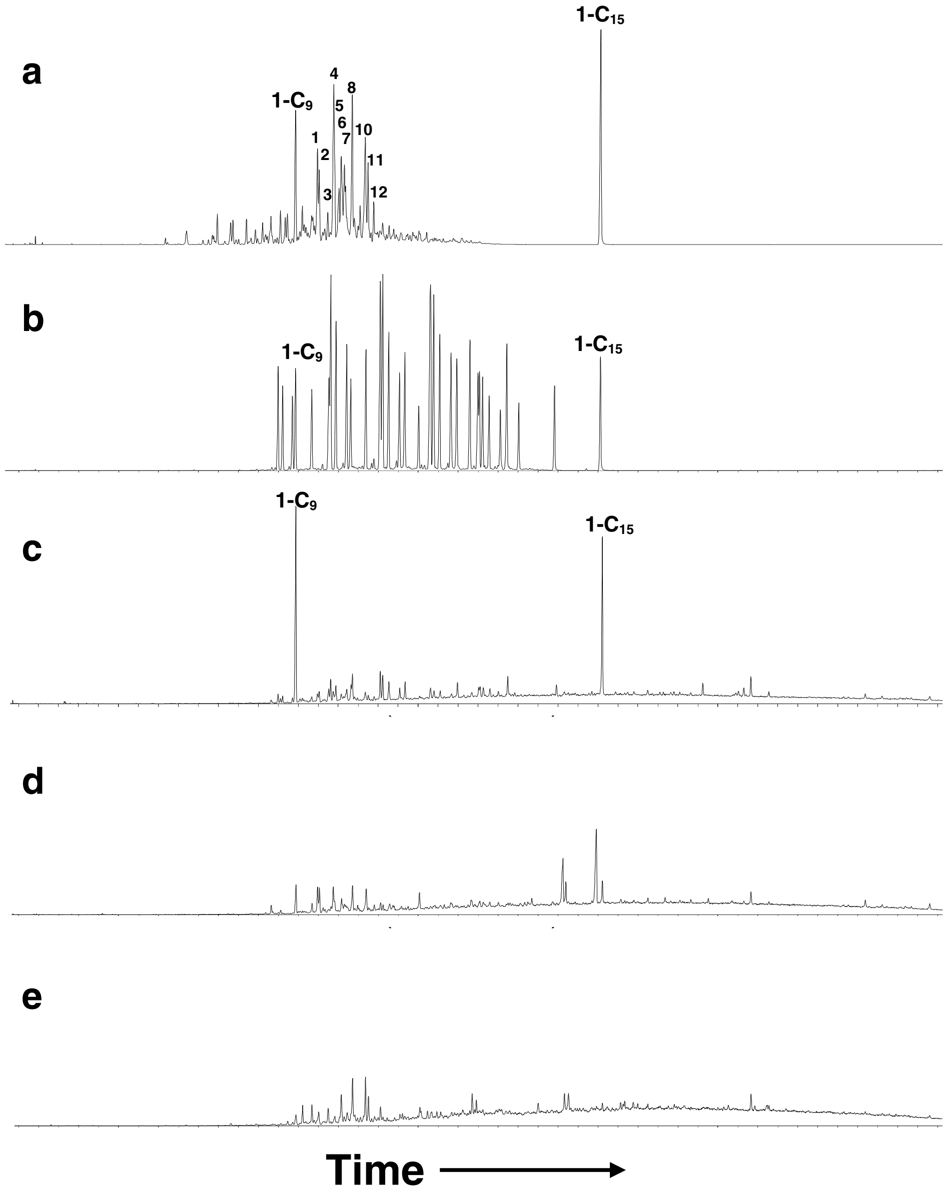

Figure S2. Total ion current (TIC) of (a) TAB calibration standard, and (b) LAB calibration standard, and mass fragmentograms for the 30-32 cm section of core 124B1-03 at (c) m/z = 91, (d) m/z =105, and (e) m/z =119.

2. Sampling Locations

Figure S3 shows the locations where sediment cores (site C), GEOPROBE ‘bag samples’ (site B), and sediment-trap samples (site A) were collected.

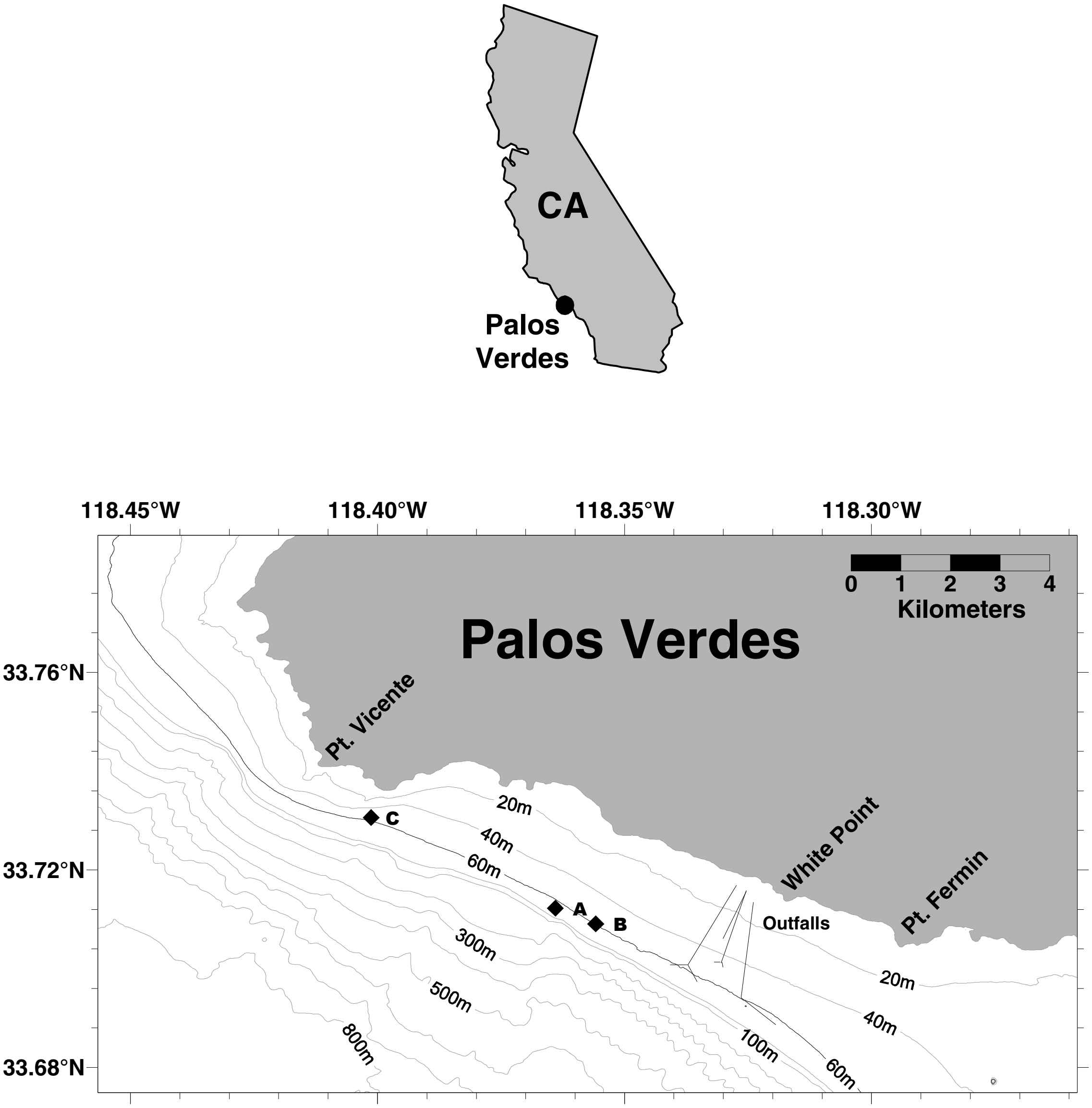

Figure S3. Location map of the Palos Verdes Shelf. USGS cores were collected at site C, near-bottom suspended particles (‘bag samples’) at site B, and sediment-trap samples at site A.

3. Concentrations of LCABs in SRM 1941a

Table S1. Concentrations of long-chain alkylbenzenes in NIST SRM 1941a (ng/dry g)[a]

Compound/peak	**This study[b]**	**av URI[c]**	**av TUAT[d]**
5-C_{10}	93.9	113.1	119.4
4-C_{10}	41.7	54.7	57.1
3-C_{10}	25.2	27.7	31.6
2-C_{10}	24.9	23.6	36.7
6-C_{11}	172.2	203.5	183.7
5-C_{11}	289.9	258.7	270.4
4-C_{11}	107.0	125.1	137.8
3-C_{11}	51.9	64.9	70.4
2-C_{11}	49.5	49.3	59.2
6-C_{12}	300.1	359.7	340.8
5-C_{12}	271.7	247.1	260.2
4-C_{12}	127.6	137.5	134.7
3-C_{12}	65.3	68.9	76.5
2-C_{12}	42.1	54.2	53.1
7-&6-C_{13}	373.2	344.5	345.9
5-C_{13}	212.3	190.4	186.7
4-C_{13}	115.3	99.2	109.2
3-C_{13}	64.2	55.8	70.4
2-C_{13}	37.1	36.2	35.7
7-C_{14}	113.7	206.3	226.5
6-C_{14}	129.9		
5-C_{14}	103.4	98.4	91.8
4-C_{14}	66.3	71.8	58.2
3-C_{14}	36.0	42.9	33.7
2-C_{14}	18.4	22.3	17.3
ΣLAB_{26}	2,930	2,960	3,010
I/E ratio[e]	2.43	2.33	2.27
TABs[d]:			
1	18.8	--[f]	--
2	8.5	--	--
3	38.8	--	--
4	34.0	--	--
5	21.6	--	--
6	16.3	--	--
7	17.8	--	--
8	27.6	--	--
9	3.4	--	--
10	27.4	--	--
11	23.2	--	--
12	15.9	--	--

ΣTAB_{12}	253.4	--	--
Avg. ‘Total TABs’	671.2	--	--

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[a] NIST = National Institute of Standards and Technology.

[b] Average concentrations (n=2).

[c] URI = University of Rhode Island (*7*).

[d] TUAT = Tokyo University of Agriculture and Technology (*7*).

[e] See text for explanation.

[f] Not reported.

4. Concentrations of LABs in Wastewater Effluent and Field Samples and Fluxes in Sediment Traps

Figure S4 summarizes data for the LAB concentrations in LACSD (Los Angeles County Sanitation Districts) effluent, particles collected in near-bottom sediment traps (site A, Figure S3), suspended particles collected during resuspension events (‘bag samples’; site B, Figure S3), and surficial sediments collected on the PVS in 1992 and 2003 (cores 124B1-92, -03, site C, Figure S3).

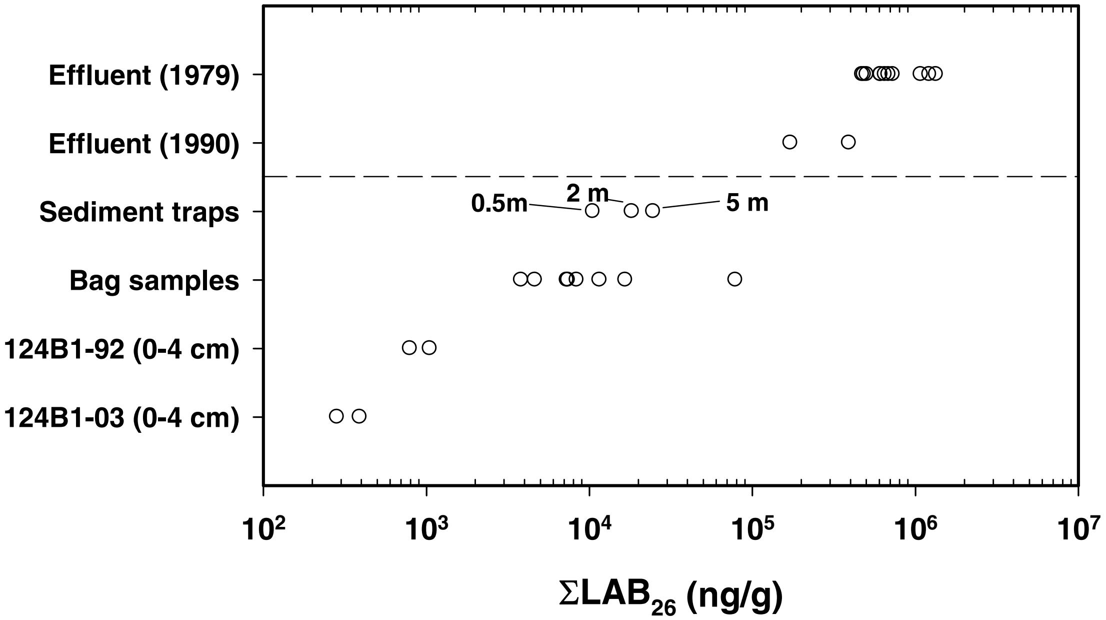

Figure S4. Concentrations of total linear alkylbenzenes (ΣLAB_{26}) in LACSD effluent samples (1979, 1990), near-bottom sediment traps (1989), ‘bag samples’ (1992, 1993), and surficial sediments (1992, 2003) collected on the Palos Verdes Shelf. Note: x-axis is logarithmic.

Concentrations of LABs in effluent particles were greater in 1979 than in 1990. This decline is likely the result of improved source control and treatment (*8*). Sediment traps at site A (Figure S3) positioned at three elevations above the seafloor showed lower ΣLAB_{26} concentrations than the effluent particles. However, concentrations increased with elevation above the sea floor. ‘Bag samples,’ collected at site B that represented particles mobilized during resuspension events, exhibited a wide range of ΣLAB_{26}

concentrations that spanned those of particles collected in sediment traps. Nevertheless, most of the data were closer to those obtained for particles collected in the sediment trap positioned 0.5 m above the seafloor. Finally, the surficial sediment samples (124B1-92, 124B1-03) showed even lower concentrations than were observed for the sediment trap and 'bag' samples. This is likely due to the fact that these samples were collected further downcurrent from the outfall system and, thus, may have experienced greater dilution from non-effluent derived particulate matter. As discussed in the main body of this paper, biodegradation following deposition (as indicated by the higher I/E ratios) served to further reduce ΣLAB_{26} concentrations.

Table S2 summarizes information on the mass fluxes and concentrations of chemical constituents in particles collected in the near-bottom sediment traps.

Table S2: Concentrations and Fluxes of Constituents Collected in Near-Bottom Sediment Traps[a]

			Solids	**TOC**[b]		**TN**[c]		**ΣLAB_{26}**	
deployment date	**days deployed**	**elevation (m)**	**flux ($g/cm^2/y$)**	**concentration (%)**	**flux ($mg/cm^2/y$)**	**concentration (%)**	**flux ($mg/cm^2/y$)**	**concentration ($\mu g/g$)**	**flux ($\mu g/cm^2/y$)**
11/28/89	36	0.5	5.73	3.55	203.	0.34	19.5	10.6	60.7
		2.0	2.42	3.60	87.1	0.35	8.5	18.3	44.3
		5.0	1.51	3.73	56.3	0.37	5.6	24.7	37.3
6/8/90	33	0.5	8.62	3.66	315.	0.35	30.2	11.4	98.3
		2.0	2.19	3.80	83.2	0.38	8.3	28.8	63.1
		5.0	1.40	3.95	55.3	0.41	5.7	-[d]	-[d]

[a] Description of the methods used for determination of TOC and TN concentration in sediment-trap particles and calculation of trap fluxes can be found in Hendricks and Eganhouse (*9*).

[b] TOC = total organic carbon.

[c] TN = total nitrogen.

[d] Sample lost during processing.

5. TAB Composition in Sediment Cores

In the original work of Eganhouse *et al*. (*10*), the strong similarity between GC/MS chromatograms of the TAB mixture obtained from Monsanto Company and those in PVS sediments near site C suggested that these compounds were well preserved. In subsequent studies Eganhouse *et al*. (*6*) presented evidence that although the TABs appear to be largely preserved, subtle changes in the relative abundances of some of the TAB peaks can be seen deeper in the sediment column. It was unclear whether these changes reflected historical variations in the composition of the TABs introduced to the LACSD or selective removal of TAB components following burial.

To expand on this concept, Figure S5 presents data on the composition of TABs in the 1992 and 2003 cores. The upper panel (Figure S5a) is a plot of the average compositions (with error bars-1 std dev) for the two cores. Although similar, the average relative abundances of the TABs in the two cores exhibited distinct differences. Notably, there were apparent decreases in the average relative abundance of TABs #10 and 11, with smaller decreases for TABs #4, 7 and 12. On the other hand, there were apparent increases in the relative abundances of other TAB peaks (#1,2,3,5,8). As indicated by the error bars, some of these differences were likely not significant (*e.g.* TABs 4,5,7,8,12). One way of resolving this is to compare compositions at depth intervals that were deposited at approximately the same time (coeval layers). The lower panel (Figure S5b) shows TAB compositions in coeval layers (30-32 cm or 29.8 g/cm^2-1992, 34.1 g/cm^2-2003). Although the patterns are similar to those seen for the whole-core averages, some relations are reversed (*e.g.* TABs #4,7,8). A notable result is the fact that the relative abundance of TAB3 (*i.e.* TAB peak #8) appears to have remained essentially constant during this time period. From these data, it is clear that some of the TABs were slowly altered under reducing conditions in sediments at this location. It must be recognized that the TABs are a complex mixture of alkylbenzenes with a range of structures. Studies ongoing in our laboratory have shown that TAB3 consists of more than one phenyldodecane and one minor phenyltridecane, structures of which are presently unknown. It is probable that differences in the structures of the alkyl chains result in differences in biodegradability. However, based on a comparison of the ΣTAB_{12} and TAB3 whole-core inventories (see main text), the effects of these transformations are not quantitatively significant; from 1992 to 2003, the change in ΣTAB_{12} and TAB3 inventories were -8.8 percent and 1.3 percent, respectively. These differences are within the estimated analytical error of about 9-11.5%. For all intents and purposes, inventories of TAB3 and the sum of the twelve TAB peaks remained constant during the period 1992-2003.

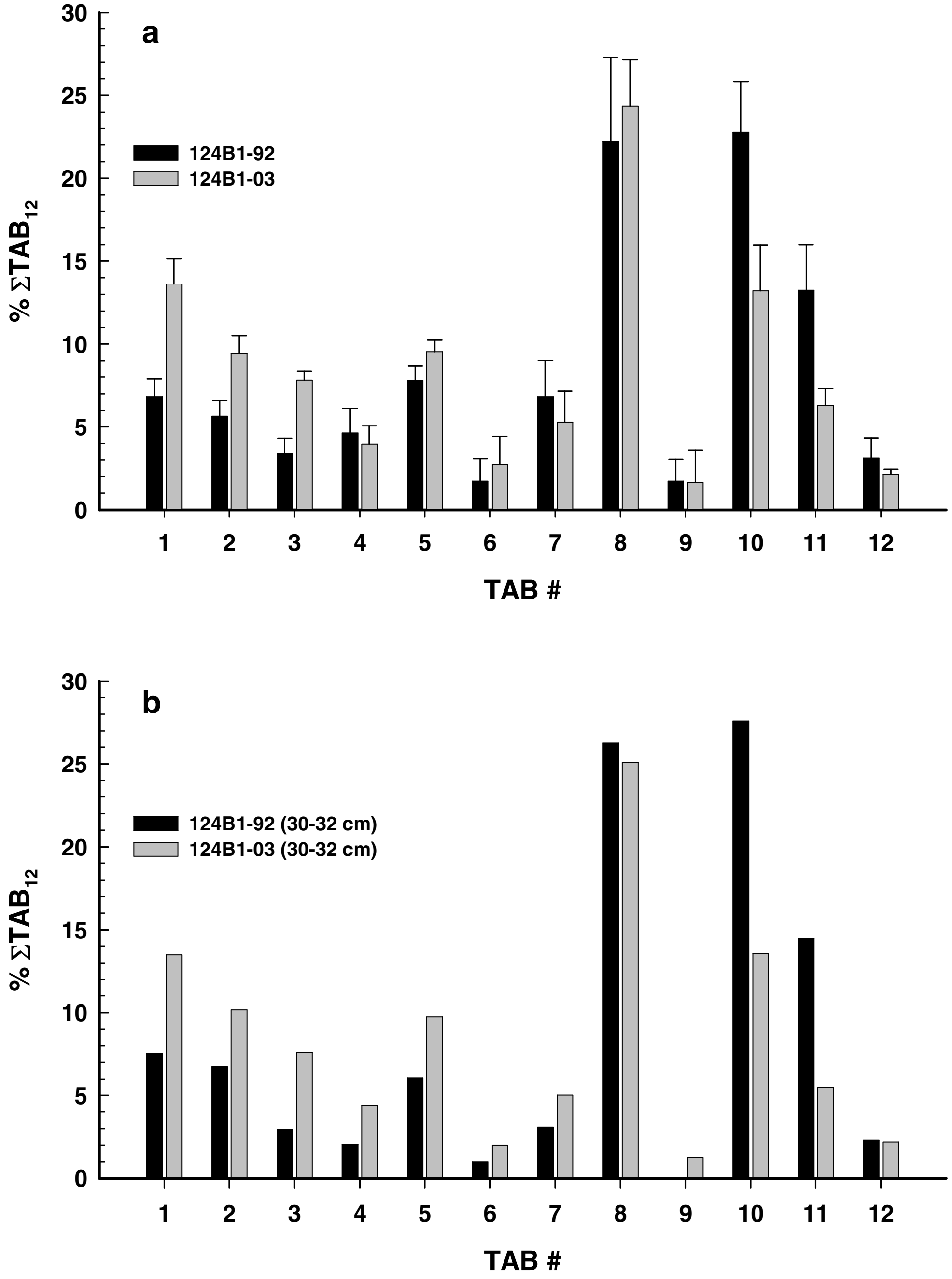

Figure S5. Relative abundances of TAB peaks in cores collected at site C in 1992 and 2003 (a) average for all depths, and (b) in coeval depth intervals.

6. Propagation of Error Calculations.

Uncertainties were estimated for first-order transformation rates and half-lives determined by comparison of whole-core inventories (WCIs) and coeval sediment layers ($C\text{-}C_{mean}$) of aligned 1992 and 2003 cores (see Table 1, main paper). Here we present an example calculation for uncertainty in the first-order transformation rate of 6-C_{12} determined by comparing concentrations in coeval sediment layers ($C\text{-}C_{mean}$) of the aligned 1992 and 2003 cores. Assumptions for this calculation include: 1) no dependency of uncertainty on sample size, 2) LAB concentrations are log-normally distributed, 3) time is constant, and 4) the error associated with determination of LAB concentrations for each core can be approximated by results of replicate analyses conducted on a single core collected on the PVS in 1990 (PVST90). These calculations were developed with the assistance of Dr. Jurate Landwehr (USGS) whose help is gratefully acknowledged.

The uncertainty in the first-order rate coefficient, σ_λ, can be expressed as:

$$\sigma_\lambda = \frac{1}{t} \bullet \sqrt{\ln(1 + rsd_{'92}^2) + \ln(1 + rsd_{'03}^2)}$$

where: $rsd_{'n}$ = relative standard deviation of the LAB concentration for the core collected in year, n, and
t = time between core collection (11.07 years).

For the LAB, 6-C_{12}, $rsd_{'92}$ is assumed to equal to $rsd_{'03} \cong 0.084$. This yields:

$$\sigma_\lambda = \frac{1}{11.07} \bullet \sqrt{\ln(1 + [0.084]^2) + \ln(1 + [0.084]^2)}$$

$\sigma_\lambda = 0.011\ \text{yr}^{-1}$ (see Table 1, main paper)

Literature Cited

(1) Swisher, R. D. *Surfactant Biodegradation*; Second Edition ed.; Marcel Dekker: New York, 1987; Vol. 18.

(2) Hons, G. Alkylarylsulfonates: History, manufacture, analysis, and environmental properties. In *Anionic Surfactants: Organic Chemistry*; Stache, H. W., Ed.; Marcel Dekker, Inc.: New York, 19958.

(3) Ötvös, I.; Iglewski, S.; Hunneman, D. H.; Bartha, B.; Balthazár, Z.; Pályi, G. Petrochemical analytical problems: II. Gas-liquid chromatographic-mass spectrometric investigation of industrial dodecylbenzenes. *J. Chrom.* **1973**, *78*, 309-316.

(4) de Almeida, J. L. G.; Dufaux, M.; Taarit, Y. B.; Naccache, C. Linear Alkylbenzene. *J. Amer. Oil Chem. Soc.* **1994**, *71*, 675-694.

(5) Grubb, H. M.; Meyerson, S. Mass spectra of alkylbenzenes. In *Mass Spectrometry of Organic Ions*; McLafferty, F. W., Ed.; Academic Press: New York, 1963.

(6) Eganhouse, R. P.; Pontolillo, J.; Leiker, T. J. Diagenetic fate of organic contaminants on the Palos Verdes Shelf, California. *Mar. Chem.* **2000**, *70*, 289-315.

(7) Hartmann, P. C.; Quinn, J. G.; King, J. W.; Tsutsumi, S.; Takada, H. Intercalibration of LABs in marine sediment SRM1941a and their application as a molecular marker in Narragansett Bay sediments. *Environ. Sci. Technol.* **2000**, *34*, 900-906.

(8) Stull, J.; Baird, R.; Heesen, T. T. Relationship between declining discharges of municipal wastewater contaminants and marine sediment core profiles. In *Ocean Processes in Marine Pollution*; Wolfe, D. A., O'Connor, T. P., Eds.; Robert E. Krieger Publishing: Malabar, FL, 1988; Vol. 5.

(9) Hendricks, T.; Eganhouse, R. P. *Modification and verification of sediment deposition models*, Southern California Coastal Water Research Project Authority: Long Beach, CA, 1992.

(10) Eganhouse, R. P.; Blumfield, D. L.; Kaplan, I. R. Long-chain alkylbenzenes as molecular tracers of domestic wastes in the marine environment. *Environ. Sci. Technol.* **1983**, *17*, 523-530.