

VALIDITY OF USING LINEAR ALKYL BENZENES AS MARKERS OF SEWAGE CONTAMINATION WITH INTERFERENCE FROM TETRAPROPYLENE-BASED ALKYL BENZENES

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Abstract—A previously developed two-component model was used to estimate the magnitude of interference from tetrapropylene-based alkylbenzenes (TABs) in measuring linear alkylbenzene (LAB) concentrations in a sediment core collected from the Palos Verdes Shelf (Los Angeles, CA, USA). The magnitude of such interference generally increased with increasing sediment core depth and was fairly high in deeper sediments, where TABs were abundant relative to LABs. Usage of LABs as sewage markers in sediments is generally valid as long as the approximate ratio of TAB to LAB concentration is less than 10.

Keywords—Linear alkylbenzenes Tetrapropylene-based alkylbenzenes Two-component model Sewage marker
Interference

INTRODUCTION

The coastal ocean off southern California (USA) has received a variety of pollutants from sources such as sewage outfalls and storm drains. Differentiating between these inputs is desirable for better management of the coastal resources. Linear alkylbenzenes (LABs), raw materials in the production of detergents, have been recognized as molecular markers of domestic waste inputs for more than a decade [1–4]. Linear alkylbenzene residues remain in detergents, survive wastewater treatment, and can be transported to the environment with treated sewage. On the other hand, tetrapropylene-based alkylbenzenes (TABs) were used as raw materials for alkylbenzenesulfonate surfactants used in detergent manufacturing until the early 1960s, when they were replaced by LABs. Because the retention times and mass spectrometric ion fragments are similar for some LAB and TAB components [1,5], usage of LABs as markers of current sewage-derived contaminant inputs may be questionable without considering the interference from TABs when both LABs and TABs are present.

In a previous article [6] we presented a two-component model that can be used to estimate quantitation errors that occur when measuring LABs in the presence of TABs using gas chromatography–mass spectrometry (GC–MS). Our approach was based on the difference in the relative abundances of two major ion fragments of individual LAB and TAB compounds. The applicability of this model was tested on several sections from a sediment core collected from station E6 (Fig. 1) in Santa Monica Bay. The quantitation errors in measurements of a few LAB compounds increased with increasing core depth, consistent with the fact that the concentration of TABs was higher in deeper sediments.

This study was intended to examine the validity of using LABs as molecular markers of sewage-derived organic con-

tamination using the two-component model. Specifically, we analyzed a full sediment core collected from the Palos Verdes Shelf near the Joint Water Pollution Control Plant (JWPCP) outfall system of the County Sanitation Districts of Los Angeles County (CSDLAC). Profiles of LABs and TABs in a sediment core collected from a nearby location (station 3C) were determined previously on the basis of the mass spectrometric abundances of m/z 91, 105, or 119 (m/z 91 and 105 for LABs and m/z 105 and 119 for TABs) [1]. Although the mutual interference between LABs and TABs could not be accounted for, these profiles at least qualitatively demonstrated the co-presence of LABs and TABs in sediments. Thus, it provided a unique opportunity to investigate the influence of TABs in quantifying LAB concentrations. In our study, we carefully extracted related data used in the model calculation. Instead of estimating the impact of TAB interference on individual LAB components, we considered the effects on total LAB concentrations to realistically assess the significance of the TAB interference on LAB measurements.

METHODS

An 80-cm sediment core was collected at station 7C (33°42.1' N, 118°20.9' W; Fig. 1) near the JWPCP outfall (60-m water depth) on October 10, 1995, using a modified gravity corer [7] and frozen immediately. The core was thawed and cut into 1-cm pieces using a stainless-steel handsaw and stored at –20°C before further treatment.

Thawed sediments were spiked with 1-phenyl nonane (surrogate standard) and extracted three times with methylene chloride using a roller table. The combined extract was concentrated, solvent-exchanged to hexane, treated with activated copper granules to remove sulfur, and subjected to a 1:2 alumina:silica gel glass column for clean-up and fractionation. The fraction containing LABs was concentrated to 1 ml using a Zymark 500 Turbo Vap concentrator. An appropriate amount

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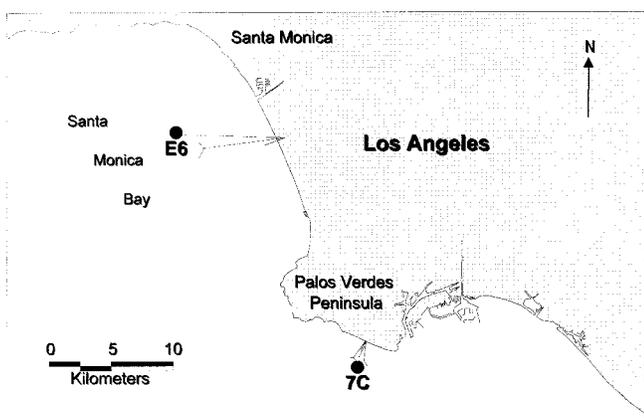


Fig. 1. Map of the sampling region in Palos Verdes Shelf and Santa Monica Bay, California, USA.

of the internal standard (1-phenyl pentadecane) was added to the extract before instrumental analysis.

Linear alkylbenzenes were measured using an HP 5890 Series II gas chromatograph with a 5970 mass selective detector equipped with a 60-m \times 0.25-mm-inner diameter (0.25- μ m film thickness) DB-5 column (J&W Scientific, Folsom, CA, USA). The column temperature was initially set at 70°C, immediately ramped to 200°C at 6°C/min and to 285°C at 10°C/min, and held for 42 min. Ultra-high-purity helium was used as the carrier gas at 2 ml/min at 70°C. The detection limit for individual LAB compounds was estimated to be 200 ng for 1 g of dry sample. Linear alkylbenzene concentrations were determined on the basis of the response factors of individual components in an LAB mixture that was quantified previously; detailed procedures are described elsewhere [6]. The surrogate standard recoveries were $90 \pm 38\%$ in 15 samples.

The calculation of quantitation errors is made possible by three assumptions: (1) only LABs and TABs contribute to m/z 91 and 119; (2) LABs contain their strongest ion fragment at m/z 91 and a minor component of m/z 119; and (3) TABs contain their strongest ion fragment at m/z 119 and a minor component of m/z 91 [6]. The exception to assumption 2 is C_i -LAB-2 (i = the number of carbon atoms on the alkyl chain). For this group of LABs, the major ion fragment is m/z 105.

For a given chromatographic peak, A and A' are defined as abundances of m/z 91 and 119, respectively; B and B' , abundances of m/z 91 and 119 contributed from an LAB component (or a mixture); and C and C' , abundances of m/z 91 and 119 contributed from a TAB component (or mixture). According to assumption 1,

$$A = B + C$$

and

$$A' = B' + C'$$

If we define $X = B'/B$ and $X' = C'/C$, we may combine the above equations to achieve

$$B = (X'A - A')/(X' - X) \quad (1)$$

The quantitation error (E) for measurements of individual LAB components is defined by

$$E (\%) = 100[(A - B)/B] \quad (2)$$

Substituting Equation 1 into Equation 2 yields

$$E (\%) = 100[(1 - \beta X)/(\beta X' - 1)] \quad (3)$$

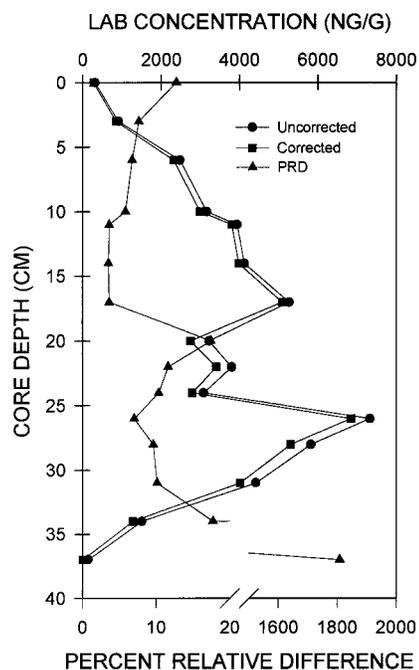


Fig. 2. Depth profiles of uncorrected linear alkylbenzene (LAB) concentration, corrected LAB concentration, and the percent relative difference (PRD) in the 7C sediment core.

with $\beta = A/A'$. As described previously [6], β can be acquired directly from the GC-MS measurements and X from analyses of a pure LAB mixture.

An average X value was obtained for each of the LAB components in four measurements of the LAB mixture; the overall relative SD (RSD) was 6.2%. X' values were obtained from analyses of a TAB mixture, but instead of assuming an identical value for all TABs [6], we estimated X' for individual TAB contributions. Procedurally, four measurements of the TAB mixture were performed, and the abundances of m/z 91 and 119 were summed around the retention times of LAB compounds, which were obtained in separate runs. The overall RSD for X' was 37%, indicating the inconsistency of finding TAB peaks at the retention times associated with the LAB compounds. To assure a positive E by definition (Eqn. 2), any values of βX and $\beta X'$ not satisfying $\beta X \leq 1$ and $\beta X' > 1$ had to be rejected.

E was estimated for each LAB component using Equation 3, which in turn was used to derive the corrected concentration B using Equation 2. The corrected total LAB concentration for each sample was the sum of the individual LAB concentrations. The extent of biodegradation of LABs can be characterized by the concentration ratio for the internal and external isomers of C_{12} -LABs, $I/E = \Sigma(6\text{-phenyl dodecane} + 5\text{-phenyl})/\Sigma(4\text{-phenyl dodecane} + 3\text{-phenyl dodecane} + 2\text{-phenyl dodecane})$ [8]. A high I/E ratio indicates a high degree of LAB biodegradation, due to the selective biodegradation of the external isomers relative to the internal isomers [8]. The corrected I/E ratio was also estimated from the corrected LAB concentrations.

RESULTS AND DISCUSSION

The percent relative difference (PRD) between the uncorrected and corrected total LAB concentrations in the sediment core varied in a narrow range between 0 and ~ 35 cm and abruptly increased below the 35-cm depth (Fig. 2). This was

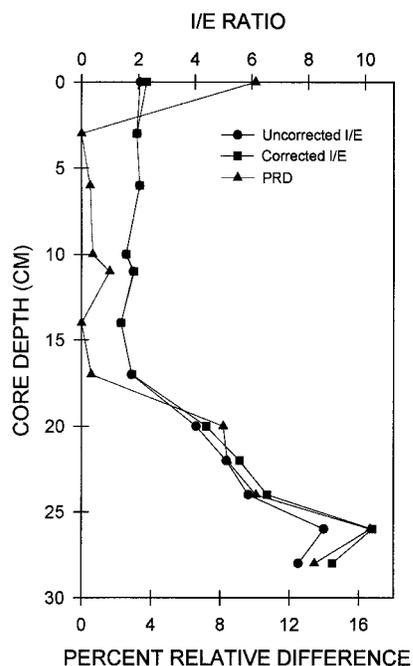


Fig. 3. Depth profiles of uncorrected internal/external isomer ratio (I/E), corrected I/E, and the percent relative difference (PRD) in the 7C sediment core.

consistent with the increasing quantitation errors for individual LAB components at deeper sediments of Santa Monica Bay [6]. Rising PRD was considerably correlated with decreasing total LAB concentration in the sediment core. Under our experimental conditions, TABs mostly interfered with C_{10} -LABs and C_{11} -LABs. The total LAB concentration, on the other hand, was the sum of C_i -LABs with $i = 10$ to 14. Thus, the overall LAB concentration was not impacted as much by TABs as were individual LAB components depicted previously [6]. The two-component model appeared to correctly appraise the magnitude of the TAB interference in sediments with both LABs and TABs present.

The similarity in the profiles of the uncorrected and corrected total LAB concentrations (Fig. 2) suggests that the presence of TABs may affect the quantitative results of LAB measurements but does not affect very much the vertical distribution of LABs after deposition in sediments. Furthermore, the generally small PRD throughout the sediment core indicates that the impact of the TAB interference was significant only when the LAB concentration was extremely low.

The I/E ratios varied in a narrow range in the upper sediment sections and started rising beyond ~ 15 cm deep in the sediment (Fig. 3), in line with the expectation that older LAB deposits were degraded to a greater extent than the more recently discharged LABs. Similar to the total LAB concentration, the corrected I/E ratio was very similar to (but always higher than) the uncorrected one; PRD varied between 0 and 17%. This discrepancy is not significant in assessing the magnitude of LAB biodegradation considering the large uncertainty in the experimental I/E-LAB degradation relationship [8].

The JWPCP is one of the largest municipal wastewater treatment plants in southern California, with a total effluent flow of 4.52×10^{11} L in 1994 [9] discharged onto the Palos Verdes Shelf at the 60-m depth. Historic emissions of LABs have not been monitored, but a few studies have measured

LABs in the JWPCP final effluents at various time periods. Eganhouse et al. [1] analyzed monthly composite effluent samples for 11 months (January to October and December) during 1979. The LAB concentrations in the particulates ranged from 472 to 1,340 $\mu\text{g/g}$ with a mean value of 763 $\mu\text{g/g}$. Chalaux et al. [10] collected one composite sample in November 1987 and obtained a particulate LAB concentration of 421 $\mu\text{g/g}$. Both studies used Whatman GF/A (1.6 μm pore size) glass fiber filters to filter suspended particles from the effluents. Hendricks and Eganhouse [11] analyzed the JWPCP effluent twice in 1990, and the total particulate LAB concentrations were 393 and 172 $\mu\text{g/g}$, respectively (suspended solids were filtered by Whatman GF/C filters, 1.2 μm pore size). On the other hand, the annual effluent flow from the JWPCP has been quite steady over the last 20 years [9]. These results suggested a general trend of decreasing LAB inputs from the wastewater effluents, which is consistent with the LAB concentration profile in the 7C sediment (Fig. 2).

The insignificant differences in the corrected and uncorrected total LAB concentrations and I/E ratios, as well as the hypothesized correlation between the historical inputs of LABs and the sediment LAB profile, validate the use of LABs as markers of sewage-derived contamination where both LABs and TABs are present in significant amounts. Although this study examined sediments from the Palos Verdes Shelf only, the conclusion should be true if the concentration of TABs is not too high compared to that of LABs. By comparing the sediment profiles of LABs and TABs at station 3C [1], we estimated that the presence of TABs would not affect the quantitation of LAB concentrations within the analytical error if the ratio of TAB to LAB concentrations is less than 10.

The two-component model reexamined in this study can be considered a special case under a general framework of mixing modeling [12]. Thus, it may be used in any other two-component systems satisfying the criteria given previously [6]. One potential application may be to separate coeluting polychlorinated biphenyl (PCB) isomers. Among the possible 209 PCB congeners, quite a few of them coelute under normal chromatographic conditions [13]. We found that in a mixture of Aroclor[®] 1242, 1248, 1254, and 1260, at least 15 chromatographic peaks contained coeluting PCB isomers that could not be separated by a quadrupole mass spectrometer. On the other hand, using the MS-MS approach, it may be possible to generate secondary ion fragments that have different relative abundances for isomeric molecules (C.C. Chou, personal communication). If this occurs with any coeluting PCB isomers, they can be quantified separately using the two-component model.

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