

Validity of Using Linear Alkylbenzenes as Markers of Sewage Contamination with Interference from Tetrapropylene-Based Alkylbenzenes

Eddy Zeng, Darwin Cheng, Azra Khan,
and Cherrie Vista

ABSTRACT

The co-presence of linear alkylbenzenes (LABs) and tetrapropylene-based alkylbenzenes (TABs) in sediments challenges the use of LABs as molecular markers of domestic wastes, due to the similar chromatographic characteristics of these two alkylbenzene types. A previously developed two-component model was used to estimate the magnitude of interference from TABs in measuring LAB concentrations in a sediment core collected from the Palos Verdes Shelf off the coast of Los Angeles, California. The results were consistent with the trend of historical inputs of domestic wastes, indicating that the presence of TABs may affect the quantitative results of LAB measurements. However, the impact of the TAB interference is significant only when the LAB concentration is extremely low. It was concluded that the use of LABs as sewage markers is generally valid as long as the ratio of TAB and LAB concentrations is approximately less than 10.

INTRODUCTION

The ocean off the southern California coast has received a variety of pollutants from sources such as sewage outfalls and storm drains. Differentiating among these inputs, and understanding the fate of these pollutants, is desirable for better management of the coastal resources. Linear alkylbenzenes (LABs), which have been used as raw materials in the production of detergents since the early 1960s, have been recognized as molecular markers of domestic waste inputs for more than a decade (Eganhouse *et al.* 1983a, Takada and Ishiwatari 1987, Eganhouse *et al.* 1988, Takada and Ishiwatari 1991). The LAB residues remain in detergents, survive wastewater

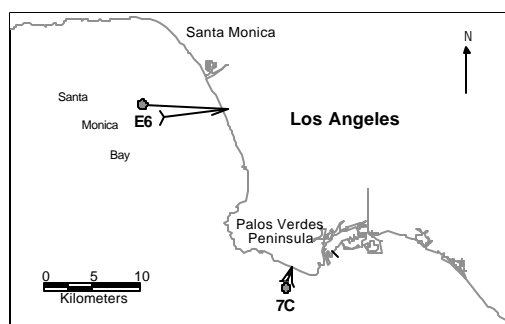
treatment, and are transported to the environment with treated sewage. Tetrapropylene-based alkylbenzenes (TABs) were used as raw materials for detergent manufacturing until the early 1960s, when they were replaced by LABs. Since the retention times and mass spectroscopic ion fragments are similar for some LAB and TAB components (Eganhouse *et al.* 1983a, Eganhouse *et al.* 1983b), the use of LABs as markers of current sewage-derived contaminant inputs may result in error unless the interference from TABs when both LABs and TABs are present is considered.

In a previous paper (Zeng and Yu 1996), a two-component model was presented that can be used to estimate quantitation errors that occur when measuring LABs in the presence of TABs (or vice versa) using gas chromatography/mass spectrometry (GC/MS). This 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 (Figure 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 is higher in deeper sediments.

The present study examined the validity of using LABs as molecular markers of sewage-derived organic contamination using the two-component model. Specifically, 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) was examined. Profiles of LABs and TABs in a sediment core collected

from a nearby location (Station 3C) were defined previously (Eganhouse *et al.* 1983a). These profiles clearly demonstrated the co-presence of LABs and TABs in sediments, thus providing a unique opportunity to investigate the influence of TABs in quantifying LAB concentrations. In

FIGURE 1. Map of the sampling region on the Palos Verdes Shelf and in Santa Monica Bay.



this study, related data used in the model calculation was carefully extracted. Instead of estimating the impact of TAB interference on individual LAB components, the effect on total LAB concentrations was determined, in order to realistically assess the significance of the TAB interference on LAB measurements.

MATERIALS AND METHODS

An 80-cm sediment core was collected at Station 7C (33°42.1' N/118°20.9' W, Figure 1) near the JWPCP outfall (60-m water depth) on October 10, 1995, using a modified gravity corer (SCCWRP 1982) and frozen immediately. The core was then thawed and cut into 1-cm pieces using a stainless steel handsaw and stored at -20°C prior to additional 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 0.5 or 1 mL under gentle nitrogen flow. An appropriate amount of the internal standard (1-phenyl pentadecane) was added to the extract before instrumental analysis.

LABs were measured using a Hewlett Packard 5890 Series II GC with a 5970 mass selective detector equipped with a 60 m × 0.25 mm i.d. (0.25 μm film thickness) DB-5 column (J&W Scientific, Folsom, California). 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/g for 1 g of dry sample. The procedure for quantifying LAB concentrations was described previously (Zeng and Yu 1996).

The quantitation error for measurements of individual LAB components is calculated using a previously published formula (Zeng and Yu 1996):

$$E (\%) = 100 \times \left(\frac{A - B}{B} \right) \quad (1)$$

or

$$E (\%) = 100 \times \left(\frac{1 - \beta X}{\beta X' - 1} \right) \quad (2)$$

with $A = B + C$, $A' = B' + C'$, $\beta = A/A'$, $X = B'/B$, and $X' = C'/C$, where A and A' were defined as abundances of m/z 91 and 119, respectively, in a given chromatographic peak;

B and B' were defined as abundances of m/z 91 and 119 contributed from a LAB component (or a mixture); and C and C' were defined as abundances of m/z 91 and 119 contributed from a TAB component (or mixture). As described previously (Zeng and Yu 1996), β can be acquired directly from the GC/MS measurements and X from analyses of a pure LAB mixture. Average X values ($n=4$) were obtained for each of the LAB components with an overall relative standard deviation of 6.2%. The X' values were obtained from analyses of a TAB mixture; but instead of assuming an identical value for all TABs (Zeng and Yu 1996), X' was estimated 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 the LAB compounds. The overall relative standard deviation for X' was 37%, indicating the inconsistency of finding TAB peaks at the retention times associated with the LAB compounds. To ensure a positive E by definition (Equation (1)), any values of βX and $\beta X'$ not satisfying $\beta X \leq 1$ and $\beta X' > 1$ had to be rejected.

The value of E was calculated for each LAB component using Equation (2), which in turn was used to derive the corrected concentration B using Equation (1). The corrected total LAB concentration for each sample was the sum of the individual LAB concentrations. In addition, the corrected I/E ratio ($\sum(6\text{-phenyl dodecane}+5\text{-phenyl dodecane})/\sum(4\text{-phenyl dodecane}+3\text{-phenyl dodecane}+2\text{-phenyl dodecane})$), an indicator of the extent of LAB biodegradation (Takada and Ishiwatari 1990), was also calculated 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 (Figure 2), indicating stronger TAB interference at deeper locations. Rising PRD was well correlated with decreasing total LAB concentration in the sediment core. Under the 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 (Zeng and Yu 1996). 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 (Figure 2) suggests that the presence of TABs can affect the quantitative results of

LAB measurements but only minimally affect the vertical distribution of LABs after deposition in sediments. Additionally, the generally small PRD found throughout the sediment core indicates the impact of the TAB interference was significant only when the LAB concentration was extremely low.

The I/E ratios generally increased with core depth (Figure 3), congruent 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 within the same range as (but always higher than) the uncorrected ratio; PRD varied between 0 and 17%. This discrepancy is not significant in assessing the magnitude of LAB biodegradation considering the high degree of uncertainty in the experimental I/E-LAB degradation relationship (Takada and Ishiwatari 1990).

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 (SCCWRP 1996) discharged onto the Palos Verdes Shelf at the 60-m depth. Historic emissions of LABs have not been monitored. Two previous studies obtained effluent particulate LAB concentrations of 1,342 $\mu\text{g/g}$ (Eganhouse *et al.* 1983a) and 421 $\mu\text{g/g}$ (Chaloux *et al.* 1992) in 1979 and 1987, respectively. In addition, the concentrations of total suspended solids, oil and grease, and other organic (e.g., PCB and DDT) and inorganic contaminants (e.g., trace metals) have drastically declined over the last 24 years (SCCWRP 1996). These results suggest that a general trend of decreasing LAB inputs from the wastewater effluents may also be present, which is consistent with the LAB concentration profile in the Station 7C sediment (Figure 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 only examined sediments from the Palos Verdes Shelf, it is expected that this conclusion can be applied in cases where the concentration of TABs is relatively low compared to that of LABs. By comparing the sediment profiles of LABs and TABs at Station 3C (Eganhouse *et al.* 1983a), it was estimated that the presence of TABs would not affect the quantitation of LAB concentrations within the analytical error if the ratio of TAB and LAB concentrations is less than 10.

The two-component model reexamined in this study can be considered a specific application under a general framework of mixing modeling (Akerjord and Christophersen

FIGURE 2. Depth profiles of uncorrected LAB concentrations, corrected LAB concentrations, and the percent relative difference (PRD) in the Station 7C sediment core collected in 1995.

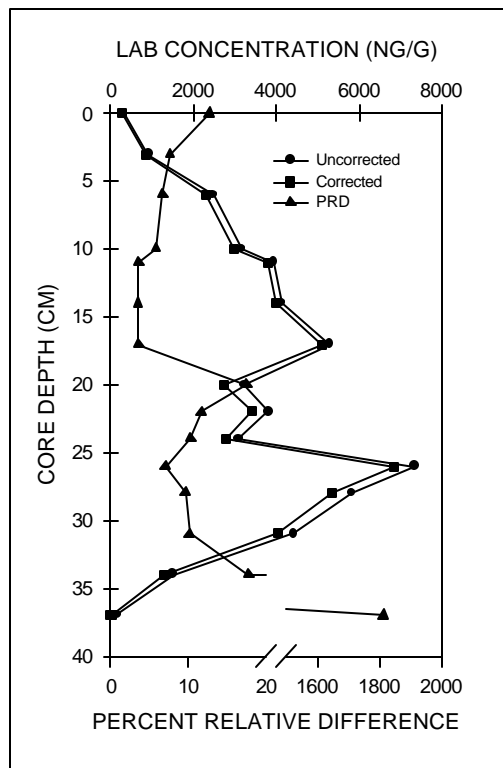
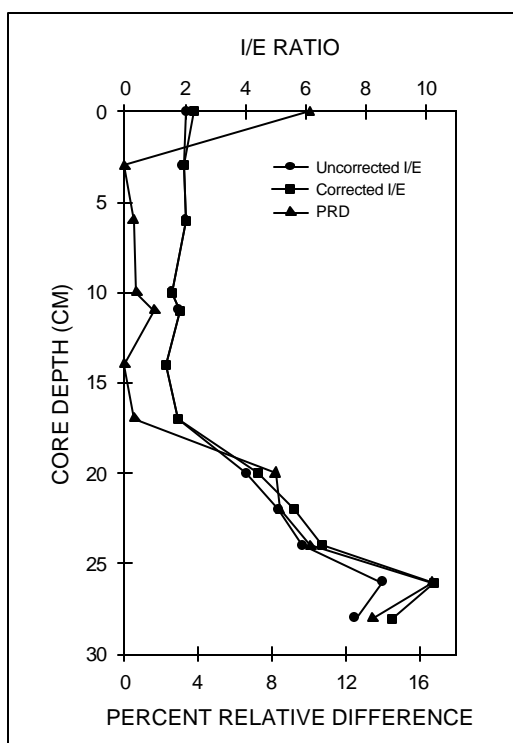


FIGURE 3. Depth profiles of uncorrected I/E ratio, corrected I/E ratio, and the percent relative difference (PRD) in the Station 7C sediment core.



1996). Thus, it can be used in any other two-component systems satisfying the criteria defined previously (Zeng and Yu 1996). One potential application may be to separate co-eluting polychlorinated biphenyl (PCB) isomers. Among the possible 209 PCB congeners, several co-elute under normal chromatographic conditions (Mullin *et al.* 1984). In a mixture of Aroclor 1242, 1248, 1254, and 1260, at least 15 chromatographic peaks contained co-eluting 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. If this occurs with any co-eluting PCB isomers, they can be quantified separately using the two-component model.

LITERATURE CITED

Akerjord, M.A. and N. Christophersen. 1996. Assessing mixing models within a common framework. *Environmental Science and Technology* 30:2,105-2,112.

Chaloux, N., J.M. Bayona, M.I. Venkatesan and J. Albaigés. 1992. Distribution of surfactant markers in sediments from Santa Monica Basin, southern California. *Marine Pollution Bulletin* 24:403-407.

Eganhouse, R.P., D.L. Blumfield and I.R. Kaplan. 1983a. Long-chain alkylbenzenes as molecular tracers of domestic wastes in the marine environment. *Environmental Science and Technology* 17:523-530.

Eganhouse, R.P., E.C. Ruth and I.R. Kaplan. 1983b. Determination of long-chain alkylbenzenes in environmental samples by argentation thin-layer chromatography/high-resolution gas chromatography and gas chromatography/mass spectrometry. *Analytical Chemistry* 55:2,120-2,126.

Eganhouse, R.P., D.P. Olaguer, B.R. Dould and C.S. Phinney. 1988. Use of molecular markers for the detection of municipal sewage sludge at sea. *Marine Environmental Research* 25:1-22.

Mullin, M.D., C.M. Pochini, S. McCrindle, M. Romkes, S.H. Safe and L.M. Safe. 1984. High-resolution PCB analysis: Synthesis and chromatographic properties of all 209 PCB congeners. *Environmental Science and Technology* 18:468-476.

Southern California Coastal Water Research Project. 1982. An improved corer for soft sediments. pp.267-271 in W. Bascom (ed.), Southern California Coastal Water Research Project Biennial Report 1981-1982. Southern California Coastal Water Research Project. Long Beach, CA.

Southern California Coastal Water Research Project. 1996. Characteristics of effluents from large municipal wastewater treatment facilities in 1994. pp.10-20 in M.J. Allen (ed.),

Southern California Coastal Water Research Project Annual Report 1994-1995. Southern California Coastal Water Research Project. Westminster, CA.

Takada, H. and R. Ishiwatari. 1987. Linear alkylbenzenes in the urban riverine environments in Tokyo: Distribution, source, and behavior. *Environmental Science and Technology* 21:875-883.

Takada, H. and R. Ishiwatari. 1990. Biodegradation experiments of linear alkylbenzenes (LABs): Isomeric composition of C₁₂LABs as an indicator of the degree of LAB degradation in the aquatic environment. *Environmental Science and Technology* 24:86-91.

Takada, H. and R. Ishiwatari. 1991. Linear alkylbenzenes (LABs) in urban riverine and coastal sediments and their usefulness as a molecular indicator of domestic wastes. *Water Science and Technology* 23:437-446.

Zeng, E.Y. and C.C. Yu. 1996. Measurements of linear alkylbenzenes by GC/MS with interference from tetrapropylene-based alkylbenzenes: Calculation of quantitation errors using a two-component model. *Environmental Science and Technology* 30:322-328.

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