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# Isomers of the dodecylbenzene in marine sediments from the Todos os Santos Bay, Bahia, Brazil

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## Abstract

Linear alkylbenzenes(LAB) have been investigated in surficial sediments from the Todos os Santos Bay, the largest on the Brazilian coast. The presence of these compounds in the environment has been related to sewage pollution because they are manufactured for the preparation of surfactants used in detergent formulations. They are usually present as an homologous series of compounds with a side chain varying from 10 to 14 carbon atoms attached to a benzene ring.

The sediment samples were collected from the intertidal area of 13 stations situated in the bay. The dried samples were solvent extracted, and after clean up and fractionation of the lipid extract by column chromatography the fraction containing the LABs were separated and identified by high resolution gas chromatography and gas chromatography coupled to mass spectrometry. Surprisingly, only the isomers of dodecylbenzene were found. The compounds were present in all stations and the concentrations ranged from 0.063 to 50.2 mg g<sup>-1</sup> total organic carbon. These values were considered very high compared to those cited in the literature.

It is not yet clear if the origin of these compounds in the sediments is related to detergent formulations. However, the results suggest that they possibly originated from a point source and dispersed in the bay probably due to water movements in the area. © 2000 Elsevier Science Ltd and AEHMS. All rights reserved.

*Keywords:* Linear alkylbenzenes; Surficial layer

## 1. Introduction

Todos os Santos Bay (TSB), the largest in the Brazilian coast with an area of approximately 1100 km<sup>2</sup>, is situated at 13°S latitude and 38°W longitude (Fig. 1). Since the late 1960s the area surrounding the bay has been subject to high industrial growth together with increasing exploitation of its natural resources. Two important industrial centers are situated in the area, the Aratu Industrial Center

and the Camaçari Petrochemical Complex, which are dedicated to metallurgy, and manufacture of synthetic fibers, plant oils, ceramics, several fine chemicals and petroleum products. Additionally there are two ports, one in Aratu Bay for industrial products and one at Salvador. The area around the bay has the largest demographic population of the state of Bahia whose capital Salvador, has about 2.5 million inhabitants. Salvador is situated at the entrance of the bay. The large expansion of the population without planning or provision of adequate basic sanitary structures, has caused a number of problems in the region, the main one being the discharge of a large amount of untreated domestic wastes into the bay. The industrial activities and the population growth have subjected

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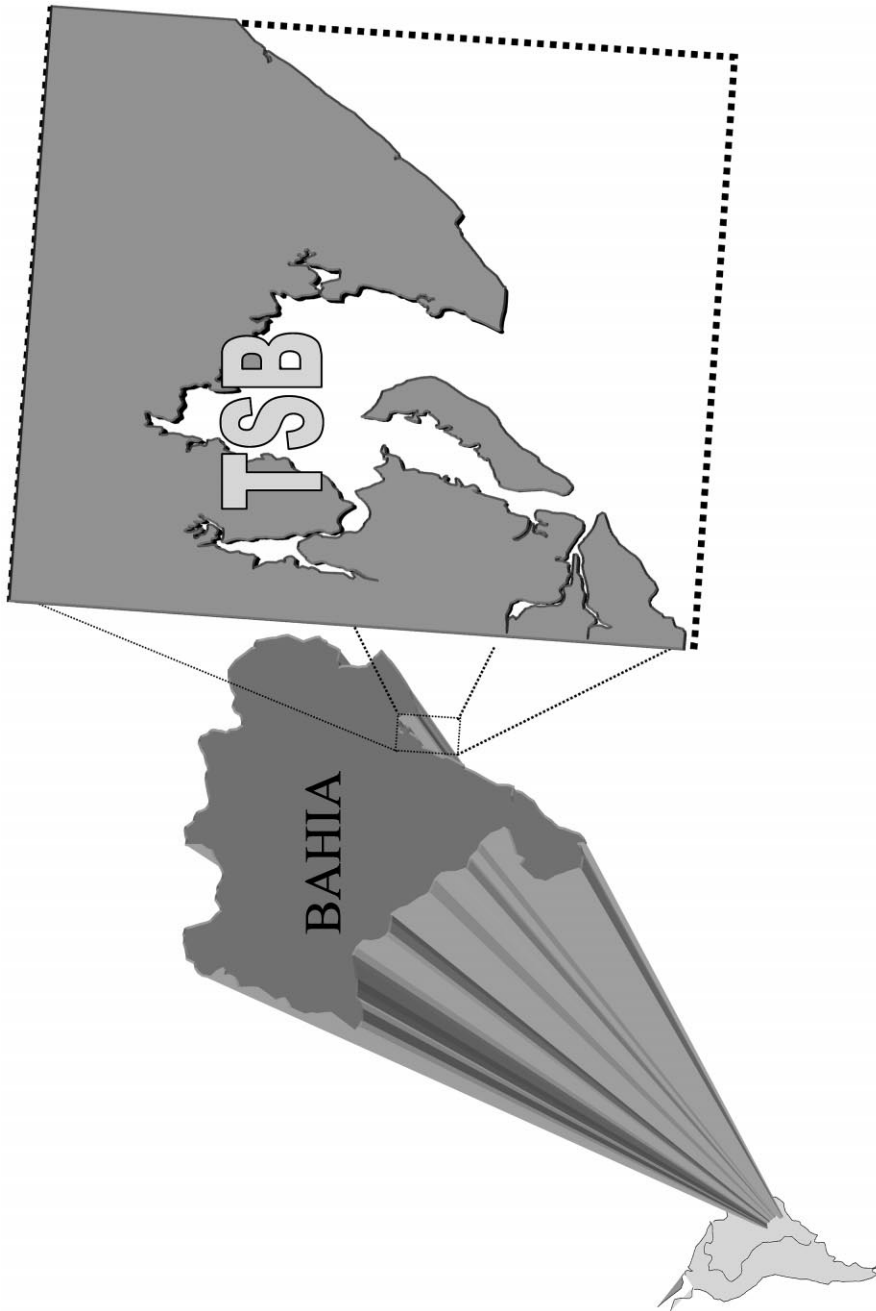


Fig. 1. Todos os Santos bay, Bahia, Brazil.

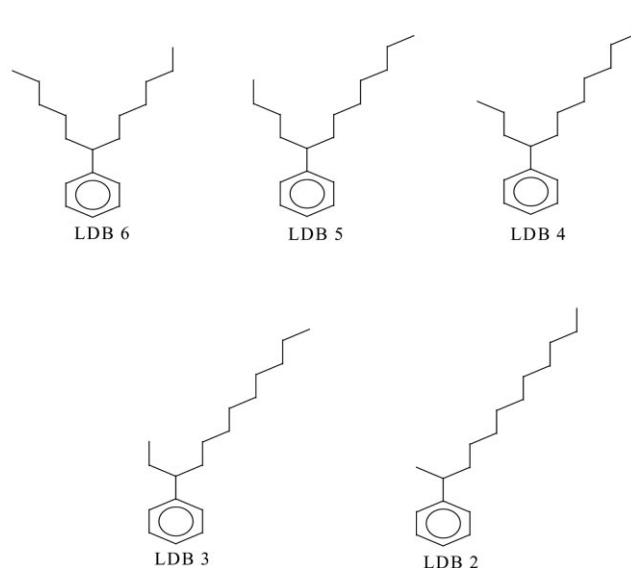


Fig. 2. The linear dodecylbenzene structures (LDB 6, 6-phenyldodecane; LDB 5, 5-phenyldodecane; LDB 4, 4-phenyldodecane; LDB 3, 3-phenyldodecane; LDB 2, 2-phenyldodecane).

TSB to increasing anthropogenic environmental impacts. In recent years a number of monitoring programs have been developed in the bay (Carvalho et al., 1985; Tavares et al., 1988, 1999; Porte et al., 1990; Tavares, 1991, 1997; Santos et al., 1997; Santos, 1998).

The linear alkylbenzenes (LAB) are a group of secondary phenyl alkanes ( $C_6H_5-C_nH_{2n+1}$ ,  $n = 10-14$ ) which are manufactured for the production of LAB sulfonates surfactants, the major constituents of commonly used synthetic detergent formulations (Fig. 2). As a result of incomplete sulfonation, the LABs remain as minor constituents of the surfactants and are subsequently carried over to the detergents. Thus, they appear in domestic wastes and some eventually find their way into the marine environment (Eganhouse et al., 1983; Ishiwatari et al., 1983).

This work is part of a program set up to investigate the quality of organic matter in sediments of the TSB. We report on the current environmental conditions of the bay and present and discuss the LABs found in sediments in the bay.

## 2. Materials and methods

All glassware was left overnight in a 40% HCl

aqueous bath, thoroughly rinsed with tap water, Milli-Q water and dried in an oven at 120°C. Cellulose thimbles were soxhlet extracted in dichloromethane for 24 h prior to use. Organic solvents were redistilled before use. At all stages regular checks were made to ensure that contamination was avoided. Full procedural blanks were done throughout.

Sediment samples were collected from thirteen stations of the intertidal area of the bay in January and February, 1994 (Table 1). Surficial composite

Table 1  
Name and location of sampling stations

Station no.	Station name	Location
1	Cabrito	12° 54,30'S 38° 29,26'W
2	Mapele	12° 46,66'S 38° 35,87'W
3	Ilha de Maré	12° 46,05'S 38° 31,00'W
4	Coqueiro Grande	12° 42,71'S 38° 33,75'W
5	Madre de Deus	12° 40,41'S 38° 37,41'W
6	Ilha de Pati	12° 42,76'S 38° 37,68'W
7	Ilha das Fontes	12° 41,58'S 38° 38,76'W
8	Don João	12° 36,62'S 38° 38,65'W
9	Salinas	12° 52,00'S 38° 45,52'W
10	Mutá	12° 59,63'S 38° 46,59'W
11	Cações	13° 01,10'S 38° 47,42'W
12	Jiribatuba	13° 03,49'S 38° 47,59'W
13	Baiacú	12° 57,78'S 38° 40,55'W

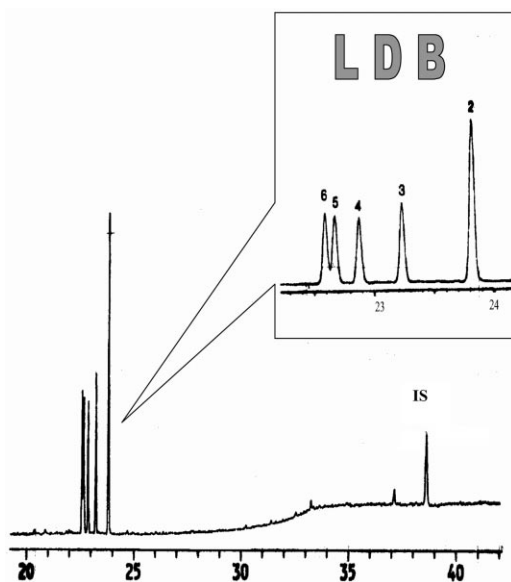


Fig. 3. Typical chromatogram of linear dodecylbenzenes from TSB surficial sediments.

samples (0–2 cm) were collected with a stainless steel spatula and placed in a precleaned glass jar and taken to the laboratory in cool boxes where they were kept frozen ( $-20^{\circ}\text{C}$ ) until analysis. The freeze-dried samples were Soxhlet extracted with a mixture of dichloromethane and methanol (2:1) for 24 h. The organic extracts were fractionated by column chromatography under 5% deactivated silica gel. The fraction where the LABs were found was eluted with 40 ml of a mixture of toluene and hexane (1:4) and its extract was separated and analyzed by high resolution gas chromatography coupled to mass spectrometry (GC-MS; Shimadzu QP 5000). Separation was performed on a DB 5 column and the oven temperature was programmed to increase from 60 to  $310^{\circ}\text{C}$  at  $8^{\circ}\text{C min}^{-1}$ . The temperature was held for 10 min. Helium was used as carrier gas. The MS was operated in full data acquisition mode. Individual compounds were identified by comparison of their relative retention times and the mass spectra with the literature. The results were calculated by comparison of peak areas in the reconstructed total ion current (TIC) chromatogram of the quantification standard ( $5\alpha(H)$ -cholestane) and the compound of interest. Relative response factors were assumed to be equal to 1, so data are semiquantitative (Goat 1981; Goat et al.,

Table 2

Concentration of isomers of the linear dodecylbenzenes (LDB)

Station	Isomers of the linear dodecylbenzenes ( $\text{mg g}^{-1}$ TOC)					Total LDB
	LDB 6	LDB 5	LDB 4	LDB 3	LDB 2	
1	0.86	1.1	0.31	1.3	1.9	5.5
2	0.01	0.01	0.01	0.01	0.02	0.06
3	0.94	0.95	1.1	1.2	0.11	4.3
4	0.44	0.63	0.44	0.50	1.0	3.0
5	5.0	5.0	5.3	6.3	17	39
6	0.33	0.39	5.1	0.63	1.6	8.1
7	0.74	0.46	1.5	2.8	0.31	5.8
8	0.06	0.06	0.07	0.08	0.21	0.48
9	11	4.1	4.0	4.9	27	51
10	2.6	2.7	3.7	3.8	8.5	21
11	4.1	4.1	4.1	5.5	12	30
12	1.3	1.7	3.0	2.1	7.8	16
13	0.70	0.73	0.82	0.87	1.8	4.9

1986; Svetashev et al., 1991; Santos et al., 1994). Full procedural blanks were carried out throughout.

### 3. Results and discussion

All of the TSB surficial sediments analyzed contain the isomers of the linear dodecylbenzenes (LDB). A typical chromatogram is shown in Fig. 3, and analytical results in Table 2. The LABs manufactured for the production of surfactants used in detergent formulations are secondary phenyl alkanes with a side chain varying usually from 10 to 14 carbon atoms. Reports in the literature refer to these compounds in sediments from several places (Eganhouse et al., 1983; Murray et al., 1987; Takada et al., 1991; Raymundo and Preston, 1992; Preston and Raymundo, 1993). In all samples from the TSB only the isomers of LDB were found. Concentrations of LDB found in all stations ranged from 0.06 to  $51 \text{ mg g}^{-1}$  TOC (Fig. 4). Stations located in the west side of the bay showed higher concentrations.

Porte et al. (1990) collected edible bivalves from nine stations in the same area in 1986 and found a set of LABs ( $\text{C}_{11}$ – $\text{C}_{13}$ ) at a station situated in the eastern part of the Aratu Bay. This station is situated close to one of the stations of the present work (Mapele Station). According to these authors, the presence of these specific compounds was related to a spill of

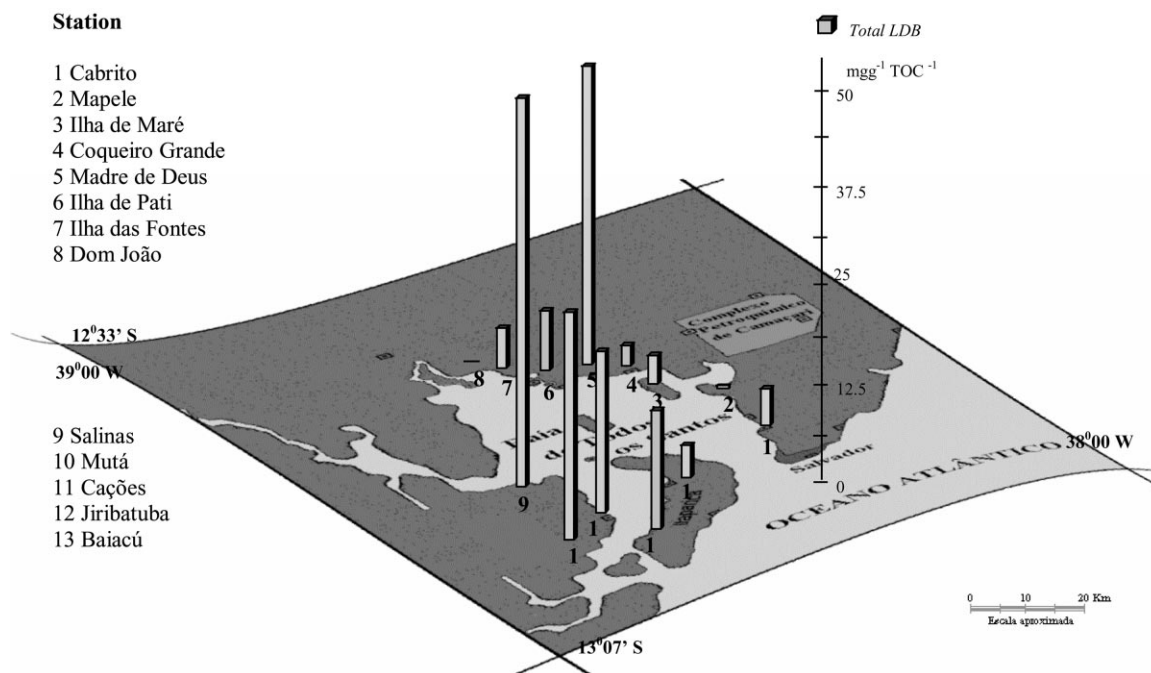


Fig. 4. Histogram showing the total dodecylbenzenes from TSB surficial sediments.

LABs from an industrial source some months before. In the present work only the isomers of the compound containing 12 carbon atoms in the side chain, that is dodecylbenzene, were detected.

#### 4. Conclusions

The results of this research indicate the presence of isomers of the linear dodecylbenzenes (LDB) in sediments sampled from the Todos os Santos bay (TSB). The origin of these compounds is not yet clear. The results suggest that the LDB found in the TSB might have been discharged from a point source in the bay and could even continue to be discharged at present. An integrated effort by the government and the researchers has been undertaken in the state of Bahia to reduce environmental impacts, and to restore and preserve the natural resources in the coastal region of the TSB. In order to detect the true origin of these LDB compounds and thus contribute to this restoration, further work will be carried out.

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