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Determination of butyltin compounds in surface sediments from the São Paulo State coast (Brazil) by gas chromatography–pulsed flame photometric detection

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Abstract

Occurrence and the effects of butyltin compounds (BTs) have been studied for some years, mainly in countries of the Northern Hemisphere. Due to widespread use of tributyltin compounds (TBTs) and considering their deleterious effects, it is necessary to conduct studies on its occurrence, especially in the marine environment because of its excessive use in coatings of ship hulls to prevent fouling. Moreover, it was important to extend the evaluation to areas where there is no current information about their occurrence. The present work reports the occurrence of BTs in marine sediments of São Paulo state, Brazil. Commercial and leisure harbor sampling sites were selected because these areas are potentially exposed to BTs from antifouling paints used on ship hulls. Analytical conditions for organotin analysis in marine sediments were optimized for GC with pulsed flame photometric detection. Detection limits ranged from 8.4 to 66.3 ng g⁻¹ using a 610-nm filter, and the linearity range was 20–500 ng g⁻¹. Concentration levels of BTs were highest in Santos harbor (360 ng g⁻¹ TBT in average) and Guarujá marina (670 ng g⁻¹ TBT in average), which seems to be related to intensive boat traffic. Lower levels of BTs were observed in Cananéia, where only fishing boats are present (50 ng g⁻¹ TBT in average).

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1. Introduction

Ship hulls immersed in the sea over any space of time are subject to the attack of fouling organisms such as barnacles and mussels, resulting in a significant decrease of operational efficiency of the boat. A 10-mm fouling in the hull means an increase of

0.3–1% in the fuel consumption [1]. For that reason antifouling paints containing tributyltin (TBT) as biocide are used [2]. Introduced first in the 1960s in the form of so-called “free-association” paints, and in the 1970s in its self-polishing copolymer (SPC) formulation, TBT rapidly established itself as the antifoulant of choice, and by the mid-1980s was used on over 80% of the commercial fleet. However, by 1980 or thereabouts, some environmental disadvantages became apparent. The effects of TBT on the reproduction of oysters in France and of dog-whelks in England were quite significant, and increasing incidence of imposex, whereby female neogastropod

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species develop male genitalia, leading to reproductive failure [3,4], were reported. Concerning all these effects, TBT has been cited as the most toxic substance ever introduced deliberately into the marine environment [5]. As a result, restrictions concerning the use of TBT were imposed throughout most of the developed world, and it was included in the European Union pollutant list.

Monitoring programmes are currently carried out in order to assess the extent of TBT pollution. Several studies have measured concentrations of TBT and other BTs, and most of the analytical procedures developed for organotin speciation are based on chromatographic separation, either GC or LC, allowing the simultaneous determination of a variety of organic tin species [6,7]. The techniques used most often are based on gas chromatography due to greater resolution and lower detection limits [8–12].

However, all the studies focusing on organotin compounds registered in the literature refer to the North and West areas of the Atlantic and Pacific oceans, embracing the North Hemisphere, where there is legislative control. Therefore, it became important to study other regions of the world, where legislation is sparse or non-existent. In Brazil, no legislation is currently in place to control the use of TBT-based paints, so the purpose of this paper is to evaluate the extent of TBT contamination in surface sediment samples of São Paulo state coast, Brazil, analyzed by gas chromatography with pulsed flame photometric detection (GC–PFPD). The optimization of PFPD for organotin compounds is described in a paper submitted for publication [13].

2. Experimental

All reagents used were of analytical reagent grade. Monobutyltintrichloride (MBTCl₃) 95%, dibutyltin-dichloride (DBTCl₂) 96%, tributyltinchloride (TBTCl) 96%, tetrabutyltin (TeBT) 98%, tricyclohexyltinchloride (TCyTCl) 90%, ammonium pyrrolidinedithiocarbamate (APDC) and pentylmagnesiumbromide (PeMgBr) 2 M in diethyl ether were purchased from Aldrich (Milwaukee, WI, USA). Tripropyltinchloride (TPrTCl) 98% was purchased from Merck (Darmstadt, Germany). Hexane, toluene

and acetic acid were purchased from Malinckrodt (Xalostoc, Mexico). Aluminium oxide (Al₂O₃) was purchased from Carlo Erba.

2.1. Sampling

Marine sediments were collected using a modified Pettersen sampler in five different areas in the São Paulo State, Brazil, namely: Ubatuba, São Sebastião, Guarujá, Santos and Cananéia, on April and December, 1998. The samples were obtained at or near the harbor dock sites where one would expect to find high OT sediment levels. For each site sampling, five separate sediment samples were taken in close proximity. The sampler used permits to collect sediment until around 15–20 cm depth. Redox potential (E_h) of sediment samples were measured *in situ* using an Ag/AgCl/Pt combined electrode. The samples were immediately frozen, and then lyophilized. Before storage they were ground and sieved in 106- μ m mesh.

Ubatuba (23°30'S/45°07'W) is a leisure boat harbor with 70–90 boats less than 50 ft. (1 ft.=30.48 cm), and the sediment samples at this point are more sandy than other sampled areas. Guarujá (23°58'S/46°18'W–24°00'S/46°17'W) is a leisure boat harbor, with traffic of 800 boats per year, and where usually the hulls are cleaned and repainted every year. São Sebastião (23°48'S/45°24'W) is a commercial ship harbor and Santos (23°55'S/46°20'W–23°59'S/46°17'W) is the biggest commercial ship harbor of South America, with a traffic of 3600 ships in 1998. Cananéia (25°01'S/47°55'W) is a fishing harbor. Fig. 1 shows the studied areas.

2.2. Methods

We used the methodology described by Abalos et al. [14] for the extraction of BTs from sediment samples. Two grams of sediment (dry mass) were extracted three times with a toluene–acetic acid (10:4, v/v) mixture in an ultrasonic bath for 5 min, and centrifuged for 5 min at 2000 rpm. To the extracts was added the complexing agent—APDC—to improve the extraction efficiency. The derivatization was carried out with PeMgBr and the cleanup with Al₂O₃ activated at 120 °C overnight. TPrTCl

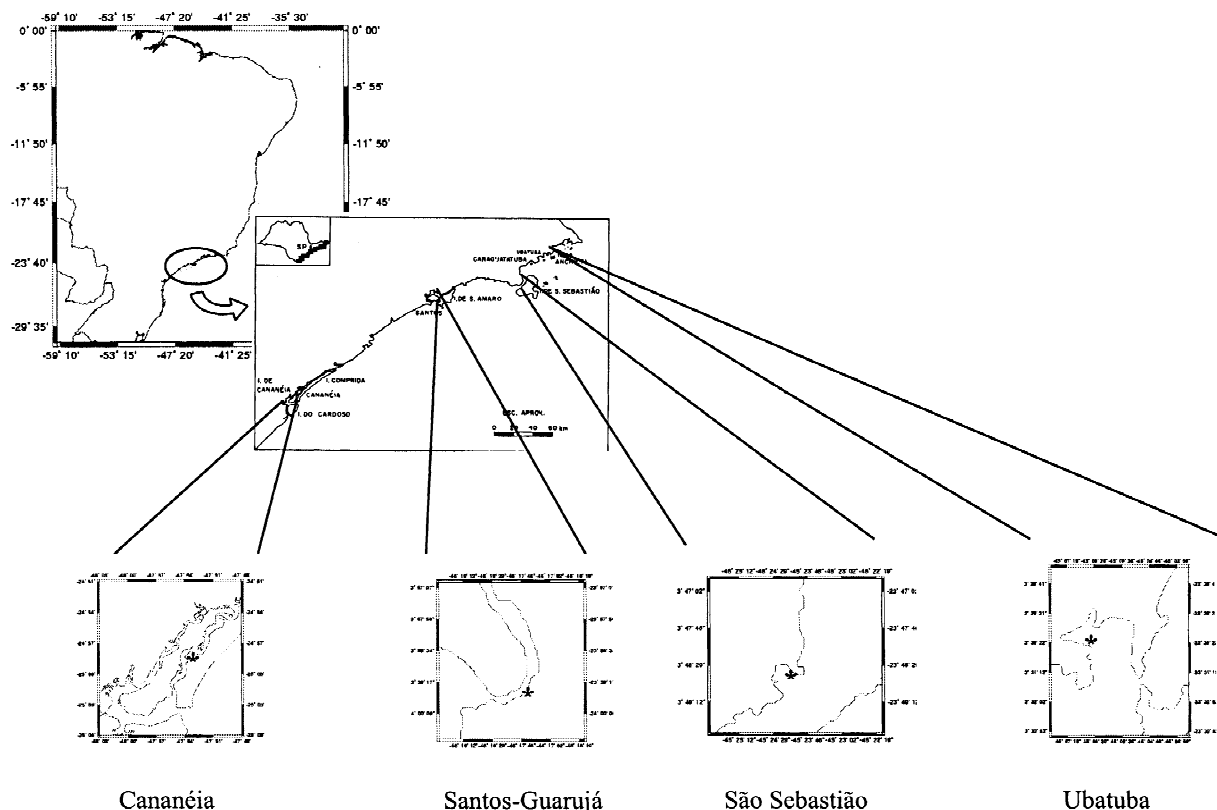


Fig. 1. São Paulo state coast and sampling site localization in the Brazilian map: Ubatuba ($23^{\circ}30'S/45^{\circ}07'W$) and São Sebastião ($23^{\circ}48'S/45^{\circ}24'W$) in the north, Santos ($23^{\circ}55'S/46^{\circ}20'W$ – $23^{\circ}59'S/46^{\circ}17'W$) and Guarujá ($23^{\circ}58'S/46^{\circ}18'W$ – $24^{\circ}00'S/46^{\circ}17'W$) in the middle, and Cananéia ($25^{\circ}01'S/47^{\circ}55'W$) in the south.

and TCyTCl were used as surrogates and TeBT as internal standard.

2.3. Apparatus

The analysis of the extracts was performed using a Varian GC 3800 gas chromatograph equipped with a PFPD system operating with a 610-nm filter. The injector was operated at $250^{\circ}C$ with the purge flow closed for 60 s. Hydrogen (ultrapure, 99.999%; flow, 1.7 ml min^{-1}) served as carrier gas. For separations, a $30\text{ m}\times 0.25\text{ mm}\times 0.25\text{-}\mu\text{m}$ VA-35 column (35% phenyl–65% methylpolysiloxane, Varian, Walnut Creek, CA, USA) was used. The following temperature program was used: $70^{\circ}C$ for 1 min, ramp at $10^{\circ}C\text{ min}^{-1}$ to $280^{\circ}C$, held for 8 min. The PFPD temperature was $300^{\circ}C$. The injections were made in triplicate.

Calibration was obtained by the internal standard method, using a blank and a set of 11 standards containing $10\text{--}500\text{ ng g}^{-1}$ of MBT, DBT, TBT, TPtT, TCyT pentylated and TeBT, freshly prepared in hexane.

For method validation a reference material (harbor sediment) PACS-2 from National Research Council of Canada (NRCC), certified for DBT and TBT concentrations, was used.

3. Results and discussion

The concentrations of BTs in the certified reference material recovered during the analyses were very close to the certified values (see Table 1). In addition, the concentration of the triplicate agreed well within the estimated errors. This means that the

Table 1
Butyltin concentrations in the reference material PACS-2 [ng(Sn) g⁻¹(dry mass)]

Compound	Certified	Analysed
MBT	300 ^a	334 (5.9)
DBT	1090±150	1030 (6.1)
TBT	980±130	986 (4.4)

^a Information value; RSD values, in percent, are between brackets.

method used here was appropriately applied in the samples and the precision and accuracy of the analytical procedure were insured. Concentration values were corrected to 65–100% recoveries.

TBT (tributyltin), DBT (dibutyltin) and MBT (monobutyltin) concentrations and redox potential (E_h) measured in the samples are presented in Table 2, which shows that the concentration levels are higher in December. This probably occurs due to the summer season, when the leisure boat traffic is intensified. Under anoxic conditions, observed here by negative values measured in the sediment samples, TBT is believed to degrade by a stepwise debutylation into DBT, MBT and inorganic tin(IV) [23], which could explain the presence of MBT and DBT in the samples.

The sites studied, Guarujá, Santos, Ubatuba, São Sebastião and Cananéia, can be classified as highly, moderately and slightly contaminated sites, respec-

tively, following a scale established by Waite et al. [15].

The Ubatuba sample chromatogram shown in Fig. 2, demonstrates a very good separation for butyltin compounds, although there were some unknown peaks. It was also possible to identify and quantify the BT peaks without interference using the 610-nm filter, which can minimize sulfur emission.

Table 3 shows the concentration levels of organotin compounds observed in different sediment samples, analyzed by different chromatographic techniques. High contamination levels are found mainly where the boat traffic is high, like commercial harbors [22]. Butyltin concentration values observed on the Brazilian coast are close to that observed in other countries and since they were high in areas dedicated to drydocking and marinas, it can be concluded that these activities are significant sources of organotin contamination of the local marine environment.

4. Conclusions

Our results confirm the current view that TBT contamination is prevalent in areas close to marinas and harbors. Also, high concentration levels for BTs were observed in December samples, probably due to increased traffic of leisure boats in the summer

Table 2
Butyltin concentrations obtained by GC–PFPD, with a 610-nm filter, and redox potential measured in the sediment samples collected in São Paulo state coast, in April and December 1998

Sampling site	Local depth range (m)	Concentration [ng (Sn) g ⁻¹ (dry mass)]			E_h (mV)
		MBT	DBT	TBT	
Ubatuba A	2–4	36 (20)	37	b	c
Ubatuba D	2–4	62 (9)	113 (7)	140 (5)	–179.1
São Sebastião	2–5	28 (16)	56 (8)	18	c
São Sebastião D	2–5	40 (11)	123 (15)	266 (14)	–250.6
Guarujá A	5–14	367 (2)	124(11)	224 (7)	c
Guarujá D	5–14	207 (9)	421 (14)	847 (8)	–368.8
Santos A	6–15	44 (5)	65 (13)	90 (9)	c
Santos D	6–15	54 (13)	176 (6)	482 (6)	–349
Cananéia A	3–7	a	14 (1)	17	c
Cananéia D	3–7	a	18 (7)	53 (12)	–310

The values for each site are mean of five points, that are taken in close proximity at each site (each point representing a specific area within the sampling area).

Between brackets are RSD values (%); a, <2.77 ng g⁻¹; b, <12.12 ng g⁻¹; c, not measured; A, April; D, December. Concentrations without RSD values were found for only one sample.

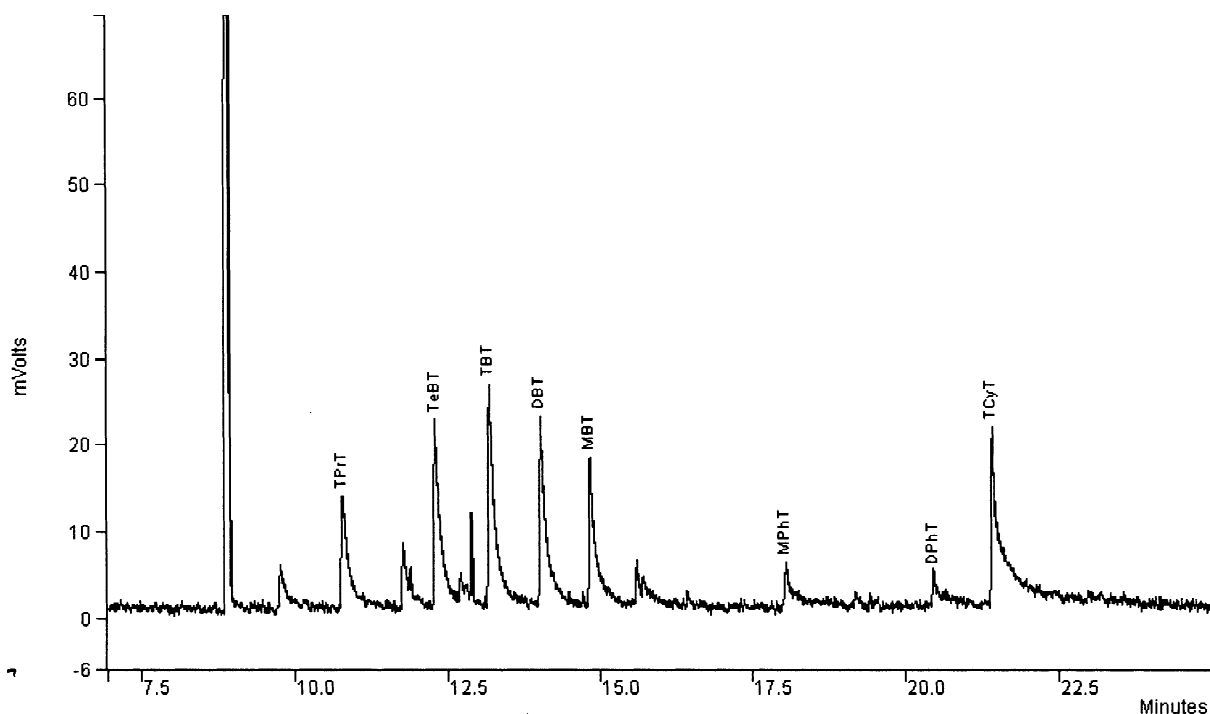


Fig. 2. Chromatogram of a sample from Ubatuba, collected in April 1998, obtained by GC–PFPD with a 610-nm filter. Injector temperature was 250 °C, hydrogen carrier gas flow 1.7 ml min⁻¹, 30 m×0.25 mm, 0.25- μ m VA-35 column (35% phenylmethylsiloxane, Varian). Temperature program: 70 °C for 1 min, ramp at 10 °C min⁻¹ to 280 °C, held for 8 min. The PFPD temperature was 300 °C, operating on 610 nm.

season, when antifouling paints are renewed and TBT release is intensified.

To our knowledge, this is the first report on the detection of butyltin compounds in surface sediments of Brazilian marine environment, representing a

preliminary diagnosis on the extension of this specific contamination in the marine environment. But it is clear that in order to control environmental risks associated with the release of TBT, both the use of TBT-based antifouling paints for leisure boats, as

Table 3

Butyltin concentrations detected in sediment samples of different countries, obtained by different techniques, and respective references

Country	Year	Technique	Concentration [ng (Sn) g ⁻¹ (dry mass)]			Ref.
			MBT	DBT	TBT	
Spain	1994	GC–FPD	–	482.0	994.0	[17]
Australia	1995	AAS	–	–	50–1350	[18]
Poland	1997	GC–FPD	–	–	1800–2900 (Σ BT)	[19]
Japan	1999	GC–MIP–AED	105	307	720	[16]
France	2000	GC–PFPD	18–30	<0.45–2.0	3–12	[10]
Switzerland	2000	GC–FPD	10–1300	30–1900	80–17000	[20]
India	2001	GC–ICP–MS	1.6–393	1.3–394	n.d.–1280	[21]
Brazil	2002	GC–PFPD	12–256	8–704	34–1388	This work

FPD, flame photometric detection; AAS, atomic absorption spectrometry; MIP, microwave-induced plasma; AED, atomic emission detection; ICP, inductively coupled plasma.

well as drydock practices, need to be controlled by appropriate regulatory measures and enforcement.

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