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Speciation of organotin compounds in sediment cores from Guanabara Bay, Rio de Janeiro (Brazil) by gas chromatography–pulsed flame photometric detection†

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The contamination of sediments by organotins poses a threat to marine biota that may last long after release of the substances. The determination of tributyltin (TBT) and its decay products in sediment cores allows elucidation of concentration and degradation trends, and is a useful tool to support management decisions. In this study, organotin speciation was performed on cores from several locations in Guanabara Bay, Rio de Janeiro, to investigate contamination trends over the last 30 years in this area, which houses the second most important harbor in Brazil. TBT concentration in surface sediments ranged from 742 μg kg^{-1} (as tin) in the vicinity of a major shipyard to 14 μg kg^{-1} (as tin) in an environmental protection area. Organotins depth profiles were, in general, very irregular, lacking evidence that TBT degradation occurs at appreciable rates in these anoxic sediments. Decay most probably takes place predominantly in the water column and at the water–sediment interface before final burial in the sediments. Data from the least contaminated area was used to estimate a first-order degradation constant of −0.37 $years^{-1}$ for dibutyltin.

KEYWORDS: speciation; organotin; GC-PFPD; sediments; geochronology; Guanabara Bay

INTRODUCTION

Organotins have been used as fungicides, catalysts, polymer stabilizers, in timber preservatives and as antifouling agents in ship-hull paints.[1,2] Tributyltin (TBT) has been considered the most hazardous compound to marine organisms[3] since its adverse effects on oyster farming near marinas were proved.[4] Triphenyltin (TPhT) has also been shown to be hazardous to aquatic life.[1] The high toxicity of TBT and TPhT, even at low concentrations, leads to shell malformation[4] and imposex, (i.e. induced sex change in marine gastropod females resulting in imposition of male sexual characteristics) in some organisms.[5,6] Numerous studies have indicated that TBT degrades by successive debutylation to the less toxic dibutyltin (DBT), monobutyltin (MBT) and inorganic tin.[7,8] In anoxic sediments, decomposition seems to occur slowly, with an estimated half-life of up to 8 years.[7] Thus, TBT can be accumulated in this compartment, leading to a persistent ecotoxicological risk.[8]

The use of TBT has been restricted or even banned in most developed countries since the mid-1980s because of the high toxicity to non-target marine organisms.[9] However, in Brazil, no legislation exists to control or limit the use of TBT-based paints, and very little is known either about its presence in marine environments or possible effects.

Guanabara Bay is a eutrophic coastal bay located in the heart of Rio de Janeiro city. The bay is severely polluted due to industrial and domestic discharges derived from several municipalities.[10,11] Besides the industrial activities

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on land, which include 6000 industries and two oil refineries, Guanabara Bay houses two naval bases, two harbors (Rio de Janeiro and Niterói), a number of shipyards and marinas, and is subject to heavy ship traffic.[11] The geochronology of contamination by trace metals and polycyclic aromatic hydrocarbons, for example, has demonstrated increasing trends over the last 50–60 years.[12–14]

The contamination of Guanabara Bay by organotin compounds was first reported by Fernandez and co-workers,[15,16] who verified the occurrence of imposex in the gastropod *Stramonita haemastoma* (Linnaeus, 1767, Gastropods, Muricidae) and determined organotins in surface sediments from suspected hotspots. These studies showed a decline in the population of *S. haemastoma* over the last 5 years in Guanabara Bay and demonstrated correlations between elevated concentrations of TBT in surface sediments and the levels of imposex in the organisms.[15] Limaverde[17] proved that the exposure of healthy *S. haemastoma* to TBT and TPhT in the laboratory induced imposex and that in Guanabara Bay the imposex levels are related to the proximity of the organism's population to the main pollution sources. Data are lacking, however, on the geochronology of contamination and on the persistence of these substances in the anoxic sediments of the bay.

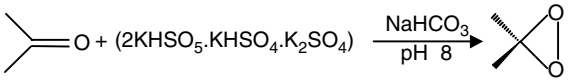
The aims of this study are: (a) the determination of TBT, TPhT and of their degradation compounds in sediment cores from Guanabara Bay to verify contamination trends as related to the use of antifouling paints based on organotin compounds, and (b) to look for indications of decay processes in the anoxic environment.

EXPERIMENTAL

Reagents

All reagents used were analytical grade. TBT chloride (TBTCl) 96%, DBT dichloride ($DBTCl_2$) 96%, MBT trichloride ($DBTCl_2$) 95%, tetrabutyltin (TeBT) 93%, tricyclohexyltinchloride (TCyTCl) 97%, pentylmagnesiumbromide ($CH_3(CH_2)_4MgBr$, Grignard reagent) 2 mol l^{-1} in diethyl ether and Oxone® ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) were purchased from Aldrich (Milwaukee, WI, USA). Tripropyltinchloride (TPrTCl) 98%, neutral aluminum oxide (Al_2O_3, 70–230 mesh), Na_2SO_4, HOAc, HCl and $NaHCO_3$ were obtained from Merck (Darmstadt, Germany); ammonium pyrrolidinedithiocarbamate (APDC, $C_5H_8NS_2{\cdot}NH_4$) 97% was purchased from Fluka (Buchs, Switzerland), toluene (ChromAR® HPLC) from Malinckrodt, 95% *n*-hexane HPLC/GC UltimAR® and acetone Nanograde from Malinckrodt or Merck.

Dimethyldioxirane (DMD) solution (about 0.08 mol l^{-1} in acetone) was synthesized according to the reaction in Eqn (1) and as described by Adam *et al*.[18] The stability of the DMD solution at −20 °C in the dark was found to be no longer than 3 months.[19]



(1)

For total tin determination, the reagents used were: HNO_3 (65.8% v/v, p.a., twofold sub-boiled), HCl (Merck) and H_2O_2 (30% v/v, p.a., Merck). Water was distilled and deionized to a resistivity of 18 MΩ cm. Argon was used for plasma operation. For organic carbon determination, H_3PO_4 (p.a., Merck) was used.

Standard preparation

Organotin chlorides and TeBT stock standard solutions were prepared at 1000 mg kg^{-1} (as tin) in toluene and remaining stable over a period of 6 months stored at −20 °C. Pentylated working solutions were prepared by diluting the stock solutions with hexane before derivatization with Grignard reagent.

Sampling area

Guanabara Bay is located at 22°40′–23°00′S and 43°00′–43°18′W. The actual bay area, the average volume and average depth are 346 km^2, 2.2×10^{18} m^3 and 7.7 m respectively (Fig. 1).[20] The residence time of water in the bay is 20 days on average. Tidal currents provide fast exchange of the waters in the central areas of the bay, but as most contaminant sources are located in the inner areas they tend to accumulate in the sediments near the river estuaries.[21] In the case of organotins, major potential sources are the harbor, marinas and anchorage areas.

Because of the diffuse character of the sources and of their major location in areas influenced by effective tidal currents, the five sampling sites in Guanabara Bay were selected so as to represent average conditions (Table 1). The region of Station 2, near the Guapimirim environmental protection area, is one of the least polluted in the bay; owing to the low water depth, boat traffic is restricted to small fishing crafts. Station 3 is at the outer boundary of the deeper central channel, where water exchange is most effective. Fishing and pleasure boats are frequently found at this site. The area of Station 4 is contaminated by industrial and domestic sewage draining from the northwestern part of the bay, and Station 5 lies in an anchorage area for large vessels, where traffic made up of small and large boats is abundant. At Station 6, at the central channel edge, contamination derives from the traffic of small and large boats allied to the nearby presence of small shipyards, a naval base, and domestic and industrial waste inputs.

Sampling

In July–September 2001, sediment cores 70–90 cm in length were collected with a Kullenberg gravity corer equipped with aluminum tubes (length 100 cm, internal diameter 5 cm). Four or five cores were collected at each station for the determination of organotin compounds, pH, redox potential E_H, sulfur content, organic carbon, total tin and ^{210}Pb dating. The cores were immediately sealed and maintained in vertical position in an ice box at 4 °C during the transport to the laboratory. Before slicing, all cores, except those for pH and

Figure 1. Sediment sampling sites in Guanabara Bay. IS: station near the Ishikawajima Shipyard.

Table 1. Sampling locations and local water depth

Station	Date	Latitude (S)[a]	Longitude (W)[a]	Depth (m)
2	20 September 2001	22°44.654′	43°04.624′	2.8
3	27 July 2001	22°47.058′	43°05.783′	6.1
4	8 August 2001	22°51.191′	43°13.287′	2.0
5	8 August 2001	22°50.890′	43°10.323′	6.1
6	27 July 2001	22°50.230′	43°07.200′	4.5

[a] Coordinates determined by global positioning system (Station 2: GPS AccuNav Sport–Eagle; other: GPS Garmin model II).

E_H measurements, were stored, standing vertically in the dark, at −20 °C.[22]

In addition to the above, analyses of TBT and degradation products were performed for the top and bottom layers of a core sampled near the Ishikawajima Shipyard.

Sample treatment

Redox potential and pH were measured immediately after arrival in the laboratory, using an Ag/AgCl/Pt combined electrode and a glass combined electrode respectively. Measurements were performed under inert atmosphere, inserting the electrode directly in the extruded sediment. The frozen cores were sliced under nitrogen into segments of different thickness depending on the known sedimentation rates (Station 2: 0.86 cm year^{-1}; Station 4: 0.49 cm year^{-1}; Station 6: 2.2 cm year^{-1})[13,23] down to 30 cm below the top layer, resulting in 51 samples. For Stations 3 and 5, where the sedimentation rates were not known, cores were sliced into 3 cm segments and thereafter dated by ^{210}Pb.[24] To avoid possible contamination from the aluminum tube, only the segment's central parts were used for further determinations.[25] Except for dating, composed sub-samples of each segment were prepared by mixing together the corresponding layer of three or four cores from each site.[26] The sub-samples were put in amber glass bottles, frozen and later freeze-dried.[27] The dried sediments were ground before storing in amber glass bottles in the dark at −20 °C.

METHODS

Elemental composition and dating

Sulfur was determined either by elemental analysis or using a Shimadzu EDX-700 energy dispersive X-ray fluorescence

spectrometer. Organic carbon was measured in 1 mg of acid-treated (20% H_3PO_4 aqueous solution) sediment using a Shimadzu SSM-5000A solid-sample combustion unit coupled to a Shimadzu TOC-5000A total organic carbon analyzer. Quantification was performed using analytical curves and potassium biphthalate as standard.[28] Dating of sub-samples of sediment cores collected from Stations 3 and 5 was carried out by the determination of excess ^{210}Pb according to methodology described in Godoy *et al*.[24] Samples were not sieved so as to avoid contamination, since from a previous study it was known that sediments from the sampled sites show 78–100% of grains <63 μm.[12]

Total tin

Total tin concentrations were determined by quadrupole inductively coupled plasma mass spectrometry (Elan 6000, Perkin Elmer-Sciex) using a cross-flow nebulizer with a Ryton® nebulization chamber for sample introduction and ^{103}Rh as internal standard. Sample digestion was performed by adding 5 ml of a 1:3 mixture of HNO_3/HCl to 0.5 g of freeze-dried sediments, leaving the mixture at room temperature overnight and then under heat (60 °C) for 2 h. After that, 2 ml of H_2O_2 were added to each sample, which remained under heat for an additional 30 min. The harbor sediment reference material PACS-2 from the National Research Council of Canada (Ottawa, Canada), certified for tin, was used for method validation. As shown in Table 2, tin concentrations found for this reference material are in good agreement with the certified value. The sample detection limit was 8 μg kg^{-1}.

Organotin compounds

Extraction procedure

The methodology adopted was modified from Baijona and co-workers[19,29,30] as appropriate to the sediments' characteristics and to the detection by pulsed flame photometric detection (PFPD).[31] Sediment (2 g, dry mass) was transferred to a glass centrifuge tube. TPrTCl and TCyTCl were added as surrogates at a spiking level of 200 ng each. The extraction step was accomplished by sonication with toluene/HOAc (10:4, v/v) for 5 min followed by centrifugation at 2000 rpm, for 5 min, and transfer of the supernatant to a separation vessel. This process was repeated twice (Fig. 2).

To the extracts, 10 ml of 0.5% APDC aqueous solution were added to partition the HOAc to the aqueous phase and improve the solubility of the mono- and di-substituted organotins in the organic phase. This step was repeated one more time and the separated organic phase was percolated through activated Na_2SO_4 and rotaevaporated to a few milliliters at about 35 °C (Fig. 2).

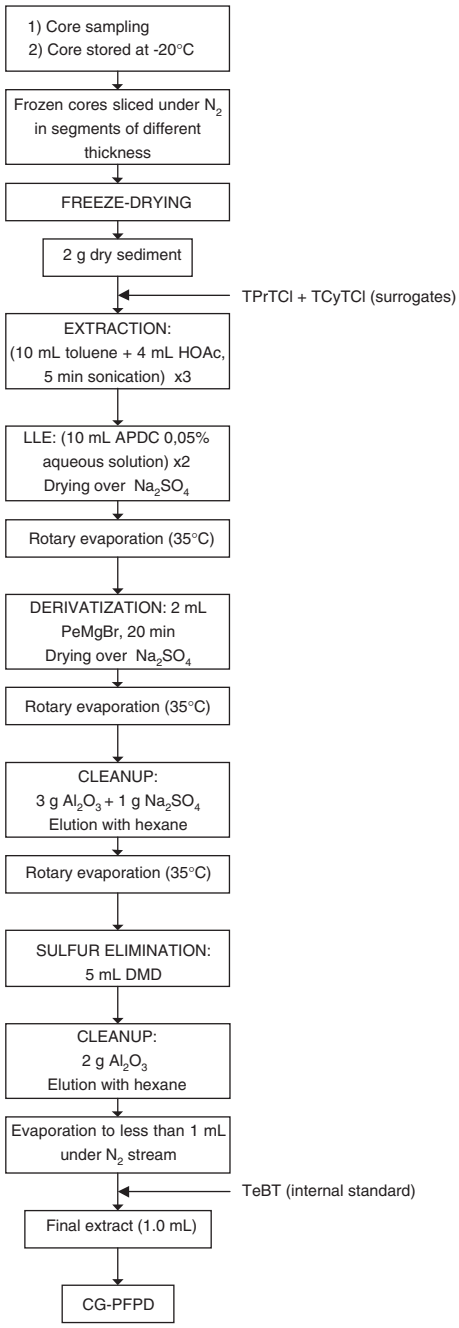


Figure 2. Flow diagram of the analytical procedure for the organotin speciation.

Table 2. Organic and Inorganic tin concentrations in the reference material PACS-2 ($n = 3$)

	[Sn] (μg kg^{-1} dry mass)	
	Determined	Certified
TBT	971 ± 142	980 ± 130
DBT	1158 ± 157	1090 ± 150
MBT	386 ± 84	300[a]
Tin	19.8 ± 3.1	19.8 ± 2.5

[a] Information value.

Derivatization, alumina cleanup and sulfur elimination

Because of the high air humidity in Rio de Janeiro (above 70%), derivatization was always carried out under inert atmosphere. After addition of 2 ml of Grignard reagent, the extract was shaken for 1 min and left standing for 20 min. Elimination of excess Grignard reagent was carried out in an ice bath by adding 10 ml of Milli-Q water and 1–2 ml of concentrated HCl. The aqueous phase was liquid–liquid extracted three times with 2 ml of hexane and the derivatized extract was then percolated through activated Na_2SO_4, recovered in a vessel and rotaevaporated to a few milliliters at 35 °C (Fig. 2).

The cleanup was made by alumina adsorption chromatography in a glass column filled with 3 g of alumina, 2% water deactivated, and 1 g of activated Na_2SO_4 packed on the top. The organic phase was percolated through the column, using hexane as eluent, and the extract recovered was once more rotaevaporated to a few milliliters at 35 °C.

For sulfur elimination, 5 ml of DMD solution, previously prepared as described above, were added to the extracts, followed by a cleanup in a Pasteur pipette containing 2 g of alumina, 2% water deactivated (Fig. 2). Finally, the extract was evaporated under a gentle stream of nitrogen down to 1 ml and TeBT was added as internal standard prior to the gas chromatography (GC)–PFPD determination.

GC–PFPD determination

A Varian CP-3800 gas chromatograph fitted with a 1177 split/splitless injector, an 8200 auto sampler and a pulsed flame photometric detector (Varian, Walnut Creek, CA, USA) was used in the measurements. The injector, kept at 250 °C, was operated in splitless mode for 60 s following injection. Separation was performed on a DB-17 (50% phenyl-methylpolysiloxane) fused-silica column of 30 m length, 0.25 mm internal diameter and 0.25 μm film thickness (J&W Scientific, Folsom, CA, USA). Nitrogen (ultra pure; flow 1.7 ml min^{-1}) was used as carrier gas. The following temperature program was used: 50 °C for 1 min, 50 to 80 °C at 50 °C min^{-1}, 80 to 140 °C at 8 °C min^{-1}, 140 to 170 °C at 2 °C min^{-1}, 170 to 280 °C at 8 °C min^{-1}, with a final hold of 5 min. The detector, fitted with a Schott BG-12 band-pass filter, was held at 300 °C. The gas flow rates were: air_1, 17.1 ml min^{-1}; air_2, 10.6 ml min^{-1}; and hydrogen, 13.5 ml min^{-1}. The best gate delay, gate width and trigger level tested in the laboratory were 5 ms, 3 ms and 200 mV respectively. The determinations were made in triplicate and the resulting chromatograms were quantified using peak area normalized to the internal standard using the Star Chromatography Workstation 5.52 software (Walnut Creek, CA, USA).

Calibration and quantification

Quantification was performed by internal standard procedure, using TeBT added after derivatization. Standards were prepared in hexane containing 1–300 ng l^{-1} (as tin) of pentylated butyltins (TBT, DBT, MBT) and pentylated phenyltins (TPhT, diphenyltin (DPhT), monophenyltin (MPhT)). Procedural blanks were carried out for every batch of samples.

Table 3. Analytical curves and linearity

Organotin	Linearity (ng ml^{-1} as Sn)	CV (%)	Analytical curves ($y = ax + b$)		
			a	*b*	R^2
TPrT	1.49–201	6	0.850	−0.0596	0.997
TBT	1.36–27.2	6	0.671	−0.0037	0.999
	30.6–183	9	0.866	−0.137	0.996
DBT	5.44–27.2	6	0.685	0.0019	0.991
	30.6–150	9	0.786	−0.0930	0.993
MBT	5.82–29.1	7	0.676	0.0007	0.991
	32.7–160	9	0.821	−0.130	0.992
TcyT	1.31–9.84	8	0.595	−0.0032	0.996
	13.1–144	9	0.875	−0.0916	0.996
TPhT	2.71–149	12	1.119	−0.106	0.977
DPhT	57.5–158	9	1.124	−0.323	0.965
MPhT	53.3–168	9	0.804	−0.224	0.977

The analytical procedure was validated by analyzing the harbor sediment reference material PACS-2 from the National Research Council of Canada (Ottawa, Canada), certified for TBT and DBT. As shown in Table 2, the results obtained for the certified material are in good agreement with the certified values. The uncertainty of the overall procedure applied to the reference material was 15% for TBT, 14% for DBT and 22% for MBT. The calibration curve parameters for all analytes are given in Table 3. The concentrations of butyltins and phenyltins were corrected for the recoveries of TPrT (from 60 to 75%) and TCyT (from 75 to 90%) used as surrogates. Derivatization yields tested in standard solutions of the several analytes were always around 80%. The tin detection limits[32] in the various organotins are: TBT, 2.2 μg kg^{-1}; DBT, 1.9 μg kg^{-1}; MBT, 2.4 μg kg^{-1}; MPhT, 2.7 μg kg^{-1}; DPhT, 2.6 μg kg^{-1}; and TPhT, 3.6 μg kg^{-1}. The mean relative standard deviation (RSD) obtained for 10 injections was 8.6%. Organotin concentrations reported are expressed as micrograms of tin per kilogram of dry sediment mass.

RESULTS AND DISCUSSION

The first report on the use of GC–PFPD for organotin speciation was published by Jacobsen *et al.*,[31] and since then, because of the good detection limit, this detector has often been employed.[15,17,33–41] However, the determination of very low concentrations of organotins may be severely affected by high levels of sulfur-containing compounds in

sediment extracts.[42] It is possible to reduce this problem by using the 610 nm optical filter, which decreases sulfur interferences; however, organotin detection limits are poor compared with those obtained with the 390 nm filter. In this study the sulfur interference was reduced by oxidation with DMD, as it was imperative to use the filter providing the best detection limit. Fernández-Escobar *et al*.[19] found that a large sulfone peak appearing just after the MBT peak could interfere with the quantification, and so introduced a cleanup by alumina adsorption chromatography after the oxidation step to eliminate the sulfone. In this study, a similar peak was observed, but this was not completely eliminated by the second cleanup step. Therefore, owing to the high sulfur content of Guanabara Bay sediments (see Table 4 for sulfur content in sediments), in addition to the above procedure, the selection of a suitable temperature program was necessary to eliminate co-elution of residual sulfur compounds interfering with the quantification of organotins.

Possible effects of the oxidation step upon analyte integrity were tested by applying the whole desulfurization procedure to the PACS-2 reference material. The results in Table 2 prove the good performance of the procedure adopted. The chromatogram for surface sediments from station 2 (Fig. 3) shows that well-resolved organotin peaks are obtained despite the presence of sulfur residues.

Total tin, TBT, DBT, MBT, total sulfur and organic carbon concentrations measured in the samples are presented in Table 4. No phenyltin compounds were found in these samples. Calculated porosity and the mass accumulation rates are also shown in Table 4.

The anoxic state of all sediment layers was confirmed by the redox potentials measured, which varied from −42.9 to −169.4 mV at Station 2, from −190.0 to −544.0 mV at Station 3, from −100.0 to −241.0 mV at Station 4, and from −130.0 to −170.0 mV at Station 6. For Station 5, data are available only for the surface layer (+20.0 mV) and for the 5–10 cm layer (−38.0 mV). At Station 3, large redox potential variations between surface and bottom layers were verified (−544.0 mV and −190.0 mV respectively).

The ^{210}Pb profile in core 3 shows that an alteration occurred at 12–15 cm depth, preceded by a period of low constant sedimentation rate. This indicates a change in the dynamics of sedimentation in the region of Station 3, since other properties measured do not suggest core disturbance by mixing processes. At Station 5, the absence of ^{210}Pb in excess and the depth variation of other properties (see Table 4) point to man-made alterations, possibly by dumping of sandy material.

The spatial distribution of inorganic tin revealed a source of contamination in the area of Station 4, which receives industrial and sewage discharges. Assuming that the values found for the core from Station 2 (in the least contaminated area) are close to the naturally expected levels for the region, them Stations 3 and 4 present two- to three-fold increases compared with this baseline estimate. The values in this study are in the range of those reported by Dahab *et al*.[43] (1.87–8.19 mg kg^{-1} of tin) for Lake Mariuty in Egypt,

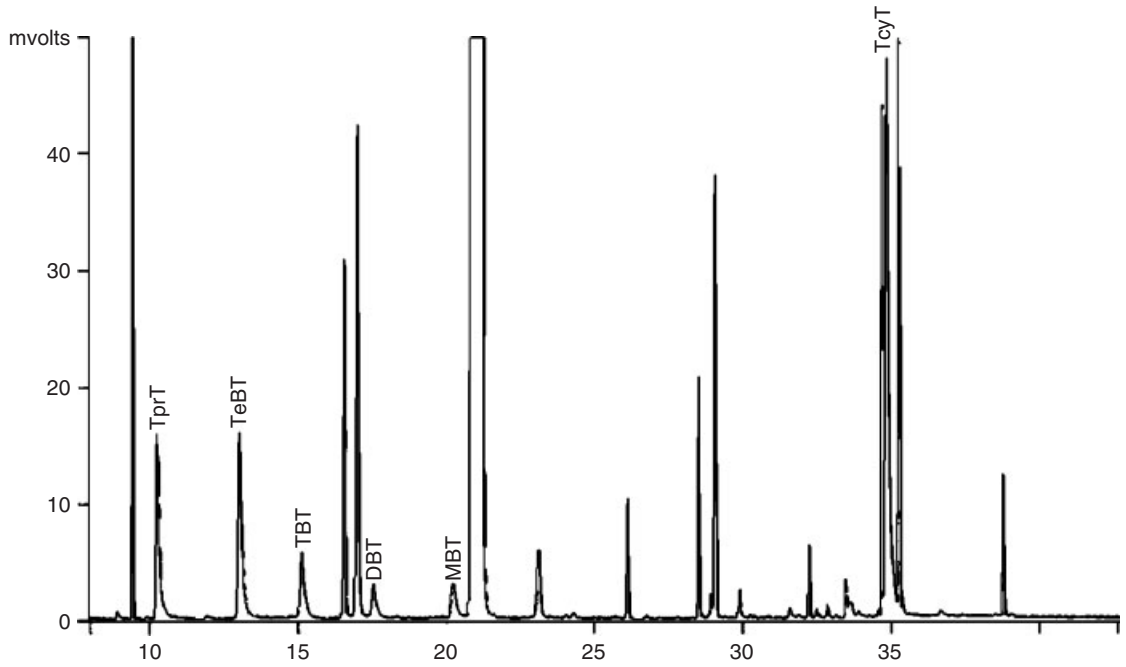


Figure 3. Chromatogram of surface sediments from Station 2 obtained by GC–PFPD with a 390 nm filter. Temperature program: 50 °C for 1 min, 50 to 80 °C at 50 °C min^{-1}, 80 to 140 °C at 8 °C min^{-1}, 140 to 170 °C at 2 °C min^{-1}, 170 to 280 °C at 8 °C min^{-1}, with a final hold of 5 min.

Table 4. Elemental composition, porosity, mass accumulation rate (MAR), and tin concentrations in sediment cores from Guanabara Bay[a]

Station	Sub-sample	Depth (cm)	Porosity[b] (%)	MAR[c] (g cm^{-2} $year^{-1}$)	C_{org} (%)	S_{total} (%)	Sn_{total} (mg kg^{-1} dry mass)	[Sn][d] (μg kg^{-1} dry mass)		
								TBT	DBT	MBT
2	2-1	0–1.5	0.85	0.36	3.90	1.74	5.74	14 ± 3	27 ± 2	<d.l.
	2-2	1.5–3	0.86	0.34	3.66	1.71	5.80	23 ± 4	12 ± 1	3.7 ± 0.2
	2-3	3–4.5	0.84	0.39	3.63	1.76	5.93	25 ± 3	8.3 ± 0.5	<d.l.
	2-4	4.5–6	0.85	0.36	3.96	1.77	5.52	6.2 ± 0.8	3.8 ± 0.3	<d.l.
	2-5	6–7.5	0.86	0.34	3.90	1.70	5.40	24 ± 3	<d.l.	8.4 ± 0.7
	2-6	7.5–9	0.87	0.31	3.33	1.67	4.79	57 ± 7	<d.l.	<d.l.
	2-7	9–13.5	0.85	0.36	3.94	1.54	5.31	15 ± 2	<d.l.	41 ± 4
	2-8	13.5–18	0.85	0.36	2.93	1.48	5.38	8.9 ± 0.9	<d.l.	15 ± 2
	2-9	18–22.5	0.85	0.36	3.22	1.33	5.72	21 ± 2	<d.l.	37 ± 5
3	3-1	0–3	0.75	n.d.	3.89	1.48	9.49	82 ± 5	3.1 ± 0.3	<d.l.
	3-2	3–6	0.79	n.d.	3.68	1.26	10.6	76 ± 9	<d.l.	<d.l.
	3-3	6–9	0.74	n.d.	3.70	1.17	10.4	29 ± 2	13 ± 2	43 ± 6
	3-4	9–12	0.78	n.d.	3.46	1.08	11.1	5.5 ± 0.2	<d.l.	12 ± 1
	3-5	12–15	0.59	n.d.	2.80	1.53	11.1	2.4 ± 0.5	<d.l.	3.5 ± 0.4
	3-6	15–18	0.75	n.d.	3.14	1.06	10.8	27 ± 1	<d.l.	<d.l.
	3-7	18–21	0.77	n.d.	3.47	1.01	10.9	59 ± 7	4.2 ± 0.6	<d.l.
4	4-1	0–1	0.85	0.21	4.08	1.48	16.6	47 ± 4	28 ± 4	<d.l.
	4-2	1–2	0.84	0.22	3.54	1.35	16.1	35 ± 2	8.3 ± 0.9	<d.l.
	4-3	2–3	0.84	0.22	2.86	1.29	15.3	33 ± 3	<d.l.	<d.l.
	4-4	3–4	0.83	0.23	3.60	1.31	15.7	48 ± 5	<d.l.	<d.l.
	4-5	4–6.5	0.83	0.23	3.65	1.26	15.3	56 ± 3	<d.l.	<d.l.
	4-6	6.5–9	0.84	0.22	3.10	1.12	13.5	4.9 ± 0.3	<d.l.	126 ± 9
	4-7	9–11.5	0.81	0.26	2.84	1.56	11.3	<d.l.	<d.l.	113 ± 17
	4-8	11.5–14	0.83	0.23	2.53	1.45	10.4	22 ± 2	<d.l.	16 ± 2
	4-9	14–16.5	0.82	0.25	2.35	1.53	10.4	< d.l.	<d.l.	39 ± 3
5	5-1	0–3	0.65	n.d.	0.77	<d.l.	4.20	30 ± 4	15 ± 2	17 ± 3
	5-2	3–6	0.64	n.d.	0.84	<d.l.	3.48	6.5 ± 0.5	5.3 ± 0.5	<d.l.
	5-3	6–9	0.61	n.d.	0.76	<d.l.	2.63	44 ± 2	3.4 ± 0.5	24 ± 2
	5-4	9–12	0.57	n.d.	0.57	<d.l.	1.44	<d.l.	2.1 ± 0.3	<d.l.
	5-5	12–15	0.57	n.d.	0.60	<d.l.	1.59	<d.l.	2.9 ± 0.3	<d.l.
	5-6	15–18	0.59	n.d.	0.72	<d.l.	1.30	<d.l.	<d.l.	<d.l.
6	6-1	0–3	0.84	0.99	2.54	1.31	7.03	73 ± 8	18 ± 2	<d.l.
	6-2	3–6	0.82	1.11	2.65	1.28	6.93	45 ± 3	7.2 ± 0.4	<d.l.
	6-3	6–9	0.83	1.05	3.22	1.18	6.63	51 ± 3	<d.l.	<d.l.
	6-4	9–12	0.82	1.11	2.62	1.07	6.71	58 ± 4	<d.l.	<d.l.
	6-5	12–15	0.81	1.17	2.52	1.09	5.79	14 ± 1	<d.l.	<d.l.
	6-6	15–18.5	0.81	1.17	2.65	1.00	5.29	12 ± 1	<d.l.	<d.l.
	6-7	18.5–22	0.80	1.23	2.51	1.35	5.30	<d.l.	2.3 ± 0.1	59 ± 7
	6-8	22–25.5	0.80	1.23	1.84	0.752	4.93	3.7 ± 0.4	12 ± 1	96 ± 8
	6-9	25.5–29	0.77	0.42	1.99	0.863	5.16	<d.l.	<d.l.	<d.l.
	6-10	29–32.5	0.77	0.42	2.01	—	4.80	13 ± 2	<d.l.	<d.l.

[a] n. d.: not determined; <d.l.: less than detection limit.
[b] Porosity $= w = \{P_d/[1 + w(P_d - 1)]\}$, where w is humidity (%)/100 and P_d is the particle density (2.8 g cm^{-3} here).
[c] MAR $= V_s P_d (1 - P)$, where V_s (cm $year^{-1}$) is the sedimentation rate in and P (%) is the porosity.
[d] Data obtained for two replicates.

by Arambarri *et al.*,[44] who found values between 11 and 113 mg kg^{-1}, for estuarine sediments in northern Spain and by DelValls *et al.*[45] (8.1–24 mg kg^{-1} of tin) for the Cadiz Gulf.

The spatial distribution of butyltin compounds in surface sediments is shown in Fig. 4. As expected, TBT concentrations are, in general, higher than DBT and MBT, except at Station 2.

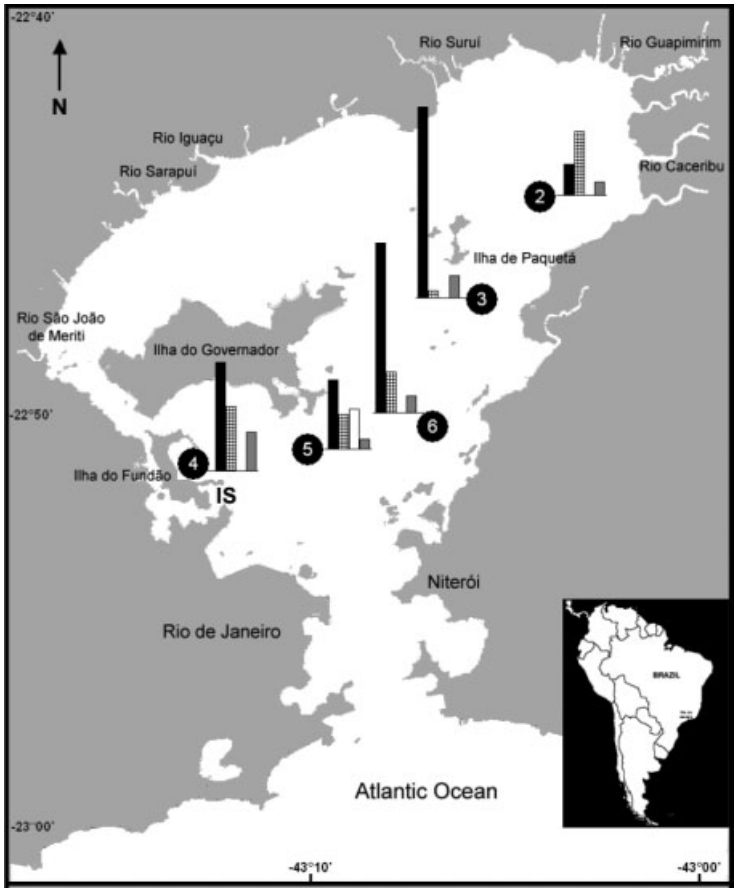


Figure 4. TBT (black column), DBT (dashed column) and MBT (white column) concentrations (μg kg^{-1} as tin (dry mass)), and total tin (gray column) concentration (mg kg^{-1} (dry mass)) found in the surface sediment.

This area of shallow waters, located near the environmental protection area of Guapimirim, is one of the least polluted in the bay. Artisan fishing, the main activity in the area, contributes little to organotin inputs, because TBT-based hull protection is too costly to be used by the low-income fishing community. Organotin compounds found here probably originate from the ship anchorage area located south of this protected site. Tidal currents of the order of 0.5–0.6 m s^{-1} in the bay are effective in conveying particulate matter carrying TBT and its degradation products from the main source areas to these remote, shallower sites, where settling of particles is favored by hydrodynamics.[11] Therefore, DBT predominance in the top sediment layer at Station 2 may derive from decay occurring during the material drift in the aerated water column. The greatest TBT level was found at Stations 3 and 6, which are both in the vicinity of ship anchorage areas.

There is a great variability in TBT concentrations throughout the cores and, in general, the organotins depth profiles do not point out significant degradation of TBT into DBT, MBT or inorganic tin. Although MBT predominated over DBT and even TBT in some sediment layers, there is no significant evidence of direct degradation of TBT to MBT, as reported by Stang and Seligman,[46] and in more than 50% of the samples both DBT and MBT values were below detection limits. The lack of relation among species concentration and the low levels of the degradation products suggest that TBT remains stable once buried in the sediments. Degradation seems to occur mainly in the water column or at the sediment–water interface from where solids containing at least 90% of water can often be resuspended due to tidal waves before final burial. This mechanism could favor the loss of the most weakly adsorbed degradation products back to the water column, resulting in impoverished sediment in these substances. Data on the adsorption of TBT degradation products on sediment particles that could be used to support this proposed mechanism are rare. However, according to Hoch *et al.*,[47] at above pH 7 the driving force for adsorption (the hydrophobic character of the neutral butyltin hydroxides) is controlled by the number and nature of the organic compounds bound to the tin cation, and an increase in adsorbability is expected with increasing hydrophobicity (TBT > DBT).

Contrary to Dahab *et al.*,[43] Stang and Seligman[46] and De Mora *et al.*,[48] who reported a rapid decrease of concentrations with depth and indications of degradation to MBT and DBT, Sarradin *et al.*[22] found, as in this study, no trends or

correlation between concentrations, degradation products and depth; they attributed such a scattered pattern to variations in the pollutant input rates, differences in sediment composition and mixing. Quevauviller *et al*.[25] measured butyltin concentrations in a sediment core from the harbor of Arcachon and found an increasing TBT gradient from the bottom to the core top, which indicated that TBT persisted within the sedimentary column over a large period of time.

Several factors may have contributed to the butyltins' variability in the sediment cores studied. As stated before, sediment resuspension is one factor influencing the very low concentrations of degradation products. Similar features could also result from time-variable inputs of organotins to the sediments due to changing oceanographic conditions and water properties (e.g. particulate matter content), since the areas sampled are not that near to the sources so as to be greatly influenced by source intensity fluctuations. The resulting concentration of DBT and MBT in the sediments may be a function of the time the parental compound remains exposed to the oxic conditions in the water column before final sedimentation. In addition, the local high mean water

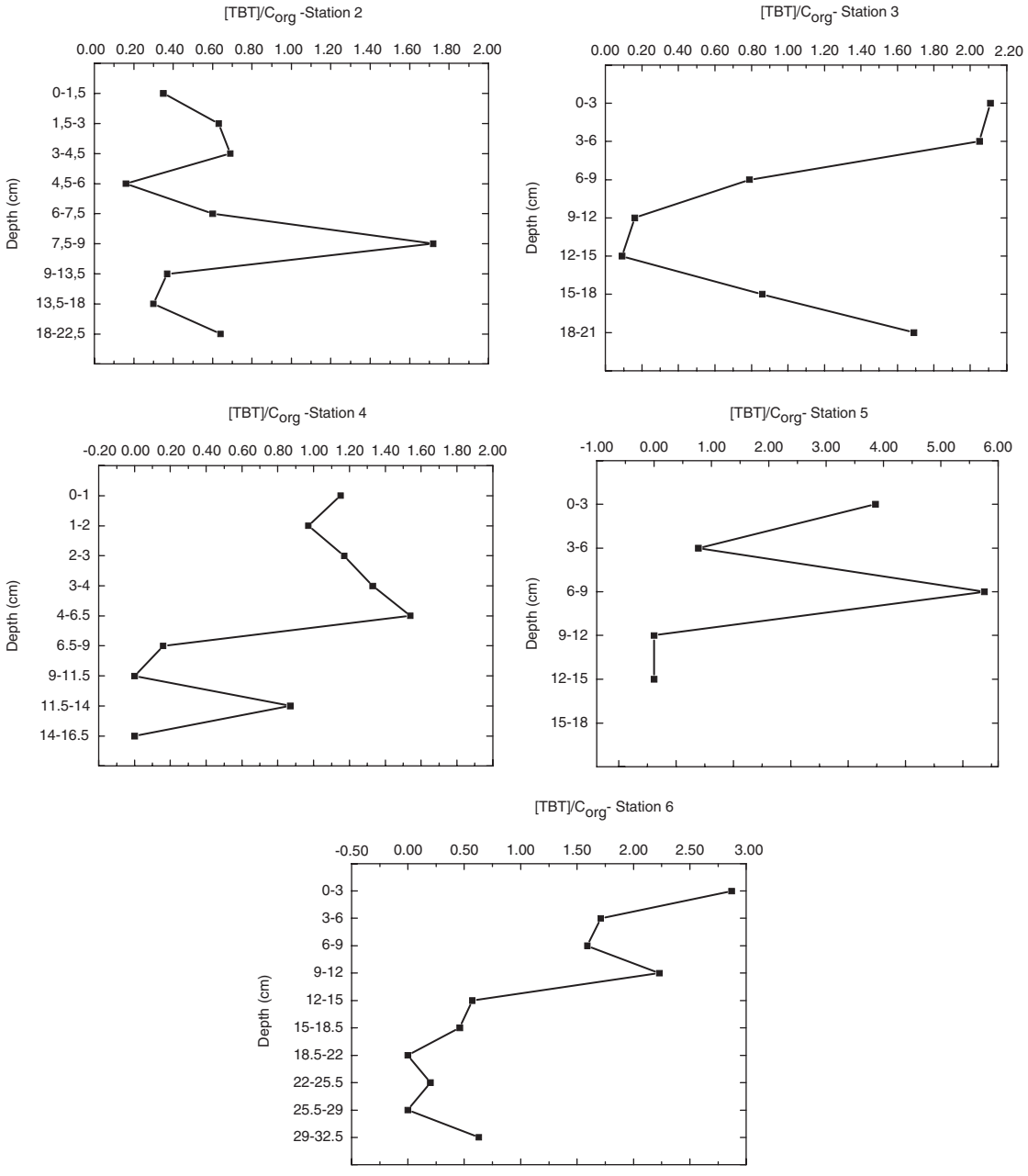


Figure 5. TBT concentrations normalized to organic carbon (C_{org}) given in mg TBT as tin per kg of organic carbon.

temperatures (24.2 ± 2.6 °C) contribute to faster degradation of labile organic substances.

There is no correlation between organotins concentration and sulfur content or redox potential, nor are there trend similarities in their depth profiles.

The sediments from Stations 2 to 6 can be classified, according to the scale established by Waite *et al.*,[49] as moderately to slightly contaminated. At Stations 4 and 6, there is evidence of a TBT concentration increase over the last 20–30 years, whereas at Station 2 no temporal trend was verified. At Station 3 the results suggest profound alterations in this area during the deposition time of the 12–15 cm layer that led to changes in sediment properties (porosity, organic carbon) and to a temporary shift in TBT concentration trend. The low absolute concentrations at Station 5 are due to the sandy characteristics of these sediments, the oxic surface layer and the low organic carbon concentrations. Because in sediments containing >0.2% organic carbon sorption of organic substances occurs preferably upon organic phases,[50] normalization of data to the organic carbon content provides a basis for evaluating the effect of different sediments' properties on the accumulation of organic pollutants. Porosity could also be used to this end; however, variations from site to site and among core samples were too small compared with those of organic carbon. Figure 5 highlights the relevance of this procedure, showing that, once normalized, TBT concentrations at Station 5 become the highest amongst all stations. This should, in fact, be expected, since Station 5 is located in the center of an anchorage area and, as a result, contains organic material highly enriched in TBT.

Figure 6 shows calculated fluxes of TBT to the sediments using the mass accumulation rates based on the existing sedimentation rates and the concentrations. Data for Stations 3 and 5 are missing due to the failure in dating these cores. The high fluxes in core 6 above a depth of 25 cm are due to a dramatic raise in sedimentation rate that occurred in the area about 15–20 years ago.

Determinations in the surface (0–5 cm) and bottom (30–35 cm) layers of a sediment core sampled near Ishikawajima Shipyard (IS, Fig. 1, coordinates 22°51.926′S latitude and 43°12.290′W longitude, 6.4 m water depth) showed high TBT concentrations in both segments (surface: 742 μg kg^{-1} as tin, bottom: 151 μg kg^{-1} as tin). In the surface sample, [DBT] = 90 μg kg^{-1} (as tin) and [MBT] = 21 μg kg^{-1} (as tin); in the bottom layer, [DBT] = 12 μg kg^{-1} (as tin) and [MBT] was below the detection limit. These results in sediments near a major source indicate that degradation of TBT is indeed a slow process in the anoxic sediments of Guanabara Bay. Only in this area was TPhT (35 μg kg^{-1} as tin) found in the surface layer.

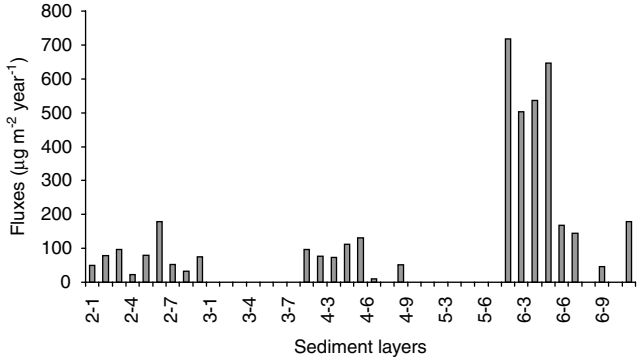


Figure 6. TBT fluxes to the sediments.

An attempt was made to estimate the degradation constant for TBT and DBT by adopting a simple first-order degradation rate model for steady-state conditions, i.e. $k = -[\ln(C_t/C_{t=0})/t]$, where C the concentration and t is the time in years,[51] and using the data from Stations 2 and 6 (where organic carbon and sedimentation rates have been constant over the last 15–20 years). Good model fitting was observed only for data from Station 6 ($r = 0.859$); however, the degradation constant result is too elevated (-0.24 $year^{-1}$). It should be stressed that degradation products were not detected in the considered depth interval unless for DBT in the first two layers. The estimated half-life of about 3 years lies within the interval of 4 months to >8 years reported by Stewart and De Mora[7] in their review on this matter. Differences in degradation rates may derive from the sediment nature and/or from differences in TBT associations in the sediment environment.

The same estimate was carried out for DBT using the data from Station 2 (the least contaminated site). An excellent fit was obtained to the first-order rate model ($r = 0.989$; $p < 0.05$), which gave a degradation constant of -0.37 $year^{-1}$ and a half-life of 2 years. These results seem to point to an ongoing degradation process of DBT at this station, although MBT was not detected in most of the sediment layers considered in the calculation.

CONCLUSIONS

The space–time distribution of organotin species in the sediments was very irregular and there is little evidence that extensive degradation has occurred after sedimentation. Depth profiles showing an increase from the bottom to top sediment layers may represent the historical record of increasing TBT use in the region. Organotin concentrations are low in comparison with those reported for Marina da Glória by Fernandez[15] with exception of the value of 742 μg kg^{-1} found near a major shipyard. This space distribution pattern confirms the tendency of organotins to settle rapidly in the vicinities of the sources. Substantive organotin contamination in Guanabara Bay seems to be restricted to areas of heavy ship traffic, marinas and shipyards. Such a trend is confirmed by the highest TBT fluxes to the sediments (500–700 μg m^{-2} $year^{-1}$) obtained for Station 6, which in

comparison with Stations 2 and 4 is the most prone to receiving major organotin inputs from nearby sources.

There were no indications of substantial TBT decay in the anoxic sediments of Guanabara Bay. Most probably, the DBT and MBT found above the detection limits in some segments of the cores were formed in the water column or at the sediment–water interface, before final burial in the sediments. This means that TBT in the bay may pose risks to the biota long after it has been released into the environment.

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REFERENCES

1. Hoch M. *Appl. Geochem.* 2001; **16**: 719.
2. Fent K. *Crit. Rev. Toxicol.* 1996; **26**: 1.
3. Wilken RD, Kuballa J, Jantzen E. *Fresenivs J. Anal. Chem.* 1994; **350**: 77.
4. Alzieu C, Sanjuan J, Deltreil JP, Borel M. *Mar. Pollut. Bull.* 1986; **17**: 494.
5. Gibbs PE, Bryan GW. Reproductive failure in the gastropod *Nucella lapillus* associated with imposex caused by tributyltin pollution: a review. In *Organotin—Environmental Fate and Effects*, Champ MA, Seligman PF (eds). Chapman & Hall: London, 1996; 259–281.
6. Horigushi T, Shiraishi H, Shimizu M, Masatoshi M. *Appl. Organometal. Chem.* 1997; **11**: 451.
7. Stewart C, De Mora SJ. *Environ. Technol.* 1990; **11**: 565.
8. Dowson PH, Bubb JM, Lester JN. *Estuar. Coast. Shelf Sci.* 1996; **42**: 551.
9. Champ M. *Sci. Total Environ.* 2000; **258**: 21.
10. Amador ES. *Baía de Guanabara e Ecossistemas Periféricos: Homem e Natureza*. Reproarte Gráfica e Editora Ltda: Rio de Janeiro, 1997.
11. Kjerfve B, Ribeiro CA, Dias GTM, Filippo A, Quaresma VS. *Cont. Shelf Res.* 1997; **17**: 1609.
12. Rebello AL, Haekel W, Moreira I, Santelli R, Schroeder F. *Mar. Chem.* 1986; **18**: 215.
13. Lima ALC. Geocronologia de hidrocarbonetos poliaromáticos (PAHs)—estudo de caso: Baía de Guanabara. MSc dissertation. PUC-Rio, Rio de Janeiro, 1996.
14. Wagener ALR, Scofield A, Hamacher C, Francioni E, Ziolli R, Carreira R. Impactos ambientais decorrentes de derramamentos de óleo na Baía de Guanabara. In *Meio Ambiente, Cultura e Desenvolvimento Sustentável. Somando Esforços, Aceitando Desafios*, vol. 2, Fonseca DPR, Siquiera JC (eds). Sette Letras: Rio de Janeiro, 2002; 73–92.
15. Fernandez MA. Compostos orgânicos de estanho na Baía de Guanabara: sua distribuição e possíveis impactos. Doctorate thesis, PUC-Rio, Rio de Janeiro, 2001.
16. Fernandez MA, Limaverde AM, Castro IB, Almeida ACM, Wagener ALR. *Cad. Saúde Públ.* 2002; **18**: 463.
17. Limaverde AM. Estudo da especiação de compostos orgânicos de estanho (COE) em Thais (Stramonita) haemastoma por GC\PFPD visando avaliar seu potencial de bioindicação. Doctorate thesis, PUC-Rio, Rio de Janeiro, 2002.
18. Adam W, Bialas J, Hadjiarapoglou L. *Chem. Ber.* 1991; **124**: 2377.
19. Fernández-Escobar I, Gibert M, Messeguer A, Bayona JM. *Anal. Chem.* 1998; **70**: 3703.
20. FEEMA. Qualidade da água da Baía de Guanabara—1990 a 1997. Secretaria de Estado de Meio Ambiente, Fundação Estadual de Engenharia do Meio Ambiente, Rio de Janeiro, 1998.
21. Rebello AL, Alevato S, Arras S. *Quim. Nova* 1981; **4**: 70.
22. Sarradin PM, Astruc A, Sabrier R, Astruc M. *Mar. Pollut. Bull.* 1994; **28**: 621.
23. Godoy JM, Moreira I, Bragança MJ, Wanderley C, Mendes LB. *J. Radioanal. Nucl. Chem.* 1998; **227**: 157.
24. Godoy JM, Moreira I, Wanderley C, Simões Filho FF, Mozeto AA. *Radiat. Prot. Dosim.* 1998; **75**: 111.
25. Quevauviller P, Donard OFX, Etcheber H. *Environ. Pollut.* 1994; **84**: 89.
26. Yonezawa Y, Fukui M, Yoshida T, Ochi A, Tanaka T, Noguti Y, Kowata T, Sato Y, Masunaga S, Urushigawa Y. *Chemosphere* 1994; **29**: 1349.
27. Quevauviller P. *Method Performance Studies for Speciation Analysis*. The Royal Society of Chemistry: Cambridge, 1998.
28. Carreira R, Wagener ALR, Readman JW, Fileman T, Macko SA, Veiga A. *Mar. Chem.* 2002; **79**: 207.
29. Abalos M, Bayona JM, Compañó R, Granados M, Leal C, Prat MD. *J. Chromatogr. A* 1997; **788**: 1.
30. Abalos M, Bayona JM, Quevauviller P. *Appl. Organometal Chem.* 1998; **12**: 1.
31. Jacobsen JA, Stuer-Lauridsen F, Pritzl G. *Appl. Organometal Chem.* 1997; **11**: 737.
32. Currie LA. *Anal. Chim. Acta* 1999; **391**: 105.
33. Bancon-Montigny C, Lespes G, Potin-Gautier M. *J. Chromatogr. A* 2000; **896**: 149.
34. Jacobsen JA, Asmund G. *Sci. Total Environ.* 2000; **245**: 131.
35. Aguerre S, Lespes G, Desauziers V, Potin-Gautier M. *J. Anal. At. Spectrom.* 2001; **16**: 263.
36. Bech M. *Environ. Pollut.* 2002; **117**: 421.
37. Kawarai M, Shirazaki T, Mizuishi K. *Bunseki Kagaku* 2002; **51**: 959.
38. Simon S, Bueno M, Lespes G, Mench M, Potin-Gautier M. *Talanta* 2002; **57**: 31.
39. Godoi AFL, Montone RC, Santiago-Silva M. *J. Chromatogr. A* 2003; **985**: 205.
40. Strand J, Jacobsen JA, Pedersen B, Granmo A. *Environ. Pollut.* 2003; **124**: 7.
41. Le Gac M, Lespes G, Potin-Gautier M. *J. Chromatogr. A* 2003; **999**: 123.
42. Almeida ACM. Geocronologia de compostos orgânicos de estanho e de alguns metais de relevância ambiental. Estudo de caso: Baía de Guanabara. Doctorate thesis, PUC-Rio, Rio de Janeiro, 2001.
43. Dahab OA, Sabrouti MA, Halim Y. *Environ. Pollut.* 1990; **63**: 329.
44. Arambarri I, Garcia R, Millán E. *Chemosphere* 2003; **51**: 643.
45. DelValls TA, Forja JM, Gómez-Parra A. *Chemosphere* 2002; **46**: 1033.
46. Stang PM, Seligman PF. In *Proceedings of the Organotin Symposium, Oceans '86 Conference*, vol. 4. IEEE: Piscataway, NJ, 1986; 1256–1261.
47. Hoch M, Alonso-Azcarate J, Lischick M. *Environ. Pollut.* 2003; **123**: 217.
48. De Mora SJ, King NG, Miller MC. *Environ. Technol. Lett.* 1989; **10**: 901.
49. Waite ME, Waldock MJ, Thain JE, Smith DJ, Milton SM. *Mar. Environ. Res.* 1991; **32**: 89.
50. USEPA. 1993; Technical basis for establishing sediment quality criteria for nonionic organic contaminants for the protection of benthic organisms by using equilibrium partitioning. Draft EPA 822-R-93-011, US Environmental Protection Agency, Office of Science and Technology, Health and Ecology Criteria Division, Washington DC.
51. Berner RA. *Early Diagenesis. A Theoretical Approach*. Princeton University Press: Princeton, 1980.

