RESEARCH ARTICLE

Distribution of butyltin compounds in Brazil's southern and southeastern estuarine ecosystems: assessment of spatial scale and compartments

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Abstract Butyltin compounds (BTs), including tributyltin (TBT) and its degradation products, dibutyltin and monobutyltin, have been found in a diversity of aquatic systems and causing toxic effects in target and nontarget organisms. They enter in coastal systems through different sources (as antifouling paints, industrial effluents, etc.) where they interact with biotic and abiotic components, and their distribution is commonly determined by the morphological and hydrodynamic conditions of the coastal systems. In this study, we discuss the contamination by BTs on a spatial scale (eight estuaries with three subareas each) and in different compartments of the estuaries (sediments, suspended particulate matter (SPM), and estuarine catfish tissues (liver and gills). Lower concentrations of BTs were found in the sediments (n.d. to 338 ng g^{-1}) in comparison to studies before a ban of TBT in antifouling paints was enacted, mostly indicating an old input or preservation related with sediment properties and composition. For SPM samples (n.d. to 175 ng L^{-1}) as well as in fish tissues (n.d. to 1426 ng g^{-1}), the presence of these compounds was frequent, especially in the fish due to their movement throughout the estuaries and the potential to assess point sources of BTs. These results indicate that BTs persist in the environment, with variation in amounts between investigated estuaries and even at locations inside the same estuary, because of ideal preservation conditions, transport to remote areas, and input from different sources.

Introduction

Estuaries are coastal ecosystems with high ecological relevance that receive a continental flux of organic and inorganic material in particulate and dissolved form, including essential nutrients for marine trophic chains (Bianchi 2006). They are also important for the protection, feeding, and reproductive processes of vertebrates and invertebrates (Dantas et al. 2010), with a diversity of resident and transient estuarine organisms using these areas as nurseries (Day et al. 1989). In addition to the ecological relevance, estuaries have economic and logistic importance based on the presence of commercial harbors and artisanal fishery activity.

Butyltin compounds (BTs) are a group of organometallic contaminants that are used in a variety of applications. Tributyltin (TBT) is the most investigated of these compounds due to its biocide properties and use in antifouling formulations. Based on these applications, BTs enter in estuarine and marine systems via different sources, including commercial harbors, navigation routes, piers, marinas, dockyards, and fishing nets. The occurrence and intensity of these compounds are related to their usage history (Antizar-Ladislao 2008). In the environment, BTs can be involved in different processes, such as lixiviation, advection, diffusion, sorption, sedimentation, biodegradation, and resuspension and can be found in the dissolved and particulate forms in the water column, in

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sediments, and even bioaccumulated in organisms (Hoch 2001; Yamamoto et al. 2009).

Although TBT in antifouling paints was banned globally by the International Marine Organization in January 2008, TBT can still be found in the aquatic environment (Filipkowska et al. 2011; Kim et al. 2011; Sant'Anna et al. 2014; Santos et al. 2010) due to its relative stability in these systems. In estuarine environments, numerous factors, including temperature, salinity, pH, redox potential, organic matter content, and grain size of sediments, can affect the distribution of BTs, and all these factors are related to the speciation, complexation, and bioavailability of BTs for aquatic biota (Hoch 2003).

Aquatic organisms are indirectly exposed to sources of contamination through the food chain or directly through uptake from water, sediment, or suspended particulate matter. In this context, fishes represent a crucial role as energy carriers from the lowest to higher trophic levels (Van der Oost et al. 2003). Fishes are able to bioaccumulate BTs at two or three levels of magnitudes (D'Agati et al. 2006), even when exposed to low environmental concentrations (ng mL^{-1} or ng g^{-1}) (Meador et al. 2002). TBT toxicity is well described in the literature, mainly with regard to the effects on the endocrine system, where cytochrome P450 is inhibited and causes masculinization in gastropod females (Fernandez et al. 2005; Leung et al. 2006). In addition, TBT toxicity has been observed in fish as masculinization and sperm damage in *Danio rerio* in concentrations between 0.1 and 100 ng L^{-1} (McAllister and Kime 2003), masculinization rates in *Paralichthys olivaceus* with doses of 0.1 to 1 μg g^{-1} diet (Shimasaki et al. 2003), and affecting the xenobiotic biotransformation system and hormonal responses in *Salmo salar* in concentrations of 50 and 250 μ L^{-1} (Mortensen and Arukwe 2007).

Because of their complex distribution in aquatic systems, BTs should be assessed and monitored in more than one compartment of the aquatic system (sediment, water, suspended particulate matter, and the tissue of organisms). In this way, contamination by and impact from these compounds can be assessed, whether they are from old or recent input into the system. Many studies have considered this broad-range monitoring through temporal and spatial scales (Berto et al. 2007; Lee et al. 2006; Meng et al. 2009; Wang et al. 2008), where the first is important for predicting the entrance of these compounds into the system, and the second provides comparison of the partitioning of BTs over different aquatic profiles and input rates. The use of different compartments (matrices) allows the understanding of BT distribution between biotic and abiotic phases or even between different sampling points inside a specific aquatic system. This was already described in Sant'Anna et al. (2014) using hermit crabs and sediments from different intertidal estuarine regions after the TBT ban. As observed in that study, it is important to choose an efficient

bioindicator species and also consider the abiotic matrix. In this way, in areas where TBT occurs in deeper sediment layers, benthic organisms or demersal fishes, such as catfishes, can be good biomonitors for this compound. In this situation, the risks to the biota can, hypothetically, be associated to the measured environmental concentration. Thus, the feeding behavior of catfishes and their important role, as fishes, in trophic chains (Van der Oost et al., 2003) associated with their broad-range temporal and spatial distribution (Azevedo et al. 1998; Araújo et al. 2002) and their use as a protein source by riverine communities elect these organisms as potential bioindicators of contaminants, including BTs, in these areas.

The aim of this study was to investigate the occurrence of BTs in different spatial scales (estuaries and areas within estuaries) and environmental compartments [sediment, suspended particulate matter (SPM), and fish tissues (liver and gills)] to reach an integrative evaluation of how BTs impact these systems over different environmental profiles. Brazil contains several important estuarine harbor areas that are located along the southern and southeastern coast, including the Santos, Sepetiba, Paranaguá, Itajaí, and Babitonga (São Francisco) harbor complexes, most of which are surrounded by marine-protected areas. Thus, the distribution of BTs over a geographical scale and within different compartments was studied in eight estuarine regions from Brazil's southern and southeastern coast, considering the sources of these compounds to the system even after the TBT ban in antifouling formulations was enacted.

Material and methods

Study area and sampling

Sampling was conducted in eight estuarine areas of the southern and southeastern Brazilian coast (Fig. 1) between June 2009 and July 2010: Itapemirim (ITP), Sepetiba (SEP), Santos (STO), Cananéia (CAN), Paranaguá (PNG), Guaratuba (GTB), Babitonga (BAB), and Itajaí (ITA). These areas were selected based on potential sources of BTs, such as harbors, marinas, and sewage effluents, as well as by the presence of the investigated fish species. Estuaries have different hydrodynamics, sediment composition, and catfish species occurrence (Table 1).

Surface sediment was obtained as a composed sample ($n = 3$ at each sampling point) using a Van Veen bottom grab. Redox potential (mV) was measured for each sample in the field. In the laboratory, samples were homogenized, freeze-dried, sieved, and stored at −20 °C. Different sieving meshes (62 to 250 μm) were used to homogenize the samples after they were freeze-dried, and total sediment was used in the analysis of the BTs. Grain size, organic matter, and sulfur content analyses were conducted on a portion of sediment that

Fig. 1 Locations of studied estuaries and sampling points along the southern and southeastern Brazilian coast (**a** *ITP* Itapemirim, **b** *SEP* Sepetiba, **c** *STO* Santos, **d** *CAN* Cananéia, **e** *PNG* Paranaguá, **f** *GTB* Guaratuba, **g** *BAB* Babitonga, and **h** *ITA* Itajaí)
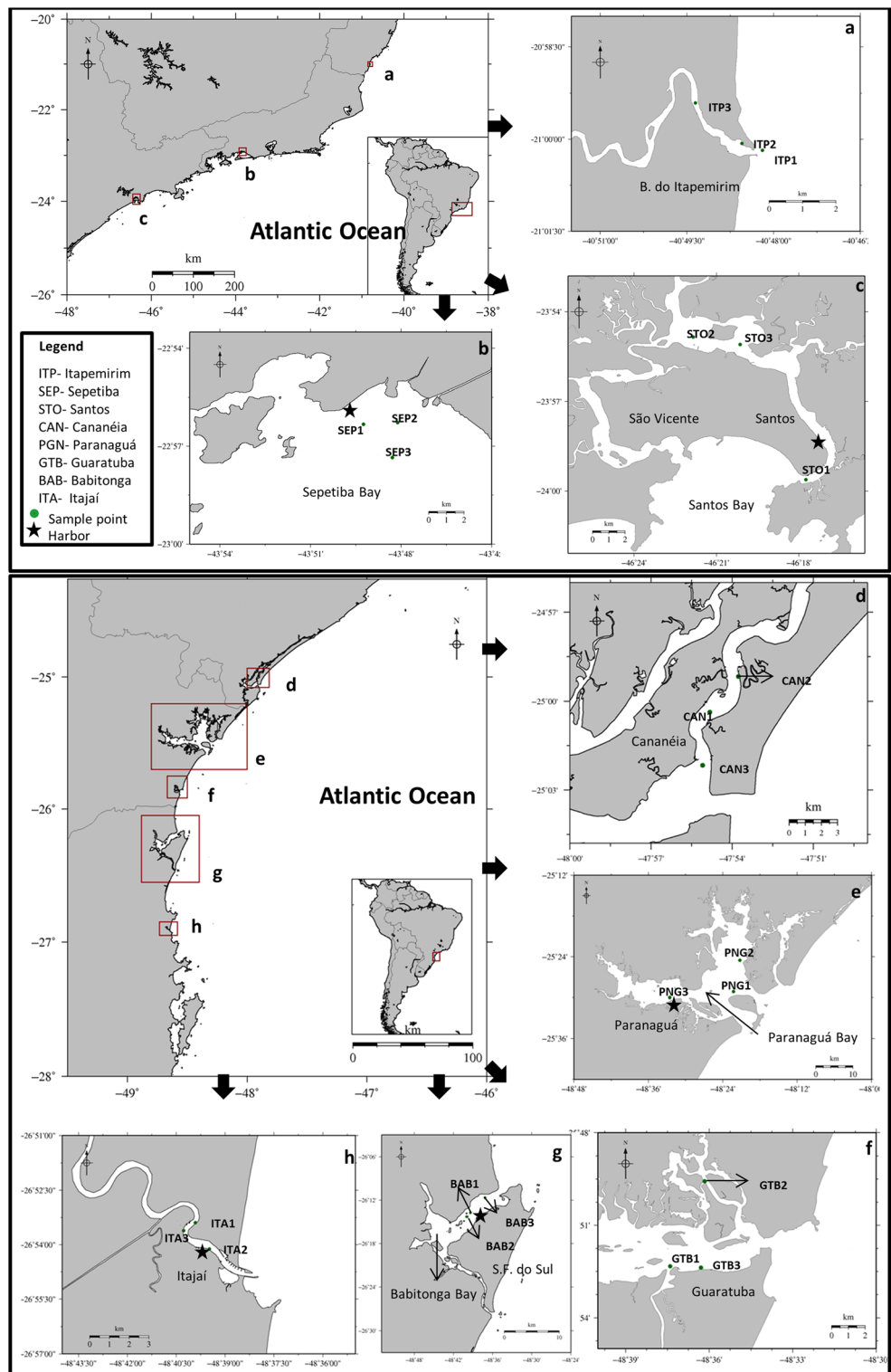
was not sieved. Triplicate bottom water samples were collected with a 2-L Niskin bottle, homogenized, and subsampled in the field for physicochemical parameters (salinity, pH, and temperature) and for SPM analysis. In the laboratory, these water samples were filtered using a Millipore® filtration kit and 0.45-μm glass fiber filters. The SPM content filter was dried at 60 °C, stored in aluminum foil, and kept frozen until analysis. Fishes were sampled using different sampling methods depending on the depth of the sampling point. Sampling was authorized by SISBIO (Authorization and

Table 1 Characterization of the sampling points (positioning, depth, and redox potential (Eh)) and compartments (water, sediment, and fish) in the investigated estuaries

Estuary/ state	Sample point	Location	Main BT source	Sediment							Water			Catfish species
				Depth (m)	Eh^- (mV)	Particle size (%)			S (%)	OM (%)	T (°C)	‰ psu	pH	
						Sand	Silt	Clay						
Itapemirim-ES	ITP 1	21° 00′ 182″ S 40° 48′ 193″ W	Navigation route	6.4	−8	99.7	0	0	0.18	0.9	24	33	7	*C. spixii*
	ITP 2	21° 00′ 019″ S 40° 48′ 548″ W	Dockyard	1.5	144	99.4	0	0	0.18	0.2	29	0	6	*G. genidens*
	ITP 3	20° 59′ 410″ S 40° 49′ 183″ W	Navigation route	2.5	201	96.4	0	0	0	0.5	30	0	6	*G. genidens*
Sepetiba-RJ	SEP 1	22° 56′ 329″ S 43° 49′ 247″ W	Harbor	6	−356	73.4	9.9	16.6	0.65	4.5	29	31	8	*G. genidens*
	SEP 2	22° 56′ 276″ S 43° 48′ 115″ W	Industrial effluents	5.5	−374	3.8	41.7	54.5	1.54	17.4	28	32	7	*C. spixii*
	SEP 3	22° 57′ 349″ S 43° 48′ 290″ W	Navigation route	6.5	−311	2.9	20.2	76.8	1.38	17.6	28	33	7	*G. genidens*
Santos-SP	STO 1	23° 59′ 622″ S 46° 17′ 747″ W	Harbor entrance/ Dockyard	5.5	−279	34.9	34.5	29.3	0.88	17.5	a	31	7	*G. genidens*
	STO 2	23° 54′ 850″ S 46° 21′ 847″ W	Industrial effluents	4.5	−235	51.9	25.8	22.3	0.95	7.1	a	27	7	*G. genidens*
	STO 3	23° 55′ 100″ S 43° 20′ 139″ W	Industrial effluents	3.5	−260	31.4	35.7	30.0	1.52	13.2	a	20	7	*G. genidens*
Cananéia-SP	CAN 1	25° 00′ 372″ S 47° 54′ 827″ W	Dockyard/Marina	7.6	−263	57	17.2	25.8	1.01	13.1	21	28	8	*C. spixii*
	CAN 2	24° 59′ 175″ S 47° 53′ 771″ W	Navigation route	8.2	−297	72.4	10.3	17.1	0.57	4.9	20	32	8	*C. spixii* *A. luniscutis*
	CAN 3	25° 02′ 168″ S 47° 55′ 093″ W	Navigation route	6.1	−237	89.6	3.4	6.8	0.42	2.4	21	35	8	*A. luniscutis*
Paranaguá-PR	PNG 1	25° 29′ 136″ S 48° 22′ 272″ W	Navigation route	8.5	−168	70.7	13.8	15.5	0.58	4.8	18	34	8	*C. spixii*
	PNG 2	25° 24′ 253″ S 48° 21′ 241″ W	Navigation route	11.5	−80	100	0	0	0.29	1.2	18	33	8	*C. spixii*
	PNG 3	25° 30′ 001″ S 48° 32′ 555″ W	Harbor/Dockyard	13	−198	a	a	a	a	a	18	33	8	*C. spixii*
Guaratuba-PR	GTB 1	25° 52′ 334″ S 48° 37′ 400″ W	Navigation route	8	−225	53.8	25.7	20.5	0.25	9.4	26	28	7	*C. spixii*
	GTB 2	25° 49′ 569″ S 48° 36′ 162″ W	Navigation route	9	−231	15.2	18.5	65.7	0.21	8.9	27	23	7	*C. spixii*
	GTB 3	25° 52′ 376″ S 48° 36′ 297″ W	Marina	5.5	−195	94.8	3.4	1.7	0.61	1.6	26	29	9	*G. genidens*
Babitonga-SC	BAB 1	26° 13′ 744″ S 48° 39′ 387″ W	Navigation route	10	−286	12.4	40	47.5	1.04	14.8	26	31	7	*A. luniscutis*
	BAB 2	26° 14′ 291″ S 48° 39′ 975″ W	Navigation route	14	−155	29.5	30.4	39.9	0.94	9.9	25	29	7	*C. spixii*
	BAB 3	26° 11′ 659″ S 48° 37′ 158″ W	Dockyard	11	56	97.8	0	0	0.20	1.6	24	32	7	*G. genidens*
Itajaí-SC	ITA 1	26° 53′ 395″ S 48° 39′ 913″ W	Dockyard	9.5	−266	5.6	44.7	49.7	1.15	9.2	a	25	7	*G. genidens*
	ITA 2	26° 54′ 119″ S 48° 39′ 484″ W	Harbor	5	−199	62.2	22.3	15.4	0.53	4.9	a	20	7	*G. genidens*
	ITA 3	26° 53′ 615″ S 48° 40′ 272″ W	Navigation route	4	−148	25.4	54.3	20.3	0.52	7.3	a	25	7	*G. genidens*

S sulfur content, *OM* organic matter content

[a] Not determined

Information Biodiversity System, no. 18305). The species collected from each sampling point are described in Table 1. A pool of ten fish tissues (liver and gill) was prepared for each sampling point and stored in aluminum foil at −20 °C until the

analysis of the BTs could be performed according to Santos et al. (2013).

Analysis of BTs

Reagents

The BTs of TBT, dibutyltin (DBT), monobutyltin (MBT), tripropyltin, and tetrabutyltin were purchased from Sigma-Aldrich (Milwaukee, WI, USA) as were the neutral aluminum oxide and Grignard reagent (2 mol L^{-1} pentylmagnesium bromide in diethyl ether). Hexane and toluene were obtained from Mallinckrodt (Xalostoc, Mexico), and methanol, chloroform, hydrochloric acid, sulfuric acid, acetic acid, sodium hydroxide, and anhydrous sodium sulfate were purchased from J.T. Baker (Xalostoc, Mexico). Ammonium pyrrolidine dithiocarbamate (APDC-98 %) was purchased from Fluka (St. Gallen, Switzerland).

Method

The analysis of the BTs followed Santos et al. (2013) and Godoi et al. (2003), for sediments and SPM, and Cristale et al. (2012), for fish tissues. The steps for this analysis included extraction using an acid (acetic acid) and a nonpolar solvent (toluene) followed by derivatization using Grignard reagent and a cleanup step using alumina or Florisil®.

The final extracts were analyzed by a Varian 3800 gas chromatograph with PFPD, equipped with a pulsed flame photometric detector using a tin filter (610 nm) and VF5 capillary column (30 m × 0.25 mm × 0.25 μm) (Varian, Walnut Creek, CA, USA). The calibration curve was checked in the linear range between 0.033 and 1.8 μg mL^{-1}. For this system, the LOD and LOQ respectively were 32 and 62, 88 and 178, and 164 and 330 pg for TBT, DBT, and MBT, respectively. The LOD and LOQ for the sediment and SPM method respectively were 3.2 and 6.6, 11 and 22, and 25 and 51 ng g^{-1}, for TBT, DBT, and MBT, respectively. The LOD and LOQ of fish tissues were, respectively, 8 and 26, 16 and 24, and 7 and 55 ng g^{-1} for TBT, DBT, and MBT. All analyses were processed in triplicate using tripropyltin as the surrogate and tetrabutyltin as the internal standard (IS) in corresponding concentrations of 0.3 and 1 μg mL^{-1}. Surrogate recovery was above 80 % in all analyses and was used to correct the final extract concentration. Other quality control parameters, such as matrix effect observed and accuracy and precision of applied methods, are described in detail in Santos et al. (2013).

Data analysis

Statistical treatment was applied with integrative results, considering each butyltin compound (TBT, DBT, and MBT) in each matrix, with normality checked by Kolmogorov-Smirnov, and the integration based on Spearman's rank analysis ($p < 0.05$) to assess the interaction of each compound in a specific matrix, BT content, and physical chemical parameters.

Results and discussion

In general, BTs were detected in all the investigated estuarine systems. The distribution was observed among estuaries, among the different points inside the same estuary, and among the investigated compartments within the same estuary varied (Table 2). This process demonstrated the complexity of the distribution of BTs in estuarine systems and may be influenced by interactions occurring between environmental processes acting in the area as well as by the intensity and frequency of the input from potential sources. Similar variation was observed by Sant'Anna et al. (2014), who compared the presence of BTs in 25 estuaries where intertidal sediments and hermit crab samples were investigated.

BTs in sediments

Sediments are commonly described as the final deposit of BTs in aquatic environments due to their hydrophobic behavior. For this reason, most monitoring and assessment studies of BTs involve this matrix to understand the associated risk of these compounds in aquatic systems. BTs in sediment samples were detected in 8 of the 24 samples investigated. However, quantification errors occurred in the samples from Itajaí and Babitonga Bays. Sample ITA1, located at 9.5 m deep, had a negative redox potential (−226 mV) and high amount of fine sediment particles (95 %), which are ideal conditions for TBT preservation. However, the ITA1 and BAB1 sediment samples also contained higher sulfur content (1.15 and 1.04 %, respectively) that directly affected the determination of BTs in the sediments and SPM because of interference to the chromatographic response during GC-PFPD analysis (Santos et al. 2013). The integration parameters for these samples (but not in the others with equal and/or high sulfur content) were influenced by the existence of a sulfur peak at the same retention time, which made the quantification unreliable. For this reason, these two sediment samples were classified as n.d. in this study.

For all the other samples, the amounts of BTs determined in the sediments are described using the surrogate recovery correction but were not adjusted according to the organic matter content due to the absence of significant correlation ($p > 0.05$). The association of BTs with fine grains (silt and clays) has been reported (Radke et al. 2008; Ramaswamy et al. 2004) and includes a discussion about the high reactive surface of these grains interacting with particulate and dissolved substances due to their double electrochemical layer and the

Table 2 Analysis of BTs in superficial sediments, SPM, and fish tissues ($n = 3$) with results expressed as averages and %RSD (in parentheses)

Sample	Sediment (ng g⁻¹ d.w.)				SPM (ng L⁻¹)				Liver (ng g⁻¹ w.w.)				Gill (ng g⁻¹ w.w.)			
	TBT	DBT	MBT	∑BTs	TBT	DBT	MBT	∑BTs	TBT	DBT	MBT	∑BTs	TBT	DBT	MBT	∑BTs
ITP 1	<LOQ	n.d.	n.d.	b	34	n.d.	n.d.	34	80 (14)	<LOQ	n.d.	80	<LOQ	n.d.	n.d.	b
ITP 2	n.d.	n.d.	n.d.	b	28	n.d.	n.d.	28	56 (14)	<LOQ	n.d.	56	<LOQ	n.d.	n.d.	b
ITP 3	n.d.	n.d.	n.d.	b	n.d.	n.d.	n.d.	b	43 (13)	n.d.	n.d.	43	<LOQ	n.d.	n.d.	b
SEP 1	n.d.	338 (14)	<LOQ	338	8	25	16	49	110 (27)	18 (17)	<LOQ	128	81 (26)	n.d.	n.d.	81
SEP 2	n.d.	n.d.	n.d.	b	a	a	a	b	<LOQ	58 (10)	n.d.	58	n.d.	n.d.	n.d.	b
SEP 3	n.d.	n.d.	n.d.	b	36	9	175	220	n.d.	n.d.	n.d.	b	58 (8)	n.d.	n.d.	58
STO 1	26 (4)	63 (4)	n.d.	89	50	7	<LOQ	57	102 (10)	91 (18)	<LOQ	193	59 (15)	n.d.	n.d.	59
STO 2	n.d.	25 (7)	n.d.	25	76	4	<LOQ	80	n.d.	221 (14)	n.d.	221	n.d.	n.d.	n.d.	b
STO 3	n.d.	30 (6.5)	<LOQ	64	25	4	<LOQ	29	n.d.	n.d.	n.d.	b	n.d.	n.d.	n.d.	b
CAN 1	<LOQ	19 (8)	n.d.	19	7	5	<LOQ	12	n.d.	n.d.	n.d.	b	b	b	b	b
CAN 2a	<LOQ	n.d.	n.d.	b	6	<LOQ	<LOQ	6	57 (12)	n.d.	n.d.	57	n.d.	n.d.	n.d.	b
CAN2b									n.d.	455 (23)	n.d.	455	n.d.	n.d.	n.d.	b
CAN 3	<LOQ	n.d.	n.d.	b	7	4	<LOQ	11	89 (10)	n.d.	n.d.	89	n.d.	n.d	n.d.	b
PNG 1	n.d.	26 (10)	64 (17)	90	54	106	166	326	66 (12)	107 (6)	n.d.	173	n.d.	n.d.	n.d.	b
PNG 2	<LOQ	n.d.	n.d.	b	32	25	89	146	121 (9)	178 (17)	n.d.	299	n.d.	27 (7)	218 (35)	245
PNG 3	279 (33)	<LOQ	289 (0.5)	568	a	a	a	b	71 (8)	302 (30)	n.d.	373	n.d.	n.d.	n.d.	b
GTB 1	<LOQ	n.d.	n.d.	b	n.d.	n.d.	121	121	65 (11)	45 (4)	94 (13)	204	<LOQ	n.d.	n.d.	b
GTB 2	n.d.	n.d.	n.d.	b	n.d.	n.d.	n.d.	b	<LOQ	n.d.	n.d.	b	<LOQ	n.d.	n.d.	b
GTB 3	n.d.	n.d.	n.d.	b	25	8	137	170	<LOQ	n.d.	n.d.	b	72 (7)	n.d.	n.d.	72
BAB 1	a	a	a	b	2.17	n.d.	60	62.17	77 (29)	n.d.	n.d.	77	n.d.	n.d.	n.d.	b
BAB 2	n.d.	n.d.	n.d.	b	4.5	n.d.	41	44.5	66 (13)	n.d.	n.d.	66	n.d.	n.d.	n.d.	b
BAB 3	n.d.	n.d.	n.d.	b	n.d.	n.d.	53	53	124 (15)	35 (9)	<LOQ	159	n.d.	n.d.	n.d.	b
ITA 1	a	a	a	b	a	a	a	b	432 (8)	1426 (25)	458 (14)	2316	129 (13)	<LOQ	n.d.	129
ITA 2	229 (21)	31 (3)	n.d.	260	<LOQ	5	<LOQ	5	78 (8)	<LOQ	n.d.	78	71 (5)	n.d.	n.d.	71
ITA 3	<LOQ	n.d.	LOQ	b	a	a	a	b	a	a	a	b	a	a	a	b

n.d. not detected = <LOD, *<LOQ* below quantification limit, *CAN2a C. spixii*, *CAN2b A. luniscutis*

[a] Dirty sample—not determined

[b] Not applicable

sorption of cationic compounds. However, the complexity of mineralogical and organic matter compositions can affect the sorption differently (Hoch et al. 2003). In some cases, as observed in the Guaratuba and Babitonga Bays, the presence of BTs in the biota or in the SPM can involve the behavior of BTs in the sediments, directly associated with several factors, including sediment composition, organic matter, frequency of input, and environmental conditions. Considering this behavior, detected levels can differ significantly on a short spatial scale (Sant'Anna et al. 2014; Santos et al., 2010). In these two areas, there is an absence of a BT hotspot close to the sampling points, and sediments were sampled mainly in navigation routes, where currents, tides, and dragging activities can inhibit the preservation of contaminants associated with this matrix. In Cananéia, the presence of DBT in low concentrations at sampling point CAN1, located in a dockyard area, indicated an old TBT input in the area. In addition, DBT sorption in sediments is favored in lower salinities (Hoch et al. 2003). This estuary was previously investigated (Sant'Anna et al. 2014) for the presence of BTs, and DBT was the most abundant (2045 ng Sn g⁻¹) BT in sediments and was related to a deactivated dockyard in the region.

In Santos estuary, BTs were detected in all three sediment samples (25 to 63 ng g⁻¹). These amounts are considered low compared to previous studies in the area: 285 ± 11 ng Sn g⁻¹ of TBT detected from 2008 to 2010 (Sant'Anna et al. 2014) and

4882 ng Sn g^{-1} of TBT detected in a 2001 sampling campaign (Godoi et al. 2003). Based on these two studies and our results, we can hypothesize that TBT concentration in the area is decreasing, probably due to the worldwide ban of TBT-based antifouling paints for large vessels. The sample STO1 was located close to the entrance of Santos harbor, whereas the two other samples were located in the northern portion of the estuary. In these two areas, the presence of TBT degradation products in the sediments may be related to degradation during transport through the estuary or even by the input of these compounds from industrial effluents. However, TBT was detected in low concentrations in SPM and fish tissues also indicating a recent TBT input as consequence of navigation activities or even industrial effluents.

In Paranaguá Bay, the favorable preservation conditions (anoxic sediments and high organic matter content as observed in sample PNG3) and the active distribution (presence of maximum turbidity zone) (Santos et al. 2009) can support the presence of BTs in the area even in areas far from the main sources. The degradation products detected in PNG1 may be associated with sediment composition, which, at this sampling point, is composed mainly of sand (70 %). The highest TBT concentration in our samples (279 ng g^{-1}) was detected in PNG3, where MBT was also detected in quite similar concentration. The most probable explanation for this is the higher adsorption for these two compounds in fine sediments due to the hydrophobic behavior as observed in Santos et al. (2009), where fine sediments close to the harbor were related to the higher amount of BTs detected. Compared to the previous study developed in 2006 undertaken before the TBT worldwide ban (Santos et al. 2009), the amount of TBT in the harbor area (1595 ng g^{-1}) decreased and may be a consequence of a lower recent input. Similarly, the results may also be a consequence of the frequent harbor channel dredging (conducted in 2009, just before sampling), where the superficial sediment layer containing TBT is likely removed, at least partially.

In sampling points located far from potential input areas such as harbors, piers, and dockyards, the presence of degradation products is expected (Felizzola et al. 2008). This aspect can also explain the result observed for PNG1, where TBT was not detected in the sediment samples but its degradation products (DBT and MBT) were. The highest DBT concentration in sediments (338 ng g^{-1}) was detected in another estuary in a harbor area (SEP) and may indicate an old TBT input with debutilation process (degradation) but may also be influenced by sediment composition (73.4 % sand) and sorption affinity. However, the opposite was observed for ITA2, another harbor area, with mostly sandy sediment and with an elevated amount of TBT (229 ng g^{-1}). This difference suggests influence by a recent/old input as, historically, high concentrations of BTs were found in Itajaí sediments with concentrations of 1136 and 94 ng Sn g^{-1} (Oliveira et al. 2010), related with dockyards and harbor activities, respectively, in this area.

In Brazil, TBT levels in sediments are described in CONAMA 454 (MMA 2012), with permitted concentrations of 100 ng g^{-1} for level 1 (NOAEL) and 1000 ng g^{-1} for level 2 (LOAEL) in sediments from dredged areas. Estuaries investigated in this study are mostly below these limits; however, level 1 was reached at sampling points PNG3 and ITA2, both of which are in harbor areas. Sample STO1 is below these Brazilian limits, however is above the recommended levels of the international Sediment Quality Guidelines (SQG), 7 ng g^{-1} in the Netherlands guideline (Stronkhorst and Hattun 2003) and 9 μg Sn kg^{-1} in the Australian guideline (CSIRO 2013).

BTs are also detected in sediments globally after the TBT ban: Ecuador 32.5 to 247 ng g^{-1} (Castro et al. 2012), Portugal 1 to 165 ng g^{-1} (Carvalho et al. 2009), Indonesia 160 to 350 ng g^{-1} (Harino et al. 2012), China 65 ng g^{-1} (Wang et al. 2008), and India <LD to 84.2 ng g^{-1} (Antizar-Ladislao et al. 2011), all of which are related to harbor areas.

BTs in SPM

As observed in this study and reported in the literature, the dynamic distribution of BTs in estuaries is also influenced by the SPM content (Langston et al. 2009). The highest TBT concentrations in SPM were observed in Santos (25 to 76 ng L^{-1}), whereas its degradation products, DBT and MBT, had higher values in Paranaguá (25 to 106 and 89 to 166 ng L^{-1}, respectively). Corneliessen et al. (2008) detected high TBT concentrations ranging from 58 to 510 ng g^{-1} in suspended particles in Oslo Harbor that originated from surface runoff. In this study, the detection of TBT in SPM samples far from harbor regions, as observed in the Paranaguá and Santos samples, may indicate a strong transport process occurring in this region affected by interactions between tides and continental runoff as well as the input from alternative sources as industrial effluents. In addition, degradation products were also detected in the SPM from Paranaguá Bay.

The presence of DBT in the SPM can be due to its major solubility in water, whereby it is easily released from sediments and distributed into the aquatic system (Hoch et al. 2003; Roberts 2012). DBT is also commonly found in industrial and urban effluents (Hoch et al. 2003). A study involving SPM in India showed concentrations of BTs from 0.60 to 29 ng Sn L^{-1}, where DBT was the most abundant (Bhosle et al. 2004). In our study, according to Spearman's rank analysis, the SPM density in the investigated estuaries was moderately related with the presence of DBT ($r = 0.36$) and MBT ($r = 0.55$), and the quantification of these two degradation products in the SPM was also correlated ($r = 0.50$). In addition to transport from another estuarine points, the presence of MBT in the SPM in the Babitonga and Guaratuba Bays may be due to the higher interaction of this compound with the inorganic fraction of SPM (Bravo et al. 2010), sorption

through electrostatic interactions (Ramaswamy et al. 2004), or even the input of this compound from other sources (Wang et al. 2008). In Itapemirim (ITP), although the sediment is composed mostly of sand (99 %), which is not favorable for the sorption of BTs, the detection of TBT in the SPM may be explained by a labile interaction associated with a recent input.

In dynamic systems, such as estuaries, the assessment of contaminants in suspended solids can contribute positively to the understanding of the distribution process among compartments. Furthermore, the detection of BTs in 16 of 24 samples also demonstrates high contamination prevalence, even in areas where these contaminants are not present in the sediments.

BTs in fish tissues

Correlations between the presence of BTs in abiotic matrices and in organisms have been reported (Harino et al. 2002). However, these studies used low-mobility organisms, such as mollusks. For fishes, Harino et al. (2012) detected TBT in the liver of *Anguila anguila*, and the results were compared with concentrations in sediments from previous studies, following the same contamination gradient in the Thames estuary in England. In some investigated estuaries, BTs were detected in sediment and fish tissues sampled at the same point. In Itajaí, higher amounts of BTs of 432, 1426, and 458 ng g^{-1} for TBT, DBT, and MBT, respectively, in fish tissues (*Genidens genidens*) were detected (ITA1). Unfortunately, we do not have sediment or SPM data for this point, considered by previous studies as a dragging discharge point and where the concentration of BTs was detected in sediments (Oliveira et al. 2010). The presence of degradation products (DBT and MBT) in the liver may be associated with the direct assimilation from sediments and SPM and by the transformation of the fishes' metabolism (debutilation). The TBT concentration detected in the sediments (229 ng g^{-1}) from ITA2 may indicate possible bioavailability of this compound for fish species where assimilation can occur directly from sediments (0.47 Spearman's correlation rank between TBT in sediment and TBT in liver) as well as through the trophic chain (Antizar-Ladislao 2008).

The assimilation of BTs through SPM can influence the presence of these compounds in gills (Roberts 2012). TBT was the most abundant BT in gills, indicating that this tissue is an important exposure route for this contaminant. Viglino et al. (2006) observed this same result using *Licodes vahlii* (eelpout), where TBT was quantified in seston samples from deep water. In Guaratuba Bay, the detection of TBT in the gills of *G. genidens* (72 ng g^{-1}) may be a result of this assimilation by the diffuse entrance of water containing TBT dissolved and/or associated with suspended particles (Viglino et al. 2006). In this way, the presence of TBT in water, associated with particles or not, may affect directly the content in gills

once the metabolism of xenobiotics fails to occur (Lee 1996). This effect was observed in the Santos, Sepetiba, and Guaratuba Bays.

However, after assimilation by the gills, diet uptake is the most common route of exposure for fishes (Michaud and Pelletier 2006), and assimilation can occur differently depending on the accumulation capacity of each species as well as its habit (pelagic or benthonic) (Lee et al. 2005). Similarly, species that travel longer distances accumulate more BTs than resident species (Takahashi et al. 2000), once they are exposed to different contamination sources. In demersal species, such as catfishes, the TBT accumulation is detected mainly in internal organs, whereas for pelagic species, the highest concentrations are in muscles (Lee et al. 2005). BTs found in fishes worldwide and in the present study are shown in Table 3.

In general, the accumulation of BTs in fishes can be measured through the TBT percentage in the liver (Ohji et al. 2006; Ohji et al. 2011), once this compound is directly assimilated from abiotic matrices, whereas the detection of degradation compounds in the liver indicates that metabolism has occurred. Accumulation of BTs in the liver can be higher than it is in other tissues, such as muscle (Kannan et al. 1995). In fish samples from ITA2, BAB1, BAB2, CAN2, CAN3, and ITA1, ITA2 and ITA3 TBT represents 100 % of the BTs in the liver. Through these results, all *Aspistor luniscutis* samples had 100 % TBT in the liver. This species is commonly found in deep regions, where TBT can stay preserved and available to them.

In Babitonga Bay, three fish species were investigated in this study. The assimilations of BTs by *A. luniscutis* (77 ng g^{-1}) and *Cathorops spixii* (66 ng g^{-1}) sampled from BAB1 and BAB2, respectively, are in accordance with their competitive behavior for food (Azevedo et al. 1998), as they occupy the same ecological niche. However, the highest TBT concentration was observed in *G. genidens* liver (124 ng g^{-1}), probably as a result of the movement of this species to the inner estuary and consequent contact with TBT-impacted sediments from other areas. The presence in the liver of DBT in *C. spixii* (455 ng g^{-1}) and TBT in *A. luniscutis* (57 ng g^{-1}) sampled in the same area (CAN2), however, can demonstrate that the exposure can be influenced by another factors as different time of exposure and metabolism. Although *C. spixii* usually is related with deep sediments, the presence of this species in shallow or intertidal waters, where TBT degradation products can be available, has also been reported (Possato et al. 2011).

Considering these results, the three species investigated can act as biomonitors for BTs, as they demonstrate the uptake capacity. The presence of sediments in their feeding behavior has already been reported, likely from accidental uptake or even to help on trituration of organisms from their diet. In these reduced sediments, degradation is observed less

Table 3 Butyltin concentrations in demersal and pelagic fishes worldwide

	Continent/country	Year	Species (habitat)	Tissue	Concentrations (ng g^{-1})			Reference
					TBT	DBT	MBT	
Asia	China, Bohai Bay	2002	*Chaeturichthys stigmatias* (demersal)	Muscle	1.3	24.4	5.4	Hu et al. (2006)
	Taiwan, Hsiao Island	[c]	*Rachicentrum canadium* (pelagic)	Liver	751	39.8	68.6	Liu et al. (2011)
				Gill	169	[a]	37.4	Liu et al. (2011)
	Taiwan, Hsingta Harbor	2003	*Pagrus major* (demersal)	Liver	779	2635	4346	Lee et al. (2005)
				Gill	424	208	655	Lee et al. (2005)
	Japan, Kyushu	2008	*Paralichthys olivaceus* (demersal)	Liver	6.6	4.7	[b]	Miki et al. (2011)
Europe	Turkey, Aegean	2009	*Mullus barbatus* (demersal)	Muscle	174	69.2	1496	Kucuksezgin et al. (2011)
	UK, Thames estuary	1999	*Anguila anguila* (demersal)	Liver	143	26	66	Harino et al. (2002)
				Muscle	60	24	66	Harino et al. (2002)
	Spain, Mediterranean	1996	*Mora moro* (demersal)	Liver	130	134	88	Borghi and Porte (2002)
				Gill	38	8.6	<1.6	Borghi and Porte (2002)
	Denmark, Coast	1998	*Platichthys flesus* (demersal)	Liver	40[d]	200[d]	19[d]	Strand and Jaconsen (2005)
Oceania	Australia, Brisbane	1990	*Platycephalus fuscus* (demersal)	Liver	6.22	3.4	250	Kannan et al. (1995)
				Muscle	2.0	3.1	24	Kannan et al. (1995)
Africa	Egypt, Alexandria	2004	*Triglaparus lastovizo* (demersal)	[c]	212[d]	20[d]	[b]	Said et al. (2006)
			Diplodua sargus (pelagic)	[c]	82[d]	16[d]	[b]	
America	Canada, Saguenay Fjord	1999/2002	*Licodes vahlii* (demersal)	Liver	115[d]	102[d]	n.d.	Viglino et al. (2006)
				Gill	185[d]	38[d]	8[d]	Viglino et al. (2006)
			Sebastes fasciatus (pelagic)	Liver	1822[d]	[a]	[a]	Viglino et al. (2006)
				Gill	435[d]	56[d]	[a]	Viglino et al. (2006)
	Brazil, south and southeastern estuaries	2009/2010	*Cathorops spixii* (demersal)	Liver	121[d]	302[d]	94[d]	This study
				Gill	[a]	27[d]	218[d]	
			Genidens genidens (demersal)	Liver	432[d]	1426[d]	458[d]	This study
				Gill	129[d]	[a]	[a]	
			Aspistor luniscutis (demersal)	Liver	89[d]	455[d]	[a]	This study
				Gill	[a]	[a]	[a]	

[a] Not detected

[b] Not analyzed

[c] Not specified

[d] Highest concentration detected

(Santos et al. 2010), and TBT uptake is favored. In addition to being bioindicators of estuarine pollution, catfishes are also important for estuarine trophic chains and are consumed broadly by riverine communities.

In Paranaguá Bay, BT occurrence in liver of *C. spixii* was previously reported (53 to 330 ng g^{-1} of TBT) in fishes sampled in 2011, close to harbor area (Santos et al. 2014). The detected levels from 2011 sampling (carried after a channel dredging) can indicate an increase of catfish exposure to TBT once in 2010 (present study), the maximum level of this contaminant was lower (71 ng g^{-1}).

Integrative results

The presence of BTs in all investigated estuaries is presented in Fig. 2. In general, low concentrations of BTs detected in surface sediments may be a result of (i) sampling location, as some samples may be located far from the main sources, (ii) a

Fig. 2 Presence of total butyltins in all investigated estuaries (sediment and fish tissues in ng g^{-1}; SPM in ng L^{-1}; *CAN2a C. spixii, CAN2b A. luniscutis*). Samples with zero level can indicate BTs not detectable or not quantified
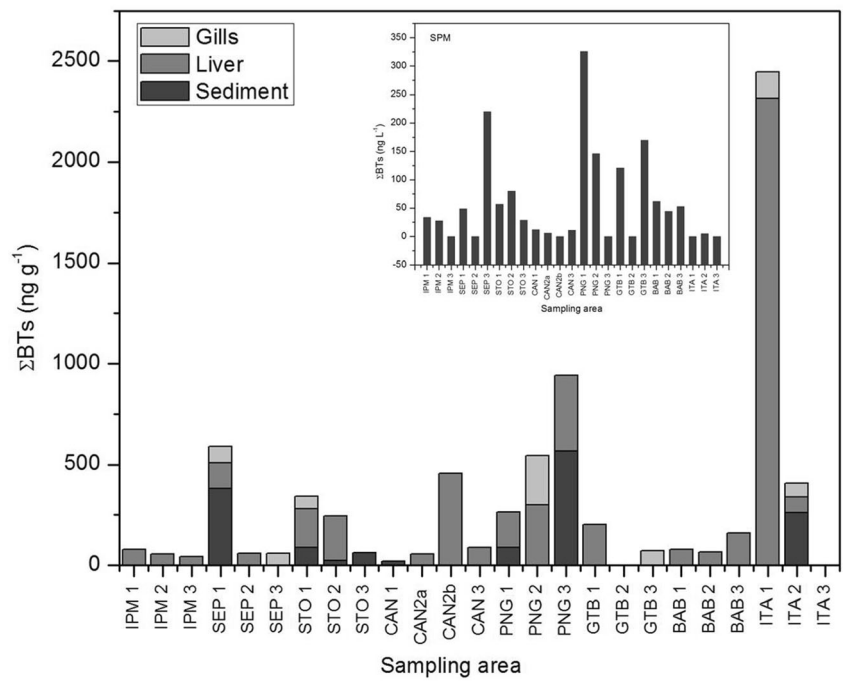
decrease in input because of the TBT-based antifouling paint ban, and (iii) degradation in the environment caused by hydrodynamic processes and human activities, such as dredging and ship traffic (Radke et al. 2008). Whereas in some environments, TBT impact was reduced after the antifouling ban (Airaksien et al. 2010; Garg et al. 2009), in other areas (mainly development countries), the concentrations detected after the ban were higher (Filipkowska et al. 2011; Kim et al. 2011; Kim et al. 2015). Corresponding with these results, Paranaguá and Itajaí (located along the Brazilian southern coast) were the most impacted estuaries, as the presence of BTs was observed in biotic and abiotic matrices. As discussed above, previous studies reported that the presence of TBT in these areas was directly related to the input by antifouling paints and the great variation in abiotic factors (such as circulation, tides, salinity, and sediment composition) that can directly affect the persistence of an old input of BTs in these areas. Besides different input sources and intensities, seasonality can also act as a factor for observed differences between estuaries, as campaigns were conducted in different months during 1 year (2009–2010) under different rainy season (dry-wet).

Of all the studied areas, Cananéia, Itapemirim, and Guaratuba can be considered the least impacted by BTs, based on sediment results, and were related to an absence of the major potential source (harbor activities) (Fig. 1 and Table 1). However, the detection of BTs in fish tissues and SPM samples indicated the presence of these compounds, even in regions primarily considered as reference areas.

Spearman's rank analysis demonstrated a moderate correlation between TBT in sediments and silt content ($r = 0.39$).

Redox potential was inversely correlated with DBT, indicating that in reduced sediments, the DBT content was lower, and TBT preservation was favored. The other environmental parameters of salinity, temperature, elementary compounds, and depth were not significantly correlated in general. Due to different sorption interactions with sediments and SPM as well as different uptake rates by organisms, the presence of BTs in the studied estuaries was analyzed separately and did not present a specific pattern.

The presence of BTs in 15 of 24 SPM samples was an important result that indicates the capacity of transport in estuaries, probably influenced by hydrodynamics conditions as well as human actions, such as dragging. The MBT presence in the SPM was related to the density of the SPM quantified ($r = 0.50$). This parameter can also influence the results for fish tissues, as assimilation by gills is favored.

The observed relationship between TBTs detected in liver samples and gills may be a consequence of direct assimilation by accidental ingestion during benthic foraging as well as the suspended particles in the sediments containing these compounds that are sorbed into the gill tissue. Degradation products in fish tissues may be a result not only of metabolism but also of assimilation directly from sediments, water, or SPM. Particularly for DBT detected in high concentration in fish liver from the ITA1 and Paranaguá, Santos, Sepetiba, and Cananéia samples, the major water solubility of DBT compared with TBT may induce its release from sediment (Roberts, 2012), increasing its bioavailability to the aquatic biota. At the same time, MBT may also be commonly found dissolved in the water phase and attributed to the secondary

sources of BTs (Wang et al. 2008), such as urban and industrial effluents, and was expected in the gill and liver tissues.

The study of spatial occurrence of BTs in different estuarine systems using different spatial scales and matrices provided a general distribution behavior determined by the different estuarine dynamics, interactions with biotic and abiotic factors, sources, and input rates. The use of fishes as biomonitors was important as a consideration for the whole system and not only the point sources of BTs and can show the impacts of BTs, even in systems where human activities are not so evident or where TBT input should be reduced after the antifouling paint ban. In this way, the ecological impact of BTs must be assessed in these areas, as the contamination affects not only the biota but also the local communities that commonly use these fish species as a protein source.

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