

**Distribution of butyltins in waters and sediments of the Mandovi and Zuari estuaries,
west coast of India**

Anita Garg*, Ram M Meena, Narayan B Bhosle
*Marine Corrosion and Material Research Division,
National Institute of Oceanography,
Council of Scientific and Industrial Research,
Dona Paula- 403004, Goa, India*

*Corresponding author E-mail anita@nio.org
Telephone +918322450202
Fax +91832450602

Abstract

Butyltins (TBT, DBT, MBT) were measured in water and sediment samples collected from various locations in the Mandovi (10 stations) and Zuari (9 stations) estuaries during November 2007. The total butyltin (TB) in water samples varied between ~12 and 73 and from 0.5 to 77 ng Sn l⁻¹ ; whereas, for the sediments it varied from ~ 15 to 118 and 6 to 119 ng Sn g⁻¹ dw for the Mandovi and the Zuari estuaries, respectively. The average TB concentration in the sediments from the Zuari estuary was higher as compared to the Mandovi estuary, whereas for the water samples it was *vice versa*. For both the water and sediment samples, MBT was generally the most predominant butyltin in these two estuaries. This suggests that the butyltins contamination was not freshly derived. Fairly good relationships between the concentrations of TB and organic carbon in water and sediment samples of these estuaries implicate the importance of adsorption/desorption processes in controlling the levels of TB in these estuaries.

Keywords TBT, DBT, MBT, water, sediment, estuaries

Introduction

Organotin compounds, mainly tributyltin (TBT), and to some degree triphenyltins (TPhT), have been widely used as antifouling agents in marine paints for more than four decades. These compounds are used as PVC heat stabilizers, catalysts, agrichemicals and in glass coatings (Bhosle 2006). The predominant source of organotins in the marine waters is related to their use as biocides in antifouling paints, especially tributyltin (TBT). In order to control biofouling about 70% of the worlds commercial ships use TBT based antifouling paints (Lee et al. 2006). Although triphenyltins (TPhT) are used in antifouling paints, their major application is in agriculture as a pesticides, insecticides, fungicides etc (Bortoli et al. 2003; Bhosle et al. 2004; 2006). These antifouling compounds enter into the marine waters through land runoff, and leaching of antifouling paints. The ecotoxicological effects of TBT in aquatic systems have been noted since the 1970s and have been well documented (Blanca 2008) which include imposex in gastropods, mussel larvae mortality and oyster shell malformation at very low (few ng l⁻¹) concentrations (Brancato et al. 2000; Konstantinous and Albanis 2004; Alzieu 2000; 2006; Díez et al. 2006; Bhosle 2007). At TBT contaminated sites, water samples may show a low presence of TBT; however, because of bioaccumulation, animal tissue or sediment will show much higher concentrations.

The half-life of TBT ranges between 6 days in summer time for turbid waters to 127 days in winter for water free of any suspended particulate matter (Alzieu 2006). However, degradation of TBT is much slower in sediments where half-lives have been estimated to last several years (Alzieu 2006). Environmental awareness about the effects of organotins compounds has increased considerably in recent years (Morabito and Massanisso 2000).

In India, organotin compounds are used as antifouling paints to control growth of fouling organisms on commercial and naval ships, and other industrial structures that use sea water. To best of our knowledge, there has been no legal ban on the use of TBT compounds in India. Moreover, there is very little knowledge about the levels of organotins in marine waters, sediments and organisms collected form coastal environment of India. Little is known about the distribution of organotin compounds in

the waters and sediments along the west coast of India (Rajendran et al. 2001; Bhosle et al. 2004; 2006).

The Mandovi and Zuari estuary are located on the west coast of India, and are used for navigation of recreational boats and fishing vessels, and for the transport of iron and manganese ores from the hinterland to the Marmugoa harbour. Along both the estuaries, there are small jetties and wharfs that are used for berthing of small recreational boats, fishing vessels, and barges. There are also small shipbuilding units located along the banks of these estuaries that are involved in construction, repair, and maintenance of small ships and barges. Both the estuaries are fringed with mangroves along the banks. Mangroves support several flora and fauna and serve as nursery grounds as well as nutrient sources to economically and ecologically important organisms such as prawn, fishes and many other invertebrates (Bhosle 2007). Therefore, the Mandovi and Zuari estuaries are sensitive ecosystems that may be subjected to organotin contamination due to shipping activities. The aim of this work was to evaluate butyltin contamination in the waters and sediments of the Mandovi and Zuari estuaries.

Materials and methods

Study area

Sampling locations in the Mandovi and Zuari estuaries along the west coast of India are shown in Fig. 1. Seawater and sediment samples were collected from 10 stations in the Mandovi estuary (Fig. 1). These areas include a creek where treated waste water is discharged (station 1) in to the Mandovi estuary, a fisheries jetty (station 2), small jetties for the berthing of small commercial vessels and passenger ferries (stations 3 and 4), a shipbuilding unit (station 5), and a few stations in the navigation channel used for the transport of ores (stations 6, 7, 8, 9 and 10). Similarly, seawater and sediment samples were collected from 9 stations in the Zuari estuary. These include a small jetty for recreational purpose (station 1), a shipbuilding unit (station 2), small jetties for passenger ferries and berthing of commercial vessels for transport of ores (station 3, 4, 5, 6, 7, and

8) and a location (station 9) where the river Zuari originates and is without any major shipping activity.

Sampling

Water and sediment samples were collected from the Mandovi and Zuari estuary during November 2007. Surface water (~ 1 m) samples were collected using a clean bucket and immediately transferred to the laboratory. Immediately after collection, seawater was filtered onto pre-ashed (450 °C for 4 h) GF/F (47 mm 0.7 µm) filter to collect suspended particulate matter. Surface sediment samples were collected using a Van Veen grab, and transported to the laboratory using a portable icebox. In the laboratory, the samples were lyophilized, powdered and sieved through 120 µm mesh and stored at -20°C until analysis.

Extraction of butyltins from water samples

Butyltin compounds were extracted and analyzed following the method of Morabito et al. (1995). In brief, 750 ml of seawater sample was taken in a teflon separatory funnel, to which 100 ml of 5% NaCl in deionised water was added and the sample pH adjusted to 2 with HCl. The sample was then spiked with internal standard tripropyltin and extracted twice for 15 minutes with 20 ml of 0.03% of tropolone in dichloromethane by shaking vigorously in a separatory funnel. The extracted organic phase was dewatered with sodium sulphate, to which 1 ml of Isooctane was added and then reduced to almost dryness under a stream of nitrogen and treated with the Grignard's reagent for 5 minutes at room temperature. The rest of the procedure followed was similar to that for the sediments, mentioned below.

Extraction of butyltins from sediments

Freeze dried and sieved (120 µm mesh) sediment samples (1 g) were spiked with internal standard tripropyltin and extracted twice for 15 minutes with 15 ml of 0.03% of Tropolone solution in methanol and 1 ml of concentrated HCl by vortexing. The extracts

were centrifuged for 10 minutes and liquid-liquid- extracted twice in a separating funnel with 15 ml of dichloromethane (CH_2Cl_2) and 100 ml of 5% NaCl in deionised water, (to avoid the formation of emulsion). The organic phase separated was dewatered with sodium sulphate and diluted with 1 ml of Isooctane and then reduced to almost dryness under a stream of nitrogen and treated with the derivatising agent pentylmagnesium bromide (Grignard's reagent) for 5 minutes at room temperature. The excess Grignard's reactant was destroyed by adding carefully, drop-by-drop 2 ml of deionised water. The derivatised butyltins were subsequently extracted twice with 2 ml of n-hexane and 5 ml of 1 M sulphuric acid. Then as a clean up step, the sample was reduced to 0.5 ml under a stream of nitrogen, and eluted with 10 ml of 1:1 hexane-toluene through a 6g column of activated flurosil. The eluate was finally evaporated to 0.5 ml under gentle stream of nitrogen and analyzed with gas chromatography. Sets of blanks and standards were also processed following the same method as for samples. Separation and quantification of butyltin compounds were performed by GCMS. 1 μl of standard and samples were injected onto the GCMS. Peak identification was based on the matching of retention times of the standard butyltin compounds.

Instrumental analysis

A GC-MS system (Shimadzu QP 2010) equipped with a gas chromatograph and mass spectrometer detector with electron impact ionization mode (70 eV) was used for the analysis. The Organotins were separated and detected using RESTEK Rtx- 5MS capillary column (30 m, 0.32 mm i.d. 0.25 μm df) and selected ion monitoring (SIM) mode. One microliter of sample or blank or standard mixtures were injected using a programmable on column injector. The injector was kept at 60 $^\circ\text{C}$ for 1 min, then temperature was raised @100 $^\circ\text{C min}^{-1}$ to 240 $^\circ\text{C}$, and maintained at the same temperature for the rest of the run time. Initial column temperature was 80 $^\circ\text{C}$. After 2 min the oven temperature was programmed to reach 280 $^\circ\text{C}$ at @ 10 $^\circ\text{C min}^{-1}$. The interface temperature of the MS was maintained at 280 $^\circ\text{C}$ and ion source temperature was maintained at 250 $^\circ\text{C}$. Helium was used as carrier gas (3 ml min^{-1}). The total run-time was 24 min. Data analysis was done by data processing software Shimadzu GC-MS solution Version 2.21.

Quantification, calibration and sensitivity

Quantification of organotins was performed by the internal standard procedure using TPrT (Tripropyltin) as internal standard. Fresh standards were prepared to obtain calibration curves. Procedural blanks and standards were carried out for every set of 12 samples. To keep a check on the quality of analysis, an in house sediment reference material was analyzed with every alternate set of samples. Linear regression coefficient displayed a suitable linear correlation ($R^2 > 0.975$). The results obtained for the percentage recovery for MBT, DBT and TBT was 99, 86 and 96 percent and relative standard deviation was 8, 10 and 5 respectively. These analyses showed adequate repeatability and precision for all the components. The minimum detection concentration for butyltins was 0.2 ng Sn g^{-1} .

Estimation of Organic carbon

Particulate organic carbon (POC) of the suspended particulate matter was analysed following the method of Parsons et al. (1984). Sediment samples were treated with 1 N HCl, and then analysed for the total organic carbon (TOC) by the CNS analyzer (Thermo electron corporation, Flash EA, 1112 series).

Results and Discussion

Butyltins in surface seawaters

The concentrations of POC, TBT, DBT and MBT for water samples in the Mandovi and Zuari estuary are presented in Table 1. Concentrations of POC varied from 1.5 to $4.5 \mu\text{g l}^{-1}$ and from 0.3 to $2.5 \mu\text{g l}^{-1}$ in the Mandovi and Zuari estuaries, respectively. For the water samples, the TB varied from 12 to 73 ng l^{-1} and 0.5 to 77 ng l^{-1} in the Mandovi and Zuari estuaries, respectively. TBT varied from 1 to 37 and 0.2 to 46 ng Sn l^{-1} and DBT from 1 to 6 and 0.05 to 13 ng Sn l^{-1} for the Mandovi and Zuari estuaries respectively. TBT levels were highest for the waters of station 5 (37 ng Sn l^{-1}) of the Mandovi estuary

and station 2 (46 ng Sn l^{-1}) of the Zuari estuary. At both these locations, shipbuilding units are located. These shipbuilding units are involved in construction, overhauling, maintenance, painting and repairs of all kinds of vessels. The high levels of TBT are most likely associated with the leaching from boats and paint waste and effluents from the shipyard in to the estuary. The other sampling sites in both the estuaries recorded low levels of butyltins, probably due to lesser maritime activities. At many of the sampling stations in both the estuaries, MBT was predominant component of TB. The MBT concentrations varied between 10 and 29 ng Sn l^{-1} and accounted for more than 70% to the total butyltins in the Mandovi estuary. A similar trend was recorded for the distribution of MBT in the Zuari estuary with exception of stations 3, 5 and 9. The observed higher abundance of MBT in these estuaries was probably because TBT is more hydrophobic and is less soluble in water as compared to DBT and MBT (Rajendran et al. 2001) or the degradation of TBT to DBT and MBT in the aquatic system via dealkylation by UV photolysis and microbial degradation (Alzieu 2006). Faster degradation of TBT in tropical water may be yet another reason for the abundance of MBT in the Mandovi and the Zuari estuaries (Gomez-Ariza et al. 1998; Rajendran et al. 2001). But recent evidence for direct inputs of DBT and MBT in to the aquatic system has been reported (Hoch 2001) as a result of leaching from PVC materials.

The mean concentration of TBT, DBT and MBT in the seawater shows a distinct distribution pattern of these compounds in the two estuaries. The mean MBT values (Table 1) for the Mandovi estuary were higher (17 ng Sn l^{-1}) than those of DBT (2 ng Sn l^{-1}) and TBT (6 ng Sn l^{-1}). Whereas, for the Zuari estuary the mean MBT values (Table 1) were lower (7 ng Sn l^{-1}) than that of TBT (8 ng Sn l^{-1}) but higher than DBT (3 ng Sn l^{-1}). However, the mean TB value was higher for the Mandovi waters (24 ng Sn l^{-1}) compared to the Zuari waters (18 ng Sn l^{-1}) indicating that the Mandovi waters are more contaminated. A wide range of butyltins suggests localized areas of contamination and the present TB values are consistent but lower than those reported earlier (Bhosle et al. 2004). Rajendran et al. (2001) reported TB values ranging from 5 to 58 ng l^{-1} from Tuticorin harbour along the east coast of India. In the present study the concentrations of TBT in the Mandovi and Zuari estuaries exceed the UK environment quality standard for seawater, 2 ng l^{-1} (UK Department of the environment 1989), an aquatic life advisory

concentration of 10 ng l⁻¹ (US EPA 1985), and the Canadian water quality guideline of 1 ng l⁻¹ (CCME 1992).

TBT exhibits both lipophilic and ionic properties (Arnold et al. 1997; Blanca 2008). This means TBT levels will be influenced by the concentrations of total lipids and organic carbon. TB concentrations in water samples showed a good positive correlation with POC for Mandovi ($R^2 = 0.724$, $p < 0.01$) and Zuari ($R^2 = 0.781$, $p < 0.01$) estuaries.

Butyltins in the sediments

The concentrations of TOC, TBT, DBT and MBT in the sediment samples are shown in Table 2. TOC for the sediments ranged between 0.7 and 4.7 %, and 0.2 and 4.8 % for the Mandovi and Zuari estuaries respectively. TB for the sediments varied from ~16 to 118 and ~ 6 to 119 ng Sn g⁻¹ dw of sediment for the Mandovi and Zuari estuaries, respectively. As compared to the water samples, concentrations of butyltins were relatively higher in surface sediments. The transport of TBT associated with suspended particles from water column to the bottom sediments could be the reason for higher levels of TBT in the sediments (Rajendran et al. 2001; Blanca 2008).

TBT was predominant in most of the sediment samples of both these estuaries, with the highest level of TBT observed for Mandovi estuary at stations 5 (43 ng Sn g⁻¹ dw) and for the Zuari estuary at station 2 (61 ng Sn g⁻¹ dw). Both these station have small- scale shipbuilding units. Release of TBT containing waste material from these units may be responsible for the higher concentration of TBT. Relatively low levels of TBT (10 to 26 ng Sn g⁻¹ dw) were recorded at other locations of both the estuaries. Interestingly, at some of the sampling sites, the concentrations of MBT were higher than that of TBT (Table 2). Station 1 of the Mandovi estuary had the highest level of MBT (34 ng Sn g⁻¹ dw) and very low level of TBT (0.2 ng Sn g⁻¹ dw). This is a site where treated municipal wastewater is released into Mandovi estuary. Greater concentration of MBT indicates microbial or photolytic degradation of TBT to MBT and/or direct release of MBT containing wastewater (Rajendran et al. 2001).

For the sediments of the Zuari estuary, although TBT was highest at station 2, the total butyltins was highest at station 5 (119 ng Sn g⁻¹ dw) followed by station 6 (116 ng Sn g⁻¹

dw). This was due to the presence of higher levels of MBT and DBT at both these sites. Similar trends were recorded at stations 1, 3, 4, 7, 8 and 9. Most of these sites are located at small old jetties, for berthing small boats and barges used for the transport of ores. Therefore higher levels of DBT and MBT strongly indicate presence of historic TBT inputs in the sediments.

The mean TBT values for the Mandovi estuary sediments were higher (17 ng Sn g^{-1}) than those of DBT (8 ng Sn g^{-1}) and MBT (12 ng Sn g^{-1}). For the Zuari estuary the mean MBT values were higher (24 ng Sn g^{-1}) than that of TBT (15 ng Sn g^{-1}) and DBT (11 ng Sn g^{-1}). However the mean concentration of TB in the sediments indicates the Zuari estuary sediments ($50 \text{ ng Sn g}^{-1} \text{ dw}$) being more contaminated compared to Mandovi estuary sediments ($38 \text{ ng Sn g}^{-1} \text{ dw}$).

A fairly good significant positive correlation was observed between the total organic carbon (TOC) and TB for both Mandovi ($R^2 = 0.726$, $p < 0.01$) and Zuari ($R^2 = 0.639$, $p < 0.05$) estuaries. We also observed a significant correlation ($R^2 = 0.891$, $p < 0.001$) between the concentrations of TB in sediments and in overlying waters of the Mandovi estuary. It is apparent from these relationships that adsorption/desorption processes played important role in controlling the levels of TB in sediments of both the estuaries and waters of the Mandovi estuary. A positive but not very significant correlation ($R^2 = 0.371$, $p < 0.1$) was observed between the concentrations of TB in water and sediment samples of the Zuari estuary perhaps due to the effects of tide and currents.

In India we do not have any guidelines for TBT contaminations. According to Australian sediment quality guidelines TBT values of 5 ng g^{-1} and $70 \text{ ng g}^{-1} \text{ dw}$ of sediment indicate low and high trigger values, respectively (ANZECC/ARMCANZ 2000). Out of the 19 sediment samples from both Mandovi and Zuari estuaries, all the sediment samples contained TBT concentration less than the suggested high trigger value, while 6 of the samples contained TBT levels lower than the low trigger value. Even at low levels ($< 10 \text{ ng l}^{-1}$) TBT can cause endocrine disruption, resulting in imposex, especially in gastropods (Hoch 2001, Blanca 2008). The observed levels of TBT compounds in both the estuaries are higher than those known to induce imposex. Moreover, imposex has been recorded in gastropods collected from Mormugao harbour (Bhosle 2007). Bhosle (2006) reported that oysters, mussels, clams and fish collected from nearby Mormugao harbour were

contaminated with TBT, and TBT can suppress the normal functioning of the immune system of mammals. In view of this, it is possible that the benthic biota especially shellfish, in these areas could be contaminated with TBT and may pose a threat to human health.

Degradation of TBT

The degradation of butyltin in the aquatic system is via dealkylation by UV photolysis and microbial degradation, and takes place in following steps, TBT → DBT → MBT and inorganic tin. For assessing the degradation of TBT, a degradation index for BT was calculated based on the following equation (Diez et al. 2006).

$$BTs \text{ deg}(\%) = \left[1 - \left(\frac{TBT}{TBT + DBT + MBT} \right) \right] \times 100$$

The lowest degradation index values suggest a recent input of TBT. As observed in figure 2, TBT degradation index was higher for the waters of the Mandovi estuary (Fig. 2a) as compared to sediments. Degradation index for the waters of the Mandovi estuary was > 80% for all the areas sampled, except for station 5 (48%). Bacterial susceptibility to TBT biodegradation has been reported earlier by Harino et al. (1997), and also warmer ambient temperature and intense sunlight are likely responsible for higher degradation index of TBT in the waters. The degradation index of TBT in the sediments was lowest (~ 20%) for stations 6, 7, 8 and 9 indicating recent inputs (Fig. 2a) while it varied between 60 to 85 % for the rest of the sampling sites. It has been reported TBT is highly adsorbed to sediment that are fine textured with abundant organic carbon (Burton et al. 2004) thus minimizing the bioavailable fraction amenable to degradation. In case of Zuari estuary (Fig. 2b) the TBT degradation index was > 60% for most of the water as well as sediment samples. It was lowest for waters of station 3 (~ 20%) followed by the water as well as sediment at station 2 (~ 40 %).

Conclusions

The levels of TBT observed both in water and sediments appear to reflect the activities performed at all the sites sampled and some of the areas showed contamination levels high enough to pose a risk to aquatic and benthic organisms. In view of this, it is necessary to form legislations to control the usage of TBT compounds in order to reduce their level in marine waters of India.

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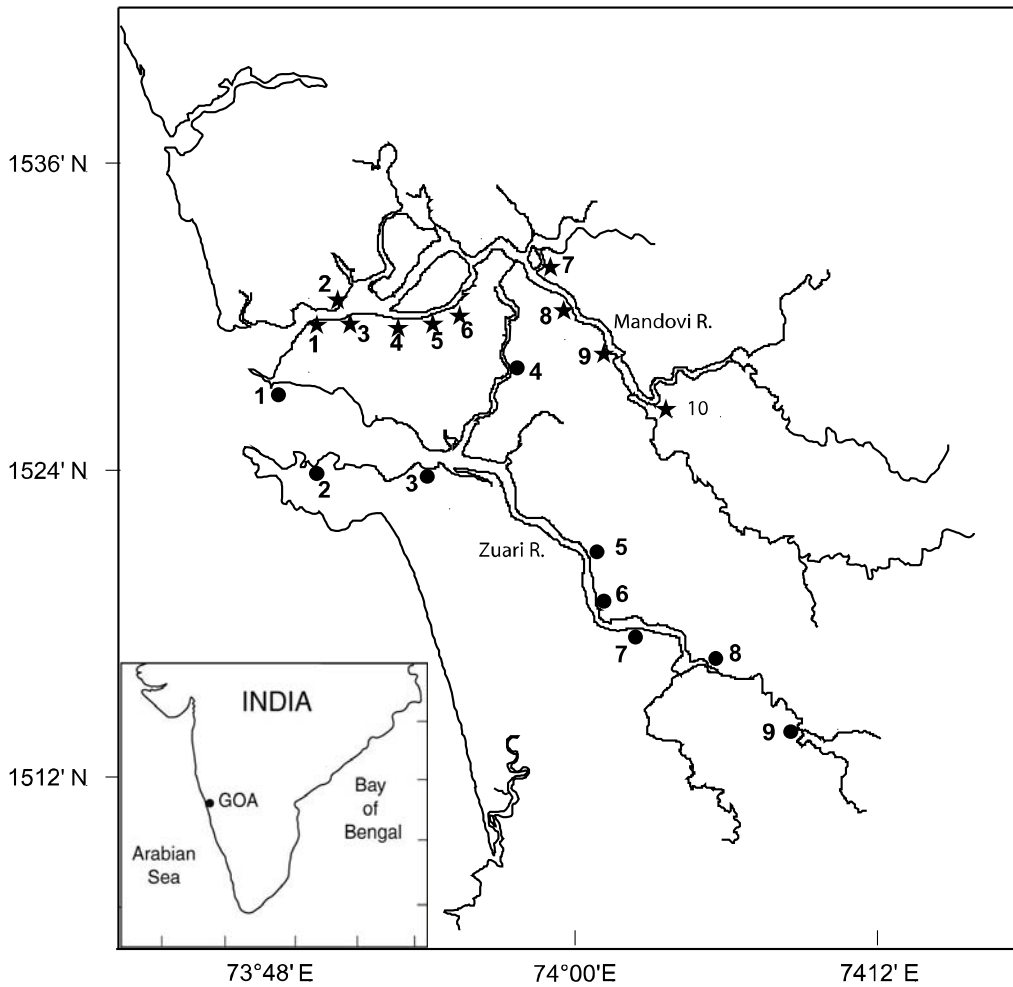
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Table 1 Concentrations (ng Sn l^{-1}) of TBT, DBT, MBT, total butyltin (TB), and particulate organic carbon (POC $\mu\text{g l}^{-1}$) in the surface waters collected from various stations in the Mandovi and Zuari estuaries during November 2007

Area	Stations	TBT	DBT	MBT	TB	POC
Mandovi estuary	1 Campal creek	1 \pm 0.0	2 \pm 0.0	10 \pm 0.8	12	1.5 \pm 0.1
	2 Fish Jetty (Malim)	2 \pm 0.3	1 \pm 0.0	18 \pm 2.8	22	2.7 \pm 0.2
	3 Capt of Ports Jetty	1 \pm 0.2	1 \pm 0.1	23 \pm 1.7	25	2.2 \pm 0.1
	4 Ribandar Ferry	3 \pm 0.4	1 \pm 0.1	15 \pm 0.4	19	3.2 \pm 0.3
	5 Dempo Shipyard	37 \pm 0.7	6 \pm 0.1	29 \pm 2.2	73	4.5 \pm 0.1
	6 Old Goa Jetty	4 \pm 0.4	1 \pm 0.3	18 \pm 5.6	23	2.5 \pm 0.0
	7 Amona	2 \pm 0.5	1 \pm 0.1	16 \pm 1.8	21	2.1 \pm 0.1
	8 Betqui	2 \pm 0.1	2 \pm 0.1	12 \pm 3.0	16	2.2 \pm 0.2
	9 Bambai	1 \pm 0.4	2 \pm 0.3	18 \pm 1.0	22	1.8 \pm 0.3
	10 Savoi Verem	2 \pm 0.5	1.6 \pm 0.0	12 \pm 0.2	16	2.5 \pm 0.5
Mean		6	2	17	24	
Zuari estuary	1 Dona Paula	1 \pm 0.0	0.05 \pm 0.0	8 \pm 0.8	10	0.9 \pm 0.0
	2 Chicalim	46 \pm 2.3	13 \pm 0.4	18 \pm 2.8	77	2.5 \pm 0.4
	3 Cortalim	14 \pm 1.1	3 \pm 0.9	1 \pm 0.1	18	1.1 \pm 0.0
	4 Cumarjua canal	2 \pm 0.3	0.3 \pm 0.0	19 \pm 0.4	21	1.6 \pm 0.4
	5 Borim	5 \pm 0.6	5 \pm 0.5	0.6 \pm 0.2	11	1.1 \pm 0.3
	6 Shiroda	2 \pm 0.0	0.9 \pm 0.1	2.3 \pm 0.1	5	1.4 \pm 0.2
	7 Curtorim	0.8 \pm 0.0	0.2 \pm 0.0	8.5 \pm 1.8	9	1.0 \pm 0.3
	8 Sanvordem	1 \pm 0.1	1 \pm 0.1	3.7 \pm 1.0	6	1.1 \pm 0.1
	9 Sanguem	0.2 \pm 0.1	0.3 \pm 0.0	0.0 \pm 0.0	0.5	0.3 \pm 0.1
Mean	8	3	7	18		

Table 2 Concentrations (ng Sn g⁻¹) of TBT, DBT, MBT, total butyltin (TB), and total organic carbon (TOC %) in the sediments collected from various stations in the Mandovi and Zuari estuaries during November 2007

Area	Stations	TBT	DBT	MBT	TB	TOC
Mandovi estuary	1 Campal creek	0.2 ± 0.1	1 ± 0.0	34 ± 3.3	35	3.3 ± 0.2
	2 Fish Jetty (Malim)	23 ± 1.4	17 ± 7.0	15 ± 8.4	55	3.3 ± 0.1
	3 Capt of Ports Jetty	6 ± 0.0	2 ± 0.0	8 ± 0.8	16	0.7 ± 0.1
	4 Ribandar Ferry	4 ± 0.5	7 ± 0.1	10 ± 1.1	22	2 ± 0.1
	5 Dempo Shipyard	43 ± 1.7	43 ± 2.8	32 ± 3.5	118	4.7 ± 0.3
	6 Old Goa Jetty	26 ± 2.1	4 ± 0.6	3 ± 1.2	33	2.8 ± 0.2
	7 Amona	12 ± 0.5	1 ± 0.1	2 ± 0.5	15	2.0 ± 0.1
	8 Betqui	24 ± 1.5	1 ± 0.3	5 ± 2.5	29	2.3 ± 0.2
	9 Bambai	25 ± 2.8	3 ± 0.1	3 ± 1.0	31	2.9 ± 0.2
	10 Savoi Verem	10 ± 10	5 ± 0.3	10 ± 0.5	25	1.6 ± 0.1
Mean		17	8	12	38	
Zuari estuary	1 Dona Paula	4 ± 0.1	1 ± 0.1	24 ± 0.3	30	0.2 ± 0.0
	2 Chicalim	61 ± 3.1	21 ± 2.3	15 ± 0.2	98	3.3 ± 0.1
	3 Cortalim	10 ± 0.5	12 ± 0.3	18 ± 0.7	39	1.0 ± 0.1
	4 Cumarjua canal	2 ± 0.1	1 ± 0.2	4 ± 0.5	7	1.1 ± 0.1
	5 Borim	22 ± 1.0	29 ± 0.8	67 ± 1.5	119	4.8 ± 0.3
	6 Shiroda	24 ± 2.1	29 ± 0.7	63 ± 2.5	116	4.6 ± 0.3
	7 Curtorim	2 ± 0.0	3 ± 0.2	6 ± 0.7	11	2.5 ± 0.2
	8 Sanvordem	11 ± 0.1	0.5 ± 0.5	16 ± 2.0	28	3.3 ± 0.2
	9 Sanguem	2 ± 0.1	1 ± 0.4	3 ± 0.2	6	0.5 ± 0.1
Mean	15	11	24	50		



- ★ Mandovi stations
 1. Campal creek, 2. Fish jetty, 3. Capt. of ports jetty, 4. Ribandar ferry,
 5. Dempo Shipyard, 6. Old Goa jetty, 7. Amona, 8. Betqui,
 9. Savoi Verem 10. Bambai
- Zuari stations
 1. Dona Paula 2. Chicalim 3. Cortalim 4. Cumbarjua canal
 5. Borim 6. Shiroda 7. Curtorim 8. Sanvordem
 9. Sanguem

Fig. 1 Sampling locations along the Mandovi and Zuari estuaries on the west coast of India.

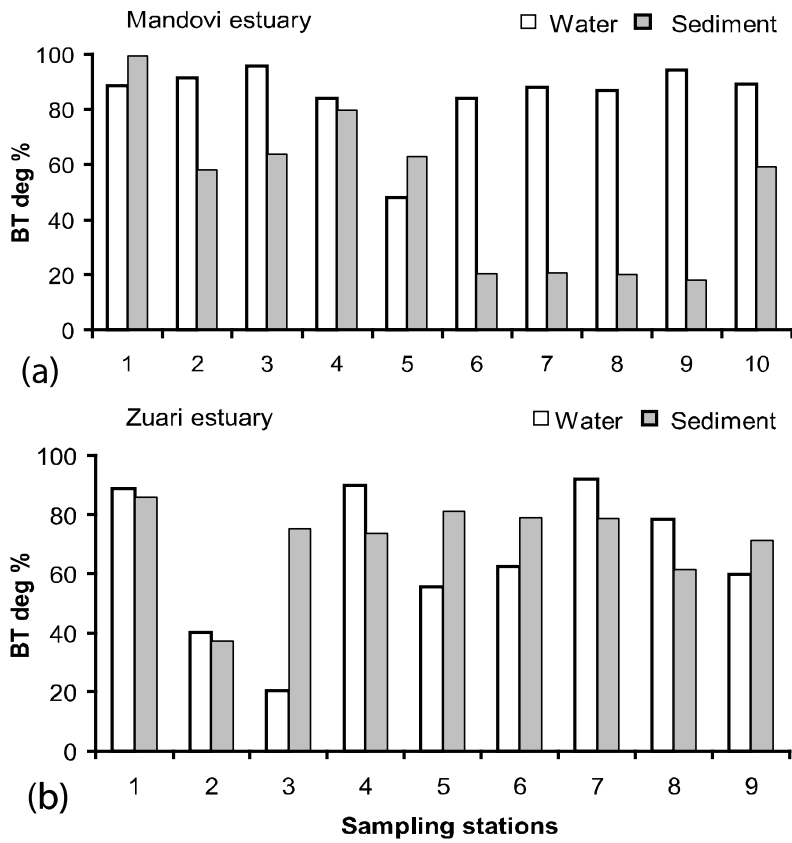


Fig. 2 Butyltin degradation index for the Mandovi (a) and Zuari (b) estuaries.