Bull Environ Contam Toxicol (2009) 82:586–589
DOI 10.1007/s00128-009-9634-7

Seasonal Variation in Organotins in the Waters of the Dona Paula Bay, West Coast of India

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Received: 30 July 2008 / Accepted: 2 January 2009 / Published online: 21 January 2009

Abstract Surface seawaters from the Dona Paula Bay, were collected at weekly intervals during March 2007 to March 2008, and analyzed for butyltins (BT) such as tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT) using a GC–MS system. The mean concentrations of TBT, DBT, MBT and total BT varied from <1–37, 4–19, 6–28 and 21–84 ng Sn L^{-1}, respectively. Highest levels of BTs were recorded during May followed by April 2007 and March 2007 probably because the shipping and tourism activities are very high during these months.

Keywords TBT · DBT · MBT · West coast of India

Organotins have been used as active agents in wide range of applications including stabilizers in the PVC industry, plastic additives, industrial catalysts, insecticides, fungicides, bactericides, wood preservatives and antifouling paints (Hoch 2001; Bhosle 2006). These tributyltin (TBT) containing antifouling paints are highly effective in controlling fouling on industrially useful surfaces. These paints are the main source of organotins in coastal waters. When released into water, organotins, especially TBTs are highly toxic even at few ng L^{-1} to non-target organisms (Alzieu 2006; Bhosle 2007). Exposure to Organotins can cause growth reduction in mussels (Salazar and Salazar 1991), larval mortality (Tanabe et al. 2000; Zhou et al. 2003), shell thickening in oysters (Alzieu et al. 1986), imposex in gastropods and snails (Law et al. 1998; Zhou et al. 2003; Evans et al. 2000; Gomez-Ariza et al. 2006) and immunological dysfunction in fishes (Zhou et al. 2003). The usage of TBT-based antifouling paints is estimated to save the shipping industry about 6 billion dollars per annum, and also results in annual fuel saving of 7 million tones per year (Bhosle 2007).

In India, TBT containing paints are used to control fouling on the hull of ships, and there is no control on the usage of organotins. Despite this, little is known about the distribution of organotins in waters of India (Rajendran et al. 2001; Bhosle et al. 2004). In view of this, the present study was carried out to assess the seasonal variation of butyltins (BT) in the seawaters of Dona Paula Bay, west coast of India.

Materials and Methods

The sampling station, Dona Paula Bay (15°27′N, 73°N, 48′E) is located along the west coast of India (Fig. 1), and is situated very close to the Marmugoa harbour. Surface seawater (~1 m) was collected at weekly intervals using a clean polycarbonate-sampling bottle. The samples were transported to the nearby laboratory, and processed immediately as described below.

Monobutyltin (MBT), dibutyltin (DBT), TBT and Tropolone were purchased from Aldrich (USA); all the compounds were of 95%–98% purity. Tripropyltin chloride (TPrTCL, 98%) was obtained from Merck (Germany), and was used as internal standard. Flurosil, diethyl ether, Mg metal, bromopentane were purchased from Sigma. Pentyl magnesium bromide (Grignard reagent) was freshly prepared in the laboratory. All other chemicals were analytical grade and were purchased from Qualigens, India. Standard solutions of the BT were prepared in methanol.

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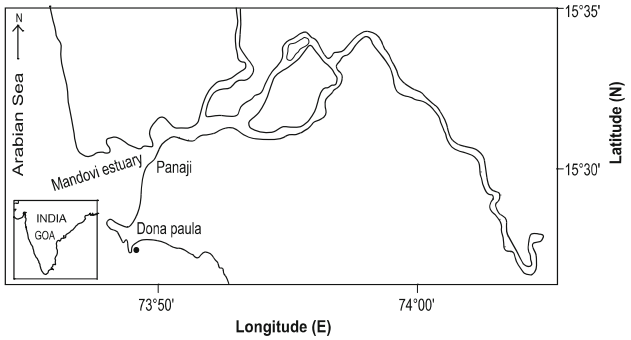

Fig. 1 Sampling site, Dona Paula Bay (west coast of India)

BT 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 min 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 min at room temperature. The excess Grignards reagent was destroyed by adding drop-by-drop 2 mL of deionized water. The derivatized organotins were extracted twice with 2 mL of *n*-hexane and 5 mL of 1 M H_2SO_4. Then as a clean up step, the sample was reduced to 0.5 mL under a stream of nitrogen gas. The concentrated sample was then loaded onto activated flurosil column and eluted with 10 mL of 1:1 hexane–toluene mixture. The eluant was finally evaporated to 0.1 mL under the stream of nitrogen and analyzed by GC–MS.

BT were separated and quantified using the GC–MS system (Simadzu Model-QP 2010) equipped with a electron impact ionization mode (70 eV) mass detector, using selected ions monitoring mode. Capillary column Rtx-5 (30 m length × 0.32 mm i.d. × 0.25 μm thickness) was use for quantification. Data analysis was done by data processing software installed in GC–MS. The relative response factors were checked by injecting standard mixture on regular basis. Peak identification was based on matching of retention times (±0.5%) and isotopic mass ratios (±20%) for diagnostic ions (Table 1).

Table 1 GC–MS SIM (selected ions monitoring) operation with the following program (dwell time was 200 ms for all ions)

Ion	Retention time (min)	*m/z*
TPrT	9.2	277, 275, 273
TBT	11.7	305, 303, 301
DBT	13.4	319, 317, 315
MBT	14.3	319, 317, 315

Table 2 Relative standard deviation (n = 8) and recovery for organotins

Compounds	RSD (%)	Recovery (%)
MBT	5.6	101
DBT	5.7	98.3
TBT	5.1	99.1

In water samples, the quantitative recoveries for BT compounds ranged between 98.33% and 101.11% and the relative standard deviation (RSD) of BTs were in the ranges of 5.17%–5.75%, with coefficient of variation of 5.13%–5.73% (Table 2). The detection limits of BTs were <1 ng L^{-1} as tin.

Results and Discussion

The distribution of BTs the seawater of Dona Paula Bay, west coast of India during the period of March 2007 to March 2008 is show in Table 3. The concentrations of TBT, DBT, MBT and BT varied between <1–36, 4–19, 6–27 and 20–83 ng Sn L^{-1}, respectively. Highest levels of TBT, DBT, MBT and BT were recorded during May 2007. Concentrations of BTs were generally high in summer (March to May) and low during the monsoon period (June to September). TBT was the most abundant (39%–43%) during pre-monsoon season, whereas MBT (29.2%–73.5%), during post monsoon period. This indicates some correspondence between the abundance of BT compounds and seasons. Seasonal changes in organotin levels have been frequently reported for water sample, and these changes have been related to seasonal changes in boating activities in the respective area (Evans and Huggett 1991; Champ 2000; Hoch 2001). In Marmugoa and Dona Paula Bay, the traffic due to ships and recreational boats is low during the monsoon season (June to September), and is high in October to May. Therefore, the observed high and low levels of the BT were probably associated with the increase or decrease in the traffic of ships and boats, and dilution of seawater due to river run-off during the monsoon season.

TBT level drastically decrease from October 2007 to March 2008. This contrasting trend was probably because all the recreational activities were stopped due to renovation and expansion of the Dona Paula jetty. Concentrations of DBT and MBT during October to March 2008 were relatively in high probably due to degradation of TBT. It is well known that TBT degradation is more rapid in sunlit

Table 3 Organotin TBT, DBT, MBT (ng Sn L^{-1}) concentrations in water sample of Dona Paula Bay, west coast of India during March 2007 to March 2008

Sampling months	TBT	DBT	MBT	∑BTs	TBT/∑BT
March-07	23.66 ± 4.6	12.81 ± 2.8	25.81 ± 2.8	62.20	0.38
April	30.01 ± 2.5	15.55 ± 2.5	25.25 ± 3.2	70.75	0.42
May	36.75 ± 4.1	19.25 ± 2.1	27.75 ± 2.5	83.75	0.44
June	14.81 ± 1.4	10.81 ± 2.2	15.61 ± 1.5	41.20	0.36
July	11.75 ± 1.5	8.75 ± 1.2	10.75 ± 1.7	31.25	0.38
August	16.75 ± 1.8	13.75 ± 1.5	27.25 ± 3.5	57.75	0.29
September	3.78 ± 0.1	11.68 ± 0.0	20.49 ± 1.4	35.94	0.11
October	11.71 ± 0.0	13.72 ± 0.9	21.34 ± 0.0	46.78	0.25
November	1.14 ± 0.1	6.70 ± 0.5	26.00 ± 2.2	33.85	0.03
December	1.71 ± 0.3	13.24 ± 0.4	7.01 ± 1.1	21.96	0.08
January-08	2.55 ± 0.2	4.28 ± 0.5	18.95 ± 1.2	25.78	0.10
February	2.31 ± 0.1	5.13 ± 0.6	17.04 ± 0.4	24.48	0.09
March	0.93 ± 0.1	13.65 ± 1.5	6.02 ± 0.7	20.60	0.05

Table 4 Distribution of TBT in water collected from various marine environments (ng Sn L^{-1})

	Study area	TBT (ng Sn L^{-1})	References
1	Dona Paula Bay	0.93–36.75	This study
2	Dona Paula Bay	10–89[a]	Bhosle et al. (2004)
3	Tuticorin harbour, west coast of India	0.3–30.4	Rajendran et al. (2001)
4	Korean coastal	5–164[a]	Choi et al. (2008)
5	Portugal coast	3–30	Diez et al. (2005)
6	Greece	2–70	Thomoaidis et al. (2007)
7	Japanese coast	3.9–27[a]	Murai et al. (2005)
8	France	0.9–280[a]	Michel and Averty (1999)
9	West coast of Spain	0.9–196	Alez (2006)

[a] TBT values in ng L^{-1}

estuarine waters. Moreover, TBT is more hydrophobic and less soluble in the seawater as compared to DBT and MBT (Rajendran et al. 2001). The TBT/∑BT ratio has been used as an approximate measure of the TBT degradation. A high TBT/∑BT ratio indicates little degradation or recent input of TBT in the marine environment (Thomoaidis et al. 2007). TBT ratio was higher during in March 2007 to August 2007 indicating recent inputs of TBT, thereafter it decreased from September 2007 to March 2008, except for October 2007, indicating low/old inputs. The observed concentrations of BTs in the Dona Paula Bay waters are comparable to those previously reported from India and coastal waters of many other countries (Table 4). The observed levels of TBT compounds are high enough to cause harmful effects in marine organisms and thus need to be monitored on a regular basis.

Acknowledgments The authors would like to thank Dr. Satish R. Shetye, the Director of the institute for their support and encouragement. We thank Dr. N. B. Bhosle for his guidance and correcting the draft of this MS. We are grateful to the European commission for financial supports under project (CLP 1674) INCO-CT-2005-510658 titled "TBT IMPACTS – Assessing the impacts of TBT on multiple coastal uses". We appreciate very much the help render by A. P. Selvam for the operation of Gas Chromatographic system during the course of the study. This is NIO contribution No. 4487.

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