Determination of butyl-, phenyl-, octyl- and tributylmonomethyltin compounds in a marine environment (Bay of Bengal, India) using gas chromatography-inductively coupled plasma mass spectrometry

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Organotin compounds (butyl-, phenyl-, octyl- and tributylmonomethyltin) and inorganic tin were quantified in sea-water and sediments from two harbours and several locations on the southeast coast of India using highly sensitive and selective gas chromatography-inductively coupled plasma mass spectrometry (GC-ICP-MS), adopting new extraction and analytical techniques with extremely low detection limits (water, 0.019–0.85 pg l^{-1}; sediment, 0.23–0.48 ng g^{-1}). The concentrations of monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT) in sea-water from Tuticorin harbour varied from 0.64 to 4.97, 3.0 to 26.8 and 0.3 to 30.4 ng Sn l^{-1}, respectively. MBT, DBT and TBT in sediments from harbour areas ranged from 1.6 to 393, 1.3 to 394 and ND (not detected) to 1280 ng Sn g^{-1} (dry weight), respectively. Natural methylation in both harbours was established by quantifying tributylmonomethyltin (TBMMT) residues (sea-water, ND–0.19 ng Sn l^{-1}; sediment, ND–765 ng Sn g^{-1} dry weight). In sea-water, octyltins were also determined as monooctyltin (MOT) > dioctyltin (DOT) > trioctyltin (TOT). Butyltin contamination in commercial harbours is evident, but other coastal waters are not contaminated with organotin residues. The high concentration of inorganic tin in estuarine sediment indicates an elevated rate of debutylation in the estuarine environment. Both methylation and debutylation of TBT in Chennai harbour were greater than in Tuticorin harbour. A significant correlation ($r^2 = 0.75$) between total butyltin and organic carbon contents in sediment was found. To our knowledge, this is the first report on the distribution of butyltins and methylated butyltin in sea-water and sediment and octyltins in sea-water in the Indian marine environment.

Introduction

Tributyltin (TBT) is an active ingredient of many bactericidal, fungicidal, insecticidal, acaricidal and wood preservation products. In 1971, it replaced copper oxide as an antifoulant paint additive. Since then it was used extensively on ship and boat hulls, cooling water pipes, docks, aquaculture cages and buoys to prevent attachment and growth of barnacles, algae, mussels, tube worms and other marine organisms until a partial restriction was enacted by some countries in the 1980s and early 1990s. Despite the partial restriction imposed by many countries, it has been estimated that around 1200 tons of TBT per year are still used for the protection of ship hulls.[1] TBT is the most effective antifoulant ever devised and brings enormous benefits to the shipping industry, because of reduced fuel costs and less frequent need to dry-dock and re-paint vessels estimated to be worth US$ 5.7 billion per annum during the mid-1990s.[2] However, a number of reports have documented that since the 1980s, extremely low environmental levels of TBT can cause lethal and sub-lethal effects on non-target organisms, e.g., imposex[3,4] or intersex[5] in several gastropod species; malformation in oysters (*Crassostrea gigas*),[6] increased mortality and retardation of growth in larvae of blue mussels (*Mytilus edulis*)[7] and disappearance of clams (*Scrobicularia plana*) in UK waters.[8]

Although the environmental level of TBT has decreased in some places,[4,6] it is still encountered in commercial harbours, marinas, near dry docks and boat wash-down facilities and busy shipping lanes.[9–11] It was reported that sedimentary concentration levels remained high owing to the long half-life.

Hwang *et al.*[12] reported the half-lives of TBT and dibutyltin (DBT) in sediments to be 6.9 and 11.6 years, respectively.

India has a long coastline, with 12 major harbours, of which five (Tuticorin, Chennai (formerly Madras), Visahapatnam, Paradip and Calcutta) are on the east coast. The shipping industry plays a vital role in India's economy, millions of tons of goods being handled in harbours every year. Studies on coastal pollution on both the east and west coasts of India have been carried out under the Coastal Ocean Monitoring And Prediction System (COMAPS) research project funded by the Department of Ocean Development, Government of India. Many workers have reported on organochlorine pesticides,[13] polychlorinated biphenyls (PCBs)[14] and trace metals[15] in the Indian marine environment. Butyltin residues in marine fishes,[16] marine mammals[17] and green mussels,[18] and imposex in a gastropod[19] (*Cronia konkanensis*) in Indian waters have also been reported. However, there has been no report on the distribution and fate of organotin compounds in water and sediment from coastal environs.

Furthermore, the use of butyltin-based antifoulant paint is not controlled in India and one of two harbours (*i.e.*, Tuticorin) is in the Gulf of Mannar region, which is India's first and most important marine bioreserve. This prompted us to carry out this preliminary survey to ascertain the distribution and fate of organotin compounds (butyl-, methylated butyl-, phenyl- and octyltins) in sea-water and sediments in two major harbours and several coastal locations on the east coast of India adopting the recently developed extraction methods for sea-water[20] and sediment[21] and analytical techniques such as improved programmed temperature vaporization (PTV) and a

shield torch under normal plasma conditions in GC-ICP-MS,[20] which enabled us to measure sub-picogram levels in sea-water.

Materials and methods

Study area

The study area and sample details are shown in Fig. 1 and Table 1, respectively. Chennai and Tuticorin harbours are the main commercial harbours chosen for this survey. Pondicherry, Cuddalore and Nagapatinam harbours are small, but commercial vessels visit occasionally. Ennore has a small fishing harbour and Mahabalipuram is only a tourist spot. Except in Chennai and Tuticorin harbours the sediment samples were collected between 0.5 and 2 nautical miles away from the harbours (coast).
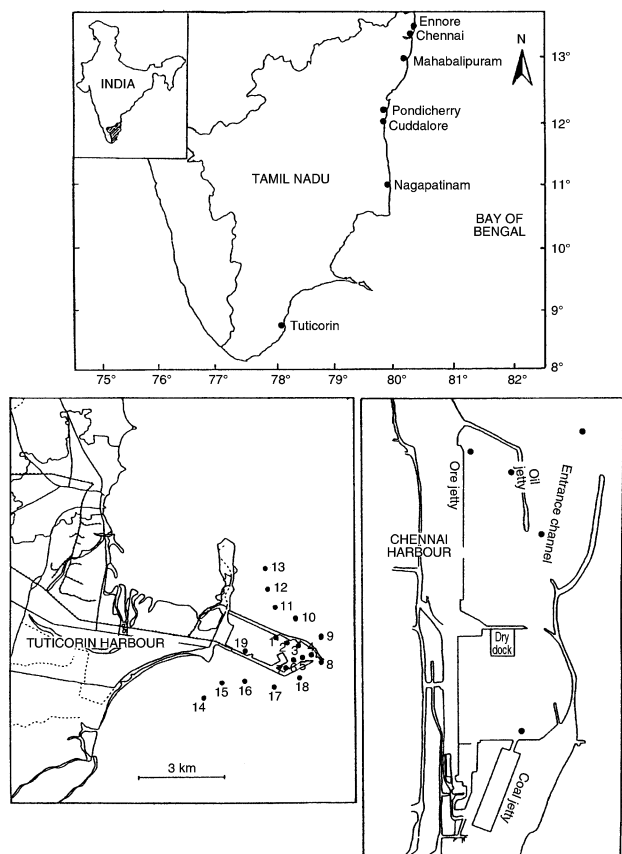
Sea-water and sediment

Much care was taken with glassware clean-up to avoid contamination. Briefly, sample bottles were cleaned with distilled water, then rinsed with concentrated HCl and kept overnight. Other glassware (Pasteur pipettes, centrifuge tubes, *etc.*) were soaked in 10% soap solution and subsequently (after washing) with 10% HNO_3 overnight. Finally, all the glassware was cleaned with distilled water, Milli-Q-purified water and acetone (pesticide grade) serially and dried in a clean room and packed in new polyethylene bags.

Sea-water samples were collected on October 4, 1999 from 10 locations in Tuticorin harbour area in pre-cleaned Pyrex glass bottles of 200 ml capacity without filtration and acidification. The bottles were rinsed thoroughly with the sample water before acquisition of samples. Plastic material was avoided to minimize contamination of samples by leaching of organotin compounds used as stabilizers. Water samples were collected 0.3 m below the surface to prevent the inclusion of the surface

Table 1 Details of sampling locations on southeast coast, India

Location		Date	Latitude	Longitude	Depth/m
Chennai harbour		13.8.1999			
	Open sea		13°07′43″	80°20′55″	20
	Entrance channel		NA[a]	NA	21
	Coal jetty		13°06′71″	80°18′18″	12
	Oil jetty		13°06′29″	80°18′19″	20
	Ore jetty		13°06′18″	80°18′05″	7
Tuticorin harbour		04.10.1999			
Station	1		08°45′12″	78°12′51″	NA
	2		08°45′09″	78°13′03″	NA
	3		08°45′05″	78°13′14″	NA
	4		08°44′55″	78°13′33″	NA
	5		08°44′50″	78°13′21″	NA
	7		08°44′39″	78°13′03″	NA
	19		08°44′59″	78°12′14″	NA
	8		08°44′45″	78°13′43″	NA
	9		08°45′13″	78°13′42″	NA
	10		08°45′36″	78°13′12″	NA
	11		08°45′51″	78°12′50″	NA
	12		08°46′10″	78°12′41″	NA
	13		08°46′35″	78°12′37″	NA
	14		08°44′05″	78°11′27″	NA
	15		08°44′21″	78°11′47″	NA
	17		08°44′18″	78°12′46″	NA
	18		08°44′29″	78°13′17″	NA
Coastal waters					
1	Ennore	03.9.1999	13°14′10″	80°20′21″	5
2	Ennore	03.9.1999	13°14′10″	80°25′25″	19
3	Ennore	03.9.1999	13°14′10″	80°30′30″	45
4	Ennore estuary	14.9.1999	13°13′92″	80°19′50″	3
5	Ennore	11.7.1999	13°13′55″	80°20′80″	9
6	Ennore	11.7.1999	13°13′55″	80°21′98″	17
7	Mahabalipuram	03.9.1999	12°28′58″	80°09′88″	5
8	Pondicherry	31.8.1999	11°54′70″	79°50′50″	7
9	Pondicherry	31.8.1999	11°54′70″	79°52′75″	19
10	Cuddalore	02.9.1999	11°42′45″	79°47′26″	5
11	Nagapatinam	01.9.1999	10°45′75″	79°51′80″	5
12	Nagapatinam	01.9.1999	10°45′75″	79°53′50″	9

[a]Not available. Tuticorin harbour: stations 1–7 and 19, inner harbour; station 8, entrance channel; stations 9–18, outer harbour.

microlayer, kept in an ice box and brought under cold conditions (4 °C) to the laboratory and stored at 4 °C in the dark until chemical extraction. Adsorption of tributyltin (TBT) was not observed in non-acidified water in Pyrex glass bottles stored at 4 °C for over 5 months[22] and it was stable for 7 months when kept at 4 °C in polycarbonate bottles without the addition of acid.[23]

Surface sediments were collected from harbours (21 samples), open sea (11 samples) and estuary (one sample) with the help of the DOD's (Department of Ocean Development, India) coastal research vessel *Sagar Purvi* between July and October, 1999, using a grab sampler, in clean polyethylene bags, sealed and brought to the laboratory under cold conditions (4 °C) using an ice-box and deep-frozen (−20 °C) in the dark in the laboratory until chemical extraction. TBT was found to be stable in wet sediment samples stored at 4 °C and in frozen sediment for 4 months.[23] Both water and sediment samples were stored at the Institute for Ocean Management (IOM), Anna University, India before being brought (with dry-ice packing) to the National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan for extraction and instrumental analyses.

Reagents and chemicals

Monobutyltin trichloride (MBT, ∼95%), monophenyltin trichloride (MPT, ∼98%), diphenyltin dichloride (DPT, ∼96%) and tripentyltin chloride (TPeT, ∼96%) were purchased from Aldrich (Milwaukee, WI, USA). Dibutyltin dichloride (DBT, ∼97%) and tributyltin chloride (TBT, ∼95%) were obtained from Wako (Osaka, Japan). Triphenyltin chloride (TPT,

Fig. 1 Map of study area and sampling sites at Tuticorin and Chennai harbours.

~97%) was purchased from Kanto Chemicals (Tokyo, Japan). Tripropyltin chloride (TPrT, ~98%) and tetrabutyltin (TeBT, ~95%) were purchased from Merck (Darmstadt, Germany). Monooctyltin trichloride (MOT, ~95%), dioctyltin dichloride (DOT, ~95%) and trioctyltin chloride (TOT, ~95%) were purchased from AZmax (Chiba, Japan). Monobutyltrimethyltin (MBTMT, ~99%), dibutyldimethyltin (DBDMT, ~99%) and tributylmonomethyltin (TBMMT, ~99%) were obtained from Tokyo Kasei Kogyo (Tokyo, Japan).

Sodium tetraethylborate (NaBEt$_4$, ~98%) was purchased from Strem Chemicals (Newburyport, MA, USA). Hydrochloric acid, acetic acid and ammonia solutions were of ultrapure grade (Merck). Sodium chloride, anhydrous sodium sulfate, tropolone (~95%), methanol and toluene were procured from Wako.

Stock standard solutions of individual organotin compounds (1 g l^{-1} as Sn) were prepared by dissolving appropriate amounts of the respective compounds in methanol (pesticide analysis grade) and stored at 4 °C in the dark until use. Working standard solutions were prepared each time by dilution of an aliquot of the stock standard solutions. TPrTCl was used as an internal standard for both sample preparation and GC-ICP-MS determination. A 5% m/v aqueous solution of NaBEt$_4$ was prepared and purified according to Tao et al.[20] Acetate buffer (1 mol l^{-1}, pH 5) was prepared by mixing acetic acid and ammonia solution. A 1 mol l^{-1} HCl–methanol solution was prepared by mixing concentrated HCl with methanol. Sodium chloride and anhydrous sodium sulfate were heated at 500 °C for 20 h to decompose organotin impurities. Tropolone solution (0.1% m/v) was freshly prepared in toluene for each batch of extraction and used without purification. The water used throughout the experiments was obtained from a Milli-Q water purification system (Milli-Q-ICP-MS, Nihon Millipore Kogyo, Tokyo, Japan). Xe gas (981 ppm diluted in Ar gas) from Takachiho Kagaku (Tokyo, Japan) was used for optimization of the ICP-MS parameters. Sediment certified reference materials (CRMs), PACS-2 and NIES No. 12 were obtained from the National Research Council of Canada and the National Institute for Environmental Studies of Japan, respectively.

Sample extraction

Sea-water was extracted according to the method of Tao et al.[20] with slight modifications. Briefly, 0.07 ml of acetic acid (1 + 1) and 0.4 ml of 1 mol l^{-1} acetate buffer were added to ~200 ml of water sample in a narrow-necked bottle and the pH was adjusted to 5. Then, 100 μl of internal standard (TPrT, 5 μg l^{-1}) and 0.5 ml of 5% NaBEt$_4$ were added. Finally 10 ml of hexane were added and stirred for 30 min using a Teflon magnetic stirring rod at room temperature. Then, Milli-Q-purified water was added gently to recover the organic phase inside the narrow neck. After clear phase separation, the hexane layer was collected with a Pasteur pipette in a glass-stoppered centrifuge tube and mixed with 2 g of anhydrous Na$_2$SO$_4$ and shaken manually for 1 min to remove traces of water, if any. After centrifuging (at 2000 rpm for 2 min), the extract was transferred into a preconcentration tube and condensed to 500 μl by passing argon gas (4 × 10^4 Pa) using a Turbovap II Concentration Workstation (Zymark, Hopkinton, MA, USA) at room temperature. The final extract was collected in a brown glass vial and kept in the dark at −20 °C until analysis by GC-ICP-MS.

Sediment samples were air dried, homogenized with a pestle and mortar and subjected to extraction. A new extraction procedure developed by us[21] was adopted. Briefly, 100 μl of a 3 μg ml^{-1} solution of internal standard (TPrTCl) were spiked into 0.5 g of sediment in a glass-stoppered tube. After 10 min, 2 g of NaCl, 12 ml of 0.1% tropolone solution in toluene and 10 ml of 1 mol l^{-1} HCl–methanol were added and extracted

using a mechanical shaker (vertical) for 60 min. After extraction, about 10 ml of pure water were added to the tube for phase separation and again shaken for 10 min, then the tube was centrifuged at 2000 rpm for 2 min and the extract (toluene layer) was collected in another tube and condensed to 5 ml by passing nitrogen gas (<1.4 × 10^4 Pa) using a Reacti-Vap evaporating unit (Model 18780, Pierce, Rockford, IL, USA). After concentration, 5 ml of 1 mol l^{-1} acetate buffer of pH 5, 15 ml of Milli-Q-purified water and 0.2 ml of 5% NaBEt$_4$ were added to the extract and shaken for ethylation and extraction for 10 min. After ethylation, the upper organic layer, which contained the compounds of interest, was collected in a tube after centrifuging, 2 g of anhydrous Na$_2$SO$_4$ were added and the mixture was shaken manually for 1 min to remove the water. Finally, a portion of the final extract was transferred to a brown glass vial and stored at −20 °C until analysis by GC-ICP-MS. Sediment organic carbon (OC) was calculated from total carbon (TC) by subtracting the inorganic carbon (IC).

Instrumentation

Organotin determination was carried out using a gas chromatograph (HP 6890, Agilent, Wilmington, DE, USA) equipped with PTV and pulsed splitless inlet systems coupled to an inductively coupled plasma mass spectrometer (HP4500, Agilent-Yokogawa, Tokyo, Japan) using a shield torch under normal plasma conditions. The analytical merits of the systems (PTV and shield torch) were reported previously.[20] The GC and ICP-MS systems were connected by a laboratory-made transfer line. Injections were made with an automatic injector (HP 6890 Series). The PTV and splitless inlet systems were used for water and sediment analysis, respectively. Optimum operating conditions for both PTV and splitless GC-ICP-MS with the transfer line were described by Tao et al.[20] and Babu Rajendran et al.,[21] respectively. The total and inorganic carbon concentrations in sediments were quantified using a Total Organic Carbon Analyzer (TOC-V Series SSM-5000A, Shimadzu, Japan).

Quality control

Both water and sediment samples were subjected to strict quality control procedures; a procedural blank was run simultaneously with each batch of five samples to ensure that potential laboratory and reagent contamination could be excluded. Plastic was not used throughout the sample extraction in order to avoid possible contamination by plastic additives and stabilizers. Sea-water samples spiked with 200 ng of each organotin species (butyl-, phenyl-, tripropyl- and tripentyltin) were processed as described previously. Recoveries of all the organotin species were good and ranged from 95 to 105%, except for diphenyltin (72.5%). In order to determine the recovery, the sediment samples were spiked with known concentrations of standard solutions of TBT, TPT and TPrT and the recoveries ($\pm s$) obtained were 102 $\pm$ 3.4, 99 $\pm$ 8.5 and 96 $\pm$ 3.4%, respectively. The method detection limit is defined as the concentration that would give three times the standard deviation of the peak areas for six replicates of the blank. The detection limit of each organotin species in water and sediment ranged from 0.019 to 0.85 pg l^{-1} and 0.23 to 0.48 ng g^{-1}, respectively. The sediment extraction method was validated using CRMs (PACS-2 and NIES No. 12). The concentrations obtained for DBT and TBT in PACS-2 and TBT in NIES No. 12 were in good agreement with the respective certified values and were discussed in an earlier paper.[21] Replicate analyses of spiked matrices revealed adequate precision with good recovery and repeatability. The concentration of the analyte was calculated by comparing the peak area of the analyte with that of the internal standard. Organotin concentrations given in this paper are expressed as tin, unless

stated otherwise, and on a dry weight basis for sediment and not corrected for the percentage recovery.

Results and discussion

Butyltin compounds

The concentrations of butyltin compounds in sea-water from Tuticorin harbour area are presented in Table 2. The MBT, DBT and TBT concentrations were higher in the inner harbour, varying from 0.8 to 4.97, 3.03 to 26.8 and 1.17 to 30.4 ng l^{-1}, than in the outer harbour, varying from 0.64 to 1.31, 3.98 to 8.60 and 0.30 to 5.16 ng l^{-1}, respectively. The concentrations in the harbour entrance channel decreased in the order TBT (13.3 ng l^{-1}) > DBT (4.48 ng l^{-1}) > MBT (1.94 ng l^{-1}). The mean concentrations of TBT and DBT in sea-water clearly show a distinct distribution pattern of these two compounds in the water column. The DBT mean values were higher (11.76 and 5.47 ng l^{-1}) than those of TBT (8.98 and 1.95 ng l^{-1}) in the inner and outer harbours, respectively. It is known that TBT is more hydrophobic and so less soluble in water and *vice versa* for DBT. The trend was opposite in the entrance channel and it was difficult to reach a conclusion with only one sample analysed. The distribution of TBT and DBT in the sediment compartment was the opposite to that in water and is discussed later.

In this study, TBT concentrations at two locations were well above the concentration reported to be toxic to many aquatic species. Stations 7 and 8 had 15 and six times higher values than the UK environmental quality standard (2 ng l^{-1}) and also seven and three times higher values than the Dutch government environmental quality limit (9.7 ng TBT$^+$ l^{-1}), respectively. Furthermore, the TBT concentrations in eight out of 10 samples (2.86–74.3 ng TBT l^{-1}) were greater than the toxicity threshold of 2 and 2.5 ng TBT l^{-1} that initiate the imposition of male sexual characteristics in the female mud snail (*Ilyanassa obsoleta*)[24] and *Nucella lapillus* and other stenoglassan gastropods,[3] respectively.

Butyl- and inorganic tin values in surface sediments are presented in Table 3. Sediment collected near the coal jetty in Chennai harbour contains very high concentrations of MBT, DBT and TBT (377, 394 and 867 ng g^{-1}, respectively), followed by the ore jetty and oil jetty. Sediment sampled near the coal jetty was clayey and black in colour, and rich in coal particles, which might be the reason for higher organic carbon content (12%). The mean concentrations of MBT, DBT and TBT in the inner harbour (coal, ore and oil jetty) were greater than in the harbour entrance channel (15.7, 22.5 and 36.7 ng g^{-1}, respectively) and decreased in another sediment sampled further away from the entrance channel, *i.e.*, open sea (8.34, 8.65 and 11.5 ng g^{-1}, respectively). Kan-Atireklap

et al.[18] recorded higher concentrations of TBT (150 ng g^{-1} wet weight) in green mussel (*Perna viridis*) collected from Chennai in 1994 than DBT (21 ng g^{-1} wet weight) and MBT (9 ng g^{-1} wet weight). They also reported higher butyltin residues in mussels collected from the east coast than the west coast of India. In Tuticorin, sediments from the inner harbour contain higher levels of butyltins, similarly to Chennai harbour, ranging from 19.5 to 393, 9.8 to 248 and 22.8 to 1280 ng g^{-1} for MBT, DBT and TBT, respectively. The sediments from the outer harbour, where vessels are anchored before berthing inside the harbour, contain lower levels of MBT, DBT and TBT, ranging from 1.6 to 4.96, 1.3 to 205 and ND (not detected) to 5.63 ng g^{-1}, respectively. The greatest DBT concentration of 205 ng g^{-1} found at station 10 in the outer harbour is two orders of magnitude higher than for other samples and also greater than three times the standard deviation of the mean. Therefore, this value was treated as an outlier and excluded from the mean calculation. The concentrations of MBT, DBT and TBT in the harbour entrance channel were 4.79, 1.70 and 5.93 ng g^{-1}, respectively. Owing to the water current, mixing and flushing are more efficient in the outer than the inner harbour, leading to lower values than those encountered in the inner harbour. Biselli et al.[25] reported lower TBT values in sea-water in North Sea marinas with strong water exchange than those in Baltic Sea marinas where the water exchange was restricted.

It was found that the sediment concentrations in Chennai and Tuticorin harbours exhibit similar trends between the inner and outer harbours. The butyltin concentrations in the outer harbour declined with distance from the source. The mean values of TBT, DBT and MBT reveal that the parent compound levels were greater than those of the metabolites, unlike in water. In addition, at Tuticorin the DBT/TBT ratio was always lower in sediments (Table 3) (inner harbour, 0.31; outer harbour, 1.08) than in water (Table 2) (inner harbour, 2.45; outer harbour, 6.99), and probably a similar ratio obtains for Chennai harbour also. The decreasing ratio of DBT/TBT from water to sediment observed in Tuticorin shows the transport of TBT associated with suspended particles in the water column and settling subsequently on the sediment surface as suggested by Valkirs et al.[26]

Langston and Burt[8] observed the disappearance of clams (*Scrobicularia plana*) from a number of locations in the UK, where the concentration of TBT in sediment approached 300 ng g^{-1} dry weight. In this study, a sediment TBT concentration of >300 ng g^{-1} dry weight was observed at one location in Chennai harbour and two locations in Tuticorin harbour, which could have some impact on sensitive benthic organisms.

One sediment sample collected from Ennore estuary, north

Table 2 Butyl-, tributylmonomethyl- and octyltins in sea-water from Tuticorin harbour area, India

Station	Concentration/ng Sn l^{-1}								
	MBT	DBT	TBT	TBMMT	MOT	DOT	TOT	DBT/TBT	TBMMT/TBT
1	0.972	7.49	2.12	0.029	0.149	0.026	0.009	3.53	0.014
3	1.91	5.25	1.46	0.055	0.244	0.111	0.005	3.60	0.038
5	1.07	3.03	1.17	0.015	0.247	0.042	0.007	2.59	0.013
7	0.802	26.8	30.4	0.175	1.93	0.503	0.186	0.88	0.006
19	4.97	16.2	9.72	0.193	0.112	0.037	–^{a}	1.67	0.02
Mean	1.95	11.8	8.98	0.093	0.536	0.144	0.052	2.45	0.018
8	1.94	4.48	13.3	—	0.14	0.023	—	0.34	—
10	1.01	8.60	5.16	0.099	1.53	0.358	—	1.67	0.019
12	1.31	3.98	1.67	—	0.215	0.074	—	2.38	—
14	0.637	5.27	0.295	—	0.119	0.02	—	17.9	—
17	0.885	4.05	0.675	—	0.419	0.061	—	6.0	—
Mean	0.961	5.47	1.95		0.57	0.128		6.99	

^{a}—, Not detected. See Table 1 for station positions. Stations 1, 3, 5, 7, 19, inner harbour; station 8, entrance channel; stations 10, 12, 14, 17, outer harbour.

Table 3 Butyl-, tributylmonomethyl- and inorganic tin in surface sediments from southeast coast, India

Location		Concentration/ng Sn g^{-1} (dry weight)						
		MBT	DBT	TBT	TBMT	DBT/TBT	TBMT/TBT	Inorganic Sn
Chennai harbour								
Coal jetty		377	394	867	765	0.45	0.88	1770
Oil jetty		21.1	180	68.3	82.2	2.64	1.20	654
Ore jetty		74.1	137	156	378	0.88	2.42	1200
Entrance channel		5.7	22.5	36.7	8.70	0.61	0.24	420
Open sea		8.34	8.65	11.5	6.80	0.75	0.59	240
Tuticorin harbour								
Station	1	393	248	1280	28.6	0.19	0.02	826
	2	45.7	24.3	116	25.1	0.21	0.22	178
	3	139	123	318	6.93	0.38	0.02	405
	4	19.5	9.8	22.8	9.10	0.43	0.40	237
	5	148	88.2	341	15.4	0.26	0.05	469
	7	47.3	32.3	91.6	48.3	0.35	0.53	239
	Mean	132	87.7	362	22.2	0.31	0.21	392
	8	4.79	1.70	5.93	—[a]	0.29	—	34.5
	9	3.47	1.47	2.0	—	0.74	—	86.0
	10	1.90	205	3.41	65.5	60.1	19.2	35.1
	11	3.06	3.16	1.90	—	1.66	—	71.9
	12	4.28	2.19	1.65	0.69	1.33	0.42	—
	13	2.30	1.70	0.90	—	1.89	—	47.1
	14	1.60	1.30	—	—	—	—	25.5
	15	1.84	2.15	5.63	—	0.38	—	31.5
	17	1.92	2.07	3.24	3.82	0.64	1.18	22.4
	18	4.96	1.73	1.94	2.03	0.89	1.05	96.6
	Mean	2.81	1.97	2.3		1.08^b		52
Coastal waters								
1	Ennore	—	—	—	—			86.0
2	Ennore	—	—	—	—			138
3	Ennore	—	—	—	—			61.6
4	Ennore estuary	8.83	8.74	4.60	—	1.9		1160
5	Ennore	—	—	—	—			300
6	Ennore	—	—	—	—			152
7	Mahabalipuram	—	—	—	—			37.0
8	Pondicherry	—	—	—	—			37.1
9	Pondicherry	—	—	—	—			15.5
10	Cuddalore	—	—	—	—			16.9
11	Nagapatinam	—	—	—	—			94.7
12	Nagapatinam	—	—	—	—			72.1

[a]Not detected. Tuticorin harbour: stations 1–7, inner harbour; station 8, entrance channel; stations 9–18, outer harbour. [b]This value was calculated by excluding an outlier value (at station 10).

of Chennai harbour, contained measurable concentrations of butyltin compounds, but the TBT concentration was lower (4.60 ng g^{-1}) than those of the degradates, MBT (8.83 ng g^{-1}) and DBT (8.74 ng g^{-1}). This shows that industrial and other wastewaters might be the reason for high MBT and DBT levels, and/or the degradation of TBT from antifouling paints. The elevated concentration (1160 ng g^{-1}) of inorganic tin shows the faster rate of debutylation of butyltins. Lee *et al.*[27] found that TBT degradation was more rapid in sunlit estuarine waters compared with incubations in the dark. It was further inferred that a land-based source might be the reason for butyltin residues in Ennore estuary (13°13′92″N; 80°19′50″E), because another two sediments collected at locations further away from the estuary (coast) (13°13′55″N; 80°20′80″E and 13°13′55″N; 80°21′98″E) contained no butyltin residues. Organotins can enter the aquatic environment not only through their use in antifouling paints, but also through other applications, which include disinfection of industrial and electrical generation plant cooling water, slime control in paper mills, as a biocide in the preservation of wood, textile, paper or stonework and as stabilizers of poly(vinyl chloride) (PVC) plastic.[28] Land-based inputs of DBT and MBT have been reported in the northeastern Mediterranean area, where relatively high concentrations of MBT and DBT compared with TBT in coastal sea-waters (MBT, 2774; DBT, 484; TBT, <8 ng l^{-1}) were observed.[29] Elevated levels of MBT and DBT among butyltins in sea-water from Tokyo Bay also suggest that there was a

source of MBT and DBT other than the degradation products of TBT.[30]

Apart from Chennai and Tuticorin harbours and Ennore estuary, 11 sediment samples collected further away from the coast at five locations were screened for organotins, but none of the sediment contained any organotin species except inorganic tin (Table 3). This supports the findings of Ko *et al.*,[31] who found extremely high levels of TBT in sediments from two shipyards in Hong Kong that ultimately decreased to background levels within 100 m of them. Similarly, imposex-free populations of dogwhelks or those with mild symptoms of imposex have been observed within a few kilometres or less of polluted areas at Loch Sween, Scotland.[32] Kiran and Anil[19] observed 90–100% imposex frequency in gastropods from Marmagoa harbour in India, which was reduced drastically (0–7%) at Dona Paula and not found in Arambol some kilometres away from the harbour. The determination of TBT in sediment and mussels (*Mytilus edulis*) from Norwegian coastal waters has also revealed elevated concentrations only close to harbours.[33]

The concentrations of triphenyltin (TPT) and its degradative products diphenyltin (DPT) and monophenyltin (MPT) were below the detection limits in all the samples, except one sediment from Chennai harbour (oil jetty, MPT 0.51 ng g^{-1}) and a water sample from Tuticorin harbour (inner harbour, TPT 0.202 ng l^{-1}). This indicates that the harbour environment is not contaminated with TPT compounds, unlike TBT.

Because TPT is mainly used in free-association paints, which have been replaced by self-polishing copolymer (SPC) paints on commercial shipping, the discharge of TPT compounds from antifouling paints is meager or has decreased drastically. Triphenyltin was not detected in sea-water along the tanker route in the Strait of Malaca and in Tokyo Bay, Japan,[30] or in Chinhae Bay, Korea,[34] but has been reported in European waters. Michel and Averty[10] studied French coastal waters and reported a maximum value of 31.7 ng TPT l^{-1}, and pointed out that concentrations were reduced considerably in 1997 compared with 1992. Tselentis et al.[35] also recorded very high concentrations of phenyltins in surface sediments in Greek coastal areas (maximum TPT level of 75 ng Sn g^{-1} dry weight with higher degradative compounds). Biselli et al.[25] observed higher concentrations in both North Sea (<17–90 ng TPTCl g^{-1} dry weight) and Baltic Sea marinas (<17–3800 ng TPTCl g^{-1} dry weight) during 1997 and 1998, where the level of the parent compound was always higher than that of the metabolites, indicating a considerable input and persistence in the sediments.

Octyltin compounds

In sea-water, apart from butyltins, octyltins were also detected (Table 2). Tri-, di- and monooctyltin concentrations were measured and found to decrease in the order MOT > DOT > TOT in the inner harbour. However, in the outer harbour only mono- and dioctyltins were detected. The half-life of octyltins might be less than that of butyltins, because no sediment contained even a trace of octyltin residues, indicating that the degradation of octyltins might be faster in the water column and/or sediment. Our group[36] reported a similar order of distribution in sea-waters from Seto Inland Sea, Japan. Octyltin is mainly leached from plastic materials where mono- and dioctyltins were used as stabilizers. Trioctyltin determined in the inner harbour may be an impurity from mono- and dioctyltins. The trioctyltin level was an order magnitude lower than those of di- and monooctyltins. Data on the toxicity of ocytltins to aquatic organisms is fragmentary, Steinhauser et al.[37] reported that dioctyltin was toxic to bacteria and water fleas (Daphnia magna), with EC_{50} values of 0.002 and 0.005 mg l^{-1}, respectively. Reports on octyltin compounds in environmental samples are scarce; we reported on Japanese waters[36] and Bancon-Montigny et al.[38] recorded high concentrations of MOT (15 ng Sn l^{-1}) and DOT (4.5 ng Sn l^{-1}) in waters from an urban treatment plant and TOT (12.4 ng Sn g^{-1} dry weight) in sludge. When compared with butyltins, the octyltin concentrations were low and could not pose any immediate threat to aquatic species along this coast.

Tributylmonomethyltin

GC-ICP-MS traces containing a TBMMT peak for sediment and sea-water are shown in Fig. 2. Methylation of butyltin species in the aquatic environment may be a significant pathway of transformation,[39] but very limited data on the environmental distribution of methylated butyltins are available.[40–42] In this study, TBMMT was quantified in sea-water (Table 2), concentrations varying from 0.014 to 0.193 ng Sn l^{-1} in Tuticorin inner harbour, but in the outer harbour out of five samples only one (station 10) contained 0.099 ng Sn l^{-1}, where the TBT concentration was also high. The concentration in Tuticorin harbour was 3–4 orders of magnitude lower than in Canadian waters (120–310 ng Sn l^{-1}),[40] but higher than in Arcachon harbour (7.57 ± 1.5 pg Sn l^{-1}),[42] and comparable to sea-water from the pearl/fish culture area of Shikoku island, Japan (0.002–2.4 ng Sn l^{-1}) (personal observation, manuscript in preparation).

Results on tributylmonomethyltin in sediments from Chennai and Tuticorin harbours are presented in Table 3. The
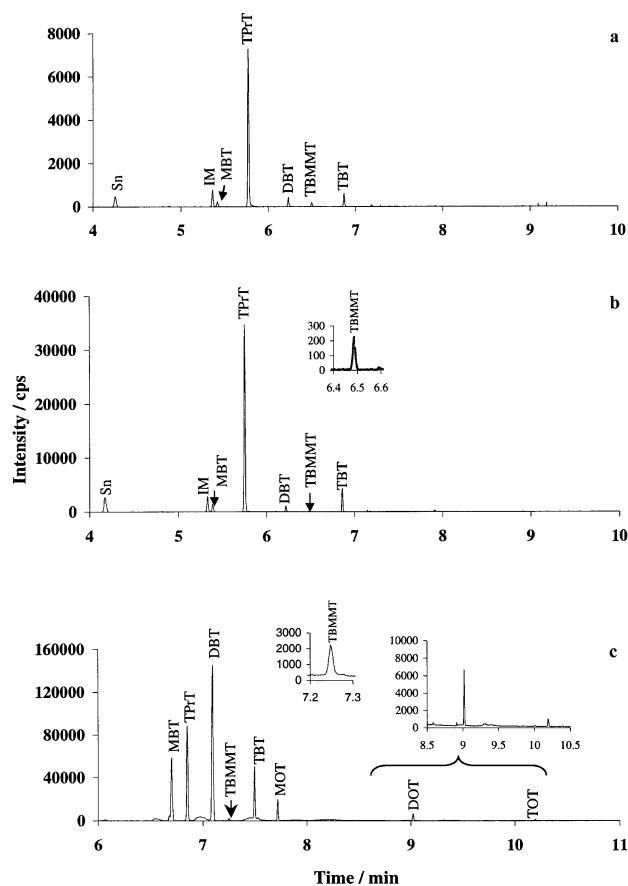

Fig. 2 GC-ICP-MS of harbour sediments [(a) Chennai and (b) Tuticorin] and sea-water [(c) Tuticorin]. IM: impurity peak.

concentration in Chennai harbour (inner) is almost equal to or more than that of TBT and the higher TBMMT/TBT ratio (mean 1.5) indicates that the methylation of tributyltin was more efficient. The higher concentration of inorganic tin than total organic tin (mono-, di- and tributyl) suggests that debutylation (biological and/or chemical) of butyltin compounds to the inorganic form was also faster. Yonezawa et al.[41] reported the transformation of TBT in marine sediments by two pathways, i.e., debutylation and methylation. They found both debutylation and methylation in sediment cores from Ise Bay, Japan. In the case of Tuticorin harbour sediments, the situation is opposite to that for Chennai harbour: the organotin concentration (sum of mono-, di- and tributyltins) was greater than that of the inorganic form and the TBT concentration was also greater than that of TBMMT (low TBMMT/TBT ratio of 0.21 in the inner harbour). Moreover, it is obvious from the Tuticorin sediment that the higher TBT concentration with lower TBMMT/TBT ratio may indicate that the methylating bacteria may be affected at higher TBT concentration, but this is not the case with Chennai harbour. Hence the transformation of organotins depends on physico-chemical and biological properties, varies from one place to another, and is different in these two harbours. The TBMMT concentration in Tuticorin harbour (mean 22.2 ng g^{-1}) is comparable to those in Toronto (22.8 ng Sn g^{-1}) and Kingston (15 ng Sn g^{-1}) harbour sediments in Canada,[39] but the Chennai harbour levels (82–765 ng g^{-1}) are an order of magnitude higher than those in Canadian harbours and 3–4 orders of magnitude higher than that in Arcachon harbour (51.4 pg Sn g^{-1} dry weight).[42] In Ise Bay surface sediment, the TBMMT concentration was about four times lower than that of TBT.[41] To compare with temperate sediments an elevated rate of TBT methylation was observed at Chennai harbour.

Relationship between total butyltin and organic carbon in sediment

A significant correlation between the organic carbon content and total butyltin (sum of MBT, DBT, TBT and TBMMT) concentrations in sediment was found ($r^2 = 0.75$) (Fig. 3). Yonezawa et al.[43] found a good relationship between butyltin concentrations and organic carbon contents in sediments from Ise Bay, Japan. Kim et al.[44] and Shim et al.[45] observed a good correlation between the total butyltin concentration and the sediment organic carbon content from Kyeonggi Bay ($r^2 = 0.678$; $p < 0.0001$) and Chinhae Bay ($r^2 = 0.43$; $p < 0.001$) in Korea. Pereira et al.[46] reported that the soil sample with the greatest concentration of organic carbon contained the highest levels of butyltins at Mare Island, San Francisco Bay. This shows that butyltins in sediment may exist as species bound to organic carbon because of the hydrophobic nature, so the organic carbon is an important parameter which controls the distribution of butyltins in sediment.

Conclusion

Based on the criteria of Dowson et al.,[4] sediments from Chennai and Tuticorin harbours belong to the highly contaminated category (100–500 ng g^{-1}). However, open sea sediments near the harbours belong to the lightly contaminated category (3–20 ng g^{-1}) and sediments other than from the harbour area are not contaminated. The concentration of butyltin compounds observed in harbour waters and sediments may have some effects such as imposex, larval mortality, etc., on the resident mollusc community and other organisms in close proximity to harbours.

Based on sediment TBMMT/TBT and DBT/TBT mean ratios, a distinct pattern of the organotin transformation process was obtained between the two harbours. At Chennai harbour methylation of TBT (TBMMT/TBT = 1.5) and debutylation to DBT (DBT/TBT = 1.32) were faster, but in Tuticorin harbour, methylation (TBMMT/TBT = 0.21) and debutylation (DBT/TBT = 0.31) of TBT were not as efficient as in Chennai harbour. This was also evident from the higher inorganic tin content (through debutylation) in Chennai than in Tuticorin harbour.

Just north of Chennai harbour a new harbour was recently constructed at Ennore and started its operation. We may expect an elevated level of butyltin contamination in future in the close vicinity of two commercial harbours and a fishing harbour. Since there is no restriction on the use of TBT-based antifouling paints in India, extensive research on imposex in gastropods is essential to assess the status of the Indian coastal environments along with the regular chemical monitoring of organotin compounds.

The environmental quality target (EQT) value for TBT in sediments, set at 1–2 ng g^{-1}, has been implemented in most European cou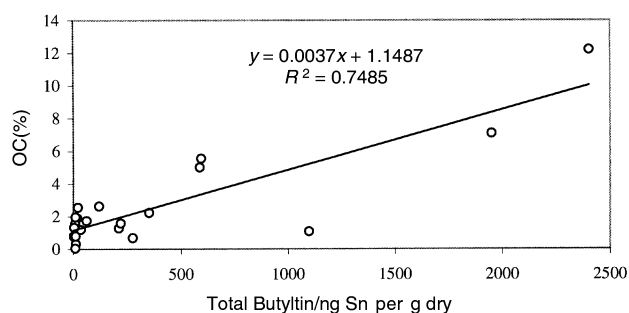ntries and should also be considered for the Indian environment to avoid any catastrophe from the increasing ship traffic and ship-scrapping industry.

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Fig. 3 Relationship between total butyltin concentration and organic carbon content (%) in sediment.

$$y = 0.0037x + 1.1487$$
$$R^2 = 0.7485$$

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