

# Occurrence of butyltin compounds in marine sediments and bivalves from three harbour areas (Saigon, Da Nang and Hai Phong) in Vietnam

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A survey of organotin compounds comprising tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) in sediment and clam (*Meretrix meretrix*) was undertaken in Vietnam in 2003. Samples were collected from dry docks and cargo harbours in Ho Chi Minh (south), Da Nang (centre) and Hai Phong (north) cities. Measurable amounts of TBT, DBT and MBT were found in all samples. The total concentration of the butyltin compounds ( $\Sigma$ BTs) in sediment from shipyards and vessel repair yards (Nam Trieu, Song Cam, Lach Tray and Ba Son) were always higher than those measured in cargo ports (Hai Phong, Da Nang, and Sai Gon). The highest  $\Sigma$ BTs concentration (as tin: 122 ng g<sup>-1</sup> dry wt) was found in the sediment from Song Cam station, where seven shipyards are located. The lowest concentrations of  $\Sigma$ BTs occurred in sediments from the Da Nang and Hai Phong cargo ports (as tin: 21–22 ng g<sup>-1</sup> dry wt). This implies that the major source of BTs in the marine environment in Vietnam is from the shipbuilding activities. The ratio of TBT to  $\Sigma$ (MBT + DBT) in sediment was  $0.67 \pm 0.03$  for all the sampling sites, indicating the recent use of TBT in Vietnam. For the clam (*M. meretrix*), the concentration of  $\Sigma$ BTs (as tin) varied in the range 11.2–60.1 ng g<sup>-1</sup> wet wt. There was a good correlation ( $R^2 = 0.85$ ) between total organic matter-normalized  $\Sigma$ BTs in sediment and hexane-extractable organic matter-normalized  $\Sigma$ BTs in clam soft tissue. The mean biota–sediment accumulation factors (organic carbon/lipid) for MBT, DBT and TBT in clam's soft tissue were found to be  $1.83 \pm 0.66$ ,  $1.44 \pm 0.23$  and  $1.16 \pm 0.47$  respectively, indicating that sediment-bound BTs might be an important source of contamination for the clam. Copyright © 2005 John Wiley & Sons, Ltd.

**KEYWORDS:** organotin compounds; tributyltin; harbour; Vietnam; clams; sediment

## INTRODUCTION

Tributyltin (TBT) compounds have been used extensively as a biocide in marine antifouling paints. Organotin-based paints have been applied to vessels of all sizes, from small yachts to supertankers, thereby ensuring the global dispersion of TBT throughout the marine environment from the coastal zone to the open ocean.<sup>1,2</sup> These compounds are persistent in the marine environment, especially in sediments, due to slow

degradation rates and the consistent flux.<sup>3,4</sup> Also, they can accumulate in a variety of marine organisms, from plankton and fish, to various marine birds and mammals.<sup>5–8</sup> Numerous deleterious biological effects of TBT on non-target organisms have been observed.<sup>9</sup> The most obvious manifestations of TBT contamination have been shell deformation in Pacific oysters<sup>10</sup> and the development of imposex/intersex (i.e. the imposition of male sex organs on females) in marine gastropods.<sup>11–13</sup> The latter effect demonstrates that TBT acts as an endocrine disrupter. Moreover, imposex is sufficiently sensitive as to be indicative of shipping density in the North Sea.<sup>14</sup>

Owing to the widespread deleterious effects on non-target organisms, the use of TBT as an antifouling agent has been regulated in developed countries for over 20 years.<sup>15</sup> France was the first country to implement a ban on the use of TBT

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antifouling paints on ships of less than 25 m at the beginning of 1982. In the following years most European countries, the USA, Canada, Australia, and New Zealand implemented similar limited legislation. More dramatically, Japan banned the use of TBT on all vessels in 1985. The International Maritime Organization (IMO) adopted an international convention on the control of harmful antifouling subsystems for ships in 2001, which banned the new application or reapplication of organotin-based paints on all vessels from 2003 and the presence of TBT on boat hulls starting in 2008. Regulations on the use of TBT compounds in Vietnam started only in 2003.

Many Asian countries rely substantially on mariculture of molluscs, crustaceans and fish. Both ongoing and historic use of TBT compounds has led to several reports of instances of organotin contamination in various Asian countries.<sup>16–18</sup> High concentrations of TBT in marine sediments, seawater, and biological samples have been detected in Malaysia,<sup>19,20</sup> Taiwan,<sup>21,22</sup> Thailand,<sup>23,24</sup> and Korea.<sup>25–27</sup> Despite the greater restrictions on TBT usage, high levels of these contaminants have still been detected in Hong Kong<sup>28,29</sup> and Japan.<sup>30,31</sup>

Vietnam is located along the South China Sea and has a coastline of ~2000 km. An important shipbuilding industry was developed many years ago. As a result, a large amount of TBT-based antifouling paint has no doubt been applied to vessels under construction and repair. Only limited data exist regarding the level of organotin contamination in the marine environment of Vietnam. Concentrations of butyltin (BT) residues were determined in muscle tissue of fish acquired from local markets and sea-food shops in several Asian countries, including Vietnam.<sup>16</sup> Similarly, samples from Vietnam formed part of a survey of green mussels (*Perna viridis*) from various Asian sites, as part of the Asia-Pacific mussel watch.<sup>18</sup> Also, organotin contamination in sediments and clams (*Meretrix meretrix*) collected from the northern and central coastal areas of Vietnam has recently been reported.<sup>32</sup>

The aim of the present study was to determine the TBT, DBT and MBT concentrations in sediments and clams (*M. meretrix*) in areas close to the shipyards and dry docks in Hai Phong (north), Da Nang (centre) and Sai Gon (south) harbours. These results not only contribute to the generally sparse data set for organotin distributions in the marine environment of Vietnam, but also can help to elucidate the role of the shipbuilding industry as a source of TBT. Moreover, *M. meretrix* is an important component in the Vietnamese diet.

## MATERIALS AND METHODS

### Samples and sampling sites

Sediment was collected using an Ekman–Birge sampler in November 2003. Samples were obtained from cargo harbours in Hai Phong (north), Da Nang (centre) and Ho Chi Minh (south) cities and from dry docks in Ho Chi Minh and Hai Phong. For the biota, ~2 kg of clams having shell lengths of between 40 and 60 mm were bought from local fishermen

harvesting in the harbours, as well as near the dry docks in Ho Chi Minh and Hai Phong.

Figure 1 maps the sampling locations in Vietnam. In Hai Phong city, samples were taken from four sites. The first site is Nam Trieu mouth (St 1), where the biggest shipyard in northern Vietnam (Bach Dang yard) is located, with the capacity to build ships up to 600 000 tons. The second sampling site in Hai Phong is Song Cam mouth (St 2), where seven shipyards and vessel repair factories are located. In this area, ships of up to 400 000 tons capacity can be made. The third site is Hai Phong cargo port (St 3), with a loading capacity of several million tons of goods per year, and the fourth site is Lach Tray dry dock (St 4), where vessels of up to 50 000 tons capacity can be repaired. In Da Nang city, samples were taken from Da Nang cargo port (St 5), which has a loading capacity of several million tons of goods per year. In Ho Chi Minh City, samples were taken from the Sai Gon river mouth (St 6), where the Ba Son shipyard is located, and from the cargo port (St 7), having a loading capacity of several million tons of goods per year.

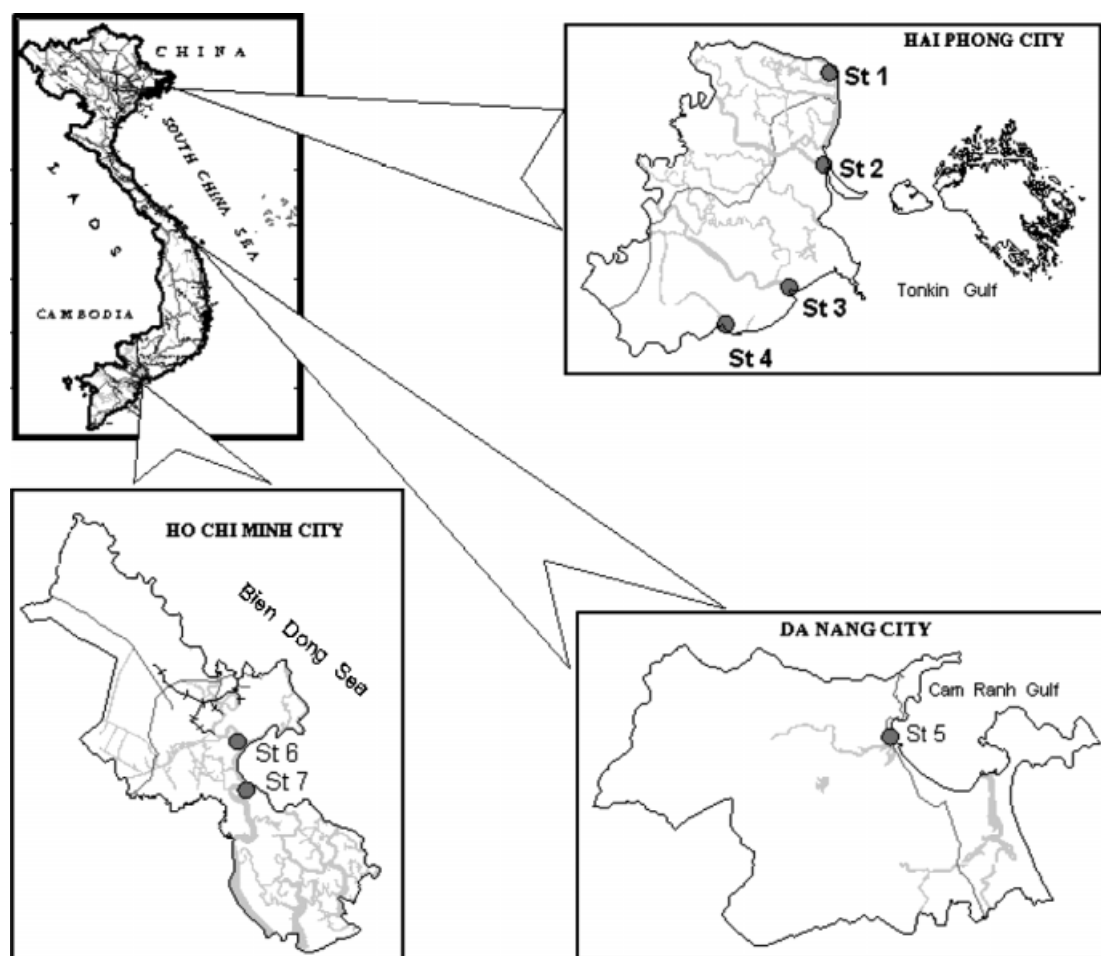
### Standards and reagents

MBT trichloride (95%) was obtained from Aldrich (Milwaukee, USA). DBT dichloride (98%), tripropyltin (TPrT) chloride (96%), TBT chloride and tetrabutyltin (TeBT; 95%) were purchased from Merck (Darmstadt, Germany). The procedure for preparing standard solutions has been described in detail elsewhere.<sup>33</sup>

NaBeT<sub>4</sub> was purchased from Wako Chem. Co., Japan, in 1 g sealed aliquots. A solution of 1% NaBeT<sub>4</sub> in 2% KOH was prepared with deionized water and stored in a freezer at –20 °C. A sodium acetate–acetic acid buffer was prepared with sodium acetate and acetic acid of PA grade from Merck. Quaternary ammonium hydroxide (0.5 M in toluene) as a tissue solubilizer with a trade name of Soluence 350 was purchased from Packard and used without dilution. HCl of PA grade, acetone, methanol, ethyl acetate and *n*-hexane of pesticide grade were purchased from Merck.

### Sample pretreatment

Sediment samples were kept in glass bottles, which were previously washed with *n*-hexane and dried at 150 °C overnight. Clam samples were wrapped in aluminium foil. All samples were kept in an icebox for transport to the laboratory for pretreatment as quickly as possible. In the laboratory, sediment was wet sieved through a metallic sieve and only the fraction of particle size less than 0.1 mm was recovered. Particles were allowed to settle overnight and the clear overlying water was decanted. The sediment samples were then air dried in the laboratory. Moisture of sediment samples was determined gravimetrically after drying at 105 °C overnight. The moisture content of the sediment samples was between 35 and 40%. Calcination of the dried sediment samples at 550 °C for 3 h was carried out to determine total organic matter (TOM, mg g<sup>–1</sup>) in sediments.



**Figure 1.** Map showing sampling locations. St 1: Nam Trieu mouth; St 2: Song Cam mouth; St 3: Hai Phong cargo port; St 4: Lach Tray mouth; St 5: Da Nang cargo port; St 6: Ba Son shipyard; St 7: Sai Gon cargo port.

Clam soft tissue was removed from the shell, briefly washed with deionized water, and the excess water was drained. The tissue was homogenized using a high-speed food homogenizer, then stored in glass bottles that had previously been thoroughly washed with *n*-hexane and dried at 150°C overnight. Both air-dried sediments and clam soft tissue homogenate were kept in a freezer at -20°C until subsequent chemical analysis.

The lipid content of clam tissue homogenate was determined as the hexane-extractable organic matter (HEOM, mg g<sup>-1</sup>). About 1 g of anhydrous Na<sub>2</sub>SO<sub>4</sub> dried tissue homogenate (tissue: reagent = 1:4, w:w) was Soxhlet extracted with 100 ml of *n*-hexane (pesticide analytical grade) for 8 h. Afterward, the extract was concentrated to ~5 ml by rotary evaporation. The moisture in the extract was removed using anhydrous Na<sub>2</sub>SO<sub>4</sub>. The extract was transferred into a vial and further concentrated under a gentle stream of dry nitrogen to 0.5 ml. HEOM was determined by weighing the residue of an evaporated aliquot on a balance.

### Sample preparation for BTs analysis

The analysis of BT compounds in sediments was based on a previously published procedure<sup>34</sup> with some modification. Sediment (1–3 g) was placed in a centrifuge tube together with an internal standard, TPrT, used to quantify the extraction process and derivatization reaction. The mixture was extracted twice by shaking for 20 min with 10 ml of 1 M HCl-methanol/ethyl acetate (1:1, vol:vol). After centrifugation, the combined supernatant was concentrated almost to dryness and then transferred to a separatory funnel with 20 ml of sodium acetate-acetic acid buffer (pH 4–5). Following the addition of 2 ml NaBEt<sub>4</sub> solution, the determinands were ethylated and extracted twice into 10 ml *n*-hexane by shaking for 10 min. The organic phases were combined, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to ~1 ml. This solution was cleaned up using a Florisil packed column. Upon eluting with 10 ml of *n*-hexane, the final solution was concentrated to 0.5 ml under a gentle stream of pure nitrogen and spiked with TeBT, acting as a internal standard during gas chromatography (GC) to quantify the recoveries of the TPrT internal standard.

A well-established method<sup>33</sup> was used for the analysis of the biota samples. Briefly, clam tissue was thawed at room temperature. Approximately 1 g (wet weight) was put into a centrifuge tube and spiked with TPrT as an internal standard. The mixture was dissolved in 10 ml of Soluence 350 by ultrasonication at 50 °C for 1.5 h. Upon buffering at pH 4–5 with acetate–acetic acid, the samples obtained were simultaneously derivatized with 1 ml of the NaBEt<sub>4</sub> and twice extracted with 5 ml aliquots of *n*-hexane. The combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated to 1 ml by evaporation, and cleaned up using Florisil. The analytes were eluted by 10 ml of *n*-hexane, concentrated to 0.5 ml and, as above, spiked with TeBT, acting as a GC internal standard to quantify the recoveries of the TPrT internal standard.

### GC–flame photometric detector analysis

An HP 5890 Series II gas chromatograph equipped with a flame photometric detector (FPD; 610 nm filter and with a hydrogen-rich flame) was used to determine all the butyltin compounds. A DB-1 (30 m × 0.25 mm × 0.25 µm) fused-silica capillary column (J&W Scientific Co. Ltd) coated with 100% dimethyl polysiloxane was used. The temperatures of the splitless injector and FPD were maintained at 250 °C and 270 °C respectively. Helium, at a flow rate of 1 ml min<sup>−1</sup>, was used as the carrier gas. The GC temperature programme was 60 °C for 2 min, then 60–270 °C at 6 °C min<sup>−1</sup> and 270 °C for 20 min.

To quantify the concentration of corresponding BT compound in samples, calibration curves (concentration versus FPD's response) were made, for a batch of five samples, by spiking known amounts of BT compounds into non-contaminated sediment or biota homogenate. For each BT compound, an average response factor was obtained from the calibration curve. The response factors were then used to quantify all BT concentrations in the samples.

Based on recovery experiments of spiked sediment and biota samples, the recoveries of all the analytes (TBT, DBT, MBT) from both sample types were in the order of 101 ± 10%. The detection limit (as tin) for each of the BTs

was 2 ± 1 ng g<sup>−1</sup>. All concentrations of BT compounds are expressed as nanograms of tin per gram on a dry weight basis for sediment and on a wet weight basis for biota.

## RESULTS AND DISCUSSION

### Sediments

The concentrations of MBT, DBT and TBT in sediments from the seven sampling sites in Hai Phong, Da Nang and Ho Chi Minh cities ranged from 3.95 to 29.7 ng g<sup>−1</sup> dry wt, from 8.13 to 42.7 ng g<sup>−1</sup> dry wt, and from 8.25 to 50.5 ng g<sup>−1</sup> dry wt respectively (Table 1). From Table 1, the total concentrations of all BTs (ΣBTs) in sediments from areas where shipyards or vessel repair facilities are located (Nam Trieu (St 1), Song Cam (St 2), Lach Tray (St 4) in Hai Phong or Ba Son (St 6) in Ho Chi Minh; Fig. 1) were always higher than those from the cargo ports (Hai Phong (St 3), Da Nang (St 5) or Sai Gon (St 7)). The concentration of individual BTs is in the rank order of TBT > DBT > MBT (Table 1). Additionally, the mean ratio of the concentration of TBT to that of the sum of MBT and DBT, i.e. TBT/(MBT + DBT), was as high as 0.67 ± 0.03 (Table 1). The high ratio indicates that TBT is still being introduced into the local environment, probably due to ongoing application of TBT-based antifouling paints on marine vessels. Thus, an important major source of TBT into the coastal environment in Vietnam seems to be shipbuilding activities.

BT concentrations in sediments from various Asian countries are compared in Table 2. Data for sediments have been reported in only one other study in Vietnam,<sup>32</sup> which found somewhat lower levels of BT than those reported here. The difference probably relates to the nature of the sampling sites. Whereas the present study investigated a number of shipyards, samples in the previous investigation were collected only from mooring places for small fishing boats.<sup>32</sup> The use of TBT-based antifouling paints on fishing boats in Vietnam has apparently been relatively restricted, with a consequent limited TBT release from this source. Table 2 also shows BT data from other Asian countries for comparison.

**Table 1.** Concentrations of BT compounds (as tin) in sediments from Vietnam

Site	Moisture (%)	TOM (mg g <sup>−1</sup> )	[Sn] (ng g <sup>−1</sup> dry wt)				TBT/(MBT + DBT)
			MBT	DBT	TBT	ΣBTs	
St 1	35.9	67.6	14.9	30.1	34.9	79.9	0.61
St 2	34.8	54.6	29.7	42.7	49.5	122	0.68
St 3	38.4	62.4	5.0	8.1	8.3	21.4	0.60
St 4	40.2	57.5	15.5	16.7	19.4	51.6	0.63
St 5	35.6	51.2	3.9	9.9	8.4	22.3	0.61
St 6	39.6	59.4	17.8	37.6	50.5	106	0.91
St 7	36.8	60.8	7.5	10.5	11.8	29.8	0.66
Mean							0.67
Std dev.							0.03

Even though the coastal areas sampled in Vietnam were often located near shipyards, the concentration of BT compounds was much lower than the maxima seen in other Asian countries. The extent of BT contamination of the marine environment in Asian countries has previously been linked to the economic status of the country, with the greatest pollution evident in the most developed nations.<sup>18,24</sup> Notwithstanding such regional differences, all sites investigated in Vietnam are considered to be contaminated with respect to TBT (i.e. TBT > 1.3 ng g<sup>-1</sup>) according to the classification scheme of Dowson *et al.*<sup>36</sup>

## Clams

The concentrations of MBT, DBT, and TBT in clams (*M. meretrix*) from the seven sampling locations ranged

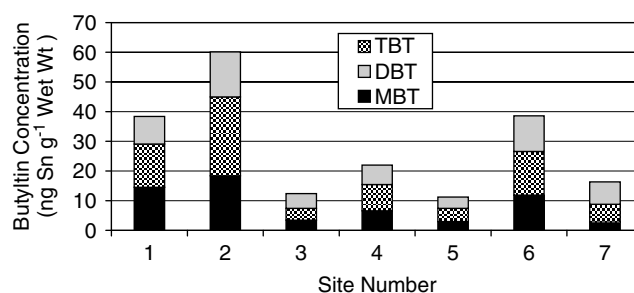
**Table 2.** BT content (as tin) in sediment from some Asian countries

Country	[Sn] (ng g <sup>-1</sup> dry wt)			Ref.
	MBT	DBT	TBT	
Hong Kong	—	—	up to 53 000	29
Korea	40–740	10–573	4–382	27
Korea	—	1.6–53.7	0.4–68.5	35
Japan	—	—	10–2100 <sup>a</sup>	31
Japan	—	—	10–640 <sup>a</sup>	30
Malaysia	—	—	<0.7–217	20
Malaysia	5.0–360 <sup>a</sup>	3.8–310 <sup>a</sup>	2.8–1100 <sup>a</sup>	19
Thailand	7–410 <sup>a</sup>	2–1900 <sup>a</sup>	4–4500 <sup>a</sup>	23
Vietnam	<0.04–11	0.64–5	0.89–34	32
Vietnam	3.9–29.7	8.1–42.7	8.3–50.5	This study

<sup>a</sup> Not normalized to tin.

2.8–18.4 ng g<sup>-1</sup> wet wt, 4.4–26.6 ng g<sup>-1</sup> wet wt, and 3.8–15.1 ng g<sup>-1</sup> wet wt respectively (Fig. 2). Comparing the mean relative composition of the BT compounds, the clams contain less TBT, but more DBT and MBT than the sediments from the same locations. This suggests that the clams can debutylate TBT and DBT, as has been noted for starfish<sup>37</sup> and mussels.<sup>38</sup> The few other data for *M. meretrix* from Vietnam are presented in Table 3. The BT concentrations were comparable to those reported in the one other study of this clam species.<sup>32</sup> Based on their deductions and the lower TBT concentrations found here, the consumption of these clams does not pose a public health threat.

Table 3 also presents data for other bivalve species from locations throughout Asia for comparison, noting that all concentrations are expressed as nanograms of MBT, DBT, or TBT per gram without normalising to tin. Overall, the concentrations of the BT compounds in clam tissue reported here were lower than in green mussel (*P. viridis*) collected from the coastal areas in Vietnam.<sup>18</sup> Considering the relative amounts of the BT compounds, the green mussels contained



**Figure 2.** Concentration of BT compounds (as tin) in the soft tissue of the clam (*M. meretrix*) from seven sites in Vietnam.

**Table 3.** BT levels (wet wt) in marine bivalves from Asian countries

Country	Bivalve species	Year sampled	MBT (ng g <sup>-1</sup> )	DBT (ng g <sup>-1</sup> )	TBT (ng g <sup>-1</sup> )	Ref.
Cambodia	<i>Perna viridis</i>	1998	<2–25	<0.98–37	2.4–88	18
Hong Kong	<i>P. viridis</i>	1999	4.2–94	4.9–76	16–330	18
Indonesia	<i>P. viridis</i>	1998	<1.5–13	<0.58–14	2.2–38	18
Japan, Osaka	<i>Mytilus edulis</i>	1996	—	—	20–390	31
Japan, Otsuchi	<i>M. edulis</i>	1995	—	—	23–1100	30
Malaysia	<i>P. viridis</i>	1998	<2.6–74	<1–160	3.5–730	18
Malaysia	<i>P. viridis</i>	1997–1998	2.3–7.4	<1.3–13	2.4–190	19
Philippines	<i>P. viridis</i>	1997–1998	<2–15	<1.3–19	0.8–47	18
Philippines	<i>P. viridis</i>	1994–1997	<3–51	<1–100	<1–787	24
South Korea	<i>M. edulis</i>	1997–1999	3.4–320	13–1100	17–1200	25
Thailand	<i>P. viridis</i>	1994–1995	<3–45	1–80	3–680	39
Thailand	<i>P. viridis</i>	1994–1997	<3–45	1–80	3–680	24
Vietnam	<i>P. viridis</i>	1998	<2.1–3.3	<0.86–19	2.1–84	18
Vietnam	<i>M. meretrix</i>	2002	0.86–29 <sup>a</sup>	0.7–6.1 <sup>a</sup>	1.4–47 <sup>a</sup>	32
Vietnam	<i>M. meretrix</i>	2003	2.8–18.4 <sup>a</sup>	4.4–26.6 <sup>a</sup>	3.8–15.1 <sup>a</sup>	This study

<sup>a</sup> Normalized to Sn.

predominantly TBT, whereas the clam had higher amounts of both MBT and DBT. There are many reasons that may account for these observations. First, the higher concentrations and predominance of TBT in the mussels could indicate a greater and/or more recent exposure to contamination. It is acknowledged that there are differences in habitat and feeding mode of the two marine organisms. The clam lives in sediment and it feeds by filtering suspended particulates from both water and sediment, but the habitat of the mussel is primarily on rocks and it feeds by filtering suspended particles from water, and the coastal waters around Vietnam are very turbid. Second, the relative importance of DBT and MBT in clams might indicate that this species can more readily debutylate BT compounds than is the case in green mussels. Other recent studies, however, have found much higher proportions of TBT metabolites in tissues of the mussels *M. edulis* compared with the clams *Mya arenaria*.<sup>40</sup> In light of that, it was suggested that body burdens in the *M. arenaria* are likely to reflect contamination for longer periods.

The levels of BTs contamination in the marine biota from the coastal areas in Vietnam are also compared with those from other Asian countries in Table 3. Clearly, the concentrations are much lower than have been measured elsewhere in Asia, and are presumably related to Vietnam's economic status as a developing country.

The biota–sediment accumulation factors (BSAFs, organic carbon/lipid) of MBT, DBT and TBT in the clam were calculated by dividing the BTs concentrations in clam soft tissue, normalized to HEOM, by the respective BTs concentrations in sediment, normalized to TOM.<sup>41</sup> The normalization of BTs concentrations to organic carbon content in sediment reduces variability due to the sediment characteristics, and the normalization of BTs concentrations in clam soft tissue to the lipid content of the organism reduces variability in tissue concentration among individuals of the same species, as well as between different species.<sup>42</sup> The mean

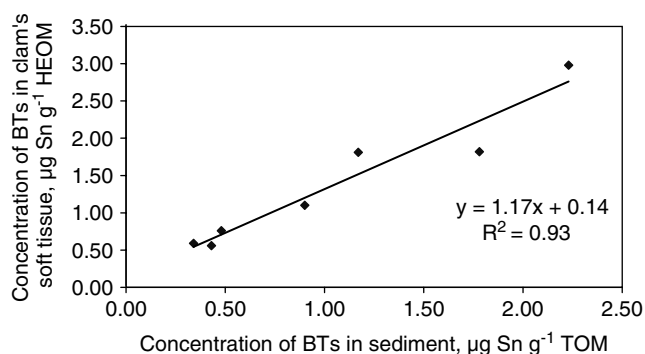
BSAF values for the seven sites were  $1.83 \pm 0.66$ ,  $1.44 \pm 0.23$ , and  $1.16 \pm 0.47$  for MBT, DBT, and TBT respectively (Table 4). These values are comparable to the BSAF of TBT (0.4 to 4.6) reported for other marine invertebrates<sup>14,43</sup> and those for neutral hydrophobic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and pesticides (0.3 to 1.4).<sup>44</sup> Much higher BSAF ranges for TBT (1.9 to 8.0) were reported for lipid tissues of the Asian clam, *Potamocorbula amurensis*, near Mare Island Naval Shipyard, San Francisco Bay, for which additional partitioning and binding processes were suggested for organotin compounds over the neutral hydrophobic PAHs and PCBs.<sup>42</sup>

The bioconcentration factor of TBT between sediment and clam without normalization to organic carbon and lipid content ( $BCF_{\text{tissue-sediment}}$ ) ranged from 0.23 to 0.60 (wet wt/dry wt) and from 1.0 to 2.7 (dry wt/dry wt). These values were in the lower range of those reported recently for *Meretrix* sp. from Vietnam ( $BCF_{\text{tissue-sediment}} = 0.56\text{--}5.5$ ),<sup>32</sup> where it was considered that the clam could take of BT from dissolved BT in water and from particulate-bound BT in sediment. The lower values measured in the present study might likely reflect the higher metabolism of TBT in the clams of the present study.

As shown in Fig. 3, the HEOM-normalized concentrations of  $\Sigma$ BTs in sediment correlate with the HOEM-normalized  $\Sigma$ BTs content in the soft tissue of clams (*M. meretrix*) from the seven sampling stations. The high correlation coefficient ( $R^2 = 0.93$ ) indicates that the sediment could act as a source of BTs for this clam. Other studies support this interpretation. Based on 60-day experiments, the  $BCF_{\text{tissue-water}}$  of TBT for the suspension-feeding clam *Ruditapes decussatus* was  $9 \times 10^4$ , whereas the  $BCF_{\text{tissue-sediment}}$  was  $<1$  (dry wt/dry wt).<sup>45</sup> Based on field survey data, the  $BCF_{\text{tissue-water}}$  and the  $BCF_{\text{tissue-sediment}}$  for the periwinkle *Littorina littorea*, living on rocks, were  $4.4 \times 10^4$  and 3.9 (dry wt/dry wt) respectively.<sup>46</sup> Considering sediment-dwelling clams in the same study, the  $BCF_{\text{tissue-water}}$  was  $9.9 \times 10^3$  for *Scrobicularia plana* and  $13.3 \times 10^4$  for *M.*

**Table 4.** TOM-normalized BT concentrations in sediment, HEOM-normalized BT concentrations in clam soft tissue, and BSAF value for BT compounds

Site	BT ratio						BSAF (organic carbon/lipid)		
	Sediment ( $\mu\text{g Sn g}^{-1}$ )			Biota ( $\mu\text{g Sn g}^{-1}$ )					
	MBT	DBT	TBT	MBT	DBT	TBT	MBT	DBT	TBT
St 1	0.22	0.44	0.51	0.68	0.69	0.44	3.09	1.57	0.86
St 2	0.54	0.78	0.91	0.91	1.32	0.75	1.68	1.69	0.82
St 3	0.08	0.13	0.13	0.16	0.19	0.24	2.0	1.46	1.85
St 4	0.27	0.29	0.34	0.33	0.44	0.33	1.22	1.52	0.97
St 5	0.08	0.19	0.16	0.15	0.22	0.19	1.90	1.13	1.15
St 6	0.30	0.63	0.85	0.56	0.69	0.57	1.88	1.10	0.67
St 7	0.12	0.17	0.19	0.13	0.28	0.35	1.06	1.64	1.81
Mean							1.83	1.44	1.16
Std dev.							0.66	0.23	0.47



**Figure 3.** Correlation between TOM-normalized  $\Sigma$ BT concentrations in sediments and HOEM-normalized  $\Sigma$ BT concentrations in the soft tissue of the clam (*M. meretrix*).

*arenaria*, but the respective  $BCF_{\text{tissue-sediment}}$  values were only 8.8 and 77.9 (dry wt/dry wt). These results suggest that TBT in the water column is the major source of uptake for suspension-feeding clams, but sediment-bound TBT can be an additional source of contamination for sediment-dwelling bivalves.

## CONCLUSIONS

This study points to shipyards and shipbuilding activities as sources of TBT to the marine environment of Vietnam. However, the level of BTs in coastal sediments was relatively low in comparison with other Asian countries. Similarly, BT concentrations in the clam *M. meretrix* were comparatively low and do not warrant concern for public health. This clam accumulates BTs in soft tissue, with a BSAF ranging from 0.7 to 3.1. Although TBT usage has been regulated in the country since 2003, continuous monitoring of BT pollutants in the environment of Vietnam is recommended to guarantee compliance with regulations, to ensure the safety of seafood, and to protect the marine environment.

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## REFERENCES

- de Mora SJ (ed.). *Tributyltin: Case Study of an Environmental Contaminant*. Cambridge University Press: Cambridge, 1996.
- Hoch M. *Appl. Geochem.* 2001; **16**: 719.
- Michel P, Averty B. *Environ. Sci. Technol.* 1999; **33**: 2524.
- Stewart C, de Mora SJ. *Environ. Technol.* 1990; **11**: 565.
- Beaumont AR, Mills DK, Newman PB. Some effects of tributyltin (tbt) on marine algae. In *International Organotin Symposium, Oceans '87*. Marine Technology Society: Halifax, 1987; 1488.
- Fent K, Woodin BR, Stegeman JJ. *Comp. Biochem. Physiol. Part C: Pharmacology, Toxicol. Endocrinol.* 1998; **121**: 277.
- St-Louis R, de Mora SJ, Pelletier É, Doidge B, Leclair D, Mikaelian I, Martineau D. *Appl. Organometal. Chem.* 2000; **14**: 218.
- Tanabe S. *Mar. Pollut. Bull.* 2002; **45**: 69.
- Fent K. *CRC Crit. Rev. Toxicol.* 1996; **26**: 1.
- Alzieu C. Biological effects of tributyltin on marine organisms. In *Tributyltin: Case Study of an Environmental Contaminant*, de Mora SJ (ed.). Cambridge University Press: Cambridge, 1996.
- De Wolf H, De Coen W, Backeljau T, Blust R. *Mar. Environ. Res.* 2001; **52**: 249.
- Gibbs PE, Bryan GW. TBT-induced imposex in neogastropod snails: masculinization to mass extinction. In *Tributyltin: Case Study of an Environmental Contaminant*, de Mora SJ (ed.). Cambridge University Press: Cambridge, 1996.
- Strand J, Asmund G. *Environ. Pollut.* 2003; **123**: 31.
- Ten Hallers-Tjabbes CC, Wegener J-W, (AGM) Van Hattum B, Kemp JF, Ten Hallers E, Reitsema TJ, Boon JP. *Mar. Environ. Res.* 2003; **55**: 203.
- Bosselmann K. Environmental law and tributyltin in the environment. In *Tributyltin: Case Study of an Environmental Contaminant*, de Mora SJ (ed.). Cambridge University Press: Cambridge, 1996.
- Kannan K, Tanabe S, Iwata H, Tatsukawa R. *Environ. Pollut.* 1995; **90**: 279.
- Keithly JC, Cardwell RD, Henderson DG. *Human Ecol Risk Assess.* 1999; **5**: 337.
- Sudaryanto A, Takahashi S, Monirith I, Ismail A, Muchtar M, Zheng J, Richardson BJ, Subramanian A, Prudente M, Hue ND, Tanabe S. *Environ. Toxicol. Chem.* 2002; **21**: 2119.
- Sudaryanto A, Takahashi S, Iwata H, Tanabe S, Ismail A. *Environ. Pollut.* 2004; **130**: 347.
- Tong SL, Pang FY, Phang SM, Lai HC. *Environ. Pollut.* 1996; **91**: 209.
- Hsia M-P, Liu S-M. *Sci. Total Environ.* 2003; **313**: 41.
- Liu LL, Chen SJ, Peng WY, Hung JJ. *Environ. Pollut.* 1997; **98**: 113.
- Kan-Atireklap S, Tanabe S, Sanguansin J. *Mar. Pollut. Bull.* 1997; **34**: 894.
- Tanabe S, Prudente MS, Kan-Atireklap S, Subramanian A. *Ocean Coast. Manage.* 2000; **43**: 819.
- Hong H-K, Takahashi S, Min B-Y, Tanabe S. *Environ. Pollut.* 2002; **117**: 475.
- Shim WJ, Kahng SH, Hong SH, Kim NS, Kim SK, Shim JH. *Mar. Environ. Res.* 2000; **49**: 435.
- Shim WJ, Oh JR, Kahng SH, Shim JH, Lee SH. *Environ. Pollut.* 1999; **106**: 351.
- Cheung KC, Wong MH, Yung YK. *Toxicol. Lett.* 2003; **137**: 121.
- Ko MMC, Bradley GC, Neller AH, Broom MJ. *Mar. Pollut. Bull.* 1995; **30**: 249.
- Harino H, Fukushima M, Yamamoto Y, Kawai S, Miyazaki N. *Environ. Pollut.* 1998; **101**: 209.
- Harino H, Fukushima M, Yamamoto Y, Kawai S, Miyazaki N. *Arch. Environ. Contam. Toxicol.* 1998; **35**: 558.
- Midorikawa S, Arai T, Harino H, Ohji M, Duc Cu N, Miyazaki N. *Environ. Pollut.* 2004; **131**: 401.
- Cassi R, Tolosa I, Bartocci J, de Mora S. *Appl. Organometal. Chem.* 2002; **16**: 355.
- Smedes F, de Jong AS, Davies IM. *J. Environ. Monitor.* 2000; **2**: 541.
- Hwang HM, Oh JR, Kahng S-H, Lee KW. *Mar. Environ. Res.* 1999; **47**: 61.
- Dowson PH, Bubbs JM, Lester JN. *Mar. Pollut. Bull.* 1993; **26**: 487.
- Mercier A, Pelletier É, Hamel J-F. *Aquat. Toxicol.* 1994; **28**: 259.
- Quevauviller P, Lavigne R, Pinel R, Astruc M. *Environ. Pollut.* 1989; **57**: 149.
- Kan-Atireklap S, Tanabe S, Sanguansin J, Tabucanon MS, Hungspreugs M. *Environ. Pollut.* 1997; **97**: 79.

40. Harino H, O'Hara SCM, Burt GR, Chesman BS, Langston WJ. *Chemosphere* 2005; **58**: 877.
41. Burkhard LP, Cook PM, Lucasewycz MT. *Environ. Sci. Technol.* 2004; **38**: 5297.
42. Pereira WE, Wade TL, Hostettler FD, Parchaso F. *Mar. Pollut. Bull.* 1999; **38**: 1005.
43. Meador JP. *Rev. Environ. Contam. Toxicol.* 2000; **166**: 1.
44. Tracey GA, Hansen DJ. *Arch. Environ. Contam. Toxicol.* 1996; **30**: 467.
45. Coelho MR, Bebianno MJ, Langston WJ. *Mar. Environ. Res.* 2002; **54**: 179.
46. Langston WJ, Burt GR, Mingjlang Z. *Mar. Pollut. Bull.* 1987; 634.