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Elevated tri(*n*-butyl)tin concentrations in shellfish and sediments from Suva Harbour, Fiji

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Tri(*n*-butyl)tin (TBT) concentrations were determined in sediments and selected shellfish from Suva Harbour, Fiji. Sediments in the immediate vicinity of foreshore slipways and boatyards were exceedingly contaminated, with a maximum observed level of 38 μg g^{-1} TBT-Sn. Concentrations were much lower in surficial sediments from commercial docks and yacht mooring areas, namely 16–83 ng g^{-1} TBT-Sn. Mangrove oysters (*Crassostrea mordax*), gastropods (*Thais mancinella*), and bivalves (*Anadara scapha*) were found to have accumulated TBT. Concentrations as high as 3180 ng g^{-1} TBT-Sn were found in mangrove oysters. With respect to the mangrove oyster, its widespread distribution, abundance and proclivity to accumulate TBT suggest that it is likely to be the best bioindicator species of TBT contamination in Fijian coastal waters.

Keywords: Tributyltin, Fiji, sediments, shellfish

INTRODUCTION

Tri(*n*-butyl)tin, commonly referred to as TBT, is widely recognized as a potent environmental toxin.[1,2] Concentrations known to cause deleterious effects in marine biota and those observed in coastal seawater adjacent to boating and shipping activities markedly overlap, resulting in widespread biological damage.[3] The most obvious manifestations are shell deformation in the Pacific oyster (*Crassostrea gigas*)[4–5] and the induction of imposex in neogastropods.[7–9] Several other organisms are also adversely affected.[10–13]

The major pathway of TBT to the marine environment is through its use as the active ingredient in antifoulant paints. These are applied to small pleasure craft, ocean-going transporters, and naval vessels. The residence time of TBT in seawater is relatively short as it is rapidly adsorbed onto suspended particles with subsequent deposition. Degradation rates within the sediments are comparatively slow with respect to those observed within the water column, and TBT can persist for decades.[14–16]

TBT acts as a localized contaminant, but has been shown to be of global concern. Due to its damaging consequences for marine ecosystems, several countries have imposed legislative controls on the usage of TBT (or all organotin compounds in some cases) in antifoulant paint formulations.[2] No regulations governing the utilization of TBT exist in Fiji. This paper presents the first environmental TBT data for Fiji. A preliminary survey of shellfish and sediments in Suva Harbour was conducted, initiating a database for future management of TBT in the South Pacific.

METHODS

Environmental setting

Shellfish and sediments were collected at various sites in Suva Harbour during 3–5 April 1991. Sample locations are shown in Fig. 1. Sediments were obtained from four locality types: a yacht moorings area (the Royal Suva Yacht Club), a commercial wharf (King's Wharf), the naval dockyard and in the immediate vicinity of several slipways. Surface benthic sediments were collected using a Van Veen grab sampler. A core was collected from the marina by divers.

Shellfish samples from Suva Harbour comprised one species of oyster and three species of gastropods. It should be noted that shellfish were not present at all sites from which sediments were collected. Mangrove oysters (*Crassostrea mordax*) were obtained from intertidal sites along the waterfront. The neogastropods (*Thais mancinella, Morula spinosa* and *Littorina scabra*) were collected from the pilings at Shed Island. This site is about 400 m off the shore and is known to be a location at which imposex in neogastropods has

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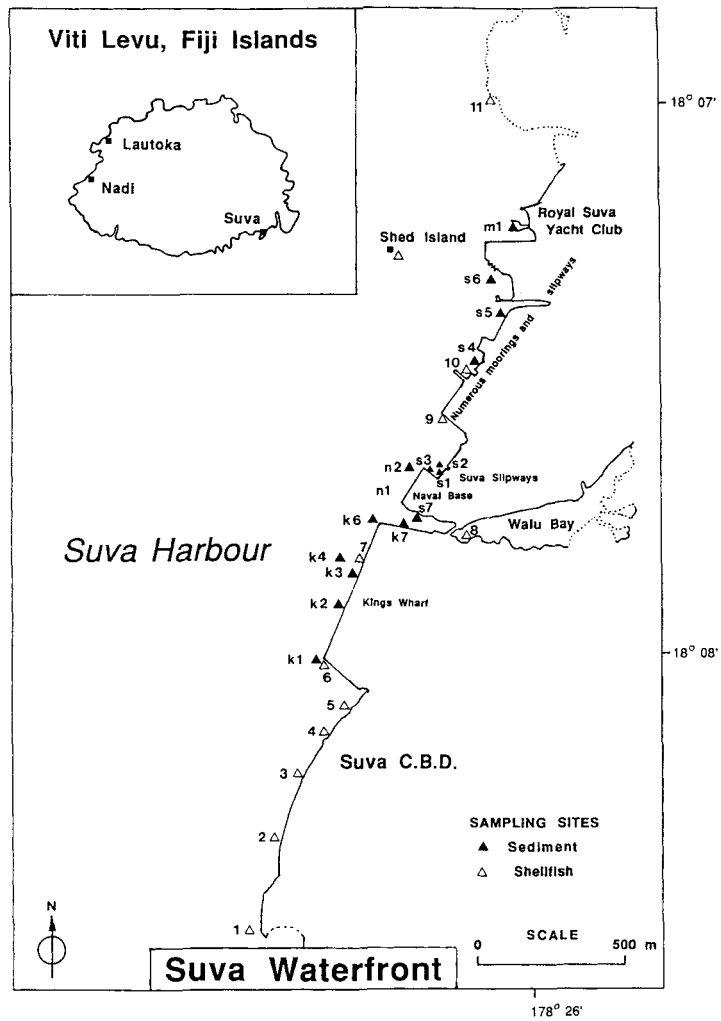

Figure 1 Sampling locations in Suva Harbour, Fiji.

been observed (Ellis, D. V., personal communication). Mangrove oysters were also collected at this location for comparative purposes. Finally, shellfish intended for human consumption were purchased at the main Suva market. Samples of the sea urchin (*Tripneustes gratilla*, local name *Cawaki*) and a marine bivalve (*Anadara scapha*, local name *Kaikoso*) were obtained.

Analyses

TBT was analysed in sediments and shellfish as described previously.[9] The TBT was desorbed from sediments (about 10–15 g wet weight) using 5 cm^3 of 2 mol dm^{-3} hydrochloric acid (HCl). TBT was then extracted into 18 cm^3 hexane. Di- and mono-butyltin compounds were removed using a backwash with 2 cm^3 of 3 % sodium hydroxide (NaOH) and then the TBT was oxidized to inorganic tin with 1 cm^3 of concentrated nitric acid (HNO_3). Following evaporation of the hexane, the volume was made up to 10 cm^3 with Milli-Q water. This solution was analysed by graphite furnance atomic absorption spectroscopy. Measurements were made at 286.3 nm using a Perkin–Elmer AAS-5000 with an HGA-500 graphite furnace and an AS-40 autosampler. Background correction was carried out using a deuterium lamp and 0.36 % $K_2Cr_2O_7$ was employed as a matrix modifier. The moisture content of a sediment subsample was determined in order to express results on a dry weight basis.

With respect to biological samples, a composite sample from each location and for each species

was produced by combining six individuals. These composite samples comprised the complete soft tissues from six individuals which had not been depurated. The composites were freeze-dried and ground to a fine powder. The TBT was solubilized from 1–2 g of sample using 2 cm^3 of concentrated HCl and thereafter analysed as described above for sediments.

The results here are reported as hexane-extractable tin in that the procedure may not distinguish between butyl- and phenyl-tin compounds. The detection limit is approximately 5 ng g^{-1} TBT-Sn for sediments, and 15 ng g^{-1} TBT-Sn for shellfish. Analytical precision is in the order of 5–10 %. The extraction efficiency from TBT-spiked sediments is 90 %.

RESULTS AND DISCUSSION

Sediments

TBT concentrations (reported here as ng g^{-1} hexane-extractable Sn) for sediments from Suva Harbour are listed in Table 1. Concentrations in surficial sediments ranged from 16 to 38000 ng g^{-1} hexane-extractable tin. This upper value is extremely high, and greatly exceeds the previously reported maximum level of 10780 ng g^{-1} TBT-Sn found in Vancouver Harbour sediments.[17] This high degree of localized contamination results from the unregulated use of TBT in Fiji and uncontrolled activities in foreshore shipyards.

The greatest concentrations of TBT in Suva Harbour were found in the vicinity of the slipways, i.e. in areas where ship hull hydroblasting and repainting operations are conducted. Waste waters from such operations are discharged without restriction into the harbour, transporting TBT-contaminated paint residues, which occasionally were evident as surface slicks. Such practices are not unique to Fiji as indeed other studies have shown slipways and dry docks to be significant sources of TBT to the marine environment, with hotspots of TBT contamination to be found in adjacent benthic and intertidal sediments.[6,18] Concentrations also tend to be elevated in sessile marine biota adjacent to slipways and, accordingly, TBT-induced biological damage tends to be most severe in these localized areas.[19,20]

The polluted samples from Site s1 were collected from an area of intertidal mud on the foreshore of the main Suva slipway. The disparate

Table 1 Hexane-extractable tin in sediments from Suva Harbour, Fiji

Site	Locality type	Water depth (m)	Hexane-extractable tin (ng g^{-1} dry weight)
Surface sediments			
s1	Slipway	Intertidal	38000
s1	Slipway	Intertidal	15200
s2	Slipway	1	4050
s3	Slipway	2	361
s4	Slipway	1	758
s5	Slipway	2	37
s6	Slipway	2	36
s7	Slipway	2	364
k1	Wharf	9	83
k2	Wharf	11	4
k3	Wharf	10	51
k4	Wharf	15	66
k5	Wharf	12	16
k6	Wharf	9	74
n1	Slipway	Intertidal	483
n2	Slipway	Intertidal	164
Core from the Royal Suva Yacht Club			
m1	Moorings	2	
		Sediment depth (cm)	
		0–2	18
		2–4	44
		4–6	28
		6–8	41
		8–10	14
		10–12	<5
		12–14	<5
		14–16	<5
		16–18	<5
		18–20	<5

TBT concentrations found in these samples are a manifestation of sediment heterogeneity, most likely due to the presence of discrete paint flakes. Similar observations have been made near the outfall from the Naval Dockyards in Auckland, New Zealand, which used to be subjected to periodic emissions of TBT antifoulant residues as a consequent of ship refit operations.[21] The presence in the sediments of persistent paint flakes has been highlighted as a possible problem in the Mediterranean Sea with respect to long-term control of TBT in the marine environment.[22]

TBT concentrations measured in samples from King's Wharf were lower, ranging between 16 and 83 ng g^{-1} hexane-extractable tin and with a mean value of 59 ng g^{-1}. These concentrations are similar to those determined in sediments from

Auckland's commercial port area, which were in the range 35–68 ng g^{-1} hexane-extractable tin.[21] Much higher concentrations have been observed in Mediterranean ports and Boston Harbour where commercial ships dock.[22,23] Clearly significant quantitites of TBT can originate from large oceangoing vessels. As indicated in Table 1, slightly higher concentrations of 164 and 483 ng g^{-1} hexane-extractable tin were found in sediments collected near the Navy wharves. Site n1 was also adjacent to a small slipway.

A core was collected from the sediments underlying the Royal Suva Yacht Club. This is relatively small moorings facility with provision for only about 50 yachts. Hexane-extractable tin was detected down to, but not below, 10 cm depth. Levels of TBT in the upper horizons ranged from 14 to 44 ng g^{-1} TBT-Sn. These quantitites are much lower than typical TBT concentrations measured in marinas elsewhere, namely 100–300 ng g^{-1} TBT-Sn in Auckland, New Zeland,[15,21] approximately 400 ng g^{-1} TBT-Sn in Lake Lucerne, Switzerland,[24] up to 518 ng g^{-1} TBT-Sn in Boston Harbour, USA,[23] and 380 ng g^{-1} TBT-Sn in Puget Sound, USA.[18] The Royal Suva Yacht Club does not have an enclosing wall, and it is probable that sedimentation rates are relatively low. Tidal flushing effectively disperses TBT leaching from yacht hulls. Whereas many marina cores exhibit decreasing TBT concentrations down the sediment profile,[14,15,24] no such trend was observed in this study.

Shellfish

TBT concentrations in four species of mollusca collected from the intertidal region of the pilings of a small shed approximately 0.5 km off the coast from the Royal Suva Yacht Club are presented in Table 2. Although the four species would have been exposed to the same ambient seawater TBT concentrations, TBT accumulation obviously has varied widely. The periwinkle *Littorina scabra* and the spiny gastropod *Morula spinosa* had not accumulated TBT to detectable levels (i.e. <15 ng g^{-1} hexane-extractable tin). In contrast, *Thais mancinella* was found to contain 443 ng g^{-1} hexane-extractable tin and the mangrove oyster *Crassostrea mordax* contained 869 ng g^{-1} tin. Inter-species differences in efficiency of TBT accumulation can be a manifestation of different feeding modes (*Littorina* is a grazer, whereas the other species are filter feeders); filtration rates (for example Pacific oysters reportedly filter up to 10 dm^3 of seawater per hour); and rates of depuration and metabolic breakdown of TBT. The degradation of TBT in the the tissues of mollusca is thought to be relatively slow, with a half-life of several months.[25]

Table 2 Hexane-extractable tin in mollusca either collected at Shed Island in Suva Harbour or purchased at the Suva Market, Fiji

Organism	Hexane-extractable tin (ng g^{-1} dry weight)
Shed Island samples	
Crassostrea mordax	869
Thais mancinella	443
Morula spinosa	<15
Littorina scabra	<15
Market samples	
Tripneustes gratilla	<15
Anadara scapha	90

As noted in Table 2, TBT accumulation is greatest in mangrove oysters. These filter feeders are abundant and widespread in Fijian coastal waters. Such attributes suggest that this organism would thus be the most suitable bioindicator of TBT contamination in the marine environment of Fiji. The hexane-extractable tin concentrations in mangrove oysters (*Crassostrea mordax*) collected along the Suva Harbour waterfront are displayed in Table 3. TBT was detected in oysters from all the sites, and ranged from 626 to 3180 ng g^{-1} hexane-extractable tin. These levels are quite high but are comparable to contaminated shellfish observed elsewhere. TBT concentrations in

Table 3 Hexane-extractable Sn in mangrove oysters from the waterfront along Suva Harbour, Fiji

Site	Hexane-extractable tin (ng g^{-1} dry weight)
1	733
2	835
3	1650
4	1110
5	2050
6	2930
7	1260
8	No live oysters found
9	626
10	3180
11	1890
Shed Island	869
Royal Suva Yacht Club	No live oysters found

Pacific oysters, *Crassostrea gigas* have been measured up to 1640 ng g^{-1} organic tin in Arcachon Bay, France,[26] and as high as 2250 ng g^{-1} TBT-Sn adjacent to a marina washdown facility in Auckland, New Zealand.[6] Also, concentrations as high as 3700 ng g^{-1} tin were measured in *Dreissena* mussels from a marina in Lake Lucerne, Switzerland.[24]

Given the exceedingly high sedimentary TBT concentrations recorded along the Suva Harbour waterfront, it is perhaps surprising that oyster body burdens of TBT are not higher. However, it should be noted that oysters could not be found in the most heavily polluted areas, such as in the vicinity of the slipway complex just north of Walu Bay (Sites s1–s32). Moreover, TBT is not a conservative contaminant and the processes acting to depurate and/or degrade the toxin may proceed more rapidly in the tropical marine environment than in temperate regions due to the warmer ambient temperature. Seawater temperatures are approximately 10 °C warmer on average throughout the year, compared with those recorded in Auckland.

At the TBT body burdens recorded in this study, there is every reason to suspect that biological damage would be sustained by marine biota. Concentrations of 200–400 ng g^{-1} TBT-Sn in the Atlantic dogwhelk *Nucella lapillus* are associated with imposex that has progressed to the point of sterility.[27] A similar situation exists for the New Zealand oyster borer *Lepsiella scobina*.[9] A limited pilot study of imposex occurrence in Fijian neogastropods has been carried out at the Shed Island site and all females in 20 specimens of *Thais mancinella* examined were definitely masculinized (Ellis, D. V., personal communication).

Human exposure to TBT tends to be rather restricted. Intake is often limited because the extreme sensitivity to TBT of many mollusca gathered as food will result either in early shellfish mortality or individuals with an obviously unhealthy appearance. Nonetheless, TBT has been detected in the flesh of maricultured salmon reared in sea pens painted with TBT antifoulant.[28,29] There is no other recorded incidence of the entry of TBT into the human diet. In this study, TBT has been detected in shellfish intended for human consumption in Suva. As shown in Table 2, the *Cawaki* or sea urchin (*Tripneustes gratilla*) did not contain measurable TBT, but the marine bivalve *Kaikoso* (*Anadara scapha*) contained 90 ng g^{-1} TBT-Sn. An acceptable daily intake (ADI) for humans is regarded as 0.006 mg kg^{-1} day^{-1};[30] thus a 20 kg child would have to eat 133 contaminated *Kaikoso* (at approximately 10 g dry weight each) per day to reach the ADI level. Thus, the observed levels are clearly not of significance with respect to public health in Fiji.

CONCLUSIONS

This study reports the first data for TBT in the marine environment of Fiji. Present unrestricted use of TBT antifoulants has resulted in the highest sedimentary TBT concentrations yet measured globally. The greatest levels, up to 38000 ng g^{-1} tin, were observed in the vicinity of foreshore slipways along the Suva Harbour waterfront. Six species of shellfish were either collected from the harbour or purchased locally. Relatively warm temperatures may mitigate against accumulation in shellfish and only mangrove oysters (*Crassostrea gigas*), the gastropod *Thais mancinella*, and the clam *Anadara scapha* were found to have accumulated TBT to varying extents. Of these, the mangrove oyster is likely to be the best bioindicator species for Fijian coastal waters.

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