A study on tributyltin contamination of marine sediments in the major ports of Fiji

Matakite Maata and Kanayathu Koshy
Department of Chemistry, School of Pure and Applied Sciences,
The University of the South Pacific, Suva, Fiji

ABSTRACT

Tri-n-butyltin (TBT) compounds are synthetic, multipurpose chemicals, which have been extensively used, in marine anti-fouling paints. They have been known to be extremely poisonous to mollusc fishery resources (oysters, clams, scallops, etc.). TBT levels in marine sediments from the main ports in Fiji were analysed using the GC/FPD method. The results indicated that these sites were among the worst polluted with TBT in the world. The most contaminated site recorded a TBT concentration of 360μgg^{-1}. TBT comprised 48-90% of the total organotins measured. Some stringent legislative means are needed to regulate the use of this contaminant in marine anti-fouling paints.

Keywords: *TBT, biocide, anti-fouling, sediments, Fiji*

1 Introduction

TBT compounds are active biocides in anti-fouling paints used on ship hulls (Evans *et al*., 1996; Stab *et al*., 1996). The wide applications of TBT began in the early 1960s when it was found that they inhibited the growth and attachment of fouling organisms such as algae, barnacles, tubeworms (Huet *et al*., 1996), mussels (Huggett *et al*., 1992) and wood worm borers (Greenwood and Earnshaw, 1993) on ship and boat hulls. It is through this use that the marine TBT finally finds its way into sediments where it eventually decomposes into the less toxic dibutyltin (DBT) and monobutyltin (MBT). This study considers these organotin (OT) species in a tropical Pacific environment taking Fiji as an example. In the present paper, an attempt has been made to summarise our studies on the quantification and degradation kinetics of TBT into its equilibrium component forms.

2 Study Sites

The sites studied included a slipway in Walu Bay, Suva, a jetty in Lautoka and jetties also in Savusavu and Labasa. These sites are shown in Figure 1.

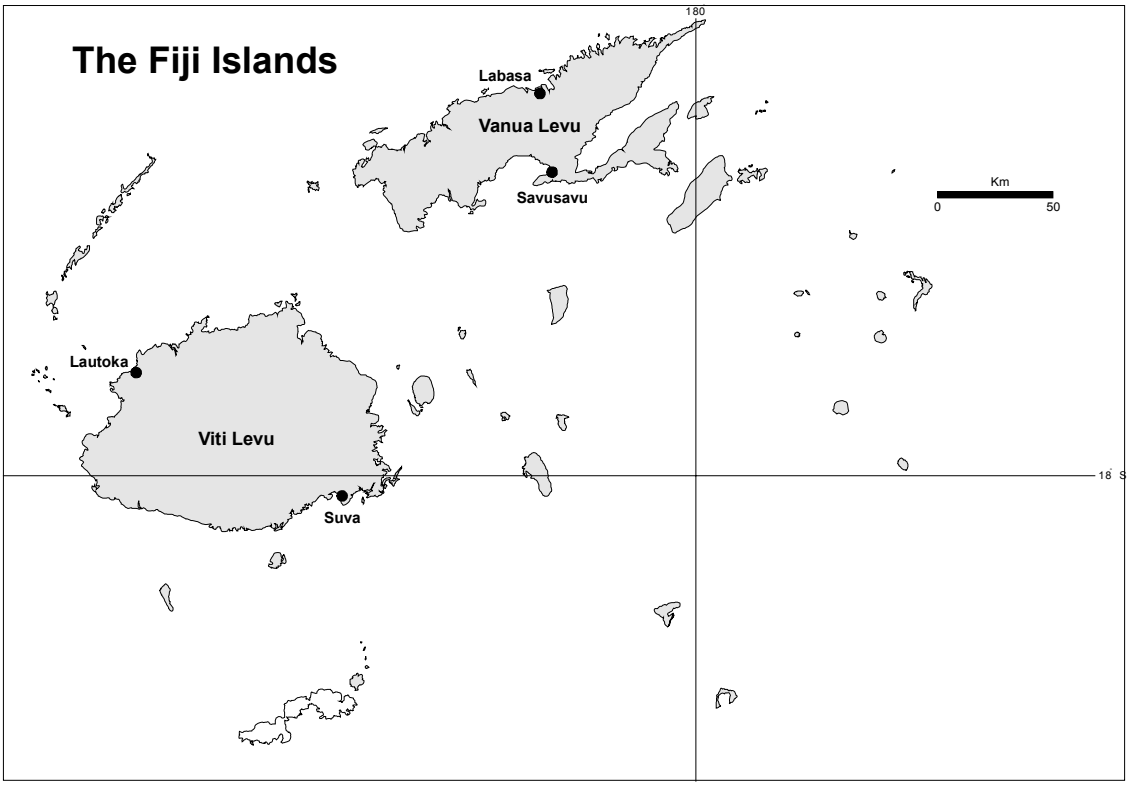

Figure 1. Fiji Islands showing the study sites.

3 Materials and Methods

Sediment samples were collected with a ponar grab sampler (or by hand when possible), and were stored frozen in polyethylene bags. These were then subsequently freeze-dried and stored till analysis.

In preparation for the organotin analysis, a slightly modified version of an extraction procedure by Krone was used. This involved extracting the TBT in sediments with methylene chloride, derivatizing it with Grignard reagent, pentyl magnesium bromide to generate the volatile tetra-alkylated organotins and detecting the tin using Gas Chromatography with a flame photometric detector (GC/FPD) (Krone, 1995). The analysis with the GC/FPD was carried out at the Institute of Ocean Sciences, Sidney, B. C., in Canada.

4 Results and Discussion

The data from the analysis of the samples from Suva (Walu Bay), Lautoka, Savusavu and Labasa are presented in Tables 1, 2 and 3. These include organotin concentrations and the ratios for [MBT]/Total [OT] and [TBT]/[DBT].

Table 1 Results of the field samples from Walu Bay showing the OT concentrations and the ratios of MBT with Total OT and TBT with DBT.

Sample No.	Date	TBT (µg/g)	DBT (µg/g)	MBT (µg/g)	Total OT (µg/g)	MBT/OT ratio	TBT/DBT ratio
10	24/4/95	116	40.4	48.4	205	0.236	2.87
28	25/5/95	132	45.4	97.7	275	0.355	2.91
37	29/6/95	72.2	19.5	7.97	100	0.079	3.7
42	12/7/95	360	91.1	45.2	496	0.091	3.95
63	24/8/95	196	86.7	90.2	373	0.242	2.26
77	1/10/95	106	17.3	45.9	169	0.271	6.13
88	2/12/95	223	175	66.5	465	0.143	1.27
92	2/2/96	91.9	26.0	15.5	133	0.116	3.53

Table 2 Results of the field samples from Lautoka wharf (LW) showing the ratios of MBT with Total OT and TBT with DBT.

Sample No.	Date	[TBT] (µg/g)	[DBT] (µg/g)	[MBT] (µg/g)	Total [OT] (µg/g)	[MBT]/Tot [OT]	[TBT]/[DBT]
9 (LW1)	20/4/95	25.0	1.35	14.2	40.55	0.35	18.5
29 (LW1)	25/5/95	52.8	3.83	16.5	73.13	0.226	13.8
30 (LW2)	25/5/95	45.5	5.00	18.7	69.2	0.27	9.1
60 (LW1)	12/8/95	43.4	2.03	8.76	54.19	0.162	21.4
61 (LW2)	12/8/95	20.4	1.97	3.45	25.82	0.134	10.4
80 (LW1)	28/10/95	37.4	4.13	12.9	54.43	0.237	9.1
81 (LW2)	28/10/95	41.6	8.52	21.0	71.12	0.295	4.9
90 (LW1)	1/2/96	15.0	1.88	2.17	19.05	0.114	8.0
91 (LW2)	1/2/96	29.3	3.46	8.12	40.88	0.197	8.5

Table 3 Results of field samples from Savusavu (SVSV) and Labasa (LBS).

Sample No.	Site	[TBT] (µg/g)	[DBT] (µg/g)	[MBT] (µg/g)	Total [OT] (µg/g)	[MBT]/Tot [OT]	[TBT]/[DBT]
32	SVSV1	39.6	1.22	4.02	44.8	0.089	32.5
33	SVSV2	15.8	0.669	2.01	18.5	0.109	22.6
34	SVSV3	21.1	0.205	6.55	27.9	0.235	103
35	LBS1	34.9	2.54	5.17	42.6	0.121	13.7
36	LBS2	89.0	4.16	5.47	98.6	0.056	21.4

The TBT concentrations were highest in the Walu Bay sediments (Figure 1), when compared with the other ports (Tables 1, 2 & 3). This can be attributed to the slipway source at this site. Out of the three organotin species, TBT is dominant in all the samples analysed. Table 4 presents some of the international TBT data compared with the data from this site. It is evident that the Fiji sediments from the two studies presented in the table are heavily loaded with this contaminant. TBT concentration as low as 0.659ng TBT g^{-1} has been reported to be toxic to molluscs (O'Connor, 1996).

Table 4 TBT concentrations from various studies

Site	Depth (cm)	Concentration (ng Sn g^{-1} dry weight)	Reference
Suva Harbour, Fiji	Surface	<5-38 000	Stewart & de Mora, 1992
Suva Harbour, Fiji	Surface	72 200-360 000	This study
Arcachon Bay, France	0-50 cm	<5-5 000	Astruc et al., 1990
Kaipara Harbour, NZ	0-40 cm	<4-759	de Mora, King & Miller, 1989
San Diego Harbour, USA	0-20 cm	8-66	Stang & Seligman, 1986
San Diego Harbour, USA	Surface	143	Stang, Lee & Seligman, 1992
North Chesapeake Bay, USA	Surface	58-570	Matthias et al., 1988
Poole Harbour, UK	Surface	8-213	Langston et al., 1987
Sado Estuary, Portugal	Surface	6-213	Quevauviller et al., 1988
Sydney Harbour, Australia	Surface	10-8 000	Batley & Brockbank, unpublished results
Georges River, Sydney, Australia	0-40 cm	<0.2-20	Kilby & Batley, 1993
Great Bay Estuary, New Hampshire, USA	Surface	4-20	Weber et al., 1988

TBT degrades to other lesser toxic organotin compounds, DBT and MBT in seawater and sediments. The half-life of TBT in sediments varies from 16 weeks to 3.5 years with the latter now believed to be representative (Ko *et al*., 1995). At the Walu Bay site, the supply of TBT into the environment can be considered to be excessive over removal by degradation.

The ratio, [MBT]/total [butyltins] is used to determine whether the discharge is recent. Low ratios (0.03-0.1) indicate recent discharge of TBT. Ratios as low as 0.03, show TBT "hot spots". In Hong Kong, measured ratios correlated with the recent release of TBT into the sediments in marinas and shipyards, which were heavily, contaminated **(**Ko *et al*., 1995). No "hot-spots" were identified from these sites although there were two samples from Walu Bay that had values <0.1 (Table 1). The remaining ports had ratio values >0.1. This is no surprise as there is a known source of TBT at this port (Stewart and de Mora, 1992).

The ratio, [TBT]/[DBT], has also been used previously as a first estimate of the stability of the organotin (Tolosa *et al*., 1992). This is because the organotin compound degradation occurs via a successive cleavage of the alkyl or aryl substituents (Maguire *et al*., 1986). In sediments, the higher ratios were found in enclosed systems, which had slower anaerobic degradation processes prevailing. The trend in the ratio is a relative decrease from organisms to sediments to seawater and this is thought to be due to a lower stability of TBT in water and/or a higher affinity for biota and sediments (Tolosa *et al*., 1992). It is obvious from the data available (Tables 1-3) that the sites had high values of this ratio, implying stability of TBT. This, however, may not necessarily be the case as the high TBT input could also be responsible for the high ratio value. This again could be attributed to the unrestricted usage of TBT in marine paints in this country.

5 Conclusions

The sediments of the major ports in Fiji contain very high concentrations of TBT. The high input of TBT into the environment and particularly sediment overrides any removal by the degradation pathway. Stringent legislative measures are needed to curb the uncontrolled usage of this contaminant in marine paints. The people who are consumers of the marine resources, which are being threatened, need awareness and education programmes on the impact of TBT on the environment. It is these people who can pressure the authorities for tougher legislation on TBT use.

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