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Detection of Organotin Compounds in the Surface Seawater and Sediments along the Coast of Okinawa Island, Japan

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Abstract

Six organotin species - tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT), triphenyltin (TPT), diphenyltin (DPT) and monophenyltin (MPT) - were investigated along the coast of Okinawa Island, Japan. Analytical conditions for organotin compounds in seawater and in marine sediments were optimized for GC with pulsed flame photometric detector. In July 2002, samples were collected at 30 locations. Butyltin species were present in all stations, but phenyltin species can be detected in only a few stations. The TBT concentration ranged from 40.2 ng L⁻¹ Sn to ND (not detected) in the seawater, and from 172 to 1.20 ng g⁻¹ Sn (dry weight) in sediments, with the highest values closely related with shipping activity and decreasing according to the distance from potential sources. A comparative study of the concentration of organotin species in 2002 and 2003 showed an increase trend.

Introduction

Marine pollution with organotin compounds has been a matter of concern in environmental and fishery science of the world. So determination of organotins level in the marine environment is of special concern.

Organotin compounds, characterized by containing at least one bond between tin and carbon and generally represented as R_nSnX_{4-n} (n=1-4; R=alkyl or aryl; X=H, halogen, etc.), are produced globally at about 51,000 tons per year (Fent *et al.*, 1996). Organotin compounds are man-made synthetic substances. They have several specific applications, where the most important are antifouling, woodpreservation, agricultural use (triphenyltin), and additive in painting and stain. Compared with private use, industrial use is dominating (Maguire *et al.*, 1987; Evans *et al.*, 1985; Blunden *et al.*, 1985).

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Tributyltin (TBT) is used primarily as an antifoulant paint additive on the ships, seawater piping systems and fishnets to prevent the growth of marine organisms (Michel *et al.*, 1999).

After TBT is released from the antifouling paint into water, due to the low water solubility, it is rapidly adsorbed to suspended matter and deposit. At the sea bottom it accumulates in the sediments. The active substance TBT is highly toxic and can damage to a multitude of species. Numerous bottom-dwelling organisms take up TBT via their food or contact with water and sediments. The compound accumulates in their tissues and causes damage such as mimic or interference with hormones, shell deformation or inhabitation of larval release, reduction of native populations (Alzieu *et al.*, 1989). Organotin compounds have high bioaccumulation potential, persistence in sediment for periods of up to several years and toxicity to marine organisms (Ritsema *et al.*, 1991). Their widespread use in conjunction with ships and fishing nets resulted in severe contamination of aquatic environments during the 1980s and early 1990s (Ambrose *et al.*, 1994). Since 1982, the partial restriction is imposed by many countries. However, based on recent reports, it can be concluded that organotin levels in water and in sediments remain relatively high, and continue to pose a toxic risk to marine organism.

In Japan, although the level of TBT concentration is low, even lower value also can cause damage to aquatic organisms. In recent years, all the studies of organotin have been focused on the mainland of Japan and determination of organotin in the marine organisms has been highlighted. To our knowledge, this is the first report on the detection of organotin compounds in the surface seawater and sediment along the coast of Okinawa Island.

In Okinawa Island, fisheries, beaches and harbors are the economic basis. Itoman harbor is the chief port, and various ships shuttle up and down every day. So it is important to ascertain the distribution of organotin compounds (butyl-, phenyl-) in the seawater and sediments along the coast of Okinawa Islands. Determination of organotin species was carried out through solvent extraction and derivatization of organotins with NaBEt₄ (sodium tetraethylborate) from samples.

After that treatment, samples were measured with the GC-FPD (Gas chromatography, in conjunction with a Flame Photometric Detector).

Experimental

1. Study area

The study area and the samples description are shown in Fig.1 and Table 1. Itoman harbor, Naha harbor and Aja harbor are the main commercial harbors. In this survey, the distribution of organotin compounds in Itoman harbor was assessed in detail.

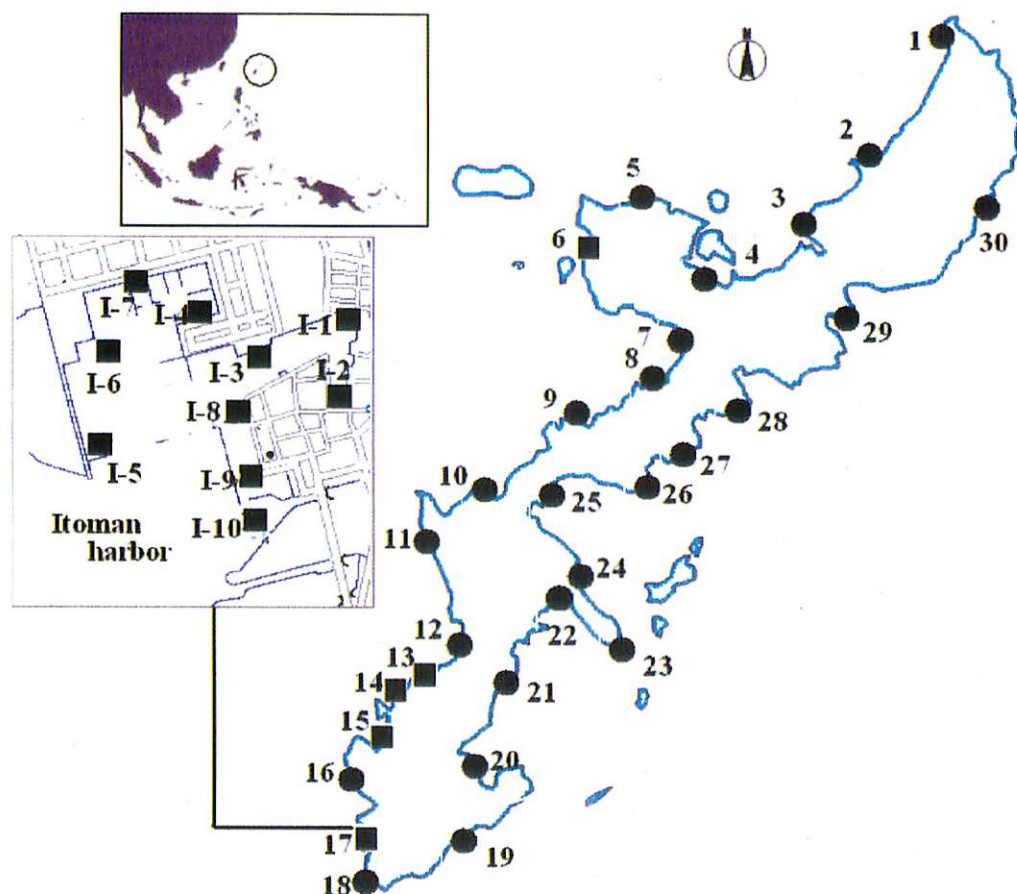


Fig. 1. Map of study area and sampling sites along the coast of Okinawa and Itoman harbor (● collected samples only in 2002, ■ collected seawater samples both in 2002 and in 2003)

2. Sample collection

Seawater samples were collected on July 26, 2002 from 30 locations along the coast of the Okinawa Island in pre-clean brown gallon glass bottle of 2 L capacity. Water samples were stored at 4°C in the dark until chemical extraction (Gomez *et al.*, 2000). On July 26, 2003, seawater samples were taken from Itoman harbor, Naha harbor, Aja harbor, Tomari harbor and Toguchi harbor.

Surface sediments and seawater were obtained on September 9, 2002 from 10 locations in Itoman harbor. Sediments were collected by a grab sampler in the clean polyethylene bottles, deep-frozen (-20°C) in dark until chemical extraction. On July 26, 2003, seawater sample was collected from the same location at Itoman harbor.

Table 1. Sampling locations around the Okinawa Island (July, 2002).

Station No.	Location	Condition
1	Ginama	open coast
2	Hentona harbor	harbor
3	Shioya bay	bay
4	Nakao	open coast
5	Nakasone	open coast
6*	Toguchi harbor	harbor
7	Nago harbor	harbor
8	Kyoda harbor	harbor
9	Onna	harbor
10	Maeda	open coast
11	Kadena	harbor located in the river
12	Chatan	river mouth
13*	Aja harbor	harbor
14*	Tomari harbor	harbor
15*	Naha harbor	harbor
16	Senaga Island	open coast
17	Itoman harbor	harbor
1- 1*		wet dockyard
1- 2*		middle mooring
1- 3*		middle mooring
1- 4*		north mooring
1- 5*		entrance harbor
1- 6*		middle mooring
1- 7*		middle mooring
1- 8*		middle mooring
1- 9*		south mooring
1-10*		outside harbor
18	Kyan cape	open coast
19	Minatogawa	river mouth, harbor
20	Shinkai	harbor
21	Nakagusuku	harbor
22	Nanbara	harbor
23	Heshikiya	harbor
24	Teruma	harbor
25	Ishikawa	river mouth
26	Kanna	beside river
27	Henoko	harbor
28	Abu	open coast
29	Kesaji harbour	harbor
30	Ada	beside river

* : Samples were collected in July, 2002 and July, 2003

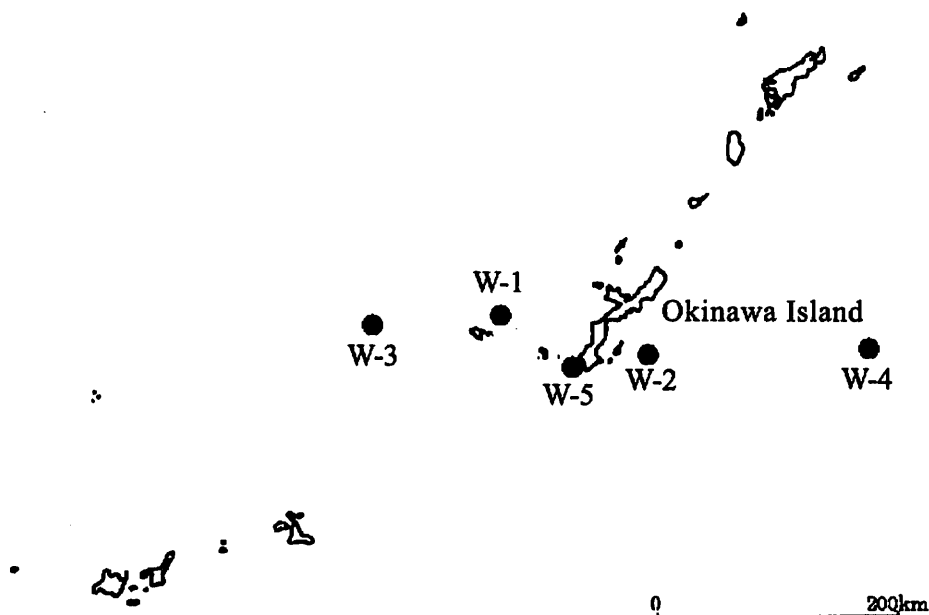


Fig. 2. Sampling points for open seawater around the Okinawa Island (2000).

We also got seawater samples from the open sea around the Okinawa Island through Nagasaki-maru expedition (Sep. 22th~Oct. 2nd, 2000). (Fig.2)

During sampling, plastic materials were avoided to minimize contamination of samples. And much care was taken with glassware clean-up. Sample bottles were cleaned with Milli-Q water, then rinse with 10% HNO_3 and kept overnight. Other glassware were soaked in 10% HNO_3 and subsequently (after washing) with 1% TMAH overnight. Finally all the glassware was cleaned with Milli-Q- purified water and dried in a clean room.

3. Reagents

Monobutyltin trichloride (MBT, 95%), monophenyltin trichloride (MPT, 98%), dibutyltin dichloride (DBT, 96%), diphenyltin dichloride (DPT, 96%), tributyltin chloride (TBT, 96%), triphenyltin chloride (TPT, 95%) and tripropyltin chloride (TPrT, 98% internal standard); TMAH (tetramethyl ammonium hydroxide, 25%) and sodium tetraethylborate (98%, NaBEt_4) were purchased from Kanto Chemicals (Tokyo, Japan). Hydrochloric acid ($\text{Sn} < 0.1 \text{ pg ml}^{-1}$), acetic acid ($\text{Sn} < 1 \text{ pg ml}^{-1}$), ammonia solution (Kanto) were of ultrapure grade, and sodium chloride, anhydrous sodium sulfate, tropolone, methanol, toluene, hexane were of pesticide-analysis-grade (Kanto).

Stock standard solutions of individual organotin compounds (1 g dm^{-3} as Sn) were prepared by dissolving appropriate amounts of the respective compounds in methanol, and

were stored at 4°C until required for use. TPrT chloride was used as an internal standard for both sample preparation and GC determination. The purification procedure for NaBEt₄ is described as follows: a 5% m v⁻¹ NaBEt₄ solution was centrifuged at 2000 rpm for 3 min to remove particulate organotin impurities. The supernatant was transferred into another centrifuge tube and extracted three times with one-tenth volume of hexane, in order to remove dissolved organotin impurities (Biselli *et al.*, 2000). Acetate buffer (1 mol dm⁻³, PH 5) was prepared by mixing acetic acid and ammonia solution. A 1 mol dm⁻³ HCl-methanol solution was prepared by mixing HCl with methanol. Sodium chloride and anhydrous sodium sulfate were heated at 500°C for 20 h to decompose organotin impurities. Tropolone was used without purification and 0.1% m v⁻¹ tropolone was freshly prepared in toluene for each extraction. The water use throughout the experiments was purified by Milli-Q water purification system (Biselli *et al.*, 2000).

4. Sample treatment

Seawater: 5 ml 1 M acetic acid/acetate buffer was added to 1 L of water sample and the pH was adjusted to 5. Then, 0.1 ml of internal standard (TPrT, 50 μg L⁻¹) and 1 ml 5% NaBEt₄ were added. Finally 30 ml hexane was added and stirred for 20 min using a Teflon magnetic stirring rod at room temperature. After clear phase separation, the hexane layer was collected with a Pasteur pipette in the centrifuged tube and mixed with 2 g anhydrous Na₂SO₄ and shaken manually for 1 min to remove traces of the water. After centrifuging at 2000 rpm for 3 min, the sample was separated the hexane layer from sodium sulfate, added 2 ml hexane to the centrifuge tube to recover the residual hexane. The extract was condensed to 1 ml by passing nitrogen gas 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.

Sediment: 0.1 ml TPrT (50 μg ml⁻¹) internal standard was added to 0.5 g frozen-dry sediment. After 10 min, 2 g of NaCl, 12 ml of toluene containing 0.1% tropolone and 10 ml of 1 mol L⁻¹ HCl methanol were added, and the mixture was extracted using a mechanical shaker for 60 min. 10 ml pure water was added into the tube, which was again shaken for 10 min. The tube was centrifuged at 2000 rpm for 3 min in order to achieve clear separation. The upper toluene layer was transferred into another centrifuge tube and evaporated to 5 ml under nitrogen gas. After evaporation, 5 ml of 1 mol L⁻¹ acetate buffer of pH 5, 15 ml of pure water and 1 ml 5% NaBEt₄ were added to the extract and shaken for 10 min for ethylation and extraction, then centrifuged for 3 min at 2000 rpm in order to achieve phase separation. The hexane layer was collected with a Pasteur pipette in the centrifuged tube and mixed with 2 g anhydrous Na₂SO₄ and shaken manually for 1 min to remove the water. Finally the extract was concentrated to 1 ml under nitrogen stream for analysis by GC.

5. GC-FPD analysis

Organotin determination was carried out using a gas chromatography (Hewlett-Packard 5890 Series) equipped with flame photometric detector (GC-FPD) and with 30 m (length) \times 0.32 mm capillary column (HP-1) coated with 0.25 μ m film (methyl siloxane). The column oven temperature was programmed from 55°C to 100°C at a rate of 15°C min⁻¹ and then a rate of 30°C min⁻¹ to a final temperature of 300°C with a 1.33 min hold time. Injector and detector temperatures were held at 250°C and 240°C, respectively (Tao *et al.*, 1999).

The concentrations of samples were calculated by comparing peak areas of organotin compounds in samples with those in internal standard.

Results and discussions

1. Organotin concentration in the harbor and along the coast

The concentrations of organotin compounds in seawater along Okinawa Island and in Itoman harbor area (2002) are listed in Table 2. The MBT, DBT and TBT concentrations were higher in the main commercial harbors, ranging from 5.54 to 18.7, 13.7 to 33.5 and from 24.9 to 40.2 ng L⁻¹ Sn, than in the small marinas, varying from ND (not detected) to 1.37, 0.31 to 5.98, and from ND to 4.62 ng L⁻¹ Sn, respectively. The highly contaminated sites, such as site 6, 13, 14, 15 and 17, reflected the intensity of the boating activity and low water exchange. Butyltin species were present in all stations, but phenyltin species can be detected in only a few stations. TBT levels below detection limit were found in the open coast and bay with the almost complete absence of moorings and marinas.

In this study, TBT concentrations at five locations were relatively high. Station 6, 13, 14, 15 and 17 had two to twenty times higher than the UK environmental quality standard (2 ng L⁻¹ Sn). These five locations might be in toxic to some aquatic organisms.

Table 2 showed the distribution of organotin species in seawater at Itoman harbor. A positive concentration gradient from the outer to the inner waters was observed. High levels of organotin compounds are observed at site I-1 and the surrounding areas, and decreasing sharply at locations far from the source. The highest concentration in waters was found in enclosed dockyard with low water turnover. I-1 is a site of wet dock for repairing, cleaning and painting operations, which indicates that antifouling paints would be the main source of TBT and site I-1 was supposed to be the main source of organotin species at Itoman harbor.

Organotin concentrations in sediments were presented in Table 3. Sediment collected at wet dock contains very high concentrations of butyltin species (MBT: 2,950 ng g⁻¹ Sn; DBT: 10,056 ng g⁻¹ Sn and TBT: 172 ng g⁻¹ Sn in dry weight). Sediment sample in wet dock was dreggy, rich in iron filing and particle attached with paint that was

Table 2. Concentration of organotin compounds in seawater (ng L⁻¹ Sn) along the Okinawa Island and at the Itoman harbor in July, 2002 (—, detection limit).

Station	MBT	DBT	TBT	MPT	DPT	TPT	Total
1	—	0.15	—	—	—	—	0.15
2	0.37	2.10	2.24	—	—	—	4.71
3	—	—	—	—	—	—	—
4	—	0.32	—	—	—	—	0.32
5	—	—	—	—	—	—	—
6	1.54	5.98	4.62	—	—	—	12.1
7	0.64	2.09	1.25	—	—	—	3.98
8	—	0.42	0.50	—	—	—	0.92
9	—	0.31	0.81	—	—	—	1.12
10	—	—	—	—	—	—	—
11	0.80	0.95	0.57	—	—	—	2.32
12	0.30	1.19	—	—	0.93	—	2.42
13	18.6	23.2	24.9	—	—	—	66.7
14	9.32	17.2	28.3	—	—	2.73	54.8
15	16.5	13.7	33.8	—	—	1.59	65.6
16	0.42	0.57	—	—	—	—	0.99
17							
I-1	9.12	33.5	40.2	1.00	1.00	1.00	85.8
I-2	5.96	18.6	36.0	—	—	0.63	61.2
I-3	5.54	21.1	35.4	—	—	0.13	62.2
I-4	4.01	14.8	11.2	—	—	0.09	30.1
I-5	1.68	2.56	1.97	—	—	—	6.21
I-6	1.86	7.63	3.57	—	—	—	13.1
I-7	1.55	7.27	3.75	—	—	—	12.6
I-8	1.69	5.60	2.50	—	—	—	9.79
I-9	2.01	13.65	23.60	—	—	—	39.3
I-10	0.34	0.66	0.10	—	—	—	1.10
18	0.47	0.15	—	—	—	—	0.62
19	0.80	—	—	—	—	—	0.80
20	1.37	1.35	—	—	—	—	2.72
21	1.13	1.98	1.20	—	—	—	4.31
22	0.63	0.90	—	—	—	—	1.53
23	0.85	1.44	1.68	—	—	—	3.97
24	1.04	2.13	1.42	—	—	—	4.59
25	0.62	1.38	—	—	—	—	2.00
26	—	0.08	—	—	—	—	0.08
27	0.67	1.86	1.36	—	—	—	3.89
28	—	0.34	—	—	—	—	0.34
29	0.98	2.75	1.65	—	—	—	5.38
30	—	—	—	—	—	—	—

Table 3. Organotin concentration in sediment (ng Sn g⁻¹, dry weight) from Itoman harbor in September, 2002 (—, detection limit; --, Could not get samples).

Station	MBT	Concentration/ng Sn g ⁻¹ In 2002					Total
		DBT	TBT	MPT	DPT	TPT	
I-1	2,950	10,056	172	7,992	139	114	2,1423
I-2	58.7	82.4	74.7	331.	5.28	2.24	554
I-3	25.1	45.6	48.4	473.1	—	—	592
I-4	39.4	55.8	113	239	1.35	0.88	449
I-5	1.36	—	7.28	4.40	—	—	13.0
I-6	--	--	--	--	--	--	--
I-7	1.42	2.46	1.45	14.5	—	—	19.8
I-8	20.6	12.8	1.32	22.6	0.84	1.12	59.3
I-9	46.6	59.1	2.36	38.8	5.89	1.75	155
I-10	1.29	2.03	1.20	44.3	—	—	48.8

expected to be peeled off from the ships, which might be the reason for higher values. The concentrations of butyltin compounds were relatively low in other stations, due to stronger water exchange in the outer harbor than in the inner harbor (Biselli *et al.*, 2000). It was found that the butyltin concentrations in sediment at Itoman harbor show the similar positive trend as observed in the seawater, declined with the distance from the source. At site I-1, the TBT concentration was lower than those of decomposed compounds, such as MBT and DBT. It shows that industrial and wastewaters might be the reason for high MBT and DBT levels, or the degradation of TBT from antifouling paints (Babu *et al.*, 2001). According to the classification proposed by Waite for the evaluation of the TBT pollution in sediments (Waite *et al.*, 1991), the surveyed areas are ranked from low contamination levels (0-20 ng g⁻¹ Sn) at stations of high water exchange with low tributyltin input, to medium contamination level (20-200 ng g⁻¹ Sn) at stations closer to harbor (Gomez *et al.*, 2001). At the Itoman harbor, the concentrations of organotin in sediment were higher than in the seawater, which suggests that sediments have a high sorption capacity for organotin species (Tolosa *et al.*, 1992). However, TBT concentrations found in sediments were below to those causing lethal effects to living organisms such as clam (300 ng g⁻¹ Sn) (Ruiz *et al.*, 1994).

2. Behavior of organotin in the harbor

Butyltin concentrations in seawater collected in July, 2003 are presented in Table 4. After comparing with the values of Butyltin species in July, 2002 in Table 2, the concentrations of butyltin in seawater collected in July, 2003 were slightly higher. Butyltin species may be derived from a little bit higher shipping density and lower yearly precipitation in 2003 than in 2002 and resuspension of settled particles by hydrographic condition (Ten *et al.*, 2003). It is also speculated that biota may release butyltin from

Table 4. Concentration of butyltin compounds in seawater (ng Sn l⁻¹) in July, 2003.

Station	Concentration/ng Sn l ⁻¹ In 2003		
	MBT	DBT	TBT
6	2.31	6.18	10.5
13	18.8	37.1	29.6
14	9.65	18.3	30.1
15	15.0	15.4	35.7
17 (<i>Itoman harbor</i>)			
I-1	10.6	42.1	42.6
I-2	5.23	18.1	37.8
I-3	6.80	27.2	38.7
I-4	2.21	30.0	13.7
I-5	1.74	3.71	2.10
I-6	2.41	12.0	5.92
I-7	2.03	8.92	7.81
I-8	1.95	5.70	3.92
I-9	3.60	18.2	27.5
I-10	0.51	0.88	0.14

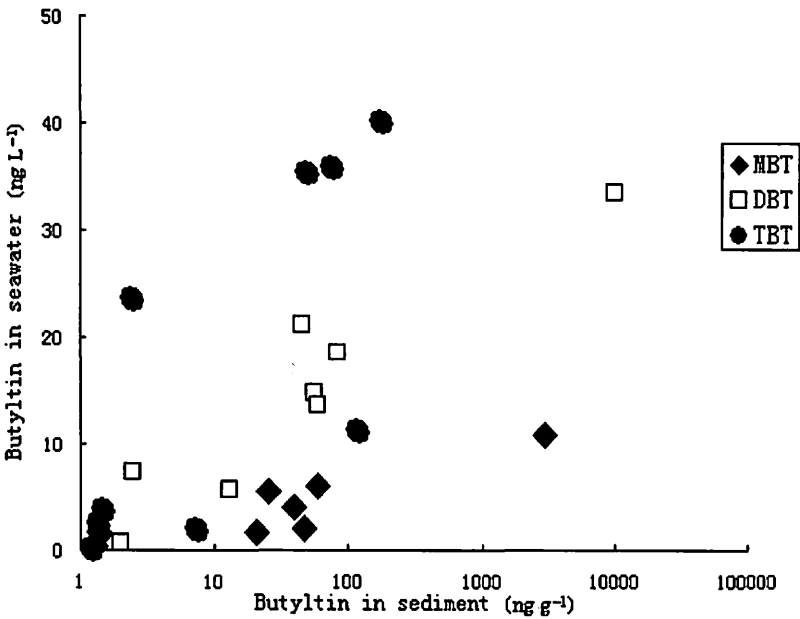


Fig. 3. The relationship of Butyltin concentration in the seawater and sediments (Itoman harbor) (in 2002).

resuspended sediment (Ritsema *et al.*, 1994), and a continuous input of the pollutant as a consequence of the use of stock TBT paints.

Figure 3 showed the relationship of butyltin concentration in the seawater and sediments at Itoman harbor. In this study, MBT mostly existed in the sediment, which might be own to degradation of TBT. DBT presented in both seawater and sediment. TBT

Table 5. Concentration of organotin compounds in seawater (ng L⁻¹ Sn) from the open sea around Okinawa Island (—, detection limit).

Station	MBT	Concentration/ng Sn L ⁻¹			In 2000	
		DBT	TBT	MPT	DPT	TPT
W-1	0.17	0.51	0.02	—	—	—
W-2	0.20	0.36	—	—	—	—
W-3	0.30	0.43	0.05	0.02	—	—
W-4	1.23	1.38	0.07	0.10	—	—
W-5	0.26	0.38	0.11	0.04	—	—

Table 6. Organotin concentration in the seawater (ng L⁻¹ Sn) reported for several areas in the world.

Station	MBT	DBT	TBT	References
European harbors and marinas	~1,200	~290	~600	Ruiz <i>et al.</i> , 1996; Ritsema <i>et al.</i> , 1998 Tolosa <i>et al.</i> , 1996 Chau <i>et al.</i> , 1997
American harbors and marinas	~460	~270	~500	
Asian and oceanian harbors and marinas	—	51	45-18,000	Harino <i>et al.</i> , 1998 Tong <i>et al.</i> , 1996
European ecological places	~110	~145	~50	Tolosa <i>et al.</i> , 1992 Ruiz <i>et al.</i> , 1996
American ecological places	~4.7	~9.3	~17.8	Chau <i>et al.</i> , 1997
Asian and Oceanian ecological places	~33	~21	~100	Tong <i>et al.</i> , 1996
Okinawa harbors and marinas	~40.2	0.3-33.5	~18.8	This research, 2002

~: Up to

was found mainly in the seawater, only a few sites showed irregularly, which maybe because the character of TBT which is not very stable or the TBT compound was supplied from other sources such as industrial factory. TBT is easy to be decomposed with sunlight or other factors (Skinner *et al.*, 1964). Another reason might be the property of seawater, usually mobility and easy to be vertically mixed or stratified.

3. Comparison of Butyltin levels

The concentration of organotin in the open sea was listed in Table 5. Comparing with the values in the harbors and marinas, the concentration was much lower, where the range of MBT, DBT and TBT concentrations were from 0.17 to 1.23 ng L⁻¹ Sn; 0.36 to 1.38 and from ND to 0.11 ng L⁻¹ Sn, respectively. Which was supposed to be far away from the source.

Butyltin levels found in this study are a little bit higher than some ecological places reported previously in different areas of the world (Table 6). As expected, those higher levels are in agreement with considering that all these studies corresponded to harbors and marinas, where TBT accumulates in sediment and shows a different behaviour due to tidal regime or dilution effects. Clear relationships could be obtained from marinas and port areas. Then, comparison with the harbors and marinas in other areas reflects that butyltin compounds in the coast of Okinawa Island occur in much lower levels. In this matter, we can assume that differences are more related to the traffic of boats which still use TBT-based antifouling paints.

Conclusions

The distribution of organotin species in seawater and in the sediment were assessed along the coast of Okinawa Island in 2002 and 2003. The harbors and marinas were the major sources of pollution, especially in the chief commercial harbors. The TBT values in seawater were above the threshold of 1 ng L^{-1} , which is known to cause toxic effects for some marine species.

In Itoman harbor, the highest concentration was found, showing 40 times higher than the toxic level. There has the ship-repairing industry, which was supposed to be the source of organotin, and a positive concentration gradient from outer to inner was found.

A comparative study of the concentration of organotin species in 2002 and 2003 showed an increase trend with year, however compared with other places in the world, Okinawa Island is a relatively clean place.

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