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Butyltin and phenyltin residues in water, sediment and biological samples collected from Otsuchi Bay, Japan

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Between 1996–2001, butyltin (BT) and phenyltin (PT) compounds were monitored in water, sediment, plankton mussels and fish from Otsuchi Bay. The changes of tributyltin (TBT) compounds in water and sediment were not observed during study period, however TBTs in plankton, mussels between 1997–1999 decreased in comparison with those in 1996. The current status of BTs and PTs in Otsuchi Bay was investigated. TBT in water, sediment, plankton, mussels and fish ranged of <0.002–0.022 $\mu g\,l^{-1}$, 0.016–0.110 mg kg^{-1} dry, 0.010–0.255 mg kg^{-1} dry, 0.012–0.048 mg kg^{-1} wet and 0.009–0.029 mg kg^{-1} wet, respectively. TBT concentrations were high near the shipyard. Triphenyltin (TPT) compounds in water and mussel were not detected. TPT in sediment, plankton and fish ranged of <0.002–0.015 mg kg^{-1} dry, <0.002–0.015 mg kg^{-1} dry and <0.003–0.017 mg kg^{-1} wet, respectively.

Key words: butyltin, phenyltin, water, sediment, biological samples

INTRODUCTION

Organotin (OT) compounds leaching from antifouling paints caused the many deleterious effects for nontarget aquatic organisms such as imposex and abnormal of shell (Gibbs et al., 1988, Waldock and Thain, 1983). As the results, OTs has led the aquatic product to decrease. Several countries have banned and are restricted its application to large vessels. In Japan, the sale and use of OTs has been regulated. That is, bis(tributyltin)oxide (TBTO) has been designated a Class 1 Specified Chemical Substance under "the Law Concerning the Examination and Regulation of Manufacture etc. of Chemical Substances" in 1990, and 7 triphenyltin (TPT) species and 13 tributyltin (TBT) species, excluding TBTO, have been designated as Class 2 Specified Chemical Substances under the same Law. In spite of the regulation of TBT, OT compounds have been still detected at higher concentrations in water, sediment and biota from harbours, marinas and estuaries, particularly where boat activity is high and water movement is restricted (Harino et al., 1998a).

Sanriku coastal area is area which marine products are rich in Japan. In particular, Otsuchi Bay, locating in the north part of Sanriku coastal area, has many fishing port and scallop farms. Harino et al. (1998b) reported that the higher concentrations of TPT as well as TBT were detected in mussel from Otsuchi Bay during 1995–1996. Therefore, it is important to research OTs concentration in aquatic environment of Otsuchi Bay of late years. The basic objective of this study is to discuss the temporal trend of OTs and assess the current status of contamination by OTs in Otsuchi Bay.

MATERIALS AND METHODS

Sample collection

Otsuchi Bay is located on the Pacific coast of Japan and it has a fishing port and several scallop farms. Water, sediment and plankton samples in Otsuchi Bay were collected from stations A1–A7 between 1996–2001 (Fig. 1). Seawater samples were obtained by using a bucket between 1996 and 1999 and sediment samples were taken by a Smith-McIntyre grab sampler during 1996–2001. Plankton samples were taken by a plankton net, 25 μm in pore size, during 1996–1999. Mussel (*Mytilus galloprovincialis*) samples were collected from stations B1–B5 between 1995 and 1999 (Fig. 1). Fish (filefish (*Navodon modestus*), surf smelt (*Hypomesus pretiosus japonicus*), greenling (*Physicalus maximowiszi*) were also collected from station A2 in 2000 (Fig. 1).

Water samples were analyzed within a week. The soft tissues of mussels and muscle tissue in fish were analyzed. Sediment and biological samples were frozen at −20°C before chemical analysis.

Analytical methods

The method used for the determination of butyltin (BT) and phenyltin (PT) compounds in water, sediment and biological samples was based on that of Harino et al. (1992) with some modifications. Analytical procedures are described briefly. One liter water samples were extracted

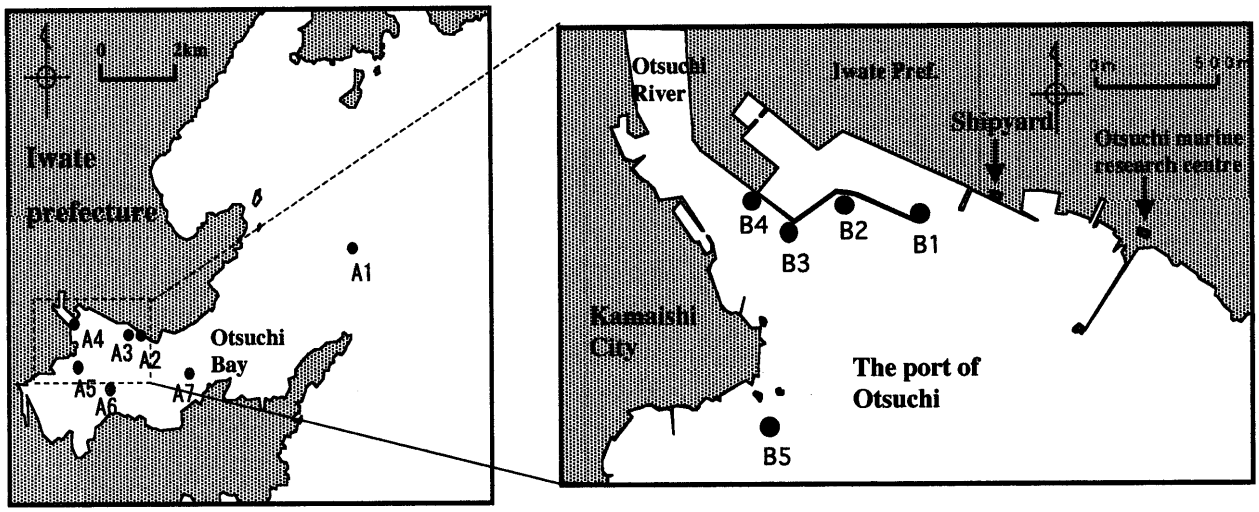

Fig. 1. Study area in Otsuchi Bay (water, sediment plankton, mussel and fish).

twice with 50 ml of 0.1% tropolone-benzene solution after adding 1 N HCl solution. The organic layer was dried with anhydrous Na_2SO_4 and concentrated up to 1 ml. After propylation with n-propyl magnesium bromide, the excess grignard reagent was destroyed with 1 N H_2SO_4. Distilled water was added to the mixtures and then the OTs were extracted twice with 10% benzene-hexane solution. After concentration up to 1 ml with a rotary evaporator, the mixtures were cleaned with florisil Sep-Pak cartridge columns (Waters Association Co. Ltd.). The analytes were determined by gas chromatography equipped with a flame photometric detector.

Ten grams of sediment and biological samples were extracted and homogenized twice with 50 ml of acetone after adding 1 N HCl, respectively. The supernatant was poured with 25% NaCl solution and analytes was re-extracted with 50 ml of 0.1% tropolone-benzene. With sediment samples, the inorganic sulphur-containing species that co-extracted with the analytes were removed with tetrabutylammonium hydrogensulphate and sodium sulphite. The organic layer was concentrated up to 1 ml after drying with anhydrous Na_2SO_4. The further procedures were identical with that for the water samples. The concentrations of the various organotin species are reported as Sn. The recoveries of OTs in water, sediment and tissue of fish were generally in the range of 84–98%, 68–109% and 84–103% in water, sediment and biological samples, respectively and relative standard deviation of OTs in water, sediment and tissue ranged from 1.0 to 5.5%, from 2.9 to 11% and from 2.5 to 12%, respectively. The detection limit for water, sediment and biological samples corresponding to a signal-to-noise ratio of three, were 0.002 $\mu g\,l^{-1}$, 0.003 mg kg dry^{-1} and 0.003 mg kg wet^{-1}, respectively.

RESULTS AND DISCUSSION

Temporal trend of orgnotin compounds

The temporal trends of water, sediment, plankton and mussel from Otsuchi Bay are shown in Table1 and the proportions of the total BT burden presented as monobutyltin (MBT), dibutyltin (DBT) and TBT were calculated from average concentration during the study period (Fig. 2). The decrease of TBT concentration in water was not observed between 1996 and 1999 and the composition of BTs in water displayed similar pattern during 1996–1999 in sequence TBT>MBT, DBT. Harino et al. (1999) monitored TBT in water from the Port of Osaka, Japan during 1989–1996. Though TBT concentration decreased dramatically in a marina and the mooring places in a one of poor flushing during 1989–1991, thereafter, TBT in water was constant level. No decreasing of TBT in sediment was observed between 1996 and 2001. The half-life of TBT in sediment was reported to be 4–5 months (Maguire and Tkacz, 1985). Dowson et al. (1993) also reported that the half-lives of TBT ranged from 360 to 775 days in surface sediments. Judging from these findings, degradation of TBT is very slow. The composition of BTs in sediment displayed similar pattern during 1996–2001. TBT in plankton were decreased from 0.199 to 0.067 mg kg^{-1} dry among 1996–1999. TBT in mussel also decreased dramatically from 0.059 to 0.033 mg kg^{-1} wet between 1995–1996, however thereafter, the changes of TBT concentrations were not observed. Mussel concentrations of TBT reflect on water within 2 or 3 months (Short and Sharp, 1989) Namely, it would be assumed that TBT concentration decreased drastically in water from Otsuchi bay before 1996. However, the composition of BTs in plankton and mussel displayed similar pattern as well as those in water and sediment in this study period, suggesting that the rates of uptake and excretion of BTs attained equilibrium in plankton and mussel.

TPT was not detected in water between 1996 and 1999. TPT in sediment during 1996–1999 were detected in the ranging of 0.006–0.012 mg kg^{-1} dry, however TPT was not detected since 2000. The concentration of TPT in plankton was decreasing from 0.055 to 0.004 mg kg^{-1} dry during 1996–1999. Though TPTs in mussel were determined in the ranging of 0.008–0.018 mg kg^{-1} during 1995–1997. TPT was not detected in 1999.

Level of organotin compounds in various compartments

The average and range of TBT concentration in water, sediment, plankton, mussels, from Otsuchi Bay are summarized in Fig. 3. TBT was detected in the range of <0.002–0.022 $\mu g\,l^{-1}$ from the water in 1999. Shim et al. (1998) reported that TBT in seawater from the Chinhae Bay from

Table 1. Temporal trend of organotin compounds is water, sediment, plankton and mussel from Otsuchi Bay.

		MBT	DBT	TBT	MPT	DPT	TPT
Water	1996	0.009 (0.007- 0.013)	0.008 (0.004- 0.028)	0.014 (0.010- 0.030)	0.004 (0.003- 0.005)	<0.002 (<0.002)	<0.002 (<0.002- 0.003)
	1997	0.008 (0.007- 0.009)	0.006 (0.006- 0.007)	0.015 (0.006- 0.024)	<0.002 (<0.002)	<0.002 (<0.002)	<0.002 (<0.002)
	1999	0.004 (<0.002-0.007)	0.007 (0.006-0.009)	0.010 (<0.002-0.022)	<0.002 (<0.002)	0.003 (<0.002-0.005)	<0.002 (<0.002)
Sediment	1996	0.016 (<0.003- 0.045)	0.021 (<0.003- 0.051)	0.062 (0.003- 0.262)	<0.003 (<0.003- 0.007)	<0.003 (<0.003- 0.005)	0.006 (<0.003- 0.013)
	1999	0.031 (0.009- 0.078)	0.019 (0.004- 0.049)	0.049 (0.008- 0.148)	0.014 (<0.003- 0.068)	0.003 (<0.003- 0.012)	0.012 (<0.003- 0.037)
	2000	0.020 (0.008- 0.035)	0.016 (<0.003- 0.044)	0.051 (0.009- 0.164)	<0.003 (<0.003)	<0.003 (<0.003)	<0.003 (<0.003)
	2001	0.017 (0.005- 0.036)	0.014 (<0.002- 0.035)	0.056 (0.016- 0.110)	<0.003 (<0.003)	<0.003 (<0.003)	<0.003 (<0.003- 0.006)
Plankton	1996	0.154 (0.057- 0.227)	0.035 (0.027- 0.058)	0.199 (0.097- 0.401)	0.089 (0.006- 0.179)	0.008 (<0.003- 0.040)	0.055 (0.007- 0.228)
	1997	0.038 (0.025- 0.052)	0.017 (0.012- 0.023)	0.101 (0.053- 0.148)	<0.003 (<0.003)	<0.003 (<0.003)	0.007 (<0.003- 0.014)
	1999	0.043 (0.015- 0.133)	0.026 (0.004- 0.098)	0.067 (0.010- 0.255)	0.010 (<0.003- 0.046)	<0.003 (<0.003- 0.006)	0.004 (<0.003- 0.015)
Mussel	1995	0.019 (0.006- 0.058)	0.024 (0.006- 0.073)	0.059 (0.022- 0.123)	<0.003 (<0.003- 0.006)	<0.003 (<0.003- 0.004)	0.008 (<0.003- 0.018)
	1996	0.021 (0.009- 0.036)	0.018 (0.006- 0.036)	0.033 (0.018- 0.075)	0.006 (<0.003- 0.012)	<0.003 (<0.003- 0.006)	0.018 (0.004- 0.043)
	1997	0.007 (<0.003- 0.011)	0.019 (<0.003- 0.037)	0.027 (<0.003- 0.058)	<0.003 (<0.003)	<0.003 (<0.003)	0.011 (<0.003- 0.023)
	1999	0.007 (0.003- 0.013)	0.007 (0.005- 0.015)	0.021 (0.012- 0.048)	<0.003 (<0.003)	<0.003 (<0.003)	<0.003 (<0.003)

Water: $\mu g\,l^{-1}$, sediment and plankton: $mg\,kg^{-1}$ dry, mussel: $mg\,kg^{-1}$ wet.

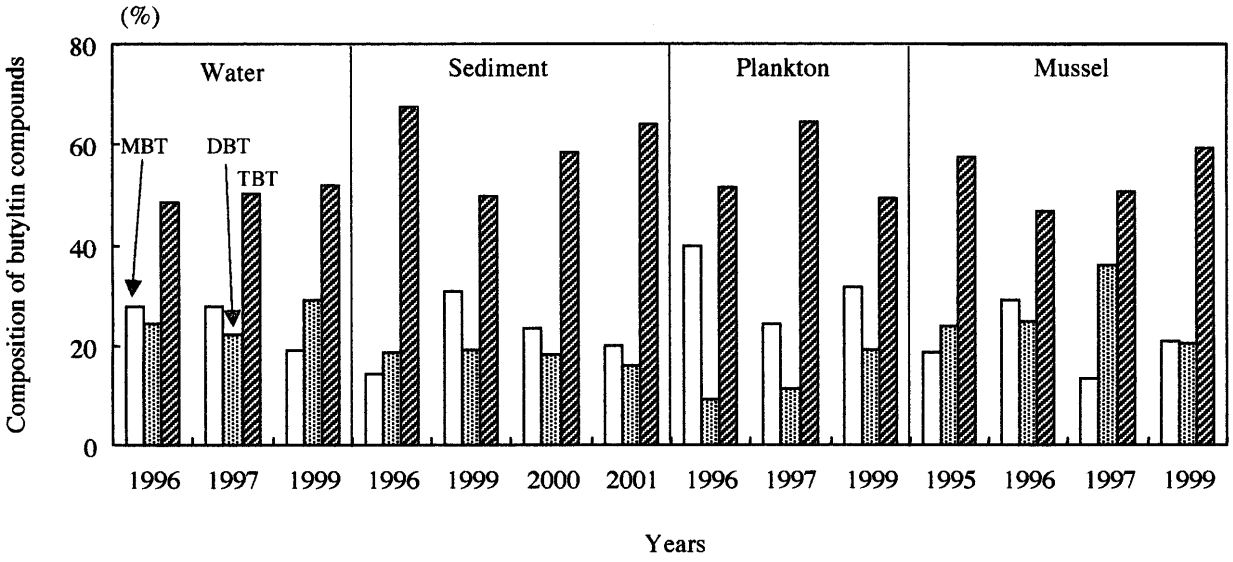

Fig. 2. The change of the composition of butyltin compounds during 1995–2001.

Korea ranged form <0.008 to 0.035 $\mu g\,l^{-1}$. TBT in water from Ayamonte-Isla Cristina area, southwest Spain ranged 0.079–0.0091 $\mu g\,l^{-1}$ (Gomez-Ariza et al., 1998). TBT in water from Eckwarderhorne of the river Elbe, Germany detected at 0.0043 $\mu g\,l^{-1}$ (Shawky and Emons, 1998). Judging from these reports, TBT levels in water from Otsuchi Bay are similar to those from the other country. From the viewpoint of the endocrine disruptant, laboratory

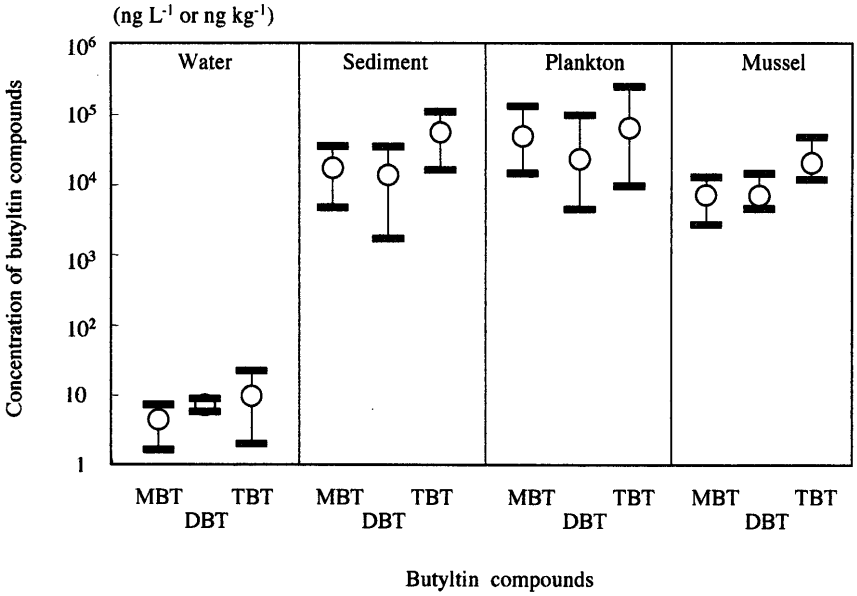

Fig. 3. The level of butyltin compounds in water, sediment, plankton and mussel from Otuschi Bay.

studies showed that concentrations as low as 0.02 $\mu g\,l^{-1}$ would produce imposex for dog whelk, *Nucella lapillus*, (Bryan et al., 1986). In a few sample from Otsuchi Bay, TBT exceeds the level at which imposex is possible.

The concentrations of TBT (0.016–0.110 mg kg^{-1} dry) in sediment, 2001 were higher than thousand times that of water. There are many reports concerning of TBT in sediments. TBT in surface sediment from Tailand, 1995 detected in the ranging of 0.002–1.84 mg kg^{-1} dry (Kan-atireklap et al., 1997). TBT in surface sediments from an enclosed by system, Korea ranged from 0.027 to 1.76 mg kg^{-1} dry (Shim et al., 1999). Elgethum et al. (2000) reported that TBT detected in the ranging of 0.024–1.20 mg kg^{-1} dry in sediment from the Coos Bay, U.S.A. TBT in sediment from St Lawrence, Canada ranged from <0.2 to 0.410 mg kg^{-1} dry. (Saint-Louis et al., 1997). TBT in sediment from Ayamonte-Isla Cristina area, southwest Spain ranged 0.003–0.015 mg kg^{-1} dry (Gomez-Ariza et al., 1998). TBT in sediment of Otsuchi Bay is considered to be lower concentrations in comparison with that of the sediment of the harbour areas in the other country.

TBT (0.010–0.255 mg kg^{-1} dry) in plankton was higher than that of sediment. There is a few papers concerning of OTs in plankton. Harino et al. (1998a) reported that TBT in plankton from the Port of Osaka were detected in the range of 0.13–1.7 mg kg^{-1} dry. TBT from Otsuchi Bay was one-tenth in comparison with that from the Port of Osaka. TBT concentration ranged from 0.012 to 0.048 mg kg dry^{-1} in soft tissues of mussel from Otsuchi Bay. The concentration of TBT ranged from 0.010–0.041 mg kg^{-1} dry in mussel from St Lawrence estuary, Canada (Pelletier and Normandeau, 1997). The concentration of TBT ranged from <0.0004–0.3784 mg kg^{-1} dry in mussel from the other area of St Lawrence estuary, Canada (Saint-Louis et al., 1997). Shawky and Emons (1998) reported that TBT in mussel from the North Sea, German were detected in the ranging of 0.010–0.022 mg kg^{-1} dry. These concentration display as a dry base. Usually, water contents of mussels are about 80–90%. Therefore it is assumed that the concentration of TBT from Otsuchi Bay is a little higher than that from the other country. Page and Widdows (1991) reported that the threshold value of the effects on scope for growth of mussels was 2 mg kg dry^{-1}. TBTs in mussels from Otsuchi Bay were lower than the threshold value. Though TBT was also detected in fish (0.009–0.029 mg kg^{-1} wet) in 2000, the levels were the lowest among all the biological samples (Fig. 4). Harino et al. (2000) surveyed the TBT concentration in muscle of 11 species in fish from the Port of Osaka, Japan. TBT ranged from 0.052 to 0.182 mg kg^{-1} wet. TBTs in fish from Otsuchi Bay are approximately one-sixth in comparison with those from the port of Osaka. Penninks (1993) derived that the tolerable daily intake (TDI) is 0.25 $\mu g\,kg^{-1}$ body weight day^{-1}. Tolerable average residue levels (TARL) for TBT in seafood products were calculated based on the TDI (Belfroid et al., 2000). TARL for TBT in seafood products in Japan was 77 $\mu g\,kg^{-1}$ wet. TBT in fish from Otsuchi Bay is lower than TARL.

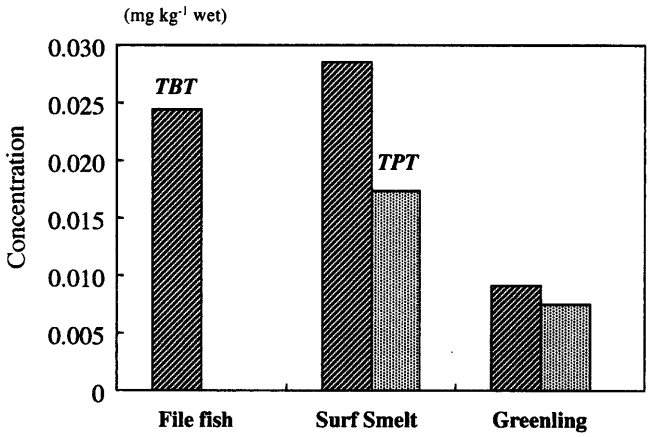

Fig. 4. Tributyltin and triphenyltin in fish from Otsuchi Bay, 2000.

TPT was not detected in the water, 1999. TPT was detected in the range of <0.003–0.006 mg kg^{-1} dry in sediment samples, 2001. TPT in plankton from Otsuchi Bay ranged from <0.003 to 0.015 mg kg^{-1} dry and TPT from

Table 2. The concentrations of organotin compounds in water, sediment, plankton and mussel from Otsuchi Bay.

			MBT	DBT	TBT	MPT	DPT	TPT
1999	Water	A2	0.007	0.009	0.022	0.002	0.005	<0.002
		A3	0.007	0.007	0.009	<0.002	0.003	<0.002
		A4	0.004	0.008	0.011	0.002	<0.002	<0.002
		A5	0.002	0.006	0.002	<0.002	0.002	<0.002
		A6	0.002	0.007	0.004	0.002	0.005	<0.002
		A7	0.005	0.007	0.010	0.002	<0.002	<0.002
2001	Sediment	A1	0.005	0.002	0.016	<0.003	<0.003	<0.003
		A3	0.021	0.035	0.110	<0.003	0.008	0.006
		A7	0.036	0.009	0.061	<0.003	0.029	<0.003
1999	Plankton	A1	0.110	0.029	0.094	0.004	0.010	<0.003
		A2	0.133	0.098	0.255	0.046	0.006	0.015
		A3	0.037	0.015	0.034	<0.003	<0.003	<0.003
		A4	0.015	0.004	0.010	<0.003	<0.003	<0.003
		A5	0.016	0.005	0.015	<0.003	<0.003	<0.003
		A6	0.015	0.006	0.023	<0.003	<0.003	0.004
		A7	0.019	0.006	0.026	0.008	<0.003	0.003
1999	Mussel	B1	0.013	0.015	0.048	<0.003	<0.003	<0.003
		B2	0.003	0.006	0.017	<0.003	<0.003	<0.003
		B3	0.005	0.005	0.012	<0.003	<0.003	<0.003
		B4	0.005	0.005	0.012	<0.003	<0.003	<0.003
		B5	0.010	0.005	0.014	<0.003	<0.003	<0.003

Water: $\mu g\,l^{-1}$, sediment and plankton: $mg\,kg^{-1}$ dry, mussel: $mg\,kg^{-1}$ wet.

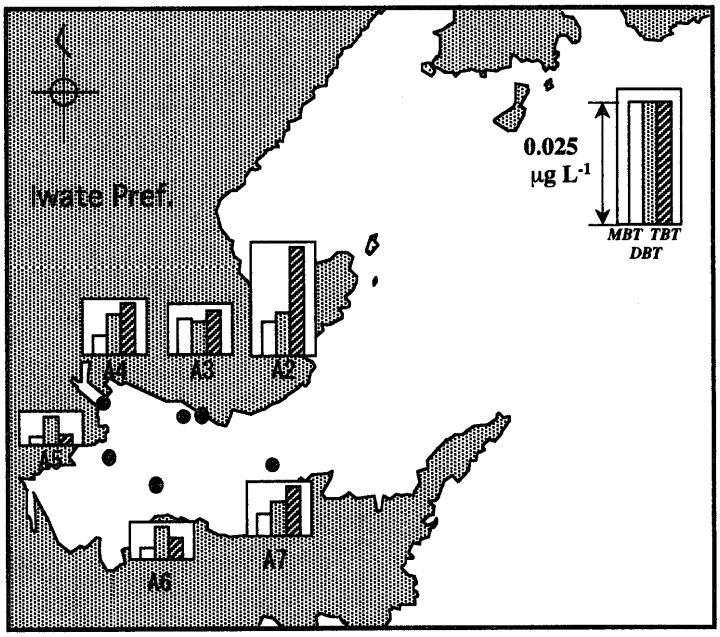

Fig. 5. Horizontal distribution of butyltin compounds in water from Otsuchi Bay, 1999.

Otsuchi Bay was similar to that of the outer part of Otsuchi Bay. TPT was not detected in mussel. TPT in fish ranged from <0.003 to 0.017 mg kg wet^{-1}.

Horizontal distribution of organotin compounds

The highest concentration of TBT in water was detected at station A2 near the shipyard and the ratio of TBT to BTs was 59% (Fig. 5, Table 2). Harino et al. (1999) reported about TBT concentration in the port of Osaka. MBT and DBT were dominant species in water from the port of Osaka in recent years. TBT among BTs was still dominant species in water samples from Otsuchi Bay. The input of

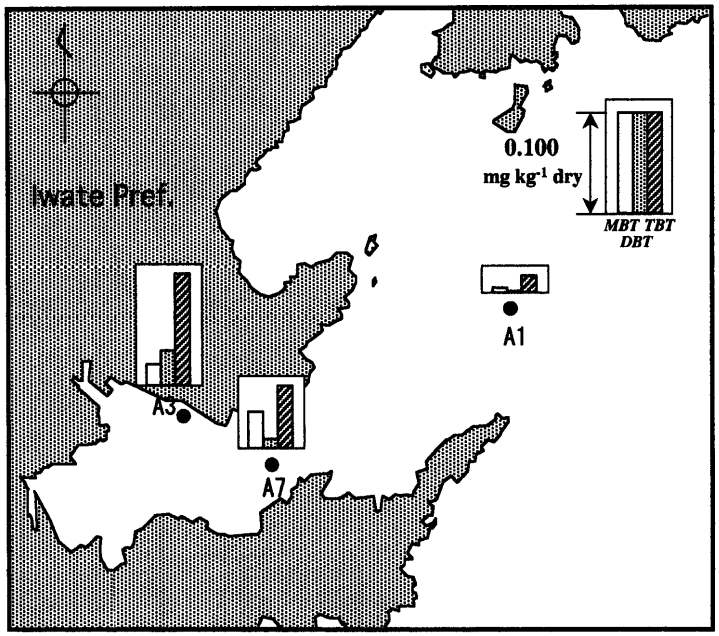

Fig. 6. Horizontal distribution of butyltin compounds in sediment from Otsuchi Bay, 2001.

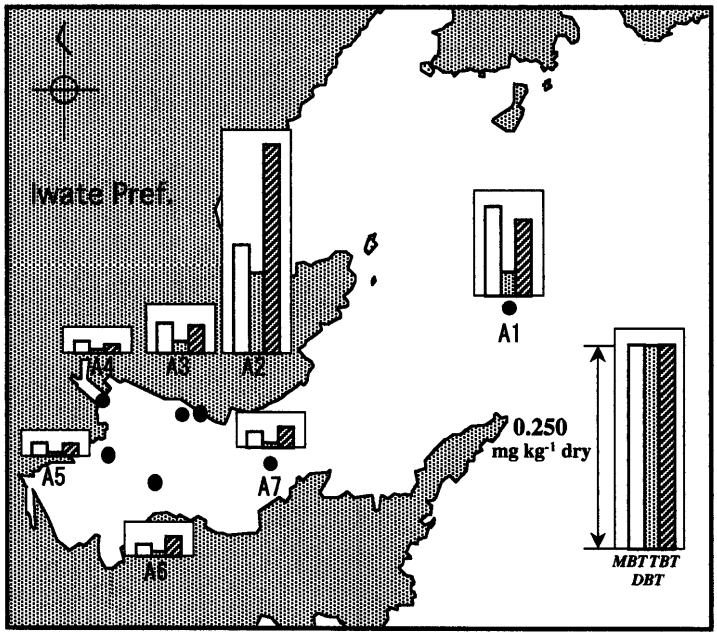

Fig. 7. Horizontal distribution of butyltin compounds in plankton from Otsuchi Bay, 1999.

TBT to water may be still continued from the other compartments in Otsuchi Bay. The concentrations of TBT in sediment were also high at station A3 near the shipyard (Fig. 6, Table 2) and TBT was dominant species among BTs. TBT in plankton showed similar trend to that in water and sediment, and the ratio of TBT to the total BTs was also high at station A2, suggesting shipyard as a point-source of TBT (Fig. 7, Table 2). Shim et al. (1999) reported that horizontal distribution of TBT concentration in surface sediments showed apparent negative gradients from harbours and shipyards. This trend coincided with our results. Mussels at stations B1–B5 were collected along the breakwater (Fig. 8, Table 2). The concentrations of TBT decreased with an increase in distance from the shipyard and the ratio of TBT in the total BTs also decreased from 64 to 48%. This indicates that TBT is probably discharged from the shipyard. TBT was dominant in BTs at most of the stations. It may be due to its hydrophobic property.

TPTs were not detected in water, 1999. While diphenyltin (DPT) and monophenyltin (MPT) were detected in the ranging of <0.002–$0.002\,\mu g\,l^{-1}$, <0.002–$0.005\,\mu g\,l^{-1}$, respectively (Table 2). These results show that there is no input of TPT to water, recently. The concentrations of TPT in sediment ($0.006\,mg\,kg^{-1}$ dry) from stations A3 were higher than those in the other sites, however degradation product, DPT of TPT was dominant among the PTs. This shows that TPT was used as an antifouling paint, past year. TPT in plankton was near the detection limit. TPT was not detected in mussel.

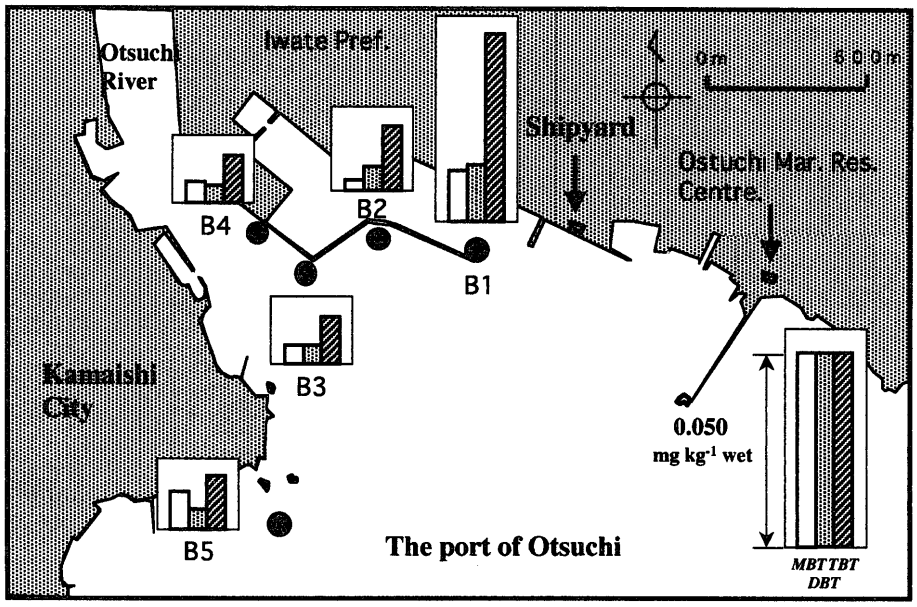

Fig. 8. Horizontal distribution of butyltin compounds in mussel from Otsuchi Bay, 1999.

CONCLUSION

Though TBTs in plankton and mussel during 1996–2001 were low in comparison with those in 1995, no changes of TBT concentrations in water and sediment were observed during study period. Moreover, in spite of lower TBT concentration in Otsuchi Bay in comparison with the other area, TBT in water was higher than level, which caused imposex and TBT concentration was still high near the shipyard. Therefore, further study is to clarify the factor, which TBT concentration in water of Otsuchi Bay did not decrease.

LITERATURE CITED

Belfroid, A. C., Purperhart, M. and Ariese, F. 2000. Organotin levels in seafood. Mar. Pollut. Bull. 40: 226–232.

Bryan, G. W., Gibbs, P. E., Hummerstone, L. G. and Burt, G. W. 1986. The decline of the gastropod *Nucella lapillus* around south-west England: evidence for the effect of tributyltin from antifouling paint. J. Mar. Bio. Assoc. U. K. 66: 615–640.

Dowson, P. H., Bubb, J. M., Williams, T. P., Lester, J. N. 1993. Degradation of tributyltin in sediment in freshwater and estuarine marina sediments. Wat. Sci. Technol. 28: 133–137.

Elgethun, K., Neumann, C. and Blake, P. 2000. Butyltins in shellfish, finfish, water and sediment from the Coos Bay estuary (Oregon, USA). Chemosphere 41: 953–964.

Gibbs, P. E., Pascoe, P. L. and Burt, G. R. 1988. Sex change in the female dog-whelk, *Nucella lapillus*, induced by tributyltin from antifouling paints. J. Mar. Biol. Assoc. U.K. 68: 715–731.

Gomez-Ariza, J. L., Morales, E. and Giraldez, I. Spatial distribution of butyltin and phenyltin compounds on the huelva coast (southwest Spain). Chemosphere 37: 937–950.

Harino, H., Fukushima, M. and Tanaka, M. 1992. Simultaneous determination of butyltin and phenyltin compounds in the aquatic environment by gas chromatography. Anal. Chim. Acta. 264: 91–96.

Harino, H., Fukushima, M., Yamamoto, Y., Kawai, S. and Miyazaki, N. 1998a. Organotin compounds in water, sediment, and biological samples from the port of Osaka, Japan. Arch. Environ. Contam. Toxicol. 53: 558–564.

Harino, H., Fukushima, M., Yamamoto, Y., Kawai, S. and Miyazaki, N. 1998b. Contamination of butyltin and phenyltin compounds in the marine environment of Otsuchi Bay, Japan. Environ. Pollut. 101: 209–214.

Harino, H., Fukushima, M. and Kawai, S. 1999. Temporal trends of organotin compounds in the aquatic environment of the Port of Osaka, Japan. Environ. Pollut. 105: 1–7.

Harino, H., Fukushima, M. and Kawai, S. 2000. Accumulation of butyltin and phenyltin compounds in various fish species. Arch. Environ. Contam. Toxicol. 39: 13–19.

Kan-atireklap, S., Tanabe, S. and Sanguansin, J. 1997. Contamination by butyltin compounds in sediments from Tailand. Mar. Pollut. Bull. 11: 894–899.

Maguire, R. J. and Tkacz, R. J. 1985. Degradation of the tri-n-butyltin species in water and sediment from Toronto harbour. J. Agric. Food. Chem. 33: 947–953.

Page, D. S. and Widdows, J. 1991. Temporal and spatial variation in levels of alkyltins in mussel tissues: atoxicological interpretation of field data. Mar. Environ. Res. 32: 113–129.

Pelletier, E. and Normandeau, C. 1997. Distribution of butyltin residues in mussels and sea stars of the St Lawrence estuary. Environ. Technol. 18: 1203–1208.

Pennisks, A. H. 1993. The evaluation of data-derived safety factors for bis(tributyltin) oxide. Food. Add. Cotam. 10: 351–361.

Shawky, S. and Emons, H. 1998. Distribution pattern of organotin compounds at different trophic levels of aquatic ecosystems. Chemosphere 36: 523–535.

Saint-Louis, R., Gobeil, C. and Pelletier, E. 1997. Tributyltin and its degradation products in the St Lawrence estuary (Canada). Environ. Technol. 18: 1209–1218.

Shim, W. J., Oh, J. R., Kahng, S. H., Shim, J. H. and Lee, S. H. 1998. Accumulation of tributyl- and triphenyltin compounds in pacific oyster *crassostrea gigas*, from the Chinhae Bay system, Korea. Arch. Environ. Contam. Toxicol. 35: 41–47.

Shim, W. J., Oh, J. R., Kahng, S. H., Shim, J. H. and Lee, S. H. 1999. Horizontal distribution of butyltins in surface sediments from an enclosed bay system, Korea. Environ. Pollut. 106: 351–357.

Short, J. W. and Sharp, J. L. 1989. Tributyltin in bay mussel (*Mytilus edulis*) of the Pacific Coast of the United States. Environ. Sci. Technol. 23: 740–743.

Waldock, M. J. and Thain, J. E. 1983. Shell thickening in *Crassostrea gigas*: organotin antifouling or sediment induced? 14: 411–415.