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Butyltin Compounds Concentrations in Masan Bay

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The occurrence of butyltin compounds in the seawater and sediment of Masan Bay was investigated. The concentrations were in the range of ND-0.059 μg/ℓ for tributyltin (TBT), ND-0.091 μg/ℓ for dibutyltin (DBT) and ND-0.720 μg/ℓ for monobutyltin (MBT) in the seawater, and ND-0.233 μg TBT/g.dry , ND-0.197 μg DBT/g.dry and ND-0.684 μg MBT/g.dry in the sediment. Among the butyltin compounds, the major component in the seawater was MBT, while the predominant species in the sediment changed with time. The tributyltin concentrations in the sediment are approximately three orders of magnitude greater than the associated water column levels. Sediment/water partition coefficients (K) of TBT were between 0.6×10^3 and 5.0×10^3.

Key words : Butyltin compounds (TBT, DBT and MBT), partition coefficients

Introduction

Tributyltin (TBT) is a very toxic molecule which has been used in marine antifouling paints since the mid-1960s. Its effect on marine biota was first described by Alzieu who correlated shell thickening and production decline in the culture *Crassostrea gigas* with TBT pollution in Arcachon Bay, France (Alzieu, 1986). Tributyltin is probably the most toxic substance ever introduced deliberately into the marine environment. At seawater concentrations of only a few ng 1 ^{1}, TBT disrupts reproduction in some molluscs (notably neogastropod whelks), and is toxic to many embryonic and larval organisms at levels of 10~100 ng 1 ^{1} (Stewark and Thomson, 1994). Several authors have shown in both the environment and the laboratory that butyltin concentrations are 1~3 orders of magnitude greater in sediment than in overlying waters (Maguire and Tkacz, 1985; Valkirs et al., 1986; Fent and Hunn, 1991; Schebak and Andrea, 1991). While tributyltin (TBT) compounds are the primary biocide, mono- (MBT) and dibutyltin (DBT) compounds as well as tributyltin have been detected in marine waters and marine sediments (Stang and Seligman, 1986). To date, little is known about the occurrence, temporal variation, and behavior of organotin compounds in Korean coastal areas (Choi et al., 1993; Kahng, 1995; Park et al., 1996). The Masan Bay is an enclosed bay that contains harbors and industrial city such as Masan and Changwon city. Therefore, it has a strong possibility on the contamination of butyltin compounds. This paper presents the results of the determination of the presence and partitioning of TBT and its degradation products (DBT and MBT) in the seawater and sediment of Masan Bay, and monitoring of short-term variations.

Materials and Methods

Sampling

Water and sediment samples were collected in May, July, and September, 1996 at ten stations in Masan Bay (Fig. 1). 1L of samples of subsurface water were collected in amber glass bottles from a depth of 0.5 m, stored at 4℃, and extracted within 1~2 days. Sediment samp-

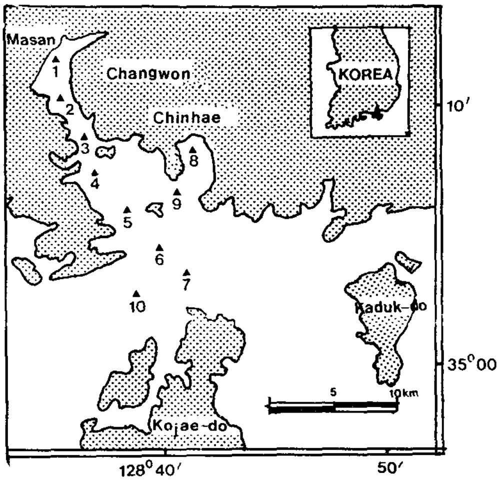

Fig. 1. Sampling stations in Masan Bay.

les were collected with gravity corer. The top 5 cm was scraped off into jars and frozen as soon as possible.

Instruments

A Varian 3400 gas chromatograph equipped with a flame photometric detector with a 610 nm cut-off interference filter was used. The separation was carried out on a capillary column (30 m×0.53 mm i.d.) coated with methylsilicone (1.5 μm). The column temperature was held at 80℃ for the first 1 min, then 160℃ at 15℃ min^{-1} and to 220℃ at 5℃ min^{-1}. Nitrogen was used as carrier gas at a flowrate of 10 mℓ min^{-1}. The flowrates of air and hydrogen for detector at 270℃ were 175 and 140 mℓ min^{-1} respectively.

Analytical procedure

Water samples. The sample of 1,000 mℓ was spiked with 0.36 μg of the internal standard (IS) tripentyltin chloride, mixed with 5 mℓ of conc-HCl and 100 g of NaCl, and extracted two times with 50 mℓ of 0.1% tropolone in benzene. The benzene extract was concentrated to approximately 5 mℓ using a rotary evaporator at 40℃. The extracted butyltins and IS were converted into chromatographically-inert n-pentyl derivatives using a Grignard reaction by adding 1 mℓ of 2 M n-pentylmagnesium bromide. The mixture was allowed to stand 30 min and the excess of reagent was destroyed by the addition of 10 mℓ of 1 N H_2SO_4. The solution was purified by passing through a florisil chromatography column. The eluate was concentrated to approximately 0.1 mℓ using N_2 gas.

Sediment samples. Approximately 20 g of wet samples was spiked with 1.8 μg of the internal standard (IS) tripentyltin chloride, mixed with 50 mℓ of 1N HCl in methanol and extracted with 50 mℓ of 0.1% tropolone in benzene. The benzene extract was concentrated to approximately 5 mℓ using a rotary evaporator at 40℃. In order to remove co-extracted inorganic sulphur-containing species, the extracts were washed with 2 mℓ of 3.3% tetrabutylammonium hydrogensulphate and 40 mℓ of 16% sodium sulphide. The extracted butyltins and IS were converted into chromatographically-inert n-pentyl derivatives using a Grignard reaction by adding 3 mℓ of 2 M n-pentylmagnesium bromide. The mixture was allowed to stand 30 min and the excess of reagent was destroyed by the addition of 10 mℓ of 1 N H_2SO_4. The solution was purified by passing through a florisil chromatography column. The eluate was concentrated to approximately 1.0 mℓ using N_2 gas.

Results and Discussions

Detection of butyltin compounds

The results for the extraction of butyltin compounds from water are given in Table 1. All the organotin compounds are converted into their chlorides by reaction with HCl and extracted. In general, hexane, dichloromethane, and benzene are used as extraction solvents. When hexane and dichloromethane were used as the solvent, the recoveries were not good except for tributyltin compounds. In this work, 0.1% tropolone in benzene exhibited high recoveries for TBT (87%) and DBT (88%), except for monobutyl compounds (146%). Approximately 100 g of NaCl was added to prevent the emulsion phenomenon. Harino et al. (1992) described the effect of NaCl on the recovery of butyltin compounds using 0.1% tropolone in benzene as solvents. Their results showed a poor recovery of TBT (37%) and DBT (36%) in 100 g of NaCl, while a good recovery of TBT (85%) and DBT (80%) in 250 g of NaCl. Monobutyltin had a high recovery above 90% for both cases. The detector response depended significantly on the air and hydrogen flowrates. The air and hydrogen flowrates were given Table 2. Most of authors reported that the flowrate of hydrogen was higher than that of air. However, we found that a low air flowrate occurred the flame out and the optimum flowrates were 140 and 175 mℓ min^{-1} for hydrogen and air, respectively. The detection limit was approximately 0.012 μg/ℓ for tri-, 0.011 μg/ℓ for di- and 0.024 μg/ℓ for monobutyltin in seawaters, while 0.005 μg/g for tri- and di-butyltins, and 0.012 μg/g for monobutyltin in sediments. The detection limit is defined here as a signal three times greater than the baseline noise.

Table 1. Recoveries of butyltin compounds from 1 L of distilled water using 0.1% tropolone in benzene

Concentration (μg)	NaCl (g)	Recovery (%)			Reference
		TBT	DBT	MBT	
0.67	100	87 ± 6.4	88 ± 4.6	146 ± 8.2	This study
0.10	100	37	36	98	Harino et al. (1992)
	250	85	80	100	

Table 2. Comparison on the effect of hydrogen and air flowrates on detector response of butyltin compounds

Hydrogen (mℓ/min)	Air (mℓ/min)	Instruments	References
140	170	Varian 3400	This study
200	100	Hewlett Packard HP 5890	Higashiyama et al. (1991)
200	40	DO Lul GC-9AM	Hattori et al. (1991)
160	120	Hewlett Packard HP 5890	Harino et al. (1992)
170	100	Hewlett Packard HP 5890	Kahng (1995)

Butyltins in Water Column

A series of butyltins were detected in marine waters. Figure 2 shows the distributions of butyltins of Masan bay. Butyltins, TBT, DBT, and MBT were found in every sample from ten stations. The concentrations were the range of ND-0.059 μg/ℓ for TBT, ND-0.091 μg/ℓ for DBT, and ND-0.720 μg/ℓ for MBT. In the relative proportions of the different butyltins, MBT was predominant and DBT followed. These observations indicated that some degradation of TBT had occurred in the seawater. Similar results were reported by Choi et al. (1993). However, butyltins values were lower than these results, ranging from ND to 0.015 μg/ℓ for TBT, ND to 0.016 μg/ℓ for DBT, 0.013 to 0.064 μg/ℓ for MBT. The highest concentration of TBT (0.059 μg/ℓ) recorded in September at station 2 located in the inner part of Masan Bay that contains harbor and areas which has a large industrial complexes from Masan and Changwon city. Next highest concentration of TBT was recorded at station 1 and 8. These results are in accordance with those found by Gabrielides et al. (1990) in the Mediterranean. Those authors have reported TBT values in the range of 1.125~12.150 μg/ℓ for industrial discharges, <0.020~0.936 μg/ℓ for harbors, 0.016~3.930 μg/ℓ for marinas and <0.002~0.017 μg/ℓ for mariculture. The concentrations of butyltins were higher level in July and September than in May. The mean concentrations were 0.014 μg/ℓ for TBT, 0.023 μg/ℓ for DBT, and 0.059 μg/ℓ for MBT in May, 0.026 μg/ℓ for TBT, 0.039 μg/ℓ for DBT, and 0.225 μg/ℓ for MBT in July, 0.027 μg/ℓ for TBT, 0.022 μg/ℓ for DBT, and 0.042 μg/ℓ for MBT in September. With respect to TBT effects on mollusc larval development, the No Observed Effect Level (NOEL) of 0.020 μg/ℓ was reported (Gabrielides et al., 1990). Therefore, the results showed that this bay exhibited more contamination by TBT. Such contamination is mainly due to the use of tir-n-butyltin compounds as antifouling agents in paint for boats and ships including industrial discharge.

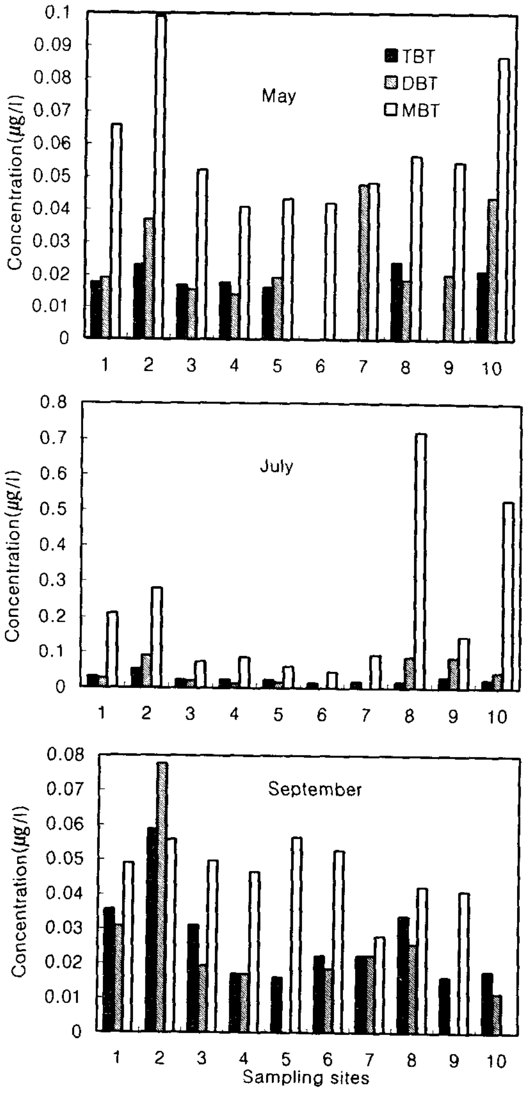

Fig. 2. Concentrations of monobutyltin (MBT), dibutyltin (DBT), and tributyltin (TBT) in seawaters.

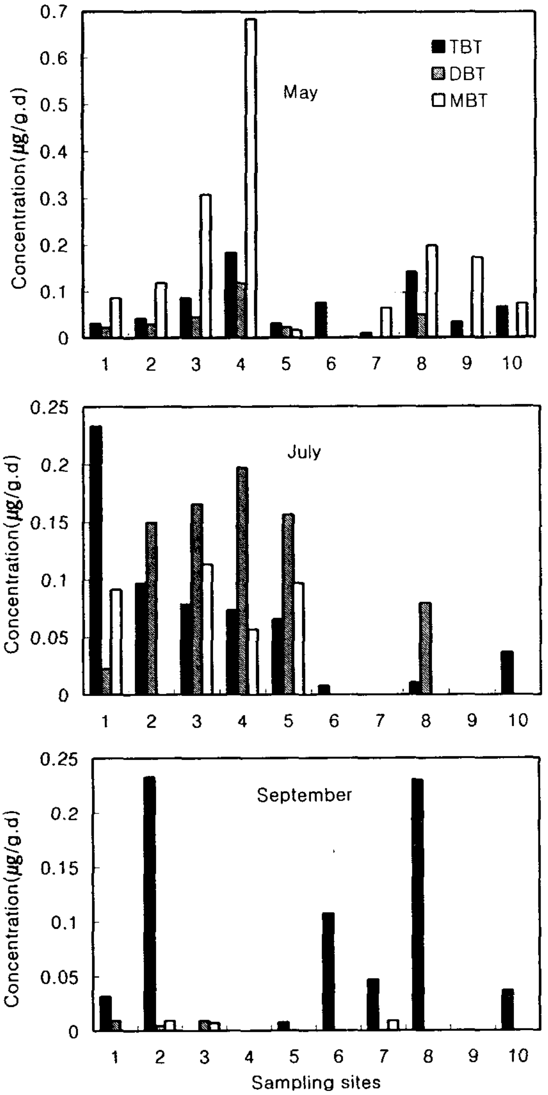

Fig. 3. Concentrations of monobutyltin (MBT), dibutyltin (DBT), and tributyltin (TBT) in sediments.

Butyltins in Sediments

A series of butyltins were detected in sediments. Figure 3 shows the distributions of butyltins of Masan bay. In most of samples, TBT, DBT, and MBT were detected. The concentrations were the range of ND-0.233 μg/g.dry for TBT, ND-0.197 μg/g.dry for DBT and ND-0.684 μg/g.dry for MBT. There are quite wide variations of the proportions of the various organotin species. The more abundant butyltin compounds were MBT in May, DBT in July and TBT in September. It must be thought both that degradation have occurred and the tin containing paints have been used. The highest peaks of contamination were observed at inner part of Masan Bay stations in July. This strong contamination may be due to increasing of ship and boat for transportation during summer season and effluents from industrial complex: The mean concentrations were 0.070 μg/g.dry for TBT, 0.029 μg/g.dry for DBT, and 0.172 μg/g.dry for MBT in May, 0.060 μg/g.dry for TBT, 0.077 μg/g.dry for DBT, and 0.036 μg/g.dry for MBT in July, 0.069 μg/g.dry for TBT, 0.002 μg/g.dry for DBT, and 0.003 μg/g.dry for MBT in September. These observations are in discordance with those found by Park et al. (1996) in Masan Bay in 1994. They have reported TBT values in the range of ND-0.056 μg/g, showing undetectable level of DBT and MBT. Several authors have shown in both the environment and the laboratory that butyltin concentrations are 1~3 orders of magnitude greater in sediment than in overlying waters (Maguire and Tkacz, 1985; Valkirs et al., 1986; Fent and Hunn, 1991; Schebak and Andrea, 1991). The most obvious feature of the TBT distribution is that a high contamination of TBT is invariably found at stations near harbors, such as station 1, 2, and 8. The highest concentrations of TBT (0.233 μg/g.dry) were observed at station 1 in July and at station 2 in September. The next highest concentration of TBT were recorded at station 8 (0.230 μg/g) in September. However, these concentrations are well below maxima observed elsewhere, e.g. 0.513 μg/g Mex Bay and 2.672 μg/g western harbor in the Alexandria (Egypt) coastal belt. (Gabrielides et al., 1990).

Partitioning between seawater and sediment

The results of partition coefficient of TBT, DBT, and MBT are presented in Table 3. A calculation of the butyltin partitioning coefficient (K) between the sediment and water column phases may be performed by dividing the butyltin concentration in the sediment fraction in μg/g by the butyltin concentration in the water in μg/ℓ. The partition coefficient values of TBT were between 0.6×10^3 and 5.0×10^3, with the majority of the values being on the order of 10^3. The highest levels of the partitioning coefficients are reported for the middle part of Masan Bay, such as station 4, 6, and 8 with a high organic contents (Table 4). Unger et al. (1986) have reported that the K values suggest some correlation to TOC and percent clay size fraction, and published K values for aqueous TBT

Table 3. Partitioning coefficients of TBT, DBT, and MBT in Masan Bay

Sampling station	TBT			DBT			MBT		
	Seawater (μg/ℓ)	Sediment (μg/g.dry)	Partition coefficient ($\times10^3$)	Seawater (μg/ℓ)	Sediment (μg/g.dry)	Partition coefficient ($\times10^3$)	Seawater (μg/ℓ)	Sediment (μg/g.dry)	Partition coefficient ($\times10^3$)
1	0.029	0.098	3.4	0.026	0.018	0.7	0.109	0.059	0.5
2	0.045	0.124	2.7	0.069	0.061	0.9	0.145	0.042	0.3
3	0.023	0.055	2.4	0.018	0.073	4.0	0.059	0.109	1.9
4	0.020	0.085	4.4	0.014	0.105	7.3	0.058	0.247	4.3
5	0.018	0.035	1.9	0.015	0.060	4.1	0.053	0.038	0.7
6	0.014	0.064	4.5	0.010	ND	–	0.047	ND	–
7	0.016	0.019	1.2	0.025	ND	–	0.057	0.024	0.4
8	0.025	0.127	5.0	0.044	0.043	1.0	0.273	0.066	0.2
9	0.019	0.011	0.6	0.038	ND	–	0.081	0.057	0.7
10	0.021	0.046	2.2	0.034	ND	–	0.212	0.024	0.1
mean	0.023	0.066	2.8	0.029	0.036	1.8	0.109	0.068	0.9

* ND : Non detected

Table 4. Contents of organic carbons in Masan Bay sediment

	Organic carbons (%)
Inner part of Masan Bay	2.28
Middle part of Masan Bay	3.19
Mouth of Masan Bay	1.85

on sediment have ranged from 3.4×10^2 to 1.9×10^6. TBT has a low aqueous solubility and relatively high affinity of TBT for particulate matter, providing a direct and potentially persistent route of entry into benthic sediments (Langston and Pope, 1995). Valkirs et al. (1986) also supported these results as showing that environmental sediments tributyltin concentrations are approximately three orders of magnitude greater than the associated water column levels. The partition coefficients of TBT between sediment and water are a key parameter for modelling to predict TBT behaviour in marine environment. The partition coefficient values of DBT and MBT were in the range of $\sim7.3\times10^3$ and $\sim4.3\times10^3$. Stang and Seligman (1986) have estimated a low values for dibutyltin and monobutyltin as 0.65 and 2.6×10^3, respectively.

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