D-2.2 The Origin and Accumulation of Hazardous Substances in East-Asian Seas (Final Report)

Contact Person   Mamoru Tominaga
Hydrospheric Environmental Protection Department,
National Institute for Resources and Environment,
Agency of Industrial Science and Technology, MITI
16-3 Onogawa, Tsukuba, Ibaraki 305-8569, Japan
Tel: +81-298-58-8338   Fax: +81-298-58-8338
E-mail: p1702@nire.go.jp

Abstract

Organohalogen and organotin compounds in seawater were measured to clarify the occurence and behavior of hazardous substances in East-Asian seas. An *in situ* filtration/adsorption water sampler was developed to collect the dissolved and suspended matters separately. Vertical profiles and isomer patterns of PCBs were determined by using this sampler and multi-dimensinal GC. The total concentrations of PCBs ranged from 150 to 1140 fg/dm^3 in Siribesi Trough. The isomer patterns of PCBs suggested that Siribesi Trough during summer is stratified into four layers (50-500, 500-1500, 1500-2500 and 3000-3500 m). Principle component analysis indicated that the PCB contamination in each layer may reflect the history of the water bodies. Gas chromatography combined with ICP-MS was developed for the determination of organotins. The detection limit was improved 100 times. The concentrations of organotins in dissolved fraction increased in the order of tri-<di-<mono-butyltin. This suggested that the hydrophobic compounds like tributyltin (TBT) were removed from water column to sediment by adsorbing to the suspended matters. Relatively high concentrations of methyltins indicated the importance of biomethylation in the behavior of tin compounds in the marine environment. The distribution of butyltins was investigated in seawater along the tanker route in the Strait of Malacca and in Tokyo Bay, areas of potential release of toxic organotins to the aquatic environment from large vessels. Relatively high concentrations of butyltins were observed along the Strait of Malacca and Tokyo Bay, high enough to cause deleterious effects on aquatic organisms, such as imposex in gastropods. The high ratio of TBT/DBT observed in the Strait of Malacca suggests that recent inputs of TBT have occurred there.

Key Words   Marine pollution, Organotin, Organohalogen Compounds, Mussel

Organohalogen Compounds

Introduction

Although it is generally believed that the world ocean is the ultimate sink of these chemicals, there are only few reliable reports on the concentration of PCBs in ocean water. This is largely due to the fact that reliable sampling has proven to be difficult as their concentrations in ocean water are extremely low. The recently developed Kiel in-situ filtration/extraction pump system (KISP)[1] allows the accurate determination of relatively apolar and polar organic compounds in seawater solution and in suspended particulate matter at extremely low concentration levels (e.g., in the fg dm^3 range). With its help, chlorobiphenyl (CB) congener-specific analyses have been carried out in the Sea of Japan to study oceanic processes.

Materials and Methods

Sampling: Surface water was taken from 6 m depth at the bow of the ship while sailing. Water was pumped with a built-in-rotary pump $(20 \text{ m}^3 \text{ h}^{-1})$. A KISP unit was connected to a pipeline that supplied seawater at 90 $\text{dm}^3 \text{ h}^{-1}$. It was pumped through a filter unit to collect SPM, and the filtrate was extracted with XAD-2 resin. The glass fiber filter was replaced at water flow rate below 60 $\text{dm}^3 \text{ h}^{-1}$. Deep water was sampled with KISP, using four units attached to the hydrographic wire at 50, 100, 1500 and 2500 m(Siribesi Trough: 42°58'N, 139°32'E). Coastal water samples (Hokkaido Coast) were collected at 50, 100, 200, and 300 m at 43°15'N, 140°06'E. The sampling locations are depicted in Fig. 1.

Analytical Procedures: The XAD-2 resin was extracted in a modified Soxhlet apparatus with water/acetonitrile (10:90). The GF/C filters were extracted in a modified Soxhlet apparatus with 80 cm^3 acetonitrile for 4 h. This extract was treated like the XAD-2 extracts. Three XAD-2 columns were used as blanks during the cruise. They were extracted and processed exactly like the sample columns. The chromatograms of their final extracts were taken as the procedural blanks. Gas chromatography-electron capture detection analyses were carried out with a Siemens Sichromat-1 GC and ^{63}Ni-ECD using a programable temperature evaporator (280 °C). A SE-54 fused silica column (50 m, 0.25 mm i.d.) was used for identification of 30 CBs.

Results and Discussion

The concentrations of 30 individual CBs and their sum (Σ CBs) in solution and suspension are given in Table 1 and 2. The concentrations of Σ CBs in solution were between 0.1 and 1.2 pg dm^{-3} (those of individual congeners between 0.001 - 0.1 pg dm^{-3}) and in suspension between 0.2 and 1.5 pg dm^{-3} (those of individual congeners between 0.01 - 0.1 pg dm^{-3}). Values in suspension exceeded those in solution in almost all samples. The vertical profiles of Σ CBs in solution and suspension in the Siribesi Trough were similar (Fig. 2). The surface water concentrations in solution were low, in fact lower than in remote areas of the Atlantic Ocean. Another contrast with findings in the Atlantic, where concentrations in solution as well as in suspension showed maxmal values at the surface and decreasing values with increasing depth, is the observation of higher concentrations in deeper water of the Siribesi Trough than near the surface.

It can be expected that homogeneity of the water column in the vertical profile would result in the establishment of particulate-solution distribution equilibria of CBs. PCA may be extremely helpful to investigate the relative roles of the mixing of water bodies and the interaction between solution and particles. Fig. 3 is a biplot of principal components (PC) 1 and 2 of the correlation matrix of mol% contributions of CBs in solution and suspension at the various depths of the Siribesi Trough. In plots of this kind, similarity of the compositions results in neighboring positions. Fig. 3a shows that this applies to the sets of samples originating from (a) 50 and 100 m; (b) 500 and 1000 m; and (c) 1500, 2000, and 2500 m. The composition of the 3000 m sample had no matching counterpart. An interesting observation is the fact that the samples split up in four groups that appear to be identical to the water mass classification of Kim et al. [2]

PC 1, accounting for 67% of the variability between the samples, represents the degree of chlorination. The loadings (the individual CBs contributing to the result) in Fig. 3a show that surface water is characterized by lower chlorinated CBs and that deep water is charactrized by higher chlorinated CBs. The water samples obtained at the various depths are thus characterized by different compositions of the mixtures of individual congeners. A

clear grouping of samples is absent in the biplot for suspensions (Fig. 3b). The percentage contributions of PC 1 and 2 differ from Fig. 3a. PC 1 contributes only 32%, and PC 2 contributes only 22%. This (PC 2) reflects most probably the variable composition of the biological material, being the main carrier of the CBs.

As the concentrations in suspension exceed those in solution in nearly all samples, any mobilization of CBs from particulates into solution should result in corresponding modifications in both concentrations and compositions of CB mixtures in solution. All these observations indicate that the concentrations of CBs in solution as well as the composition of their mixture at any position in the Siribesi Trough can be considered as independent from concentrations and composition in particulate suspended forms in that area and can be considered to reflect primarily the history of the water bodies concerned.

Surface and bottom waters have the lowest concentrations. The different concentration regimes may be due to different source regions of the waters concerned. It was suggested by Kim and Kim [3] that the mode of deep water formation in the region has changed from bottom water formation to intermediate/deep water formation in recent years. As the anthropogenic contaminants such as CBs in deeper waters have their sources in the sea surface, higher concentrations at the present time would be expected in the intermediate/deep waters rather than in bottom waters. This expectation is supported by observations (Fig. 3a). The compositions of the CBs mixture in surface water in the Japan Sea region are quite variable. This can explain the correspondingly large differences between the CB compositions in the different water masses present in the vertical profile of Fig. 3a resulting from different source regions.

The low values in bottom water are similar to those in surface water. The presence of surface-derived constituents may be due to mixing of deep and bottom water, but it cannot be excluded that surface water is a direct source to bottom water. These latter facts are consistent with the estimated relatively low turnover time of total deep and bottom water of about 80 years [3], quite different from the situation in the North Atlantic.

Sources of Contamination: The ultimate sources of CBs are industrially produced technical mixtures of various overall chlorine content (in the 30-60% range). They have been produced under different names, e.g., Aroclors and Phenoclors. Of particular relevance for the area under consideration are the Russian (Sovol) and Japanese (Kanechlor) formulations. A comparison between their compositions of the mixtures with those found in the Sea of Japan may be interesting for identifying sources. The score plots of the PCA involving water samples and the four major Kanechlor (KC) and Clophen (A) formulations (eg., KC 300, 400, 500, and 600 with 30, 40, 50, and 60% chlorine, respectively) and Sovol (50-60%) [4] are represented in Fig. 4. The surface water resembles KC400; the deep water and bottom water resemble Sovol and KC500, respectively. Gamo et al. [5] suggested that surface water in the northern or northwestern part of the Sea of Japan gets dense enough in strong winters to sink to the bottom. The newly formed bottom water would have sufficient kinetic energy to maintain active vertical mixing. The resemblance between the CB compositions in these deep and bottom waters and Sovol supports this.

It can be concluded that these findings on the distribution of CBs are in agreement with the presence of different water masses in the Sea of Japan, as suggested by Kim and Kim [3] and characterized by different concentrations and compositionsof CBs.

Organotin Conpounds
Introduction

Tributyltins (TBT) have been widely used as antifouling agents in marine paints for commercial and pleasure vessels. They cause deleterious effects on aquatic organisms, such as shell anomalies in oysters [6] and imposex in gastropods [7]. It was also reported that TBT has probably reduced the embryonic development of the bivalve Scrobicularia plana [8]. Triphenyltin (TPT) was used as an effective antifouling agent for paints in Japan but production has been regulated. Many countries have regulated the use of antifouling paints containing TBT for small boats. Subsequently, decreases of organotin levels in the water column [9] and of imposex levels in gastropods [10] have been observed in coastal areas. However, the use of organotin-based antifouling paints on large vessels has not been regulated yet, and about 69% of ships still use them [11]. Thus, the organotin antifouling paint regulations have been effective in decreasing TBT concentration in areas dominated by small boats, but less effective in reducing TBT levels in areas used by large vessels [12]. There have been many investigations on the contamination of coastal sea areas by organotins [12, 13], but few in the open ocean [14].

The purpose of this study was to investigate the distribution of organotins in the tanker route and in selected coastal areas subject to heavy shipping. The areas chosen were the Strait of Malacca and Tokyo Bay which have heavy shipping activity, and the Bay of Bengal where many oil slicks are caused by large vessels such as oil tankers. High levels of organotin contamination have been recorded in Tokyo Bay in the past [15]. Neogastropod imposex has been reported in coastal areas of Singapore and in Tokyo Bay [16].

Materials and Methods
Development of GC-ICP-MS

The transfer line designed to interface the GC and the ICP-MS is described in Fig. 5. It was composed of two concentric stainless-steel pipes. Electronically controlled heating wires and thermocouples were inserted between the inner and the outer stainless-steel pipes and all along the transfer line up to respectively 30 mm and 95 mm before the plasma. Thus any risk of condensation of high boiling species was avoided. The transfer line was directly inserted in the torch and positioned 2 mm before the tip of the torch central tube. The transfer line could be uniformaly heated up to 300°C. Designed to remain flexible before the torch-box, the transfer line was rigidly fixed at the entrance of the ICP torch to stay aligned, centered and avoid mechanical efforts on the quartz torch. The detection limits of this method were 170 fg for MBT (monobutyltin), 40 fg for DBT (dibutyltin), 60 fg for TBT, 60 fg for MPT (monophenyltin), 40 fg for DPT (diphenytin), and 20 fg for TPT.

Dissolved Concentration of Organotins: Water samples from Tokyo Bay were filtered immediately after sampling and analyzed by GC-ICP-MS. Fig. 6 shows the chromatogram obtained on mass 120. Peak integration gave concentrations as Sn of 20 pg g^{-1} for Me$_3$SnCl, 1.20 pg g^{-1} for Me$_2$SnCl$_2$, 1.10 pg g^{-1} for MBT, 0.30 pg g^{-1} for DBT and 0.09 pg g^{-1} for TBT. This suggested that the hydrophobic compounds like TBT were removed from water column to sediment by adsorbing to the suspended matters. Relatively high concentrations of methyltins indicated the importance of biomethylation in the behavior of tin compounds in the marine environment.

Distribution of Butyltin Compounds in the Strait of Malacca and in Tokyo Bay
Sampling: There were 20 sampling stations (n=69) as shown in Fig. 7. Seawater (4-15 l) was collected during the cruise of the R.V. Shinyo Maru in Feb. 1996 from the Strait of Malacca to the Bay of Bengal. Seawater (1.2 l) was also collected by the research vessel

(Hiyodori) in Tokyo Bay during 1993, 1994 and 1996. Samples were taken 1.5 m below the surface to prevent potential contamination from the surface micro-layer, using a GoFlo sampler whose inner side was coated with Teflon.

Analytical procedure: Tripentyltin chloride (0.5 ng) as an internal standard, 25 g of NaCl, and 20 ml of 6 M HCl were added to each bottle containing 1.2 kg of unfiltered seawater. After the addition of 5 ml of 0.25% tropolone-C_6H_6 and 5 ml of $CH_3COOC_2H_5$ to each bottle, the mixture was stirred magnetically with a Teflon coated bar for 10 min. Following this extraction, a further 5 ml of 0.25% tropolone-C_6H_6 and 5 ml of $CH_3COOC_2H_5$ were added to the residue and the organotins were extracted again. After the removal of water with anhydrous Na_2SO_4, the organic layer was concentrated to 1 ml and the solvent was exchanged with n-hexane under a gentle stream of N_2. One ml of 2 M n-propylmagnesium bromide was added to the concentrate and kept for 30 min at room temperature and the excess reagent was decomposed by the addition of 4 ml of 10% NH_4Cl solution. The mixture was passed through a silica/alumina (1:2 w/w, 1.5g) column for clean-up. The remaining solution was used for the determination of organotins. The precision of the measurements through triplicate extractions and GC-FPD analysis was about 8%; the detection limit was about 0.1 ng l^{-1}. The recoveries of standard spikes were about 80 to 90 %. No organotins were detected in the reagent and procedure blanks.

Results and Discussion
Concentrations and distribution of butyltins: As shown in Table 3, organotins were detected in most seawater samples: TBT in 61 out of 69 samples, DBT in 57 out of 69 samples and MBT in 53 out of 69 samples. No TPT, DPT or MPT was detected in any sample. Relatively high concentrations of butyltins were observed along the Strait of Malacca (St. 12-16), while lower values were observed in the Bay of Bengal (St. 17-20). The concentrations of TBT in sea water in the Strait of Malacca were almost the same as those in Tokyo Bay in Dec. 1996. These TBT levels were comparable to those which caused imposex in gastropods in Singapore and in Tokyo Bay.

There were spatial gradients in the concentrations of organotins. Levels of TBT and total butyltins (BTs=TBT+DBT+MBT) in the seawater samples decreased with increasing distance from Singapore along the Strait of Malacca. This distribution pattern of butyltins in the Strait of Malacca and in the Bay of Bengal were consistent with those of oil slicks due to the volume of oil tanker traffic, suggesting that the main source of the contamination by butyltins was large vessels in these area.

Sources of Contaminations in the Strait of Malacca and Tokyo Bay: The proportions of MBT, DBT and TBT in the Strait of Malacca in Feb. 1996 and in Tokyo Bay in Dec. 1993, Jan. 1994 and Dec. 1996 are shown in Fig. 8. Since the ratio of TBT/DBT presumably decreases over time, the high ratio of TBT/DBT (217%) observed in the Strait of Malacca suggests that recent inputs of TBT were made there. A much lower ratio of TBT/DBT was observed in Tokyo Bay in the same period (16%). Both the ratio of TBT/DBT and concentration of BTs in seawater of Tokyo Bay dropped from 1993 to 1996. It is possible that the legislation enacted in 1990, which relates to small vessels, is already having some effect in Tokyo Bay. However, concentrations of TBT in fish and crustaceans collected in Tokyo Bay (fish muscle: 6-423 ng TBTCl g^{-1} wet weight, crustaceans: 16-56 ng TBTCl g^{-1} wet weight) remain high [17]. The half-life of TBT in marina sediments was reported to be about 2.5 years [18]. Thus, organotins in sediment may continue to be a major source of those in fish and crustaceans, even after water column

concentrations decline.

In contrast, we found remarkably high concentrations of DBT (44.7 ng l^{-1}) and MBT (70.1 ng l^{-1}) compared to those of TBT in seawater in Tokyo Bay in Dec. 1996. The levels of MBT and DBT among butyltins in Tokyo Bay were relatively high which suggests that there has been a source of MBT and DBT other than the degradation products of TBT. TBT has been detected in sewage discharges [19], and sewage discharges have been reported as one of the sources of TBT in harbors [13]. We measured the organotins in effluent from a wastewater treatment plant (St. a) in Dec. 1996. The concentrations of TBT, DBT and MBT were 12.2, 21.7, and 58.4 ng l^{-1}, respectively. The concentrations of MBT and DBT were as high as those at St. 1 (Table 3), suggesting that wastewater effluent may be one of the sources of organotins to the seawater in Tokyo Bay.

Conclusions

BTs contamination of seawater in the Strait of Malacca, although low compared to that in Tokyo Bay, was high enough to cause imposex in gastropods. The data further suggest that there was a recent source of TBT from shipping there. The input of organotins in the Strait of Malacca and in the Bay of Bengal demonstrates the need for international control of the use of antifouling paints containing organotins for commercial vessels. The results in Tokyo Bay also show the need to control the pollution of organotins by wastewater.

References

1) Petrick, G., Schulz-Bull, D. E., Martens, V., Scholz, K., Duinker, J. C.: Mar. Chem., 1996, 54, 97-105.
2) Kim, K., Kim, K.-R., Kim, Y.-G., Cho, Y.-K., Chung, J.-Y., Choi, B.-H., Byun, S.-K., Hong, G.-H., Takematsu, M., Yoon, J.-H., Volkov, Y., Danchenkov, M.: J. Korean Soc. Oceanogr., 1996, 31, 155-163.
3) Kim, K.-R., Kim, K.: J. Korean Soc. Oceanogr., 1996, 31, 164-172.
4) Kannan, N., Schulz-Bull, D. E., Petrick, G., Duinker, J. C.: Int. J. Environ. Anal. Chem., 1992, 47, 201-215.
5) Gamo, T., Nozaki, Y., Sakai, H., Nakai, T., Tsubota, H.: J. Mar. Res., 1986, 44, 781-793.
6) Alzieu, C., Sanjuan, J., Deltreil, J. P., Borel, M.: Mar. Pollut. Bull., 1986, 17, 494-498.
7) Bryan, G. W., Gibbs, P. E., Huggett, R. J., Curtis, L. A., Bailey, D. S., Dauer, D. M.: Mar. Pollut. Bull., 1989, 20, 458-462.
8) Ruiz, J. M., Bryan, G. W., Wigham, G. D., Gibbs, P. E.: Mar. Environ. Res., 1995, 40, 363-379.
9) Dowson, P. H., Bubb, J. M., Lester, J. N.: Mar. Pollut. Bull., 1993, 26, 487-494.
10) Evans, S. M., Evans, P. M., Leksono, T.: Mar. Pollut. Bull., 1996, 32, 263-269.
11) Ambrose, P.: Mar. Pollut. Bull., 1994, 28, 134.
12) Smith, P. J.: Mar. Pollut. Bull., 1996, 32, 362-365.
13) Minchin, D., Storoben, E., Oehlmann, J., Bauer, B., Duggan, C. B., Keatinge, M.: Mar. Pollut. Bull., 1996, 32, 188-195.
14) Hallers-Tjabbes, C. C. T., Kemp, J. F., Boon, J. P.: Mar. Pollut. Bull., 1994, 28, 311-313.
15) Higashiyama, T., Shiraishi, H., Otsuki, A., Hashimoto, S.: Mar. Pollut. Bull., 1991, 22, 585-587.
16) Horiguchi, T., Shiraishi, H., Shimizu, M., Morita, M.: J. Mar. Biol. Ass. U.K., 1994, 74, 651-669.

17) Takayama, T., Hashimoto, S., Tokai, T., Otsuki, A.: Environmental Sciences, 1995, 8, 1-9.

18) de Mora, S. J., Stewart, C., Phillips, D.: Mar. Pollut. Bull., 1995, 30, 50-57.

19) Donard, O. F. X., Quevauviller, Ph., Bruchet, A.: Wat. Res., 1993, 27, 1085-1089.
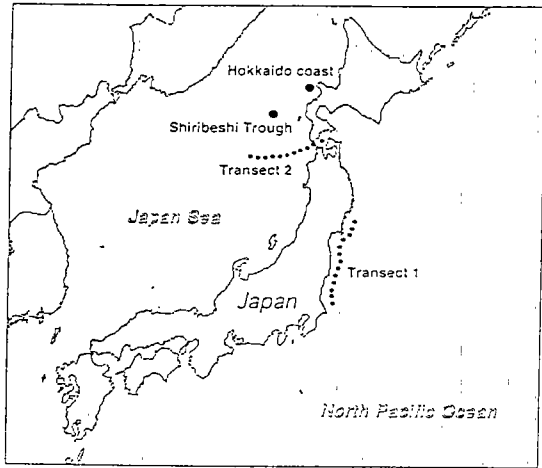
Fig. 1 Station of sampling chlorobiphenyls
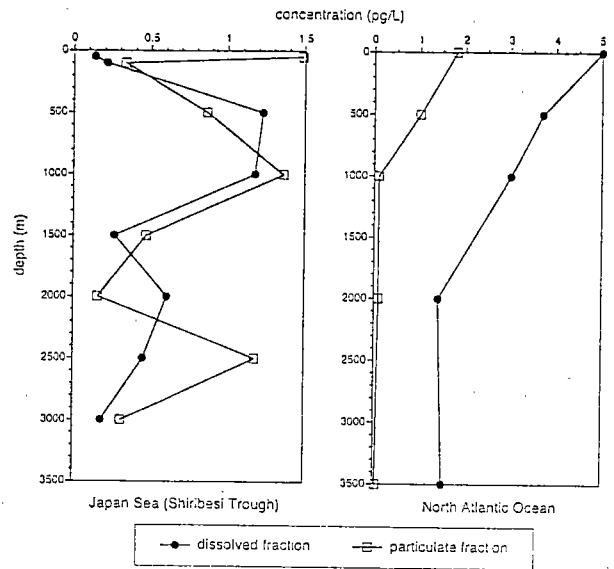
Fig. 2 Sum of 30 CBs in solution and suspension in vertical profile of Siribesi Trough and in the North Atlantic

Fig. 4 Score plots of principal components 1 and 2 derived from the correlation matrix of % contribution of 30 CB congeners to sum CBs in Clophen A30-A60, in Kanechlor KC300-KC600, in Sovol, and in vertical samples (solution) of Siribesi Trough.

Fig. 3 (a) Solution and (b) suspension: Biplot of pricipal components 1 and 2 derived from the correlation matrix of mol % contribution of 11 dominant individual CBs in samples of the vertical profile in the Siribesi Trough. Stars (★) represent scores, and the numbers refer to the depth of sampling in meters. The component loadings are represented by diamonds (◆), along with corresponding CB numbers.

— 154 —

TABLE 1. Concentrations (fg dm⁻³) of Individual CBs and Their Sums and the Sum of Nonylphenols (NoPhs) in Solution (Depth in m)[a]

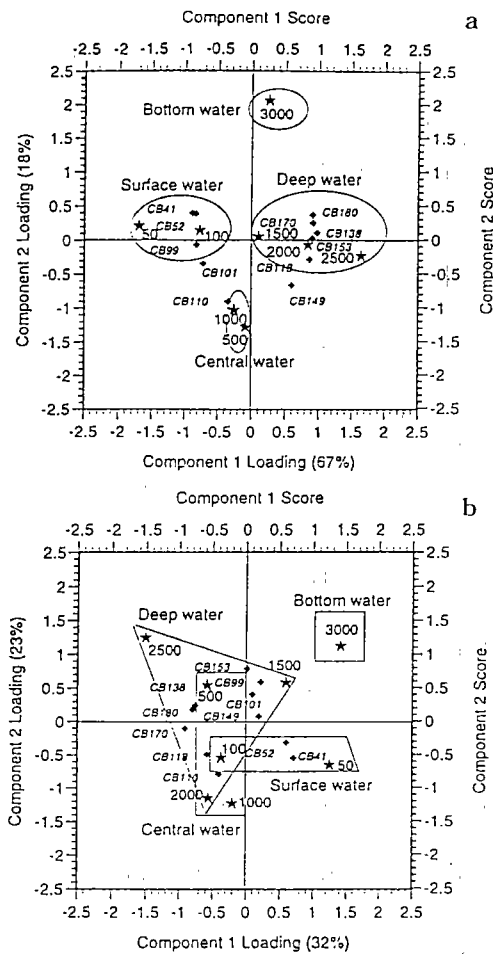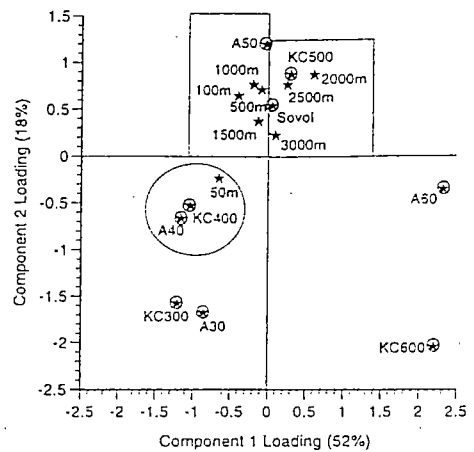| CB no.	Siribesi Trough								Hokkaido Coast				Tracks 1/6	Tracks 2/6
	50	100	500	1000	1500	2000	2500	3000	50	100	200	300	6	6
41	6.6	10	40	48	11	9.4	12	9.4	2.6	0.29	14	13	5.4	10
44	10	16	63	75	15	15	21	14	43	26	25	25	8.4	16
49	14	16	66	71	17	14	21	18	44	30	19	31	10	15
52	14	18	76	70	16	17	22	16	49	31	22	25	12	16
60	4.6	5.5	31	39	10	5.5	10	5.9	12	8.9	9.0	8.4	4.3	11
70	10	17	69	76	19	22	24	10	41	25	25	18	9.4	14
82	3.9	5.8	14	19	5.5	22	6.6	4.3	11	6.8	4.2	6.1	1.1	2.3
84	4.8	15	81	43	16	16	28	3.8	30	19	14	6.4	3.1	7.0
85	0.6	2.1	18	15	3.5	6.3	5.3	1.6	5.6	2.3	3.7	2.3	1.9	1.0
87	5.8	10	60	57	10	24	18	5.8	27	11	16	10	6.4	9.3
97	3.2	6.1	30	30	6.3	14	10	3.2	16	7.0	9.1	5.9	4.2	8.5
99	5.0	7.7	37	34	11	11	11	4.0	22	9.4	11	7.3	5.0	7.6
101	10	16	110	106	12	34	28	11	46	29	23	18	10	16
110	10	17	121	121	21	53	37	11	54	23	30	20	12	23
118	1.9	7.9	58	40	10	44	22	5.5	28	7.3	13	7.0	6.2	12
128	1.6	1.8	2.6	11	0.6	11	5.6	2.8	6.9	3.5	3.5	2.2	1.0	0.9
135	0.7	1.9	25	18	2.5	8.6	7.2	0.76	9.1	3.0	5.5	2.2	1.3	4.9
136	3.6	4.0	32	25	3.5	4.4	6.1	2.8	8.5	3.6	2.6	2.9	1.5	2.8
138	2.7	7.8	58	55	17	65	35	11	36	14	15	12	7.8	12
141	0.30	1.9	18	15	3.0	13	9.0	1.9	6.8	2.3	4.0	2.0	1.8	1.7
146	0.26	0.2	8.6	8.0	1.0	7.3	5.4	0.8	3.4	0.3	0.8	1.0	0.5	0.9
149	3.6	7.0	102	77	17	41	31	6.5	40	12	17	12	6.6	16
153	3.1	4.6	56	43	8.6	45	30	8.5	26	8.7	13	6.1	4.9	0.9
156	0.3	1.9	6.4	7.5	2.7	16	4.3	2.4	5.6	3.2	4.0	2.7	1.8	2.2
170	0.36	1.5	7.2	10	2.9	18	7.2	3.5	7.2	3.5	2.5	3.2	2.0	6.4
176	7.2	4.2	10	15	13	3.9	11	6.3	7.2	7.1	12	2.4	2.5	2.7
177	0.2	1.3	7.3	9.5	3.0	9.2	4.8	3.0	2.9	3.2	3.3	3.5	3.1	2.1
180	0.2	1.5	10	14	3.3	23	11	5.6	19	4.2	5.5	5.4	2.5	3.3
183	0.2	0.8	7.0	6.7	1.3	8.1	6.2	2.5	7.8	2.7	2.9	2.1	0.8	0.9
187	7.8	2.9	2.3	16	3.3	24	3.8	0.7	2.9	4.9	3.2	4.1	1.8	0.8
ΣCBs, fg dm⁻³	136	213	1226	1176	265	604	452	183	619	312	330	266	138	228
ΣCBs, fmol dm⁻³	0.4	0.7	3.8	3.7	0.8	1.8	1.4	0.6	1.9	0.9	1.0	0.9	0.4	0.7
ΣNoPhs, pg dm⁻³	3	2	28	145	92	4	4	9	34	58	21	24	11	93

[a] Tracks indicate space-integrated sampling at 6 m depth while cruising. CBs are identified by numbers according to Schulz et al. (11).

TABLE 2. Concentrations (fg dm⁻³) of Individual CBs and Their Sums in Suspension

CB no.	Siribesi Trough								Hokkaido Coast			
	50	100	500	1000	1500	2000	2500	3000	50	100	200	300
41	128	7.0	32	46	16	8.2	7.0	12	1.9	32	33	27
44	143	13	37	32	14	16	52	10	20	8.6	14	34
49	116	15	34	84	5.8	12	36	14	20	29	40	34
52	88	28	30	94	55	11	39	27	26	47	33	28
60	76	33	34	75	14	1.7	61	4.8	20	57	1.2	23
70	116	28	43	104	23	13	55	7.7	30	42	41	34
82	36	12	19	1.6	8.7	1.7	25	6.5	14	11	23	18
84	40	8.4	20	48	8.7	1.7	13	4.3	15	18	10	13
85	24	8.2	37	1.8	4.3	1.6	44	4.3	10	35	34	88
87	60	12	39	62	17	8.8	46	8.6	31	30	40	23
97	28	3.5	19	40	8.7	6.9	15	6.0	10	15	14	10
99	32	8.2	25	1.6	8.7	1.6	28	9.1	16	20	21	13
101	100	18	54	96	32	1.6	69	18	47	48	58	41
110	108	23	61	106	32	12	82	19	57	58	58	44
118	48	17	29	106	20	6.9	58	11	40	24	29	28
128	4	2.8	9.0	13	5.8	1.6	16	1.7	3	8.6	5.4	8.8
135	24	9.4	13	1.7	5.8	1.5	24	13	18	29	21	8.8
136	12	4.2	17	30	2.3	1.5	16	29	15	29	10	13
138	68	16	63	88	29	13	124	17	50	54	95	43
141	12	6.8	17	36	8.7	2.9	27	3.6	6.9	4.5	18	9.4
146	12	4.2	10	45	4.3	1.5	13	2.9	8.9	7.4	9.1	5.6
149	100	4.2	34	62	26	12	76	17	31	11	20	34
153	32	10	42	53	27	5.2	66	28	37	42	66	27
156	10	4.7	15	13	8.7	1.4	19	1.9	12	10	7.4	9.4
170	12	6.8	25	29	8.7	5.2	45	2.2	21	23	27	13
176	24	3.5	6.0	28	23	1.4	6.6	7.2	7.9	5.6	19	11
177	8	6.3	10	23	4.3	1.4	23	0.7	7.9	7.1	1.2	2.5
180	16	13	35	39	14	1.4	61	2.6	31	30	4.5	20
183	4	4.0	7.2	1.6	2.9	1.5	20	12	2	10	12	6.9
187	8	2.0	49	1.6	29	1.4	14	10	1.9	4.3	47	2.4
ΣCBs, fg dm⁻³	1484	332	865	1362	470	159	1179	311	607	748	812	672
ΣCBs, fmol dm⁻³	4.7	1.0	2.6	4.2	1.4	0.5	3.6	0.9	1.8	2.3	2.5	2.1

[a] Sampling depths in meters are indicated at the top. CBs are identified by numbers according to Schulz et al. (11).
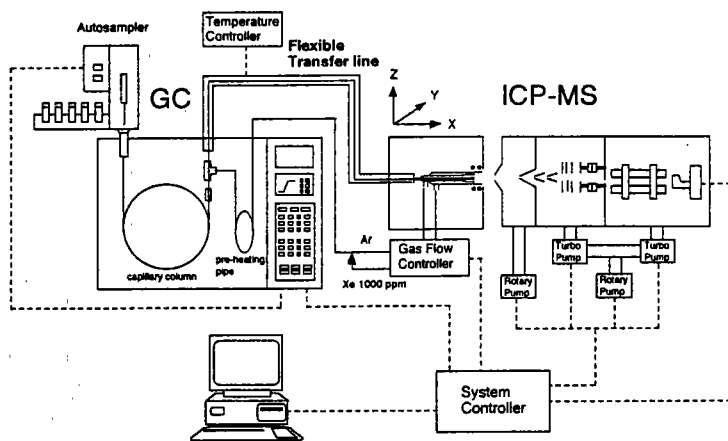
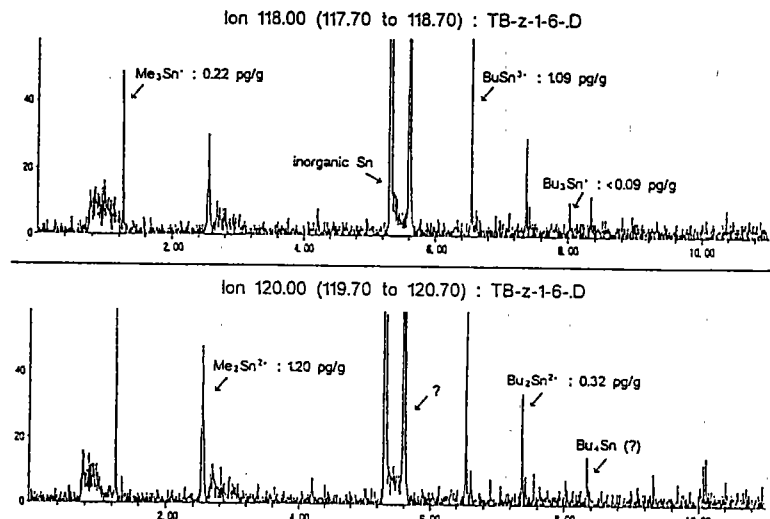Fig. 5 A schematic diagram of GC-ICP-MS

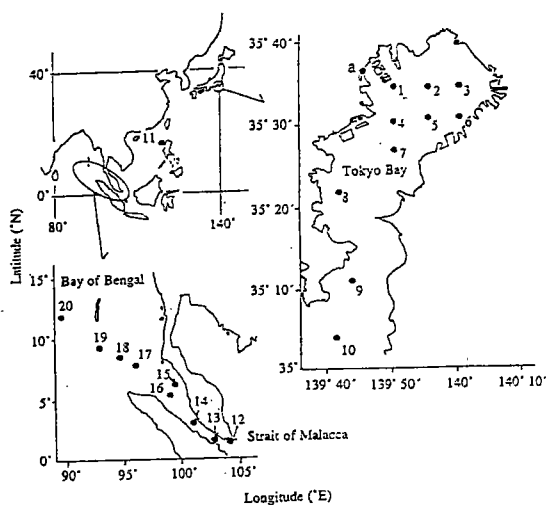Fig. 6 Chromatogram of organotins in filtered seawater in Tokyo Bay

Fig. 7 Stations for sampling butyltins.

Table 3 Concentration of butyltins in surface sea water (ng l as chlorides)

|	MBT	DBT minimum - maximum, mean	TBT
Strait of Malacca (Feb. 1996)			
Sta. 12	5.4 - 5.9, 5.7	2.0 - 2.2, 2.1	5.1 - 5.2, 5.2
Sta. 13	1.1	< 0.1	2.9
Sta. 14	0.4	0.9	0.7
Sta. 15	1.0 - 1.2, 1.1	1.8 - 2.4, 2.1	1.8
Sta. 16	0.2 - 0.3, 0.3	< 0.1	0.1 - 0.2, 0.2
Open Ocean (Feb. 1996)			
Sta. 11	< 0.1	< 0.1	< 0.1
Sta. 17	0.2	< 0.1	0.3
Sta. 18	< 0.1	< 0.1	< 0.1
Sta. 19	< 0.1	< 0.1	< 0.1
Sta. 20	< 0.1	< 0.1	< 0.1
Tokyo Bay (Dec. 1993)			
Sta. 1	14.5 - 16.3, 15.4	23.0 - 28.2, 25.6	8.7 - 9.7, 9.2
Sta. 2	3.0 - 3.9, 3.5	22.4 - 26.5, 24.4	7.4 - 9.3, 8.4
Sta. 3	5.5 - 6.1, 5.8	29.5 - 32.9, 31.2	7.7 - 8.0, 7.9
Sta. 4	7.6 - 10, 8.8	17.3 - 23.9, 20.6	6.6 - 8.0, 7.3
Sta. 5	8.9 - 12.1, 10.5	5.3 - 8.1, 6.7	8.7 - 11.1, 9.9
Sta. 6	< 1	8.7 - 11.3, 10.0	5.2 - 7.5, 6.4
Sta. 7	5.7 - 8.9, 7.3	9.8 - 11.8, 10.8	8.2 - 11.8, 10.0
Sta. 8	9.3 - 11.6, 10.7	7.1 - 8.9, 8.0	4.2 - 5.0, 4.6
Sta. 9	5.6 - 6.6, 6.1	2.6 - 3.2, 2.9	4.0 - 4.8, 4.4
Sta. 10	7.9 - 10.1, 9.0	3.5 - 4.5, 4.0	4.1 - 5.9, 5.0
Sta. 1 (Jan. 1994)	16.2 - 19.2, 17.7	24.5 - 29.5, 27.0	9.1 - 11.3, 10.2
Sta. 2	3.1 - 3.9, 3.5	29.6 - 36.2, 32.9	7.4 - 9.3, 8.4
Sta. 3	2.1 - 2.7, 2.4	29.8 - 35.0, 32.4	6.1 - 9.3, 7.7
Sta. 4	8.5 - 11.3, 9.9	35.2 - 44.8, 40.0	6.2 - 8.4, 7.3
Sta. 5	9.2 - 11.7, 10.5	43.2 - 53.4, 48.3	8.6 - 11.1, 9.9
Sta. 6	2.0 - 2.5, 2.3	45.4 - 49.3, 47.3	5.8 - 7.6, 6.7
Sta. 7	< 1	34.4 - 43.9, 39.1	6.1 - 7.9, 7.0
Sta. 8	0.7 - 1.2, 1.0	29.8 - 38.0, 33.9	9.2 - 11.4, 10.3
Sta. 9	< 1	16.3 - 20.1, 18.2	3.0 - 4.0, 3.5
Sta. 10	< 1	21.4 - 26.3, 23.8	3.1 - 3.5, 3.3
Sta. 1 (Dec. 1996)	59.6 - 72.8, 66.2	39.3 - 50.1, 44.7	4.2 - 5.6, 4.9
Sta. 2	37.0 - 47.1, 42.1	9.1 - 11.7, 10.4	2.4 - 3.1, 2.7
Sta. 3	13.0 - 14.1, 13.6	7.1 - 9.0, 8.1	1.9 - 2.5, 2.2
Sta. 4	17.7 - 22.7, 20.2	17.3 - 22.1, 19.7	5.5 - 7.4, 6.5
Sta. 5	34.2 - 43.6, 38.9	5.4 - 7.1, 6.2	0.8 - 1.4, 1.1
Sta. 6	61.6 - 78.6, 70.1	12.5 - 16.1, 14.3	2.9 - 3.7, 3.3
Sta. 7	19.5 - 23.5, 21.5	20.4 - 26.3, 23.3	< 1
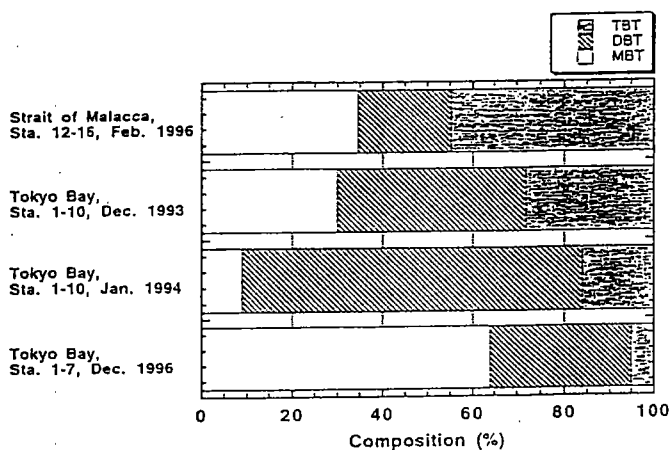
Fig. 8 Proportions of MBT, DBT and TBT in seawater in the Strait of Malacca and Tokyo Bay.