APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **12**, 819–825 (1998)

Measurement of Butyltin Contamination of Water and Sediment in Osaka Bay, Japan

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The concentration of tributyltin (TBT) in surface water from Osaka Bay ranged from 0.023 to 0.061 μg l^{-1} in 1989 and from not detected (ND) to 0.059 μg l^{-1} in 1990 while the proportion of TBT as a percentage of the total butyltins (BTs) was more than 40%. The concentration of TBT was also surveyed in the Port of Osaka and the Yodo River basin. TBT levels were highest in the estuary (the Port of Osaka), followed by sea areas (Osaka Bay) and rivers (Yodo River basin). A fairly high correlation coefficient between TBT concentration and salinity in water from the estuary and the sea areas was observed. This result shows that the TBT in the estuary water is diluted by seawater. Generally, the TBT concentrations in the water columns were distributed uniformly and the composition of the BTs was also constant. TBT was detected in sediment from Osaka Bay in the range from ND to 0.023 mg kg^{-1} dry weight with a high ratio of monobutyltin (MBT) to the total BTs. TBT in sediment core was also measured; its concentration decreased with core depth. It was estimated from these measurements that the release of TBT into Osaka Bay began in the 1960s. © **1998 John Wiley & Sons, Ltd.**

Keywords: monobutyltins; dibutyltins; tributyltins; water; sediment; Osaka Bay

Received 9 January 1998; accepted 24 April 1998

INTRODUCTION

Tributyltin (TBT) have been widely used as a biocide in antifouling paints. However, it was found to cause damage to the marine organisms, such as imposex and deformity in molluscs.[1] Investigation of the aquatic environment has shown that high concentrations of TBT have frequently been found in water, sediment and biota from coastal area.[2,3] Cocchieri *et al.*[4] also reported that organotin (OT) concentrations exceeded the level that was toxic to certain sensitive marine species, even in the relatively uncontaminated areas of the Gulf of Naples. It was also reported that TBT concentrations in sediment from San Diego Bay ranged from 0.002 to 1.1 mg kg^{-1} dry wt during 1988–1990.[5] There are thus many reports of contamination with OTs in Europe and the USA. However, reports on the current status of OTs in Japan have been comparatively few.[6]

TBT leached from paint is extremely active and the most important sink process is adsorption to particulate material with subsequent sedimentation. It is well known that TBT concentrations in sediment are a thousand times higher than in water.[7] OTs are also stable in sediment.[8] it is therefore important to clarify the vertical distribution of butyltins (BTs) in sediment cores in order to elucidate the history of OT contaminants.

The object of this research is to assess the extent of TBT contamination as well as the presence of its degradation products such as dibutyltin (DBT) and monobutyltin (MBT) in Osaka Bay, and to estimate temporal trends from profiles of OTs in sediment core.

MATERIALS AND METHODS

Sampling Procedure

Figure 1 shows the sampling sites. Osaka Bay is

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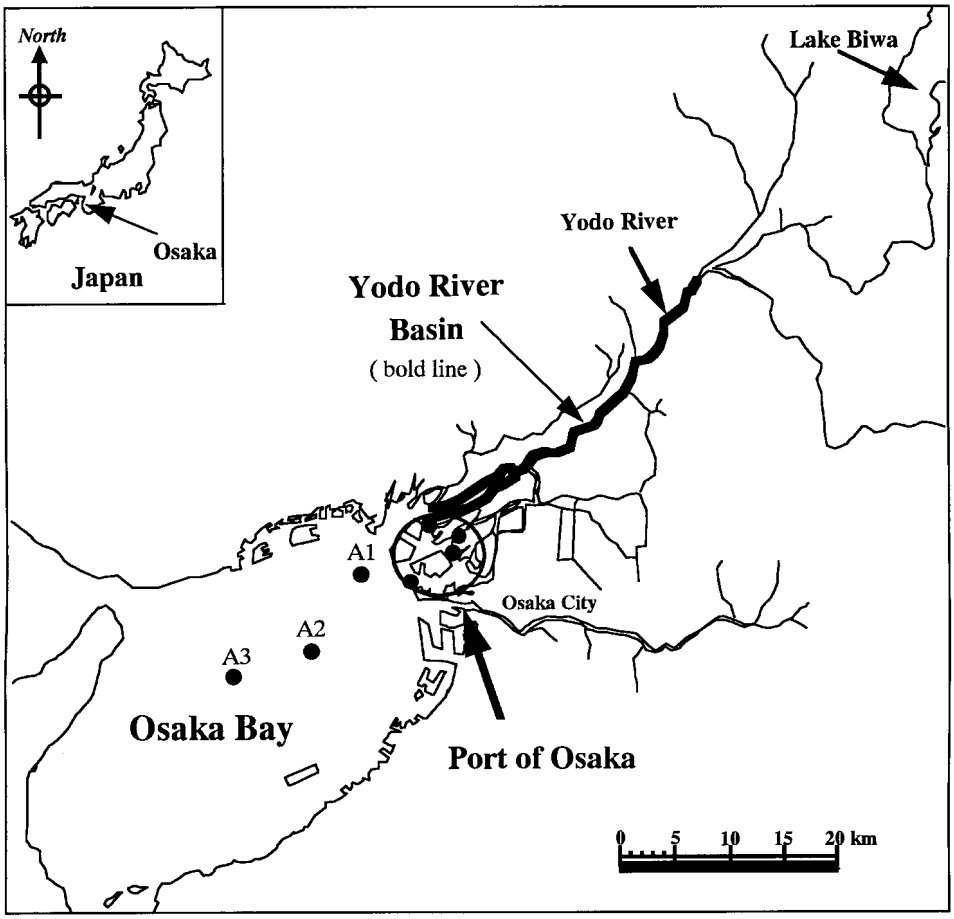

Figure 1 Sampling sites.

located in mid-western Japan and its average depth is about 30 m. The peripheral area of Osaka Bay is an industrial zone with trading ports, industrial plant and similar installations. Many rivers flow into Osaka Bay, Yodo River is the largest of them and its discharge comprises about 80% of the total river discharge into the bay. The Port of Osaka, situated in the north-east of the bay, is a prominent international trading port in Japan — about 80 000 ships enter the Port of Osaka in a year.

Both water and sediment samples from Osaka Bay were collected from 15 sites in November and December 1989, and 25 sites in May 1990. Water-column and sediment cores were taken at stations A1–2 and at station A3, respectively. Water samples from rivers (Yodo river basin) were taken from 10 sites in February 1989 and May 1990, and estuary water and sediment samples (the Port of Osaka) were taken from four sites in December 1989 and May 1990.

Determination of sedimentation rate

Sediment (3 g) from station A3 in Osaka Bay was dried at 105 °C. The activities of radionuclides ^{238}U and ^{210}Pb in this sediment sample were determined, using a γ-ray spectrometer with a planer Ge (Li) detector, from the areas of the photopeaks due to 63.1-keV γ-rays of ^{234}Th (daughter nuclide of ^{238}U), 67.4-keV γ-rays of ^{230}Th and 46.5-keV γ-rays of ^{210}Pb.[9] In order to calculate the sedimentation rate, it is assumed that (1) the flux of excess ^{210}Pb to the sedimentation is constant, (2) the sedimentation rate is constant at all times, (3) there is no postdepositional migration of ^{210}Pb within the

sediment and (4) depth profiling of ^{210}Pb-supported ^{238}U in the sediment is not uniform. The accumulation rate at the surface was calculated from the vertical distribution of excess ^{210}Pb.[10]

Analytical procedure

The method used for the determination of BTs in water and sediment was based on that of Harino *et al.*,[11] with some modifications. Analytical procedures are explained briefly in the following. Water samples (1 l each) were extracted twice with 0.1% tropolone–benzene solution after adding 1 M HCl solution. The benzene layer was dried with anhydrous Na_2SO_4 and concentrated to 1 ml. After propylation with *n*-propyl magnesium bromide, the analytes were determined using a gas chromatograph equipped with a flame photometric detector.

Portions of sediment (10g) were extracted twice with acetone after addition of 1 M HCl. The supernatant was re-extracted with 25% NaCl solution and 0.1% tropolone–benzene. Inorganic sulphur-containing species co-extracted with the analytes were removed with tetrabutylammonium hydrogensulphate–sodium sulphide. The organic layer was concentrated to 1 ml after drying with anhydrous Na_2SO_4. Further procedures were identical with those for water samples. OTs concentrations are expressed as those of the cation. The recoveries for OTs were typically in the range 73–100% in water and 68–109% in sediment samples, while the detection limits for water and sediment samples were 0.003 μg l^{-1} and 0.005 mg kg^{-1} dry wt, respectively.

RESULTS AND DISCUSSION

Butyltins in water

Figure 2 shows the distribution of BTs in water

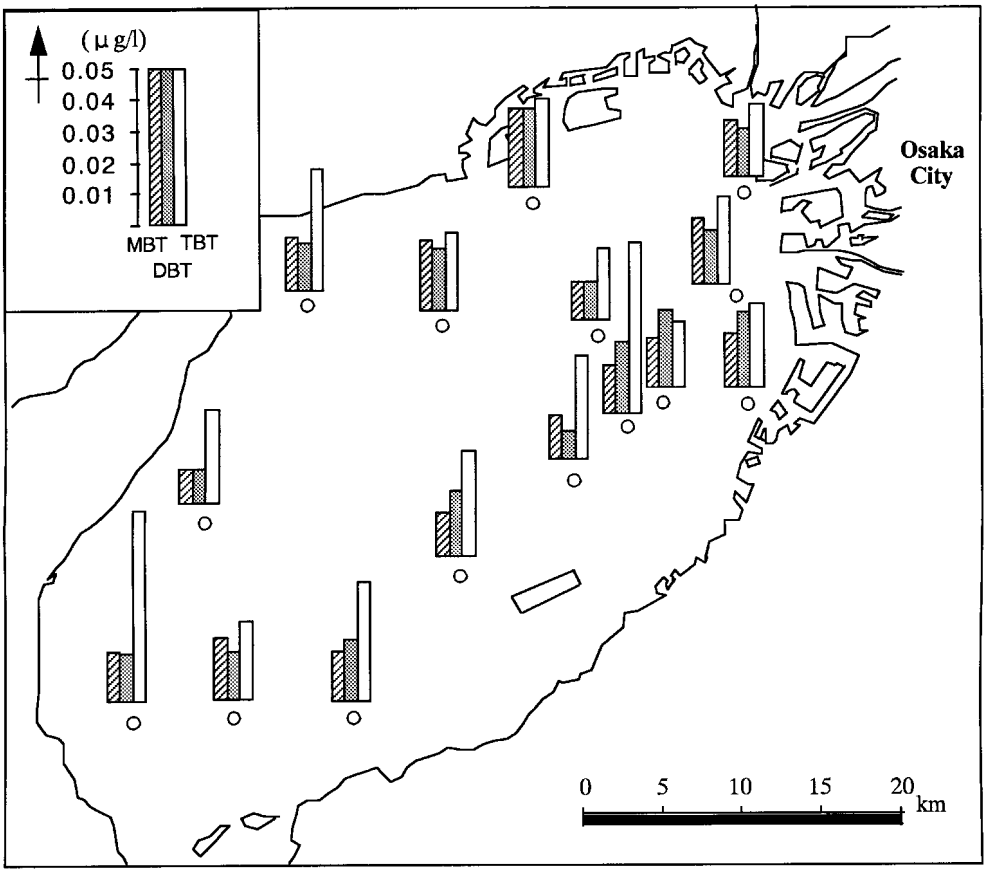

Figure 2 Horizontal distribution of butyltins in water from Osaka Bay in 1989.

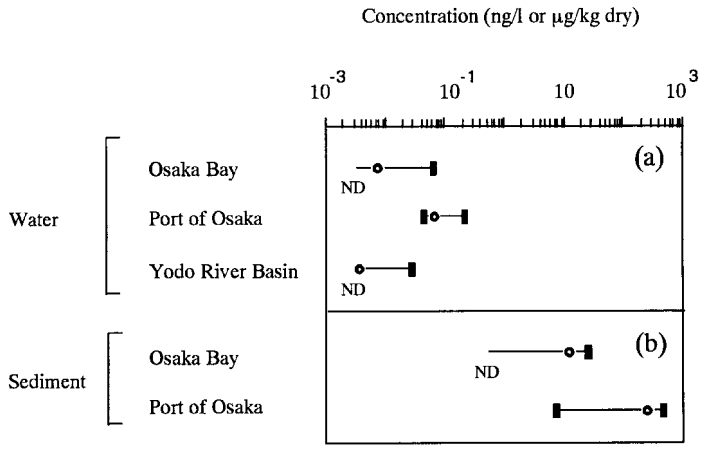

Figure 3 Levels of butyltins in water and sediment from Osaka Bay, the Port of Osaka and the Yodo River basin in 1990. Solid lines and circles indicate ranges and medians, respectively.

from Osaka Bay in 1989. TBT concentrations ranged from 0.023 to 0.061 μg l^{-1} and were distributed uniformly at 15 sites in Osaka Bay. This is due to TBT from sailing vessels. On the other hand, it is reported that TBT is degraded to DBT and MBT by bacteria in water[12,13] and the half-life of TBT is in the range of 4–19 days.[14,15] Furthermore Seligman *et al.*[16] report that TBT is adsorbed to particulate material easily, with subsequent sedimentation. However the ratio of TBT to the total BTs in water from Osaka Bay was generally high, suggesting recent input from ships.

BTs in water were also measured at 25 sites in Osaka Bay in 1990. The concentration of TBT in water from Osaka Bay ranged from not detected (ND) to 0.059 μg l^{-1} and was the same as in 1989. The concentration of TBT in the estuary (the Port of Osaka) and the rivers (Yodo River Basin) was also investigated and compared with that in the sea areas (Osaka Bay) (Fig. 3a). The concentrations of TBT in the estuary were the highest among the three

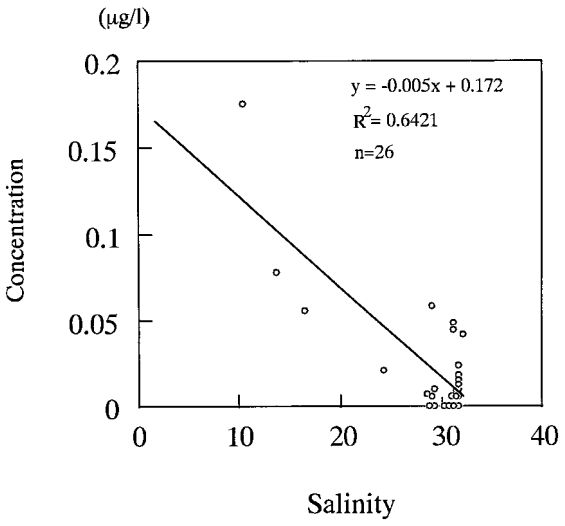

Figure 4 Correlation between concentration of TBT and salinity in water.

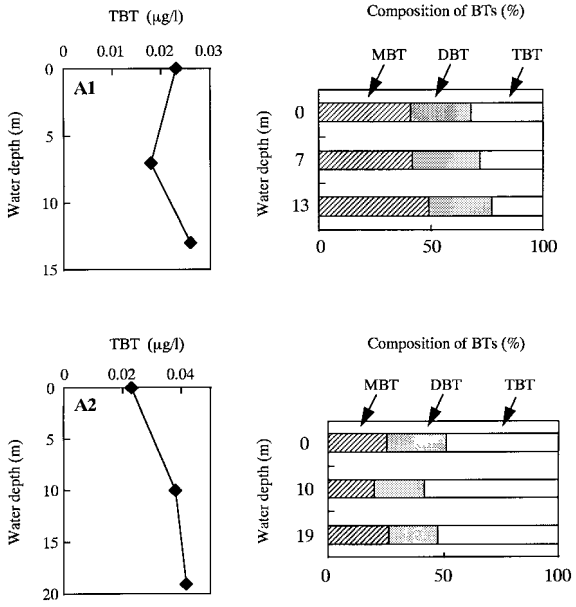

Figure 5 Vertical distribution of butyltins in water columns from stations A1 and A2 in Osaka Bay.

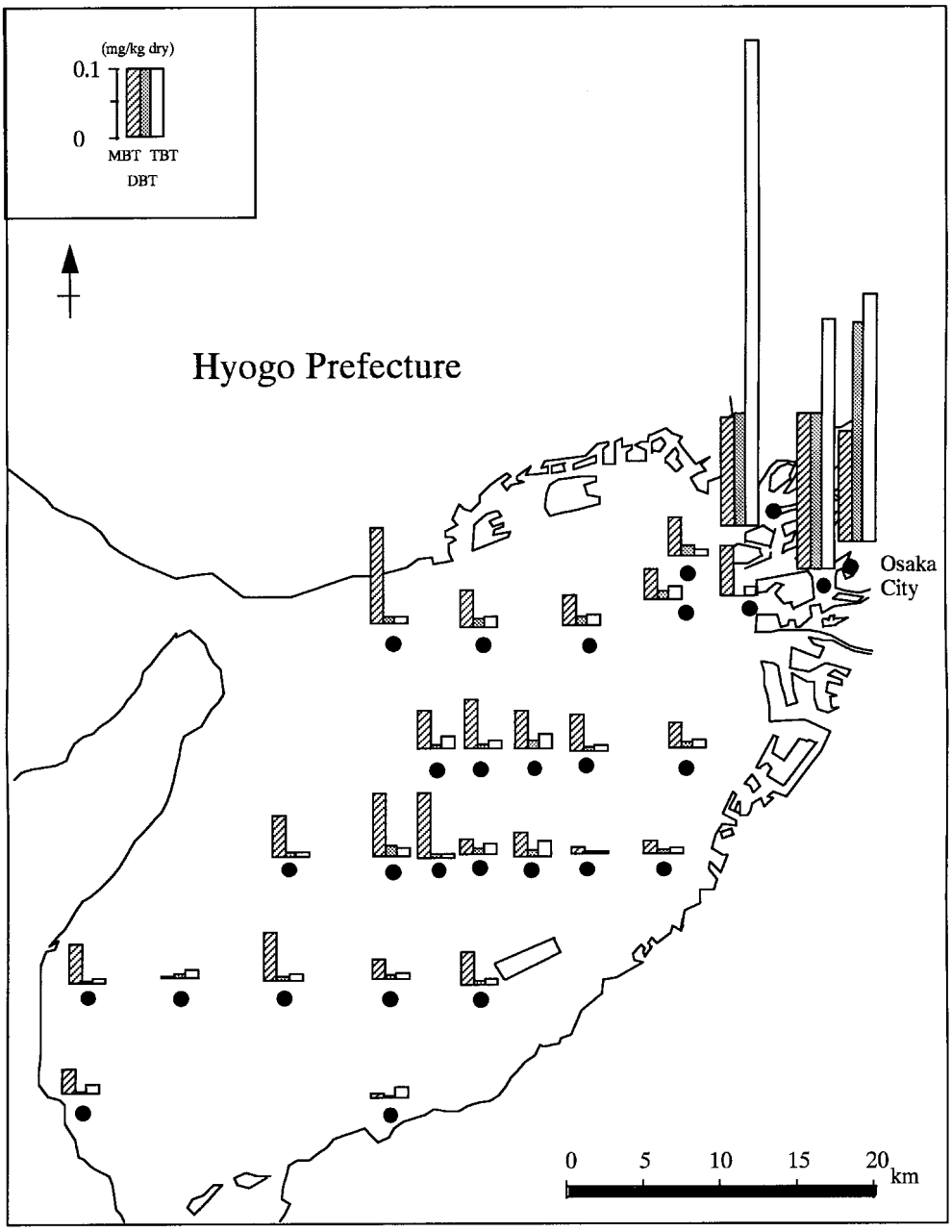

Figure 6 Concentration of butyltins in sediment from Osaka Bay in 1990.

areas and was in the range 0.040 – 0.067 μg l^{-1}. The levels of TBT in the sea areas were lower, while TBT was scarcely detected in the rivers, where MBT and DBT were however present.

Figure 4 shows the correlation between TBT concentration and salinity in water from the sea areas and the estuary. The graph had a downward slope, showing that the lower the salinity, the higher the TBT concentration in water. This result indicates that the estuary is heavily contaminated with TBT and that TBT from the estuary to offshore is diluted with seawater.

The BTs in the surface, middle and bottom layers of the water columns are shown in Fig. 5. The concentration of TBT at stations A1 (water depth 14 m) and A2 (water depth 20 m) were almost uniform throughout water column. The composition of the BTs was also uniform throughout the water column. The salinity in the surface (A1:28.36, A2:32.34), middle (A1:30.89, A2:32.34) and bottom (A1 31.98; A2 32.34) layers was also almost the same, suggesting vertical mixing. Accordingly, differences in the OTs concentration were not observed in the water columns.

Butyltins in sediment

Figure 6 shows the TBT concentrations in sediments from Osaka Bay and the Port of Osaka. The concentrations of TBT in Osaka Bay and the Port of Osaka ranged from not detected (ND) to 0.023 mg kg^{-1} dry wt and from 0.011 to 0.692 mg kg^{-1} dry wt, respectively, showing that the Port of Osaka had higher TBT levels in sediment than Osaka Bay (Fig.3b). This investigation was carried out before the regulation of TBT. It is therefore difficult to compare these results with TBT levels in other areas of Japan after regulation. However, as it is reported that TBT in sediment is stable,[8] TBT levels in sediment from Osaka Bay and the Port of Osaka were compared with those in sediment from Ise Bay, which is adjacent to Osaka Bay, in 1992.[6] The concentration of TBT in Ise Bay ranges from ND to 0.11 mg kg^{-1} dry wt. The concentration of TBT in the Port of Osaka was remarkably high compared with that of Ise Bay.

Because the Port of Osaka is an international trading port, there are many moorings and heavy sea traffic, and it is a zone of poor flushing. This is why the level of TBT is high in the estuary. The ratio of TBT to the total BTs was high in the Port of Osaka, whereas MBT was dominant in Osaka Bay. This means that the TBT loading of sediment in the Port of Osaka is higher than in Osaka Bay.

Figure 7 shows the concentration of BTs in sediment core from Osaka Bay. The descending orders of BT concentrations were MBT > TBT > DBT in surface sediment. It is reported that TBT persists for several years within sediment.[7] Accordingly, it is possible to estimate the times when release of TBT began in this area from the profile of TBT in sediment core. The concentration of TBT in the top 10 cm from station A3 was higher than in the other sediment core. The deposition rate of sediment at station A3 was estimated to be 3.1 mm per year. Consequently, it is estimated that TBT has been used since approximately 1960s. Our results were therefore in agreement with the general assertion that TBT has been in use since the 1960s. BTs were detected in segments from less than 10 cm deep (especially, sediment at depths between 18–20 cm and 26–28 cm). It may be the bioturbation.

CONCLUSION

A relatively high concentration of TBT was observed in water and sediment from Osaka Bay in comparison with other areas of Japan. In particular, TBT in estuary samples showed high levels. These results indicated that the main source of TBT is sailing vessels. To decrease TBT levels in the aquatic environment, the use of TBT on ships should therefore be controlled.

The relationship between the deposition rate of suspended solid (SS) in sediment and the TBT concentration in sediment cores suggests estimated that use of TBT in this area started in the 1960s. Further study is required to monitor OT concentra-

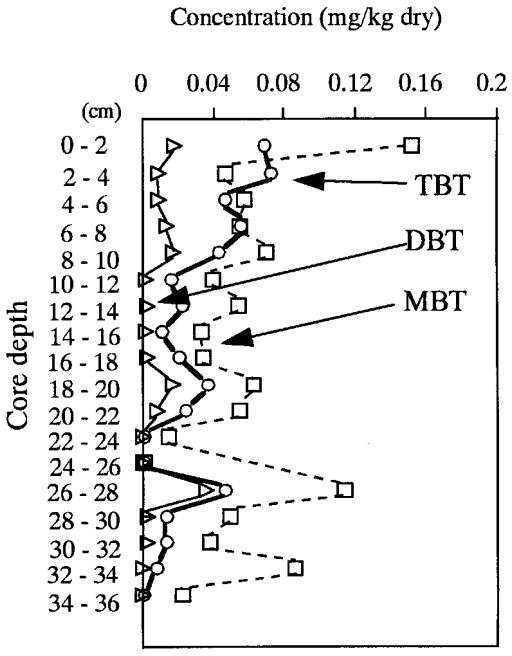

Figure 7 Vertical distribution of butyltins in sediment core from station A3 of Osaka Bay.

tions in each area of the aquatic environment, in order to clarify the temporal trend.

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