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Desorption of Tributyltin, Dibutyltin and Zinc from Resuspended Sediment

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Adsorption–desorption equilibrium and desorption kinetic studies were conducted in order to assess desorption of tributyltin (TBT), dibutyltin (DBT) and zinc from resuspended sediment. Equilibria were described in terms of linear adsorption. Desorption kinetics were represented by a two-site model which assumed that desorption consisted of rapid desorption and first-order kinetic desorption. TBT desorbed the most easily. Desorption kinetic parameters were related to adsorption mechanisms. Some experimental results did not correspond with the theoretical model. This was thought to be caused by natural organic ligands originally held in the sediment. Zinc deviated the most, because it was affected by the natural organic ligands more strongly than butylins. For example the partition coefficient of zinc varied by up to 1000-fold, and re-adsorption to sediment of the zinc that had been discharged to the water took place. Release of chemicals induced by remedial dredging was assessed. Desorbed TBT may pose a high risk. Among remediation alternatives, capping or leaving the sediment to stand prior to *in situ* degradation are preferred. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

The majority of tributyltin (TBT) in the aquatic environment is held in the sediment instead of in the water compartment.[1–3] Thus it is generally true for other heavy metals also. It is of interest to assess the amount of contaminant that will be released when the contaminated sediment is resuspended. In Japan, mercury-contaminated sediments were removed by dredging for remediation purposes from the 1970s to the 1980s.[4] Release of mercury in the dissolved phase was reported not to be observed there.[5] However, careful examination is needed before the same situation is assumed for other contaminants, such as TBT.

There are two possible sources of discharged contaminant from the resuspended sediment to the overlying water. One is released interstitial water. The other is desorption of the contaminant from the scattered sediment soil. For highly adsorptive chemicals such as TBT, the latter mechanism becomes more important.

Desorption kinetics have been proposed in many models; we selected a two-site model[6] as a practical means to characterize the desorption phenomena. The two-site model in this paper assumes that adsorption consists of a loose and a strong form. On the other hand, it is known that non-ionic/physical adsorption operates over longer distances but with weaker energies than ionic/electrostatic adsorption.[6] Furthermore, organometallics can behave as both ionic and non-ionic substances.[7, 8] These properties bring validity to the use of a two-site model for desorption of organometallics from resuspended sediment soil. In comparison, it is very interesting to apply the same model to a heavy metal which is believed to be a cation in water (i.e. zinc).

We carried out the experiments on adsorption and desorption equilibria first. Desorption kinetic parameters were obtained experimentally with a suspended sediment—water continuous contactor. Tributyltin and dibutyltin (DBT) were used as organometallics. Zinc was selected as a cationic heavy metal. The different equilibrium and kinetic behavior of butyltins and zinc was

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explained on the basis of the adsorption mechanism and included also some contribution from natural organic ligands. Finally, remediation alternatives for TBT-contaminated sediment were discussed.

EXPERIMENTAL

Sample collection and preparation

Muddy sediment soil was collected by an Ekman dredge at the mouth of the Kamo River, Toba Estuary, Mie Prefecture, Japan, on 21 December 1990. Butyltin concentrations were measured by hydrochloric acid–methanol extraction from the sediment followed by quartz-furnace hydride-generation atomic absorption spectrometry (HGAAS) using a liquid nitrogen trap and chromatographic separation.[9, 10] The concentrations of TBT and DBT were 334 μg Sn kg^{-1} dry wt and 115 μg Sn kg^{-1} dry wt, respectively.

In order to avoid decomposition during analysis of the hydrides, the normal U-shaped trap was replaced by a W-shaped trap. The first dip was empty and acted as a trap to prevent water from soaking into packing contained in the second dip. The second dip was packed with 3% OV-1 on Chromosorb W AW-DMCS 40/60 mesh. This prevented water from soaking into the packing phase and allowed moisture to pass as vapor through the packing phase. Silanization was also carried out.

For adsorption–desorption equilibrium studies, several grams of sediment soil was dried at 105–110 °C and ground up.

For the desorption kinetic studies, a highly spiked sediment was prepared as follows; 700 g wet wt sediment soil was added to 500 ml seawater and made homogeneous by a hand-drill mixer. A mixture of 10 g of zinc sulfate powder, and TBT (0.6 g Sn) and DBT (0.4 g Sn) (as chlorides) dissolved in 30 ml methanol, was poured into the slurry, which was kept homogeneous by stirring for a further 5 min. The slurry was left in the container for a month; afterwards the wet sediment was stored in a sealed plastic container in a refrigerator. The concentrations of TBT, DBT and zinc in the highly spiked sediment were measured to be 848 mg Sn/kg dry wt, 656 mg Sn kg dry wt and 3690 mg Zn kg^{-1} dry wt, respectively. Nitric acid–sulfuric acid digestion followed by flame atomic absorption spectrometry was used for zinc determination. At the same time the leachate above the sediment was sampled and analyzed and considered to be interstitial water. Concentrations were 581 μg Sn l^{-1}, 369 μg Sn l^{-1} and 220 mg Zn l^{-1}, respectively, for TBT, DBT and zinc. Moisture content was 41.7%. For the sediment analysis 1 g of wet sediment was treated with 5 ml of HNO_3 and a small amount of water and heated on a hotplate for one hour; 2 ml of HNO_3 and 5 ml of H_2SO_4 (1 : 1) were added. The mixture was heated for 1 h and the extract was diluted with water to 100 ml.

Adsorption–desorption equilibria

Six 50 ml centrifuge tubes with Teflon-lined screw-caps were used as batch reactors. Samples comprising 0.1, 0.2, 0.3, 0.5 and 1.0 g dry wt of sediment soil were placed in five of the tubes, with a remaining tube used as a blank with no soil. Then 30 ml of seawater spiked with TBT (200 μg Sn l^{-1}), DBT (50 μg Sn l^{-1}) and zinc (100 mg l^{-1}) was poured into each tube. They were shaken for 24 h at room temperature with the sediment soil and then they were centrifuged. The supernatant liquid was sampled and analyzed (for the adsorption study). After all the supernatants had been removed, 30 ml of fresh seawater (unspiked) was added, then the same protocol was carried out for the desorption study. The concentrations of chemicals in the sediment soil were calculated from the change of concentration in the water. Initial concentrations of TBT in unspiked sediment soil were so low compared with spiked seawater as to be negligible, viz. for TBT in soil 334 ng in 1 g, total = 334 ng; for DBT 115 ng in 1 g, total = 115 ng. In spiked seawater there was 200 ng TBT/ml in 30 ml, i.e. 6000 ng and 50 ng DBT/ml in 30 ml, i.e. 1500 ng.

Desorption kinetics

A suspended sediment–sea water continuous contactor was built, as depicted diagrammatically in Fig. 1. This consisted of lower, middle and upper parts which were separated by two glass fiber filters (GA100, Advantec Toyo, Japan.) A certain amount of highly spiked sediment soil (0.29 and 1.47 g dry wt in runs 1 and 2, respectively) in a wet condition was placed in the middle part. Seawater was introduced into the lower part (using a peristaltic pump) at a rate of 90 ml min^{-1} and 26 ml min^{-1} in runs 1 and 2, respectively. Use of a magnetic

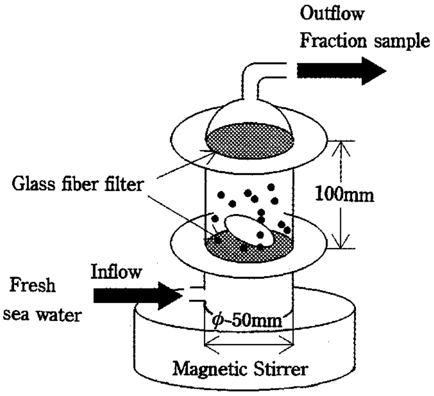

Figure 1 Sediment seawater continuous contactor.

Table 1 Partition coefficients (K_p) for zinc

Wt of sediment soil (g)	Partition coefficient K_p ($l\,kg^{-1}$)	
	Adsorption	Desorption
0.1	8	7100
0.2	2	238
0.3	10	270
0.5	15	98
1.0	29	278
Spiked sediment	17[a]	17[a]

[a] Value obtained from interstitial water analysis of spiked sediment.

stirring bar made the middle part homogeneous. Samples were collected from the top 1-min fractions. Concentrations of TBT, DBT and zinc in the sampled water were measured.

RESULTS AND DISCUSSION

Partition coefficient (K_p)

K_p values for both TBT and DBT were in the range 1500–3000 $l\,kg^{-1}$; moreover, they showed little difference for adsorption and desorption through concentration levels of 10 μg Sn l^{-1} to 1 mg Sn l^{-1} (Fig. 2). However, K_p tended to become larger as the concentration decreased. This corresponds well with the results of Unger *et al.*[11] The equation widely used in adsorption analysis, viz. Eqn [1], was applied:

$$K_p = \frac{q^{i}_{sed}}{C^{eq}_{w}} \cdot \frac{V_w}{m}\left(\frac{C^{i}_{w}}{C^{eq}_{w}} - 1\right) \qquad [1]$$

where q_{sed} = concentration of TBT or DBT in sediment soil; C_w = concentration of TBT or DBT in sample; V_w = volume of the sample; m = weight of suspended soil; and superscripts i and eq denote initial and equilibriated, respectively.

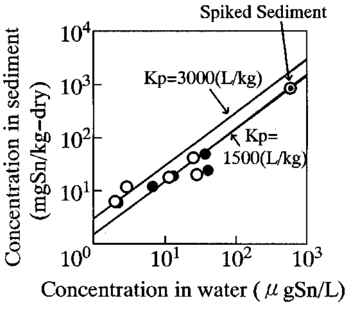

Figure 2 Adsorption and desorption equilibria of TBT. ●, Adsorption; ○, desorption.

However, K_p for zinc varied severely: values are listed in Table 1. For the adsorption study K_p was less than 30 $l\,kg^{-1}$, whereas K_p was in the range 100–7000 $l\,kg^{-1}$ for the desorption study.

This 1000-fold variation of K_p, for zinc is probably due to organic matter held in natural sediment soils, e.g. fulvic acids.[12] A possible mechanism is illustrated in Fig. 3. Some organic matter is known to act as ligands to prevent metallic cations from being adsorbed to negatively charged surfaces. They alter metallic cations to electroneutral or hydrophobic complexes. The water in the batch reactors had been supplied with such organic matter from the sediment in the adsorption study; however, if the water was replaced by seawater (this operation was conducted in the desorption study) it resulted in the washing-off of the organic matter. Evidence of organic-matter-rich status during the adsorption experiment was provided by experimental observations; i.e. the water was coloured yellow or brown in the adsorption study. On the contrary a colorless water phase was observed in the desorption experiment. This indicated an organic-matter-poor status. Some humic acids have been noted as being yellow.[12]

It is interesting that DBT and TBT did not show such behavior. The K_p values of butyltins were stable throughout the adsorption and desorption experiments. Butyltins have been known to behave as both hydrophobic and ionic substances. However the result of the adsorption–desorption study indicates that butyltins are

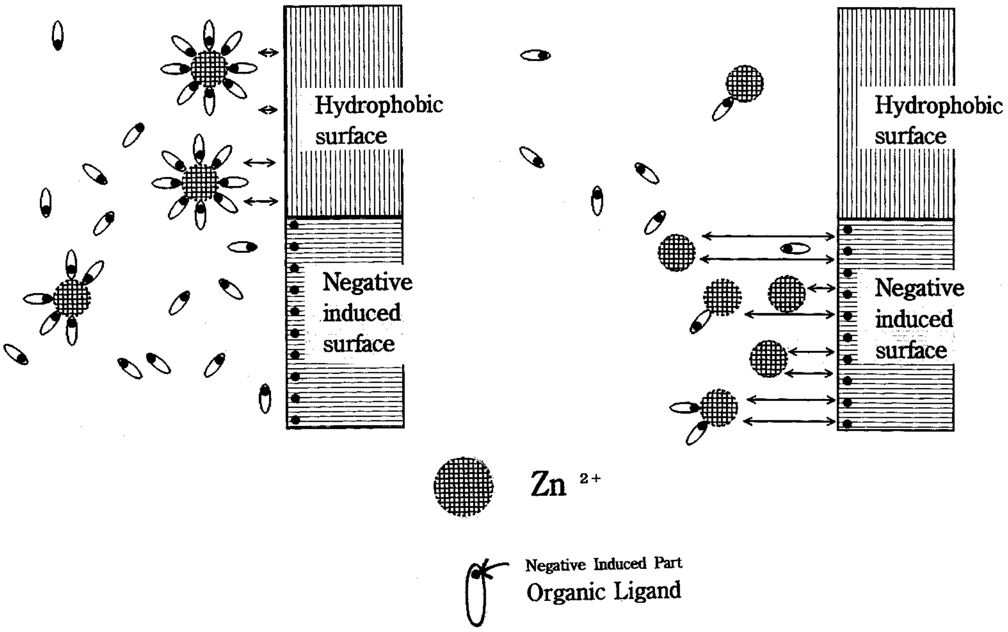

Figure 3 Organic ligands wash-off mechanism.

not affected in the same way by organic ligands as is zinc, although butyltins may be partially ionic.

Continuous contactor experiment

Figure 4 shows the result for TBT in run 1. The concentrations of TBT in the effluents are described with rectangular shapes. The remaining fraction of TBT in the sediment soil was calculated and plotted from the data with dots and a line. The basic equations are presented in Eqns [2] to [4].

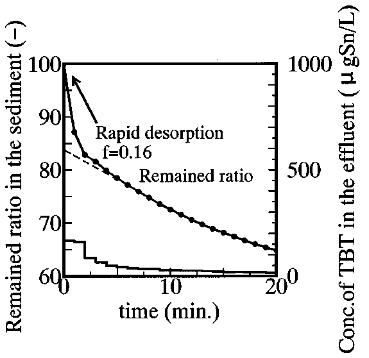

Figure 4 Desorption of TBT from suspended sediment (run 1). Flow rate 90 ml min^{-1}.

Changes in the amounts of chemical in the middle part of the reactor are caused by both movement of effluent (loss) and desorption (generation), i.e.

$$V\frac{dC_w}{dt} = -QC_w + \phi_{des} \qquad [2]$$

where V = volume of middle part (= 100 ml); C_w = concentration of the chemical effluent in the effluent sample (measured value) (μg l^{-1}); t = time (min); Q = flow rate (90 or 26 ml min^{-1}); ϕ_{des} = amount of desorbed chemical in each minute (μg min^{-1}).

Desorption of a chemical from the suspended sediment soil causes a decrease in the concentration of the chemical in the soil, i.e.

$$\frac{dq}{dt} = -\phi_{des}/m \qquad [3]$$

where q = concentration of the chemical in the sediment soil (μg g^{-1}); m = weight of suspended soil in the middle part of the contactor (= 0.29 or 1.47 g dry wt).

The remaining fraction is defined as in Eqn [4] i.e.

$$\text{Remaining fraction} = \frac{q}{q_0} \qquad [4]$$

where q_0 = initial concentration of the chemical in the sediment soil (µg g^{-1}).

The equations shown above are mathematically continuous. Therefore whereas the experimental data were obtained in disperse fashion. Therefore the equations were converted into disperse form in order to allow computer treatment.

A two-site model has been applied to the phenomenon. Desorption has been considered to consist of rapid desorption and first-order kinetic desorption. The rapid desorption ratio f was derived by drawing a tangent along the ‘remaining fraction’ curve towards the y-axis; thus $f=0.16$ was found for TBT.

It must be carefully considered whether or not the chemical in the interstitial water would contribute to apparent rapid desorption. However, this was trivial because 1 g of sediment soil binds as much as 1500-fold (equal to K_p) fold more of the chemical than is bound by 1 ml of interstitial water.

First-order kinetic desorption is described by Eqn [5]:

$$\frac{dq}{dt} = \phi(K_p C_w - q) \quad [5]$$

where ϕ = first-order kinetic desorption rate (min^{-1}); K_p = partition coefficient (l kg^{-1}).

The rate ϕ determined by Eqn [5] for TBT was $(1.4 \pm 0.5) \times 10^{-2}$ min^{-1}.

The concentrations of DBT and zinc in the effluents in run 1 were too low to detect. Hence run 2, which involved more soil and a slower flow rate, was designed to meet this analytical limit.

Figures 5 and 6 show the results for DBT and zinc, respectively, in run 2. However, TBT concentrations in the effluent in run 2 were too high to calculate the parameters. Table 2 presents the parameters f and ϕ for TBT, DBT and zinc.

These data mean that TBT can be released from sediment more easily than DBT and zinc. Considerable amounts of TBT, as much as 16% of that initially adsorbed to sediment soil, may be released when a sediment is vigorously resuspended. Afterward, the resuspended sediment releases 1.4% of TBT per minute, when the concentration of TBT in water around the

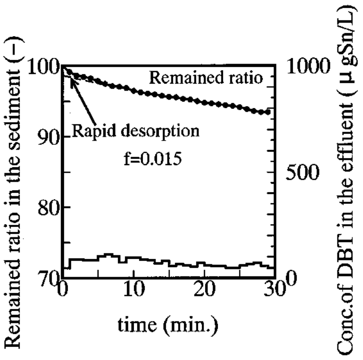

Figure 5 Desorption of DBT from suspended sediment (run 2). Flow rate 26 ml min^{-1}.

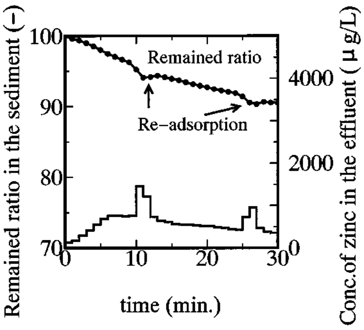

Figure 6 Desorption of zinc from suspended sediment (run 2). Flow rate 26 ml min^{-1}.

Table 2 Desorption kinetic parameters of TBT, DBT and zinc

			TBT		DBT		Zinc	
	Sediment soil (g dry wt)	Flow rate (ml min^{-1})	f^a	ϕ^b (min^{-1})	f	ϕ (min^{-1})	f	ϕ (min^{-1})
Run 1	0.29	90	0.16	$(1.4 \pm 0.5) \times 10^{-2}$		N.C.[c]		N.C.[c]
Run 2	1.47	26		N.C.[d]	0.015	$(2.5 \pm 1.3) \times 10^{-3}$	0	$(2.9 \pm 1.1) \times 10^{-3}$

[a] f, Rapid desorption ratio.
[b] ϕ, First-order kinetic desorption rate.
[c] Not calculated because the concentrations in the effluents were too low to detect.
[d] Not calculated because the concentrations in the effluents were too high.

sediment soil is sufficiently low.

The rapid desorption of DBT is only 1.5% of that initially adsorbed; this is much less than for TBT. First-order kinetric desorption of DBT is slower than that of TBT: only 0.25% of DBT desorbs in each minute.

In Fig. 6, two peaks of concentration for zinc in the effluent appeared; afterwards, the concentration rapidly decreased to the previous level. Destruction of aggregates was observed at these points. This means that first zinc desorbed from the sediment soil rapidly with destruction of the aggregate; and secondly, re-adsorption to the sediment soil took place. The re-adsorption phenomenon was not observed in the DBT experiment, although the experimental run was the same. This issue is discussed later.

Desorption kinetic parameters and adsorption mechanisms

The difference in values of the parameters between the chemical species are considered to be caused by the difference in adsorption mechanisms. The adsorption of zinc cations to sediment soil is believed to be governed by an ionic/electrostatic mechanism. On the other hand, organometallic compounds have both ionic and non-ionic aspects. However, TBT is more hydrophobic than DBT because of the aquatic solubilities of their chlorides[7] and their octanol–water partition coefficients.[8, 13] The adsorption of TBT is considered to be relatively dominated by a non-ionic/physical mechanism.

Physical adsorption has a weaker bonding energy than electrostatic sorption.[6] This means that a physically adsorbed species can be detached more easily than an electrostatically adsorbed one. Relative large values of the rapid desorption ratio f and ϕ for TBT agree well with predictions from this hydrophobic property of TBT. The adsorption of DBT was supposed to be partly physical because some rapid desorption was observed.

Re-adsorption and natural organic ligands

The adsorption–desorption equilibrium study proved that K_p for zinc varied up to several thousand-fold. An organic ligand wash-off mechanism was proposed to explain the variation as described in Fig. 3. It is not doubted that a similar phenomenon occurred in the continuous contactor experiment, too. ‘Wash-off’ of organic ligands was common: a batch wash-off was involved in the adsorption–desorption study, whereas there was a flow-mode wash-off in the continuous contactor experiment. (If ambient sediments become eroded, wash-off can occur.)

The rapid desorption of zinc involved by aggregate destruction meant that the bond affinity was weak inside on aggregate. The zinc cation was surrounded by organic ligands, and so its adsorption to the soil surface was dominated by a physical mechanism.

However, once the aggregate has been destroyed, the ligands were washed off, and afterwards the zinc cation was stripped. Consequently the zinc cation could adsorb to negatively charged soil surfaces electrochemically (re-adsorption). Its affinity had become stronger than the previous physical adsorption.

The observed lack of release of dissolved mercury from dredged sediment in previous Japanese remediation was assumed to be due to a similar mechanism.

Remediation alternatives for TBT-contaminated sediment

Three methods may be proposed for remediation of contaminated sediment: removal, capping and leaving it to stand. Removal involves dredging which are better processes, avoided because considerable TBT may be released from the contaminated sediment to the ambient water. For metallic cations such as zinc, re-adsorption may be expected when a contaminated sediment is dredged. Unfortunately TBT will show little re-adsorption.

Degradation half-lives of TBT are typically a few weeks in water[14] and less than two years in sediments.[15] We have indicated that release of TBT from sediment to overlying water in a non-disturbed condition is comparable with degradation *in situ* for removing TBT.[15] Moreover, as TBT is released to the overlying water, it will be degraded rapidly in the water.

This information should be useful for deciding on a remediation method. It is common, for both capping and leaving to stand, to expect degradion of TBT *in situ*. However, leaving to stand is more rapid than capping because leaving *in situ* utilizes degradion in the water, followed by non-disturbed release. Of course TBT will remain in the water at a low concentration level while TBT is being released from the contaminated sediment. Capping will decrease the concentration level in the water; however it needs a longer period to complete the remediation.

CONCLUSION

Adsorption–desorption equilibria of tributyltin (TBT), dibutyltin (DBT) and zinc were studied. The experimental results were explained by adsorption mechanisms. Consistent partition coefficients (K_p) over a range of organic matter concentrations were observed for TBT and DBT, whose adsorption mechanisms were relatively dominated by non-ionic/physical mechanisms. On the other hand, K_p for zinc varied with the change of organic matter concentration in the batch reactor. Under organic-matter-rich conditions, zinc was assumed to be surrounded by organic ligands and physically adsorbed to soil surfaces, giving rather small K_p values of $\tilde{3}$0 kg. However the zinc cation adsorbed to negatively charged soil surfaces gave large K_p values of ~7000 l kg^{-1} when organic matter was washed off.

A two-site model was presented to describe the desorption kinetics. Desorption consisted of rapid desorption and first-order kinetic desorption. The rapid desorption ratios for TBT, DBT and zinc were 0.16, 0.015 and 0, respectively. First-order kinetic desorption rates were 1.4×10^{-2}, 2.5×10^{-3} and 2.9×10^{-3} min^{-1}. TBT desorbed the most easily. Considering that physical adsorption is looser than electrostatic adsorption, the hydrophobic character of TBT corresponds well with the experimental results.

Re-adsorption of zinc was observed in the experiment. This was also explained by the organic matter wash-off model. This effect did not occur in the behavior of TBT and DBT.

Among the TBT-contaminated sediment remediation alternatives, removal of the sediment involving dredging processes should be avoided. Capping or leaving to stand, prior to degradation *in situ*, are preferred.

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