



## RELEASE AND DEGRADATION HALF LIVES OF TRIBUTYLTIN IN SEDIMENT

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### Abstract

The flux of tributyltin (TBT) from contaminated sediment was estimated using a film transfer model. Mass transfer coefficient was around  $10^{-6}$  (m/sec) and showed diversity according to the turbulence of overlaying water. Release to the overlaying water and degradation in the sediment itself were compared in regard to contributions to removal of TBT from sediment. Releases are greater when sediment has a large porosity, whereas degradation tends to contribute more with rather smaller porosity.

### Introduction

Concentration of tributyltin (TBT) in water has been reported to decrease after the restriction of usage of TBT (1). But its concentration in sediment does not appear to decrease swiftly. TBT in water can be removed by advective flow and degradation. Water advection and degradation which involves photodegradation and biodegradation are expected to bring half life of a few days to a few weeks (2, 3). However no advective flow is expected to sediment, moreover degradation half life is estimated to be more than a few hundred days (4–8). When an argument is made on the half life of TBT in sediment, release of TBT from sediment to the overlaying water must be taken into consideration.

Chemical transfer around sediment has been described with different modelling. Diffusion of chemicals in pore water has been well studied (9, 10). Diffusion coefficient in an actual sediment is affected by water current and bioturbation etc. The nearer the overlaying water, the greater are such effects. Hence diffusion calculation does not seem to be suitable to surface sediment.

On the other hand film model approach fits for an interface (11–13). This model assumes that transfer of chemical is proportional to the difference of dissolved phase concentration between sediment and overlaying water as in the equation (1):

$$(\text{flux}) = \beta (C_p - C_w) \quad (1)$$

(flux): Chemical flux across the interface ( $\text{mol}/(\text{m}^2 \cdot \text{sec})$ )

$\beta$  : Mass transfer coefficient (m/sec)

$C_p$  : Dissolved phase concentration of chemical in sediment ( $\text{mol}/\text{m}^3$ )

$C_w$  : Dissolved phase concentration of chemical in water ( $\text{mol}/\text{m}^3$ )

To connect the dissolved phase concentration to the corresponding sorbed phase concentration, linear and reversible sorption/desorption is assumed using partition coefficient  $K_p$ :

$$q = K_p C_w \quad (2)$$

$q$  : Sorbed phase concentration of chemical in sediment (mol/kg)

$K_p$  : Partition coefficient ( $\text{m}^3/\text{kg}$ )

$\beta$  and  $K_p$  allow an estimation of chemical flux with this model. We have tried to obtain these value for TBT and dibutyltin (DBT) by laboratory experiments (8).  $\beta$  was affected by turbulence of overlaying water.  $K_p$  was found to be consistent with the results from Unger et al (14). Formerly we have established a compartment model for TBT in an imaginary aquatic environment at steady state (8), where a typical value of  $\beta$  was only applied. However, sufficient practical applications of this model and parameter values have not yet available. The most interesting theme is competition of degradation and release for removal of TBT.

In this paper, first, the experimental results are presented. Secondly, the discussion about the limitation and implicit assumption of the model is done. Lastly, an argument was made on removal of TBT in sediment from the point of view of competition of degradation and release. Half lives of TBT by each mechanism were compared under the assumption of homogeneous sediment of various depths.

## Experiments and Results

### Experiments

The experimental device is shown in Figure 1. Sediment (20(g-wet): ca.10(g-dry)) on a plate (area of  $64(\text{cm}^2)$  and depth of 5(mm)) was inserted into an one litre beaker filled with sea water, various degrees of water currents were built using different sizes of stirring bar. Concentrations of DBT and TBT in the water were monitored by hydride generation/atomic absorption spectrometry (15). Spiked sediment was used for release (sediment to water) study. Spike protocol was as follows: TBT and DBT dissolved in ethanol was poured to the slurry sediment which was kept vigorously stirred with a drill mixer, afterward it was air dried for a few months. The concentration of DBT and TBT were measured to be 656 (mgSn/kg-dry) and 848 (mgSn/kg-dry), respectively. For penetration (water to sediment) study,

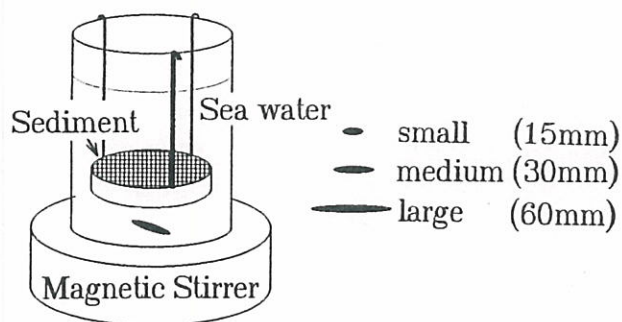


Figure 1 Experimental Device: a Sediment Bed inserted into Sea Water

unspiked sediment was used and DBT and TBT were spiked to the water. Sorption/desorption were determined reversibly with a partition coefficient of  $1.5 \text{ (m}^3/\text{kg)}$  at 10 to 1000 ( $\mu \text{ gSn/L}$ ) level(8).

### Results

Figure 2 represents results of the release study. The concentration of DBT and TBT in water appeared to increase fast with a large size stirring bar and slow with a small one. In the penetration study, the larger the size stirring bar, the faster the concentration in the water decreased.

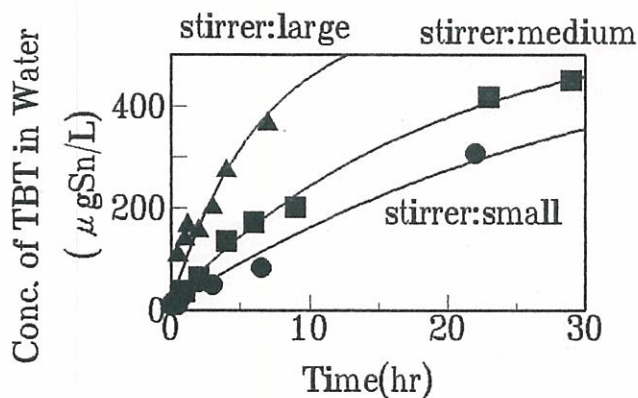


Figure 2 Concentration of TBT in the Sea Water (Release Study)

### Calculation

$\beta$  was calculated with the regression equation as follows: concentration of a chemical in the water is due to the flux across the water sediment interface which is represented by film transfer model.

$$V_w \frac{dC_w}{dt} = A(\text{flux}) = A \beta (C_p - C_w) \quad (3)$$

$V_w$ : Volume of sea water ( $=1 \times 10^{-3} \text{ (m}^3\text{)}$ )

$A$ : Surface area of sediment ( $=6.4 \times 10^{-3} \text{ (m}^2\text{)}$ )

$t$ : Time (sec)

Equation (3) was integrated under the initial condition of  $C_w = C_{\text{initial}}$  and the assumption that  $C_p$  kept constant ( $= q/K_p$ ) throughout the course of the experiment. The initial concentration increase ( $C_{\text{initial}}$ ) was due to the slight erosion which was involved in the insertion of the sediment bed plate into the sea water. The assumption that  $C_p$  kept constant was reasonable, because the 10 g-dry sediment carried 15 times more TBT/DBT than 1 litre sea water even if they were in equilibrium, therefore, release/penetration caused little change to the concentration in the sediment. Integrated form of the equation (4) is as below:

$$C_w = C_{\text{initial}} + (C_p - C_{\text{initial}})(1 - \exp(-\frac{A}{V_w}\beta t)) \quad (4)$$

$C_{\text{initial}}$ : Concentration of the chemical in the water at  $t = 0$  (measured value)

Experimental data were regressed to the equation (4). As the value of  $A$  and  $V_w$  were known,  $\beta$  was obtained from each experimental run. The value ranged around  $10^{-6}$  (m/sec). Previously reported value were compared at the right hand. These value were derived from different experiments or calculations: Boudreau *et al.*(11) estimated using chemical engineering calculation, Raaphorst *et al.*(12) obtained them from measurement of phosphate and calcium flux from a sediment core and Watanabe *et al.*(13) performed experiments using heavy metals, polymethylsiloxane and PCBs.

### Discussion

#### Mass transfer coefficient ( $\beta$ )

$\beta$  had been idealistically thought to be affected by water current and the condition of sediment surface and independent from chemical species and direction of transfer. But the experimental results showed contradictions against the hypothesis.  $\beta$  for TBT and DBT in the same experimental run showed different values, in addition, there was difference of  $\beta$  values for both directions.

These phenomena are probably due to sorption/desorption kinetics of which we did not consider in the equation (1) and (2). When a chemical in pore water is released to the overlaying water, desorption from sediment solid to pore water must take place simultaneously. This argument can be translated to resistance terms as expressed below.

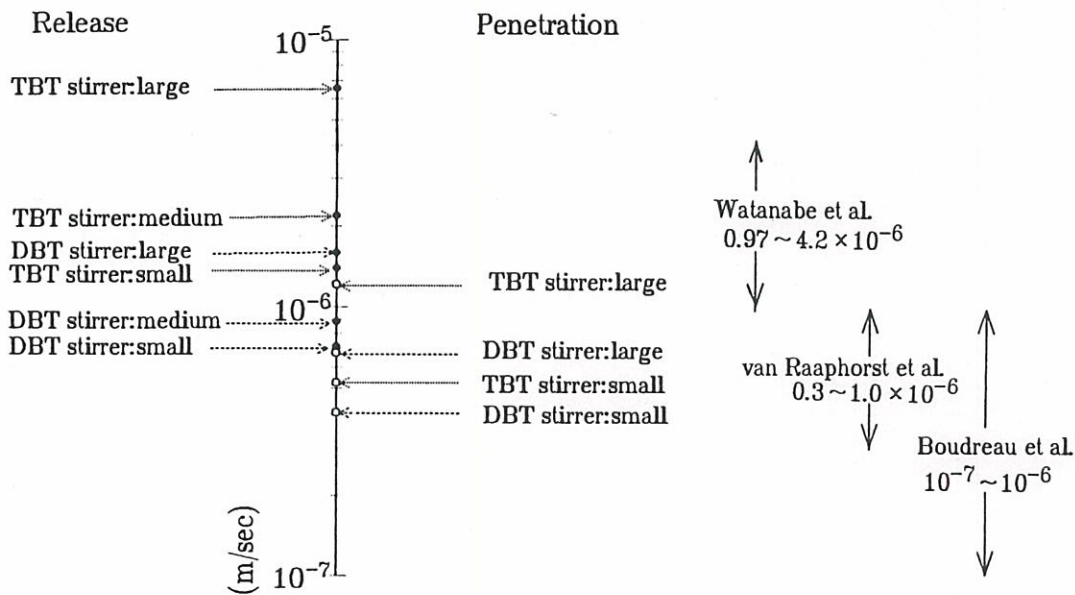


Figure 3 Mass Transfer Coefficient at Water-Sediment Interface:

$$\text{overall resistance} = \text{transport resistance} + \text{sorption/desorption resistance} \quad (5)$$

From this point of view slow sorption/desorption makes overall resistance higher, which gives smaller  $\beta$  value. Desorption kinetics of DBT and TBT was studied using continuous water - suspended solid contactor(8). Spontaneous desorption ratio was determined as 0.16 and 0.015 (-) while first order kinetic desorption rate were  $2.3 \times 10^{-4}$  and  $0.42 \times 10^{-4}$  (1/sec) for TBT and DBT, respectively. These mean that DBT is less desorptive than TBT. This was consistent with rather smaller  $\beta$  value of DBT than that of TBT.

$\beta$  for penetration must have relationship with adsorption kinetics, however adsorption kinetic parameters have not been available yet. Nevertheless, it seemed that TBT showed more rapid adsorption than DBT because TBT had relatively larger value of  $\beta$ .

#### *Applicability of this model to other chemicals*

Common  $K_p$  in sediment and overlying water is needed, moreover sorption/desorption must be reversible in the film transfer model. TBT showed such characters with the sediment soil used in this experiment. However, common  $K_p$  and reversible sorption/desorption are not true of many chemicals. Organic ligands may exist in pore water that will stabilize dissolved chemicals and prevent them from adsorption to solid. This brings different  $K_p$  between pore water and overlying water(16,17). We also experienced such phenomenon when we tried similar experiment with zinc sulfate, from which  $K_p$  was supposed to be 10 to 50 (L/kg) in pore water whereas ca. 1000 (L/kg) was obtained near the surface of the sediment.

*Half life of TBT in Sediment*

Removal of TBT from contaminated sediment is carried out by both degradation and release. It is interesting to compare their contributions. First order kinetics are applied not to only degradation but also release, so that the comparison by half lives are made available. It is assumed that the sediment is homogeneous to the depth of  $d$  (m), and chemical release is governed by the film transfer model. Equation (6) represents decrease of chemical in sediment induced by release and degradation.

$$V_{\text{sed}} \frac{dC_{\text{sed}}}{dt} = -A \beta (C_p - C_w) - r_{\text{deg}} V_{\text{sed}} C_{\text{sed}} \quad (6)$$

$V_{\text{sed}}$  : volume of sediment (homogeneous zone) ( $\text{m}^3$ )

$C_{\text{sed}}$  : overall concentration of chemical in sediment ( $\text{mol}/\text{m}^3$ )

$A$  : contacting area of overlaying water and sediment ( $\text{m}^2$ )

$r_{\text{deg}}$  : degradation rate (1/sec)

Concentration in pore water ( $C_p$ ) is converted into overall concentration in the sediment ( $C_{\text{sed}}$ ) using porosity ( $\epsilon$ ), solid density ( $\rho$ ) and  $K_p$  as in equation (7).

$$C_{\text{sed}} = \{ \epsilon + (1 - \epsilon) \rho K_p \} C_p \quad (7)$$

Assuming  $C_w$  to be zero, this hypothesis means restriction or ban of TBT, the following equation is derived:

$$\frac{dC_{\text{sed}}}{dt} = - \frac{\beta}{d} \cdot \frac{1}{\epsilon + (1 - \epsilon) \rho K_p} C_{\text{sed}} - r_{\text{deg}} C_{\text{sed}} \quad (8)$$

$d$  : depth of sediment ( $=V_{\text{sed}}/A$ ) (m)

Release and degradation half lives are calculated by equation (9) and (10), respectively.

$$T_{1/2, \text{release}} = 0.693 \frac{d}{\beta} \{ \epsilon + (1 - \epsilon) \rho K_p \} \quad (9)$$

$$T_{1/2, \text{degradation}} = \frac{0.693}{r_{\text{deg}}} \quad (10)$$

In calculation of equation (9), the value of parameters for sediment character were assumed in two cases:  $\epsilon = 0.85$  (-) and  $0.95$  (-) which gave water content of 69 (%) and 88 (%) under the common assumption of  $\rho = 2500$  ( $\text{kg}/\text{m}^3$ ). Value of  $3$  ( $\text{m}^3/\text{kg}$ ) (equal to  $3000$  ( $\text{L}/\text{kg}$ )) were employed to  $K_p$  instead of  $1.5$  ( $\text{m}^3/\text{kg}$ ) because ambient level of TBT is lower than  $\mu$  g/L where  $K_p$  were observed to increase to 3(8). The depth of homogeneous zone in sediment was assumed to be 10, 20, 30 and 50 (mm).

Figure 4 shows the estimated release half life of TBT. Two figures represent the half lives under different conditions of  $\epsilon$  : (a) is based on  $\epsilon = 0.95$  and (b) on  $\epsilon = 0.85$ . Half life under any depth and  $\beta$  can be derived from each graph.

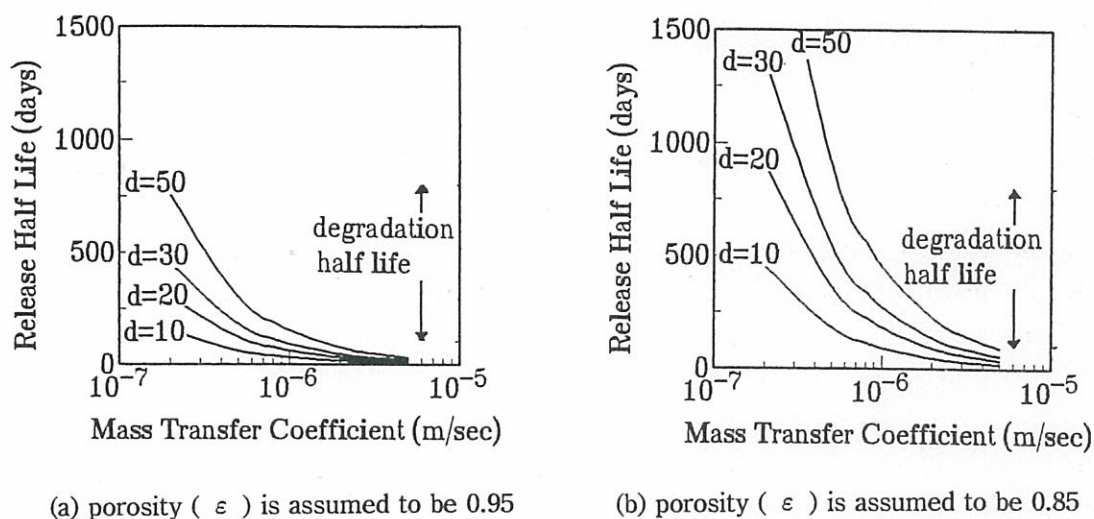


Figure 4 Half Life of TBT in Sediment

Degradation of TBT in sediment have been studied with various half lives. Maguire et al.(4) showed 112 days in a water-sediment mixture, Stang et al.(5) reported 164 days in aerobic sediment. These value are thought to be representative for semi-aerobic condition. de Moira(7) found 1.85 years from the core sample in situ. Our experimental result gave a half life of 460 days from measurements of TBT in sediment packed in test tubes(8). The longest half life was reviewed to be 815 days by U.S.EPA(6). It can be stated that degradation half life is in the range of 100 to 800 days, in addition, rather aerobic conditions bring half life shorter.

The shortest half life of a few days demonstrated by Stang et al.(18) was thought to be applicable to only dissolved TBT instead of paint chips or sorbed phase TBT, thus this information was excluded from the estimation of degradation half life in sediment.

With large porosity( $\epsilon = 0.95$ ; Figure 4(a)), release half life is the same with or shorter than degradation half life for any homogeneous zone depths. While release half life tends to be longer than degradation half life with  $\epsilon$  of 0.85 (Figure 4 (b)).

Large porosity means that sediment is slurry like. Such a sediment shows so active release that release contributes to removal of TBT from sediment as same as or more than degradation in sediment. On the other hand compacted sediment ( $\epsilon = 0.85$ ) release little, hence degradation contributes the same as or more than release to the overlaying water.

### Conclusion

A film transfer model was used to estimate the flux of butyltins across an water-sediment interface. Mass transfer coefficient was in the order of  $10^{-7} \sim 10^{-6}$  (m/sec) and varied according to the water current. The coefficient was thought to be affected by sorption/desorption resistance not only by transport resistance. Constant partition coefficient across the interface is indispensable for the simple film transfer model.

Removal of tributyltin from contaminated sediment is caused by both degradation in sediment and release to the overlying water. Comparison was made by estimating those half lives. Degradation half life is estimated to be 100 ~ 800 days, which shows variation with aerobic/anaerobic condition. Release half life depends not only on water current but also porosity of the sediment. With large porosity of the sediment, release half life is somewhat shorter than degradation half life. On the other hand release half life tends to be longer than degradation half life with small porosity of the sediment.

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