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Transport Dynamics of Tributyltin Between the Surface Microlayer and Subsurface Water

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The transport dynamics of tributyltin (TBT) between the surface microlayer and subsurface water were studied in experimental systems which simulated different surface sea states. A dynamic model was derived from a diffusion equation to describe the dynamics of the TBT transport process. With this dynamic model diffusion coefficients were determined, and the effects of surface sea states and temperature on the TBT transport process between the surface microlayer and subsurface water were also studied. Turbulence, breaking waves and elevated temperature can accelerate this transport. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Tributyltin (TBT) compounds have been widely used as industrial biocides, e.g. as wood preservatives and antifouling paints. Tributyltin and its degradation products, dibutyltin (DBT) and monobutyltin (MBT), have been detected in many aquatic environments around the world.[1] Due to TBT's high toxicity to aquatic organisms, there has been a great deal of interest in the environmental chemistry and toxicology of this compound. Higher concentrations of tributyltin have been observed in the surface microlayer of natural waters relative to subsurface waters.[2–5]

The surface microlayer at the air–water interface has special physical, chemical and biological characteristics different from the subsurface water.[6] Its thickness usually ranges from 60 to 200 μm, depending on the type of collector used.[7–9] The surface microlayer, as a special interface in the environment, influences the geochemical cycling of pollutants.[8] It is of great environmental significance to study the occurrence, transport and fate of pollutants at the air–water interface. There has been much work to demonstrate that contaminants and microorganisms are accumulated in the surface microlayer,[10–12] but little has been published on the transport and fate of pollutants in the surface microlayer.

The aim of the present paper was to investigate the transport dynamics of TBT between the surface microlayer and subsurface water under controlled conditions. A dynamic model was established to study quantitatively the effects of surface sea states and temperature on the transport of TBT between the surface microlayer and subsurface water.

EXPERIMENTAL

Chemicals

Tributyltin chloride (TBT) was obtained from Aldrich Chemical Company Inc. (Milwaukee, WI, USA). A standard TBT solution (10^3 μg Sn ml^{-1}) was prepared by dissolving appropriate amounts of tributyltin chloride in ethanol.

Experimental systems and simulated environmental conditions

To simulate different surface sea states, three experimental systems were designed (see Fig. 1).

Each tank contained 40 l of seawater. 'State a' simulated the surface sea state without turbulence. i.e. in ideal quiescent conditions. 'State b' simulated the surface sea state without wind, and a stainless steel stirrer was used to create turbulence in the water column. To simulate the effect of breaking waves caused by wind, above the water surface the stirring bar in 'state c' was separated at

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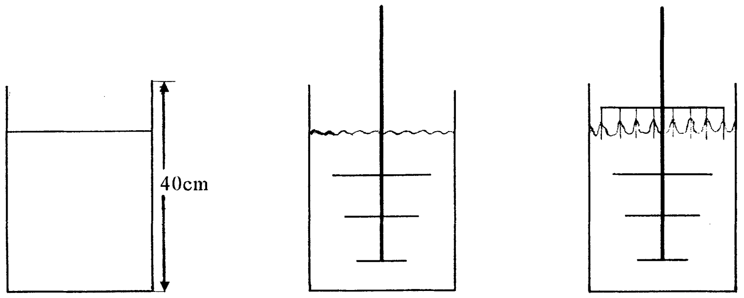

State a: Ideal quiescence simulation

State b: Quiescent simulation

State c: Breaking waves simulation

Figure 1 Experimental systems simulating different surface sea states.

equal intervals by eight stainless steel rods (2 mm o.d.) which were immersed in the water to a depth of about 2 cm through the surface microlayer. Thus the rotation of the stirrer resulted in a breaking of the water surface. In both states b and c, the rotation speed could be adjusted so as to control the intensity of the turbulence and the breaking waves. Under different simulated conditions (see Table 1), seven experiments were conducted in order to study the effects of surface sea states and temperature on the transport dynamics of TBT between the surface microlayer and subsurface water.

Procedure

At the beginning of each experiment, after the state, temperature and speed of rotation had been set up, 4.0 ml of 10^3 μg Sn ml^{-1} TBT solution in ethanol was rapidly and uniformly sprayed onto the surface microlayer. Then the surface microlayer and subsurface water samples were collected at various times. The subsurface water samples were collected through a siphon half-way up the water column. The surface microlayer was sampled at a thickness of about 50–80 μm with a glass plate sampler.[8] To reduce the error caused by the decline in the mass of TBT, each sample should be small enough in volume, if possible, to reach the detection limit. The sample volumes of the surface microlayer and subsurface water were designated (see Table 2).

Water samples previously acidified to pH 1 were extracted with benzene. The extracts were then reacted with 1.0 ml of *n*-pentylmagnesium bromide solution (1.0 mol l^{-1}). The excess of *n*-pentylmagnesium bromide was destroyed by shaking with 5 ml of 0.5 mol l^{-1} H_2SO_4. The volume of the extracts was reduced to 0.5 ml with a stream of nitrogen gas at room temperature. A 5 μl aliquot of the sample was injected into the gas chromatography–atomic absorption spectrometry (GC AA) system for analysis. The GC AA system was described in a previous publication.[13] A 2 m glass column with 3% OV-225 on Chromosorb was used. The temperatures of the injection port, the column

Table 1 Experimental conditions

Expt no.	Simulation		Temperature	Speed of rotation
n	State	Conditions	(°C)	(rpm)
1	a	Ideal quiescence	15 ± 1	—
2	b	Quiescence	15 ± 1	40 ± 5
3	c	Breaking waves	15 ± 1	40 ± 5
4	b	Quiescence	15 ± 1	70 ± 5
5	c	Breaking waves	15 ± 1	70 ± 5
6	a	Ideal quiescence	20 ± 1	—
7	a	Ideal quiescence	25 ± 1	—

Table 2 The sample volumes of the surface microlayer and subsurface water

Time	Sample volume (ml)	
(min)	Surface microlayer	Subsurface water
5	10	100
10	10	100
30	20	100
60	20	100
120	50	100
180	50	100
240	50	100
300	50	100

and the transfer line were 250, 160 and 300 °C, respectively. The AA furnace gases were hydrogen (118 ml min^{-1}) and air (56 ml min^{-1}) and the temperature of the quartz furnace was 850 °C. The detection limit for TBT was 0.15 ng and the recovery for TBT in seawater reached over 95%.

DESCRIPTION OF THE MODEL

The volatilization of TBT from distilled water is negligible over a period of at least two months.[14] It has previously been demonstrated that there was negligible adsorption of TBT on the wall of the tank and the stirrer over the experimental period of 4 h. Thus there was only the TBT transport process between the surface microlayer and subsurface water in the experimental systems. For the purposes of modelling, it is assumed that the amount (M) of TBT applied to the surface microlayer was instantaneously mixed uniformly throughout the surface microlayer. Diffusion of TBT from the surface microlayer to the subsurface water could be considered as approximately the diffusion of a plane source in one dimension.[15] That is to say, the total amount of substance (M) diffuses in a cylinder which has infinite length and unit cross-section. The diffusion equation can be expressed as[15]

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad [1]$$

by applying dimensional analysis to Eqn [1], Eqn [2] is obtained as a solution:

$$C = \frac{MB}{A\sqrt{Dt}}\exp\left(\frac{-x^2}{4Dt}\right) \qquad [2]$$

where C = concentration (μg cm^{-3});
x = diffusional distance (cm);
t = diffusional time (s);
D = diffusion coefficient ($\text{cm}^2\ \text{s}^{-1}$);
A = area of the surface microlayer (cm^2);
B = an arbitrary constant.

The total amount of diffusing substance remains constant and equals the amount originally deposited on the surface water plane ($x = 0$). Thus

$$M = \int_0^{+\infty} AC\,\mathrm{d}x \qquad [3]$$

By substituting Eqn [2] into Eqn [3], the constant B is obtained:

$$B = \sqrt{\pi}$$

$$C = \frac{M}{A\sqrt{\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right) \qquad [4]$$

and hence Eqn [4] is the solution of Eqn [1] which describes diffusion of an amount of substance M deposited at $t = 0$ on the surface microlayer (i.e. the plane $x = 0$).

When $x = 0$,

$$C = \frac{M}{A\sqrt{\pi Dt}} \qquad [5]$$

Equation [5] is the model which describes changes in the concentration of TBT with time in the surface microlayer.

There are three sources of error in this model: (1) the tank used in the experiment has a certain height, so the boundary condition set up in this experiment was not $(0, +\infty)$; (2) the mass of the substance (M) did not remain constant when water was being continuously sampled for analysis; and (3) the surface microlayer with a certain thickness (50–80 μm) was not the plane $x = 0$. The errors can be reduced by increasing the height of the tank used in the experiment, by decreasing the amount of each sample and by sampling only a small thickness of the surface microlayer.

RESULTS AND DISCUSSION

TBT concentrations in the surface microlayers and subsurface water under various experimental conditions are shown in Table 3.

TBT concentrations in the surface microlayers were gradually reduced, and at the same time TBT concentrations in the subsurface water gradually increased, until equilibrium was reached after about 4 h.

The diffusion coefficients (D) can be calculated on the basis of regression analysis, by plotting TBT concentration in the surface microlayer against $1/\sqrt{t}$ (see Eqn [5]). The regression model is $Y = a + bX$. The slope (b) is obtained from the regression equation, and

$$D = \frac{M^2}{\pi A^2 b^2} \qquad [6]$$

Results of regression analyses are listed in Table 4. The regression coefficients (0.946–0.988) clearly demonstrated that this model can describe the experimental data very well. However, the y intercepts are not at the origin (i.e. $a \neq 0$), indicating

Table 3 Concentrations of TBT (μg Sn ml^{-1}) in the surface microlayer and subsurface water at various times.

Time (min)	Experiment no. *n*											
	1		2		3		4		5		6	7
	SML[a]	SSW[b]	SML	SSW	SML	SSW	SML	SSW	SML	SSW	SML	SML
5	4.001	0.004	1.185	0.059	0.912	0.061	0.916	0.020	0.875	0.030	2.104	1.214
10	1.529	—	1.081	—	0.672	—	0.613	—	0.348	—	0.777	0.973
30	1.268	0.006	0.728	0.048	0.424	0.069	0.147	0.019	0.123	0.034	0.372	0.378
60	0.839	0.006	0.283	0.077	0.292	0.063	0.111	0.032	0.093	0.061	0.168	0.115
120	0.307	0.007	0.080	0.066	0.149	0.055	0.076	0.048	0.041	0.050	0.035	0.036
180	0.172	0.028	0.079	0.082	0.072	0.049	0.090	0.066	0.068	0.065	0.038	0.043
240	0.117	0.056	0.087	0.081	0.057	0.045	0.074	0.065	0.078	0.063	0.037	0.032
300	—	—	0.065	0.076	—	—	—	—	—	—	—	—

[a] SML, surface microlayer. [b] SSW, subsurface water.

Table 4 Regression and diffusion coefficients

Expt no. *n*	*a* (μg ml^{-1})	*b* ($\text{min}^{\frac{1}{2}}$ μg ml^{-1})	Regression coefficient *r*	Diffusion coefficient D_n (cm^2 s^{-1})
1	−0.509	9.034	0.957	3.90×10^{-4}
2	−0.106	3.252	0.960	3.01×10^{-3}
3	−0.047	2.226	0.990	6.42×10^{-3}
4	−0.137	2.288	0.979	6.08×10^{-3}
5	−0.137	1.987	0.946	8.14×10^{-3}
6	−0.433	5.026	0.959	1.26×10^{-3}
7	−0.234	3.391	0.988	2.77×10^{-3}

that there are errors in this model as pointed out in the section ‘Description of the model’.

Influence of turbulence in the subsurface water on the TBT transport process

The effects of turbulence in the subsurface water on TBT transport between the surface microlayer and subsurface water were investigated through experiments 1, 2 and 4, which were conducted under conditions of similar temperature and no waves. There was only molecular diffusion in experiment 1, simulating ideal quiescent conditions. As the rotation of the stirrer caused turbulence in the subsurface water, there was turbulent diffusion as well as molecular diffusion in experiments 2 and 4, and the turbulence in experiment 4 was more intense than that in experiment 2. From Table 4, it is clear that $D_4 > D_2 > D_1$. D_4 and D_2 were greater than D_1 by about one order of magnitude, which demonstrated that the rate of the TBT transport process between the surface microlayer and subsurface water rises with increasing turbulence, and turbulent diffusion is significantly faster than molecular diffusion. When turbulent diffusion exists, molecular diffusion becomes less important.

Influence of breaking waves on the TBT transport process

Comparing experiment 2 with experiment 3, and experiment 4 with experiment 5 under similar conditions of temperature and turbulence, it can be seen that $D_3 > D_2$ and $D_5 > D_4$ (see Table 4). The above results indicate that the rates of the TBT transport process between the surface microlayer and subsurface water under simulated breaking waves are faster than without breaking waves, i.e. breaking waves have a promoting effect on the transport process of TBT. Breaking waves not only intensify the turbulence of the surface water, but also cause vertical migration of the surface water which can accelerate the TBT transport process. Therefore breaking waves have an additional accelerative effect on the TBT transport process between the surface microlayer and subsurface water.

Influence of temperature on the TBT transport process

Experiments 1, 6 and 7, simulating ideal quiescent conditions, were conducted at different temperatures. There was only molecular diffusion in these

Table 5 Concentration of TBT and its concentration factors in the surface microlayer

Expt no.	TBT concentration ($\mu g\ l^{-1}$)		
n	In surface microlayer	In subsurface water	Concentration factor
1	117	56	2.1
2	82	77	1.1
3	65	47	1.4
4	80	60	1.3
5	73	64	1.1

experiments. The experimental results (see Table 4) show that diffusion coefficients increase with temperature.

Enrichment of TBT in the surface microlayer

From the changes in TBT concentration with time (Table 3), we can estimate the equilibrium concentration of TBT in the surface microlayer and subsurface water. The ratios of TBT concentrations in the surface microlayer to those in the subsurface water (see Table 5), illustrate TBT enrichment, on which, turbulence and breaking waves have no significant effect, in the surface microlayer.

CONCLUSION

The dynamic model (Eqn [5]) that has been established can describe the changes in TBT concentrations with time in the surface microlayer when TBT is transported from the surface microlayer to the subsurface water. Diffusion coefficients, which depict the rate of the TBT transport process between the surface microlayer and subsurface water, can be determined via this model. The influences of turbulence, breaking waves and temperature on the TBT transport process between the surface microlayer and subsurface water have been studied under controlled conditions. Turbulence, breaking waves and increasing temperature can accelerate the rate of the TBT transport process. Among these, breaking waves have the largest effect on the rate of the transport process. Enrichment of TBT in the surface microlayer has been demonstrated by the experiments.

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