

EXAMINATION FOR DEGRADATION PATHS OF BUTYLTIN COMPOUNDS IN NATURAL WATERS

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ABSTRACT

Examination of individual degradation paths (biodegradation and photolysis) of butyltin compounds (especially tributyltin : TBT) in natural waters was performed. Biodegradation of TBT and dibutyltin (DBT) in an unfiltered sea water in summer is rather fast; their half life is about a week. But pretreatment with glass fiber filter makes the half life of TBT much longer (about 80 days). Photolysis of TBT in sea water by sun light is rapid (half life is about 0.5 days), and faster than in distilled water or in fresh water. Degradation rates of each process for TBT are calculated in various conditions of sea water, and contribution rates are compared. Biodegradation will be the main degradation process in an "SS-rich" area such as a marina, but photolysis will exceed that in a "clean" area. Over all half lives of TBT in sea water vary from 6 days to 127 days considering seasons and presence of SS.

KEYWORDS

Biocide; Trace organics; Marine pollution; Tributyltin; TBT; Biodegradation; Photolysis; Evaporation; Environmental behavior; Fate.

INTRODUCTION

Pollution in coastal areas caused by butyltin compounds from hull paint or anti-fouling paint is growing to be a world wide problem. Imposex of neogastropods which is reportedly caused by tributyltin (TBT), is observed in many areas (Bryan *et al.*, 1989; Alvarez and Ellis, 1990; Ellis and Patisina, 1990). TBT concentration in sea water is around 10 ngSn/L in areas used by shipping (Unger *et al.*, 1988) and as high as 100 ngSn/L is reported in some cases such as marinas (Maguire, 1987). Dibutyltin (DBT) and monobutyltin (MBT) which are thought to be degradation products of TBT are also detected in the same areas.

Researching the environmental behavior of biocide released to the environment provides a means to evaluate analysis data from the actual environment. Estimating the fate and paths of the released chemical, a process known as fate prediction, can be completed only by integrating the basic processes. The basic processes involved in fate prediction are transfer, accumulation and degradation. It is generally agreed that TBT is of low volatility, is highly absorptive and degrades rather easily in the marine environment (Maguire, 1986, 1987; Clark *et al.*, 1988; Müller *et al.*, 1989; Cardwell and Meador, 1989).

Degradation has been considered of such importance that many researchers have conducted experiments concerning biodegradation and photolysis (Maguire *et al.*, 1983, 1985; Seligman *et al.*, 1986, 1988; Takahashi *et al.*, 1987; Thain *et al.*, 1987; Hattori *et al.*, 1988; Francois *et al.*, 1989; Lee *et al.*, 1989). But results varied in a wide range. Half life of biodegradation observed ranges from 3 days (Lee *et al.*, 1989) up to 300 days (Maguire *et al.*, 1985). And it remains difficult to develop quantitative discussion of the photolysis rate in water by sun light, since Maguire *et al.* (1983) reported values ranging from less than 1 day to more than 89 days. Moreover, quantitative examination of the contribution rate of both processes has not been examined comprehensively. Variation of the rate of each process in different conditions also has to be investigated. The aim of this report is 1) to observe the rate variation of the biodegradation process according to acclimation, season and filtering pretreatment, 2) to examine the possibility of photolysis by sunlight, and 3) to estimate the overall half life of TBT in water.

METHOD

Biodegradation Experiment. Highly contaminated marina sea water (TBT concentration in the order of 100 ngSn/L is usual) and slightly contaminated well flushed coastal sea water was collected from Toba bay, Mie prefecture, Japan. Pond water which has never exposed to butyltin contamination was collected. To investigate the contribution of suspended solid (SS), filtered water with GF/B (Whatman; 1.0 μm) or membrane (Millipore; 0.22 μm) filter and unfiltered water (for summer season coarsely filtered water by qualitative filter No.2 (Toyo; 5~10 μm) was also defined as "unfiltered", since some silt particles were observed) were prepared. TBT (DBT in some experiments) in ethanol or diluted nitric acid were added to 1 ~ 3 L of these watersamples to obtain initial concentrations of 1.5 ~ 2 $\mu\text{gSn/L}$ (up to 4 $\mu\text{gSn/L}$ in a few experiments). It resulted in giving the water considerable organic matter to add TBT in ethanol solution (10 μL of ethanol equivalent to 18.5 mg of oxygen demand). Polycarbonate or pyrex bottles containing these samples were set by an east-facing laboratory window (Figure 1). All bottles were stirred magnetically to maintain aerobic conditions, and the tops of the bottles were loosely covered with aluminium foil. 2 L of autoclaved (120 $^{\circ}\text{C}$, 2 atm., 1 hr) sea water was used as control. Concentrations of TBT and DBT were analysed periodically. Analytical samples of 50 mL with 1 ml of 1N HNO_3 added were stored in a refrigerator to await analysis, when immediate analysis was not practical.

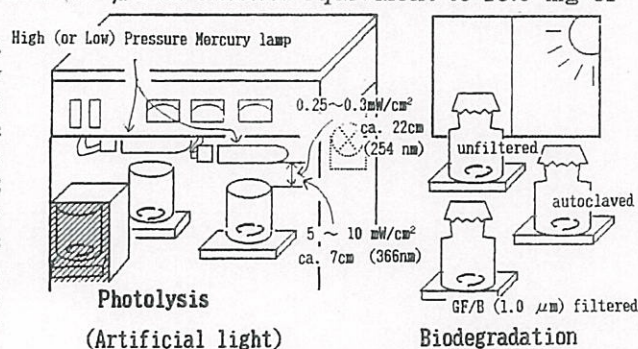


Fig. 1. Degradation experiments

Photolysis Experiment. Sea water and fresh water collected in winter as described above, distilled water and sodium chloride solution (40 gNaCl/L) were used. Natural water samples were filtered with GF/B or membrane filter to make biodegradation negligible. TBT in ethanol was added to 500 mL of the matrix water with 50 μL of micro pipet to obtain the initial concentration of 10 $\mu\text{gSn/L}$. 500mL beakers were set under an artificial light source and magnetically stirred (Figure 1). Two kinds of artificial light source were used: 10 W low pressure mercury lamp with main wave length of 254 nm and 100 W high pressure mercury lamp equipped with pyrex glass filter with main wave length of 366 nm. Intensity of irradiation was measured by UVR-1 intensity meter (Topcon), and adjusted to 0.25 ~ 0.3 mW/cm^2 for low pressure mercury lamp and 5 ~ 10 mW/cm^2 for high pressure mercury lamp. Beakers were cooled by water jacket so as not to increase the water temperature in the experiment with high pressure mercury lamp. Water temperature was 20 ~ 25 $^{\circ}\text{C}$ in all experiments. To avoid the effect of ozone induced by the lamp, all experiments were conducted in a closed box well ventilated. Nonirradiated sample was set in the same box for the control experiment.

For experiments involving sun light photolysis beakers were set on the roof and not

stirred. They were irradiated during only fine weather, and stored in refrigerator during cloudy or rainy days and at night; concentration decrease was not observed in this period. One beaker wrapped with aluminium foil was treated in the same way as other beakers as control.

Amount of water was measured following the last experiments to check the loss of water by evaporation.

Analysis. Hydride generation purge/trap atomic absorption spectrometry (HGAA) was used for determination of the DBT and TBT content in water samples (Donard *et al.*, 1986; Stallard *et al.*, 1989). In this method hydride of tin compounds generated by injection of NaBH_4 solution are purged from water and transferred to a trap/column immersed in a liquid nitrogen bath. As the trap/column is heated slowly, each butyltin hydride is flushed out of the trap/column chromatographically and detected by atomic absorption spectrometry using an air - H_2 flame in a heated quartz tube (600 °C). Triethyltin bromide is used as internal standard. W-shaped silanized glass tube containing 1g of 3% OV-1 on Chromosorb W AW-DMCS 40/60 mesh in the later U-shaped part was used as the trap/column. Deterioration of the packing phase caused by water vapor and salt fumes is well suppressed as they are stopped at the former U-shaped empty part. Previous workers reported only 15 samples were analyzed with one column, when U-shaped glass tube fully packed with the same packing phase was used (Donard *et al.* 1986). Instead, this W-shaped column achieved more than 100 samples with only one packing. Detection limits (S/N = 2) are 0.8 ngSn for DBT and 2 ngSn for TBT at the detector.

RESULT AND DISCUSSION

Biodegradation. Regression based on the assumption of the first-order kinetic was used to calculate the half lives and degradation rates as follows:

$$\frac{dC}{dt} = -rC \quad (1)$$

$$T_{1/2} = 0.693 / r \quad (2)$$

C: Concentration of the contaminant in the water ($\mu\text{gSn/L}$)

t: Time (days or hours)

r: Degradation rate (1/day or 1/hour)

$T_{1/2}$: Half life (days or hours)

90% confidence intervals by Student's t distribution estimation method are additionally presented (Table 1). Biodegradation rate in unfiltered water varies seasonally: 0.5 ~ 1 week in summer and autumn when many algae are presumed to exist, and 4 weeks in winter. DBT, which is one of the degradation products of TBT, was not seen to increase in most of the experiments. This agrees with the fact that DBT is biodegraded at the same rate as TBT. Difference of the half lives in summer and winter are presumed to be caused by the population of algae and the water temperature (more than 20°C in summer, less than 15°C in winter).

Acclimation effect was not observed since the half lives in samples whose degree of contamination are rather different are nearly the same (summer experiment). This agrees with the result of Lee *et al.* (1989). On the other hand half lives were drastically extended by filtering pretreatment (Figure 2). This shows the fact that most TBT degradable microbes are larger than 1 μm in any water samples used. And it is suggested that TBT is hardly biodegraded in clean natural water where SS or turbidity are low. Thain *et al.* (1987) and Hattori *et al.* (1988) reported variation of half lives in sea water: one week in heavily contaminated areas and slightly degraded in clean water. This shows good agreement between our result and theirs.

On the contrary, half life of 2.5 days for biodegradation of TBT in GF/A (Whatman, 1.2 μm) filtered sea water is reported (Francois *et al.*, 1989). In these experiments MBT and DBT remained for a long period after the TBT disappeared. Increase of DBT was not found in

our experiments, therefore this suggests a difference in degradability between some microbes.

Table 1 Biodegradation of TBT in Water

Matrix Water	Season	Pretreatment	Initial Concentration	Half Life (days)
Marina	Summer	Coarsely (5~10 μm) filtered	TBT 1.4 μgSn/L with EtOH	5.3~ 7.1~10.8 (r ² =0.765)
Sea Water	Summer	Coarsely (5~10 μm) filtered	DBT 1.5 μgSn/L with EtOH	3.7~ 3.8~ 3.9 (r ² =0.973)
	Winter	unfiltered	TBT 2.9 μgSn/L	24.1~25.9~28.1 (r ² =0.921)
	Winter	GF/B(1.0 μm) filtered	TBT 2.2 μgSn/L	39.7~56.2~96.5 (r ² =0.567)
	Winter	0.22 μm Membrane filtered	TBT 1.5 μgSn/L	44.3~59.0~88.2 (r ² =0.578)
Well Flushed	Summer	Coarsely (5~10 μm) filtered	TBT 1.6 μgSn/L with EtOH	4.7~ 5.1~ 5.5 (r ² =0.946)
Sea water	Summer	Coarsely (5~10 μm) filtered	DBT 1.5 μgSn/L with EtOH	9.8~10.6~11.5 (r ² =0.940)
	Autumn	unfiltered	TBT 1.3 μgSn/L	5.8~ 6.5~ 7.4 (r ² =0.888)
	Autumn	GF/B(1.0 μm) filtered	TBT 1.1 μgSn/L	35.4~37.9~40.6 (r ² =0.937)
	Autumn	autoclaved	TBT 1.1 μgSn/L	60.4~65.9~72.5 (r ² =0.910)
Uncontaminated	Summer	Coarsely (5~10 μm) filtered	TBT 2.0 μgSn/L with EtOH	4.4~ 5.3~ 6.5 (r ² =0.862)
Fresh Water	Summer	Coarsely (5~10 μm) filtered	DBT 1.5 μgSn/L with EtOH	9.3~ 9.9~10.5 (r ² =0.956)
	Winter	unfiltered	TBT 3.3 μgSn/L	23.1~25.9~29.5 (r ² =0.859)
	Winter	GF/B(1.0 μm) filtered	TBT 4.2 μgSn/L	34.1~47.5~78.3 (r ² =0.591)
	Winter	0.22 μm Membrane filtered	TBT 3.8 μgSn/L	51.1~126.0~∞ (r ² =0.578)

Decrease of TBT concentration was also observed in autoclaved sea water. Possible processes are mild photolysis caused by attenuated light from windows and the container, oxidization by air, evaporation and effect of air borne microbes which may enter during this long term. None of these processes may involve a reasonable contribution, but it is necessary to consider these processes especially in appreciating the long half life of biodegradation as in winter. Evaporating loss of TBT from a experimental water column has already been suggested (Adelman *et al.*, 1990).

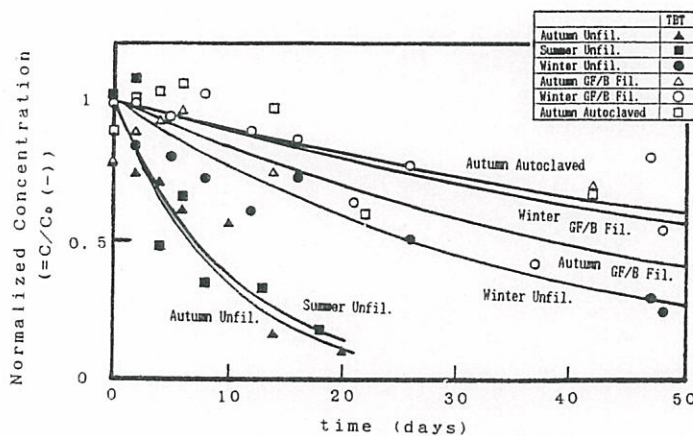


Fig. 2. Biodegradation of TBT in water

Loss of TBT by evaporation is estimated as follows. Vapor pressure for TBT is reported for bis-tributyltin oxide (TBTO) and tributyltin acetate (TBTAc) (Blunden and Chapman, 1986):

$6.4 \times 10^{-7} \sim 1.2 \times 10^{-4}$ mmHg for TBTO

2.7×10^{-3} mmHg for TBTAc.

Assuming 10 mgTBTCl/L for the water solubility of TBT (this assumption is reasonable for the variation of the vapor pressure), Henry's constant is calculated:

$$H = 1.14 \times 10^{-6} \sim 4.83 \times 10^{-8} \text{ (-)} \tag{3}$$

Loss rate of TBT by evaporation may be calculated with an assumption that mass transfer coefficients at the ocean surface (Liss and Slater, 1974) can be applied (Mackay and Leinonen, 1975). Half life of TBT by evaporation from the container we used (2 L of volume and 100 cm² of air-water interface, which yield depth of 20 cm) will be calculated over a wide range:

$$T_{1/2} = 1.24 \sim 3585 \text{ (days)} \tag{4}$$

It is reported that 60% of TBT in sea water is in the form of tributyltin chloride (Laughlin et al., 1986), so the behavior of TBT in sea water is supposed to be nearer to TBTAc than TBTO. This suggests the possibility of loss by evaporation. Calibration by control experiment is preferred to be conducted when we estimate the biodegradation rate for TBT in the marine environment.

Photolysis. Results of these experiment are presented in Table 2. In these experiments opened container top, wide air-water interface and direct irradiation may cause the concentration process induced by water loss. So calibration is conducted with the assumption that loss of TBT by evaporation is negligible:

$$r = r_{\text{observed}} - \frac{1}{V} \frac{dV}{dt} \tag{5}$$

r_{observed} : observed rate obtained

It was obvious that U.V. light of wave length: 254 nm easily decomposes the TBT in a water (Blunden and Chapman, 1982) and it is affected by presence of photo-sensitizer such as fulvic acid (Maguire et al., 1983), however the difference of rate according to the kind of natural water is revealed in this experiment. Figure 3 shows the fact TBT in sea water is degraded more rapidly (half life: 3.8 hrs) than distilled water (15.2 hrs) and fresh water (24.1 hrs) under the irradiation by U.V. light of wave length: 254 nm. On the other hand the difference of half lives between matrices is rather small when U.V. light of wave length: 366 nm is used; their half lives are in the range of 30 ~ 45 hrs. This shows good agreement with the fact reported by Takahashi et al. (1987) (irradiation of TBT in a natural sea water in a pyrex flask by 8.68 mW/cm² of U.V. light of wave length: 366 nm resulted in 40 % loss of TBT after 2 days.).

DBT, which is a degradation product of TBT, increased in sea water and fresh water but did not increase in distilled water. At the end of the experiment of 254 nm irradiation, the sum of remained TBT and DBT accounted 70 % and 90 % of the initial TBT for sea water and fresh water. It is concluded that DBT in distilled water is easily degraded but not in sea water or fresh water. This suggests

Table 2 Photolysis of TBT in Water

Matrix	Irradiating light	Half Life (hrs) (before calibration)
Distilled Water	L.P.*	9.2~ 9.4~ 9.6 (9.4~ 9.7~ 9.9, r ² =0.987)
	H.P.**	33.5~ 34.4~ 35.4 (38.8~ 40.1~ 41.5, r ² =0.975)
	Sun Light	39.6~ 54.2~ 85.9 (Concentration Increased, r ² =0.530)
Sea Water	L.P.	3.6~ 3.8~ 4.0 (3.6~ 3.8~ 4.0, r ² =0.979)
	H.P.	27.8~ 30.5~ 33.8 (31.4~ 34.8~ 39.2, r ² =0.919)
	Sun Light	9.6~ 10.5~ 11.6 (12.8~ 14.4~ 16.5, r ² =0.900)
	Dark (L.P. exp.)	71.0~129.7~741.7 (100.5~278.8~ ∞, r ² =0.173)
	Dark (Sun Light exp.)	60.2~ ∞ ~ ∞ (63.0~ ∞ ~ ∞, r ² =0.015)
Fresh Water	L.P.	21.9~ 24.1~ 26.8 (23.6~ 26.2~ 29.4, r ² =0.909)
	H.P.	43.7~ 46.2~ 48.9 (53.3~ 57.0~ 61.3, r ² =0.950)
	Sun Light	26.3~ 29.3~ 32.7 (81.3~116.0~203.0, r ² =0.711)
Salt Water (40gNaCl/L)	L.P.	5.0~ 5.3~ 5.5 (5.1~ 5.3~ 5.5, r ² =0.971)

* Low Pressure Mercury Lamp
main wave length: 254 nm
irradiation intensity:
0.25~0.3mW/cm²

** High Pressure Mercury Lamp
main wave length: 366 nm
irradiation intensity:
5~10mW/cm²

photolysis of DBT in a water is also strongly affected by substrate present in the water.

These results seem to indicate that TBT in water may be readily degraded by sun light (wave length > 290 nm). Maguire *et al.* (1983) reported the long half life of >89 days for TBT photolysis in an air tight pyrex tube. But the preferred experimental method for environmental water is to directly irradiate the water surface and to keep adequate contact with air through the interface. Unfortunately, this method results in pretty high water loss, so data will be doubtful. But we found the differences of TBT degradation according to the matrices (Figure 4). Concentration of TBT decreased obviously in the sea water, and slightly in the fresh water. Instead TBT increased in the distilled water caused by concentration by water evaporation. Increase of concentration of DBT were observed in all matrices. Calibrated half life of sun light photolysis of TBT in the sea water is 10.5 hrs (14.4 hrs prior to calibration). Half life in fresh water (116.1 \rightarrow 29.2hrs) and in distilled water (concentration increased \rightarrow 54.3 hrs) are thought to be uncertain because the obtained data showed little change in TBT concentration. However increase of concentration of DBT and results by artificial light show that the sun light photolysis is a possible process in environmental water.

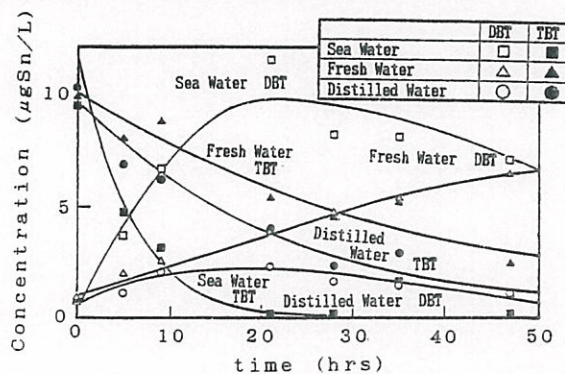


Fig. 3. Photolysis of TBT in water by U.V. light: 254 nm

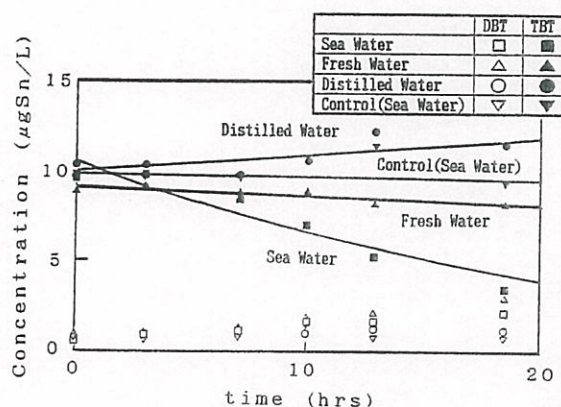


Fig. 4. Photolysis of TBT in water by sun light

Rapid degradation of TBT in sea water is thought to be the effect of chloride ions in the water. So we tested TBT photolysis in sodium chloride solution by U.V. light of wave length: 254 nm. TBT was degraded as rapidly as the sea water (5.3 hrs for the NaCl solution and 3.8 hrs for the sea water).

Contribution rates for the TBT degradation in a water. Examination for degradation paths and their contribution rates for TBT in sea water can be performed with data obtained in this experiment. The photolysis rate in summer for TBT is acquired from the result of the sun light experiment and assumption of 5 hrs/day of duration of sun-shine considering cloudy and rainy days. Photolysis rate in winter is thought to be 1/10 of the rate in summer appreciating the difference in the intensity of U.V. region (Zepp and Cline, 1977) and the water temperature. Biodegradation rates for various conditions (summer or winter, SS-rich or clean) are calculated from the result of the experiment on the sea water. Calibration by evaporation loss is applied assuming the half life of evaporation loss in the container is 70 days.

Table 3 Degradation Rate Coefficients for TBT in Sea Water

	Summer	Winter
Photolysis	0.33	0.033
Biodegradation	0.103 (SS rich Area) 0.0083 (Clean Area)	0.0168 (SS rich Area) 0.0020 (Clean Area)

*unit: 1/day

Now we work on the basis of a water column of 10 m depth. Attenuation rate of light in sea

water is close to that in distilled water (Zepp and Cline, 1977). The photo effective depth to which the photolysis rate can be applied is assumed to be 50 cm for SS-rich water and 1 m for clean water. Biodegradation rates are applied to the entire water column. The degradation rate for individual process (degradation rate coefficient \times effective depth / 10 m) and evaporation rate are calculated.

Table 4 Degradation Rates for TBT by Individual Process in Sea Water and Their Contribution Rates

	Summer		Winter	
	SS-rich Area	Clean Area	SS-rich Area	Clean Area
Biodegradation	0.103 (86.1%)	0.0082 (19.8%)	0.0165 (90.4%)	0.0002 (36.8%)
Photolysis	0.0165 (13.8%)	0.0330 (79.9%)	0.00165 (8.8%)	0.0033 (60.6%)
Evaporation	0.00014 (0.1%)	0.00014 (0.3%)	0.00014 (0.8%)	0.00014 (2.6%)
Total	0.11196	0.04134	0.01859	0.00544
T1/2(days)	5.8	16.8	37.3	127.39

*unit:1/day

Overall half life in the water column varies from a week to more than 100 days according to the conditions. The contribution of biodegradation becomes the highest (up to 90 %) in marinas. Rapid degradation of TBT in previous reports (Seligman *et al.*, 1986, 1988; Thain *et al.*, 1987; Hattori *et al.*, 1988; Francois *et al.*, 1989; Lee *et al.*, 1989) is supposed to be attributable to SS-rich water in summer. Instead the biodegradation rate is so limited in clean water such as the ocean that TBT degradation is mainly due to photolysis (80 %). It is noticed that 1 m of surface layer acts as the main degradation sink in these cases. The degradation rate in winter is very slow. Comprehensive appreciation to the value of degradation rate coefficient is needed when one estimates the fate of TBT in the environment.

The evaporation loss seems not to play an important role. However, since Henry's constants for all forms of TBT remains uncertain, the suggestion of considerable evaporation loss of TBT from the mesocosm by Adelman *et al.* (1990) must be considered.

For fresh water the biodegradation is thought to be similar to that in sea water and the photolysis rate is thought to be 1/3 of that in sea water. It is expected that the overall half life in fresh water will be longer than sea water.

DBT is found accompanied by TBT in the environments where we collected sea water. DBT is as readily biodegraded as TBT in SS-rich sea water, but more stable with regard to light than TBT. This suggests that occurrence of DBT in the area we studied is due to the photolysis of TBT near the surface.

CONCLUSION

TBT is readily degraded by both artificial light and sun light. Photolysis rate is affected by matrices type: sea water shows the fastest photolysis. DBT in natural water is thought to be more stable with regard to light. Both TBT and DBT are biodegradable. Biodegradation rate is as short as 6 days in warm SS-rich water such as in a marina in summer. However, filtering pretreatment makes the half life much longer. Precise evaporation rate of TBT has not been quantified as yet. But it seems not to be significant factor. Biodegradation is the major process in SS-rich sea water; but photolysis exceeds that in clean sea water. Overall half lives of TBT in sea water vary from 6 days to 127 days according to seasons and presence of SS. This wide range of degradation rate must be appreciated in estimating the fate of TBT in the environment.

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