

**CALIFORNIA DEPARTMENT OF TOXIC SUBSTANCES CONTROL
HUMAN AND ECOLOGICAL RISK DIVISION (HERD)**

HERD ECOLOGICAL RISK ASSESSMENT (ERA) NOTE

HERD ERA NOTE NUMBER: 3

ISSUE DATE: December 15, 1999; Revised September 2, 2003

ISSUE: Calculation of an action level/preliminary cleanup goal for dibutyltin (DBT) in surface, ground, and sediment interstitial water for protection of saltwater aquatic life.

GUIDANCE: HERD recommends an action level/preliminary cleanup goal for DBT in surface, ground, and sediment interstitial water that is equal to 0.1 µg/L [100 times more than the proposed U.S. EPA Ambient Water Quality Criterion of 0.001 µg/L for tributyltin (TBT) in saltwater]. The HERD recommended DBT action level/preliminary cleanup goal should only apply in situations where DBT is detected in water (i.e., surface water or sediment interstitial water), but not TBT. In situations where both DBT and TBT are detected in water, HERD recommends that a toxic equivalency factor (TEF) approach be used. In this approach, the relative potency of DBT detected in water is calculated and added to the concentration of TBT detected in water. For example:

In a given water sample, the measured concentration of TBT = 0.001 µg/L; the measured concentration of DBT = 0.08 µg/L. Assume TEF for DBT = 0.01.

- First, calculate the relative potency of DBT versus TBT using the TEF approach:

$$0.08 \mu\text{g/L} \times 0.01 = 0.0008 \mu\text{g/L (TBT equivalents)}.$$

- Second, add the concentration of TBT to the concentration of TBT equivalents:

$$0.001 \mu\text{g/L} + 0.0008 \mu\text{g/L} = 0.0018 \mu\text{g/L}.$$

The final concentration, 0.0018 µg/L, is greater than the criterion of 0.001 µg/L for TBT. Therefore, in this example, the action level/preliminary cleanup goal for TBT/DBT has been exceeded.

To accurately predict the bioavailable fraction of TBT in sediments, U.S. EPA Region 10 strongly recommends that sediment monitoring include interstitial water sampling (U.S. EPA, 1996). Therefore, HERD recommends that monitoring of TBT contamination include measurement of sediment interstitial water. HERD also recommends that TBT/DBT monitoring be conducted at all sites contaminated with TBT.

BACKGROUND

The purpose of this ERA Note is to provide guidance for evaluating and monitoring marine or freshwater sediments contaminated with TBT and to present an action level/preliminary cleanup goal for DBT. This ERA Note also provides (1) the rationale and justification for the proposed DBT action level/preliminary cleanup goal, and (2) a discussion of the uncertainties in deriving the action level/preliminary cleanup goal. The proposed U.S. EPA Ambient Water Quality Criterion for TBT in saltwater is 0.001 µg/L (4 day average). The criterion was developed to protect saltwater organisms from the adverse reproductive effects of TBT that have been observed in laboratory and field studies and because exposure to TBT can make saltwater organisms more vulnerable to infection from pathogens (U.S. EPA, 2002).

RATIONALE FOR MONITORING AND DERIVING AN ACTION LEVEL/PRELIMINARY CLEANUP GOAL FOR DIBUTYLTIN

Environmental Degradation of Dibutyltin

TBT is a potent biocide that was once used in the United States and Canada as an antifouling compound in marine paints. TBT contamination is typically found in harbors and nearshore environments where commercial and/or recreational boats are used, stored, or painted. For example, high concentrations of butyltin compounds (e.g., tri-, di-, mono- butyltin) have been detected in fish, shellfish, and sediments collected from the southwestern coast of British Columbia, Canada (Stewart and Thompson, 1994). TBT is degraded in the marine environment to DBT, monobutyltin (MBT), and inorganic tin (Sn). Figure 1 provides a probable degradation scheme. The reaction rates for the cleavage of tin-carbon bonds are generally greater for TBT to DBT versus DBT to MBT or MBT to inorganic tin (Eisler, 1989). Therefore, DBT may persist and co-occur in sediments contaminated with TBT. Sunlight (UV irradiation) and biological metabolism (e.g., microbacterial) are important processes by which TBT is degraded in marine environments.

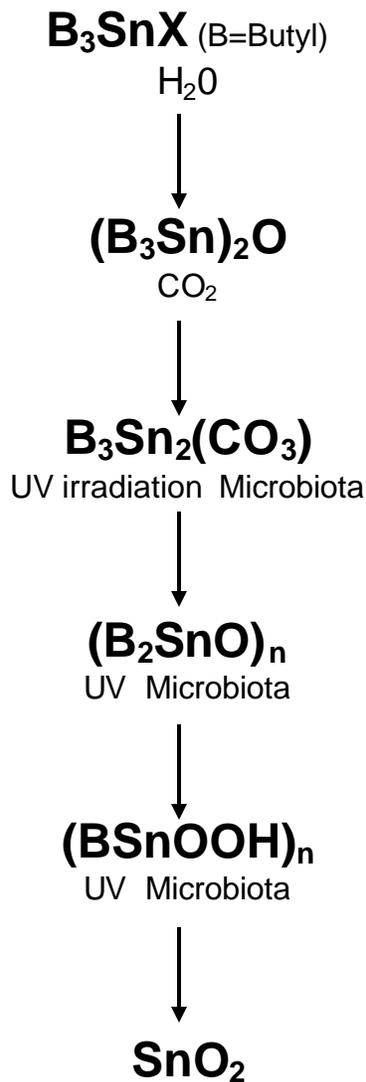


Figure 1. Environmental degradation scheme for TBT compounds. Adapted from Eisler (1989)

Toxicity of Organotin Compounds

Organotin compounds, especially TBT, are extremely toxic to aquatic life. The early developmental stages of aquatic organisms are particularly sensitive to the toxic effects of organotin compounds (Eisler, 1989). In an effort to evaluate the toxicity of DBT, HERD reviewed available toxicity literature for butyltin compounds. The review focused on marine invertebrates because of their high toxicological sensitivity to butyltin compounds (Eisler, 1989).

Very little invertebrate toxicity information is available for DBT; almost all available literature focuses on TBT. TBT effect concentrations for marine invertebrates can range from 0.001 µg/L for reproductive effects in dogwhelk (*Nucella lapillus*) to 5 µg/L for complete mortality [96 hr lethal concentration (LC) 100%] in mussels (*Mytilus edulis*) (Eisler 1989). Table 1 shows a comparison of effects ranges in marine invertebrates exposed to either TBT or DBT. Effects concentrations for DBT range from one to three orders of magnitude less than TBT. Of three studies evaluated, two studies with embryonic tunicates (Cima et al., 1996) and larval marine crabs (Laughlin et al., 1985) showed toxicity effects within one to two orders of magnitude of TBT; one study with larval mussels (Lapota et al., 1993) showed toxic effects within three orders of magnitude. The Laughlin et al. (1985) study with marine crabs concluded that the toxicity appears to be a function of hydrophobicity of the organotin compounds (i.e., hydrophobicity of TBT > DBT > MBT). Similar results have been demonstrated in other invertebrate species (Cima et al., 1985; Eisler, 1989; Laughlin et al., 1985; Thomulka and Lange, 1996).

In general, MBT and inorganic tin are much less toxic to biota than TBT and DBT (Eisler, 1989; Thomulka and Lange, 1996). For example, in the fish *Leuciscus idus melanotus*, the LC50 for MBT is more than 4 orders of magnitude greater than the LC50 for TBT (Blunden and Chapman, 1986 as cited in Eisler, 1989).

Table 1 Marine Invertebrate Toxicity Information for Tri- and Di- Butyltin						
Selected Marine Invertebrate Species ¹	Organotin Compound		Toxic Effect Evaluated		TEF ²	Reference
	DBT	TBT	Toxicity Value	Effect		
Mussel (<i>Mytilus edulis</i>)	2 µg/L	0.006 µg /L	NOEC	Growth and Survival	0.0025	Lapota et al. (1993)
	20 µg /L	0.05 µg /L	LOEC			
	6.3 µg /L	0.017 µg /L	Chronic Toxicity Value			
Tunicate (<i>Styela plicata</i>)	1.0 µM	0.1 µM	LOEC	Inhibited Embryonic Metamorphosis	0.1	Cima et al. (1996)
Marine Mud Crab (<i>Rithropanopeus harrisi</i>)	250 µg /L	10 µg /L	LOEC	Survival	0.04	Laughlin et al. (1985)

1. Toxicity studies are conducted during larval or embryonic stages of development.
2. Toxic equivalency factors (TEFs) are calculated as the relative potency of DBT versus TBT (e.g., LOEC DBT/LOEC TBT = TEF).

DBT = dibutyltin
TBT = tributyltin
NOEC = no observable effect concentration
LOEC = lowest observable effect concentration
µg/L = micrograms per liter
µM = micromolar

UNCERTAINTY IN DERIVING AN ACTION LEVEL/PRELIMINARY CLEANUP GOAL FOR DIBUTYLTIN

A number of uncertainties should be considered in the derivation of an action level/preliminary cleanup goal for DBT. Pending additional toxicity information, the value proposed in this ERA Note may need to be revised. Uncertainties to be considered include the following:

- *Limited number of DBT toxicity studies.* Most toxicity studies with DBT have been conducted in mammals; only a few studies have been conducted in aquatic organisms. Because of limited information, risks posed by dibutyltin may be under or over-estimated.
- *Mixture toxicity interactions (particularly with other organic and inorganic tin compounds).* Thomulka and Lange (1996) demonstrated that mixtures of organotin compounds may interact additively or synergistically to cause toxicity in the marine bacterium *Vibrio harveyi*. For example, mixtures of DBT and TBT were found to cause toxicity in an additive fashion. Mixtures of DBT or TBT with inorganic tin were found to cause toxicity in a synergistic fashion. For purposes of this evaluation, the toxicity of TBT and DBT are assumed to interact in an additive fashion. Risks posed by DBT may be under- or over-estimated in cases where toxicity is synergized or antagonized by other compounds.
- *Toxicity of other breakdown products of TBT.* Eisler (1989) summarizes several potential degradation products of TBT. As described above, MBT and inorganic tin are formed from the degradation of TBT. The toxicity of these compounds, singularly or in combination with TBT or DBT is not addressed in this evaluation. Other potential forms of TBT and DBT that may form after biological activity in sediments, including tributylmethyltin and dibutylmethyltin (Eisler, 1989), are also not addressed in this evaluation. Because other breakdown products of TBT are not considered, risks are underestimated.
- *Immunotoxic effects of organotin compounds.* Recent studies with marine invertebrates have shown that the immunotoxic effects of DBT exceed that of TBT. Bouchard et al. (1999) showed that the in vitro phagocytic activity of hemocytes from three marine bivalve species is reduced in the following order of potency: DBT > TBT > MBT. Immunotoxic effects may compromise an organisms ability to defend against disease (e.g., bacterial, viral, and parasitic). Because the potential immunotoxic effects of DBT are not considered in this evaluation, risks may be underestimated.
- *Bioavailability.* For purposes of establishing the action level/preliminary cleanup goal for DBT, a measured concentration in the water column is assumed to be 100% bioavailable. This assumption may be overly conservative because DBT may bind to dissolved organic carbon and be less than 100% bioavailable. Because bioavailability

is not considered in the development of the action level/preliminary cleanup goal, risks may be overestimated.

- *Exposure pathways.* The action level/preliminary cleanup goal for DBT only addresses the surface/interstitial water exposure pathway. Marine organisms may consume sediment or other suspended particulates that are contaminated with DBT. Because alternate exposure pathways are not considered in the development of the action level/preliminary cleanup goal, risks are under-estimated.
- *Bioaccumulation.* The action level/preliminary cleanup goal for DBT does not address the potential for food chain bioaccumulation and trophic transfer of DBT. For example, butyltin compounds (TBT, DBT, MBT) have been measured in sea otters (*Enhydra lutris nereis*) found dead along California coastal waters and may be associated with adverse effects in those animals (Kannan et al., 1998). Because bioaccumulation is not considered in the development of the action level/preliminary cleanup goal, risks may be underestimated.

METHODS USED TO CALCULATE ACTION LEVEL/PRELIMINARY CLEANUP GOAL FOR DIBUTYLTIN

The available aquatic toxicity information indicates that DBT is 10 to 400 times less potent than TBT (Table 1). Since two of three available studies (Cima et al., 1996; Laughlin et al., 1985) indicate that DBT is within one to two orders of magnitude less potent than TBT, HERD has selected a provisional toxic equivalency factor (TEF, see definition in Table 1) of 0.01. Therefore, HERD recommends an action level/preliminary cleanup goal for DBT in surface, ground, and sediment interstitial water that is equal to 0.1 µg/L (100 times more than the proposed U.S. EPA Ambient Water Quality Criterion of 0.001 µg/L for TBT in saltwater).

The HERD recommended DBT action level/preliminary cleanup goal should only apply in situations where DBT is detected in water, but not TBT. In situations where both DBT and TBT are detected in water, HERD recommends that a TEF approach, as presented in Table 1, be used. In this approach, the relative potency of DBT detected in water is calculated and added to the concentration of TBT detected in water. For example:

In a given water sample, the measured concentration of TBT = 0.001 µg/L; the measured concentration of DBT = 0.08 µg/L. Assume TEF for DBT = 0.01.

- First, calculate the relative potency of DBT versus TBT using the TEF approach:

$$0.08 \mu\text{g/L} \times 0.01 = 0.0008 \mu\text{g/L (TBT equivalents).}$$

- Second, add the concentration of TBT to the concentration of TBT equivalents

$$0.001 \mu\text{g/L} + 0.0008 \mu\text{g/L} = 0.0018 \mu\text{g/L}.$$

The final concentration, 0.0018 $\mu\text{g/L}$, is greater than the criterion of 0.001 $\mu\text{g/L}$ for TBT. Therefore, in this example, the action level/preliminary cleanup goal for TBT/DBT has been exceeded.

ENVIRONMENTAL MONITORING OF TBT CONTAMINATED SEDIMENTS

To accurately predict the bioavailable fraction of TBT in sediments, U.S. EPA Region 10 strongly recommends that sediment monitoring include interstitial water sampling (U.S. EPA, 1996). Therefore, HERD recommends that TBT monitoring include measurement of sediment interstitial water. Furthermore, HERD recommends that DBT monitoring be conducted at all sites contaminated with TBT.

REFERENCES

- Bouchard, N., Pelletier, E., and Fournier, M. 1999. Effects of Butyltin Compounds on Phagocytic Activity of Hemocytes from Three Marine Bivalves. *Environmental Toxicology and Chemistry*, 18(3):519-522.
- Cima, F., Ballarin, L., Bressa, G., Martinucci, G., and Burighel, P. 1996. Toxicity of Organotin Compounds on Embryos of a Marine Invertebrate (*Styela plicata*; Tunicata). *Ecotoxicology and Environmental Safety*, 35:174-182.
- Eisler, R. 1989. Tin Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. Contaminant Hazard Reviews. Biological Report 85(1.15). January.
- Kannan, K., Guruge, K.S., Thomas, N.J., Tanabe, S., and Giesy, J.P. 1998. Butyltin residues in southern sea otters (*Enhydra lutris nereis*) found dead along California coastal waters. *Environmental Science and Technology*, 32(9):1169-1175.
- Lapota, D., Rosenberger, D.E., Platter-Rieger, M.F., and Seligman, P.F. 1993. Growth and Survival of *Mytilus edulis* Larvae Exposed to Low Levels of Dibutyltin and Tributyltin. *Marine Biology*, 115:413-419.
- Laughlin, R.B., Johannesen, W., French, H., Guard, H., Brinckman, F.E. 1985. Structure-activity Relationships for Organotin Compounds. *Environmental Toxicology and Chemistry*, 4:343-351.
- Stewart, C. and A. J. Thompson. 1994. Extensive Butyltin Contamination in Southwestern Coastal British Columbia, Canada. *Marine Pollution Bulletin*, 28(10):601-606.

Thomulka, K.W. and J. H. Lange. 1996. A Mixture Toxicity Study Employing Combinations of Tributyltin Chloride, Dibutyltin Dichloride, and Tin Chloride Using the Marine Bacterium *Vibrio harveyi* as the Test Organism. *Ecotoxicology and Environmental Safety*, 34:76-84.

U.S. EPA. 1996. Recommendations for Screening Values for Tributyltin in Sediments at Superfund Sites in Puget Sound, Washington. DCN 4000-09-013-AADS, 13-01-AADK, and 33-01-AAAV. Prepared by Roy F. Weston, Inc., Seattle, Washington. Prepared for U.S. EPA Superfund Program, Region 10, Seattle, Washington.

U.S. EPA. 2002. Notice of Draft Ambient Water Quality Criteria Document for Tributyltin (TBT). United States Environmental Protection Agency, Office of Water. EPA-822-F-02-003. December.

HERD ISSUE CONTACT PERSON: Michael Anderson, Staff Toxicologist
(916) 255-6625 Voice
(916) 255-6657 Facsimile
Manders7@dtsc.ca.gov