



## Canadian Water Quality Guidelines for the Protection of Agricultural Water Uses

## ORGANOTINS

tributyltin  
triphenyltin  
tricyclohexyltin

Organotin compounds have been used in a number of industrial and agricultural applications, including polyvinyl chloride stabilizers, catalysts, industrial and agricultural biocides, and wood-preserving and antifouling agents (Bock 1981; Jones et al. 1982; Moore et al. 1992). Organotins are characterized by the presence of at least one covalent carbon-tin bond. Published environmental and toxicity levels of organotins are expressed as concentrations of (1) tin, (2) the alkyl- or aryltin, or (3) the organotin cation and associated anion. All concentrations in this fact sheet have been converted to milligrams or micrograms of organotin cation per litre so that measured concentrations of organotins can be compared.

The physical and chemical properties of organotins vary widely, according to the number and type of organic and inorganic moieties bonded to the tin atom. Moore et al. (1992) published the physical and chemical properties for 110 organotin compounds. Water solubilities for organotin compounds typically range from 5 to 50 mg·L<sup>-1</sup> and are inversely proportional to the number and molecular weight of the organic groups attached to the tin atom (NRCC 1985; Eisler 1989). Most commercially used organotins have low mobility in aquatic environments as a result of low aqueous solubility, low vapour pressure, and a high affinity for aquatic sediments (Blundin and Chapman 1982).

Although the major use of organotins in Canada is for the heat stabilization of polyvinyl chloride products, use of organotin biocides can be a threat to the aquatic environment. Several organotin compounds are used in paints to prevent water damage and biological fouling of exposed underwater surfaces. The widespread use of organotin-based antifouling paints on boat hulls, lobster traps, and fishing nets has resulted in elevated concentrations of these compounds in freshwater, estuarine, and marine environments (NRCC 1985; Anderson and Dalley 1986; Maguire et al. 1986; Laughlin and Linden 1987; Clark et al. 1988). Mandatory registration of antifoulants under the Pest Control Products Act reduced organotin use in antifoulants and led to the banning of organotin products on nets and lobster traps.

Tributyltin compounds occur at high concentrations in water, sediment, and biota associated with harbour locations. In 10% of freshwater samples from 265 locations across Canada, tributyltin was found at

levels  $\geq 0.2 \mu\text{g}\cdot\text{L}^{-1}$  (Maguire 1987, 1989). Dibutyltin and monobutyltin were also found in approximately 10% of the samples collected across Canada. Dibutyltin and monobutyltin contamination is believed to result from tributyltin degradation rather than from direct input (Maguire 1989).

The persistence and fate of organotins in the aquatic environment are functions of such factors as aqueous solubility and vapour pressure of the compound, adsorption to suspended matter and sediments, and abiotic and biotic methylation and demethylation. The degradation of an organotin compound may be defined as the sequential removal of the alkyl or aryl groups attached to the tin atom, for example:



Inorganic tin is the end product of organotin degradation in the aquatic environment. Inorganic tin has the potential to be methylated, producing mono-, di-, tri-, and tetramethyltin compounds that were not previously introduced to the area (Maguire et al. 1986). Chau et al. (1981) demonstrated that both Sn (II) and Sn (IV) undergo microbial transformation to methyltin compounds in water. Volatilization of mono-, di-, and triorganotins is likely negligible because of the tendency of these compounds to strongly adsorb to suspended solids and sediments (Maguire and Tkacz 1985). Owing to their high sediment/water partition coefficients (e.g., tributyltin  $K_{oc} = 3370$ ), adsorption of organotins to suspended solids and sediments is potentially an important mechanism for their removal from water (Cardwell 1988). However, caution is warranted in viewing adsorption to suspended solids and sediments as the ultimate fate of organotins in aquatic environments, as toxic residues may be mobilized through desorption, sediment resuspension, or uptake by benthic

**Table 1. Water quality guidelines for organotins for the protection of agricultural water uses (CCME 1992).**

Use	Guideline value ( $\mu\text{g}\cdot\text{L}^{-1}$ )
Irrigation water	NRG*
Livestock water	
Tributyltin	250
Triphenyltin	820 <sup>†</sup>
Tricyclohexyltin	250 <sup>†</sup>

\* No recommended guideline.

<sup>†</sup> Interim guideline.

biota (NRCC 1985). For more information on the use, environmental concentrations, and chemical properties of organotins, see the fact sheet on organotins in Chapter 4 of *Canadian Environmental Quality Guidelines*.

### Water Quality Guideline Derivation

The Canadian water quality guidelines for organotins for the protection of livestock water were derived using the following formula (CCME 1992; Moore et al. 1992):

$$CWQG = [(TDI \cdot UF \cdot bw) / WIR] \cdot PDWC$$

where

TDI = tolerable daily intake rate ( $\text{mg} \cdot \text{kg}^{-1}$  per day)  
 WIR = daily water intake rate ( $200 \text{ L} \cdot \text{d}^{-1}$ )  
 UF = uncertainty factor (0.1)  
 bw = maximum body weight of dairy cattle (820 kg)  
 PDWC = percentage drinking water contribution (20%)

### Livestock Water

The number and composition of the organic moieties bonded to the tin atom determine the toxicity of organotin compounds to livestock and related biota (Moore et al. 1992). Organotin toxicity to mammals generally decreases from tri- to monoorganotins. Tetraorganotins have similar toxicities to triorganotins, but the effects of tetraorganotins are often less and somewhat delayed by comparison. Mammalian toxicity within each class of organotin compounds is determined by the number of carbon atoms per side chain. Increases in the n-alkyl chain length generally reduce mammalian toxicity (Snoeijs et al. 1987). The octanol-water partition coefficients (up to 7000) for high-molecular weight organotins suggest a potential for bioaccumulation (Laughlin et al. 1986).

#### *Tributyltin*

A summary of the acute oral toxicity of several tributyltin compounds is found in Moore et al. (1992). Rat  $LD_{50}$  values based on the total tributyltin compound (i.e. tributyltin + anion) range from 94 to 224  $\text{mg} \cdot \text{kg}^{-1}$  bw. In mice,  $LD_{50}$ s range from 46 to 230  $\text{mg} \cdot \text{kg}^{-1}$  bw. Death and inflammation of the hepatic bile duct occurred in 9 of 24 rat pups orally exposed to 3  $\text{mg} \cdot \text{kg}^{-1}$  tributyltin acetate for 28 d (Mushak et al. 1982). The mechanism of toxic action of trialkyltins is thought to be the inhibition of a reaction in the energy transforming chain between electron transport and the formation of adenosine triphosphate (ATP) (McCollister and Schober 1975).

Bis(tributyltin) oxide has not been shown to induce point mutations or DNA damage in the majority of the in vitro microbial and mammalian cell test systems tested. A single report of a mutagenic response (Davis et al. 1987) could not be confirmed during a re-evaluation of the data (Schweinfurth and Gunzel 1987).

Maternal doses as high as 6  $\text{mg} \cdot \text{kg}^{-1}$  bis(tributyltin) oxide produced no teratogenic effects in mice. Doses of 11.7  $\text{mg} \cdot \text{kg}^{-1}$ , and higher, produced maternal toxicity and are thought to have caused an increase in the frequency of cleft palates in offspring of surviving females (Schweinfurth and Gunzel 1987).

The Canadian water quality guideline for tributyltin for the protection of livestock water is  $0.25 \text{ mg} \cdot \text{L}^{-1}$  ( $250 \mu\text{g} \cdot \text{L}^{-1}$ ). This value was calculated using the LOEC (3  $\text{mg} \cdot \text{kg}^{-1}$  tributyltin acetate for rat pups) as the TDI and the guideline derivation procedure previously described (Mushak et al. 1982; CCME 1992; Moore et al. 1992).

#### *Triphenyltin*

Uptake studies conducted on rats, using radioactive triphenyltin, demonstrated that 80–88% of the orally administered triphenyltin is eliminated in feces and urine within 7 d. Metabolism of triphenyltin does not occur through the mixed-function oxygenase system. Bock (1981) examined triphenyltin breakdown and found that following oral and intravenous administration there is little change in the parent compound before it is eliminated from the body.

For oral ingestion of triphenyltin, reported  $LD_{50}$ s for mice, guinea pigs, and rabbits are 80–1000, 10–41.2 and 30–140  $\text{mg} \cdot \text{kg}^{-1}$  bw, respectively (Moore et al. 1992). Chronic ingestion studies have found that rats, guinea pigs, and dogs have a similar sensitivity to triphenyltin (Bock 1981). Guinea pigs fed 10  $\text{mg} \cdot \text{kg}^{-1}$  per day of triphenyltin, for 2 years suffered significant histopathological changes in cells of the liver and heart. Using this LOEC as the TDI and the guideline derivation procedure described above, the triphenyltin interim guideline value for the protection livestock water is calculated to be  $0.82 \text{ mg} \cdot \text{L}^{-1}$  ( $820 \mu\text{g} \cdot \text{L}^{-1}$ ).

#### *Tricyclohexyltin*

Toxicity data for tricyclohexyltin is limited, though results indicate response thresholds similar to those of triphenyltin. Rats, for example, have a reported acute oral  $LD_{50}$  of 540  $\text{mg} \cdot \text{kg}^{-1}$  bw (McCollister and Schober 1975).

Chronic dietary studies with dogs and rats found decreased growth rates at 3 and 6 mg·kg<sup>-1</sup> per day, respectively (McCullister and Schober 1975). Using the LOEC of 3 mg·kg<sup>-1</sup> per day and the guideline derivation procedure previously described, an interim Canadian water quality guideline for livestock water of 0.25 mg·kg<sup>-1</sup> (250 µg·L<sup>-1</sup>) tricyclohexyltin was calculated.

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