Canadian Water Quality Guidelines for the Protection of Aquatic Life

ORGANOTINS

tributyltin
triphenyltin
tricyclohexyltin

Organotin compounds have been used in a number 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). Organotin compounds 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 micrograms of organotin cation per litre to compare measured concentrations of organotins.

The physical and chemical properties of organotins vary widely according to the numbers and types of organic and inorganic moieties bonded to the tin atom. (See Moore et al. 1992 for a table of the physical and chemical properties of 110 organotin compounds.) Water solubilities for organotin compounds typically range from 5 to 50 $mg \cdot L^{-1}$ 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 are characterized by low mobility in the aquatic environment 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 as preservatives against water damage and fouling biological growths on 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; Clark et al. 1988; Laughlin and Linden 1987). Mandatory registration of antifoulants under the Pest Control Products Act reduced organotin use as antifoulants and led to the banning of organotin products on nets and on lobster traps.

Methyltin compounds, which result from anthropogenic sources as well as biotic and abiotic methylation of inorganic tin, have been detected in various natural waters, sediments, and biota (NRCC 1985). Maguire et al. (1982, 1986) reported that Kingston Harbour had the highest Canadian concentrations for monomethyltin and dimethyltin (1.22 and 0.32 $\mu g \cdot L^{-1}$, respectively). The highest level of trimethyltin was found in Vancouver Harbour (0.248 $\mu g \cdot L^{-1}$). In the only survey of methyltin concentrations in Canadian aquatic biota, Chau et al. (1984) found that monomethyltin levels in fish from several Lake Ontario harbours ranged from 250 to 990 $\mu g \cdot kg^{-1}$.

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 of 0.2 $\mu g \cdot L^{-1}$ (Maguire 1987, 1989). Dibutyltin and monobutyltin were also found in about 10% of the samples collected across Canada. Rather than resulting from direct input, dibutyltin and monobutyltin contamination is believed to have resulted from tributyltin degradation (Maguire 1989). Few studies have been conducted in Canada to determine butyltin levels in aquatic biota. In Vancouver Harbour, tri-, di-, and monobutyltin concentrations of 580, 98, and 90 $\mu g \cdot kg^{-1}$ ww were found, respectively, in fish samples (Maguire et al. 1986). In Nanoose Bay, British Columbia, tributyltin concentrations, in oyster tissue samples were as high as 1 800 $\mu g \cdot kg^{-1}$ dw. The major source of tributyltin at this location was from the use of tributyltin as a marine growth retardant on salmon nets (Harding and Kay 1988).

The persistence and fate of organotins in the aquatic environment are functions of such factors as aqueous solubility and vapour pressure of the compound,

Table 1. Water quality guidelines for organotins for the protection of aquatic life (CCME 1992).

Aquatic life	Guideline value ($\mu g \cdot L^{-1}$)		
	Tributyltin	Triphenyltin	Tricyclohexyltin
Freshwater	0.008*	0.022*	NRG†
Marine	0.001*	NRG†	NRG†

*Interim guideline.
†No recommended guideline.

adsorption to suspended matter and to 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:

$$R_4Sn \rightarrow R_3SnX \rightarrow R_2SnX_2 \rightarrow RSnX_3 \rightarrow SnX_4.$$

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) underwent 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 biota (NRCC 1985).

The potential for aquatic biota to bioconcentrate organotins from the environment depends on the specific number and types of organic moieties attached to the tin atom. The greater the number and molecular weight of the organic groups bound to the tin atom, the more lipophilic the compound and the greater the potential for bioconcentration (NRCC 1985). Most organotins have a moderate octanol–water partition coefficient (K_{ow}), indicating that these compounds have the potential to bioaccumulate in biota. BCFs for tributyltin have been found to range from 200 in the muscle tissue of Chinook salmon *(Oncorhynchus tshawytscha)* (Short and Thrower 1986a, 1986b) to 4580 in the viscera of sheepshead minnows *(Cyprinodon variegatus)* (Ward et al. 1981). See Moore et al. (1992) for an extensive review of the literature on organotin bioaccumulation.

Water Quality Guideline Derivation

The interim Canadian water quality guidelines for organotins for the protection of aquatic life were developed based on the CCME protocol (CCME 1991).

Freshwater Life

Tributyltin

Seven primary studies of the acute toxicity of tributyltin to freshwater fish were found. The 96-h LC_{50}s ranged from 2.6 to 12.7 $\mu g \cdot L^{-1}$. The 33-d LOEL for growth in juvenile fathead minnows (*Pimephales promelas*) was 0.08 $\mu g \cdot L^{-1}$ (Brooke et al. 1986). *Daphnia magna* was found to be the most sensitive invertebrate to tributyltin exposure. Brooke et al. (1986) found a significant reduction in offspring survival following a 21-d exposure to 0.2 $\mu g \cdot L^{-1}$ tributyltin. The most sensitive algal study was Wong et al. (1982), who reported a 4-h IC_{50} for decreased primary production of 3 $\mu g \cdot L^{-1}$ in a mixed assemblage of Lake Ontario algae.

The interim water quality guideline for tributyltin for the protection of freshwater life is 0.008 $\mu g \cdot L^{-1}$ (CCME 1992). It was derived by multiplying the 33-d LOEL for growth of 0.08 $\mu g \cdot L^{-1}$ for juvenile fathead minnows (Brooke et al. 1986) by a safety factor of 0.1 (CCME 1991).

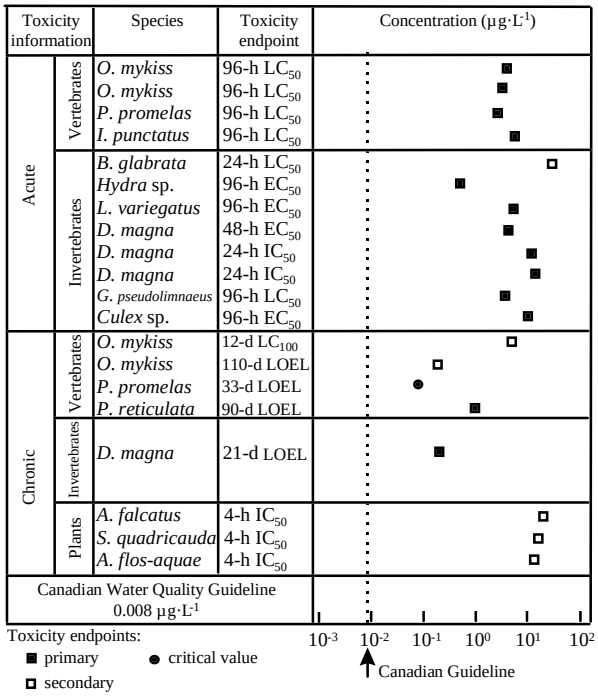

Figure 1. Select freshwater toxicity data for tributyltin.

Triphenyltin

The acute effects of triphenyltin on freshwater fish ranged from a 96-h EC_{50}, (behavioural changes) of 3.5 $\mu g \cdot L^{-1}$ for

juvenile fathead minnows (Jarvinen et al. 1988) to a 24-h LC_{100} of 860 µg·L^{-1} for the eel *Anguilla anguilla* (Gras and Rioux 1965). In the most sensitive chronic fish study, Jarvinen et al. (1988) reported a 30-d LOEL for reduced growth in juvenile fathead minnows of 0.22 µg·L^{-1}. Among the invertebrates, the cladoceran *Ceriodaphnia dubia* was found to be the most sensitive, with a 48-h EC_{50} (immobilization) of 10.8 µg·L^{-1} (Kline et al. 1989). The most sensitive algal study reported a 4-h IC_{50} of 2.0 µg·L^{-1} for a mixed assemblage of Lake Ontario algae (Wong et al. 1982).

The interim water quality guideline for triphenyltin for the protection of freshwater life is 0.022 µg·L^{-1} (CCME 1992). It was derived by multiplying the 30-d LOEL for growth of 0.22 µg·L^{-1} for juvenile fathead minnows (Jarvenin et al. 1988) by a safety factor of 0.1 (CCME 1991).

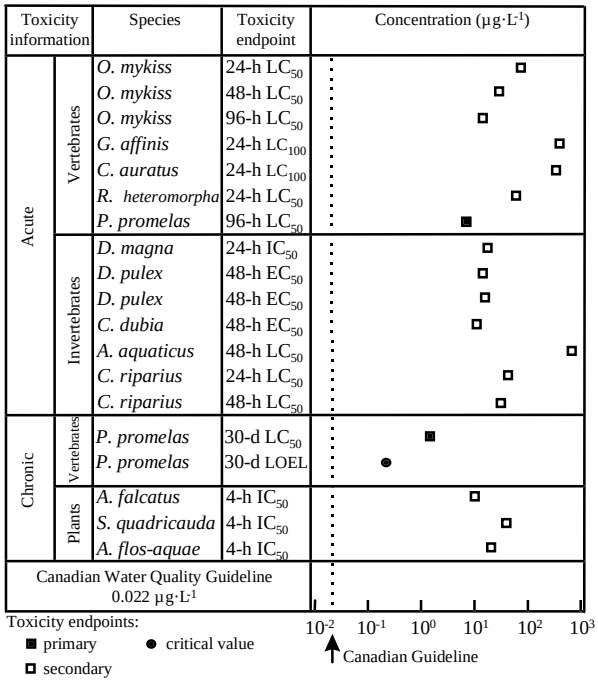

Figure 2. Select freshwater toxicity data for triphenyltin.

Marine Life

Tributyltin

Chronic toxicity data were found for three species of marine fish. The most sensitive study was Hall et al. (1988), who reported that a 28-d exposure to a tributyltin concentration of 0.093 µg·L^{-1} resulted in a significant decrease in the growth of inland silverside *(Menidia beryllina)* larvae. Survival of the inland silverside was not

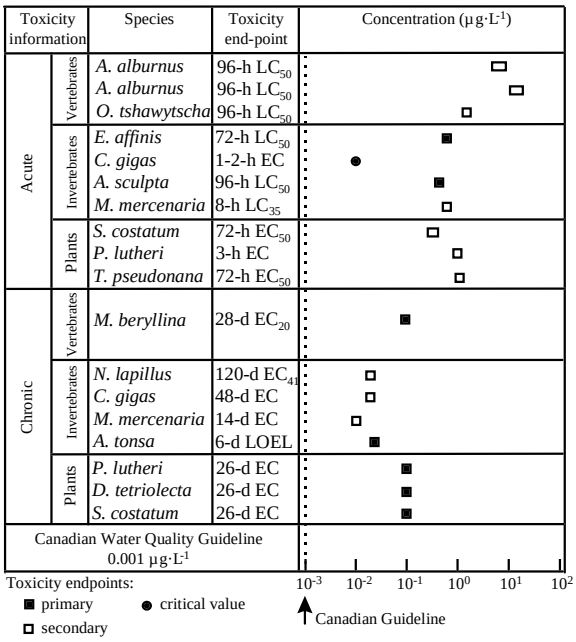

Figure 3. Select marine toxicity data for tributyltin.

significantly affected at this concentration of tributyltin. Acceptable tributyltin toxicity studies were found for 18 marine invertebrate species. The most sensitive organism was the spat of the oyster *Crassostrea gigas*, which had a reduced ability to compensate for hypoxia when exposed for 1–2 h to a tributyltin concentration of 0.01 µg·L^{-1} (Lawler and Aldrich 1987). Similarly, Laughlin et al. (1988) found growth inhibition occurred in the clam *Mercenaria mercenaria* following a 14-d exposure to a bis(tributyltin) oxide concentration of 0.01 µg·L^{-1}. The interim water quality guideline for tributyltin for the protection of marine life is 0.001 µg·L^{-1} (CCME 1992). It was derived by multiplying the 14-d LOEL of 0.01 µg·L^{-1} for the clam *M. mercenaria* by a safety factor of 0.1 (CCME 1991).

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Excerpt from Publication No. 1299; ISBN 1-896997-34-1

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