Canadian Water Quality Guidelines for the Protection of Aquatic Life

METHYL TERTIARY-BUTYL ETHER (MTBE)

Methyl tertiary-butyl ether (MTBE, CAS registry number: 1634-04-4) is a colourless, flammable, volatile liquid most commonly used as a fuel oxygenate to boost octane levels and reduce carbon monoxide emissions when blended with gasoline. MTBE is an aliphatic ether with a molecular mass of 88.15 $g \cdot mol^{-1}$. This synthetic compound boils between 53.6 and 55.2 °C, is highly miscible in water (up to 54 $g \cdot L^{-1}$) (Jacobs et al. 2002), and has a low log octanol/water coefficient (K_{ow}) of 1.3 (Veith et al. 1983). MTBE has a relatively high vapour pressure of 245 mmHg at 25 °C and the odour resembles turpentine (Squillace et al. 1996). Given these properties, it has a low taste/odour threshold (0.02 - 0.04 $mg \cdot L^{-1}$) (USEPA 1997) for humans when present in water.

MTBE does not occur naturally in the environment and is synthesised specifically for commercial applications. It is manufactured from the petroleum refining by-product isobutene. Currently, there is only one manufacturer of MTBE in Canada. The majority of MTBE used domestically is produced outside of Canada and is imported, either as a blended component of gasoline (10-15% by volume) or in its pure state for use at processing facilities and service stations within Canada. MTBE may enter the environment at any point during its manufacture, transport, storage, and use. The largest potential sources of MTBE are from leaking underground storage tanks, spills associated with manufacture and transport, runoff from residues deposited through automobile use, and motorized water craft (Squillace et al. 1996). Initial modelling estimates by Environment Canada (Government of Canada 1992) suggested that environmental concentrations in Canada, based on production levels, could reach levels of 75 $ng \cdot m^{-3}$ in air and 6 $ng \cdot L^{-1}$ in water. Data from Environment Canada's National Pollutant Release Inventory (NPRI) report an average of 143.8 tonnes of MTBE accidentally released by manufacturing and processing facilities from 1994 to 2000. Reported releases peaked at 208.1 tonnes in 1999. These values are expected to decline in the future, due to ongoing reductions in the processing and use of MTBE in Canada.

Once released into the environment, the majority of MTBE is expected to partition into the atmosphere, given its high volatility. Significant amounts of MTBE may also be found in groundwater supplies due to its aqueous solubility. MTBE is not expected to accumulate significantly in aquatic food chains on account of its low affinity for lipids (low K_{ow},) and its low tendency to associate closely with colloidal organic matter. In the environment, MTBE is susceptible to photo-oxidation and biodegradation (Squillace et al. 1998). There is a wide variation in the persistence of methyl tertiary-butyl ether dependent on local environmental conditions, with half-life potentials ranging from a few days in air (Squillace et al. 1997) to over ten years in groundwater (Johnson et al. 2000).

Soil and water contamination by MTBE has been detected at several sites throughout the United States, with an increasing number of reports from within Canada. Recent surveys, conducted under the Canadian Environmental Protection Act by Environment Canada (Government of Canada 2001), identified 233 cases of groundwater contamination from across the country. The highest incidences of contamination were reported in British Columbia (147 cases) and Prince Edward Island (31 cases). The majority of known cases of groundwater contamination are associated with sites involving service stations and/or fuel storage facilities. Although it appears that most cases are concentrated in two coastal provinces, these numbers most likely reflect the nature of reporting and sampling as MTBE is expected to be found in any areas where blended gasoline has been used.

Water Quality Guideline Derivation

Table 1. Water quality guidelines for methyl tertiary-butyl ether for the protection of aquatic life.

Aquatic life	Guideline value ($mg \cdot L^{-1}$)
Freshwater	10
Marine	5*

*Interim guideline.

The Canadian water quality guideline for MTBE, for the protection of aquatic life, was developed according to CCME protocol (CCME 1991). The majority of the toxicity studies evaluated as acceptable under the protocol and used for guideline derivation, were conducted by private laboratories. The timing of these studies coincide with a period when concerns over the potential environmental effects of MTBE were initially considered, and most recently in an attempt to satisfy data requirements for ongoing MTBE water quality guideline development by the USEPA.

Freshwater Life

Acceptable data on the toxicity of MTBE to freshwater organisms were available for three species of fish, six species of aquatic invertebrates, and three species of plants. Only information classified as a primary study was used in the guideline derivation for aquatic life. Toxicity values across species ranged from 100 $mg \cdot L^{-1}$ *(Daphnia magna)* (Drottar and Krueger 1999a) to 4789 $mg \cdot L^{-1}$ *(Selenastrum capricornutum)* (Rousch and Sommerfield 1998).

Acute toxicity values (96-h LC_{50}) for fish ranged from 887 $mg \cdot L^{-1}$ for the rainbow trout *(Oncorhynchus mykiss)* (Hockett 1997a) to 1054 $mg \cdot L^{-1}$ for the bluegill sunfish *(Lepomis macrochirus)* (Hockett 1999a). The 96-h LC_{50} estimate for juvenile fathead minnows *(Pimephales promelas)* was 980 $mg \cdot L^{-1}$. Acute toxicity values for invertebrates ranged from 340 $mg \cdot L^{-1}$ (48-h LC_{50}) for *Ceriodaphnia dubia* (Hockett 1997b) to 1742 $mg \cdot L^{-1}$ (48-h EC_{50}, survival) for *Chironomus tentans* (Hockett 1999b).

Chronic toxicity values for fish were estimated using the fathead minnow *(P. promelas)*. Estimates of 7-d LOECs carried out by Hockett at ENSR laboratories (1997e) ranged from 388 $mg \cdot L^{-1}$ (growth) to 658 $mg \cdot L^{-1}$ (survival). The same study indicated a delay in timing of hatching for fathead minnows, while growth was affected at an IC_{25} of 288 $mg \cdot L^{-1}$. In a subsequent 31-d test conducted by Hockett (1999d), fathead minnow growth was affected at an IC_{25} of 308 $mg \cdot L^{-1}$. The lowest estimate of chronic toxicity for invertebrates was 100 $mg \cdot L^{-1}$ (21-d LOEC) for *D. magna* based on reduction in reproductive rates (Drottar and Krueger 1999a). Whole body exposure of adult *C. dubia* over five days, resulted in reduced survival at 580 $mg \cdot L^{-1}$ (LOEC) (Hockett 1997d).

Toxicity estimates for plants showed reductions in growth rates for green algae *(S. capricornutum)* as low as 103 $mg \cdot L^{-1}$ (IC_{20}) over a 96-h exposure (Hockett 1999c), to tolerances of up to 4789 $mg \cdot L^{-1}$ over a 5-d exposure (Rousch and Sommerfield 1998).

The water quality guideline for MTBE for the protection of freshwater aquatic life is 10 $mg \cdot L^{-1}$. This value was derived by multiplying the 21-d LOEC (reproduction) of 100 $mg \cdot L^{-1}$ for the most sensitive organism to MTBE, the water flea *(D. magna)* (Drottar and Krueger 1999b), by a safety factor of 0.1 (CCME 1991).

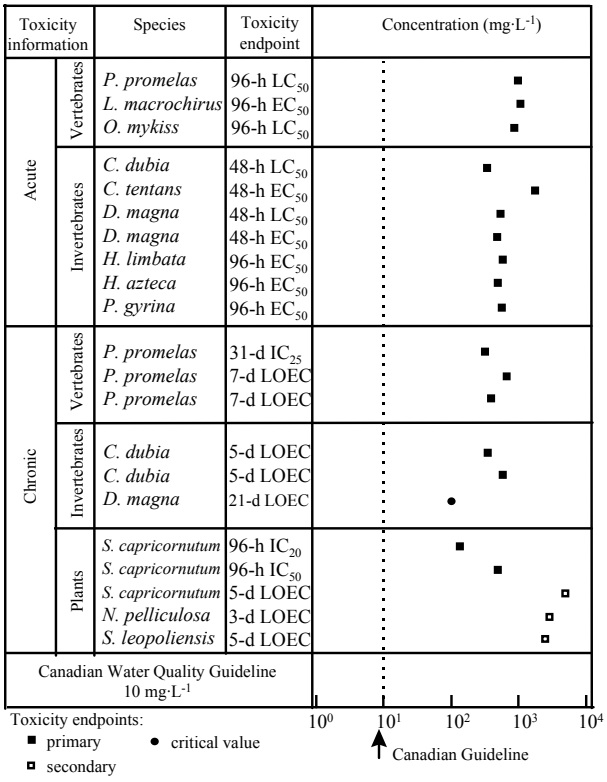

Figure 1. Select freshwater toxicity data for MTBE.

Marine Life

Data on the toxicity of MTBE was available for nine species of marine organisms. The range of studies included six species of invertebrates, two species of fish, and one marine plant. Studies classified as either primary and secondary (CCME 1991) were used for interim guideline derivation. Toxic sensitivity values varied among species, from as low as 50 $mg \cdot L^{-1}$ *(Mysidopsis bahia)* (Drottar and Krueger 1999b) up to 1950 $mg \cdot L^{-1}$ *(Mytilus galloprovinciallis)* (Stewart 2000).

Acute toxicity values for marine fish ranged from 297 $mg \cdot L^{-1}$ (96-h EC_{50}, behaviour) for the threespine stickleback *(Gasterosteus aculeatus)* (Palmer and Krueger 1999a) to 1358 $mg \cdot L^{-1}$ (96-h LC_{50}) for the sheepshead minnow *(Cyprinodon variegatus)* (Palmer and Krueger 1999b). Acute toxicity values for marine invertebrates indicated that the grass shrimp *(Palaemonetes pugio)* exhibited the lowest acute sensitivity threshold at 123 $mg \cdot L^{-1}$ (96-h LOEC) based on changes to behaviour and survival (Mank and Krueger 1999). Mediterranean mussels *(M. galloprovinciallis)* were able to survive under concentrations of up to 1950 $mg \cdot L^{-1}$ (48-h EC_{50}), despite some incidences of anomalous shell development

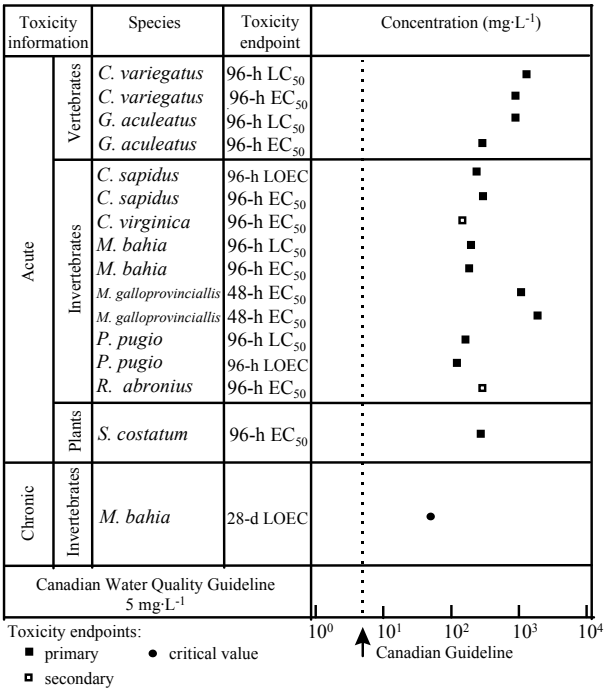

Figure 2. Select marine toxicity data for MTBE.

(Stewart 2000).

There were no chronic toxicity results available for marine fish. Values of chronic toxicity to invertebrates were based on a single study of the saltwater mysid *(M. bahia)* conducted by Drottar and Krueger at Wildlife International laboratories (1999c). Results of the 28-d exposure indicated growth (20% reduction) and reproduction (88% reduction) to be the most sensitive biological endpoints monitored. The LOEC based on reproduction was 50 $mg \cdot L^{-1}$.

Acceptable toxicity data was available for only one species of marine plant, the diatom *(Skeletonema costatum)*. The 96-h exposure experiment (Palmer and Krueger 2000) examined the effects of MTBE on algal growth rate. Results produced a 96-h EC_{50} value of 139 $mg \cdot L^{-1}$. Results also indicated that MTBE was algicidal at 725 $mg \cdot L^{-1}$ but only algistatic at concentrations of 368 $mg \cdot L^{-1}$ and lower.

The interim water quality guideline for methyl tertiary-butyl ether for the protection of marine life is 5 $mg \cdot L^{-1}$. This value was calculated by multiplying the most sensitive chronic endpoint, a 28-d LOEC (reproduction) for the saltwater mysid *(M. bahia)* of 50 $mg \cdot L^{-1}$ (Drottar and Krueger 1999b), by a safety factor of 0.1 (CCME 1991).

Currently available data on marine organisms do not meet the requirements of a full marine guideline in accordance with the CCME protocol (CCME 1991). At present data are only sufficient to support an interim guideline. Although toxicological data are available for three species of fish (Bengtsson and Tarkpea 1983; Palmer and Krueger 1999a; Palmer and Krueger 1999b) all are acute studies. At least two chronic fish studies (partial or full lifecycle) are required for full guideline derivation. Data exists for several species of marine invertebrates, but only one was of a chronic exposure design (Palmer and Krueger 2000). The protocol requires at least two chronic (partial or full lifecycle) studies from marine invertebrates of different classes for full guideline classification. Before the current interim guideline can be re-evaluated for complete guideline status two additional studies examining chronic toxicity for at least two different species of fish and one additional study examining the chronic toxicity for another species of invertebrate are required.

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