Canadian Water Quality Guidelines for the Protection of Aquatic Life

DIMETHOATE

Dimethoate ($C_5H_{12}NO_3PS_2$) is a broad-spectrum organophosphorus pesticide used in a wide variety of agricultural applications in Canada. It has a CAS name and number of O,O-dimethyl S-[2-(methylamino)-2-oxoethyl] phosphorodithioate and 60-51-5, respectively. Dimethoate has the IUPAC names O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate and 2-dimethoxyphosphinothioylthio-N-methylacetamide. In Canada, dimethoate is registered under the trade names Cygon (Cyanamid), Lagon (U.A.P.), Hopper Stopper (Peacock Industries), and Sys-Tem (Chipman) (CCME 1993).

Dimethoate is an insecticide and acaricide that exhibits both contact and systemic activity. Agricultural uses of dimethoate in Canada include pest control in barley, canola, oats, pastures, rye, wheat, alfalfa, beans, clovers, corn, flax, mushrooms, peas, potatoes, sugar beets, and sunflowers (Ali et al. 1989). Dimethoate is also used to control pests on ornamental plants in field and greenhouse applications (Agriculture Canada 1991). Target pests in agricultural applications include aphids, grasshoppers, leafhoppers, lygus bugs, mites, plant bugs, say stink bugs, sweet clover weevils, tarnished plant bugs, and thrips (Ali et al. 1989). Dimethoate is effective as a residual spray on the walls of farm buildings for fly control. In forestry applications, dimethoate is used as a foliar spray to control spruce budworm, pine shoot moth, and seed and cone insects (Adams 1988).

In Canada, pesticide products containing dimethoate are primarily sold as emulsifiable concentrates and bran baits. Dimethoate-based pesticides may be applied using either aircraft or ground spray equipment. Bran baits are frequently used to control grasshoppers, with labelled application rates of 2.0–3.0 kg a.i.·ha^{-1} (Ali et al. 1989).

Constable and Bharadia (1990) summarized the existing information on the sales of dimethoate in Canada from 1983 to 1987 and found that the bulk of the dimethoate sold in Canada was used in Ontario and the Prairie provinces. Quebec, the Atlantic provinces, and British Columbia also reported dimethoate sales during this time.

The use of dimethoate varied significantly on an annual basis due to large oscillations in populations of target pest species. Peak sales of dimethoate in the prairie provinces (1986) coincided with grasshopper infestations in Alberta and Saskatchewan and wheat midge outbreaks in Saskatchewan. In 1988, dimethoate was used for Russian wheat aphids in winter wheat, fall rye, triticale, and barley. This may have increased sales and use in the Prairie provinces in the late 1980s (Constable and Bharadia 1990).

The low log K_{oc} of dimethoate (0.96–1.44 mg·L^{-1}) and high water solubility (25 g·L^{-1}) indicate that dimethoate has a low affinity for most soil types and therefore a relatively high potential for movement through agricultural soils. Irrigation or rain following dimethoate applications could lead to detectable concentrations in agricultural runoff and leaching into groundwater.

The only reported concentrations of dimethoate in Canadian freshwater are in Quebec, where values ranged from the limit of detection (0.015 µg·L^{-1}) to 2.9 µg·L^{-1} (Giroux et al. 1997).

Although research indicates that dimethoate tends to rapidly degrade in water, it may be relatively persistent in Canadian freshwaters under some conditions. In general, degradation rates depend on temperature, pH, and the presence of microbiota and heavy metal ions. Dimethoate is considered to be thermally unstable, therefore, transformation rates are temperature dependent (El Beit et al. 1978a, 1978b). Since hydrolysis is a major transformation process in water, degradation rates of dimethoate are likely to be variable in the environment depending on ambient temperature.

If dimethoate enters natural waters, hydrolysis is the most predominant fate process, with warmer temperatures and alkaline pH increasing the rate of degradation. Photodegradation, volatilization, adsorption to sediment, and bioconcentration are not expected to be significant pathways. A typical half-life for dimethoate may be as long as 8 weeks, and possibly longer under conditions that do not favour degradation.

Table 1. Water quality guidelines for dimethoate for the protection of aquatic life (CCME 1993).

Aquatic life	Guideline value (µg·L^{-1})
Freshwater	6.2*
Marine	NRG†

*Interim guideline.

†No recommended guideline.

No studies were found on the potential for bioaccumulation of dimethoate in freshwater fish, amphibians, invertebrates, or aquatic plants as a result of chronic exposures in water. The relatively low log K_{ow} of 0.70–0.78 (WHO 1989; Worthing and Hance 1991) suggests that dimethoate would not bioaccumulate in aquatic organisms.

Water Quality Guideline Derivation

The interim Canadian water quality guideline for dimethoate for the protection of freshwater life was developed based on the CCME protocol (CCME 1991).

Freshwater Life

Data on the acute and/or chronic effects of dimethoate exist for 13 species of freshwater fish representing seven families. Acute toxicity values for the three fish species found in Canada ranged from 6.0 $mg \cdot L^{-1}$ for bluegill *(Lepomis macrochirus)* (96-h LC_{50}) to 22.4 $mg \cdot L^{-1}$ for carp *(Cyprinus carpio)* (7-d LC_{50}). Three other fish species not native to Canada had similar sensitivities to dimethoate.

A wide range of sublethal effects has been reported in freshwater fish chronically exposed to dimethoate. Studies on the chronic toxicity of dimethoate were found for six species of freshwater fish representing five families. Of these, only one species (carp) is native to Canada. Basak and Konar (1978) reported a number of histological effects on carp exposed to 5.6 $mg \cdot L^{-1}$ dimethoate for 62 d.

Dimethoate is a potent acetylcholinesterase (AChE) inhibitor, and most of its toxic effects stem from the inhibition of these enzymes (Coppage 1972). Effects on growth, feeding rate, and activity level are all related to AChE inhibition (Hameed and Vadamalai 1986). In addition, a number of morphological and histological changes have been associated with exposure (Basak and Konar 1978; Dalela et al. 1979; Gill et al. 1988). There is some indication that chronic exposure to dimethoate may result in teratogenic effects, such as the induction of Siamese twins (Manna and Sadhukhan 1986).

Studies on the acute toxicity of dimethoate were found for several species of freshwater amphibians. The 96-h LC_{50} static renewal tests on the frog *Rana cyanophlyctis* were 36.0 and 39.0 $mg \cdot L^{-1}$ for females and males, respectively (Mudgall and Patil 1987). Khangarot et al. (1985) reported that the newly hatched tadpoles of a related species in India (*R. hexadactula*) were very sensitive to dimethoate, with a 96-h LC_{50} of 0.0078 $mg \cdot L^{-1}$.

Chronic tests (100 d) on the South African clawed frog *(Xenopus laevis)* beginning from the tadpole lifestage showed that they were relatively sensitive to dimethoate. The no-observed-lethal concentration (NOLC) was 1 $mg \cdot L^{-1}$, and the NOEC based on growth and development was 32 $mg \cdot L^{-1}$ (Sloof and Canton 1983).

Studies on the acute toxicity of dimethoate were available for 13 species of freshwater invertebrates. Of the organisms tested, two snails were found to be the most sensitive; however, these subtropical species are not native to Canada and have not been introduced. Acute toxicity values ranged from 0.024 $mg \cdot L^{-1}$ for subtropical gastropods *(Limnaea acuminata* and *Thiara lineata)* (48-h LC_{50}) to 2.63 $mg \cdot L^{-1}$ for freshwater prawn *(Macrobrachium lamerrii)* (72-h LC_{50}).

Studies on the chronic effects of dimethoate were found for four invertebrates. Beusen and Neven (1989) reported 23-d EC_{50} values of 0.13 and 0.15 $mg \cdot L^{-1}$ for the immobilization of *Daphnia magna* by a 10% emulsifiable concentrate (EC) formulation and a 99% pure form of dimethoate, respectively. The LOEC for reproduction was 0.062 $mg \cdot L^{-1}$ for the EC formulation (Beusen and Neven 1989). A 16-d EC_{50} of 0.31 $mg \cdot L^{-1}$ for reproduction was also reported for daphnids by Hermens et al. (1984). Sloof and Canton (1983) reported a 21-d NOLC of 0.032 $mg \cdot L^{-1}$ for *D. magna* but did not specify a LOEC.

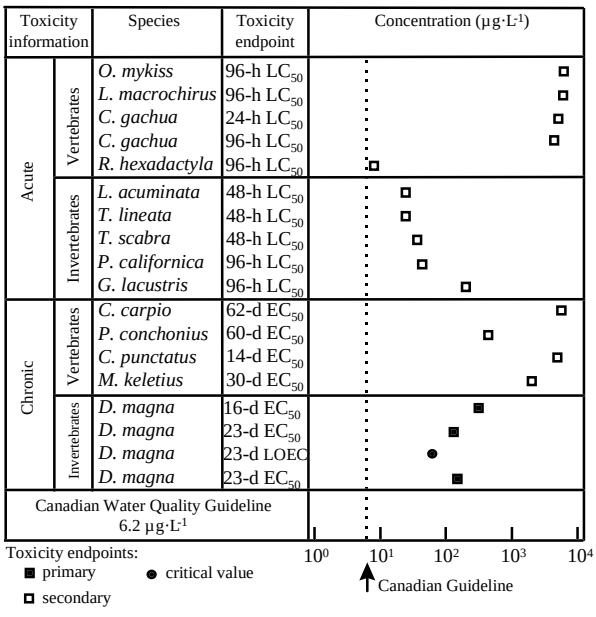

Figure 1. Select freshwater toxicity data for dimethoate.

Sloof and Canton (1983) reported a NOEC (endpoint = changes in growth and biomass) for dimethoate of 100 mg $\cdot L^{-1}$ for the alga *Scenedesmus pannonicus* in 4-d static bioassays. They also found a 7-d NOEC of 32 mg$\cdot L^{-1}$ for the duckweed *Lemna minor* using specific growth rate as the endpoint.

The database on the toxicity to freshwater biota was insufficient to derive a full Canadian water quality guideline for dimethoate. This will require an additional primary study on the chronic exposure of dimethoate to a coldwater fish and on the phytotoxicity to an algal species. Adequate data, however, were available to derive an interim water quality guideline (CCME 1991). Unfortunately, no data were found on the toxicity of dimethoxon to freshwater organisms; therefore, the guideline refers only to the parent compound, dimethoate. Studies with dimethoate should account for some of the effects of dimethoxon since dimethoate is metabolized to dimethoxon and is responsible for actual toxicity in nontarget organisms (O'Brien 1967).

The interim water quality guideline for dimethoate for the protection of freshwater life is 6.2 µg$\cdot L^{-1}$ (i.e., 0.0062 mg$\cdot L^{-1}$). It was derived by multiplying the LOEL from a chronic study using a nonlethal endpoint (reduced reproduction) of 0.062 mg$\cdot L^{-1}$ for the most sensitive organism, *D. magna* (Beusen and Neven 1989), by a safety factor of 0.1 (CCME 1991).

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