Canadian Water Quality Guidelines for the Protection of Aquatic Life

METRIBUZIN

Metribuzin ($C_8H_{14}N_4OS$) is a member of the triazine family of herbicides. It has a CAS name and number of 4-amino-6- (1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazine-5(4H)-one and 21087-64-9, respectively. Metribuzin has a low vapour pressure (0.058 mPa at 20ºC) and octanol–water partition coefficient (37.6 at pH 5.6, 20ºC) and a high water solubility (1.05 $g \cdot L^{-1}$ at 20ºC). Tradenames include Sencor and Lexone (Tomlin 1994).

Metribuzin was first registered in Canada in 1971 and is used for pre- and post-emergence control of broadleaf and grass weeds in spring wheat and barley (Agriculture and Agri-Food Canada 1997). It is a selective systemic herbicide that inhibits photosynthesis (Tomlin 1994).

From 1986 to 1988, use of metribuzin ranged between 370 kg to 258 t, with most being used in eastern Canada (Seatech Investigation Services Ltd. 1988; Moxley 1989).

Contamination of surface waters by metribuzin could result from accidental discharge or direct application to watercourses, spray and vapour drift, precipitation, or surface runoff and groundwater intrusions from treated lands. Losses of soil-applied metribuzin primarily occur through movement in the water phase through soil runoff as opposed to translocation with eroded soil sediment (Glotfelty et al. 1984). Runoff events occurring within 2 weeks after soil application are the most important with respect to delivery to watercourses.

Concentrations of metribuzin detected in Canadian freshwater range from 0.001 $\mu g \cdot L^{-1}$ in Ontario (Frank et al., 1987) to 187 $\mu g \cdot L^{-1}$ in New Brunswick (O'Neill et al. 1988).

Data on the aquatic fate of metribuzin are scarce. The half-life of metribuzin in natural water bodies ranges from 2.5 to 6.5 d (Shaw and Flint 1971; CCME 1990). Volatilization to the atmosphere is not a major fate process for metribuzin in water because of its low vapour pressure (Muir 1991).

Little information was found on the adsorption of metribuzin to aquatic sediment. No metribuzin was detected in 45 suspended solids samples collected from 12 Ontario streams flowing into the Great Lakes between 1974 and 1976 (detection limit 0.05 $\mu g \cdot g^{-1}$) (Frank et al. 1979).

Metribuzin does not appear to bioaccumulate in aquatic organisms, which is supported by its low octanol–water coefficient. No metribuzin residues were detected in whole fish homogenate of brown bullheads *(Ictalurus nebulosus)*, gizzard shad *(Dorosoma cepedianum)*, and black crappie *(Pomoxis nigromaculatis)* collected in 1974 even though metribuzin had been found in 4.4% of the water samples collected between 1973 and 1975 (Roberts et al. 1979).

Water Quality Guideline Derivation

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

Freshwater Life

Metribuzin is moderately toxic to aquatic invertebrates and vertebrates. Reported acute toxicities (96-h LC_{50}) are 80–>100 $mg \cdot L^{-1}$ for bluegill sunfish; 42–76 $mg \cdot L^{-1}$ for rainbow trout *(Oncorhynchus mykiss)*; 140 $mg \cdot L^{-1}$ for harlequin fish; and >100 $mg \cdot L^{-1}$ for channel catfish (Mayer and Ellersieck 1986; Worthing and Walker 1987). A 48-h LC_{50} of 150 $mg \cdot L^{-1}$ was reported for a mixed culture of the copepods *(Diaptomus mississippienis* and *Eucylops agilis)* (Naqvi et al. 1981).

Inhibition of aquatic plant growth by metribuzin occurs at concentrations lower than those affecting invertebrates and fish. A concentration of 50 $\mu g \cdot L^{-1}$ of metribuzin was found to significantly inhibit the growth of five species of algae from 24 to 62% over 6 d (Arvik et al. 1973). Metribuzin concentrations ≥428.6 $\mu g \cdot L^{-1}$ over 96-h were found to reduce *Euglena* chlorophyll content 36% and inhibit

Table 1. Water quality guidelines for metribuzin for the protection of aquatic life (CCME 1990).

Aquatic life	Guideline value ($\mu g \cdot L^{-1}$)
Freshwater	1.0*
Marine	NRG†

*Interim guideline.

†No recommended guideline.

photosynthesis (Richardson et al. (1979). Eley et al. (1983) reported that 100 $\mu g \cdot L^{-1}$ reduced growth and oxygen production rates of log-phase blue-green alga *Anacystis nidulans* by 25 and 18%, respectively.

The interim water quality guideline for metribuzin for the protection of freshwater life is 1.0 $\mu g \cdot L^{-1}$ (CCME 1990). It was derived by multiplying the LOEC, based on a reduction of growth and reproduction, of 10 $\mu g \cdot L^{-1}$ (Forney and Davis 1981) for duckweed *(Lemna perpusilla)* by a safety factor of 0.1 (CCME 1991).

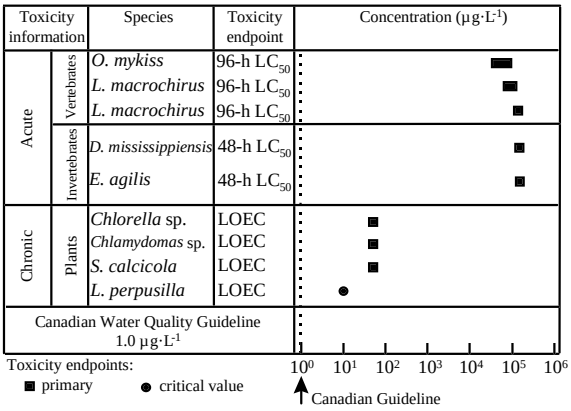

Figure 1. Select freshwater toxicity data for metribuzin.

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