Canadian Water Quality Guidelines for the Protection of Aquatic Life

DICLOFOP-METHYL

Diclofop-methyl ($C_{16}H_{14}Cl_2O_4$) is a polycyclic alkanoic acid herbicide with a CAS name and number of (methyl)-2-[4-(2,4-dichloro-phenoxy) phenoxy] propionic acid and 51338-27-3, respectively (Tomlin 1994). Diclofop-methyl undergoes hydrolysis to form diclofop-acid (referred to here as diclofop), a compound that also exhibits herbicidal properties (Swanson and Lintott 1989). Diclofop-methyl was registered in Canada in 1977 and is sold under the tradename Hoe-Grass (Agriculture and Agri-Food Canada 1997).

Diclofop-methyl is used for postemergence control of wild oats, wild millets, and other annual grass weeds in wheat, barley, rye, red fescue, and broad-leaved crops such as soya beans, sugar beet, flax, legumes, potatoes, and cucumbers. Diclofop-methyl is a selective systemic herbicide that is used primarily in the prairies. It destroys the cell membrane, prevents the translocation of assimilates to the roots, reduces the chlorophyll content, and inhibits photosynthesis and meristem activity (Tomlin 1994). In 1988, over 1×10^6 kg of diclofop-methyl were used in Canada (Agriculture Canada and Environment Canada 1987).

Erosion of diclofop-methyl adsorbed to soil and, to a small extent, its desorption and solubilization into water are the possible main routes for entry into the environment (Hickman et al. 1983). Concentrations in Canadian aquatic environments range from 0.11 to 6.1 $\mu g \cdot L^{-1}$ (Grover 1983; Waite et al. 1986).

In a laboratory microcosm study diclofop-methyl underwent almost complete hydrolysis within the first 8 h in the water column. Its depletion occurred concurrently with a rapid increase in the activity of diclofop, which peaked 4 h after the addition of diclofop-methyl. The diclofop slowly degraded to 50% of the peak concentration 11 d after the initial diclofop-methyl spike (Lintott 1993).

Walker et al. (1988) studied the biodegradation of diclofop-methyl in sterilized and unsterilized estuarine water/sediment slurries. The mean half-life of diclofop-methyl in nonsterile estuarine water was 9.2 h. When a nonsterile sediment slurry was added to this water, the mean half-life value was reduced to 4.5 h. A reduction in mean half-life was also observed when sterile sediment was added to sterile estuarine water (value decreased from 160.6 h to 48.5 h). This suggests that the addition of sediment assists in catalyzing diclofop-methyl hydrolysis. When the addition of sterile and nonsterile sediment to nonsterile estuarine water was compared, however, degradation was greater in the presence of nonsterile sediment (values for sterile sediment = 51.7, 49.9, and 43.8 h, versus values for nonsterile sediment = 2.6, 3.1, and 7.9 h). This shows the important role that microorganisms associated with sediment play in the biodegradation of diclofop-methyl.

Information on the bioaccumulation of diclofop-methyl was limited to a 28-d study conducted by Gildemeister et al. (1991) using Hoe 023408-^{14}C. BCFs of 112–643 for whole fish, 34–95 for edible tissue, and 225–1113 for nonedible tissue were reported in bluegill sunfish *(Lepomis macrochirus)*. The peak concentrations in the different fish parts were reached after 7 d, followed by a steady decline to half that concentration in nonedible parts and constancy in the edible parts. After being placed in clean water, concentrations decreased significantly within the first 24–72 h. Clearance from whole fish was an 88%, reduction in edible parts and 70–82% reduction in nonedible parts over 14 d.

Water Quality Guideline Derivation

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

Freshwater Aquatic Life

Acute toxicity values (96-h LC_{50}s) for fish range from 150 to 540 $\mu g \cdot L^{-1}$ for bluegill *(L. macrochirus)* (Mayer and Ellersieck 1986; Smith and Schweitzer 1990). Hoe-Grass (36% a.i.) produced 96-h LC_{50}s of 90, 180, and 270 $\mu g \cdot L^{-1}$ for fingerling rainbow trout *(Oncorhynchus mykiss)* with decreasing water hardness of 44.8, 37.1, and 25.8 $mg \cdot L^{-1}$

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

Aquatic life	Guideline value ($\mu g \cdot L^{-1}$)
Freshwater	6.1
Marine	NRG*

*No recommended guideline.

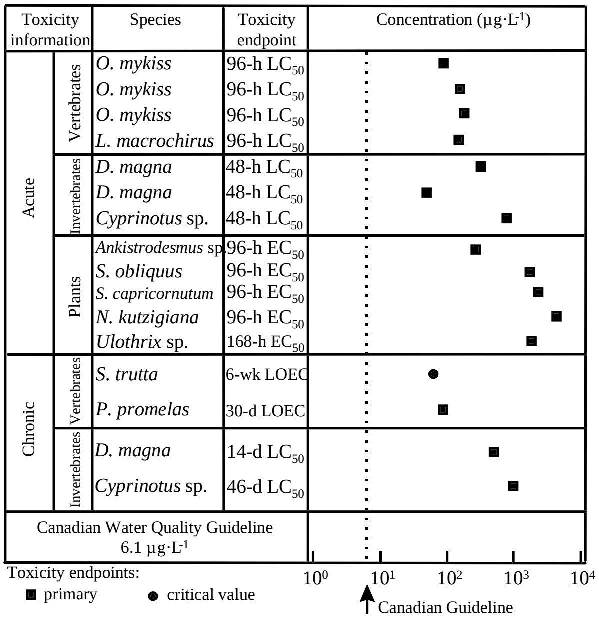

Figure 1. Select freshwater toxicity data for diclofop-methyl.

of $CaCO_3$, respectively (Matthiessen et al. 1988).

A chronic 6-week study on brown trout *(Salmo frutta)* reported a NOEC of 8 µg·L^{-1} based on egg mortality and fry and embryo development, and a LOEC of 61 µg·L^{-1} based on a decreased rate of fish fry development (Fischer and Knauf 1981). In a 30-d study on egg hatchability and survival and growth of fathead minnow *(Pimephales promelas)* larvae, a NOEC of 39 µg·L^{-1} and a LOEC of 86 µg·L^{-1} Hoelon (36% a.i.) were recorded (EG&G Bionomics 1981).

The acute toxicity values for invertebrates ranged from a 48-h LC_{50} of 317 µg·L^{-1} for *Daphnia magna* to a 48-h LC_{50} of 778 µg·L^{-1} for *Cyprinotus* sp. (Lintott 1993). An unacceptable study, however, reported a 48-h LC_{50} value for *D. magna* of 4030 µg·L^{-1} (WSSA 1989).

In a chronic study, using Hoe-Grass, a significant (50%) decrease in population size of *D. magna* was observed at 500 µg·L^{-1} after 14 d of treatment. Exposure of *Cyprinotus* sp. to diclofop-methyl showed no significant growth inhibition until 46 d had elapsed, when a statistically significant (20%) decrease in the population growth was reported at 1000 µg·L^{-1}. It was suggested by Lintott (1993) that the ostracod population was affected by consumption of sediment-bound diclofop.

Information on the phytotoxicity (EC_{50}s) of Hoe-Grass (28.4% a.i.) for algal species ranged from 268 µg·L^{-1} for *Ankistrodesmus* sp. to 4357 µg·L^{-1} for *Nitzschia kutzigiana* (Lintott 1993).

The water quality guideline for diclofop-methyl for the protection of freshwater life is 6.1 µg·L^{-1} (CCME 1993). It was derived by multiplying the 6-week LOEC of 61 µg·L^{-1} (Fischer and Knauf 1981) for the most sensitive organism, the brown trout *(S. trutta),* by a safety factor of 0.1 (CCME 1991). Since diclofop-methyl hydrolyzes quickly to diclofop, it is assumed that this guideline provides protection against the adverse effects of both compounds.

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