Canadian Water Quality Guidelines for the Protection of Aquatic Life

BROMOXYNIL

Bromoxynil is the common name for a group of benzonitrile herbicides, including bromoxynil phenol (the parent compound) and ester derivatives. The parent compound ($C_7H_3Br_2NO$) is a colourless, odourless solid with a CAS name of 3,5-dibromo-4-hydroxybenzonitrile. It is also known as 4-hydroxy-3,5-dibromo-benzonitrile. The octanoate ester, chemically known as 2,6-dibromo-4-cyanophenyl octanoate or 3,5-dibromo-4-octanoyloxy-benzonitrile, is a waxy, brown solid. The CAS registry numbers for bromoxynil phenol and octanoate ester are 1689-84-5 and 1689-99-2, respectively.

Used as a contact, post-emergent herbicide, bromoxynil selectively controls annual and perennial broadleaf weeds (e.g., buckwheat, lamb's-quarters) in cereal crops (Agriculture and Agri-Food Canada 1997). Bromoxynil decreases cellular ATP levels by de-coupling oxidative phosphorylation. Bromoxynil is commonly formulated with other herbicides (e.g., MCPA and diclofop-methyl) to control a broader spectrum of weeds (Nalewaja and Skrzypczak 1985). Herbicide products may be formulated using the phenol form of bromoxynil, its potassium salt, or one of its four common esters (octanoate, heptanoate, pentanoate, and butyrate). In Canada, bromoxynil products are typically sold as emulsifiable concentrates using the octanoate and pentanoate esters (Agriculture and Agri-Food Canada 1997).

Contamination of surface water occurs directly via spray drift from aerial or ground boom spraying operations and indirectly through soil erosion runoff from treated areas, and deposition of dust particles with adsorbed bromoxynil. Extreme contamination may result from pesticide spills, deliberate dumping of tank residues, or improper equipment-washing operations (Frank et al. 1987). In Saskatchewan, only 1 out of 42 samples (from seven watercourses) collected in 1988–89 contained a detectable level (0.04 $\mu g \cdot L^{-1}$) of bromoxynil (SEPS 1990). Of 22 samples collected from each of the Turtle and Ochre Rivers, Manitoba, four and five samples, respectively, had detectable residues (>2 $ng \cdot L^{-1}$) (Muir and Grift 1987). Bromoxynil phenol is thought to have a low potential to leach through soils and seldom is detected in groundwater (Frank et al. 1987; McRae 1991; Waite et al. 1992).

Bromoxynil phenol is moderately soluble in water (solubility = 130 $mg \cdot L^{-1}$) but because of its acidic nature, bromoxynil tends to form potassium (K) and sodium (Na) salts which dissolve readily in water (The Merck Index 1989). Photolysis and hydrolysis are important to the removal of bromoxynil from water. Bromoxynil phenol degrades rapidly (half-life < 30 min) at wavelengths around 313 nm (Plimmer 1970; Kochany et al. 1990). The half-life of octanoate ester in sterile water and under artificial light is 4.6 d (Rhône-Poulenc 1991a). Hydrolysis half-lives for the phenol range from 34.1 d at pH 5 to 1.7 d at pH 9 (Rhône-Poulenc 1990a). Though bromoxynil octanoate is virtually insoluble in water (solubility = 80 $\mu g \cdot L^{-1}$) it rapidly hydrolyzes to the phenol at alkaline pH (Rhône-Poulenc 1991b). Muir et al. (1991) reported 42% hydrolysis of esters in 4 h in fortified pond water.

The half-life of bromoxynil phenol for prairie wetland ponds is reported as 9–17 d, though residues (>2 $ng \cdot L^{-1}$) may remain up to 120 d after application (Muir et al. 1991). A 1:1 mixture of octanoate and butyrate esters degrades rapidly (within 1 h) to bromoxynil phenol when applied (450 $g \cdot L^{-1}$ a.i.) to a prairie wetland mesocosm (pH = 8.2) (Muir et al. 1991). Bromoxynil phenol distributes rapidly throughout the water column while the hydrophobic octanoate and butyrate esters remain in the surface microlayer or sorb to sediments (Muir et al. 1991).

No information exists on bromoxynil accumulation in aquatic biota. Although octanoate ester has a relatively high log K_{ow} = 5.46, it likely degrades faster than it can be taken up by aquatic organisms (Loken 1988; Muir et al. 1991; Rhône-Poulenc 1991b).

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

Aquatic life	Guideline value ($\mu g \cdot L^{-1}$)
Freshwater	5.0
Marine	NRG*

*No recommended guideline.

Water Quality Guideline Derivation

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

Freshwater Life

Lethal concentrations (LC_{50}s) of bromoxynil (phenol and esters) in fish range from 4 to 60 000 µg·L^{-1} (Alabaster 1969; Muir et al. 1991). The toxicity of the phenol depends on pH and water hardness. Under basic conditions, bromoxynil phenol ionizes (pK_a = 4.06) to the less toxic phenolate anion (USEPA 1984; Merck Index 1989). Reported 96-h LC_{50} values of bromoxynil phenol to golden orfe fish *(Leuciscus idus melanotus)* are 200, 2000, and 20 000 µg·L^{-1} at pH 6.2, 7.2, and 8.2, respectively (Grohmann and Sobhani 1980). A ten-fold increase in water hardness (20 to 250 mg·L^{-1}) corresponded to a increase in 48-h LC_{50}s (5000 to 60 000 µg·L^{-1}) for harlequin fish *(Rasbora heteromorpha)* (Alabaster 1969).

Fish are more sensitive to the octanoate ester than the phenol. For example, the 96-h LC_{50}s for rainbow trout *(Oncorhynchus mykiss)* to the octanoate and phenol forms are reported as 100 and 2000 µg·L^{-1}, respectively (Rhône-Poulenc 1981a, 1985a). Similarly, bluegill sunfish *(Lepomis macrochirus)* have 96-h LC_{50}s for the octanoate and phenol forms of 61 and 4000 µg·L^{-1}, respectively (Rhône-Poulenc 1981b, 1985b).

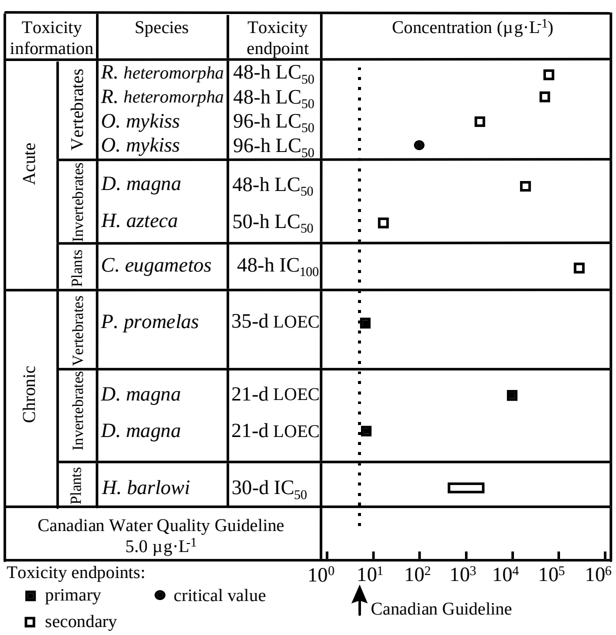

Figure 1. Select freshwater toxicity data for bromoxynil.

Limited data are available on the chronic toxicity of bromoxynil to fish. Fathead minnows *(Pimephales promelas)* exposed to the octanoate ester for 35 d have a LOEC and NOEC of 5.7 and 3.4 µg·L^{-1}, respectively (Rhône-Poulenc 1991c). Fathead minnow embryos and larvae exposed to bromoxynil octanoate for 21 d have a NOEC of 9.0 µg·L^{-1} (Rhône-Poulenc 1987).

The bromoxynil octanoate ester also appears more toxic than bromoxynil phenol to invertebrates. For example, water fleas *(Daphnia magna)* have 48-h EC_{50}s of 110 and 19 000 µg·L^{-1} for octanoate and phenol, respectively (Rhône-Poulenc 1981c, 1985c). For 21-d exposures, the NOEC and LOEC for bromoxynil octanoate are 2.5 and 5.9 µg·L^{-1}, while the NOEC and LOEC for bromoxynil phenol are 3 100 and 9 800 µg·L^{-1}, respectively (Rhône-Poulenc 1991d, 1991e). Amphipods *(Hyalella azteca)* caged in prairie wetland ponds suffered significant mortality at concentrations of 1:1 octanoate:butyrate ester >52.1 µg·L^{-1}, although natural populations of *H. azteca* or other aquatic invertebrates were unaffected (Muir et al. 1991). A 50-h LC_{50} is estimated at 16.8 µg·L^{-1}.

The 30-d IC_{50}s for bromoxynil phenol for growth inhibition of green algae (Chlorophyta) range from 500 µg ·L^{-1} *(Hormidium barlowi)* to >10 000 µg·L^{-1} for 13 other species (Cullimore 1975). Extremely high concentrations of bromoxynil phenol (277 000 µg·L^{-1}) are required to completely inhibit the growth (as measured by cell counts) of *Chlamydomonas eugametos* (Hess 1980). Duckweed *(Lemna gibba)* has a 5-d IC_{50} of 250 µg·L^{-1} for bromoxynil octanoate (Rhône-Poulenc 1990b).

As the octanoate ester is more toxic than the phenol form, but is much less persistent, the guideline derivation could be based on either an acute study using the octanoate ester or a chronic study using the phenol form (whichever is more sensitive). Using these criteria, the LOEC for bromoxynil is 100 µg·L^{-1} octanoate ester for rainbow trout (Rhône-Poulenc 1981b). This value, multiplied by a safety factor of 0.05 provides a water quality guideline of 5.0 µg·L^{-1} (CCME 1991, 1993). This value refers to the total concentration of bromoxynil phenol and its derivatives in water.

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