Canadian Water Quality Guidelines for the Protection of Agricultural Water Uses

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 and number of 3,5-dibromo-4-hydroxybenzonitrile and 1689-84-5, respectively. Bromoxynil is also known as 4-hydroxy-3,5-dibromo-benzonitrile. The octanoate ester is a waxy, brown solid and has a CAS name and number of 2,6-dibromo-4-cyanophenyl octanoate or 3,5-dibromo-4-octanoyloxy-benzonitrile and 1689-99-2, respectively.

Used as a contact, post-emergent herbicide, bromoxynil selectively controls annual and perennial broadleaf weeds (e.g., buckwheat and lamb's-quarters) in cereal crops (Agriculture and Agri-Food Canada 1997). Bromoxynil decreases cellular ATP levels by de-coupling oxidative phosphorylation. Bromoxynil's selectivity results from differences in plant morphology and rates of adsorption, translocation, and degradation (Buckland et al. 1973; Frear 1976). To control a broader spectrum of weeds, it is commonly formulated with other herbicides (e.g., MCPA and diclofop-methyl) (Nalewaja and Skrzypczak 1985). In Canada, bromoxynil products are typically sold as emulsifiable concentrates using the octanoate and pentanoate esters (Agriculture and Agri-Food Canada 1997).

Bromoxynil may adversely affect sensitive nontarget crops if elevated residue levels are present in irrigation waters. Irrigation waters may become contaminated through return flows from bromoxynil-treated fields, leaching into groundwater supplies, and from improper handling practices.

Very limited data exist regarding biotic uptake and accumulation of bromoxynil. Data from a study on two Holstein cows indicate that as much as 70% of ingested bromoxynil phenol may be retained over 9 d (St. John and Lisk 1967). A more recent study reported that cows, goats, hens, and rats readily metabolize bromoxynil octanoate to the phenol form and excrete it primarily through urine (P. McCahon, 1992, Rhône-Poulenc, Mississauga, Ontario, pers. com.)

For more information on the use, environmental concentrations, and chemical properties of bromoxynil, see the fact sheet on bromoxynil in Chapter 4 of *Canadian Environmental Quality Guidelines*.

Water Quality Guideline Derivation

The Canadian water quality guidelines for bromoxynil for the protection of agricultural water uses were developed based on the CCME protocol (CCME 1993a).

Irrigation Water

Cereal crops are relatively resistant to bromoxynil. For example, yields of canary grass *(Phalaris canariensis)*, barley *(Hordeum vulgare)*, and wheat *(Triticum aestivum)* are unaffected by bromoxynil applications of 0.3, 0.55, and 0.55 $kg\cdot ha^{-1}$, respectively (Holt and Hunter 1987; Martin et al. 1988, 1989). Some legumes are more sensitive to bromoxynil than other nontarget crop species. For example, 11 of 27 strains of soybeans *(Glycine max)* suffered severe mortality 4 weeks after treatment with 0.3 $kg\cdot ha^{-1}$ a.i. of bromoxynil phenol (Malik and Waddington 1990). Hurrelbrink soybeans have an estimated EC_{50} of 0.07 $kg\cdot ha^{-1}$ a.i. for the phenol (Malik and Waddington 1990). Alfalfa *(Medicago sativa)* is slightly more tolerant of bromoxynil phenol with a 25% reduction in crop vigour observed at 0.3 $kg\cdot ha^{-1}$ a.i. (Malik and Waddington 1990).

Sunflowers *(Helianthus annuus)*, poppies *(Papaver somniferum)*, and immature bulb onions *(Allium cepa)* are highly sensitive to bromoxynil octanoate, with 100% mortality seen at application rates of 0.3, 0.66, and 0.57 $kg\cdot ha^{-1}$ a.i., respectively (Simmonds 1968; Horowitz 1979; Gillespie and Miller 1984). Sunflowers have a NOEAR and a LOEAR of 0.07 and 0.14 $kg\cdot ha^{-1}$ a.i., respectively (Andersen et al. 1973). Flax *(Linum*

Table 1. Water quality guidelines for bromoxynil for the protection of agricultural water uses (CCME 1993b).

Use	Guideline value ($\mu g\cdot L^{-1}$)
Irrigation water	0.33*
Livestock water	11†

*Value has been revised to conform with published protocol (CCME 1993a). Values that appear in CCME (1993b) were derived according to provisional protocol, which differed with respect to AAR calculations.

†Interim guideline (CCME 1993b).

usitatissimum) is more tolerant to the octanoate, with only slight delays in maturity at application rates up to 1.12 kg·ha^{-1} a.i. (Nalewaja and Bothum 1969).

To derive irrigation guidelines, acceptable application rates (AARs) for each nontarget crop species are calculated by dividing the geometric mean of the LOEAR and the NOEAR and by an uncertainty factor of 10 (Fletcher et al. 1990; CCME 1993a). Where a NOEAR of 0 is reported, the NOEAR is estimated by dividing the LOEAR by 4.5 (CCME 1993a). The SMATCs are then calculated by dividing each AAR by the maximum irrigation rate (10^7 L·ha^{-1} per year) used in Canada. The lowest SMATCs for the three major groups of nontarget crops are 2.5 µg·L^{-1} for tame hay and cereals (wheat), 0.33 µg·L^{-1} legumes (soybeans), and 1.0 µg·L^{-1} other crops (sunflowers). Of these values, the lowest (0.33 µg·L^{-1}) is adopted as the Canadian water quality guideline for irrigation water (CCME 1993a, 1993b).

Livestock Water

Acute toxicity data for rodents and rabbits indicate that bromoxynil is toxic to mammals at relatively low levels. Of the species tested, guinea pigs are the most sensitive, with an oral LD_{50} for the phenol of 63 mg·kg^{-1} (Worthing and Walker 1983). Mice, rats, and rabbits are more tolerant, with oral LD_{50}s of 100–245, 190–440, and 260–2000 mg·kg^{-1}, respectively (Ben-Dyke et al. 1970; Worthing and Walker 1983; USEPA 1984a, 1984b; Worthing and Hance 1991). Rat studies also show that bromoxynil is more toxic when administered orally than dermally. Rabbits experience mild irritation of abraded skin when dermally exposed (WSSA 1989; P. McCahon, 1992, Rhône-Poulenc, Mississauga, Ontario, pers. com).

Rats fed bromoxynil octanoate for 2 years have a NOEL of 7.3 mg·kg^{-1} per day (IRIS 1990). The chronic NOEL for the phenol is >50 mg·kg^{-1} per day (Kenaga 1979). A 91-d NOEL of 5 mg·kg^{-1} per day has been reported for growth effects in dogs (USEPA 1984a).

Oral teratology studies indicate that bromoxynil phenol increases the incidence of fetal malformations when fed to pregnant rats. The LOEL for teratogenic effects is 35 mg·kg^{-1} per day and NOELs range from 1.5 to 15 mg·kg^{-1} per day (Agriculture Canada 1989; IRIS 1990). Maternally toxic doses of bromoxynil phenol (15 mg·kg^{-1} per day) and octanoate (21.8 mg·kg^{-1} per day) correlate with increased incidence of supernumerary ribs in rats and mice (Rogers et al. 1991).

Dietary studies with bromoxynil indicate moderate toxicity in birds. Acute oral toxicity (LD_{50}) of bromoxynil ranges from 50 mg·kg^{-1} for pheasants to >5000 mg·kg^{-1} for Japanese quail (Hill and Camardese 1986; Worthing and Hance 1991). Ring-necked pheasants also have an 8-d LC_{50} of 440 mg·kg^{-1} for the phenol (Worthing and Walker 1983). Mallard ducks *(Anas platyrhynchos)* exposed to 16.6–54 mg·kg^{-1} per day of bromoxynil octanoate suffer no adverse effects at the lower dose but experience a slight increase in regressing ovaries and a decrease in egg production at the higher dose (Rhône-Poulenc 1991a). A similar 24-week study with bobwhite quail *(Colinus virginianus)* reported a NOEL and LOEL of 11.5 and 37.2 mg·kg^{-1} per day, respectively, for increased feed consumption (Rhône-Poulenc 1991b).

Sufficient information is available to derive an interim water quality guideline for the protection of livestock watering (CCME 1993a). To develop the interim guideline, ADIs are calculated. An ADI of 15 µg·kg^{-1} per day for rats was calculated by dividing the NOEL (1.5 mg·kg^{-1} per day) by an uncertainty factor of 100 (CCME 1993a, 1993b). An RC of 57 µg·L^{-1} was calculated by multiplying the ADI by the lowest body weight:water intake rate ratio (3.8 for white leghorn chickens). To account for exposure to bromoxynil from sources other than water, the lowest RC is multiplied by an apportionment factor of 0.2, to give an interim water quality guideline of 11 µg·L^{-1} for the protection of livestock (CCME 1993a, 1993b).

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