Canadian Water Quality Guidelines for the Protection of Aquatic Life

MCPA

MCPA ($C_9H_9ClO_3$)is a systemic phenoxyacetic acid herbicide used to control a suite of broadleaf weeds in agricultural and noncropland applications (Agriculture and Agri-Food Canada 1997). MCPA has a CAS name and number of 4-chloro-2-methylphenoxy acetic acid and 94-74-6, respectively. The parent compound (MCPA-acid) is a colourless crystalline solid, but MCPA is formulated into a number of esters, salts, and amine derivatives, and primarily sold as a liquid herbicide and to a lesser extent as an emulsifiable concentrate (WSSA 1989). MCPA is often tank-mixed and applied with various other herbicides to improve control over some weeds (Alberta Agriculture 1989). Trade names of registered products in Canada include MCPA Ester, MCPA Amine, and Buctril M, among others.

In 1990, a total of 3417 t of MCPA was sold to Canada, with 94% being sold to the Prairie provinces (Agriculture Canada and Environment Canada 1990). A survey conducted in Ontario in 1983 indicated that MCPA was being used extensively in grain production (154 t) and sparingly in field corn production (1.5 t) (McGee 1984).

MCPA is a plant growth regulator and is exceptionally effective because uptake occurs bilaterally through roots and foliage, and translocation to all tissues is rapid (WSSA 1989; Tomlin 1994). MCPA has selective herbicidal properties with differences in absorption, translocation, and metabolic degradation rates among species (Frear 1976). Many plants degrade MCPA to less toxic metabolites or conjugates through decarboxylation reactions or by complexing with plant proteins (WSSA 1989).

Surface water contamination may result directly from spray drift or indirectly from runoff and/or leaching. Extreme contamination may result from spills, deliberate dumping of tank residues, or equipment-washing operations. Groundwater contamination may occur through improper handling procedures or through normal use in areas with shallow aquifers. Contamination of water with MCPA is rare despite its extensive application, high water solubility (825 $mg \cdot L^{-1}$), and low affinity for most soils (Maathuis et al. 1988). For example, 98% of 2886 surface water samples collected from Prairie provinces had nondetectable levels of MCPA (NAQUADAT 1989). Only 5 out of 447 samples collected from the Thames, Grand, and Saugeen Rivers through 1981 to 1985 contained residues >0.1 $\mu g \cdot L^{-1}$ (Frank and Logan 1988). No detectable levels of MCPA occurred in 26 samples from 13 Alberta municipalities (Hiebsch 1988). A relatively high frequency of groundwater contamination, however, was reported in Outlook Irrigation District, Saskatchewan, where 13 out of 41 samples contained residues up to 0.53 $\mu g \cdot L^{-1}$ (Maathuis et al. 1988). MCPA was detected in 31% of samples collected from numerous rivers in Quebec from 1993 to 1995 (Giroux et al. 1997). The maximum level recorded was 1.3 $\mu g \cdot L^{-1}$.

Ester, salt, and amine derivatives dissociate in alkaline water to MCPA acid (MCPA Task Force II, 1993c). For example, the half-life for MCPA 2-ethylhexyl ester (2-EHE) is 76 d at pH 7, but is 117 h at pH 9 (MCPA Task Force II, 1993a). MCPA acid, however, does not readily hydrolyze in sterile water at pHs 5–9 (Chau and Thomson 1978; MCPA Task Force II 1993b). Aerobic biodegradation of MCPA is significant, with microbes degrading 95% of dosed MCPA within 13 d (Soderquist and Crosby 1975). Benoit-Guyod et al. (1986) reported rapid degradation by ozonolysis in the dark, with half-lives from 4.2 to 11.5 h. Photodegradation half-life estimates are 1 h to 5 d (Soderquist and Crosby 1975; MCPA Task Force II 1993d).

MCPA does not accumulate in the environment because of its rapid degradation rates. In an aquatic–terrestrial laboratory model treated with 5 $kg \cdot ha^{-1}$ MCPA (99% Na-salt), for example, residues after 3 d were 27.7 $\mu g \cdot g^{-1}$, 10.196 $\mu g \cdot g^{-1}$, and 45 $\mu g \cdot L^{-1}$ for terrestrial plants, soil, and water, respectively (Virtanen et al. 1979). BCFs for fish *(Cyprinus carassius)* and snails *(Lymnea stagnalis)* were <1, with tissue concentrations of <0.024 and 0.87 $\mu g \cdot g^{-1}$, respectively (Virtanen et al. 1979). Brown

Table 1. Water quality guidelines for MCPA for the protection of aquatic life (CCME 1995).

Aquatic life	Guideline value ($\mu g \cdot L^{-1}$)
Freshwater	2.6*
Marine	4.2*

*Interim guideline.

trout *(Salmo trutta)* exposed to 10–30 mg·L^{-1} of MCPA for 28 d had similar tissue residues (3–4 mg·kg^{-1}) at all test concentrations (Hattula et al. 1978). Fish similarly exposed to 100 mg·L^{-1} MCPA for 3–5 d also accumulated residues of <4 mg·kg^{-1} (Hattula et al. 1978).

Water Quality Guideline Derivation

The interim Canadian water quality guidelines for MCPA for the protection of aquatic life were developed based on the CCME protocol (CCME 1991).

Freshwater Life

MCPA exhibits a broad range of toxicity to fish with 96-h LC_{50} values for rainbow trout *(Oncorhynchus mykiss)* from 3.6 to 748 mg·L^{-1}, depending on life stage and MCPA formulation (MCPA Task Force II 1991; Rhône-Poulenc 1992b). Carp *(Cyprinus carpio)* and white aspe *(Leucaspius delineatus)* have 48-h LOECs of 10 and 100 mg·L^{-1}, respectively (Pravda 1973). The 2-EHE and isooctyl ester formulations are most toxic to fish and invertebrates, with the former having a 96-h LC_{50} of 3.16–4.64 mg·L^{-1} for bluegill sunfish and the latter having a NOEC of 0.003 mg·L^{-1} for rainbow trout, bluegill sunfish, fathead minnows, and *Daphnia magna* (Alexander et al. 1985; Rhône-Poulenc 1992a). The EC_{50}s for impaired motility of *D. magna* are 0.28 and >230 mg·L^{-1} for 2-EHE and dimethylamine (DMA) salt, respectively (Rhône-Poulenc 1992c, 1992d). Scuds *(Gammarus pulex)*, isopods *(Asellus aquaticus)*, flatworms *(Planaria gonocephala)*, and segmented worms *(Tubifex* sp.*)* have 48-h LOECs of 10 mg·L^{-1} for MCPA Na salt and Na/K salt. Snails *(Lymnaea stagnalis)* are slightly more tolerant to these formulations, with a 48-h LOEC of 100 mg·L^{-1} (Pravda 1973). Toxicity of MCPA to amphibians is variable. For example, the LT_{50} at 1600 mg·L^{-1} MCPA (Na salt) for crested newts *(Triturus cristatus carnifex)* is 35–45 h, while the 48-h LC_{50} for tadpoles of *Rana temporaria* is 10 mg·L^{-1} (Pravda 1973; Pacces Zaffaroni et al. 1986).

Limited chronic toxicity data show that MCPA inhibits growth (50 mg·L^{-1}) of rainbow trout and increases mortality (100 mg·L^{-1}) of juvenile brown trout *(Salmo trutta)* (Hattula et al. 1978; Davies and Cook 1990). Further, skeletal deformities occur in regenerating limbs of newts exposed to 115 and 457 mg·L^{-1} MCPA 4 d per week for 11 weeks (Arias et al. 1989).

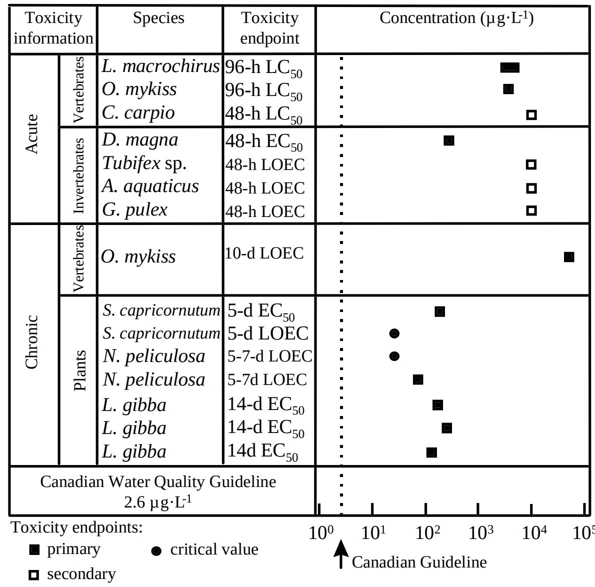

Figure 1. Select freshwater toxicity data for MCPA.

MCPA seems to be most toxic to plants. For example, 14-d EC_{50}s for reduced frond density of duckweed *(Lemna gibba)* are 0.13, 0.17, and 0.25 mg·L^{-1} for 2-EHE, MCPA acid, and DMA, respectively (MCPA Task Force II 1993i, 1993l). The 5-d EC_{50}s for reduced cell densities of the green alga *Selenastrum capricornutum*, however, are 0.19 and 0.25 mg·L^{-1} for DMA salt and 2-EHE, respectively, and LOECs for the diatom *Navicula pelliculosa* are 0.073 and 0.077 mg·L^{-1}, respectively (Rhône-Poulenc 1992e, 1992g; MCPA Task Force II 1993h, 1993k). *S. capricornutum* and *N. pelliculosa* have similar toxicities to MCPA acid, with NOECs and 5-d LOECs of 0.009 and 0.026 mg·L^{-1}, respectively (MCPA Task Force II 1993e, 1993f).

The interim water quality guideline for MCPA for the protection of freshwater life is 2.6 µg·L^{-1} (CCME 1995). It was derived by multiplying the LOEC of 0.026 mg·L^{-1} MCPA acid for *S. capricornutum* and *N. pelliculosa* by a safety factor of 0.1 (CCME 1991). Note that toxicity values for ester formulations were not considered owing to their fast hydrolysis rate. The guideline value applies to the total concentration of all forms of MCPA and transformation products in freshwater environments.

Marine Life

As with freshwater organisms, ester formulations are most toxic to marine fish and invertebrates. For example, 96-h LC_{50}s for butoxyethyl ester are 1.15 and 4.3 mg·L^{-1} for immature bleak *(Alburnus alburnus)* and harpacticoid *(Nitrocra spinipes)*, respectively (Lindén et al. 1979). Those for MCPA acid are 133 and 231 mg·L^{-1} for Atlantic silverside *(Menidia menidia)* and pink shrimp *(Penaeus duorarum)*, respectively (MCPA Task Force 1987a, 1987b). The 96-h LC_{50}s for DMA salt are 441 and 301 mg ·L^{-1} for tidewater silverside *(Menidia beryllina)* and *P. duorarum*, respectively (MCPA Task Force 1987c, 1987d).

Five-day LOECs and EC_{50}s for diatom *(Skeletonema costatum)* cell density are 0.042 and 0.3, 0.017, and 0.085, and, 0.10 and 1.5 mg·L^{-1} for MCPA acid, 2-EHE and DMA salt, respectively (MCPA Task Force II 1993d, 1993j, 1993h).

The interim water quality guideline for MCPA for the protection of marine life is 4.2 µg·L^{-1} (MCPA Task Force II 1993d; CCME 1995). It was derived by multiplying the LOEC for MCPA acid of 0.042 mg·L^{-1} for a diatom, *S. costatum*, by a safety factor of 0.1 (CCME 1991).

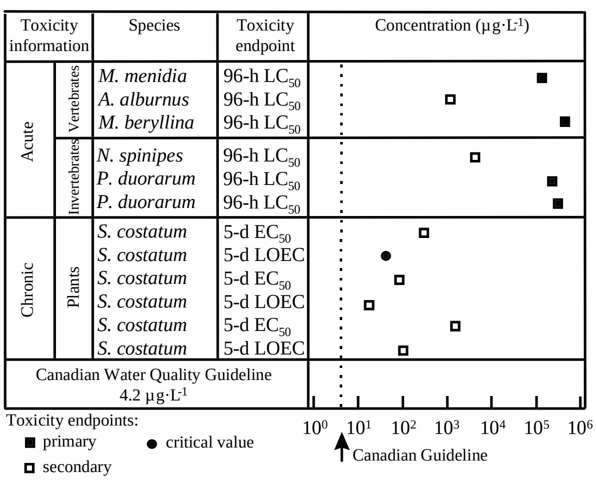

Figure 2. Select marine toxicity data for MCPA.

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