Canadian Water Quality Guidelines for the Protection of Aquatic Life

PICLORAM

Picloram ($C_6H_3Cl_3N_2O_2$; CAS 1918-02-1), the common name for 4-amino-3,5,6-trichloro-picolinic acid (IUPAC), is a white powder with a chlorine-like odour. The amine and potassium salts of picloram are soluble in water and constitute the active ingredients of several herbicides. At present, three Tordon products are registered for use in Canada: Tordon 22K, Tordon 101, and Tordon 202C (Agriculture and Agri-Food Canada 1997). Tordon 22K contains 240 $g \cdot L^{-1}$ picloram as isooctyl esters or as the potassium salt in liquid form. Tordon 22K, also contains glycol and sorbitol ester-type wetting agents along with alcohol and water. Picloram organic salts (triisopropanolamine and triethylamine) and the isooctyl ester are used in combination with other herbicides. Tordon 101 is a mixture of 10.2% picloram and 39.6% 2,4-D, both as triisopropanolamine salts. This mixture also contains a glycol derivative sequestrant and glycol wetting agent along with alcohol and water. Tordon 202C contains 200 $g \cdot L^{-1}$ 2,4-D and 12 $g \cdot L^{-1}$ picloram. All soil-applied granular formulations of picloram have been discontinued for use in Canada because of concerns with groundwater contamination.

Picloram is used in Canada primarily as a wide-spectrum herbicide for the control of woody and herbaceous broad-leaved plants (i.e., Canada thistle, clover, ragweed, dandelion, goldenrod, burdock, fleabane, and vetch) along rights-of-way. Picloram-formulated herbicides may be applied by ground or aerial application equipment. Foliage sprays are usually applied during active growing periods. Sprays may also be applied to the bark of trees.

Picloram can enter the atmosphere through spray drift during application and as a result of vaporization after application. Several incidents of damage to nontarget plants as a result of picloram spray drift have been reported. For instance, the NRCC (1974) reported an incident in which trees 50 m from a treated area were killed by spray drift after picloram application.

Picloram is rapidly absorbed by plant roots and to a lesser extent by foliage. Unabsorbed picloram may move downward or laterally through the soil due to its high solubility and low adsorption on some soils. The major factor controlling the extent of adsorption is soil organic matter content (Grover 1977). Adsorption generally increases in acidic soils and is much lower in neutral and alkaline soils. The formulation of picloram may also affect its movement.

Microbial degradation is the principle method by which picloram is broken down in soil (Mullison 1985). The degradation of picloram in soil is inversely related to the picloram concentration; as picloram concentrations increase, degradation decreases (Mullison 1985). Half-order rates for picloram degradation in soil for Alberta and Saskatchewan were 5.3 and 2.9 $g \cdot ha^{-1}$ per month, respectively, and were correlated with temperature (Hamaker et al. 1967; NRCC 1974). Other degradation rates were reported to be 4% in 15 d by plant-root micro-organisms (Meikle et al. 1966) and 0.24–1.21% over 83 d by different types of bacteria and fungi exposed to 1 $mg \cdot L^{-1}$ (Youngson et al. 1967). Photodecomposition is an additional pathway for picloram degradation on plant or soil surfaces or in water. Photodecomposition of the picloram molecule is slower and more variable in natural sunlight than under UV irradiation in laboratory studies (Bovey et al. 1970; Norris and Moore 1970; Bovey and Scifres 1971; Mosier and Guenzi 1973). For instance, when spread on a glass surface, 60% of picloram was degraded by UV light (155 $\mu W \cdot cm^{-2}$ within 48 h), but only 35% was degraded in the same time by natural sunlight (Merkle et al. 1967). Volatilization is not expected to be a major mechanism of loss from soil due to the low vapour pressure of picloram and its various formulations.

Picloram was found in surface and subsurface waters within 100 m of transmission line rights-of-way after aerial and ground applications (Wilson and Wan 1975; Varfalvy and Seguin 1987). Samples of water collected ranged from nondetectable to 181 $mg \cdot L^{-1}$. A maximum picloram concentration of 104 $mg \cdot L^{-1}$ was reported in groundwater immediately adjacent to the treated rights-of-way (Varfalvy and Seguin 1987).

The rate of hydrolysis of the acid is very slow, with >90% of the initial picloram remaining unhydrolyzed after 70 d

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

Aquatic life	Guideline value ($\mu g \cdot L^{-1}$)
Freshwater	29*
Marine	NRG†

*Interim guideline.

†No recommended guideline.

at 45°C. Under these conditions, the half-life would be approximately 2 years (Mullison 1985).

Laboratory studies indicate that photolysis is the primary mechanism for picloram degradation in water (Hall et al. 1968; Haas et al. 1971; Mosier and Guenzi 1973; Ghassemi et al. 1981). In areas of abundant sunlight, picloram decomposed rapidly in distilled water with a half-life of 6-8 d. With the exception of the highest picloram concentrations (e.g., 2500 $mg \cdot L^{-1}$), a 30-d exposure resulted in 90% picloram decomposition (Hedlund and Youngson 1972). Picloram photo-decomposition in water is proportional to the light intensity and depth of solution, but is independent of the initial concentration (Hedlund and Youngson 1972).

The hydrolysis of picloram is negligible, as it was reported to be stable in groundwater at 10°C and 25°C for up to 15 months (Weidner 1974) and in darkened controls maintained during photolysis experiments (Hedlund and Youngson 1972).

Volatilization is not expected to be a major mechanism for loss of picloram from water due to the low vapour pressure of picloram and its various formulations (NRCC 1974)

Water Quality Guideline Derivation

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

Freshwater Life

The vertebrate aquatic toxicity database for picloram consists of data for 17 fish species, including 240 acute toxicity tests and 6 chronic studies.

The isooctyl ester of picloram is the most toxic formulation to rainbow trout *(Oncorhynchus mykiss)* (96-h LC_{50} = 4.0 $mg \cdot L^{-1}$) (Johnson and Finley 1980). The toxicity of the carboxylic acid and the isooctyl ester were similar (96-h LC_{50}s of 14–32 $mg \cdot L^{-1}$ acid equivalent [a.e.] and 10.4 $mg \cdot L^{-1}$ a.e., respectively) for the goldfish *(Carassius auratus)* (Kenaga 1969). The 96-h LC_{50} data presented by Mayer and Ellersieck (1986) ranged from 3.9 $mg \cdot L^{1}$ *(Salmo clarki)* to 23.3 $mg \cdot L^{-1}$ *(Lepomis macrochirus).*

A 192-h LC_{50} of 14 $mg \cdot L^{-1}$ and a NOAEL of 6.9 $mg \cdot L^{-1}$ were found for *Salmo gairdneri*. Toxicity tests using the embryo–larval stages of the same species over approximately 70-d produced a NOAEL of 0.55 $mg \cdot L^{-1}$ and a SMATC of 0.70 $mg \cdot L^{-1}$ (Mayes et al. 1987).

Woodward (1979) simulated the effects of pulse exposure on an early life stage (3-d posthatch) of the cutthroat trout *(S. clarki)* using technical grade picloram (90% a.i.). Picloram exposure was terminated on day 24, but observations were continued until day 60. The lowest concentration in an exposure regimen that adversely affected the test fish was 0.790 $mg \cdot L^{-1}$. No significant differences in development, growth, and survival among the alevins and fry and the controls in the 0.290 $mg \cdot L^{-1}$ exposure regimen were noted.

The invertebrate toxicity database consists of 18 acute toxicity tests with six different species from six different families and one 21-d chronic test.

The 24-h LC_{50}s for invertebrates ranged from 20 $mg \cdot L^{-1}$ *(Gammarus pseudolimnaeus)* to 140 $mg \cdot L^{-1}$ for >90% picloram a.i. (Mayer and Ellersieck 1986). The 48-h LC_{50}s for picloram (>90% a.i.) as the acid range from 50.7 to 76 $mg \cdot L^{-1}$ *(Daphnia magna)* (Mayes and Dill 1984; Mayer and Ellersieck 1986). The 96-h LC_{50}s ranged from 16.5 $mg \cdot L^{-1}$ *(G. pseudolimnaeus)* picloram (Mayer and Ellersieck 1986) to 48 $mg \cdot L^{-1}$ *(P. californica)* picloram as the acid (Johnson and Finley 1980). A SMATC (14.6 $mg \cdot L^{-1}$) was derived using *D. magna* exposed to picloram as the acid (93.8% a.i.) for 21 d (Gersich et al. 1985). The formulated products containing lower percentages of picloram as the potassium salt produced higher median lethal values.

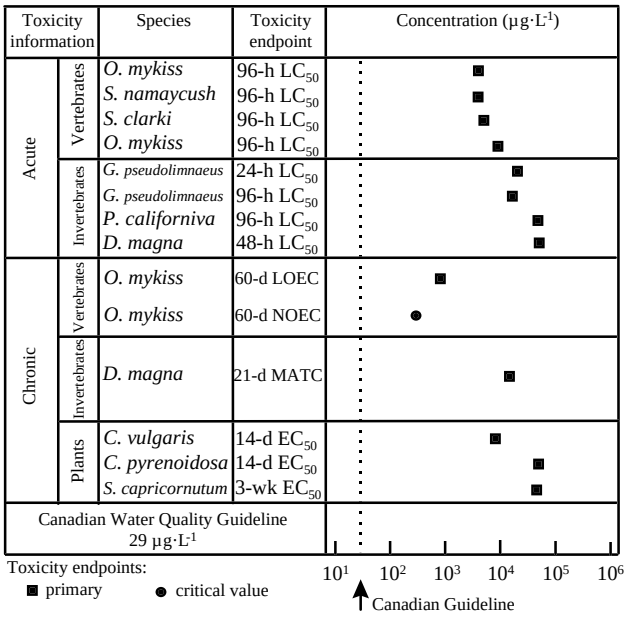

Figure 1. Select freshwater toxicity data for picloram.

The aquatic plant toxicity database includes acute and chronic tests with three common green algae: *Selenastrum capricornutum* and two species of *Chlorella*.

One 24-h EC_{50} of 115 $mg \cdot L^{-1}$ for *S. capricornutum* was based on oxygen evolution (Turbak et al. 1986). Growth (assessed using cell counts and optical density measurements) and photosynthesis (rate of carbon fixation) of various species of freshwater and marine algae (species not given) were not affected by doses of picloram of up to 240 $mg \cdot L^{-1}$ (NRCC 1974).

Kratkey and Warren (1971) reported a <50% inhibition of *Chlorella* cell growth after an 18- to 36-h exposure to picloram concentrations of 1 or 10 $mg \cdot L^{-1}$. A paper disc agar diffusion method for algal sensitivity demonstrated that 1000 $mg \cdot L^{-1}$ picloram did not inhibit the growth of *Chlorella* on agar outside the diameter of the paper disc containing the picloram (Thomas et al. 1973).

Algal chronic toxicity data are represented by 10- to 14-d exposures of *Chlorella vulgaris* and *Chlorella pyrenoidosa* to picloram as the acid and as the decarboxylated derivative measured in a microplate assay system (Baarschers et al. 1988). This produced growth EC_{50}s for picloram of >160 $mg \cdot L^{-1}$ for both species. The decarboxylated picloram was more toxic, producing EC_{50}s of 8 and 49 $mg \cdot L^{-1}$ for the two species, respectively. An EC_{50} of 44.8 $mg \cdot L^{-1}$ Tordon 22K, based on reductions in cell biomass, resulted from a 2- to 3-week exposure using *S. capricornutum* (Turbak et al. 1986).

A 17-d exposure of five species of aquatic macrophytes to 10 $mg \cdot L^{-1}$ picloram under greenhouse conditions (21–27°C) found only one species *(Lysimachia nummularia)* exhibited a negative response with significant (50%) injury. No obvious damage to aquatic macrophyte beds adjacent to a surface water sampling site, where 1.15 $mg \cdot L^{-1}$ of picloram was detected, was reported in a field study of picloram contamination (Waite et al. 1986).

The interim water quality guideline for picloram for the protection of freshwater life is 29 $\mu g \cdot L^{-1}$. It was derived by multiplying the NOEL value of 290 $\mu g \cdot L^{-1}$ (Woodward 1979) by a safety factor of 0.1 (CCME 1991). This guideline is given interim status due to missing chronic data for invertebrates and plants.

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