Canadian Water Quality Guidelines for the Protection of Aquatic Life

ATRAZINE

Atrazine ($C_8H_{14}ClN_5$) is a selective, systemic herbicide with the CAS name and number 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine and 1912-24-9, respectively. Tradenames for this herbicide include AAtrex, Aktikon, Atranex, Bicep, Blazine, Cekuzina-T, Fogard, Gesaprim, Griffex, Maizina, Mebazine, Primaextra, Sutazine, and Vectal (Tomlin 1994). Atrazine is used for the control of annual broadleaf and grassy weeds in corn and lowbrush blueberries, and nonselective weed control on noncropland. The principal mode of action of atrazine is the inhibition of photosynthesis and the interference with other enzymic processes (Tomlin 1994).

Atrazine was first introduced in Canada in 1960, and more than 1 200 000 kg (a.i.) were sold in Canada in 1990 with over 90% being sold to Ontario and Quebec (Agriculture Canada/Environment Canada 1995). The use of atrazine is now declining, however, because of rising environmental concerns. For example, in 1993 only 589 852 kg of atrazine was used on field crops, fruits, and vegetables in Ontario. This is approximately half of that used in 1983 (Hunter and McGee 1994). It is no longer used for algae control in ornamental ponds and aquariums.

Atrazine may enter the aquatic environment through runoff from treated fields, or from spillage or accidental discharge during production, packaging, storage, and waste disposal. Reported concentrations of atrazine in Canadian freshwater samples ranged from 0.01 to 74 $\mu g \cdot L^{-1}$ (Muir et al. 1978; Frank et al. 1987a, 1987b). Atrazine was detected in 77–89% of samples in monitoring studies (Frank et al. 1979; Roberts et al. 1979).

The half-life for atrazine in aquatic environments ranges from 3.2 d (Kosinski 1984) to 7–8 months (Dewey 1986). Photodegradation of atrazine in surface waters is not a significant fate process (Ghassemi et al. 1981). The primary pathways of atrazine degradation in sediments are chemical hydrolysis to hydroxyatrazine and biological dealkylation (Hance and Chesters 1969; Goswami and Green 1971).

Colloidal organic matter from an estuarine environment was found to have a high adsorptive capacity for atrazine, with a linear Freundlich adsorption constant of 1850. Comparative values for sediments ranged from 78 to 213. Normalized for the organic carbon content, colloidal material was 10 to 35 times more adsorptive as a substrate for atrazine than sediment or soil organic matter. The presence of colloids in natural waters was postulated to be important in the transport and distribution of atrazine in aquatic systems (Means and Wijayaratne 1982; Means et al. 1983).

Bioconcentration factors for atrazine range from 0.8 for crayfish *(Orconectes virilis)* to 480 for mayfly nymphs (*Baetis* sp.) (Lynch et al. 1982). In the bullhead catfish *(Ictalurus melas),* depuration half-lives of 26 h and 5 h were found following exposure to 0.01 and 0.8 $mg \cdot L^{-1}$, respectively (Ellgehausen et al. 1980).

Water Quality Guideline Derivation

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

Freshwater Life

Acute toxicity values (LC_{50}s) for fish ranged from 0.55 $mg \cdot L^{-1}$ (24 h) for harlequin fish *(Rasbora heteromorpha)* (Alabaster 1969) to 100 $mg \cdot L^{-1}$ (96 h) for crucian carp *(Carassius carassius)* (Bathe et al. 1975). Rainbow trout *(Onchorynchus mykiss)* and the guppy *(Lebistes reticulata)* appeared to be two of the more sensitive North American species, with 96-h LC_{50}s of 4.5 and 4.3 $mg \cdot L^{-1}$, respectively (Bathe et al. 1975, 1976).

Chronic studies using the channel catfish *(Ictalurus punctatus*) exposed from the fertilized egg through 96-h posthatch produced an LC_{50} of 0.22 $mg \cdot L^{-1}$ (Birge et al. 1979, 1983). Brook trout *(Salvelinus fontinalis)* fry showed increased mortality at 0.24 $mg \cdot L^{-1}$, while adult mortality was unaffected by 0.72 $mg \cdot L^{-1}$ during 44 weeks of exposure (Macek et al. 1976).
The acute toxicities (96-h LC_{50}s) for invertebrates ranged

Table 1. Water quality guidelines for atrazine for the protection of aquatic life (CCME 1989).

Aquatic life	Guideline value ($\mu g \cdot L^{1}$)
Freshwater	1.8
Marine	NRG*

*No recommended guideline.

from 0.094 mg·L^{-1} for *Acartia tonsa* to >29 mg·L^{-1} for the fiddler crab *(Uca pugilator)* (Ward and Ballantine 1985). The most sensitive invertebrates were midge larvae *(Chironomus tentans)*, with a 48-h LC_{50} of 0.72 mg·L^{-1}. Exposures to 0.23 mg·L^{-1} for two generations caused reduced hatching success, increased larval mortality, retarded development, and reduced rates of pupation and emergence. The NOEL for the same exposure time was 0.11 mg·L^{-1} (Macek et al. 1976).

For phytoplankton and periphyton, 24-h EC_{50}s (inhibition of ^{14}C uptake) ranged from 0.019 to 0.325 mg·L^{-1} (Larsen et al. 1986). Blue-green algae experienced over 90% inhibition of chlorophyll production during 7-d exposures to atrazine concentrations as low as 0.001 mg·L^{-1} (Torres and O'Flaherty 1976). The use of this response variable is somewhat problematic since a consistent response pattern does not exist for aquatic plants and atrazine. Simple algal growth inhibition tests conducted with unicellular chlorophytes reported an EC_{50} for growth (11-d standing crop estimates) of 25 µg·L^{-1} for *Chlorella vulgaris* (Burrell et al. 1985). A complement of eight species of green and blue-green algae produced a range of EC_{50}s (^{14}C uptake following 24-h exposure) from 19 to 325 µg·L^{-1}. The lowest mean value was an EC_{50} of 37.0 µg·L^{-1} for *Chlamydomonas reinhardtii* (Larsen et al. 1986).

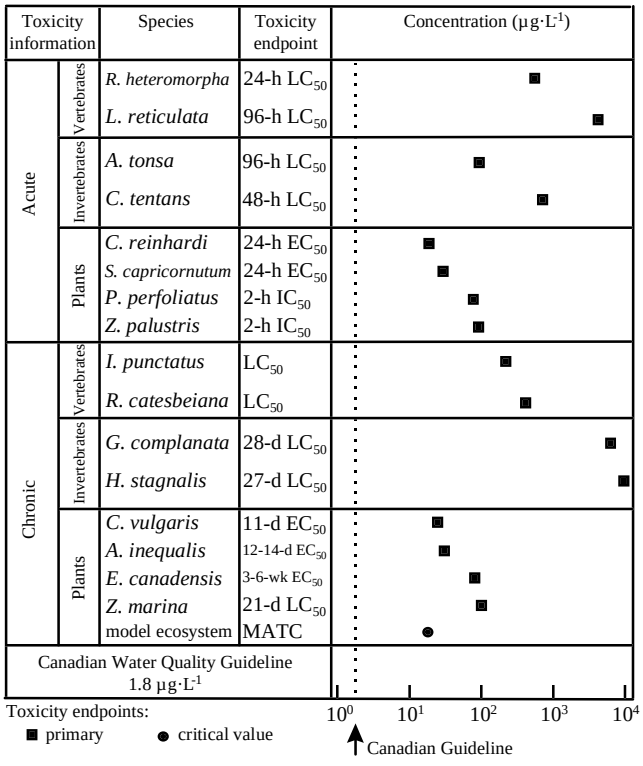

Figure 1. Select freshwater toxicity data for atrazine.

Significant reductions in aquatic vascular plant biomass were reported after single exposures to atrazine concentrations ranging from 12 to 1000 µg·L^{-1} (Correll and Wu 1982; Cunningham et al. 1984). Annual additions of atrazine during a 3-year period for a final concentration of 20 µg·L^{-1} reduced macrophyte coverage in experimental ponds by about 90% (Kettle et al. 1987). Chronic nonlethal levels of atrazine (EC_{50}, growth) for the macrophyte *Vallisneria americana* under freshwater conditions ranged from 163 to 532 µg·L^{-1} (Forney and Davis 1981).

A number of reports described the effects of atrazine additions to laboratory and field microcosms. In these studies, the introduction of atrazine (50–100 µg·L^{-1}) had an immediate and significant effect on phytoplankton and vascular plants. In phytoplankton assemblages, concentrations ranging from 20 to 60 µg·L^{-1} reduced oxygen production and inorganic carbon uptake, and changed species composition (deNoyelles et al. 1982). In microcosm studies, the concentration of atrazine required to elicit effects varied widely. A single dose resulting in a concentration of 1000 µg·L^{-1} had no effect on *Daphnia magna* in a wetland/marsh microcosm (Johnson 1986). Conversely, the same species was eliminated from a lake water column simulation by three additions of atrazine (within 5 d), producing a final concentration of 221.4 µg·L^{-1} (Millard et al. 1979). Also, in a prairie wetland microcosm, 30-d exposures to atrazine concentrations of 10 and 100 µg·L^{-1} did not affect submerged macrophyte or phytoplankton growth, although varying effects on other individual components occurred. Aquatic community gross primary productivity measured by dissolved oxygen production was significantly reduced (23%) by a concentration of 10 µg·L^{-1} (Johnson 1986).

In a model ecosystem study of atrazine toxicity, artificial floating substrates were used to measure structural (species numbers and biomass) and functional (colonization rates, O_2 production, protein and nutrient levels) responses to naturally derived microbial communities (Pratt et al. 1988). Oxygen production and the ability of communities to sequester magnesium and calcium were the most sensitive indicators of atrazine stress.

The interim water quality guideline for the protection of freshwater life is 1.8 µg·L^{-1}. It was derived by multiplying the lowest MATC (based on NOELs and LOELs) of 17.9 µg·L^{-1} by a safety factor of 0.1 (CCME 1989).

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