Canadian Water Quality Guidelines for the Protection of Aquatic Life

CYANAZINE

Cyanazine ($C_9H_{13}CN_6$) is a selective systemic triazine herbicide that inhibits photosynthesis (Tomlin 1994). It is used for general weed control in dry bulb onions and corn (Agriculture and Agri-Food Canada 1997). Cyanazine is the trade name for 2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile (CAS 2175-46-2). Its common names include Bladex, Fortol, and Payze. At standard temperature and pressure, cyanazine is a white, crystalline, odourless solid. Cyanazine has an aqueous solubility of 171 mg·L^{-1} at 25°C (Worthing and Walker 1987), a low vapour pressure (200 nPa at 20°C) (Worthing 1987), and a log octanol–water partition coefficient (3.68) (Banerjee et al. 1980).

Cyanazine is formulated as either a wettable powder, a liquid flowable suspension, or as wettable or soluble granules (Smith et al. 1982; USEPA 1988; Agriculture and Agri-Food Canada 1997). Cyanazine can be incorporated into the soil as a pre-plant treatment or applied pre- or postemergence to crops. Cyanazine may be formulated with atrazine as Blazine, with MCPA as Blagal, or with butylate, metolachlor, or dicamba (OMAF 1988).

Cyanazine can enter the environment through application to crops or accidental spills. Translocation of cyanazine to surface waters results from direct deposition of spray or from vapour drift or precipitation. Surface runoff and groundwater intrusions from treated lands also carry cyanazine to watercourses (Smith et al. 1982; Pionke et al. 1988). Losses of soil-applied triazine herbicides such as cyanazine are dominated by movement in the water phase as opposed to movement with eroded soil sediment (Baker et al. 1976; Leonard et al. 1979; Johnson and Baker 1982, 1984).

Cyanazine runoff losses have been reported between <0.01% to an average of 11%. Leonard et al. (1979) found that cyanazine is transported primarily in solution rather than adsorbed to soil particles, and cyanazine concentrations in the particles were 2 to 5 times higher than in an equivalent amount of water. Runoff losses of cyanazine vary with tillage plots and soil types (Baker et al. 1976; Hall et al. 1984).

Isensee et al. (1988) studied the movement of cyanazine from soil into wells sunk into field plots. The range of concentrations was 0.1–0.7 µg·L^{-1}. The concentration of cyanazine in the pit water at the base of a corn field over 2 years averaged 29.3 µg·L^{-1} (maximum 73.0 µg·L^{-1}), but the herbicide was found in only 16 of 327 samples (4.9%). The average concentration in pit bottom soil was approximately 40.3 µg·g^{-1} (maximum of 125 µg·g^{-1}), and cyanazine was found in 3.4% of pit bottom samples (Kadoum and Mock 1978).

Cyanazine may also move into groundwater. Muir and Baker (1976) found cyanazine (applied at 3.36 kg·ha^{-1}) in tile outlets draining a corn field in Quebec in concentrations ranging from <0.01 to 0.68 µg·L^{-1}. A metabolite of cyanazine, cyanazine amide, was found in similar concentrations.

In Ontario, cyanazine was found in only 2 out of 360 samples (detection limit 0.02 µg·L^{-1}), and the maximum concentration was 13 µg·L^{-1} (Roberts et al. 1979). Frank and Logan (1988) analyzed water samples collected from the mouth of the Grand, Saugeen, and Thames rivers in southwestern Ontario from 1981 to 1985. Out of 440 water samples, cyanazine was found in 45 (10.2%, detection limit <0.02 mg·L^{-1}). The highest mean annual concentration measured was 2.6 ± 4.3 µg·L^{-1}. In Quebec, cyanazine was detected at levels as high as 11 µg·L^{-1} (Giroux et al. 1997).

Cyanazine was not found in wells (detection limit 0.1 µg·L^{-1}) in any of the water samples collected from 26 farms where cyanazine had been used as a herbicide that year (Ripley et al. 1986; Frank et al. 1987). Cyanazine was found (with a concentration of 0.1 µg·L^{-1}) in 1 of 112 wells investigated for contamination from surface runoff and spray drift, and in 6 out of 48 wells where contamination resulted from spills. The maximum reported concentration of cyanazine resulting from a spill was 125 mg·L^{-1}. After sampling 351 private wells in 1985 and analyzing 1881 samples, the Ontario Ministry of the Environment reported cyanazine contamination in 17 wells with a maximum concentration of 4.0 µg·L^{-1} (OMOE 1987a).

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

Aquatic life	Guideline value (µg·L^{-1})
Freshwater	2.0*
Marine	NRG†

*Interim guideline.

†No recommended guideline.

Out of the 422 raw surface-water samples collected at 25 different municipal waterworks, cyanazine was detected in 34 samples from 13 of the waterworks. Reported levels were from <0.08 to 6.8 µg·L^{-1}. In another study, cyanazine was not detected in 747 groundwater samples from 37 domestic wells and five municipal groundwater supply wells in southern Ontario (OMOE 1987b).

Soil degradation of cyanazine results from both chemical and biochemical processes, but the primary route of cyanazine degradation in soil is through microbial activity (USEPA 1987). Metabolic degradation of cyanazine involves removal of the ethyl group, hydration of the cyano group, and exchange of the chlorine atom with a hydroxyl group (WSSA 1983). When wheat and potatoes were grown in soils treated with ^{14}C-cyanazine, the cyanazine breakdown products in the crops were the result of hydrolysis reactions of the nitrite and chlorine groups and of de-N-alkylation reactions; the residues were present in both free and conjugated states (Beynon et al. 1972). Under field conditions, losses by either photodecomposition or volatilization are minimal (WSSA 1983; USEPA 1987).

The longest half-lives for hydrolysis of cyanazine in soil have occurred near neutral pH and at room temperature. The compound is stable to degradation at pH values of 5, 7, and 9 for greater than 30 d (USEPA 1988). Cyanazine half-life estimates are generally 2 months or less.

Data on the aquatic fate of cyanazine are limited. The USEPA (1988) indicated that cyanazine persistence in water was not known and that the aquatic half-life had not yet been determined. Bioaccumulation from water should be negligible, as suggested by the low log K_{ow} (3.68) (Banerjee et al. 1980). Volatilization to the atmosphere is not a major fate process for cyanazine in water (Smith et al. 1982).

The fate of ^{14}C-labelled cyanazine in a model aquatic ecosystem was investigated by Yu et al. (1975). After 35 d, a concentration of 3.21 µg·L^{-1} of cyanazine was measured in the water after an application equal to 0.78 kg ·ha^{-1}. The half-life of cyanazine in this model ecosystem was less than 35 d. Degradation of the triazine ring to CO_2 proceeded slowly in the water, as indicated by the persistence of the radioactivity, but cyanazine and its metabolites did not biomagnify in the food web.

In another study, cyanazine was applied at a rate of 60 µg·L^{-1} in an aquatic microcosm consisting of pond sediment, water, and plants (Roberts 1974). The half-life in water was 14 d, but in sediment, cyanazine was degraded more slowly, with a half-life greater than 28 d.

Sanborn (1974) studied the fate of cyanazine in a model terrestrial/aquatic ecosystem. The aquatic plant *Elodea* accumulated 0.621 µg·g^{-1} of the cyanazine, while the crab *Uca manelensis* accumulated 0.172 µg·g^{-1} of N-de-ethylated cyanazine after 33 d. None of the other test organisms (algae, *Daphnia*, fish, mosquito larvae, and snails) had residues of identifiable metabolites. At the end of the experiment, the concentration of cyanazine in the water was calculated to be 3.2 µg·L^{-1}. Neither cyanazine nor its metabolites accumulated in the components of the model ecosystem.

Metcalf and Sanborn (1975) reported that the behaviour of cyanazine in the model ecosystem would indicate that it was susceptible to degradation; only the water plant *Elodea* contained cyanazine residues. The authors concluded that the continued use of cyanazine should not result in its accumulation in aquatic food chains.

Leung et al. (1981) demonstrated that, although cyanazine was detected in the Des Moines River and Saylorville Reservoir at a mean concentration of 0.09 µg·L^{-1}, no cyanazine residues were detected in any of the seven local warm-water fish species (detection limit approximately 10 µg·kg^{-1}).

Water Quality Guideline Derivation

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

Freshwater Life

Discussions of the aquatic toxicity of cyanazine usually take into account its phytotoxic mechanism through the inhibition of photosynthesis. Because of this primary mode of action, much of the published information deals with the effect of cyanazine on aquatic macrophytes and algae. Data on cyanazine levels in aquatic biota are extremely limited. This is a reflection of cyanazine's low bioaccumulation potential and the low environmental concentrations to which biota are exposed.

Using algae, Foy and Hiranpradit (1977) found that cyanazine levels of 0.052–0.208 mg·L^{-1} stimulated *Chlamydomonas reinhardtii* chlorophyll production, but 0.416 and 0.832 mg·L^{-1} reduced chlorophyll content by 40.8 and 80.3%, respectively. In the same experiment, *Chlorella* sp. chlorophyll production was reduced by 35.8% when the culture was treated with 0.208 mg·L^{-1} cyanazine.

Aly et al. (1984) carried out a toxicity bioassay using a continuous culture of the freshwater green alga *Scenedesmus quadricauda,* which was subjected to increasing dosages of cyanazine for periods of 17–22 d. Cyanazine concentrations of 0.01, 0.02, and 0.04 mg·L^{-1} were added to the culture. Growth (as determined by chlorophyll *a* content) was inhibited for 14 d at herbicide concentrations of 0.01 and 0.02 mg·L^{-1}, after which recovery was noted. After a treatment of 0.04 mg·L^{-1}, growth was suppressed for the duration of the experiment (20 d). Final chlorophyll content in this latter culture was about 90% of control after 20 d.

Cyanazine is moderately toxic to freshwater fish and aquatic invertebrates (USEPA 1988). The lowest reported 96-h LC_{50} for a fish species is 4.8 mg·L^{-1} for *Labeo rohita*, an Indian freshwater fish (Rao and Dad 1979; Dad and Tripathi 1980). The 96-h LC_{50} for rainbow trout (*Onchorhynchus mykiss*) is 9.0 mg·L^{-1} (Mayer and Ellersieck 1988). Midge larvae *(Chironomus tentans)* and freshwater scud *(Gammarus fasciatus)* have 96-h LC_{50} values of 6.6 and 2.0 mg·L^{-1}, respectively. For *Daphnia magna*, the 48-h EC_{50} is 84 mg·L^{-1} (Nebeker et al. 1986). Misra and Saxena (1985) concluded that cyanazine was more toxic than simazine, but only provided their LC_{50} estimates in days. For the Indian freshwater fish *Nemoria esthamus*, a static LC_{50} occurred after 70 d with a cyanazine concentration of 10 mg·L^{-1}, and after 87 d with a concentration of 0.10 mg·L^{-1}.

Information on the aquatic fate of cyanazine is limited; the half-life of the compound in water is expected to be less than a month, but persistence of residues in sediments remains unknown. Exposure via waterborne concentrations running off agricultural areas would be of short duration and associated with the period following soil application. Chronic exposure through contaminated sediment, however, cannot be discounted. Several studies have addressed acute lethality to fish and several invertebrate species. Data are limited, however, on aquatic plants and on sublethal effects. The interim water quality guideline for cyanazine for the protection of freshwater organisms is 2.0 µg·L^{-1}. It was derived by multiplying the LOEL, which caused an inhibitory effect with a 35% decrease in cell chlorophyll content of 0.208 mg·L^{-1} for the green alga *Chlorella* sp. (Foy and Hiranpradit 1977), by a safety factor of 0.01 (CCME 1991).

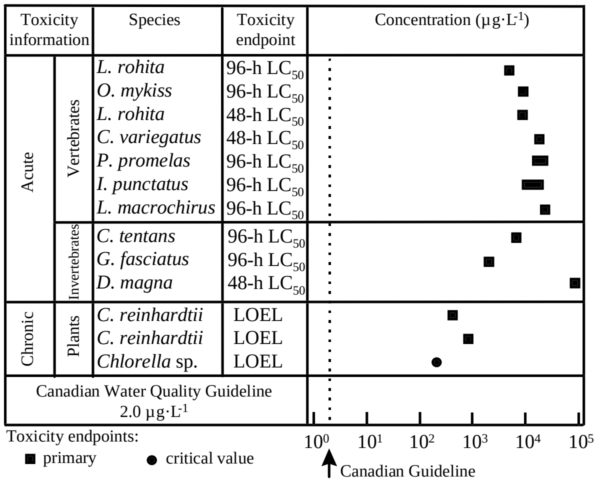

Figure 1. Select freshwater toxicity data for cyanazine.

The aquatic life guideline is given an interim status because of the limited information available on the environmental fate of cyanazine in aquatic systems, the lack of chronic toxicity information, and the fragmentary nature of the phytotoxicity data.

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