

Canadian Water Quality Guidelines for the Protection of Aquatic Life

TRIFLURALIN

rifluralin ($C_{13}H_{16}F_3N_3O_4$) has an IUPAC name of α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine. Trifluralin is an orange crystalline solid compound with a molecular weight of 335.5 and a CAS registry number of 1582-09-8. The water solubility of trifluralin is 0.05–4 mg·L⁻¹ (Verschueren 1983; Huckins et al. 1986; Poe et al. 1988). The octanol–water partition coefficients are 3.06–5.34 (Brown and Flagg 1981; Newsome et al. 1984; Suntio et al. 1988). The Henry's law constant is 4.02 Pa·m³·mol⁻¹ (at 20°C).

Trade names for trifluralin and its formulations registered in Canada include Treflan, Triflurex, Co-op Garden Weed Preventer, Heritage Selective Granular Herbicide, Rival, and Fortress (Agriculture and Agri-Food Canada 1997). Trifluralin is used to control a wide range of annual grasses and broadleaf weeds in canola, sunflowers, root crops, vegetable crops, flowers, woody nursery stock, and established shelterbelts (OMAF 1989). Trifluralin is usually preplant incorporated due to its volatility (Maguire et al. 1988).

Trifluralin appears to act as a mitotic poison affecting root growth (Ashton and Crafts 1973; Poe et al. 1988). Trifluralin may also affect other metabolic reactions such as lipid synthesis (Sparchez et al. 1987). Studies indicate that trifluralin inhibits energy-dependent calcium uptake in plant mitochondria at concentrations less than those interfering with tubulin polymerization (Hertel and Marme 1983).

Volatilization is a major dissipation pathway. Trifluralin has been found in air at concentrations as high as 160 ng·m⁻³ in regions of Canada where it is used extensively (Grover et al. 1988). The occurrence of trifluralin in air generally follows the seasonal use patterns for this herbicide. Soil moisture and rainfall events can also influence the timing and concentrations in the air (Grover et al. 1988).

Another transport pathway allowing trifluralin dispersion in the environment is surface water runoff from treated fields (Willis et al. 1975). Trifluralin is expected to exhibit minimal movement from soils because of its low solubility and strong adsorption to soil (Helling 1971). Trifluralin concentrations in runoff from treated fields typically range from below detection limits (about 0.01 mg·L⁴) to 0.04 mg·L⁻¹ in bulk water samples (Rhode et al. 1980; Grover 1983; Willis et al. 1983). Herbicide

concentrations can generally be two to three orders of magnitude higher in sediments than in the associated water (Wauchope 1978).

Trifluralin concentrations in streams in areas where the herbicide is used range from 0 to 1.8 $\mu g \cdot L^4$ and are frequently below detection limits. The lowest detection limit reported was 3 $ng \cdot L^{-1}$. The concentration of trifluralin in surface waters increases during spring runoff and again during autumn rains when erosion is expected to be greatest, particularly on the prairies (Williamson 1984). Increased concentrations in surface waters, however, are also a result of deposition of trifluralin vapours or dust particles with adsorbed trifluralin from neighbouring applications (Muir and Grift 1987).

The dinitro functional group in trifluralin and other dinitroaniline herbicides extensively decreases the molecules' water solubilities as it makes hydrogen bonds with alkyl groups of surrounding molecules (Weber 1987). The various processes governing the persistence and fate of trifluralin in the environment include volatilization, photodegradation, and microbial degradation.

Cool, dry climates favour greater persistence than warmer, more moist conditions (Jensen et al. 1983; Weber 1990). The absence of a soil microbial community also appeared to increase persistence in soils (Mostafa et al. 1982).

Under static conditions, BCF estimates for fish species ranged from 1030 for rainbow trout (*Oncorhynchus mykiss*) to 6000 for minnows (*Notropis* sp.) (Spacie and Hamelink 1979). Snail (*Helisoma* sp.) BCFs in static microcosms generally ranged from 10 to 100 (Yockim et al. 1980). The BCFs for the filamentous green alga *Oedogonium cardiacum* were about 100 for static microcosms and in the 1000 and 10 000 range in continuously dosed microcosms.

Table 1. Water quality guidelines for trifluralin for the protection of aquatic life (CCME 1992, 1993).

Aquatic life	Guideline value (µg·L ⁻¹)			
Freshwater	0.20			
Marine	NRG [*]			
*				

No recommended guideline.

Fathead minnows (*Pimephales promelas*) exhibited a BCF of 3261, and the uptake of trifluralin from water was linear with a rate constant of 755.98 per day. Transfer of fish to uncontaminated water resulted in first-order depuration with a rate constant of 0.231 84 per day (Spacie and Hamelink 1979).

Static microcosm studies by Kearney et al. (1977) showed that BCFs for algae (276), snails (400), *Daphnia* (92), and mosquito fish (33) were a result of polar metabolites, not trifluralin. Microcosms simulating a northern prairie wetland were exposed to $4 \, \mu g \cdot L^{4-14}$ C-trifluralin in a sediment—water mixture for 6 weeks (Huckins et al. 1986). Midge larvae (*Chironomus riparius*), macrophytes, and algae contained trifluralin/trifluralin metabolites in the range of $40-260 \, ng \cdot g^{-1}$, while *Daphnia* accumulated $566 \, ng \cdot g^{-1}$ (Huckins et al. 1986).

Water Quality Guideline Derivation

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

Freshwater Life

The vertebrate acute toxicity database for trifluralin consists of tests on seven freshwater fish species and an amphibian. The ranges of 96-h LC₅₀ values were $10-330 \,\mu \text{g} \cdot \text{L}^4$ for rainbow trout (O. mykiss), 8.4-400 µg·L⁴ for bluegill sunfish (*Lepomis macrochirus*), 105–160 µg·L¹ for fathead minnows (*Pimephales promelas*), and 210–2200 µg·L⁴ for channel catfish (Ictalurus punctatus) (Mayer and Ellersieck 1986). For Fowler's toad (Bufo woodhousei fowleri), 24-h and 96-h LC₅₀s were $180-200 \mu g \cdot L^4$ and $110-115 \mu g \cdot L^4$, respectively (Mayer and Ellersieck 1986). Toxicity tests using trifluralin adsorbed onto soil required as much as 227 times the amount of trifluralin to produce 50% mortality among bluegill (L. macrochirus). Therefore, the possibility of acutely toxic quantities of trifluralin washing into an aquatic environment from an adjacent treated field seem remote (Parka and Worth 1965).

Invertebrate acute toxicity data for trifluralin include 14 species of freshwater invertebrates. The 48-h LC_{50} s ranged from 50 to 625 μ g·L¹ (Cope 1966; Sanders and Cope 1966; Macek et al. 1976; Mayer and Ellersieck 1986; Naqvi et al. 1987).

A trifluralin concentration of 335.5 µg·L¹ has been found to decrease growth of single-cell green alga (*Chlamydomonas eugametos*) populations (Hess 1980)

and a 50% decrease in the optical density of a green flagellated alga (*Dunaliella bioculata*) (Felix et al. 1988).

Fathead minnows (*P. promelas*) that were exposed to mean concentrations of 5.1 μ g·L¹ died during the 163–263 d portion of a 425-d test. Surviving fish spawned 100 d later than the control fish and fish exposed to 1.9 μ g·L¹. Based on survival, the estimated SMATC for this species is between 1.95 and 5.1 μ g·L¹ (Macek et al. 1976).

In the laboratory, Atlantic salmon (*Salmo salar*) were exposed to 0.5 mg·L⁻¹ trifluralin for 11 h and observed for the following 12 months. Nine of the 100 fish died soon after exposure ceased, and the survivors were more susceptible to fungal infection. Vertebral deformation occurred in the fish with trifluralin concentrations of approximately 100 mg·kg⁻¹ (maximum) (Wells and Cowan 1982).

The estimated SMATC for *D. magna* continuously exposed through three generations is between 2.4 and 7.2 µg·L¹, based on survival (Macek et al. 1976). A study of tubificid worms (*Tubifex tubifex*) demonstrated that a trifluralin sediment concentration of 1.2 mg·kg⁻¹ did not affect the survival or normal functioning of these burrowing worms (Karickhoff and Morris 1985).

The toxic effect of trifluralin on various types of aquatic communities has been investigated using microcosms.

Toxi inform		Species	Toxicity endpoint		Conce	entration (μg·L ⁻¹)	
Acute	Vertebrates	O. mykiss L. macrochirus P. promelas I. punctatus B. fowleri B. fowleri	96-h LC ₅₀			=		
	Invertebrates	Daphnia sp. Eucyclops sp. Cypria sp. M. edulis	48-h LC ₅₀ 48-h LC ₅₀ 48-h LC ₅₀ 48-h LC ₅₀					
	Plants	C. eugametos D. bioculata	LOEC LOEC					
	Vertebrates	P. promelas P. promelas C. variegatus C. variegatus C. variegatus	425-d MATC 425-d MATC 28-d LOEL 570-d LOEL 570-d LOEL		•			
	Invertebrates	D. magna D. magna C. magister	64-d MATC 64-d MATC 80-d MATC					
		n Water Quality G 0.20 μg·L ⁻¹	uideline		ı	ı		
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Figure 1. Select freshwater toxicity data for trifluralin.

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Studies showed that $10\,000\,\mu g\cdot L^4$ trifluralin had no effect on algal communities during 3 weeks (Kosinski 1984; Kosinski and Merkle 1984), and $1000\,\mu g\cdot L^4$ trifluralin did not adversely affect phytoplankton populations, gross primary productivity, or macrophytes over 30 d (Johnson 1986). Another study of microcosms containing snails (*Helosoma* sp.), algae (*Oedogonium cardiacum*), and mosquito fish received continuous inputs of ^{14}C -trifluralin for 30 d. Both the fish and snails reproduced during the test period, but adult fish and offspring exhibited abnormal behaviour and spinal curvature. The range of $9.3–29.8\,\mu g\cdot L^4$ trifluralin was not acutely toxic (Yockim et al. 1980).

The derivation of the guideline value for freshwater aquatic life was initiated with the lowest or most sensitive SMATC from the literature. The lower limit of the SMATC for the 425-d trifluralin exposure for fathead minnows is 1.95 $\mu g \cdot L^1$ (Macek et al. 1976). Vertebral dysplasia and histopathological changes in the pituitary gland of sheepshead minnows, however, have been demonstrated to occur in the 1–5 $\mu g \cdot L^1$ range (Couch 1984).

In the original publication of the guideline (CCME 1992), the $1\,\mu g\cdot L^1$ effect level by Couch (1984) was used to define the LOEC to derive the initial guideline value. However, in 1993 a re-evaluation was done and an errata issued (CCME 1993). The revised water quality guideline for trifluralin for the protection of freshwater life is now 0.20 $\mu g\cdot L^1$. It was derived by multiplying the 425-d SMATC for fathead minnows of 1.95 $\mu g\cdot L^1$ (Macek et al. 1976) by a safety factor of 0.1 (CCME 1991). Given the wide range of half-lives reported for trifluralin in the environment, some of which indicate that the compound is persistent, as well as the bioaccumulation potential of this compound, it is appropriate that a safety factor of 0.1 be chosen.

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