Fluorine (CAS No. 7782-41-4, atomic mass 18.998) is a ubiquitous element of the lithosphere. It belongs to group VII of the periodic table of elements and exists under standard conditions as a pale yellow-green pungent, acrid gas.

The most important natural source of inorganic fluoride in the environment is bedrock from which inorganic fluoride-containing minerals are leached by groundwater and thence into surface water and seawater. In nature, hydrogen fluoride (HF) (molecular weight 20.01 g·mol^{-1}, density 0.991 g·L^{-1}) is the most reactive form of fluorine. Other inorganic fluorides of environmental importance include calcium fluoride (CaF_2) (fluorite or fluorspar; molecular weight 78.08 g·mol^{-1}), sodium fluoride (NaF) (molecular weight 41.99 g·mol^{-1}), and sulfur hexafluoride (SF_6) (molecular weight 146.05 g·mol^{-1}).

These four inorganic fluorides have varied uses in Canada. Hydrogen fluoride is used in the production of synthetic cryolite, aluminium fluoride, motor gasoline alkylates, and chlorofluorocarbons (CFCs) (CIS 1996). Calcium fluoride is used as a flux in steel, glass, and enamel production, as the raw material for the production of hydrofluoric acid and anhydrous hydrogen fluoride (Neumüller 1981), and as a molten electrolyte for the separation of oxygen and alumina (Al_2O_3) in aluminium production. Sodium fluoride is used in drinking water fluoridation, as a preservative in glues, in glass and enamel production, and as a flux in steel and aluminium production (Neumüller 1981). Sodium fluoride is also registered for use as a wood preservative in Canada. Sulfur hexafluoride is extensively used as an insulation and current interruption medium in electrical switch gear such as power circuit breakers, compressed gas transmission lines, and various components in substations (James 1992; Environment Canada 1993).

The total estimated annual release of inorganic fluorides from anthropogenic sources to the Canadian environment is in excess of 12 400 t·a^{-1}. Releases of inorganic fluorides in effluents account for at least 5 500 t (44.7%), whereas over 5 200 t (42%) are emitted in atmospheric outputs (predominantly as HF). Releases of inorganic fluorides to land are estimated to exceed 1 650 t (13.3%). The known major sources of inorganic fluoride releases to the environment include aluminium smelting and phosphate fertilizer production. Collectively, these two major sources account for over 8 700 t (70%) of total inorganic fluorides released (Government of Canada 1993; P. Paine 2000, Environment Canada, pers.com.).

Environmental concentrations in freshwater vary depending on the hydrogeological characteristics. The weathering of alkalic and silicic igneous and sedimentary rocks (e.g., shales) contributes much of the fluoride to natural waters (Warrington 1990). The mean inorganic fluoride level in freshwater across Canada is 0.05 mg F$^-$·L^{-1} (0.01–11.0 mg F$^-$·L^{-1}, n = 51 299) (GSC 1991; Parker 1992). Inorganic fluoride levels in the Great Lakes range from 0.05 to 0.14 mg F$^-$·L^{-1} (Warrington 1990). Seawater shows higher fluoride concentrations than freshwater, with a mean inorganic fluoride concentration of 1.3 mg F$^-$·L^{-1} (Dobbs 1974). Levels of inorganic fluoride in groundwater vary considerably depending on the hydrogeological characteristics of the underlying bedrock. In Canada, concentrations of fluorides in groundwater vary from 0.02 to 1.2 mg F$^-$·L^{-1} and may reach levels as high as 15 mg F$^-$·L^{-1} (Lalonde 1976; Warrington 1990; Boyle and Chagnon 1995).

In water, inorganic fluorides remain dissolved in solution under acidic conditions, low hardness, and the presence of ion-exchange material (e.g., bentonite clays and humic acid) and calcium or aluminium ions (Coker and Shilts 1979; Pickering et al. 1988; Sahu and Karim 1989). Fluoride is important for mobilizing aluminium into soluble complexes and, in acidic waters (pH 2–5), fluoride is almost entirely complexed with aluminium (Skjelkvåle 1994; Radic and Bralic 1995).

Inorganic fluoride taken up by aquatic plants is accumulated in cells and cell walls causing chlorosis,

Table 1. Water quality guidelines for inorganic fluorides for the protection of aquatic life (Environment Canada 2001).

Aquatic life	Guideline value (mg·L^{-1})
Freshwater	0.12[*]
Marine	NRG[†]

[*]Interim guideline.
[†]No recommended guideline.

peripheral necrosis, and leaf distortion and malformation (WHO 1984). Animals take up inorganic fluorides from food and drinking water. Approximately 99% of the body burden of fluoride is accumulated in bones and teeth, substituting the hydroxyl groups in the bone apatite $[Ca_5(OH,F)(PO_4)_3]$ (WHO 1997). Fluoride can also be accumulated in soft tissue (Neuhold and Sigler 1960; Wright and Davison 1975; Wright 1977). The accumulation of inorganic fluorides in aquatic biota is primarily determined by the route of exposure, levels of bioavailable inorganic fluorides, and uptake/excretion kinetics. There is no evidence that inorganic fluorides bioaccumulate through aquatic food chains; however, inorganic fluorides have been found to accumulate to potentially toxic levels in dairy cows fed bonemeal as a food supplement.

Water Quality Guideline Derivation

The interim Canadian water quality guideline for inorganic fluorides for the protection of freshwater life was developed based on the CCME protocol (CCME 1991). Due to insufficient data, no guideline for inorganic fluorides in marine waters could be derived (Environment Canada 2001).

Freshwater Life

Studies for freshwater fish focused predominantly on survival of rainbow trout *(Oncorhynchus mykiss)* and brown trout *(Salmo trutta)*. For acute studies (72–192 h), LC_{50}s ranged from 20 to 223 mg $F^-·L^{-1}$ for these species (Wright 1977; Camargo 1991). In longer term studies (10–21 d), LC_{50}s ranged from 2.3–7.3 to 75–91 mg $F^-·L^{-1}$ for juvenile rainbow trout and brown trout fry, respectively (Angelovic et al. 1961; Neuhold and Sigler 1960). Pimentel and Bulkley (1983) recorded a 96–h LC_{50} of 51.0 mg $F^-·L^{-1}$ at 17 mg $CaCO_3·L^{-1}$ for rainbow trout averaging 58 mm in length. These authors demonstrated a linear relationship between water toxicity and hardness.

Field and laboratory studies demonstrating the sublethal effects of fluorides are available also. Migration patterns of chinook *(O. tschawytscha)*, chum *(O. keta)*, and coho *(O. kisutch)* salmon were disrupted when fish were exposed to fluoride levels of 0.5 mg $F^-·L^{-1}$ prior to and during migration runs. For these species, the authors suggest a threshold for fluoride sensitivity of 0.2 mg $F^-·L^{-1}$ (Damkaer and Dey 1989). In the field part of this study, aluminium levels in the river may have been a confounding factor.

With regard to invertebrates, neonates of *Daphnia magna* experienced impaired reproduction and reduced hatchability at fluoride levels of 34 mg $F^-·L^{-1}$ beginning on day 12 of a 21-d exposure test (Fieser et al. 1986). In contrast, Dave (1984) estimated the 21-d NOEL for growth and reproduction in *D. magna* to be an order of magnitude lower, between 3.7 and 7.4 mg $F^-·L^{-1}$ in reconstituted hard water (250 mg $CaCO_3·L^{-1}$); however, there was no clear dose–response relationship in this study. Sanders and Cope (1966) investigated survival of *D. pulex* and *Simocephalus serrulatus*. The 48-h EC_{50}s for immobilization of *D. pulex* and *S. serrulatus* were 2.71 and 5.43 mg $F^-·L^{-1}$, respectively. Cryolite (Na_3AlF_6) was used as a test substance, therefore, aluminium-based toxicity could be a confounding factor to these results. The exposure of fingernail clams *(Musculium transversum)* to 2.8 mg $F^-·L^{-1}$ during an 8-week bioassay led to 60% mortality compared to 25% among control clams (Sparks et al. 1983).

A series of acute static tests on eight species of net-spinning caddisflies was conducted by Camargo (1996), Camargo et al. (1992), and Camargo and Tarazona (1991) among others. *Hydropsyche bronta* was the most sensitive species with 48-, 96-, and 144-h LC_{50} values of 52.6, 17.0, and 11.5 mg $F^-·L^{-1}$, respectively (Camargo et al. 1992). Camargo (1996) re-evaluated some of these data and reported a slightly lower 96-h LC_{50} of 15.8 mg $F^-·L^{-1}$. Sublethal effects were also tested in five of the eight species. The 96-h EC_{50}s for net larvae migration ranged from 22.95 mg $F^-·L^{-1}$ for *H. bulbifera* to 43.09 mg $F^-·L^{-1}$ for *H. lobata*; *H. bronta* was not tested (Camargo and Tarazona 1990; Camargo and La Point 1995). Water quality conditions were similar among tests (e.g., water hardness varied from 12 to 40 mg $CaCO_3·L^{-1}$).

Most plant species were not as sensitive as fish and invertebrate species, with one exception. The green alga *Chlorella pyrendoidosa* showed a growth inhibition of 37% after 48 h exposure to fluoride levels as low as 2.0 mg $F^-·L^{-1}$ (Smith and Woodson 1965).

The interim guideline for total inorganic fluorides is 0.12 mg $F^-·L^{-1}$. This guideline is derived from the lowest acceptable adverse effect level reported: a 144-h LC_{50} value of 11.5 mg $F^-·L^{-1}$ for the caddisfly *Hydropsyche bronta* (Camargo et al. 1992; Camargo 1996). Sodium fluoride was used as the fluoride-containing compound. Duplicate tests were conducted with a control and five different fluoride concentrations. Throughout the experiment, fluoride concentrations and physicochemical parameters were measured. The water quality conditions (temperature of 18°C; pH 7.8, 9.5 mg·L^{-1} for dissolved

oxygen; water hardness of 40.2 mg $CaCO_3 \cdot L^{-1}$) are suitable for *H. bronta* and applicable to Canadian freshwaters. Moreover, *Hydropsyche bronta* is a caddisfly species found in Canada. As the LOEL of 11.5 mg $F^- \cdot L^{-1}$ value is an acute, lethal endpoint, a safety factor of 0.01 was applied.

Toxicity information		Species	Toxicity endpoint	Concentration (mg·L⁻¹)
Acute	Vertebrates	*O. mykiss*	96-h LC_{50}	
		S. trutta	90-h LC_{50}	
		O. mykiss	192-h LC_{50}	
		S. trutta	192-h LC_{50}	
	Invertebrates	*H. bronta*	48-h LC_{50}	
		H. bronta	96-h LC_{50}	
		H. bronta	144-h LC_{50}	
		H. bulbifera	96-h EC_{50}	
		H. lobata	96-h EC_{50}	
		D. magna	48-h EC_{50}	
		D. magna	24-h EC_{50}	
		D. magna	48-h EC_{50}	
		D. pulex	48-h EC_{50}	
		S. serrulata	48-h EC_{50}	
	Plants	*C. pyrendoidosa*	48-h EC_{50}	
Chronic	Vertebrates	*O. mykiss*	20-d LC_{50}	
		C. carpio	20-d LC_{50}	
		O. mykiss	10-d LC_{50}	
	Invertebrates	*D. magna*	14-d EC_{100}	
		M. transversum	56-d LC_{50}	
Canadian Water Quality Guideline 0.12 mg·L⁻¹				

Toxicity endpoints:
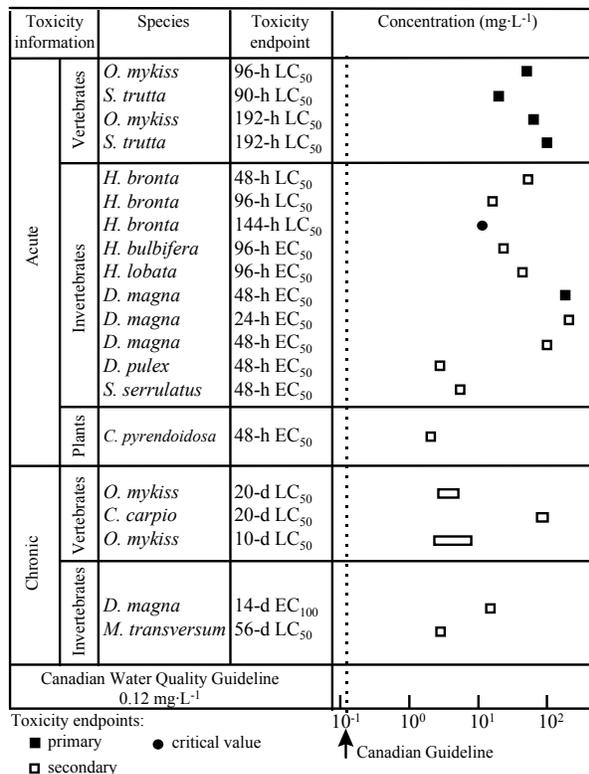■ primary ● critical value
□ secondary ↑ Canadian Guideline

Figure 1. Select freshwater toxicity data for inorganic fluorides.

Several studies have shown that inorganic fluoride toxicity is negatively correlated with water hardness and positively correlated with ambient temperature (Angelovic et al. 1961; Pimentel and Bulkley 1983; Smith et al. 1985; Fieser et al. 1986); however, there currently are insufficient data to develop a quantitative correlation or a guideline matrix. Further multifunctional experiments at various combinations in the parameters (i.e., water hardness and temperature) are needed to derive Canadian water quality guidelines that are based on these parameters. Nevertheless, it is expected that factors such as water hardness and temperature, the presence of cations such as calcium, magnesium (Pimentel and Bulkley 1983; Smith et al. 1985), and, potentially, selenium (Pang et al 1996) or anions such as chloride (Neuhold and Sigler 1962) can reduce the toxicity of inorganic fluorides on a site-specific basis.

In contrast, fluoride toxicity to aquatic plants (Husaini et al. 1996; Rai et al. 1998) and, potentially, aquatic animals is enhanced by the presence of metals, especially aluminium. In water, inorganic fluorides remain dissolved in solution under acidic conditions, low hardness, and the presence of ion-exchange material (e.g., bentonite clays and humic acid) and of calcium or aluminium ions (Coker and Shilts 1979; Pickering et al. 1988; Sahu and Karim 1989). Fluoride is important for mobilizing aluminium into soluble complexes. At pH 5 and below, fluoride is almost entirely complexed with aluminium (Skjelkvåle 1994; Radic and Bralic 1995). Therefore, judiciousness is required when using guidelines at a specific site. For more information on the toxicity of aluminium, see also the Canadian water quality guideline for the protection of aquatic life for aluminium.

Lastly, migratory anadromous fish should be considered in the development of site-specific objectives, where appropriate. Anadromous fish species appear to be more sensitive to inorganic fluorides in freshwater (effects observed at levels as low as 0.5 mg $F^- \cdot L^{-1}$) than in marine water where the natural concentration inorganic fluoride averages 1.3 mg $F^- \cdot L^{-1}$ (Damkaer and Dey 1989; Dobbs 1974).

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