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A comparative analysis of water quality guidelines for fluoride in Canada and Spain

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ABSTRACT

A comparative analysis of water quality guidelines for fluoride in Canada and Spain

Although anthropogenic fluoride (F^-) pollution is a serious worldwide environmental problem, only a few countries have currently established national water quality criteria for the protection of freshwater biota. Since Canada is a global leader in biodiversity conservation that exhibits restrictive water quality benchmarks, I carry out a comparative analysis of water quality guidelines for fluoride in Canada and Spain. The Canadian water quality benchmark of 0.12 mg F^-/l (maximum allowable concentration) prevents Canada's fresh waters from significant adverse events of fluoride pollution, thereby protecting sensitive native aquatic invertebrates and adult-migrating Pacific salmon. By contrast, the Spanish water quality benchmark of 1.7 mg F^-/l (annual mean concentration) allows not only continuous levels of fluoride pollution more than six times higher than natural fluoride concentrations in the fresh waters of mainland Spain, but also much higher discontinuous levels of fluoride pollution (> 15 mg F^-/l). This unacceptable scenario is contrary to the current environmental goal of "zero pollution" in the European Union. In view of the existing toxicological data, a Spanish water quality guideline of 0.15−0.3 mg F^-/l (maximum allowable concentration) seems much more reasonable. The recommended water quality guideline for fluoride would much better protect sensitive native fish and invertebrate species, and prevent significant bioaccumulation of fluoride in tolerant freshwater organisms.

Key words: fluoride pollution, toxicity, freshwater biota, water quality benchmarks

RESUMEN

Un análisis comparativo de las directrices de calidad del agua para el fluoruro en Canadá y España

Aunque la contaminación antropogénica por fluoruro (F^-) es un grave problema ambiental a escala mundial, solo unos pocos países han establecido actualmente criterios nacionales de calidad del agua para proteger la biota de agua dulce. Dado que Canadá es un líder mundial en la conservación de la biodiversidad que exhibe estándares de calidad del agua restrictivos, realizo un análisis comparativo de las directrices de calidad del agua para el fluoruro en Canadá y España. La norma canadiense de calidad del agua de 0.12 mg F^-/l (concentración máxima permitida) evita que las aguas dulces de Canadá sufran eventos adversos significativos de contaminación por fluoruro, protegiendo de este modo a los salmones adultos migrantes del Pacífico y a los sensibles invertebrados acuáticos nativos. Por el contrario, la norma española de calidad del agua de 1.7 mg F^-/l (concentración media anual) permite no solo niveles continuos de contaminación por fluoruro más de seis veces superiores a las concentraciones naturales de fluoruro en las aguas dulces de la España peninsular, sino también niveles discontinuos de contaminación por fluoruro mucho más elevados (> 15 mg F^-/l). Este escenario inaceptable es contrario al actual objetivo ambiental de "contaminación cero" en la Unión Europea. En vista de los datos toxicológicos existentes, una norma española de calidad del agua de 0.15−0.3 mg F^-/l (concentración máxima permitida) parece mucho más razonable. La directriz recomendada de calidad del agua para el fluoruro protegería mucho mejor a las especies nativas sensibles de peces e invertebrados y evitaría una bioacumulación significativa de fluoruro en organismos de agua dulce tolerantes.

Palabras clave: *contaminación por fluoruro, toxicidad, biota de agua dulce, estándares de calidad del agua*

INTRODUCTION

The first major natural source of fluoride (F^-) in surface and ground waters is the mechanical and chemical weathering of F-containing minerals such as villianmite (NaF), fluorite (CaF_2), sellaite (MgF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5(PO_4)_3F$) (Brindha & Elango, 2011; Malago et al., 2017; Fuge, 2019; Schlesinger et al., 2020). Volcanoes represent the second major natural source by the release of ash and fumes containing fluorine (as HF, mainly) into the atmosphere and the subsequent deposition of atmospheric fluoride (Brindha & Elango, 2011; Malago et al., 2017; Fuge, 2019; Schlesinger et al., 2020). Globally, rivers deliver millions of tons of particulate and dissolved fluorine to the oceans every year, being removed from seawater primarily by the deposition of terrigenous and authigenic sediments (Schlesinger et al., 2020).

Fluoride concentrations in unpolluted waters generally range from 0.01 to 0.3 mg F^-/l for fresh surface water, from 0.1 to 1.2 mg F^-/l for groundwater, and from 0.9 to 1.5 mg F^-/l for seawater (Warner, 1971; Gupta et al., 1978; Fuge & Andrews, 1988; Skjelkvåle, 1994; Camargo, 2003; Millero et al., 2008; Brindha & Elango, 2011; Ali et al., 2016; Malago et al., 2017; Fuge, 2019; Schlesinger et al., 2020). In various regions of the world (e.g., Western USA, Northern Mexico, Chaco-Pampean Plain, North Africa, East African Rift Valley, Canary Islands, Indo-Gangetic Basin, North China Plain), surface and ground waters can however present higher fluoride concentrations due to geological characteristics (Li et al., 2015; Malago et al., 2017; Mukherjee & Singh, 2018; Zhang et al., 2019; Rubio et al., 2020; Schlesinger et al., 2020; Cao et al., 2022). As a result, water supplies in those geographic areas often exhibit fluoride concentrations above 1.5 mg F^-/l. This is the upper limit for fluoride in drinking water recommended by the World Health Organization to prevent dental, skeletal and non-skeletal fluorosis in humans (WHO, 2011), and many countries have established drinking water quality standards below 1.5 mg F^-/l. Fortunately, defluoridation techniques, such as adsorption, electrocoagulation, ion exchange, reverse osmosis, filtration, precipitation and phytoremediation, can be used to remove fluoride from water supplies and wastewater (Loganathan et al., 2013; Karmakar et al., 2016; Mobeen & Kumar, 2017; Yadav et al., 2018; Katiyar et al., 2020; Solanki et al., 2021).

In addition to natural sources, certain human activities can significantly increase fluoride concentrations in aquatic ecosystems, in some cases more than 100 times the natural background level (Camargo, 2003). Major anthropogenic sources of fluoride are the combustion of coal, the extraction of groundwater, the smelting of aluminium, the mining of fluorapatite deposits, the manufacture of phosphate fertilizers, the production and use of fluoride chemicals, the manufacture of bricks, ceramics and glass, and the fluoridation of municipal waters (within a recommended range of 0.5–1.5 mg F^-/l; WHO, 2011) to prevent dental caries (Camargo, 2003; Jha et al., 2011; Ali et al., 2016; Fuge, 2019; Lacson et al., 2020; Schlesinger et al., 2020). According to Schlesinger et al. (2020), human activities have currently more than doubled the global flux of fluoride into the atmosphere and in rivers.

Increased fluoride concentrations from human activities can cause toxicity to aquatic organisms (Camargo, 2003; Lacson et al., 2020). This toxicity resides in the fact that fluoride ions inhibit the normal activity of numerous enzymes (phosphoryl-transfer enzymes, primarily) that are essential for key metabolic pathways such as the production of energy and the biosynthesis of nucleic acids and proteins (Camargo, 2003; Johnston & Strobel, 2020). Because certain freshwater animals appear to be relatively sensitive to fluoride toxicity, water quality criteria below 0.5 mg F^-/l have been recommended in the past (Camargo, 2003).

Nonetheless, an examination of available national water quality guidelines shows that only a few countries have currently established water quality benchmarks for fluoride to protect freshwater biota. As far as I know, Canada with a water quality benchmark of 0.12 mg F^-/l (EC, 2001; CCME, 2002), Spain with a water quality benchmark of 1.7 mg F^-/l (MAGRAMA, 2015), and Philippines with a water quality benchmark of 1.0 mg F^-/l (DENR, 2016). Since the available toxicological information on the Philippine water quality benchmark is very limited, and most importantly because Canada is a global leader in biodiversity conservation (UNBC, 2022), exhibiting restrictive water quality benchmarks (CCME, 2023), I compare water quality guidelines for fluoride in Canada and Spain. In view of scientific discoveries derived from field and laboratory studies with fluoride and native species, this comparative analysis highlights that the Canadian water quality benchmark is much more rational than the Spanish one, which must be substantially reduced to adequately protect sensitive native fish and invertebrate species from fluoride pollution events.

THE CANADIAN WATER QUALITY GUIDELINE FOR FLUORIDE

Over time, the Canadian Council of Ministers of the Environment has published specific documents that explain in detail how and why Canadian water quality guidelines have been established for numerous chemical elements and compounds (CCME, 2023). Regarding fluoride, the Canadian water quality guideline is mainly based on the ecotoxicological study conducted by Camargo et al. (1992). These authors examined the short-term (6 days) toxicity of fluoride to last instar larvae of three Nearctic caddisfly species in soft water (total hardness = 40.2 mg $CaCO_3$/l) at 18 ºC. They estimated 144 h LC_{50} values (mg F^-/l) of 24.2 for *Cheumatopsyche pettiti*, 21.4 for *Hydropsyche occidentalis* and 11.5 for *Hydropsyche bronta*, concluding that fluoride pollution could have some relevance in structuring net-spinning caddisfly guilds in a polluted reach of the Cache la Poudre River (Colorado). Subsequently, the Canadian Council of Ministers of the Environment established an interim water quality benchmark of 0.12 mg F^-/l (maximum allowable concentration) by dividing the 144 h LC_{50} value of 11.5 mg F^-/l for *H. bronta* by a standard safety factor of 100 (EC, 2001; CCME, 2002). Considering the upper 95 % confidence limit of the 144 h LC_{50} value for *H. bronta* (14.8 mg F^-/l; Camargo et al., 1992), the Canadian water quality guideline for fluoride might be increased to 0.15 mg F^-/l.

Since the mean level of fluoride in freshwater across Canada is 0.05 mg F^-/l (EC, 2001; CCME, 2002), the Canadian water quality benchmark of 0.12 mg F^-/l (or 0.15 mg F^-/l) prevents Canada's fresh waters from significant adverse events of fluoride pollution. Actually, this water quality benchmark can protect not only sensitive Nearctic caddisflies (Camargo et al., 1992), but also sensitive Nearctic amphipods and mayflies (Metcalfe-Smith et al., 2003), as well as adult-migrating Pacific salmon (Damkaer & Dey, 1989), from anthropogenic fluoride pollution.

Damkaer & Dey (1989) conducted stream mesocosm studies to examine the toxic effect of fluoride on the behaviour of adult-migrating Pacific salmon. After performing numerous behavioural experiments at Big Beef Creek Fish Research Station (Washington) during 1983 and 1984, they found that a one-hour exposure to 0.5 mg F^-/l was enough to adversely affect the upstream migration of the chinook salmon *Oncorhynchus tshawytscha* and the coho salmon *Oncorhynchus kisutch*. Damkaer & Dey (1989) concluded that a concentration of 0.2 mg F^-/l would be the threshold for fluoride sensitivity in these two salmonid species.

Metcalfe-Smith et al. (2003) carried out short-term (48–96 hours) laboratory experiments to examine the acute toxicity of fluoride to four invertebrate species in hard water (total hardness = 140–150 mg $CaCO_3$/l) at 20 ºC. They estimated the following median lethal concentrations: a 48 h LC_{50} value of 283 mg F^-/l for neonates of the water flea *Daphnia magna*; a 48 h LC_{50} value of 14.6 mg F^-/l for juveniles of the amphipod *Hyalella azteca*; a 96 h LC_{50} value of 32.3 mg F^-/l for nymphs of the giant mayfly *Hexagenia limbata*; a 96 h LC_{50} value of 124 mg F^-/l for larvae of the midge *Chironomus tentans*. If we divide the estimated LC_{50} values for *H. azteca* and *H. limbata* by a standard safety factor of 100, the resulting safe concentrations for these two sensitive Nearctic freshwater invertebrate species are close to, but above, the Canadian water quality benchmark of 0.12 mg F^-/l.

Some researchers (McPherson et al., 2014; Parker et al., 2022) have however considered the Canadian water quality guideline of 0.12 mg F^-/l to be overly conservative. Those authors, using toxicological data derived from published toxicity studies with Nearctic native species, invasive alien species, and even species from other biogeographic realms, developed general pro-

Table 1. Short-term toxicity of fluoride to aquatic organisms (algae, macrophytes, invertebrates and fish) inhabiting fresh waters of the Iberian Peninsula. Only native species (from endemic to cosmopolitan) are considered. Safe concentrations were estimated by dividing median lethal or effective concentrations (LC_{50} or EC_{50}) by a standard safety factor of 100. Exposure times (hours) in parentheses with LC_{50} and EC_{50} values. *Toxicidad a corto plazo del fluoruro para organismos acuáticos (algas, macrófitos, invertebrados y peces) que habitan las aguas dulces de la Península Ibérica. Solo se consideran especies nativas (desde endémicas hasta cosmopolitas). Las concentraciones seguras se estimaron dividiendo las concentraciones letales o efectivas medias (CL_{50} o CE_{50}) entre un factor estándar de seguridad de 100. Los tiempos de exposición (horas) entre paréntesis con los valores de CL_{50} y CE_{50}.*

Species	EC_{50} or LC_{50} (mg F^-/l)	Toxicological effect	Reference
Algae			
Chlamydomonas reinhardtii	289 (72 h) 2.89	Growth inhibition (safe concentration)	Chae et al. (2016)
Chlorella pyrenoidosa	118 (72 h) 1.18	Growth inhibition (safe concentration)	Li et al. (2013)
Macrophytes			
Lemna minor	391 (168 h) 3.91	Growth inhibition (safe concentration)	Pearcy et al. (2015)
Invertebrates			
Austropotamobius pallipes	28.9 (192 h) 0.29	Mortality in adults (safe concentration)	Aguirre-Sierra et al. (2013)
Chimarra marginata	44.9 (96 h) 0.45	Mortality in larvae (safe concentration)	Camargo and Tarazona (1990)
Daphnia magna	283 (48 h) 2.83	Mortality in neonates (safe concentration)	Metcalfe-Smith et al. (2003)
Echinogammarus calvus	10.8 (48 h) 0.11	Mortality in adults (safe concentration)	Gonzalo and Camargo (2013)
Hydropsyche bulbifera	26.3 (96 h) 0.26	Mortality in larvae (safe concentration)	Camargo and Tarazona (1990)
Hydropsyche exocellata	26.5 (96 h) 0.27	Mortality in larvae (safe concentration)	Camargo and Tarazona (1990)
Hydropsyche lobata	48.2 (96 h) 0.48	Mortality in larvae (safe concentration)	Camargo and Tarazona (1990)
Hydropsyche pellucidula	38.5 (96 h) 0.39	Mortality in larvae (safe concentration)	Camargo and Tarazona (1990)
Hydropsyche tibialis	30.6 (96 h) 0.31	Mortality in larvae (safe concentration)	Camargo (2004)
Physella acuta	120 (96 h) 1.20	Mortality in adults (safe concentration)	Camargo and Alonso (2017)
Fish			
Salmo trutta	165 (96 h) 1.65	Mortality in fingerlings (safe concentration)	Camargo (1991)

tective values of fluoride for freshwater life that are much less restrictive: 1.94 mg F^-/l (McPherson et al., 2014) and 4.0 mg F^-/l (Parker et al., 2022). However, these water quality benchmarks would allow fluoride pollution levels 40–80 times higher than natural fluoride concentrations in the fresh waters of Canada. Moreover, they are much higher than the estimated threshold for fluoride sensitivity in adult-migrating Pacific salmon, and the estimated safe concentrations for sensitive Nearctic freshwater invertebrates. See also Sinclair & MacDonald (2015) and Camargo (2022) for deeper critical analyses of McPherson et al.'s (2014) and Parker et al.'s (2022) papers.

THE SPANISH WATER QUALITY GUIDELINE FOR FLUORIDE

In 2015, the former Spanish Ministry of Agriculture, Food and Environment published the Royal Decree 817/2015, establishing the criteria for monitoring and evaluating the ecological status of surface waters, as well as the water quality standards for many chemical elements and compounds (MAGRAMA, 2015). Additionally, Pujante et al. (2016) explained the methodology used to establish reference conditions and limits between classes of ecological status in Spanish rivers. Nevertheless, it is not clear with what accuracy the Spanish water quality benchmarks were established, nor which aquatic organisms were specifically considered. The Royal Decree 817/2015, in its annex VII, only indicates the following general rules: 1) to develop water quality standards, the core set of taxa must be composed of primary producers, *Daphnia*, and fish; 2) safety factors should vary from 1000 to 10, depending on whether selected toxicological data are median lethal (or effective) concentrations or no observable effect concentrations; 3) in the event that data on persistence and bioaccumulation are available, they should be taken into account; 4) the resulting water quality standards should be compared with possible evidence from field studies in order to calculate, if necessary, a more precise safety factor; 5) the resulting water quality standards will also be subjected to critical expert review and public consultation in order, among other things, to allow the calculation of the most accurate safety factor.

The problem with the Spanish water quality guideline for fluoride (1.7 mg F^-/l; annex V in MAGRAMA, 2015) is that this water quality benchmark cannot adequately protect sensitive native freshwater invertebrates, such as amphipods, caddisflies and crayfish (see Table 1), from anthropogenic fluoride pollution. Furthermore, the problem would be worse, affecting other native freshwater species, because the Spanish water quality benchmark of 1.7 mg F^-/l does not refer to a maximum allowable concentration of fluoride (as is the case with the Canadian water quality benchmark of 0.12 mg F^-/l), but it refers to an annual mean concentration of fluoride. In consequence, as fluoride concentrations in unpolluted freshwater across continental Spain usually are lower than 0.3 mg F^-/l (MITECO, 2023), the Spanish water quality guideline of 1.7 mg F^-/l allows not only continuous levels of fluoride pollution more than six times higher than natural fluoride concentrations in the fresh waters of mainland Spain, but also much higher discontinuous levels of fluoride pollution. For example, assuming a monthly sampling period to annually assess fluoride pollution, a pollution level of 16 mg F^-/l could be allowed for one month if during the remaining eleven months the fluoride concentration is $\leq$ 0.3 mg F^-/l. This huge discontinuous level of fluoride pollution would cause significant impacts on freshwater communities. Furthermore, this unacceptable scenario contrasts dramatically with the current environmental goal of “zero pollution” in the European Union (EEA, 2020).

From a simple comparison of toxicological data in Table 1, we can see that native amphipods (*Echinogammarus calvus*), caddisflies (*Chimarra marginata*, *Hydropsyche bulbifera*, *H. exocellata*, *H. lobata*, *H. pellucidula* and *H. tibialis*) and crayfish (*Austropotamobius pallipes*) are more sensitive to fluoride toxicity than other native freshwater organisms, such as the green algae *Chlamydomonas reinhardtii* and *Chlorella pyrenoidosa*, the duckweed *Lemna minor*, the water flea *Daphnia magna*, the snail *Physella acuta*, and the trout *Salmo trutta*. In this regard, the relatively high concentration of the Spanish water quality guideline for fluoride (1.7 mg F^-/l) could basically be a consequence of the first general rule for developing water quality standards, that is, the core set of taxa must be composed of primary producers, *Daphnia*, and fish (annex VII in MAGRAMA, 2015). However, taking into account the other four general rules (annex VII in MAGRAMA, 2015), it is difficult to understand why toxicological studies with fluoride and sensitive native species (Camargo & Tarazona, 1990; Camargo, 2004; Aguirre-Sierra et al., 2013; Gonzalo & Camargo, 2013) were apparently overlooked.

RECOMMENDING A MORE RESTRICTIVE SPANISH WATER QUALITY GUIDELINE FOR FLUORIDE

The best and most reasonable national water quality guidelines for fluoride should match the natural fluoride levels in the fresh waters of each country (Camargo, 2022). A less restrictive but still reasonably valid alternative is to establish water quality guidelines for fluoride that essentially protect the most sensitive native species, especially if those species contribute significantly to the structure and function of aquatic ecosystems (Camargo, 2022). This is the case of freshwater amphipods, caddisflies and crayfish in the Iberian Peninsula (Table 1). By contrast, the use of toxicological data for native species that are relatively tolerant to fluoride toxicity (e.g., *Chlamydomonas reinhardtii*, *Daphnia magna*, *Lemna minor*; Table 1), as well as the use of toxicological data for invasive alien species and species from other biogeographic realms, seem unreasonable to develop proper national water quality criteria for fluoride (Camargo, 2022).

Although fluoride toxicity to freshwater invertebrates tends to decrease with increasing the water content of calcium and chloride (Camargo, 2003, 2004; Gonzalo & Camargo, 2012; Pearcy et al., 2015), field and laboratory studies have shown that *Echinogammarus calvus* is very sensitive to fluoride toxicity in hard waters with relatively high ionic content (Gonzalo & Camargo, 2013). Based on the 48 h LC_{50} value of 10.8 mg F^-/l for *E. calvus* (Gonzalo & Camargo, 2013), a safe concentration of 0.11 mg F⁻/l may be estimated (Table 1). However, considering the upper 95 % confidence limit of the 48 h LC_{50} value for *E. calvus* (12.5 mg F⁻/l; Gonzalo & Camargo, 2013), and the maximum fluoride concentration measured in its natural (unpolluted) habitat (0.15 mg F⁻/l; Gonzalo & Camargo, 2013), a water quality benchmark of 0.15 mg F⁻/l may be adequate to protect *E. calvus* from anthropogenic fluoride pollution. For other sensitive native freshwater invertebrates, such as *Austropotamobius pallipes*, *Chimarra marginata*, *Hydropsyche bulbifera*, *H. exocellata*, *H. lobata*, *H. pellucidula* and *H. tibialis*, a slightly less restrictive water quality benchmark of 0.3 mg F⁻/l might be enough to protect them, since their estimated safe concentrations are in the range of 0.26–0.48 mg F⁻/l (Table 1).

Obviously, the proposed water quality benchmarks of 0.15 and 0.3 mg F⁻/l refer to a maximum allowable concentration of fluoride and not to an annual mean concentration of fluoride (as is the case with the current Spanish regulation). I must also point out that these water quality benchmarks would not be applicable in the Canary Islands. Because of their volcanic origin, naturally high levels of fluoride in surface and ground waters can be found in this archipelago, particularly in the island of Tenerife where fluoride concentrations in the range of 4–7 mg F⁻/l have been reported (Rubio et al., 2020; Revelo-Mejía et al., 2023).

The recommended Spanish water quality guideline for fluoride (0.15−0.3 mg F⁻/l) might also prevent significant bioaccumulation of fluoride in the tissues of tolerant freshwater organisms. Gonzalo & Camargo (2013) conducted field studies in the middle Duraton River (Central Spain) and found that fluoride bioaccumulation in aquatic macrophytes (*Fontinalis antipyretica* and *Potamogeton pectinatus*) and invertebrates (*Ancylus fluviatilis* and *Pacifastacus leniusculus*), living downstream from an industrial effluent (mean river fluoride concentration = 0.82 mg F⁻/l), was significantly higher than the fluoride content in individuals of the same four species living upstream from the industrial effluent (mean river fluoride concentration = 0.14 mg F⁻/l). Besides, while *Echinogammarus calvus* was relatively abundant upstream from the industrial effluent, it was absent downstream (Gonzalo & Camargo, 2013).

On the other hand, several studies have shown that other chemical pollutants can similarly alter the spawning river migration of Atlantic and Pacific salmons (see, for example, Saunders & Sprague, 1967; Goldstein et al., 1999; Tierney et al., 2010; Ross et al., 2013). Thus, if we consider that a fluoride concentration as low as 0.5 mg F⁻/l can adversely affect the behaviour of adult-migrating Pacific salmon (Damkaer & Dey, 1989), the recommended Spanish water quality guideline for fluoride (0.15−0.3 mg F⁻/l) could protect adult-migrating Atlantic salmon (*Salmo salar*) from anthropogenic fluoride pollution.

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