Letter to the Editor

Letter to the Editor on Parker et al. 2022 "Development of Fluoride Protective Values for Aquatic Life Using Empirical Bioavailability Models"

Julio A. Camargo*

Departamento de Ciencias de la Vida, Unidad Docente de Ecología, Universidad de Alcalá, Alcalá de Henares, Madrid, Spain

To the Editor:

Despite human activities have currently increased the global flux of fluoride into the atmosphere and in rivers by more than a factor of 2 (Schlesinger et al., 2020), national water quality criteria for fluoride to protect freshwater biota have been established in only a few countries. The Canadian Council of Ministers of the Environment developed an interim water quality guideline of 0.12 mg F^-/L (Environment Canada, 2001) by multiplying the 144 h median lethal concentration (LC50) value of 11.5 mg F^-/L for the caddisfly *Hydropsyche bronta* (Camargo et al., 1992) by a safety factor of 0.01. This Canadian water quality guideline for fluoride appears to be adequate to protect sensitive native freshwater animals from anthropogenic fluoride pollution.

Parker et al. (2022), however, have considered the Canadian water quality guideline for fluoride to be overly conservative, developing fluoride protective values for freshwater life that are much less restrictive. Based on Pearcy et al.'s (2015) work, Parker et al. (2022) conducted a meta-analysis of available aquatic toxicity literature for fluoride to evaluate the utility of water hardness, alkalinity, and chloride as toxicity modifying factors (TMFs) in multiple linear regression-based bioavailability models of freshwater taxa. When considering TMFs, they developed chronic protective values ranging from 3.4 to 10.4 mg F^-/L, while they estimated a chronic protective value of 4.0 mg F^-/L without considering TMFs. Parker et al. (2022) concluded that suitable water quality benchmarks for fluoride would range from 3.4 to 10.4 mg F^-/L, depending on the presence of TMFs (notably chloride and alkalinity).

In contrast to Parker et al.'s (2022) meta-analysis, Pearcy et al. (2015) conducted acute toxicity tests using juveniles of the amphipod *Hyalella azteca* and fry of the salmonid *Oncorhynchus mykiss* with varying concentrations of water hardness, chloride, and alkalinity as possible toxicity modifying factors for fluoride. They found that chloride played a major role in modifying fluoride toxicity when hardness and alkalinity were held constant: estimated 96 h LC50 values for *H. azteca* were 8.1, 11.0, 17.8, and 24.8 mg F^-/L with 3, 6, 12, and 25 mg Cl^-/L, respectively, in moderately hard water (80 mg $CaCO_3$/L) and low alkalinity (20 mg $CaCO_3$/L); estimated 96 h LC50 values for *O. mykiss* were 27.7, 49.9, 55.1, and 90.9 mg F^-/L with 4, 8, 16, and 32 mg Cl^-/L, respectively, in soft water (10 mg $CaCO_3$/L) and very low alkalinity (4 mg $CaCO_3$/L). Pearcy et al. (2015) also found that alkalinity was not a toxicity modifying factor, whereas hardness did not appear to be a primary toxicity modifying factor. In addition, Pearcy et al. (2015) conducted chronic toxicity tests with varying concentrations of chloride (2, 6, and 18 mg Cl^-/L), finding that chloride also reduced fluoride toxicity in both test species: estimated 14 days LC50 values for *H. azteca* were 4.8, 8.6, and 12.9 mg F^-/L in moderately hard water (88–90 mg $CaCO_3$/L), and estimated 7 days LC50 values for *O. mykiss* were 11.5, 25.4, and 40.9 mg F^-/L in soft water (6 mg $CaCO_3$/L). The ameliorating effect of chloride might be due to an intensified competition between F^- and Cl^- ions for carriers in the membranes of epithelial cells, decreasing the influx of fluoride into cells as the concentration of chloride in the aquatic medium increases (Camargo, 2004; Gonzalo & Camargo, 2012). In fact, fluoride bioaccumulation in signal crayfish significantly decreased with increasing water chloride content (Gonzalo & Camargo, 2012). Nevertheless, according to Pearcy et al. (2015), chloride did not decrease the acute toxicity of fluoride to *O. mykiss* in moderately hard water, and the role of chloride as a primary toxicity modifying factor for fluoride was inconsistent in chronic toxicity tests with the cladoceran *Ceriodaphnia dubia* and the cyprinid *Pimephales promelas*.

In my opinion, Parker et al. (2022) have not properly considered Pearcy et al.'s (2015) findings, particularly that alkalinity was not a toxicity modifying factor for fluoride. Furthermore, after reviewing available aquatic toxicity literature for fluoride, I have not found any study showing that alkalinity is a toxicity modifying factor (see also Camargo, 2003). On the other hand,

* Address correspondence to julio.camargo@uah.es
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Parker et al.'s (2022) chronic protective values (3.4–10.4 mg F^-/L) exhibit serious drawbacks that invalidate them as a suitable alternative to the Canadian water quality guideline of 0.12 mg F^-/L (Environment Canada, 2001).

To develop their water quality benchmarks, Parker et al. (2022) have used a heterogeneous mix of toxicological data derived from chronic and subchronic toxicity studies not only with native species, but also with invasive alien species (e.g., *Branchiura sowerbyi*, *Cyprinus carpio*, *Potamopyrgus antipodarum*, *Salmo trutta*) and species from other biogeographic realms (e.g., *Austropotamobius pallipes*, *Acipenser baerii*, *Daphnia carinata*). In my opinion, to develop fluoride protective values for freshwater life in relation to a biogeographic realm or country (e.g., the Nearctic realm or Canada), it is not appropriate to use toxicological data derived from toxicity studies with invasive alien species and species from other biogeographic realms (e.g., the Palearctic and Australasian realms). Only toxicological data derived from toxicity studies with native species, in particular those relating to sensitive native species, should be taken into account. Unfortunately, Parker et al. (2022) did not consider toxicological data for sensitive adult-migrating Pacific salmons (Damkaer & Dey, 1989) and Nearctic caddisfly larvae (Camargo, 1996; Camargo et al., 1992).

Damkaer and Dey (1989), after observing in the Columbia River near John Day Dam (USA) that fluoride pollution from an aluminium smelter outfall caused migration delays of adult Pacific salmons, conducted stream mesocosm studies to verify if fluoride could affect the migratory behaviour of upstream migrating salmons. To avoid the potential influence of unknown pollutants in the Columbia River, stream mesocosm studies were carried out at Big Beef Creek Fish Research Station on Hood Canal, Washington (Damkaer & Dey, 1989). They performed numerous behavioural tests during 1983 and 1984 using a concrete walled spawning channel furnished with a two-choice longitudinal flume. Adult-migrating fish of the chinook salmon *Oncorhynchus tshawytscha*, the coho salmon *Oncorhynchus kisutch*, and the chum salmon *Oncorhynchus keta* were exposed to 0.5 mg F^-/L (equivalent to the highest fluoride level in the Columbia River) for 60 min in 1983 tests, whereas adult-migrating fish of *O. tshawytscha* and *O. kisutch* were exposed to 0.2 mg F^-/L (equivalent to the normal fluoride level in the Columbia River) for 20 min in 1984 tests. All test fish were captured in a weir trap that blocked the upstream movement of salmons into Big Beef Creek. Fish were tested one at a time and were allowed to acclimate for approximately 10 min in the holding area downstream from the two-choice longitudinal flume. When a fish moved upstream beyond the funnel trap in either side of the flume within the allowed time, the test was finished and the choice was recorded (fluoride or nonfluoride side). However, if a fish did not move upstream into either side of the flume within the allowed time, the test was recorded as "no choice."

Results from 1983 tests (using 0.5 mg F^-/L) were 16 fluoride side choices, 42 nonfluoride side choices (significantly higher than the number of fluoride side choices), and 54 no choices with chinook salmon; 21 fluoride side choices, 41 nonfluoride side choices (significantly higher than the number of fluoride side choices), and 35 no choices with coho salmon; 25 fluoride side choices, 35 nonfluoride side choices, and 17 no choices with chum salmon. Results from 1984 tests (using 0.2 mg F^-/L) were 25 fluoride side choices, 20 nonfluoride side choices, and 52 no choices with chinook salmon; 19 fluoride side choices, 15 nonfluoride side choices, and 17 no choices with coho salmon. Damkaer and Dey (1989) concluded that a fluoride concentration as low as 0.5 mg F^-/L could adversely affect the upstream migration of adult Pacific salmons in the Columbia River, also concluding that a concentration of 0.2 mg F^-/L would be the threshold for fluoride sensitivity in *O. tshawytscha* and *O. kisutch*. Thus, 0.5 and 0.2 mg F^-/L may be viewed as lowest-observable-effect-concentration and no-observable-effect-concentration values, respectively.

Camargo et al. (1992) conducted short-term (6 days) fluoride toxicity studies with last-instar larvae of competing Nearctic caddisflies in soft water (total hardness = 40.2 mg $CaCO_3$/L) at 18 °C. They estimated 96 and 144 h LC50 values of 42.5 and 24.2 mg F^-/L for *Cheumatopsyche pettitti*, 34.7 and 21.4 mg F^-/L for *Hydropsyche occidentalis*, and 17.0 and 11.5 mg F^-/L for *H. bronta*. Subsequently, Camargo (1996), using multifactor probit analysis software (Lee et al., 1995; US Environmental Protection Agency, 1991) with mortality data, estimated safe concentrations (as LC0.10 values for infinite hours of exposure) of 0.2 mg F^-/L for *H. bronta*, and 0.7 mg F^-/L for *H. occidentalis* and *C. pettitti*. Owing to the differential sensitivity to fluoride among competing caddisfly larvae, it was concluded that fluoride pollution could have some relevance in structuring net-spinning caddisfly guilds through competitive interactions between more-resistant and more-sensitive species (Camargo, 1996; Camargo et al., 1992).

In addition to the caddisflies *C. pettitti*, *H. bronta* and *H. occidentalis*, other Nearctic freshwater invertebrates can be considered relatively sensitive to fluoride. Actually, Pearcy et al.'s (2015) toxicity studies showed that the amphipod *Hyalella azteca* is one of the most sensitive freshwater invertebrates. Furthermore, prior to Pearcy et al.'s (2015) experiments, Metcalfe-Smith et al. (2003) had exposed juveniles of *H. azteca* and nymphs of the mayfly *Hexagenia limbata* to fluoride in hard water (140–150 mg $CaCO_3$/L), estimating a 48 h LC50 value of 14.6 mg F^-/L for *H. azteca*, and a 96 h LC50 value of 32.3 mg F^-/L for *H. limbata*. If these 48 and 96 h LC50 values are multiplied by an application factor of 0.016, derived from toxicological data for Nearctic caddisfly larvae (Camargo, 1996; Camargo et al., 1992), estimated safe concentrations (as LC0.10 values for infinite hours of exposure) are 0.23 mg F^-/L for *H. azteca* and 0.52 mg F^-/L for *H. limbata*.

Lastly, because the mean level of fluoride in freshwater across Canada is 0.05 mg F^-/L (Environment Canada, 2001), Parker et al.'s (2022) water quality benchmarks (3.4–10.4 mg F^-/L) would allow fluoride pollution levels 70–200 times higher than natural fluoride levels.

It should be evident that the best and most reasonable national water quality criteria for fluoride would be those that match natural levels of fluoride in the fresh waters of each country. 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. This is the case of freshwater caddisflies, mayflies, amphipods, and upstream migrating salmons. Therefore, in the event that the interim Canadian water quality guideline of 0.12 mg F^-/L (Environment Canada, 2001) must be revised upwards, I recommend raising it to a maximum level of 0.2 mg F^-/L.

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