

Fluoride Regulatory Framework and Aquatic Toxicity Review

Phase I Investigation

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Fluoride Regulatory Framework and Aquatic Toxicity Review - Phase I Investigation

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Acronyms

°C	degrees Celsius
µg	micrograms
ACR	acute-to-chronic ratio
AEL	associated emission level
AF	assessment factor
AFR	Africa
AIC	Akaike information criterion
ANZ	Australia/New Zealand
BAF	bioaccumulation factor
BAT	best available technique
BIC	Bayesian information criteria
BREF	BAT reference document
bw	body weight
CCME	Canadian Council of Ministers of the Environment
CDC	Centres for Disease Control and Prevention
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CI	confidence interval
cm	centimetre
CMC	criteria maximum concentration
CNA	China
CONAMA	National Environmental Council (Brazil)
CS	chronic aquatic life standards
CWA	Clean Water Act
DEP	Department of Environmental Protection
dw	dry weight
EC	effects concentration
EDO	environmental discharge objective
EMA	Environmental Management Act
ETMF	exposure and toxicity-modifying factor
EU	European Union
EUR	Western Europe
FAV	final acute value
FCV	final chronic value
g	grams
GCC	Gulf Cooperation Council
GMAV	genus mean acute value
GTC	gas treatment centre
ha	hectare



HC	hazard concentration
HF	Hydrofluoric acid
HHS	human health standard
IAI	International Aluminium Institute
IC	inhibition concentration
IED	Industrial Emissions Directive
INSAC	Illinois Nutrient Science Advisory Committee
IOM	Institute of Medicine
kg	kilogram
KY	Kentucky
L	litre
LC	lethal concentration
LOAEL	lowest observed adverse effects level
LOEC	lowest observed effect concentration
m	metre
m ³	cubic metre
MAC	maximum acceptable concentration
MATC	maximum acceptable toxicant concentration
MCL	maximum contaminant level
MDR	minimum data requirement
MELCC	<i>Ministère de l'Environnement et de la Lutte contre les Changements Climatiques</i> or Ministry of Sustainable Development, Environment, and Fight Against Climate Change
mg	milligram
MLR	multiple linear regression
mmol	millimole
mol	mole
MT	Montana
NAM	North America
NASA	National Aeronautics and Space Administration
NOAEL	no observed adverse effects level
NOEC	no observed effect concentration
NPDES	National Pollutant Discharge Elimination System
NY	New York
OAS	Other Asia
OCA	Oceania
OER	environmental release objectives (translated from French)
OR	Oregon
PNEC	probable no effects concentration
ppb	part per billion
ppm	parts per million
ppt	parts per thousand



ROE	Russia and Other Europe
RSD	relative standard deviation
s	second
s.u.	standard unit
SAM	South America
SCHER	Scientific Committee on Health and Environmental Risks
SD	standard deviation
SEPP	State Environmental Protection Policy
SGR	specific growth rate
SMAP	Soil Moisture Active Passive
SMAV	species mean acute value
SMCL	secondary maximum contaminant level
SPL	spent pot lining
SSD	species sensitivity distribution
t	ton
TBEL	technology-based effluent limitation
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WA	Washington
WDR	Waste Discharge Regulations
WHO	World Health Organization
WQBEL	water quality-based effluent limitation
WQG	water quality guideline



Executive Summary

The regulation of inorganic fluoride in surface waters is highly variable across regions of aluminium production globally. With the goal of effectively managing acceptable levels of surface water fluoride risk to aquatic receptors, this review summarizes the distribution of background fluoride conditions in the environment, regulatory frameworks in key regions of aluminium production and the available scientific aquatic ecotoxicity literature and guideline derivation approaches for aquatic life criteria. The information presented herein will help inform and guide stakeholders on best practices for managing and communicating acceptable levels of risk associated with fluoride in the aquatic environment, especially where local guidelines do not consider site-specific water quality conditions.

Tractable and pragmatic frameworks are needed because few remedial approaches exist to treat fluoride and these remedial approaches are not cost-effective. The aluminium industry recognizes that effective management of fluoride releases to the aquatic environment requires careful consideration of regional and site-specific factors to ensure acceptable water quality limits are attained in the receiving environment. The aim of this work is to provide a scientifically sound basis to inform the development of robust aquatic fluoride regulation and management practices. This work is focused on the fluoride management around aluminium production facilities – specifically aluminium production facilities with smelters. Findings from this review may also be relevant to alumina refineries; however, these types of facilities were outside the scope of this review. Details presented herein have been synthesized using publicly available datasets, peer-reviewed primary literature, and site and/or facility-specific information provided by participating stakeholders from the focused aluminium smelting regions. The evaluation is focused on select primary aluminium smelting regions that are representative of stakeholders within the International Aluminium Institute (IAI) across North America (NAM), Western Europe (EUR), Russia and Other Europe (ROE), Gulf Cooperation Council (GCC), China (CNA) and Oceania (OCA).

A strong understanding of fluoride behaviour in the environment and knowledge of background fluoride conditions in surface waters form the foundation of sound management strategies. This assessment included a comprehensive review of background surface water fluoride conditions to understand the natural and anthropogenic pathways that introduce fluoride to the environment, the fate and mobility of fluoride in receiving water bodies, and the geologic, hydrologic and geochemical variables that determine the distribution of fluoride concentrations in water bodies at various scales. In addition, this assessment sought to understand the ranges of naturally occurring surface water fluoride concentrations that exist in the environment, and whether aluminium smelting operations or other anthropogenic sources affect the concentrations of fluoride in surface water.

The tiered assessment framework employed in this review highlights the importance of geogenic sources, as well as major anthropogenic sources not attributed to smelting, that are primarily responsible for fluoride conditions in the environment. The biogeochemical processes that influence the fate and transport of fluoride also have an important role in mediating or ameliorating the toxicity of fluoride to aquatic receptors and need to be considered when managing aquatic fluoride.

Existing regulatory frameworks are inconsistent across regions, and aquatic fluoride criteria are likely overly conservative due to the absence of regulatory mechanisms to account for physical attenuation through mixing or the ameliorating effect of other water quality compounds on fluoride toxicity. The aquatic ecotoxicity review demonstrates that more scientifically robust approaches to derive criteria can be employed for fluoride and that these advances will have a significant effect on the current regulatory limits. This is particularly relevant for regions where freshwaters are ion rich



or in marine environments where current criteria are overly conservative and do not reflect the current state of the science.

This work was motivated by several core questions. The answers to which could be used to facilitate better management of aquatic fluorides. Key findings of this work addressed these questions, which are listed below.

Background Fluoride Review:

- *What are the dominant anthropogenic and geogenic fluoride sources globally?*
The dominant source of fluoride to the environment is through the weathering of minerals in groundwater that discharges into surface water. After geogenic sources associated with mineral weathering, the contributions from the agricultural application of phosphate-based fertilizer, brick kilns, and coal combustion are the next three largest anthropogenic sources of fluoride. Collectively, these three anthropogenic sources contribute over **100 times more** fluoride to the environment than aluminium production facilities.
- *What are typical naturally occurring surface water fluoride concentrations on a continental scale and in North American surface waters?*
At the continental scale, median fluoride concentrations in freshwaters ranged from 0.11 milligrams per litre (mg/L) in Asia to 0.30 mg/L in Africa. Concentrations were more variable at local (state) scales in the United States. Mean surface water fluoride ranged from 0.09 mg/L in New York to 0.72 mg/L in Arizona.
- *To what extent does regional geology govern fluoride concentrations in surface waters?*
Based on preliminary findings from publicly available datasets and peer-reviewed literature, regional geology is the single most influential factor in determining fluoride concentrations in surface water systems.
- *To what extent do aluminium smelting operations or other anthropogenic sources affect fluoride concentrations in surface waters?*
A sensitivity analysis was conducted to determine how surface water mixing drives the attenuation of fluoride discharges in surface water. Fluoride releases have a negligible influence on fluoride concentration in large riverine systems with established mixing zones. The range of influence can be less than the natural variability in background conditions noted in surface waters throughout a given year.

Fluoride Regulatory Review:

- *What are the ranges of drinking water guidelines across regulatory regions and what commonalities exist in their derivation?*
Drinking water guidelines typically range from 1.0 to 4.0 mg/L fluoride. Drinking water quality guidelines, particularly maximum acceptable concentrations (MACs), are largely informed by conditions that may result in increased risk for moderate dental fluorosis, whereas the United States maximum contaminant level (MCLs) are based on increased potential for more pronounced effects, such as the long-term risk for skeletal fluorosis over long exposure durations (10+ years). Among the values identified for the protection of drinking water, the concentration of 1.5 mg/L fluoride had the greatest incidence of occurrence.
- *What are the ranges of aquatic life surface water guidelines across regulatory regions and what commonalities exist in their derivation?*
The aquatic life criteria information is either antiquated or a paucity of information exists. Guideline values range from 0.12 mg/L to 4.0 mg/L; however, the upper end of the range is based on the drinking water human health MCL. In both fresh and marine waters, limited chronic toxicity information supports the derivation of aquatic life guidelines. In addition,



there are instances where freshwater and marine criteria are at or below the background surface water fluoride concentration for the region that the criteria were derived.

- *What are examples of successful means to mitigate or reduce fluoride releases to surface waters at aluminium production facilities?*

Roof vent emissions and runoff from soil or ground surface deposition were identified as important sources of fluoride at aluminium production facilities. Since stormwater is often the main transport mechanism from sources to the receiving environment, one way to mitigate or reduce fluoride releases at smelting facilities is to carefully manage stormwater. Some aluminium production facilities have novel water management approaches that use stormwater as a water source for industrial processes and in doing so dramatically reduce the fluoride discharge on an annual basis. Stormwater infrastructure and dynamic management systems are advantageous in temperate regions, with high rainfall, to provide a source of low fluoride, freshwater to mitigate and manage effluent releases containing fluoride.

Fluoride Aquatic Ecotoxicity Review:

- *Does the detailed review of available peer-reviewed literature on toxicity to freshwater and marine organisms provide any new information that could support the development of more robust fluoride guidance?*

Generally, increased fluoride concentration, exposure time and water temperature enhance the toxic effects of fluoride on aquatic organisms. Above certain concentrations, water quality constituents, such as chloride and hardness, can ameliorate the toxic effects fluoride exerts on organisms. Many of the existing aquatic life guidelines have been derived several decades ago. Since the time of derivation, more research exists to support the ability to predict fluoride toxicity based on water quality conditions.

- *How do certain factors, such as physical or chemical water quality conditions, ameliorate or modify the toxicity of fluoride? Particularly, can the recently promulgated USEPA aluminium guidance that uses multiple linear regression (MLR) approaches be used as a model for the development of more robust fluoride aquatic life criteria?*

Several studies have focused on the ameliorating effect of chloride and hardness on fluoride toxicity. However, these studies have relied on simple statistical approaches that examine one variable at a time. A metanalysis conducted as part of this review indicates that multiple water quality variables must be considered to predict fluoride toxicity. An MLR approach was employed to develop preliminary site-specific fluoride guidance. Expansion of this approach will ensure that the development of future aquatic life criteria appropriately considers site-specific water quality conditions.

- *Can more robust fluoride aquatic life criteria be derived using approved guidance on criteria derivation within the study focus area?*

Yes. This assessment successfully demonstrated that preliminary acute and chronic guidelines can be derived using approaches widely accepted by regulatory bodies across IAI regions. Preliminary chronic criteria ranged from 1.7 to 11.8 mg/L depending on the water quality conditions present. The **5- to 7-fold** increase in chronic criteria indicates that existing aquatic life guidelines are too conservative and more scientifically robust approaches need to be adopted.

Additional details on fluoride background conditions in surface water, current regulatory limits, and findings from the aquatic ecotoxicity and preliminary guideline derivation process are summarized below.



The predominant pathway by which fluoride enters surface water is through interactions between groundwater and fluorine-bearing rocks and minerals. Fluoride is also introduced to the environment through anthropogenic activities. Worldwide, the largest anthropogenic sources of fluoride to the environment are through agricultural phosphate fertilizer application, brick manufacturing and coal combustion. Other industrial sources, such as smelters or steel furnaces, emit significantly less fluoride on an annual basis. Once delivered to circumneutral or alkaline freshwater systems, fluoride can be difficult to remove due to its high electronegativity that favours its persistence as a free anion. Freshwater systems with high pH, high bicarbonate and/or low calcium will further promote fluoride mobility by preventing precipitation of fluoride minerals from solution.

Based on a review of publicly available surface water data spanning six continents (40 countries), typical freshwater fluoride concentrations fall between 0.1 and 0.3 mg/L. However, at regional and local scales fluoride concentrations in freshwater can be variable and geology can have a disproportionate effect on background concentrations in natural waters. Geology was determined to be the primary driver of surface water fluoride concentrations. In the surface water systems evaluated in the United States, predominately large rivers, aluminium production facilities did not have any discernible effect on surface water fluoride concentration.

Fluoride is a ubiquitous component of marine waters. It occurs naturally at concentrations 5 to 6 times greater than concentrations observed in most freshwaters (approximately 1.3 mg/L). Seasonal changes in sea ice distribution and greater evaporation in mid-latitudes drive gradients in seawater concentrations. Seas or embayment waters that are isolated from the open ocean, particularly in arid regions, tend to have the greatest marine water fluoride concentrations with concentrations as high as 1.5 mg/L.

Surface water fluoride aquatic life guidelines and regulatory frameworks were reviewed to provide a balanced perspective on issues pertaining to the management of fluoride-related risks to fresh and marine surface waters. The review provides additional context as to the varying approaches used to establish limits for fluoride throughout regions where stakeholders operate. Findings from the regulatory review indicated that surface water fluoride regulations rely heavily on limits for safe drinking water to prevent deleterious human health effects. Drinking water guidelines are not necessarily transferrable (and are potentially overly conservative) to the protection of aquatic receptors. The application of drinking water criteria for the protection of aquatic receptors has arisen due to the historical paucity of information directly related to chronic fluoride ecological toxicity in both fresh and marine waters. Whilst some jurisdictions have implemented aquatic life criteria for fluoride that are not based on drinking water guidelines, many of these criteria either lack sound scientific rationale or are based on antiquated approaches to deriving guideline values (e.g., approaches that do not consider water quality parameters, such as hardness). The more recent scientific literature on ecotoxicity should be incorporated into guidance to enable a more robust understanding of acceptable fluoride levels in the aquatic environment.

Most regulatory approaches do not account for background water quality conditions, which can have an important function of ameliorating the toxicity of fluoride to aquatic organisms. Additionally, the role of mixing zones (designated areas where effluents mix with background water sources) as important mechanisms for physical attenuation of fluoride is not always considered in existing regulatory frameworks. The regulatory review supports the recommendation that guidelines need to be developed that take hydrological, ecological, and geochemical characteristics of receiving water bodies into consideration. As appropriate aquatic life criteria will ultimately be location-



specific, the setting of aluminium production facilities is an important factor that will drive surface water management strategies.

In consideration of the key recommendations identified in the regulatory review, a detailed assessment of fluoride ecotoxicity literature was conducted for the aquatic environment. The aquatic fluoride ecotoxicity review summarized the available peer-reviewed literature on freshwater and marine organisms; evaluated how certain factors, such as physical or chemical water quality conditions, can ameliorate or modify the toxicity of fluoride; and developed preliminary fluoride aquatic life criteria using approved guidance. The approaches for fluoride criteria derivation leveraged the use of MLR as a tool to best predict fluoride toxicity. Acute and chronic ecotoxicity data were examined for freshwater and marine waters. In the absence of sufficient data to develop more robust criteria using approved approaches, the process itself was used to identify information gaps or uncertainties where additional information is needed to derive more technically sound guideline values. The review highlights the need to incorporate water quality parameters in the development of fluoride aquatic life criteria. Moreover, the review constrained the uncertainty surrounding some existing guidelines that employ overly conservative assumptions. Key findings of the freshwater and marine ecotoxicity review are provided below.

In freshwaters, increased fluoride concentration, exposure time, and water temperature were found to be key factors that enhance the toxic effects of fluoride to aquatic invertebrates and fish. Invertebrates tended to be the most sensitive taxonomic group to fluoride, followed by fish and algae. Surface water chloride was shown to have a greater ability to reduce the toxicity of fluoride to freshwater organisms than calcium carbonate; however, further assessment indicated that multiple factors contribute to the amelioration of fluoride toxicity in freshwater. Although the minimum data requirements (MDRs) put forth in regulatory frameworks for criteria derivation in the United States, Canada, Europe and Australia/New Zealand were not always met for the freshwater acute and freshwater chronic data reviewed, however, the datasets were able to be assessed in detail to provide important insight into criteria derivation approaches that are more technically sophisticated and leverage the most recent scientific understanding. Unlike the reviewed literature that emphasized the importance of chloride and hardness as univariate factors that influence aquatic toxicity, this assessment found that multiple water quality parameters should be evaluated together to best predict the ameliorating effect to aquatic toxicity.

An optimized model using chloride, hardness, and alkalinity was developed to enable the normalization of acute freshwater ecotoxicity data. Preliminary criteria dependent on site-specific water quality conditions were derived. Final acute values (FAVs) were calculated under low ion and high ion freshwater scenarios. The low ion water scenario was similar to surface waters present in the Northwest United States and Southwest Canada. The high ion water was similar to surface water in the Great Lakes and St. Lawrence River basins. High and low ion water scenarios resulted in FAVs of 35.4 and 5.2 mg/L, respectively. Surface water quality characteristics exhibiting hard water (high ion) resulted in a 7-fold increase in FAVs. The acute toxicity of the most sensitive species used in FAV derivation, *Hyalella azteca*, influenced the resulting FAV estimation. A more thorough review of the suitability of inclusion of sediment benthic crustaceans, *H. azteca*, in water-only toxicity testing is recommended.

Application of acute-to-chronic ratios (ACRs) was used to estimate preliminary chronic criteria from FAVs. Mean \pm standard deviation ACRs for *O. mykiss* and *H. azteca* were 3.3 ± 1.5 and 2.8 ± 0.5 , respectively. Estimated preliminary chronic criteria, final chronic values (FCVs), were calculated using the ACR and ranged from 1.7 mg/L to 11.8 mg/L fluoride in low and high ion water scenarios, respectively. Using the hardness concentrations of the low and high ion scenarios for the hardness-



specific chronic criteria developed for the protection of aquatic life in Illinois, Michigan, and New York, USA and British Columbia, Canada results in fluoride limits of 2.2 mg/L and 2.6 mg/L, respectively. Therefore, the ACR derived chronic value is comparable for low ion regions but highlights the importance of thorough considerations of fluoride toxicity where waters are heavily ionized. Moreover, increasing chloride and alkalinity is a common pattern in surface waters throughout the Northeast United States and other regions globally. Preliminary criteria derived using acute freshwater toxicity values highlight the strength of MLR approaches to adequately constrain estimates of toxicity and the utility of ACRs.

An assessment of chronic criteria was also conducted that leveraged available 10 percent effects concentrations (EC_{10}) and no observed effect concentration (NOEC) measurements in several genera. Species sensitivity distribution (SSD) approaches were used to develop preliminary chronic criteria for freshwater and marine environments. SSD derived fluoride criteria did not consider water quality conditions. Within the reviewed literature, insufficient information was available to provide an MLR-based approach using multiple water quality parameters to predict chronic toxicity. Using an SSD approach, an FCV of 2.8 mg/L fluoride was estimated in freshwater and somewhere between 4 and 30 mg/L in marine water. The 95 percent confidence interval of the freshwater FCVs captures much of the variation that exists in current freshwater criteria for aquatic life. Additional work into the marine guideline value represents an important data gap.

In summary, the multi-tiered assessment approach was effective at synthesizing a comprehensive understanding of fluoride background conditions, regulatory limits, and preliminary guidelines that should be considered when managing fluoride releases for the protection of aquatic life. The presence of chloride, hardness, and alkalinity are critical factors that ameliorate the toxicity of fluoride in surface water and need to be considered in developing appropriate management limits.



1 Introduction and Background

1.1 Aims and Objectives

Fluoride-containing compounds are critical to the production of aluminium and many other industrial processes. Increasingly stringent regulation of releases to the aquatic environment presents a challenge to industries that consume and discharge fluoride. Tractable and pragmatic frameworks are needed because limited remedial approaches are available to treat fluoride and they are not cost-effective. This exacerbates efforts to effectively manage and dispose of fluoride-containing by-products. The aluminium industry recognizes that effective management of fluoride releases to the aquatic environment requires careful consideration of regional and site-specific factors to ensure acceptable water quality limits are attained in the receiving environment.

The aim of this work is to provide a scientifically sound basis to inform the development of aquatic fluoride regulation and management. This work is focused on the fluoride management around aluminium production facilities – specifically aluminium production facilities with smelters. Findings from this review may also be relevant to alumina refineries; however, these types of facilities were outside the scope of this review. Details presented herein have been synthesized using available public datasets, peer-refereed primary literature, and site and/or facility-specific information provided by participating stakeholders from the focused aluminium smelting regions (**Section 1.2**).

The topics discussed herein represent the first phase of a two-phase study. The first phase is focused on a critical review and synthesis of available aquatic toxicity data and how that information is linked to regulatory frameworks of focused regions of global aluminium production. The second phase of the study is focused on addressing the critical data gaps identified through a combination of metadata analyses, fate and transport assessments and toxicity modelling.

The objectives of this report are to 1) provide a critical review of existing aquatic fluoride guidance and regulations governing the release of fluorides to surface waters, 2) assess regional background concentrations of fluoride in surface waters and 3) review aquatic ecotoxicological literature from both primary sources and literature supporting the determination of aquatic life criteria. The scope of this review is international in scale, but with a particular focus on selected primary aluminium smelting regions representative of stakeholders within the International Aluminium Institute (IAI) across North America (NAM), Western Europe (EUR), Russia and Other Europe (ROE), Gulf Cooperation Council (GCC), China (CNA) and Oceania (OCA).

It is necessary to collate and synthesize this information in order to assess the technical veracity of relevant fluoride toxicological studies and their use in informing regulations. This information will assist stakeholders in defining the significance of the information gaps and uncertainties in the context of current and future regulation of fluoride discharges to surface water.

1.2 Study Area Focus

The evaluation is focused on select primary aluminium smelting regions representative of stakeholders within NAM, EUR, ROE, GCC, CNA and OCA (**Figure 1-1**). The review focuses on aquatic fluoride guidelines within NAM, EUR and OCA on a federal, state and/or provincial level to the extent practicable. These regions were selected as the initial focus because regulatory models/frameworks implemented within these regions can influence management decisions in other regions. Outside of these regions, the review is specific to areas of operational aluminium production facilities as



identified by stakeholders. Background assessment leverages publicly available datasets and therefore is dependent on the presence and distribution of long-term monitoring stations of surface waters within those regions. Additional details of the distribution of monitoring locations are provided in **Section 2**.

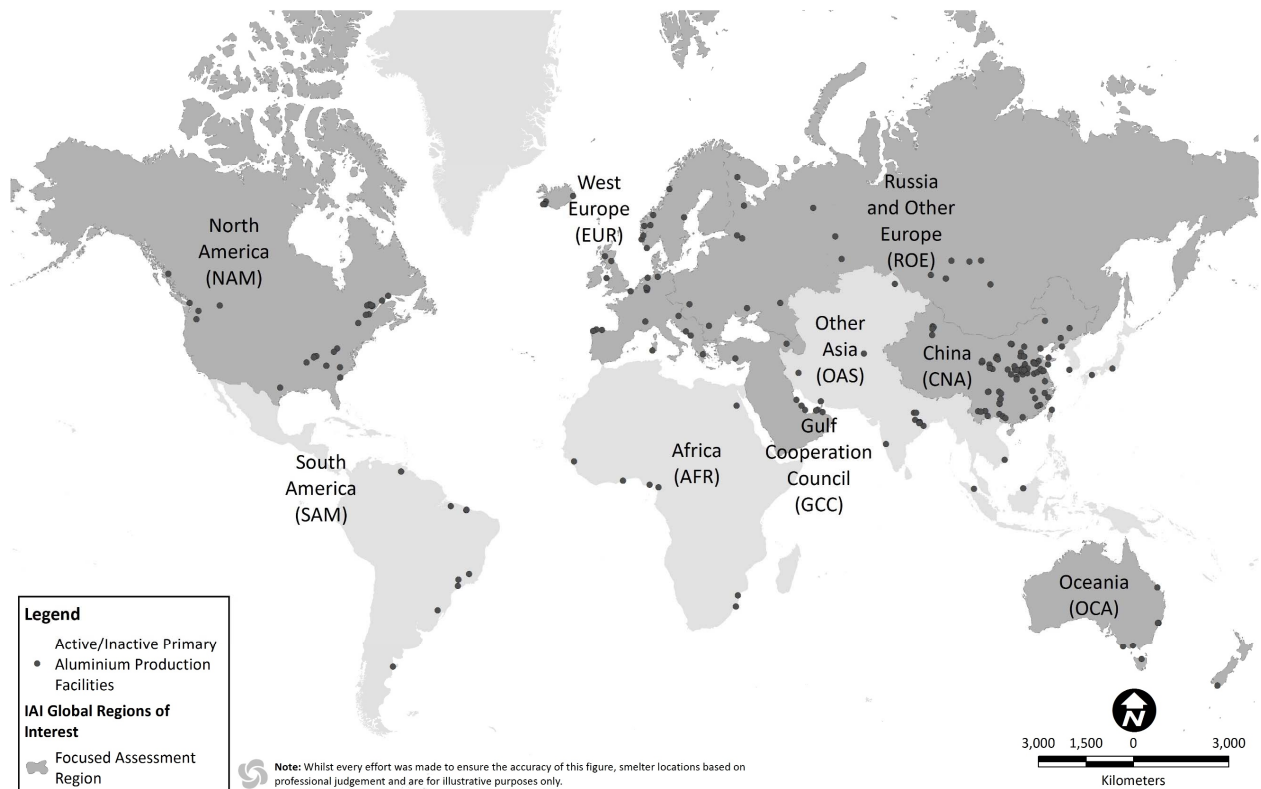


Figure 1-1 Global distribution of primary aluminium production facilities and focused regions of assessment

1.3 Report Structure

The document is structured as follows:

- **Section 2 – Background Fluoride Conditions in Surface Water** – Details the comprehensive metanalysis of background fluoride conditions in fresh and marine surface water across critical regions of aluminium production.
- **Section 3 – Surface Water Fluoride Aquatic Life Guidelines and Regulations** – Describes the focused review of surface water fluoride guidance for aquatic life, including the basis and associated toxicological studies supporting the guidance, if relevant, and regulations governing the release of fluoride to surface waters.
- **Section 4 – Fluoride Aquatic Ecotoxicity Literature Review** – Provides a summary of the state of the science regarding the toxicity of fluoride to aquatic receptors.
- **Section 5 – Conclusions** – Provides a synthesis of key findings.
- **Section 6 – Data Gaps and Recommendations** – Provides a synthesis of key recommendations and data gaps.
- **Section 7 – References** – List of works cited in this report.

Additional background on the use of fluoride in primary aluminium production is provided in **Section 1.4**.



1.4 Fluoride in Primary Aluminium Production

Fluoride is an essential feedstock to the production of aluminium. Similarly, the management of fluoride-containing by-products, as well as liquid and solid residual wastes, is of importance to the aluminium industry. Discussion of the role of fluoride feedstocks and by-products in the production of aluminium is provided in **Section 1.4.1**.

1.4.1 Role of Direct Fluoride Feedstocks

Fluoride is integral to the electrolysis process. Fluoride is used as the flux in the electrolysis of alumina (aluminium oxide) to produce aluminium. The benefit of fluoride during electrolysis is that it promotes a eutectic system with alumina, which is when a mixture of substances melts at a single temperature that is lower than any of the contributing constituents. Alone, aluminium oxide has a melting point in excess of approximately 2,000 degrees Celsius (°C). Without the use of fluoride to reduce the melting temperature of alumina in the electrolysis cells (pots), aluminium production would not be feasible due to the increased energy demand and heat required within the system.

By dissolving alumina in a bath of molten cryolite (Na_3AlF_6) and aluminium fluoride (AlF_3), the main sources of fluoride in electrolysis, the melting temperature is reduced significantly to approximately 1,000 °C, which therefore reduces energy demand.

The exact amount of fluoride used as feedstock varies by region and facility. Aluminium fluoride inputs range from 13 to 21 kilograms (kg) per tonne of aluminium across IAI regions where data is available (NAM, EUR, GCC, OCA and South America [SAM]) (IAI, 2017).

Fluoride is internally recycled to minimize emissions (**Figure 1-2**). The electrolysis within the pots produces a variety of gases including fluoride-containing compounds, such as hydrogen fluoride and perfluorocarbons. Through a process called evolution, the gases released by the pots are routed through alumina powder to sequester hydrogen fluoride and fluoride condensates, such as sodium tetrafluoroaluminate (NaAlF_4) (Kvande and Drabløs, 2014). The alumina powder that receives evolved gases can be directly added to the pots, thus substantially reducing the quantity of fluoride needed when compared to production if no dry scrubbing of evolved gases was conducted (**Figure 1-2**).

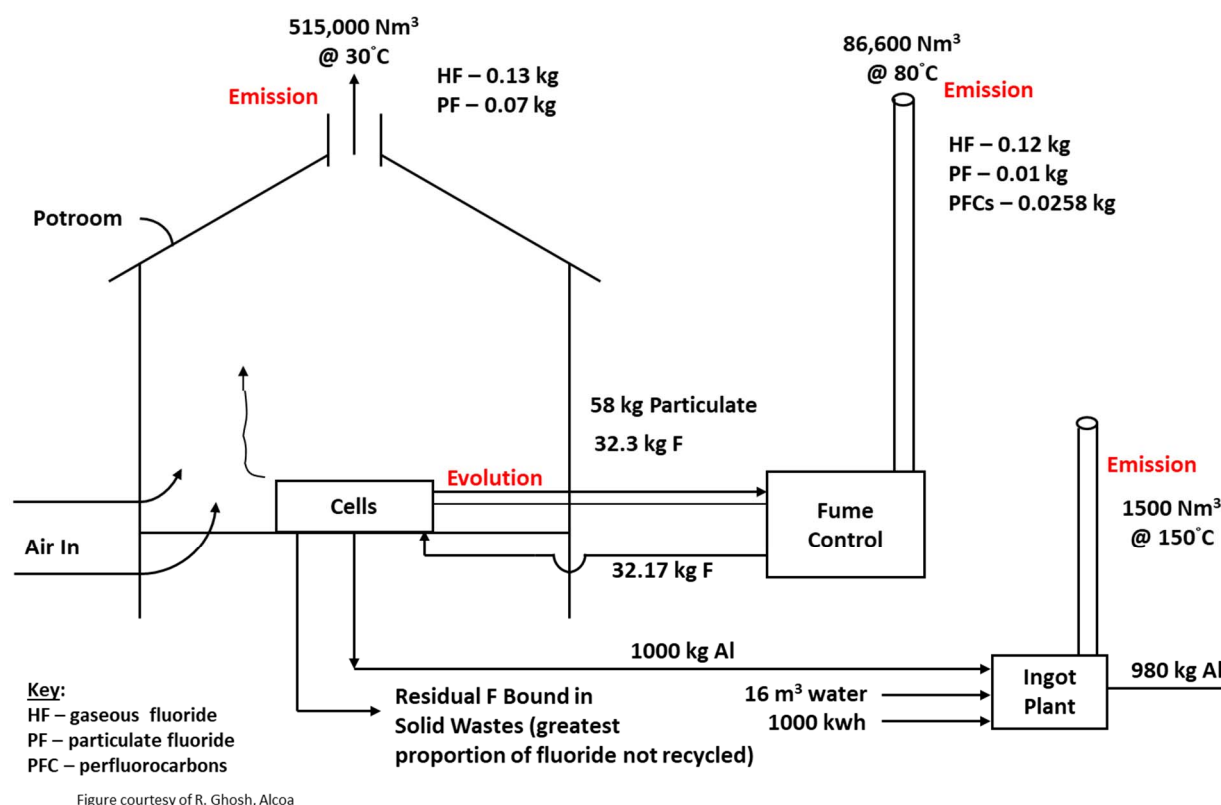


Figure 1-2 Smelting and casting fluoride mass balance per 1000 kg of aluminium for a smelter with a gas treatment centre (GTC)

In addition to the role of fluoride in electrolysis cells, fluoride-containing compounds may be used as feedstocks in other aspects of an integrated aluminium production facility. For example, hydrofluoric acid is often used at facilities with rolling mills for certain chemical treatment processes. Similarly, hydrofluoric acid may be stored at a facility to serve as an intermediate compound used in the production of fluoride-containing feedstocks for electrolysis.

1.4.2 Fluoride-Containing By-products and Wastes

Atmospheric emissions, as well as solid and liquid waste streams containing fluoride, are discussed below. The arrangement of the fume control system at aluminium production facilities often influences the types of solid and liquid residual wastes generated. Other important fluoride-containing by-products/wastes include anode/anode butt wastes and spent pot lining (SPL). Ultimately, stormwater runoff and/or process-related water containing fluoride compounds are the primary interest of this guidance, and factors influencing effluents will be discussed in detail in **Section 3.3**.

Evolution and dry scrubbing with alumina enable significant quantities of fluoride to be internally recycled and reduces overall atmospheric emissions. Although this process has remarkably high recovery rates of fluoride, it is not 100 percent effective. Emissions not captured by dry scrubbing systems are carefully regulated through air permitting requirements outside of the scope of this report. Roof vent emissions associated with changing spent anodes is also an important process for gaseous releases of fluoride (Girault et al., 2016). Implementation of manifolds and other technologies can greatly reduce the fluoride emissions that occur during anode replacement (Gagné et al., 2010).



In some aluminium production facilities, wet scrubbing systems are also employed in conjunction with dry scrubber systems. Wet scrubber systems typically occur at coastal facilities where saline water is abundant. Wet scrubbing systems are primarily intended to reduce sulphur dioxide emissions. However, given the chemical composition of the saline water and the abundance of magnesium cations, wet scrubber systems also retain some fluoride compounds.

The manner in which dry and/or wet scrubbing systems are used is site-specific. However, it is important to note the trade-off with these systems. Dry scrubber systems tend to generate solid residual waste streams (mainly filter bags) that contain fluoride whereas wet scrubbers generate liquid residual waste streams. Given the quantity of water used in wet scrubber systems, facilities that operate wet scrubbers often have larger volumes of 'process-related' water to manage than facilities that operate only with dry scrubbers (provided that the water from the wet scrubbers undergoes pre-treatment prior to discharge).

Components of the pots also contribute to the generation of solid residual by-products or wastes containing fluoride. Anode production in pre-bake type aluminium smelting facilities often incorporates recycled components of used anodes after installing new ones. The remaining portion of anodes is referred to as anode butts. The proportion of anode butts used in new anodes can vary by facility but is typically between 15 percent and 25 percent (Kvande and Drabløs, 2014). Since anodes assimilate fluoride-containing compounds during service, processes involving anode butts are a source of fluoride. Atmospheric emissions of fluoride can also occur as a result of the baking of anodes at facilities that manufacture them on-site. The presence of dry scrubbers and alumina at the carbon bake oven can be employed to capture fluorides and reduce emissions.

SPL, which is the residual cathode and isolation material (refractory brick) that is left behind in a pot after its service cycle has ended, also contains fluoride. SPL can contain up to 20 percent by mass fluoride (Chanania and Eby, 2000), however, the leachable fluoride content is highly variable. Detailed considerations of SPL management can be found in *Sustainable Spent Pot Lining Management Guidance* (IAI, 2020). The role of SPL in fluoride sources, migration routes and exposure pathways is discussed in **Section 1.4.3**.

Stormwater and process water may also be important sources of fluoride-containing wastes from aluminium production facilities. The specific nature of stormwater and process water management at aluminium production facilities varies by design, location, and other considerations (i.e., year built). Stormwater runoff from site surfaces where raw materials or by-products and/or solid wastes have been handled can contain fluoride. Additionally, localized deposition of fluoride from dust or emissions to soils can be mobilized by stormwater runoff. A variety of operations may contribute to process water that contains fluoride, such as the wet scrubber systems, casting operations, rolling mills, etc.

It should be noted that there is an absence of proven remedial technologies to sustainably remove fluoride from by-products and waste streams. This is attributed to the propensity of fluoride to remain in a dissolved phase in natural waters. Once dissolved, it is difficult to remove large amounts of the element cost-effectively. Major techniques used to remove fluoride from drinking waters include coagulation, adsorption, ion exchange, electrochemical methods and membrane techniques (Ayoo et al., 2008). These techniques have been employed with varying degrees of success. However, most suffer from high operational and maintenance costs, generation of secondary pollutants, limited efficiency, or complicated treatment procedures (Bhatnagar et al., 2011) and are therefore not effective industrial-scale solutions. A summary of available fluoride treatment technologies is provided below.



1.4.2.1 Fluoride Treatment Technologies

Several treatment technologies and materials have been utilized for addressing elevated natural and industrial fluoride in surface and groundwater with varying levels of success. Treatment technology methods rely on the principles of fluoride geochemistry. These methods include adsorption, precipitation/coagulation, membrane filtration (reverse osmosis) and electrodialysis. In some cases, these technologies are used together in series. Reverse osmosis and electrodialysis are effective at fluoride removal, are useful for removing other ions of concern, and can operate at high salinities, but come with high operating costs and can be fouled by water with high turbidity or suspended solids. Two examples of established and effective ion exchange technologies (i.e., adsorption and precipitation) are given below. However, these methods are ultimately quite costly.

Adsorption – Fluoride is removed from water by passing it through a granular filter where it is absorbed. Commercially available alumina (a form of Al_2O_3) is the most widely used (Habuda-Stanić et al., 2014). Al_2O_3 becomes hydrated on contact with water (e.g., $\text{Al}(\text{OH})_3$). Fluoride is substituted for OH ions in the hydrated alumina at optimal pH levels (pH 4-6) and can achieve better than 85 percent fluoride removal (Pickard and Bari, 2004). Most absorption media work in a restricted pH range (Rubel and Woolsley, 1979), therefore careful monitoring and pH adjustment are necessary.

Precipitation – An example of precipitation is the Nalgonda technique, a method that involves mixing aluminium chloride and sodium aluminate (with a bleach agent to raise pH) with water and removing the subsequent flocculant (Nawlakhe and Bulusu, 1989). A drawback of this method is the generation of toxic aluminium-bearing sludge (Habuda-Stanić et al., 2014).

1.4.3 Fluoride Sources, Migration Routes, and Exposure Pathways

This section describes some of the key processes that influence the fate and transport of fluoride at an aluminium production facility. **Figure 1-3** illustrates conceptual source areas, migration routes and exposure pathways of fluoride.

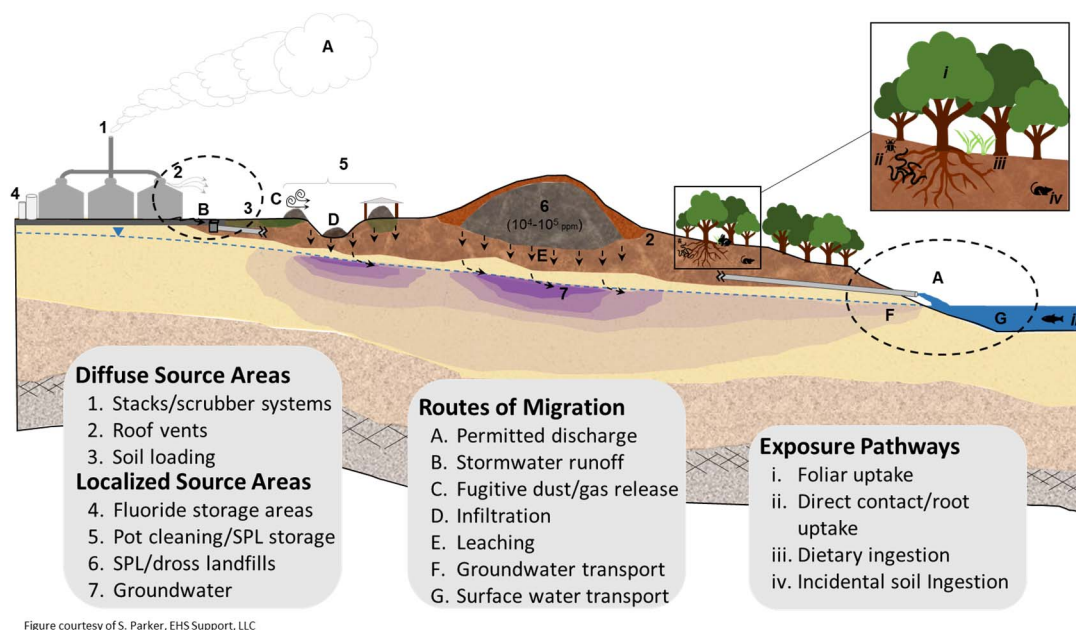


Figure 1-3 Fluoride source areas, migration routes, and exposure pathways at a hypothetical aluminium production facility



Diffuse source areas are broadly distributed, non-point sources of fluoride. Diffuse sources include emissions from stacks/scrubber systems, roof vents, and soil loading. Atmospheric emissions and fugitive dust are largely responsible for the diffuse sources around an aluminium production facility. Localized source areas are specific point sources or those directly related to legacy sources, such as groundwater. The presence of localized source areas may be attributed to past operational practices that occurred prior to the advent of robust guidance on sustainably handling waste products, such as SPL. Localized sources include fluoride storage areas, pot cleaning/anode butt/SPL storage areas, SPL/dross landfills and groundwater.

Routes of migration are factors that affect the fate and transport from the hypothetical aluminium production facility to some receiving environment. Permitted discharges include both atmospheric releases of fluoride and stormwater/process water releases to surface water. Stormwater runoff, groundwater transport and surface water transport are also important routes of migration that will be discussed herein along with the permitted surface water releases. The other migration mechanisms noted include fugitive dust, infiltration and leaching. These are more general physical processes that may ultimately play some part in the nexus of fluoride between a hypothetical aluminium production facility and the downgradient environment.

As the aquatic environment is the focus of this assessment, the primary exposure pathway of interest is direct contact with aquatic receptors. Other exposure pathways such as foliar uptake, dietary ingestion and incidental soil ingestion are focused on the terrestrial environment. Details about particular exposure pathways and their relevance are provided in **Section 4**.

Migration and exposure pathways of fluoride may be considerably different between active and inactive/legacy sites. In addition, the regulatory frameworks that govern appropriate criteria points of compliance may also be fundamentally different. Details of these differences are addressed in **Section 3**.



2 Background Fluoride Conditions in Surface Water

2.1 Introduction

A strong understanding of background fluoride concentrations in surface waters is critical to establishing meaningful guidelines consistent with site and regional-specific conditions. Effective criteria for maintaining acceptable levels of fluoride in surface waters need to be established at the scales over which fluoride concentrations vary. Because concentrations in natural waters span several orders of magnitude and are strongly influenced by climate, local geology and geochemistry, there is a need for criteria that take these location-specific factors into account in order to effectively inform management. To this end, an analysis of publicly available data on fluoride concentrations in surface waters was undertaken on a global scale. A review of anthropogenic and naturally occurring fluoride sources and fate and transport characteristics in the environment is provided as context for understanding why fluoride concentrations are spatially and temporally variable. The assessment of fluoride distribution in surface waters was carried out at multiple spatial scales.

A continental level analysis was undertaken to understand the distribution of fluoride across broad geographic regions. For this assessment, available fluoride surface water data was examined within global regional boundaries established by the IAI. The next assessment level occurred across countries where sufficient fluoride surface water data exists. Given an extremely robust dataset within the United States, comprised of information from the United States Geological Survey (USGS) and other public entities, more predictive evaluations could be investigated in the United States. In particular, the available fluoride surface water dataset helped to address the following questions:

- What are the dominant anthropogenic and geogenic fluoride sources globally?
- What are typical naturally occurring surface water fluoride concentrations on a continental scale and in North American surface waters?
- To what extent does regional geology govern fluoride concentrations in surface waters?
- To what extent do aluminium smelting operations or other anthropogenic sources affect fluoride concentrations in surface waters?

In addition, a global assessment of background fluoride in seawater was conducted using known stoichiometric ratios between fluoride, chloride and salinity to estimate fluoride concentrations in all marine water bodies where accurate salinity data is available.

2.1.1 Key Findings

The key findings provided below are intended to succinctly address the objectives and core questions of the review in the form of a question and answer format. Questions are presented in italicized text and the key findings are provided in normal text.

- *What are the dominant anthropogenic and geogenic fluoride sources globally?*
The dominant source of fluoride to the environment is through the weathering of minerals in groundwater that discharges into surface water. After geogenic sources associated with mineral weathering, the contributions from the agricultural application of phosphate-based fertilizer, brick kilns, and coal combustion are the next three largest anthropogenic sources of fluoride. Collectively, these three anthropogenic sources contribute over **100 times more** fluoride to the environment than aluminium production facilities.



- *What are typical naturally occurring surface water fluoride concentrations on a continental scale and in North American surface waters?*
At the continental scale, median fluoride concentrations in freshwaters ranged from 0.11 milligrams per litre (mg/L) in Asia to 0.30 mg/L in Africa. Concentrations were more variable at local (state) scales in the United States. Mean surface water fluoride ranged from 0.09 mg/L in New York to 0.72 mg/L in Arizona.
- *To what extent does regional geology govern fluoride concentrations in surface waters?*
Based on preliminary findings from publicly available datasets and peer-reviewed literature, regional geology is the single most influential factor in determining fluoride concentrations in surface water systems.
- *To what extent do aluminium smelting operations or other anthropogenic sources affect fluoride concentrations in surface waters?*
A sensitivity analysis was conducted to determine how surface water mixing drives the attenuation of fluoride discharges in surface water. Fluoride releases have a negligible influence on fluoride concentration in large riverine systems with established mixing zones. The range of influence can be less than the natural variability in background conditions noted in surface waters throughout a given year.

2.2 Sources of Fluoride in Freshwater

2.2.1 Natural Sources of Fluoride in the Environment

Fluorine (F) is an abundant trace element with typical concentrations in the earth's crust of 625 milligrams per kilogram (mg/kg) (Edmunds and Smedley, 2013). Fluorine is typically found in fluorite (CaF_2), fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), cryolite (Na_3AlF_6), topaz ($\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$), biotites, amphiboles and mica minerals. The weathering of these minerals is the dominant source of naturally occurring fluoride in freshwater globally. The distribution of these mineral deposits is predominately controlled by tectonic activity, and a close spatial association exists between F mineral deposits and major fault zones (Shawe et al., 1976). Alkalinity, pH and calcium content of groundwater that comes into contact with these minerals are all major factors that determine the extent to which F will leach into groundwaters (Vithanage & Bhattacharya, 2015; Saxena & Ahmed, 2003). Aquatic systems with high pH will favour the desorption of fluoride from mineral surfaces as well as the dissolution of fluoride from mineral structures due to the high electronegativity of the fluoride ion and the ability of the hydroxyl ion to substitute for fluoride in mineral structures resulting from the similar ionic radii of both anions (Edmunds & Smedley, 2013; Jha et al. 2011). Similarly, systems with high bicarbonate and low calcium content will promote the dissolution of fluoride as precipitation of calcite will be favoured over the precipitation of fluorite (Hayes et al. 2017; Saxena & Ahmed, 2003).

2.2.2 Anthropogenic Sources of Fluoride in the Environment

Whilst F occurrence in natural waters is most closely related to its abundance in local minerals and rocks (Edmunds and Smedley, 2013), there are also various anthropogenic sources that release F into the environment. It is estimated that 6.4 billion kg of F are released annually as a result of industrial activity worldwide and that roughly 3.6 billion kg of F enter fresh surface and groundwater (Ermakov, 2004). In agricultural lands, large amounts of F are applied directly to soils through the use of phosphate fertilizers that typically contain 1,400 to 13,300 mg/kg F (Ramteke et al., 2018) and may contain up to 38,000 mg/kg F (Kabata-Pendias & Pendias, 1984). The application of phosphate



fertilizer adds an estimated 2.3×10^9 kg F to soils annually and is likely the single largest anthropogenic source of F to the environment (**Figure 2-1**; Fuge, 2019; Pyle and Mather, 2009).

Other sources include coal burning, oil refining, steel production, glass, brick, clay, chemical and ceramic manufacturing and aluminium smelting (Ozsvath, 2009; Pickering, 1985; Vithanage & Battacharya, 2015). Coal combustion and brick manufacturing are thought to be the two greatest anthropogenic sources of F release to the atmosphere due to the high F content in clays and coals (Fuge, 2019). **Figure 2-2** illustrates the global distribution of coal-fire power plants by country. Clays range in F content from 100 to 2,500 mg/kg and on average contain 1,000 mg/kg (Dai et al. 2004). Coal typically contains between 20 and 300 mg/kg F (Godbeer & Swaine, 1987; Guohua et al., 2019) with a global average F content of 88 mg/kg (Ketriss and Yudovich, 2009). Fluorine content in coal varies regionally, however, and concentrations up to 3,575 mg/kg have been reported in some provinces of China (Dai et al., 2015). Upon heating, either in the process of brick production or coal-fired electricity generation, F is liberated and emitted to the atmosphere as hydrofluoric acid (HF) and other inorganic gases (SiF_4 , F_2 , SF_6 , H_2SiF_4) and particulate species (CaF_2 , NaF, Na_2SiF_6 , NaAlF_4 ; Jayarathne et al., 2014; Ozsvath, 2009). It is estimated that brick manufacturing releases 1.8×10^9 kg of F annually and that F release from coal combustion is in the range of $2\text{--}3 \times 10^8$ kg annually (Fuge, 2019). These activities dwarf all other anthropogenic sources of atmospheric F (**Figure 2-1**).

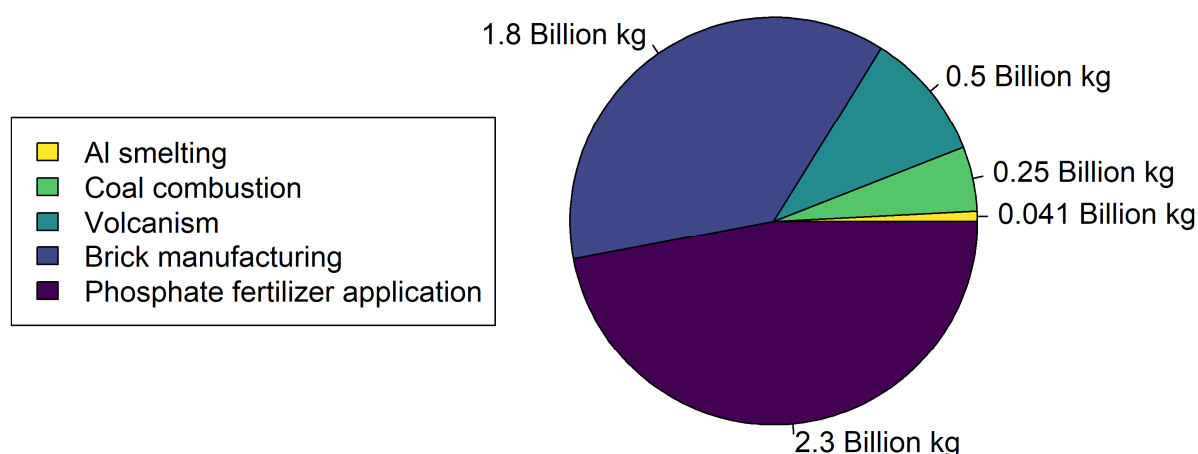


Figure 2-1 Global annual estimates of fluoride released to the environment by source. Estimates sourced from Fuge (2019) and Pyle and Mather (2009).

China currently accounts for 52 percent of global coal consumption (BP, 2020), and it is estimated that 162,161,000 kg of F were released into the atmosphere in 2009 from coal combustion in China alone (**Table 2-1**; Chen et al. 2013). In areas of the world where coal combustion is the dominant source of energy such as China and India, coal-fired powerplant F emissions may be introducing excess F to surface waters. While peak coal consumption occurred worldwide in 2013, many Asian-Pacific countries including Bangladesh, India, Indonesia, Malaysia, Pakistan, Philippines and Vietnam have increased their coal consumption by 2-7 times since 2007 (BP, 2020 and 2011), suggesting that coal combustion F emissions in the Asian-Pacific region have also been increasing. The global distribution of coal-fired powerplants is depicted in **Table 2-1**. Whilst limited information is available on the contributions of coal combustion-related F emissions to surface waters, it is certainly an F source that warrants further investigation and represents a key data gap in the understanding of anthropogenic F loading to surface waters globally.



Table 2-1 Estimated global annual fluoride emissions from coal combustion

Annual F Emissions in China (kg)		China's Proportion of Global Coal Consumption	Global Annual F Emissions (kg)
Estimate	162,161,000	51.9%	312,448,940
Source	Chen et al., 2013	BP, 2020	Estimated

Notes:

BP. (2020). Statistical Review of World Energy.

Chen, J., Liu, G., Kang, Y., Wu, B., Sun, R., Zhou, C., & Wu, D. (2013). Atmospheric emissions of F, As, Se, Hg, and Sb from coal-fired power and heat generation in China. *Chemosphere*, 90(6), 1925–1932.

<https://doi.org/10.1016/j.chemosphere.2012.10.032>

F is also emitted to the atmosphere from natural sources, particularly volcanic degassing, which accounts for an estimated 3×10^8 to 7×10^8 kg F annually (Pyle & Mather, 2009). Most of these emissions (greater than 90 percent) are from degassing while less than 10 percent are from explosive eruptions (Symonds et al., 1988). Marine aerosols also contribute F to the atmosphere, albeit at a much lower rate. Global estimates for F emissions from oceans are approximately 2×10^7 kg annually (Cadle, 1980). Another potential source of fluoride to surface waters is effluent from water treatment plants in communities that fluoridate drinking water supplies. Camargo et al. (1992) found elevated fluoride concentrations downstream of a wastewater treatment plant in the Cache la Poudre River in Colorado.

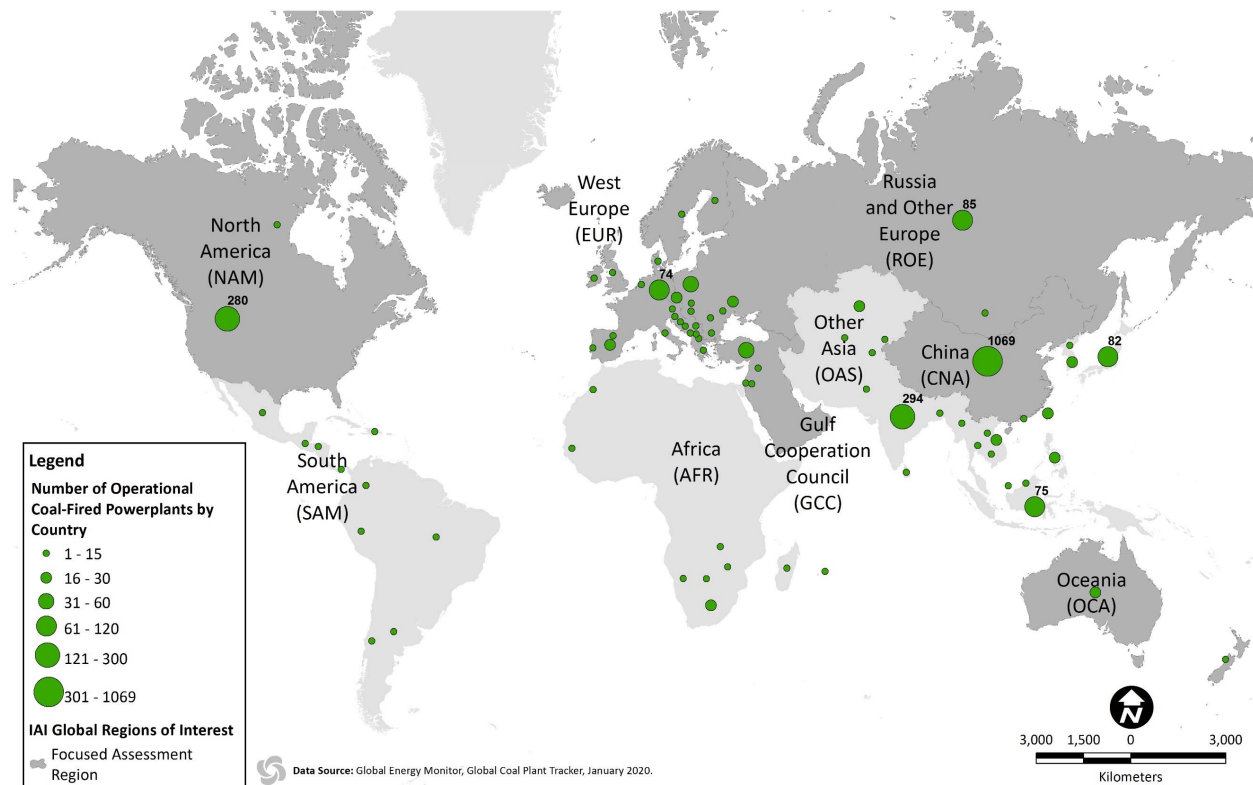


Figure 2-2 Number of coal-fired power generation facilities by country

2.3 Nature of Fluoride in Freshwater

2.3.1 Fluoride Speciation in Freshwater Systems

F is the most electronegative element on the periodic table and the most chemically reactive of all elements. In natural waters, F is overwhelmingly present as free fluoride (F^-) with only minor amounts complexed with major cations such as calcium, sodium and magnesium (Chapter 1 *Fluorine in the Context of the Environment* of Garcia and Borgnino, 2015; Jha et al. 2011). Under slightly acidic conditions (pH 5.5 to 6.5) fluoride sorption is maximized, and fluoride ions demonstrate a strong affinity for clay mineral surfaces, as well as surfaces of freshly precipitated iron and aluminium hydroxides (Edmunds & Smedley, 2013; Farrah et al. 1987). At lower pH (less than 5.5) fluoride forms strong complexes with Al such as $[AlF]^{2+}$ and $[AlF_2]^+$ and these species will predominate over free fluoride (**Figure 2-3**; Deng et al. 2011; Farrah et al. 1987; Wenzel & Blum, 1992). Due to its strong electronegativity, fluoride sorption is limited at pH greater than 6.5, and free fluoride will therefore be the dominant dissolved F species in most circumneutral or alkaline freshwater systems.

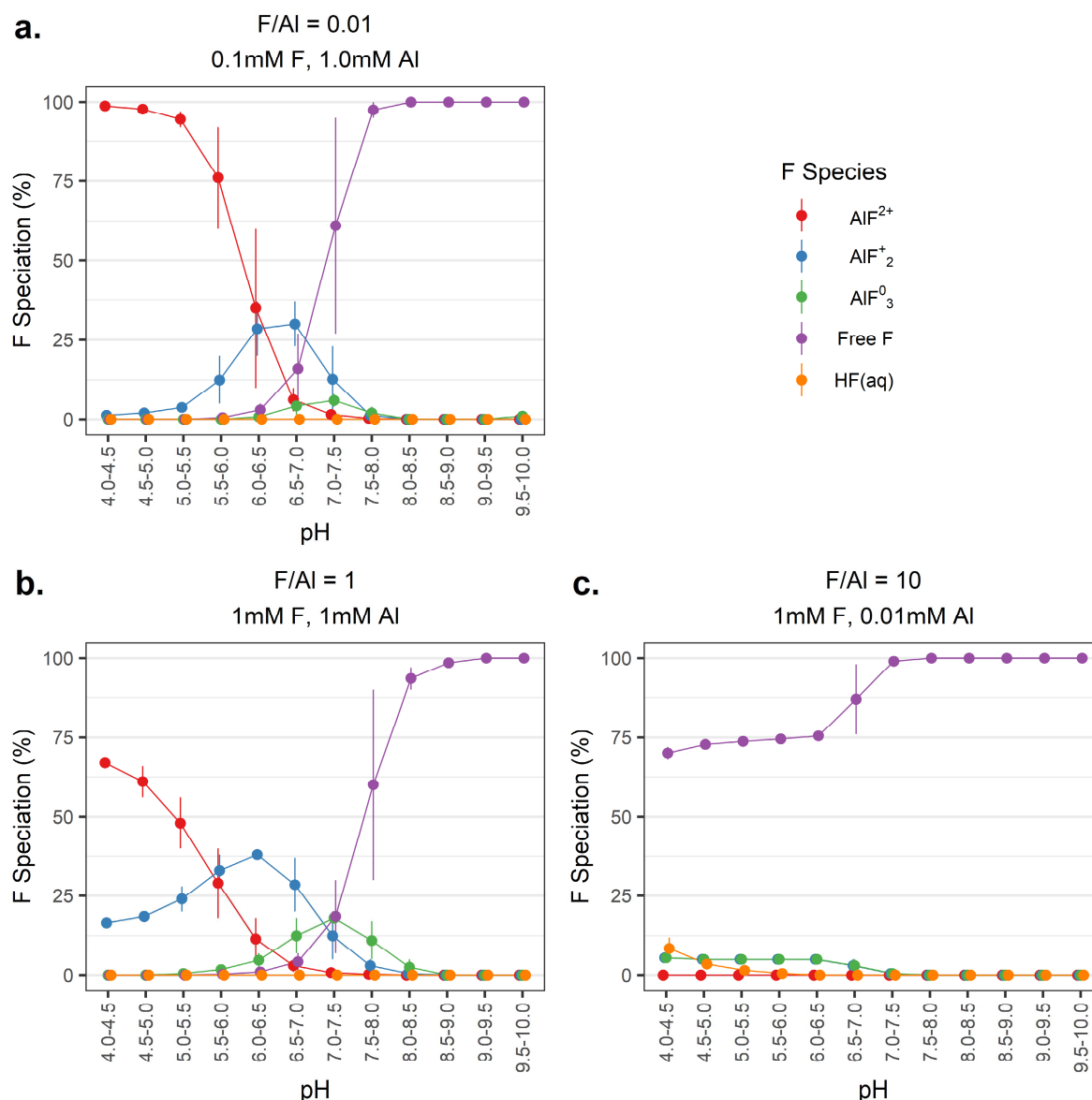


Figure 2-3 Simplified speciation diagram depicting the relative proportions of aqueous fluoride species across a range of pH values at A) 1:10 ratio of fluoride to aluminium, B) 1:1 ratio of fluoride to aluminium, and C) 10:1 ratio of fluoride to aluminium [Figure adapted from Deng et al. (2011)]

2.3.2 Mobility of Fluoride in the Environment

The solubility of F can be highly variable and is dependent on a suite of geochemical parameters including pH, alkalinity, temperature and the concentrations of calcium, sodium and aluminium in solution (Deng et al., 2011; Edmunds & Smedley, 2013; Jha et al. 2011; Vithanage & Battacharya, 2015). Due to the extreme electronegativity of the fluoride ion, dissolved fluoride has a strong affinity for positively charged mineral surfaces and its mobility in aqueous systems is therefore highly pH-dependent. The lowest solubility (and thus mobility) of fluoride is thought to occur between pH 5.5 and 6.5 because this is where sorption on the surface of aluminium hydroxides is maximized (Farrah et al. 1987; Wenzel & Blum, 1992). As pH increases above 6.5, mineral surfaces become more negatively charged and electrostatic repulsion promotes the desorption of fluoride ions into solution (Jha et al., 2011; Wenzel & Blum, 1992). At pH greater than 6.5, dissolution from F-



bearing minerals is also favoured as a result of increasing concentrations of the hydroxyl ion (OH^-) which readily substitutes for fluoride in mineral structures due to their common charge and similar ionic radii ($\text{F}^- = 1.36 \text{ \AA}$; $\text{OH}^- = 1.40 \text{ \AA}$; Garcia & Borgnino, 2015; Shawe et al. 1976). At lower pH (less than 5.5), fluoride mobility also increases due to the formation of highly stable soluble complexes with aluminium such as $[\text{AlF}]^{2+}$ and $[\text{AlF}_2]^+$ (Deng et al., 2011; Farrah et al., 1987; Wenzel & Blum, 1992). This complexation of fluoride with aluminium is one of the reasons why fluoride is so difficult to remove from natural waters. As pH decreases, mineral and particle surfaces become increasingly positively charged. Although these positively charged surfaces would have the ability to adsorb the free fluoride anion, positively charged aluminium-fluoride complexes such as $[\text{AlF}]^{2+}$ and $[\text{AlF}_2]^+$ are the dominant aqueous F species in this pH range (**Figure 2-3**) and will not adsorb to positively charged surfaces (Loganathan et al. 2013). Thus, solely on the basis of pH, F mobility in aqueous systems will be greatest at pH less than 5.5 and pH greater than 6.5.

Other geochemical variables that exert strong control over aqueous F mobility include bicarbonate and calcium ion concentrations in solution. Systems with high bicarbonate and low calcium content will promote fluoride release from fluorite as the precipitation of calcite will drive fluorite dissolution (Hayes et al., 2017; Jha et al., 2011; Saxena & Ahmed, 2003). A simplified version of this reaction is depicted in **Figure 2-4**, which can also be expressed as: $\text{CaF}_2 + \text{HCO}_3^- \rightleftharpoons \text{CaCO}_3 + 2\text{F}^- + \text{H}^+$.

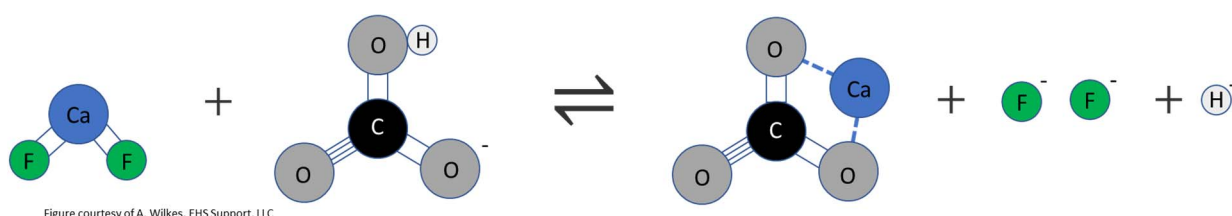


Figure 2-4 Equilibrium reaction demonstrating the relationship between fluorite (CaF_2), bicarbonate (HCO_3^-) and calcite (CaCO_3)

This reaction demonstrates that the addition of bicarbonate in the presence of fluorite will result in the dissolution of fluoride ions into solution (shift the equilibrium to the right). Conversely, the addition of protons (H^+) to a calcite-rich system in the presence of free fluoride will drive dissolution of calcite and coprecipitation of fluoride and calcium to form fluorite (shift the equilibrium to the left).

The solubility of fluorite is also temperature-dependent, and higher aqueous fluoride concentrations may therefore be expected in warmer systems or warmer seasons (Edmunds & Smedley, 2013). Residence time has also been shown to impact F mobility, particularly in groundwater aquifers, where F dissolution from rocks increases with increasing residence time (Edmunds & Smedley, 2013). These effects are particularly pronounced in arid climates, where slow groundwater infiltration and flow rates allow for prolonged interaction between water and rocks, leading to enhanced F dissolution. Conversely, high F concentrations are less common in humid tropical climates where rainfall has a more significant diluting effect on groundwater composition (Edmunds & Smedley, 2013; Jha et al., 2011) due to the typically low F concentrations found in rainwater (Barnard & Nordstrom, 1982).

2.4 Nature of Fluoride in Seawater

Contrary to freshwater systems, where F speciation is dominated by the free fluoride ion, only 51 percent of F in seawater is present as fluoride while 47 percent is complexed with magnesium as MgF^+ and approximately 2 percent is complexed with calcium as CaF^+ (Rude & Aller, 1993; Warner,



1971). Fluorine concentrations in seawater are typically higher than those found in freshwater with a global median concentration of 1.3 parts per million (ppm) (Ermakov, 2004; Garcia & Borgnino, 2015; Hayes et al. 2017). In seawater, F is a conservative constituent and the ratio of F:Cl on a mass basis has been empirically determined to be 6.75×10^{-5} to 1 (Warner, 1971). Chlorine (Cl) is also conservative in seawater and is related to salinity by **Equation 2-1**:

Equation 2-1 Salinity = $1.80655 \times [\text{Cl}]$

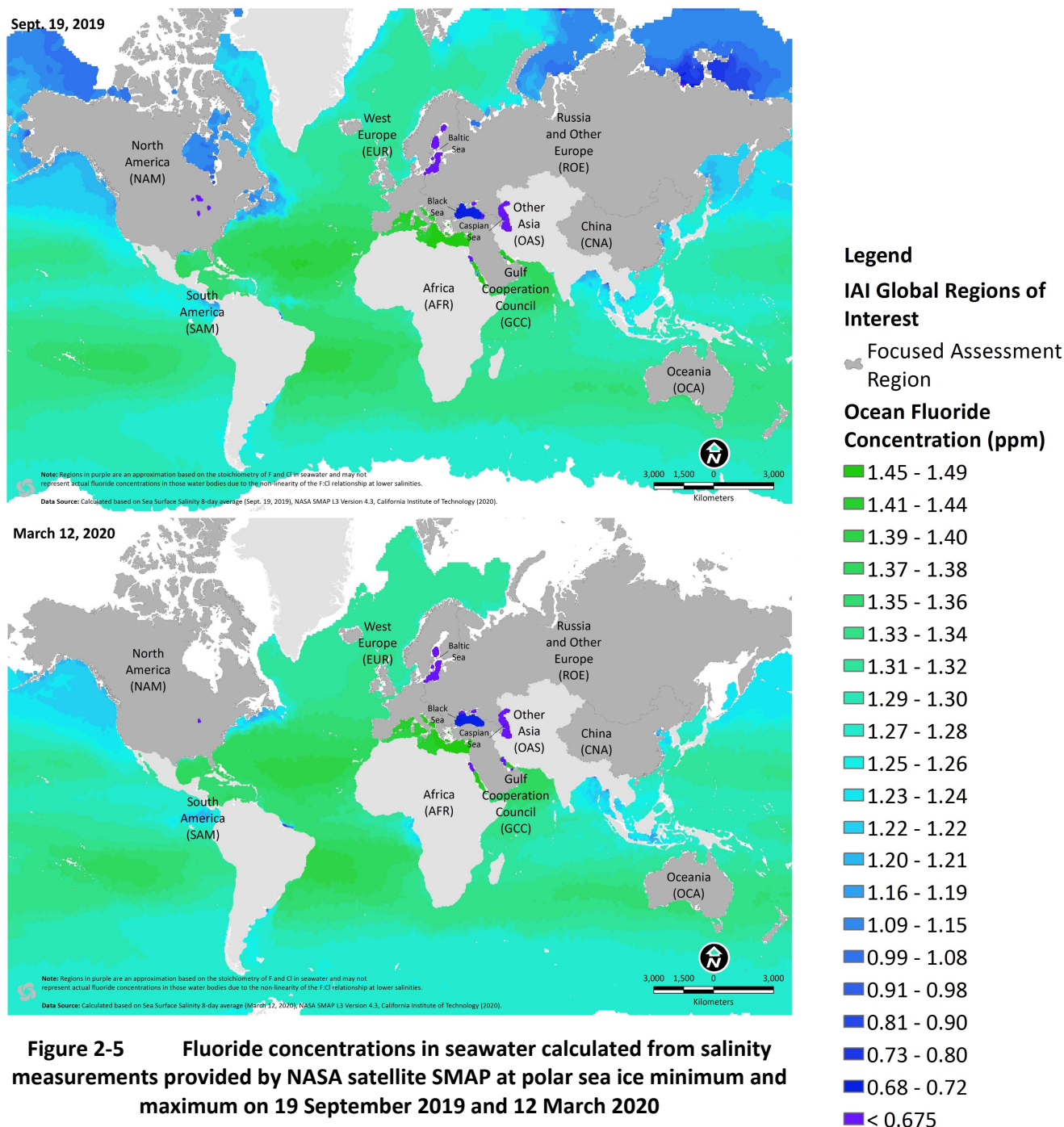
Where Salinity and Cl are each expressed in parts per thousand (Lewis, 1980).

While recent peer-reviewed literature on F in seawater is sparse and represents an information gap, the empirical relationships between [F], [Cl], and salinity indicate that F concentrations can be determined in normal seawater if salinity or [Cl] is known. Salinity concentrations of all global seawater are measured daily by the National Aeronautics and Space Administration (NASA) satellite SMAP (Soil Moisture Active Passive) and can be used to predict marine F concentrations. Information from the SMAP satellite was used to estimate marine F concentrations on a global scale with the same degree of spatial and temporal resolution as the salinity data it collects. **Figure 2-5** illustrates the global distribution of fluoride in surface water at the ocean surface during the last Arctic sea ice minimum and maximum, which occurred on 19 September 2019 and 12 March 2020.¹

Because F is a conservative constituent of seawater, its distribution in the open ocean is almost entirely dependent on the balance between evaporation and precipitation. This is apparent in **Figure 2-5** where maximum F concentrations occur in the mid-latitudes due to net evaporation while lower F concentrations occur at the equator and near the poles due to net precipitation. A seasonal pattern is also apparent near the poles where seawater F concentrations were diluted in September 2019 compared to March 2020 when sea ice extent in the Arctic was greatest. Removal mechanisms of F from seawater are limited to aerosolization although sedimentation via precipitation of F as carbonate fluorapatite may also occur (Garcia & Borgnino, 2015).

As the empirical relationship between F and Cl is linear down to approximately 10 parts per thousand (ppt) Cl (Windom, 1971), F concentrations calculated in this manner are assumed to be accurate at salinities above approximately 18 ppt. In less saline waters, the F:Cl is higher as a result of the low chlorinity of inflowing freshwater. Therefore, accurate determination of F concentrations based on satellite salinity data is possible for some of the more saline large seas. For example, estimated F concentrations for the Black Sea (salinity approximately 17 ppt) should be fairly accurate while estimated F concentrations for the Baltic and Caspian Seas may underestimate F due to the lower salinity (and chlorinity) of these systems. Studies conducted in other coastal and estuarine systems indicate that F:Cl range from $7\text{--}37 \times 10^{-5}$ to 1 when Cl concentrations are between 1 and 10 ppt (Windom, 1971; Zingde & Mandalia, 1988). Recent studies on this relationship in brackish environments are notably absent from the literature, thus F concentrations calculated for systems with less than 10 ppt Cl should be treated with caution and present an opportunity for further research, particularly in regions where aluminium production facilities are situated.

¹ Source: <https://nsidc.org/arcticseaicenews/charctic-interactive-sea-ice-graph/>. Accessed: 22 May 2020.



2.5 Background Fluoride Levels in Freshwaters

As discussed above, the background assessment of fluoride in fresh surface waters was conducted across several spatial scales. The following sections discuss the continental scale, national scale and sub-national scale evaluation of fluoride. **Figure 2-6** illustrates the global extent of surface water datasets leveraged for the assessment of fluoride in fresh surface waters.

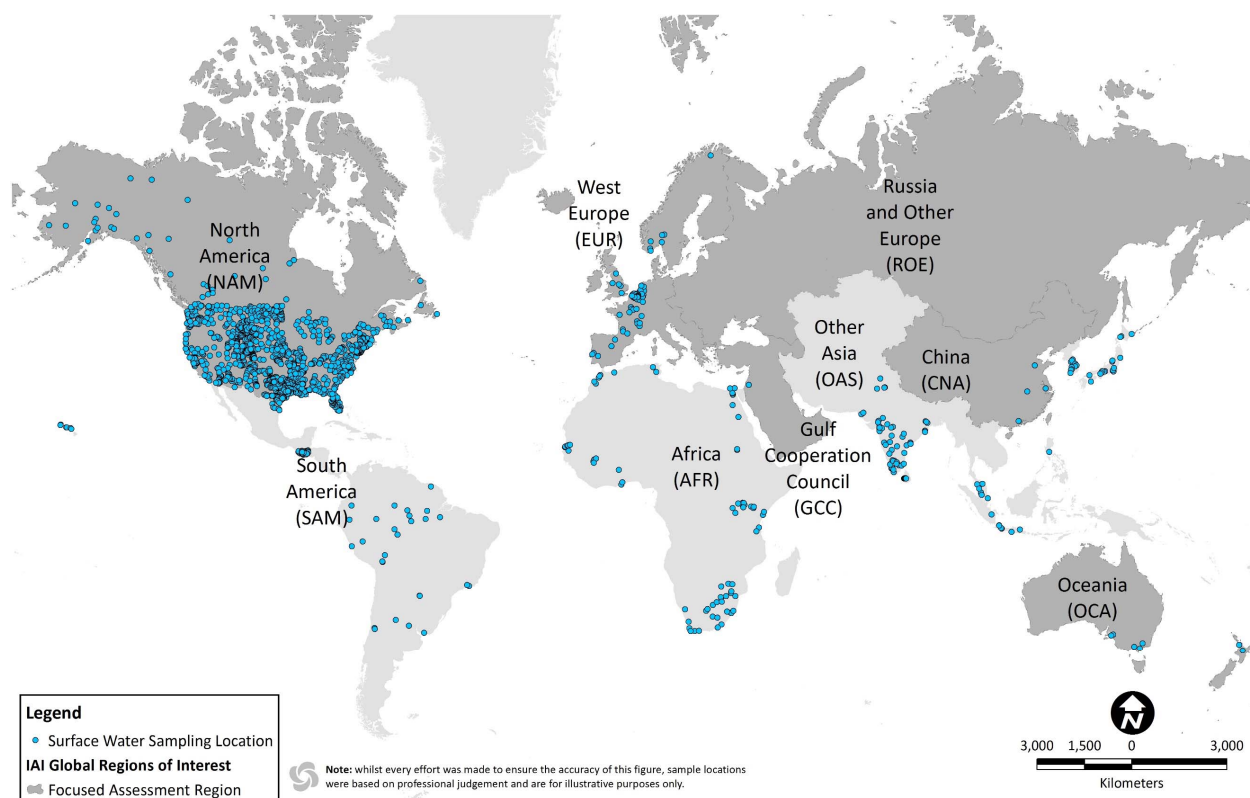


Figure 2-6 Locations of surface water sampling stations leveraged for the assessment of global fluoride concentrations

2.5.1 Continental Scale Fluoride Concentrations

Based on a review of publicly available surface water data spanning six continents (40 countries), typical freshwater fluoride concentrations fall between 0.1 and 0.3 milligrams per litre (mg/L) (**Table 2-2**). At the continental scale, median fluoride concentrations in fresh surface waters range from 0.11 mg/L in Asia to 0.30 mg/L in Africa. Mean and median concentrations were generally the same in Europe, North America, and South America, however, intra-continental variability was much greater as evidenced by the standard deviations relative to the mean concentrations (relative standard deviation [RSD] = 51 to 186 percent; **Table 2-2**).

Elevated fluoride concentrations in African surface waters are well documented and have been attributed to a variety of natural factors including high rates of chemical weathering arising from high average temperatures, volcanic rocks that contain higher F content than volcanic rocks in other parts of the world (Gaciri & Davies, 1993), and freshwater systems, particularly in the East African Rift region, that naturally contain low concentrations of Al, Ca, Fe and Mg that might otherwise remove fluoride from solution through adsorption or precipitation (Gaciri & Davies, 1993; Gizaw, 1996). High bicarbonate in natural waters of the region resulting from carbon dioxide (CO₂) outgassing and slightly alkaline pH both enhance Ca and Mg removal from natural waters and promote dissolution and desorption of fluoride from mineral phases into solution (Gizaw, 1996; Shen & Schäfer, 2015).



Table 2-2 Summary statistics for fluoride concentrations measured in surface waters at the continental scale

IAI Region	Date Range	Number of Stations	Number of Samples	Minimum (mg/L)	Maximum (mg/L)	Median (mg/L)	Mean (mg/L)	Geometric Mean (mg/L)	Standard Deviation (mg/L)
AFR	1977-2012	75	13,761	0.001	9.35	0.30	0.35	0.30	0.24
OAS/CNA	1979-2016	116	7,275	0.003	4.48	0.11	0.17	0.12	0.24
EUR	1978-2011	83	8,427	0.009	9.8	0.20	0.35	0.23	0.65
NAM	1965-2020	1,627	276,482	0	133	0.20	0.33	0.22	0.64
OCA	1979-2004	7	523	0.02	1	0.16	0.17	0.16	0.09
SAM	1979-2012	98	1,778	0.004	4	0.20	0.30	0.19	0.27

Notes:

All data sourced from publicly available databases. North America fluoride data is from the United States Geological Survey (USGS) and Open Canada. All other data is from GEMStat (United Nations Environment Programme).

AFR = Africa

CNA = China

EUR = Western Europe

IAI = International Aluminium Institute

mg/L = milligrams per litre

NAM = North America

OAS = Other Asia

OCA = Oceania

SAM = South America

2.5.2 National Scale Fluoride Concentrations

At the national scale, there is significant variability in surface water fluoride concentrations (**Figure 2-7**). While variability in data quality between nations precludes a more robust statistical analysis, it is evident from the available data that natural phenomena, such as geology and climate, govern global trends in surface water F concentrations to a far greater extent than anthropogenic activity. For example, Kenya, Tanzania and South Africa have some of the highest mean F concentrations in surface water out of all countries for which data was available (**Figure 2-7**). These countries represent areas of the East African Rift Valley known to be among some of the most severely fluoride-affected areas in the world owing both to the high F content of volcanic rocks and arid climate throughout much of the region (Gaciri & Davies, 1993; Jha et al., 2011).

At the other extreme are countries that likely experience dilution of F in surface and groundwaters as a result of high precipitation owing to their proximity to the equator. Ecuador, Sri Lanka, and the Philippines, which all have humid tropical climates, had the lowest mean F concentrations in surface water out of countries for which data was available (**Figure 2-7**).

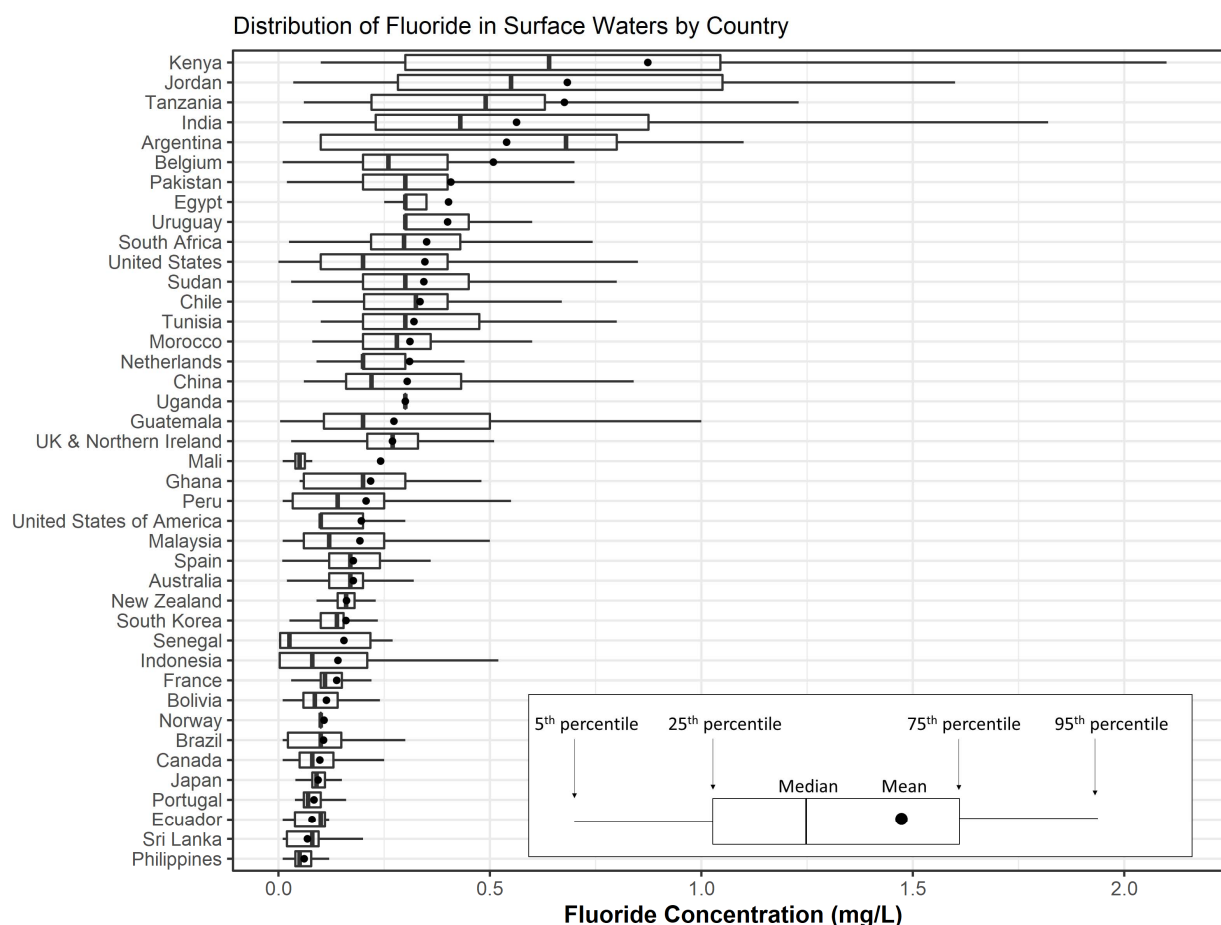


Figure 2-7 **Distribution of surface water fluoride concentration by country**

2.5.3 Fluoride Concentrations within North America

In the United States, the USGS operates a large network of surface water quality monitoring stations. A subset of the stations collects samples for fluoride analysis. Data was downloaded for the period between 1970 and 2020 from 1,580 different monitoring stations. The robust dataset had 260,267 water quality samples for fluoride spanning all 50 states. Fluoride surface water data was compiled to review spatial and temporal trends in the United States where primary and secondary aluminium smelters are located (**Figure 2-8**). Typical concentrations were found to be highly variable between states, with mean surface water fluoride ranging from 0.09 mg/L in New York to 0.72 mg/L in Arizona (**Figure 2-9**; **Appendix A - Supplemental Figure A-1**). Concentrations were found to be generally low in eastern states, whilst the highest concentrations in surface waters occur in western and southwestern states where fluoride levels in groundwater are also elevated due to regional geology (**Figure 2-10**). The major exception to this trend is Florida, where fluoride concentrations in surface waters are highly skewed (**Figure 2-9**) and instances of elevated F in surface waters have been attributed to phosphate rock mining that has occurred in the state since at least 1891 (PBS&J, 2007).

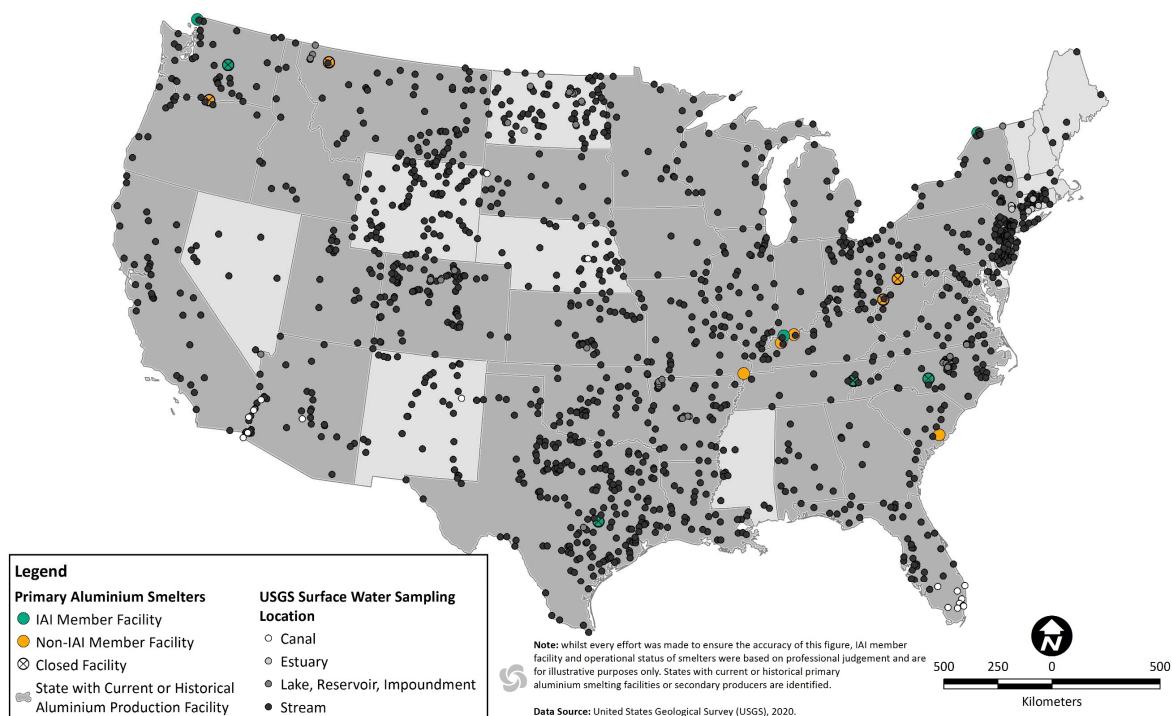


Figure 2-8 USGS surface water sampling station and primary aluminium smelter locations in the United States (NAM)

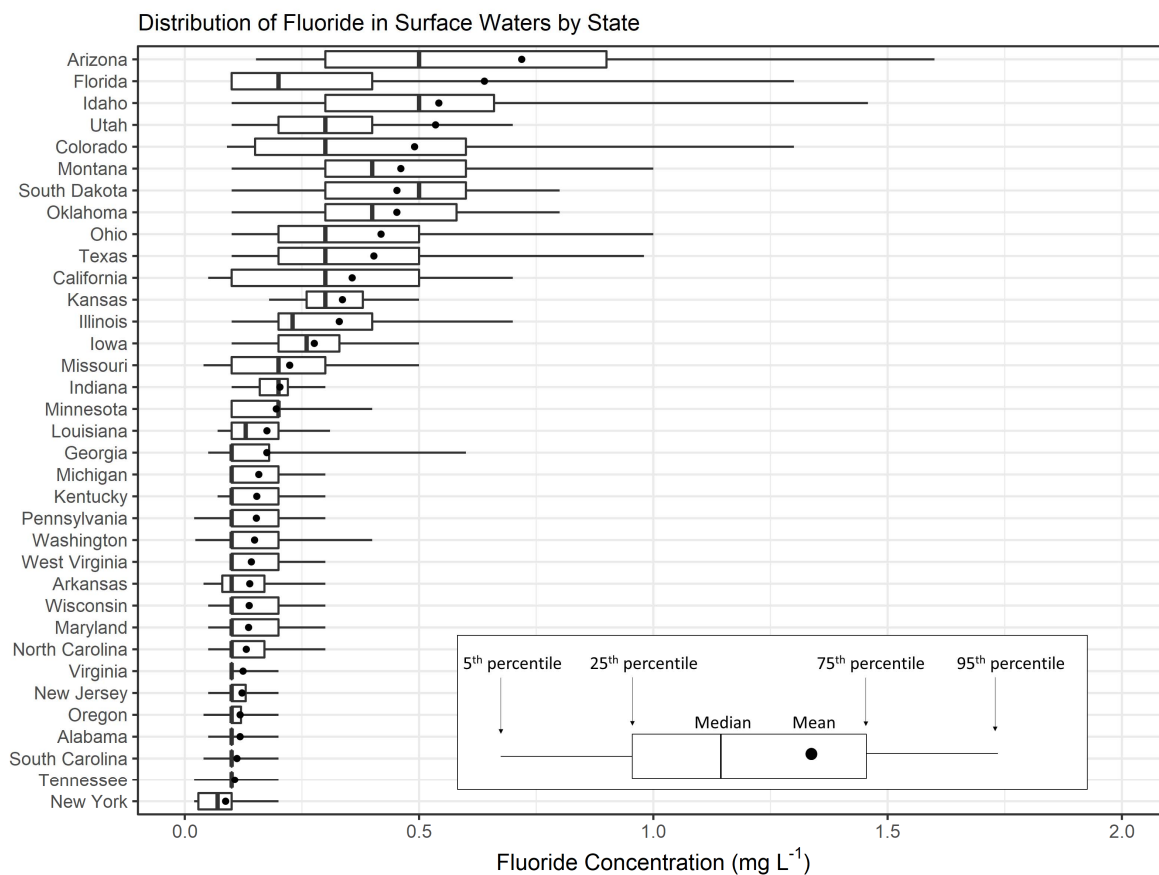


Figure 2-9 Distribution of surface water fluoride concentration by state in the United States (NAM) for states with primary or secondary aluminium smelters

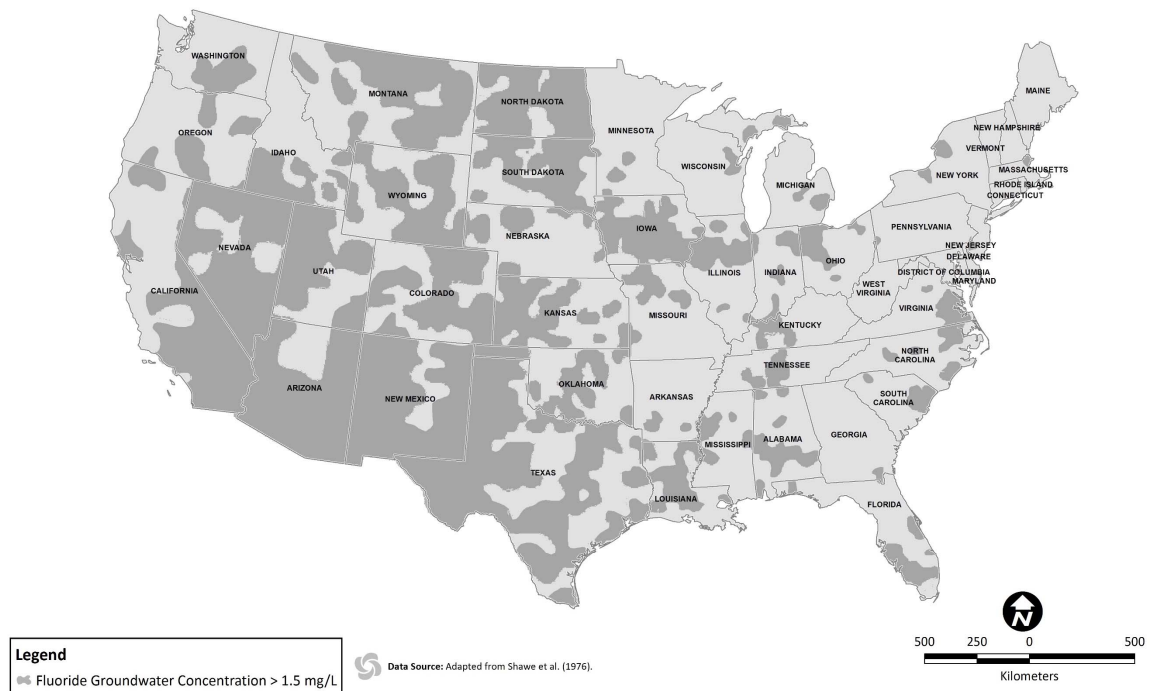


Figure 2-10 Groundwater distribution of fluoride throughout the United States

Based on available data, surface water concentrations in Canada are lower than those in the United States (**Figure 2-7**). The central tendency of fresh surface water fluoride presented in **Figure 2-7** is similar to an assessment presented by the Canadian Council of Ministers of the Environment (CCME, 2002). The review described by the CCME found mean inorganic fluoride levels in freshwater across Canada to be 0.05 mg/L. The fluoride concentrations in the 51,299 freshwater fluoride samples ranged from 0.01 to 11.0 mg/L (CCME, 2002).

In British Columbia, the Environmental Monitoring System program maintains a robust dataset of fluoride data across the province that allowed for a more detailed assessment of fluoride concentrations in both surface water and groundwater. Data from 1965 through 2020 was examined for 1,887 surface water monitoring stations containing 48,374 fluoride samples (**Figure 2-11**).

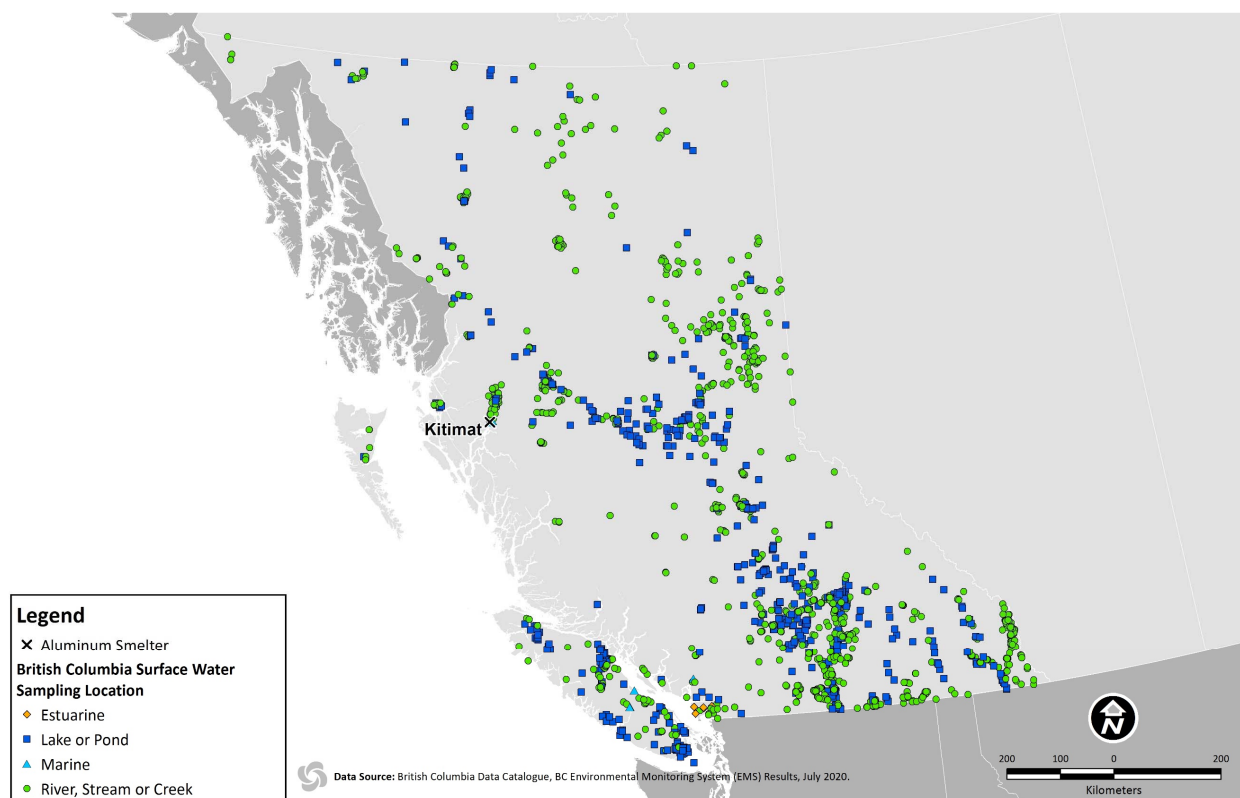


Figure 2-11 British Columbia surface water sampling locations

Fluoride concentrations in British Columbia surface waters were found to be generally low and consistent with background fluoride concentrations throughout Canada (**Table 2-3**). Areas of elevated fluoride concentrations in fresh surface waters were limited to discrete areas impacted by industrial activity, with particularly high fluoride concentrations noted in the St. Mary River basin in Kimberley, where a former fertilizer plant was located. Unlike the USGS dataset, where elevated surface water fluoride concentrations were typically attributable to local geology, geogenic fluoride signatures were less pronounced in British Columbia surface water data. In groundwater, however, areas of geogenic influence on fluoride distribution were much more obvious.

Table 2-3 Summary of fluoride concentrations by water body type across British Columbia

Waterbody Type	Date Range	Number of Stations	Number of Samples	Minimum (mg/L)	Maximum (mg/L)	Median (mg/L)	Mean (mg/L)	Geometric Mean (mg/L)	Standard Deviation (mg/L)
Lake or Pond	1967-2020	631	5,990	0.005	9.63	0.09	0.12	0.08	0.30
River, Stream, Creek	1965-2020	1,249	42,283	0.005	33	0.09	0.14	0.09	0.45
Marine and Estuarine	1988-2019	17	101	0.05	1.2	1.0	0.79	0.63	0.36
Groundwater	1974-2020	1,829	15,462	0	18.7	0.10	0.22	0.09	0.59

Notes:

mg/L = milligrams per litre



Groundwater data were available for 1,829 monitoring stations across British Columbia from 1974-2020, which allowed for a more thorough assessment of fluoride sources in the province. Mean fluoride concentrations in groundwater were both higher and more variable than mean concentrations in fresh surface waters (**Table 2-3**). Furthermore, elevated fluoride concentrations in groundwater were found to be isolated to areas in the southern region of British Columbia, which have previously been identified by the British Columbia Ministry of Environment as areas with elevated fluoride in monitoring wells (BCGA, 2007). High fluoride concentrations in groundwater in these areas can likely be attributed to geogenic influence, as fluorite deposits have been identified in some of these mainland regions (Simandl, 2009). Interestingly, many of the monitoring stations with the highest groundwater fluoride concentrations in British Columbia are located in the Gulf Islands, including Salt Spring Island, Hornby Island and Thetis Island. Due to the lack of fluoride-intensive industry in these locations, it is likely that the elevated fluoride in groundwater here is also of geogenic origin.

2.6 Geogenic and Anthropogenic Factors Affecting Fluoride Concentration

2.6.1 Case Study Evaluation of Regional Geology within the United States

Based on preliminary findings from publicly available datasets and peer-reviewed literature, regional geology is the single most influential factor in determining fluoride concentrations in surface water systems. This is apparent at the continental scale, where elevated fluoride concentrations in Africa are attributed to geologic drivers and also at smaller-scales such as across individual states within the United States, where the highest surface water concentrations are in states with large deposits of fluorite, topaz and fluorapatite.

Fluorite deposits are plentiful in Arizona, New Mexico, and Colorado (Shawe et al., 1976) and these states rank first, third and eighth, respectively in highest mean fluoride concentrations in surface water based on available USGS data (**Figure 2-9**). The observed regional trends in surface water fluoride concentrations across the United States mirror concentrations found in groundwater (**Figure 2-10**) which, according to Shawe et al. (1976), are proportionate to the fluorine content of the rocks that are in contact with that groundwater. Thus, in states where groundwater represents a significant proportion of riverine baseflow and fluoride concentrations in groundwater are high, fluoride concentrations in surface water can also be expected to be high.

2.6.2 Case Study Evaluation within Targeted NAM Water Bodies

To evaluate the impacts of aluminium smelter effluent discharge on fluoride concentrations in surface waters, USGS sampling stations located downstream of smelter operations were examined in closer detail. Five smelters (two active; three inactive/historical) were identified in locations upstream of USGS sampling stations (**Table 2-4**). Two of these smelters are located on the Columbia River in Oregon and Washington. The other three are located on the Flathead River in Montana, USA the St. Lawrence River on the border between New York, USA and Ontario, Canada and the Green River in Kentucky, USA. The available period of record for fluoride concentration data in each river ranged from 12 to 46 years and covered operational periods for each smelter. A summary of fluoride concentrations for each of these five USGS stations is provided in **Figure 2-12**. The mean and median fluoride concentrations at each of these downstream locations were found to be lower than the mean and median fluoride concentrations for surface waters in the United States at large. Furthermore, on the Columbia River, where USGS data is more abundant, mean and median fluoride concentrations at sampling locations upstream and downstream of the identified smelters are generally the same.



Table 2-4 Summary of fluoride concentrations measured downstream of aluminium smelters

State	USGS Site	River	Number of samples	Minimum (mg/L)	Maximum (mg/L)	Median (mg/L)	Mean (mg/L)	Geometric Mean (mg/L)	Standard Deviation (mg/L)
KY	3321230	Green	111	0.10	0.40	0.10	0.13	0.13	0.06
MT	12363000	Flathead	81	0	2.10	0.10	0.14	0.12	0.24
NY	4264331	St. Lawrence	299	0.07	0.30	0.11	0.13	0.12	0.05
OR	14128910	Columbia	182	0.10	0.70	0.20	0.18	0.17	0.07
WA	12472900	Columbia	175	0.05	0.30	0.10	0.12	0.11	0.04

Notes:

KY = Kentucky

mg/L = milligrams per litre

MT = Montana

NY = New York

OR = Oregon

USGS = United States Geological Survey

WA = Washington

Based on this overview it is apparent that aluminium production facilities and their corresponding permitted release requirements are not materially affecting fluoride concentrations along the river reaches where water quality data is available. This is due to the large volume of water in these river systems that rapidly attenuates fluoride contributions in permitted releases.

To demonstrate the impacts of mixing in these systems, a sensitivity analysis, modelled after the Columbia River, was conducted. According to the USGS, the mean discharge for the Columbia River is approximately 8.8 million litres per second (L/s) and the lowest measured discharge is approximately 3 million L/s. Assuming low flow conditions and a background fluoride concentration of 0.150 mg/L, an effluent flux of 50 L/s at a fluoride concentration of 50 mg/L would be required to raise the fluoride concentration of the well-mixed river by 1 part per billion (ppb), i.e., from 0.150 mg/L to 0.151 mg/L (**Figure 2-12**). Even in smaller systems like the Green River in Kentucky (mean discharge equals 500,000 L/s), an effluent flux of 50 L/s at a fluoride concentration of 50 mg/L would only raise fluoride concentrations in the well-mixed river by 5 ppb, i.e., from 0.150 mg/L to 0.155 mg/L.

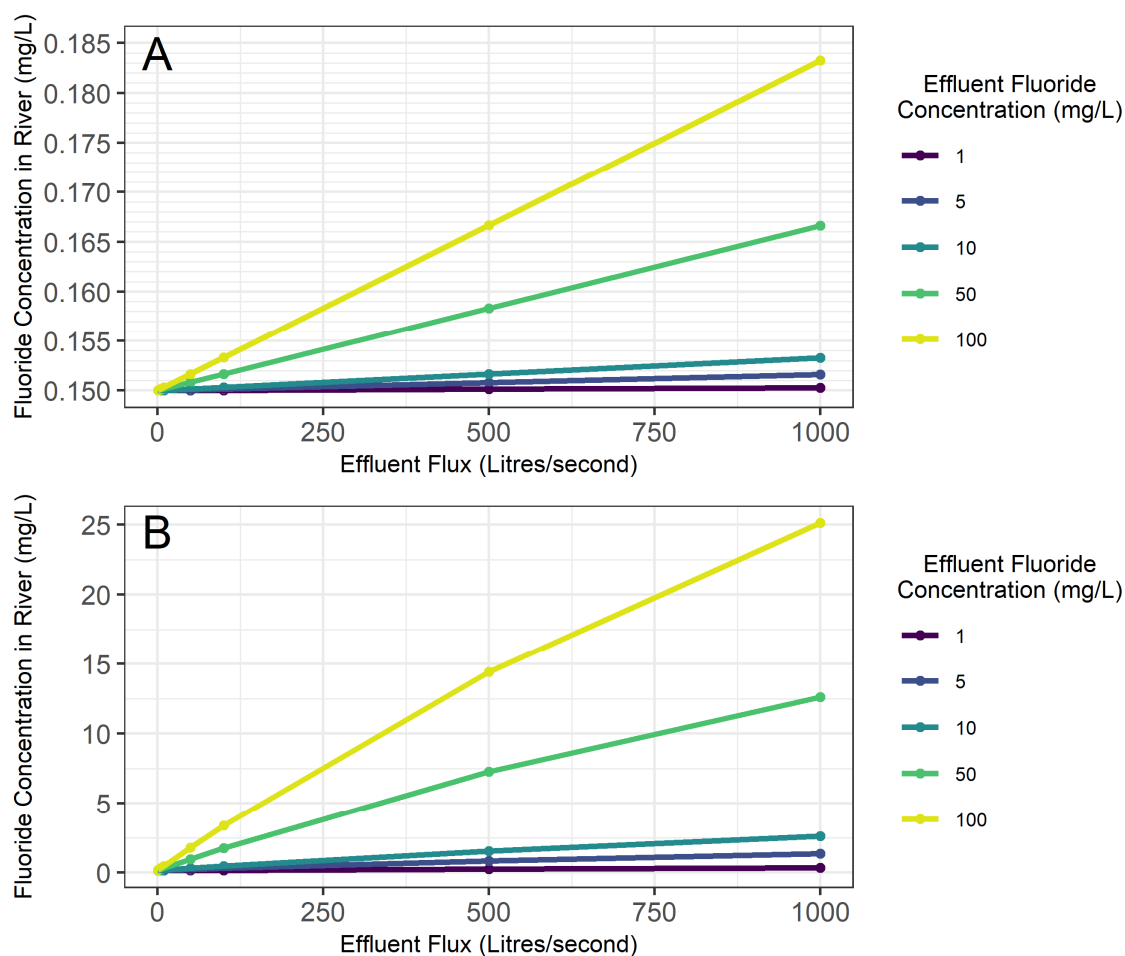


Figure 2-12 Sensitivity analysis for A) mixing in the Columbia River assuming lowest measured discharge ($3,000,000 \text{ L s}^{-1}$) and a background fluoride concentration of 0.150 mg/L and B) mixing in a river system assuming discharge of $3,000 \text{ L s}^{-1}$ and a background fluoride concentration of 0.150 mg/L

This sensitivity analysis highlights the negligible influence of releases on large riverine systems with established mixing zones. In addition, the range of influence is less than the natural variability in background conditions noted in surface waters throughout a given year. This is particularly true in river systems that are heavily impacted by annual snowmelt, such as the Columbia River, as fluoride concentrations would be further diluted by the larger volume of water being transported during peak snowmelt. Similar processes would be at play in areas that experience wet and dry seasons. Seasonality may therefore be an important consideration in determining the extent to which fluoride in industrial effluent may impact surface water concentrations.

2.7 Summary of Review, Data Gaps, and Recommendations

The continental level analysis was undertaken to understand the distribution of fluoride across broad geographic regions. For this assessment, available fluoride surface water data was examined within global regional boundaries established by the IAI. At the continental scale, median background fluoride concentrations in fresh surface waters range from 0.11 mg/L in Asia to 0.30 mg/L in Africa. Although the median freshwater fluoride concentrations were relatively low, naturally occurring background fluoride is greater than some conservative aquatic life guidelines in some regions.



Although the freshwater fluoride surface water concentrations were relatively constrained at the continental scale, the high variability of concentrations became more apparent at the national scale and within the localized assessment of the United States. In freshwaters, this variability is predominantly a reflection of local geology, which was found to be a primary driver of surface water fluoride concentration. Regions with abundant fluorine-containing mineral deposits tend to have the highest fluoride concentrations in surface water. Therefore, knowledge of regional mineralogy or geology would greatly improve constraining estimates of background freshwater fluoride.

Based on the available data for large river systems in the United States, aluminium production facilities did not have any discernible effect on surface water fluoride concentrations. Due to the natural background levels of fluoride in major river systems within the United States and high rate of flux, it is difficult to detect the influence of any anthropogenic F inputs considering the natural weathering rates. Even at sampling locations downstream of plausible sources of fluoride, little changes in concentration were noted. This assessment, in conjunction with the knowledge of the high degree of fluoride loading from phosphate fertilizer application and significant atmospheric releases of fluoride associated with coal-fired power plants, supports the conclusion that aluminium production facilities have minimal effects at broader scales.

Fluoride in marine waters is naturally more abundant than freshwater and has an average concentration of approximately 1.3 mg/L versus the global freshwater median of 0.2 mg/L. Certain, more isolated coastal marine water bodies may have even greater fluoride due to limited exchange and high evaporation rates. Elevated fluoride and other ions have been observed in coastal wetlands. Whilst F is a conservative constituent of seawater and concentrations can be reasonably estimated for the open ocean, anomalies certainly exist near coastal regions, estuaries and hydrologically isolated saltwater bodies that are not well captured in the scientific literature. The higher typical F concentrations in marine waters and the large capacity to physically mix with fresh surface waters lends support to situating aluminium production facilities near marine systems, if possible.

Throughout this review, data gaps were identified with respect to spatial and temporal coverage of fluoride data. While expected, certain countries have more publicly available data on freshwater fluoride concentrations than do others. This leads to challenges in comparing the extent of surface water fluoride between nations, particularly in countries that have aluminium production facilities but not a robust dataset of background surface water fluoride. This data gap would be of greatest importance in countries with a high incidence of aluminium production facilities where surface waters might be expected to be naturally high in F due to geology. For example, publicly available data on fluoride concentrations in Chinese surface waters is very limited. Information on natural background conditions may improve the management of fluoride releases within the CNA considering its importance to the global aluminium market. Similarly, understanding the extent to which coal-fired powerplants may be impacting fluoride concentrations in surface waters is integral to the determination of what constitutes natural background fluoride concentrations, particularly in the CNA, where coal-fired powerplants are abundant.

Another key data gap identified in this review is background fluoride concentrations in coastal regions. While fluoride concentrations were estimated for seawater globally, the spatial resolution of these estimations is limited by the resolution of the salinity data provided by the SMAP satellite. In coastal regions, fluoride concentrations likely change rapidly over very short distances due to freshwater infiltration into marine water bodies, and the resultant fluoride gradient is likely not captured in sufficient detail here to inform management decisions in these areas. Furthermore, these fluoride gradients in coastal water bodies are likely to be highly variable and dependent on



location-specific physical, chemical and geological factors as well as the nature of contributing surface water sources.

In both freshwater and marine systems, these conclusions highlight the importance of understanding the characteristics of natural background as well as mixing zones at facilities. The size and extent of the mixing zones and the assumptions for their establishment should be understood for each facility to enable more insightful understanding of the capacity of the receiving water body. Similarly, the ranges of receptors present are an important consideration as misalignment may exist between the extent of detectable changes in fluoride concentration and the area used by receptors. This relationship will be explored in greater detail in **Section 4** and **Section 5**.



3 Surface Water Fluoride Aquatic Life Guidelines and Regulations

3.1 Introduction

Globally, surface water fluoride regulations are largely based on limits for safe drinking water. Fluoride maximum acceptable concentrations (MACs) exist at federal, state and provincial levels to prevent human health effects, such as dental or skeletal fluorosis. Although MACs are important benchmarks for establishing safe limits for human ingestion exposure pathways, these guideline values are not necessarily transferable to understanding and managing risks to aquatic receptors where surface water discharges occur. Nevertheless, numerous instances exist whereby drinking water criteria have been applied to wildlife receptors or for the management of surface water releases from industrial facilities. Widespread recognition of the appropriate targeted receptors and technical basis for criteria is needed for the suitable application of derived aquatic fluoride criteria.

Inappropriate use of drinking water criteria to address surface water fluoride ecological risks is attributable to the few aquatic life criteria that exist. For example, Canadian guidance exists for the protection of freshwater aquatic life, but the criteria are considered interim guidance. In the United States, no formal federal guidance is offered. Provincial and state criteria are also sparse, and both countries lack marine criteria. The absence of widespread promulgated guideline values for ecological receptors has been driven by the quality or availability of toxicity literature for a wide range of receptor species and water types at the time of criteria derivation. Available guidelines for understanding the potential for unacceptable risk to aquatic organisms can use antiquated scientific literature or overly conservative approaches to derive values that reflect the paucity of literature. A more robust approach is needed to inform criteria derivation based on a strong knowledge base of potential ecological risks of fluoride in the aquatic environment. Comprehensive knowledge of the toxicity literature and other assumptions supporting existing aquatic life criteria is needed to establish a more unified approach to fluoride management.

The widespread use of human health criteria for fluoride management in the aquatic environment and an absence of sufficiently robust criteria specific to ecological receptors have created a regulatory climate for the management of fluoride that is extremely variable across jurisdictions and has a profound and direct impact on industries that use fluoride. The objective of this surface water fluoride aquatic life guidelines and regulatory review is to provide a balanced perspective on issues pertaining to the management of fluoride-related risks to fresh and marine surface waters within the focused assessment region.

This section is comprised of the following review topics:

- Summary of drinking water fluoride guidelines
- Existing surface water fluoride aquatic life criteria and basis
- Guidelines governing surface water fluoride releases from aluminium production facilities (permit limits and associated frameworks)

These topics are addressed by assessment region. The regulatory review is accompanied by case studies highlighting novel approaches to fluoride discharge management. This information will help identify gaps in management approaches to better inform a more unified basis of guideline values derivation and regulations of aquatic fluoride.



3.1.1 Key Findings

The key findings provided below are intended to succinctly address the objectives and core questions of the review in the form of a question and answer format. Questions are presented in italicized text and the key findings are provided in normal text.

- *What are the ranges of drinking water guidelines across regulatory regions and what commonalities exist in their derivation?*
Drinking water guidelines typically range from 1.0 to 4.0 mg/L fluoride. Drinking water quality guidelines, particularly maximum acceptable concentrations (MACs), are largely informed by conditions that may result in increased risk for moderate dental fluorosis, whereas the United States maximum contaminant level (MCLs) are based on increased potential for more pronounced effects, such as the long-term risk for skeletal fluorosis over long exposure durations (10+ years). Among the values identified for the protection of drinking water, the concentration of 1.5 mg/L fluoride had the greatest incidence of occurrence.
- *What are the ranges of aquatic life surface water guidelines across regulatory regions and what commonalities exist in their derivation?*
The aquatic life criteria information is either antiquated or a paucity of information exists. Guideline values range from 0.12 mg/L to 4.0 m/L; however, the upper end of the range is based on the drinking water human health MCL. In both fresh and marine waters, limited chronic toxicity information supports the derivation of aquatic life guidelines. In addition, there are instances where freshwater and marine criteria are at or below the background surface water fluoride concentration for the region that the criteria were derived.
- *What are examples of successful means to mitigate or reduce fluoride releases to surface waters at aluminium production facilities?*
Roof vent emissions and runoff from soil or ground surface deposition were identified as important sources of fluoride at aluminium production facilities. Since stormwater is often the main transport mechanism from sources to the receiving environment, one way to mitigate or reduce fluoride releases at smelting facilities is to carefully manage stormwater. Some aluminium production facilities have novel water management approaches that use stormwater as a water source for industrial processes and in doing so dramatically reduce the fluoride discharge on an annual basis. Stormwater infrastructure and dynamic management systems are advantageous in temperate regions, with high rainfall, to provide a source of low fluoride, freshwater to mitigate and manage effluent releases containing fluoride.

3.2 Summary of Existing Drinking Water Guidelines

Fluoride has beneficial effects on teeth at low concentrations in drinking water, but excessive exposure to fluoride in drinking water, or in combination with exposure to fluoride from other sources, can give rise to multiple adverse effects. These range from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases. Crippling skeletal fluorosis is a significant cause of morbidity in some regions of the world (WHO, 2006).

This summary of existing drinking water guidelines provides context to the range of values globally considered protective of human health. Drinking water MACs for fluoride range between 1.4 and 4.0 mg/L. **Table 3-1** summarizes the drinking water quality guidelines by region, country, and



state/province. A brief discussion of the assumptions that form the basis of the more widely adopted criteria is provided below.

Table 3-1 Fluoride drinking water quality criteria summary by region, country, state/province

Region	Country	State/Province	Criteria Value (mg/L)	Source Notes
NAM	Canada	All provinces.	1.5	Maximum Acceptable Concentration (MAC); Canada Minister of Health. 2010. Guidelines for Canadian Drinking Water Quality: Guideline Technical Document – Fluoride. Water Quality and Health Bureau, Healthy Environments and Consumer Safety Branch, Ottawa, Ontario.
	United States	Alabama, Arizona, Connecticut, Indiana, Kentucky, Minnesota, Missouri, Montana, Nebraska, North Dakota, Ohio, South Carolina, Utah, West Virginia, Texas*	4.0	United States Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL)
		Delaware, Kansas, Minnesota, Mississippi, Nevada, Pennsylvania, Wyoming, California	2.0	USEPA Secondary MCL (SMCL) and California Primary MCL
		New York, Florida	1.5	N.Y. Comp. Codes R. & Regs. tit. 6, § 703.5 Water quality standards for taste-, colour- and odour-producing, toxic and other deleterious substances; Ambient Water Quality Standards (June 1998); Class I Surface Waters – Potable Drinking Water
		West Virginia, Illinois	1.4	Ill. Admin. Code tit. 47 § 302.304. Public and Food Processing Water Supply Standards. Effective January 28, 2008.
		Ohio	1.0	Ohio Admin. Code R. 3745-1-32. Table: 32-2. Ohio River Water Quality Criteria for the Protection of Human Health. Effective August 28, 2018.
EUR	European Union	n/a	1.5	Drinking Water Directive (Council Directive 98/83/EC) of 3 Nov 1998 on the Quality of Water Intended for Human Consumption



Region	Country	State/Province	Criteria Value (mg/L)	Source Notes
	United Kingdom	n/a	1.5	United Kingdom Health Protection Agency
OCA	Australia	All states	1.5	National Water Quality Management Strategy – Australian Drinking Water Guidelines 6 (2011). Updated May 2019.
	New Zealand	n/a	1.5	Chapter 10 – Guidelines for Drinking-water Quality Management for New Zealand.

Notes:

* - Other states do not explicitly mention fluoride in guidance and would default to USEPA MCL and SMCL values.

** - Ohio and West Virginia have criteria that specify Ohio River and Class A water bodies, with specific considerations beyond drinking water guidance.

EUR = Western Europe

mg/L = milligrams per litre

n/a = not applicable

NAM = North America

OCA = Oceania

Dental fluorosis is the most widely and frequently studied of all adverse effects of fluoride. It is the effect occurring at the lowest level of fluoride exposure in the population (Canada Minister of Health, 2010). Consequently, a MAC of 1.5 mg/L fluoride, which is protective of dental fluorosis, is the modal criteria value across the regions and countries evaluated. A brief discussion of the assumptions that have contributed to this modal value as described by the World Health Organization (WHO) in *Fluoride in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality* (WHO, 2004) and *Guidelines for Canadian Drinking Water Quality: Guideline Technical Document – Fluoride* (Canada Minister of Health, 2010). In addition, a discussion of the MCL and secondary MCL (SMCL) derivations in the United States is also provided.

In general, dental fluorosis does not occur in temperate areas at concentrations below 1.5 to 2 mg/L F (WHO, 2004). The 1.5 mg/L drinking water quality guideline developed by the WHO was established based on epidemiological evidence (dose-response relationship) that concentrations above this value carry a potentially-increased risk of moderate dental fluorosis. This value was recommended by WHO as a level at which dental fluorosis should be minimal (WHO, 1984). The WHO guideline value is not a “fixed” value but is intended to be adapted to take account of local conditions (e.g., diet, water consumption, etc.). Additionally, at progressively higher drinking water fluoride concentrations (greater than 10 mg/L) the potential for risks of crippling skeletal fluorosis increases.

Since the guideline value was derived in the early 1980s it has been periodically re-evaluated to assess whether assumptions that contributed to its derivation are in alignment with the current state of scientific understanding. The latest review occurred in 2004. The WHO concluded that there is no evidence to suggest that the guideline value of 1.5 mg/L F set in 1984 and re-affirmed in 1993 needs to be revised.

In 2010 the Canadian Ministry of Health (Health Canada) also conducted an updated assessment of the available scientific literature to assess the MAC of 1.5 mg/L fluoride in drinking water. The drinking water criteria value was established to be protective of the population most at risk of



developing dental fluorosis, children 1 to 4 years old. Available data on the relationship between total daily fluoride intake and the prevalence of dental caries and dental fluorosis in children was assessed. Considering daily fluoride intake from all potential sources of exposure (drinking water, food, soil and air), the drinking water value of 1.5 mg/L would not result in a total daily intake greater than tolerable upper intake level of 100 micrograms per kilogram of body weight per day ($\mu\text{g/kg bw/day}$) established by the Institute of Medicine (IOM) in the United States for infants, toddlers and children through 8 years of age, based on the absence of moderate dental fluorosis (IOM, 1997).

The assessment concluded that the weight of evidence from all currently available studies does not support a link between exposure to fluoride in drinking water at 1.5 mg/L and any adverse health effects, including those related to cancer, immunotoxicity, reproductive/developmental toxicity, genotoxicity and/or neurotoxicity. Mild to moderate dental fluorosis is not considered to be an adverse health effect. However, in the assessment, a concentration of 1.5 mg/L was considered unlikely to cause moderate dental fluorosis in the Canadian population. As reported by Health Canada, recent Canadian Health Measures Survey data have shown that the prevalence of Canadian children with moderate dental fluorosis is too low to be reported. This MAC has been adopted widely throughout Canadian provinces.

As noted earlier, skeletal fluorosis is the most serious adverse health effect clearly associated with prolonged exposure to high levels of fluoride in drinking water. It has been estimated that the development of crippling skeletal fluorosis in man requires the consumption of 20 mg or more of fluoride/person/day over a 20-year period, i.e., 0.28 mg/kg/day (USEPA, 1985). The current enforceable drinking water standard in the United States (USEPA MCL of 4 mg/L) has been established to protect against this endpoint and included an applied safety factor (resulting in a safe exposure level of 0.12 mg fluoride/kg/day).

In addition to the MCL, a non-enforceable SMCL has also been established in the United States for use by community water systems. However, states may choose to adopt SMCLs as enforceable standards. The secondary standard of 2.0 mg/L is intended as a guideline for an upper boundary level in areas which have high levels of naturally occurring fluoride. The level of the SMCL was set based upon balancing the beneficial effects of protection from tooth decay (dental caries) and the undesirable effects of excessive exposures leading to discolouration (dental fluorosis).

Implementation of the MCL and SMCL within the United States varies due to the structure of the Clean Water Act (CWA) and the interaction between federal and state environmental policy. Individual states can promulgate standards at or below the federal MCL of 4.0 mg/L.

Similar to other regions, fluoride is voluntarily added to some drinking water systems in the United States as a public health measure for reducing the incidence of cavities among the treated population. The decision to fluoridate a water supply is made by the local municipality and is not mandated by the United States Environmental Protection Agency (USEPA) or the state. Naturally occurring levels of fluoride are used to determine whether fluoridation is necessary. The United States Centers for Disease Control and Prevention (CDC) currently recommends a fluoridation level of 0.7 mg/L, which is considered the optimal level of fluoride in drinking water to prevent tooth decay (USPHS, 2015).



3.3 Existing Surface Water Fluoride Aquatic Life Criteria

Surface water aquatic life criteria provide a specific concentration threshold (or range of thresholds) in which an exceedance may indicate some level of unacceptable risk to aquatic life. The specific approach taken to derive guidelines varies by governing body. Because many factors can contribute to the guideline derivation process and those vary by governing body, it is important to understand those assumptions and the toxicity data that informs them.

The discussion herein provides a critical review of the existing aquatic life criteria and what factors contributed to their derivation. Since aquatic life standards may or may not be promulgation values for regulatory purposes, this section also reviews the precedence of aquatic life criteria for the basis of regulations pertaining to the discharge from industrial facilities.

Table 3-2 summarizes the available aquatic life criteria by region. Details regarding the key assumptions that contributed to the aquatic life criteria guidelines are provided for NAM, EUR and other regions of primary aluminium production below. It should be noted that there has been some reliance on the MCL and SMCL fluoride criteria values in the absence of state-specific aquatic life criteria.

Table 3-2 Fluoride aquatic life criteria summary by region, country, state/province

Region	Country	State/Province	Criteria Value (mg/L)	Source Notes
NAM	Canada	Federal Criteria – Canadian Council of Ministers of the Environment (CCME)	Chronic: 0.12	Canadian Council of Ministers of the Environment. (2002). Canadian Water Quality Guidelines for the Protection of Aquatic Life - Inorganic Fluorides
		British Columbia - Ministry of Environment	Freshwater Acute: $WQG = [-51.73 + 92.57 \log_{10}(\text{hardness})]$ Freshwater Acute: $WQG = [-51.73 + 92.57 \log_{10}(\text{hardness})] \times 0.01$ Marine Acute: 1.5	British Columbia Ministry of Environment & Climate Change Strategy. (2019). British Columbia Approved Water Quality Guidelines: Aquatic Life, Wildlife and Agriculture, Victoria B.C.
		Quebec - Ministry of Environment	Freshwater Acute: 4.0* Freshwater Chronic: 0.2* Marine Chronic: 1.5	Quebec Surface Water Quality Criteria. Freshwater acute and chronic criteria based on SERT, 1989* and marine chronic criteria based on Warrington, 1990.
	United States	Federal Criteria – United States Environmental	Freshwater Chronic: 2.1194	United States Environmental Protection Agency



Region	Country	State/Province	Criteria Value (mg/L)	Source Notes
		Protection Agency (USEPA)	Marine Chronic: 2.1194	(USEPA). 2006. Region III BTAG Freshwater and Marine Screening Benchmarks.
		Florida – Department of Environmental Protection (DEP)	Class III Freshwater: 10.0 Class III Marine: 5.0	Fla. Admin. Code 62-302.530(32). Table: Surface Water Quality Criteria. Effective March 27, 2018.
		Illinois – Environmental Protection Agency	Freshwater Acute: $\exp^{(6.7319 + 0.5394 \times \ln[\text{HARDNESS, mg/L}])}$ Freshwater Chronic: $\exp^{(6.0445 + 0.5394 \times \ln[\text{HARDNESS, mg/L}])}$ with a F limit of 4 mg/L	Illinois Nutrient Science Advisory Committee (INSAC). 2018. Recommendations for Numeric Nutrient Criteria and Eutrophication Standards or Illinois Streams and Rivers. Prepared for Illinois Environmental Protection Agency. December.
		Indiana – Department of Environmental Management	Freshwater Chronic: 1.0 – 2.0 mg/L	Ind. Admin. Code tit. 327, § 2. Table 6-1. Surface Water Quality Criteria for Specific Substances. Effective May 20, 2015.
		Michigan – Department of Environmental Quality	Freshwater Acute: $\exp^{(0.1776 \times [\ln(\text{Hardness, mg/L})] + 8.8927)}$ Freshwater Chronic: $\exp^{(0.1776 [\ln(\text{Hardness, mg/L})] + 6.9017)}$	Mich. Admin. Code R. 323.1057 § 4. Water Quality Standards. Effective January 13, 2006.
		Minnesota – Pollution Control Agency	Freshwater: 4.0 Freshwater (Secondary): 2.0	Minn. R. 7050.0220. Specific Water Quality Standards by Associated Use Classes. Effective February 12, 2020.
		New York – Department of Environmental Conservation	Freshwater Acute: $\exp^{(7.394 + 0.907 \times \ln[\text{HARDNESS, mg/L}])} \times 0.1$ with a hardness limit of 200 mg/L Freshwater Chronic:	N.Y. Comp. Codes R. & Regs. tit. 6, § 703.5 Water quality standards for taste-, colour- and odour-producing, toxic and other deleterious substances.



Region	Country	State/Province	Criteria Value (mg/L)	Source Notes
			$\exp^{(7.394 + 0.907 \times \ln[\text{HARDNESS, mg/L}])} \times 0.02$ with a hardness limit of 200 mg/L	
		North Carolina - Department of Environmental Quality	Freshwater: 1.8	North Car. Admin. Code tit. 15A, § 02B.0211. Fresh Surface Water Quality Standards for Class C Waters. Effective July 24, 2018.
SAM	Brazil	Federal Criteria – Brazilian National Environmental Council (CONAMA)	Freshwater: 1.4 Marine/Brackish: 1.4	CONAMA Resolution 357, 2005.

Notes:

* = Please note that the freshwater Quebec criterion is qualified as provisional and for low hardness (<120 mg/L calcite [CaCO₃]).

mg/L = milligrams per litre

NAM = North America

SAM = South America

WQG = Water quality guideline

3.3.1 North American Surface Water Fluoride Aquatic Life Criteria Review

3.3.1.1 Canada

Canadian surface water quality guidance for the protection of aquatic life criteria exist as interim guidance put forth by the CCME and as provincial guidance in British Columbia and Quebec. Discussion of the respective surface water criteria is provided below.

The CCME developed interim freshwater guidance for the protection of aquatic life in 2002 with a guideline value of 0.12 mg/L fluoride. At the time of its derivation, insufficient toxicological information existed to derive freshwater guidelines for the protection of aquatic life in Canada (CCME, 2002) based on the methodology to derive Canadian Water Quality Guidelines (CCME, 2007). The interim guidelines include a thorough review of toxicity literature and discussion of exposure and toxicity-modifying factors (ETMFs). Acute (less than 144-h) toxicity information was only available for nine organisms across three taxonomic groups. Chronic (greater than 7 days) information was only available for four organisms across two taxonomic groups.

In the absence of sufficient toxicity information at the time of review, the most sensitive 50 percent lethal concentration (LC₅₀) from an acute (144-h) fluoride toxicity test for the freshwater invertebrate *Hydropsyche bronta* was selected as the critical value for the derivation of the interim criteria. Since the toxicity test for *H. bronta* conducted by Camargo et al (1992) was for an acute duration and lethal endpoint, the critical value was divided by an assessment factor of 100 to derive the interim guideline value of 120 µg/L fluoride. No marine guideline value was recommended at the time of publication. Based on the review discussed in **Section 3**, the interim freshwater guideline value is less than the median surface water fluoride concentration in NAM.

The British Columbia Ministry of the Environment (2011) provide both fresh and marine water aquatic life criteria for fluoride. Freshwater criteria for the protection of aquatic life is considered



tentative and has two components. If hardness is less than or equal to 10 mg/L calcite (CaCO_3), then the total fluoride in waters shall not exceed 0.4 mg/L. If hardness is greater than 10 mg/L CaCO_3 , the water hardness concentration should be able to predict specific concentrations in which fluoride would cause an LC_{50} effect. This is based on work described in Angelovic et al., (1961a and 1962b), anon. (1973), and Pimental and Bulkley, (1983). The hardness-specific short-term acute concentration is then multiplied by a factor 0.01 to provide a conservative estimate of chronic levels of protection.

Marine criteria for fluoride in British Columbia appear to be based on background concentrations; however, no clarification is provided in the guidance to establish the specific source of this information as its origin was from an anonymous publication by the USEPA. The potential for effects level exposure conditions to exist at concentrations comparable to marine background concentrations is not an appropriate representation of effective risk-based decision making and should be treated with caution.

Quebec has a provisional acute and chronic freshwater criteria for waters with low hardness containing less than or equal to 120 mg/L CaCO_3 (*Service d'Expertise en Evaluation des Rejets Toxiques* [SERT], 1989). The acute criteria are 4.0 mg/L fluoride and the chronic effect value is 0.2 mg/L. Acute toxicity criteria were established using LC_{50} or EC_{50} for seven freshwater species found in NAM. The species used include the stickleback (*Gasterosteidae*), fathead minnow (*Pimephales promelas*), bluegill (*Lepomis macrochirus*), *Philodina* sp. (rotifer), *Ceriodaphnia affinis*, *Daphnia magna*, and trout (species unspecified). The ranked sensitivity of the acute toxicity tests was used to obtain a final acute value (FAV) and subsequently acute toxicity criterion by dividing the FAV by 2. Since no acute-to-chronic ratio (ACR) was available, the chronic value was obtained by dividing the FAV by 45. The application of generic ratios for both acute and chronic toxicity values introduces uncertainties into provisional criteria.

The marine criteria for Quebec have been sourced from British Columbia (Warrington, 1990), which based its guidance value on an anonymous USEPA publication from the 1970s discussed above.

In summary, the current available aquatic life criteria in Canada are based largely on toxicity information that is over 40 years old and applies assessment factors or generic ACRs to determine appropriate benchmarks. Although the values that exist are noted to be provisional, they have been widely accepted and leveraged for planning and regulatory purposes. A more thorough review of the existing toxicity literature is needed to determine if guidelines can be revised in accordance with the CCME methodologies.

3.3.1.2 United States

Surface water quality fluoride guidance for the protection of aquatic life is limited in the United States. State-specific guidance exists in Florida, Illinois, Indiana, Michigan, Minnesota, New York and North Carolina. No formal federal guidance is available for the protection of fresh or marine aquatic life from fluoride. Common themes and the approach taken in the derivation of the criteria are discussed below.

Guidance in Minnesota and Florida is similar in that the specific basis of the identified aquatic life protection criteria is not provided. In Minnesota, the criteria of 2.0 and 4.0 correspond to the SMCL and MCL values; however, these criteria are deemed to be protective of “cold water aquatic life and habitat, also protected for drinking water” and “cool and warm water aquatic life and habitat, also protected for drinking water.” The use of drinking water criteria for aquatic life protection does not



align the appropriate receptors with the guideline value. In Florida, given the wide range of aquatic habitats present, the Rule 62 regulations specify criteria to determined water classes. Fluoride criteria for the protection of aquatic life are linked to fish harvesting or propagation for fresh and marine waters (Class III), which are 10 and 5 mg/L fluoride, respectively. The specific assumptions contributing to the derivation of these values is not provided. It should be noted that Florida has a number of phosphate mines for fertilizer production and fluoride concentrations can range widely as a result of the natural and anthropogenically sourced fluoride (PBS&J, 2007).

Illinois, Michigan, and New York have hardness-specific fluoride criteria. These approaches are among the few examples of using criteria that is consistent with site-specific biogeochemical parameters known to affect the toxicity of fluoride in freshwater. Criteria were predominately based on relationships between reduced acute toxicity and increasing freshwater hardness. Limits for chronic endpoints were achieved through the conversion using generic ACRs. A brief discussion of the sensitivity of each equation to protect aquatic life across varying degrees of hardness is provided in **Figure 3-1**.

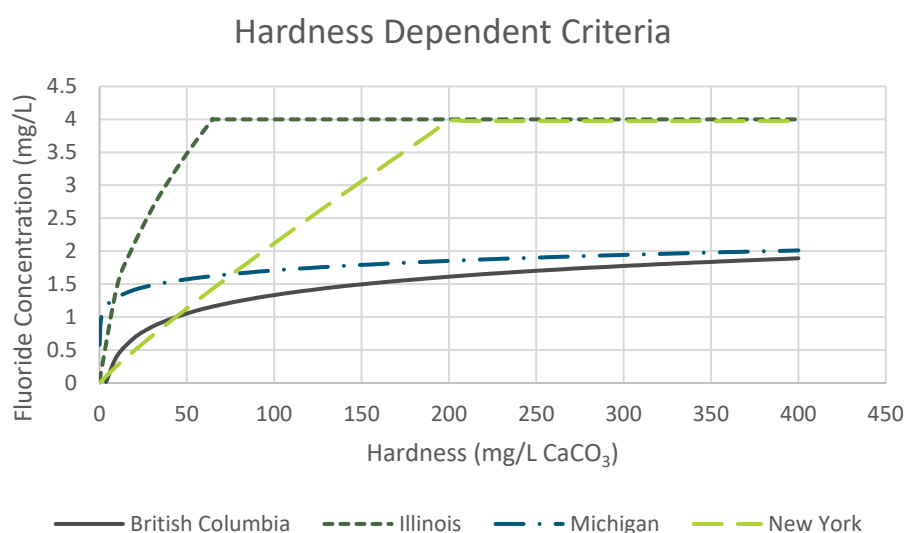


Figure 3-1 Hardness dependent chronic aquatic life criteria

All three of the hardness-specific criteria developed by states within the United States are decades old. In comparison to the British Columbia criteria, the United States hardness-specific criteria are less conservative. The hardness-specific relationship developed for New York has the most robust supporting documentation and was developed in 1984. The criteria are based on the relationship between acute fluoride LC₅₀ toxicity values in rainbow trout and corresponding hardness data obtained from four literature sources. The modelled fit between the relationship was used to develop an acute predictive equation. Through the multiplication of an application or assessment factor (AF) of 0.02, the acute criterion for fluoride could be pro-rated to address long-term, chronic effects. Chronic criteria are not to exceed 4.0 mg/L regardless of hardness in surface waters.

The Illinois chronic hardness-specific relationship has a similar limit to the chronic value of 4.0 mg/L, but it is more sensitive to variations in hardness below approximately 60 mg/L CaCO₃. Limited details are provided on the derivation of the hardness-specific relationship. The acute and chronic relationships in Illinois are applied to all waters of the Lake Michigan basin. Additionally, chronic aquatic life standards (CS) must not be exceeded outside of waters in which mixing is allowed pursuant to Sections 302.102 and 302.530 by the arithmetic average of at least four consecutive



samples collected over at least four days. The samples used to demonstrate compliance with the CS or human health standard (HHS) must be collected in a manner that assures an average representation of the sampling period. The hardness-specific aquatic life criteria for the Lake Michigan basin is complemented by a set threshold for the open waters of Lake Michigan, which cannot exceed 1.4 mg/L. Other criteria are provided for specific waterbodies, but they are of similarly derived or less conservative in nature.

Michigan hardness-specific relationships have the strongest alignment with the British Columbia guidance. However, details pertaining to the derivation of the guidance have not been identified in the Michigan hardness-specific relationship.

Indiana aquatic life criteria are variable depending on the water body and are as low as 1 mg/L within the Ohio and Wabash Rivers. All other surface waters have criteria of 2.0 mg/L. The basis of the criteria put forth is unclear. Criteria apply to waters outside of the mixing zone, which has implications for aluminium production facilities that are present along the Ohio River.

North Carolina has freshwater aquatic life criteria of 1.8 mg/L. In 1987, an assessment of fluoride toxicity was conducted by Shealy Environmental Services, Inc. to determine whether updates to the existing aquatic life criteria were needed. Five acute tests and one chronic test were conducted to assess the toxicity of fluoride to aquatic organisms in low hardness and low-temperature conditions. Toxicity tests included rainbow trout, water flea, snail, mayfly and amphipod species. Additional toxicity data was sourced from the primary literature. The fluoride FAV was an estimated 0.53 mg/L. Given complications in chronic toxicity testing, no chronic criteria were able to be calculated. As a result, the conclusion was reached by Shealy Environmental Services that the previous guideline was suitably protective.

Other states with active/inactive aluminium production facilities include Oregon, Washington, Montana, South Carolina, Texas, Tennessee, Missouri, Kentucky, and West Virginia. No available aquatic life criteria exist in these states. This may promote a disconnect between the management of operational facilities versus inactive facilities through National Pollutant Discharge Elimination System (NPDES) versus other regulatory frameworks such as the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA; herein “Superfund”). Additional discussion of regulatory frameworks in NAM is discussed in **Section 3.4**.

3.3.2 European Surface Water Fluoride Aquatic Life Criteria Review

3.3.2.1 European Commission

The European Commission’s Scientific Committee on Health and Environmental Risks (SCHER) conducted a critical review of any new evidence on the hazard profile, health effects, and human exposure to fluoride and the fluoridating agents of drinking water (SCHER, 2011). As part of this review, aquatic effects from the primary literature were reviewed and recommendations made as to potentially acceptable limits for fluoride in surface waters.

This work relied heavily on the review conducted by Camargo (2003), which found that net-spinning caddisfly larvae and upstream-migrating adult salmons, living in soft waters with low ionic content, were found to be the most sensitive organisms, affected by fluoride concentrations higher than 500 µg/L. The assessment assumed that concentrations lower than 500 µg/L are safe for these extremely sensitive organisms, and therefore appropriate for use for the protection of aquatic ecosystems. This assessment also included the calculation of probable no effects concentration (PNEC), which was



estimated to be 290 µg/L. These limits are in line with regional background conditions of certain regions of Europe and should be examined carefully in the context of appropriate values for the protection of aquatic life.

Based on the review of available public information sources and stakeholder provided information, other European country-specific criteria for the protection of aquatic life from fluoride exposure have not been identified.

3.3.3 Other Region Surface Water Fluoride Aquatic Life Criteria Review

Aquatic life-specific criteria beyond the values developed in NAM and EUR are limited for other regions. Brazil and its states have aquatic life criteria for fresh and marine waters developed by the National Environment Council (CONAMA). The CONAMA Resolution 357/05 stipulates that freshwater and brackish surface water both have aquatic life criteria of 1.4 mg/L fluoride. The rationale for the selected criteria is not provided.

Australia/New Zealand (ANZ) Water Quality Guidelines are in the process of being systematically revised. Where surface water guidelines of low quality exist or where surface water quality guidelines are absent, such as the case with fluoride, a prescriptive approach to deriving aquatic life protection criteria is taken. This approach is based on guidance developed by Warne et al. (2018) and leverages species sensitivity distributions (SSD) chronic no observed effects concentration (NOECs), 10 percent effects concentrations (EC₁₀) or PNECs affecting growth, reproduction or mortality to determine acceptable percentages of species protection that correspond to beneficial land and water uses. The appropriate percentages of species protection are typically established through local State Environmental Protection Policy (SEPP) guidance.

3.4 Factors Influencing the Regulation of Surface Water Fluoride

This section focuses on key trends observed through the review of permit requirements at aluminium production facilities across the assessment area. To provide context, a brief overview of regulatory frameworks, where established, are provided.

3.4.1 Regulatory Frameworks Overview

3.4.1.1 NAM

General discussion on the regulatory frameworks influencing the release of process-related water or stormwater from aluminium production facilities to downgradient water bodies is discussed below for Canada and the United States.

Some water-related legislation exists in Canada at the provincial and federal level. The management of fisheries, shipping and navigation typically comes under the purview of the federal government, whereas management of water resources within provincial borders are typically conducted by individual provinces.² The CCME serves as an inter-governmental organization with members across federal-provincial and territorial governments. The CCME has various task groups that help address Canada-wide standards, such as the interim guidance for the protection of aquatic life. Although CCME guidance serves as useful recommendations given its transdisciplinary nature, ultimately the provincial governments have the authority to manage surface waters. The CCME has no authority to

² https://lop.parl.ca/sites/PublicWebsite/default/en_CA/ResearchPublications/201386E#a6



implement or enforce legislation. Specific policies related to the regulation of surface water releases in British Columbia and Quebec are discussed below.

Apart from the aquatic life criteria described above, the Province of British Columbia Ministry of Environment and Climate Change Strategy regulates waste discharges for aluminium smelters under the Environmental Management Act (EMA). Waste authorizations are required to discharge or release wastes to the air, water and land. Schedule 1 Waste Discharge Regulations (WDRs) govern industries and activities that are unique, complex or have variable technology. Fluoride releases from aluminium production facilities can be regulated under Schedule 1 WDRs. Fluoride releases under the WDR schedules are typically expressed as a concentration (mass per volume), with designated maximum and average attainment criteria.

The Quebec *Ministère de l'Environnement et Lutte contre les Changements Climatiques* (MELCC) or the Ministry of Sustainable Development, Environment, and Fight Against Climate Change provide oversight and regulation of industrial wastewater discharges as well as surface water protection. The ministry has developed an approach to determining environmental discharge objectives (EDOs) based on surface water quality criteria, hydrodynamic conditions and uses of the environment. In addition, the EDOs are informed by past operational data from a facility in efforts to reduce limits under future operating conditions. The EDO approach enables the determination of concentrations and loads of constituents within effluent that can be released into the aquatic environment whilst attaining quality. The EDOs help address existing or planned discharges and environmental release objectives (OERs) are specific values determined from the characteristics of the receiving environment to maintain desired beneficial uses, if required. The EDO approach sets mass per unit time regulatory limits for constituents, such as fluoride. Released masses are pro-rated based on the capacity of a given aluminium production facility.

In the United States, the CWA is a primary regulatory framework governing industrial water management. Originally published in 1972, it is a United States federal law that establishes the basic structure for regulating both the discharge of pollutants into United States waters, and the quality standards for surface waters.³ Under this law, the USEPA implemented the NPDES permit program, which regulates discharges from point sources into surface waters. Regulations vary by discharge type; both industrial stormwater discharges and industrial process water discharges are considered point sources and are administered by the NPDES program. Most states in the United States have obtained USEPA approval to issue and administer their own NPDES permits; where this is not the case, USEPA Regions are responsible for issuing permits.⁴

NPDES permits include effluent limits, or acceptable levels of a pollutant or pollutant parameters which may be discharged, as well as monitoring and reporting requirements. Effluent limits are developed with consideration given to the technology available to control the pollutants (technology-based effluent limitations, TBELs) and existing water quality standards protective of receiving water bodies (water quality-based effluent limitations, WQBELs).

Federal regulations allow states to adopt additional policies, with USEPA approval, into their water quality standards, which may affect how those standards are applied (40 Code of Federal Regulations [CFR] § 131.13). For example, general policies authorizing mixing zones may be implemented at the state level. Per USEPA guidance, a mixing zone is defined as “a limited area or volume of water where initial dilution of a discharge takes place and where certain numeric water

³ <https://www.epa.gov/laws-regulations/summary-clean-water-act>

⁴ <https://www.epa.gov/npdes/npdes-program-authorizations>



quality criteria may be exceeded.”⁵ In addition to state-level mixing zone policies, individual, site-specific mixing zones may be defined through the NPDES permitting process. Individual mixing zones are used to establish appropriate WQBELs for a particular NPDES-permitted facility, based on site-specific conditions.

3.4.1.2 EUR

The emissions from industrial installations in Europe are regulated under the framework of the Industrial Emissions Directive (Directive 2010/75/EU)⁶. This Directive by its nature needs to be translated into legislation at Member States level (i.e., every country produces a version of the directive in their own language for its application at the national level).

The key of the Industrial Emissions Directive (IED) is the establishment of documents gathering information on industrial practices at the sector level as featured in its Annex I. Thanks to having these documents which are specific to industrial activities – for the case of aluminium it would be the report known as Best Available Techniques (BAT) Reference Document for the Non-Ferrous Metals Industries⁷ – the industry participates in building a repository of industrial and process-related information (these are called the Reference documents or BAT reference documents [BREFs]⁸) and this process results in guidelines that will dictate how to comply with emissions of pollutants. The agreed-upon values for these pollutant emissions will appear in the environmental permit for the installation and the installation abides by them.

In order to enforce unanimously the pollutant emissions from an industrial activity across all Member States, the European Authorities (i.e., the European Commission) issued the BAT for the Non-Ferrous metals industry - which is publicly available and is in force since 2016 (Table 3-3). The BATs concerning fluoride emissions are BAT 60, BAT 61 and BAT 67.

Consequently, facilities operating under an environmental permit in Europe need to comply with the following associated emissions to air (AEL) limit values for fluoride (**Table 3-3**):

Table 3-3 Commission Implementing Decision (EU) 2016/1032 of 13 June 2016 establishing best available techniques (BAT) conclusions, under Directive 2010/75/EU (excerpt)

BAT number	Scope of BAT	Parameter	BAT-AEL (mg/Nm ³)
BAT 60	Baking plant in an anode production plant integrated with a primary aluminium smelter	HF	0.3-0.5 (as daily average)
		Total fluorides	≤ 0.8 (as an average over the sampling period)
BAT 61	Baking plant in a stand-alone anode production plant	HF	≤ 3 (as daily average)

⁵ <https://www.epa.gov/sites/production/files/2014-09/documents/handbook-chapter5.pdf>

Accessed: August 7, 2020

⁶ <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32010L0075&from=EN>

Accessed: September 19, 2020

⁷ https://eippcb.jrc.ec.europa.eu/sites/default/files/2020-01/JRC107041_NFM_bref2017.pdf

Accessed: September 19, 2020

⁸ <https://eippcb.jrc.ec.europa.eu/reference> Accessed: September 19, 2020



BAT number	Scope of BAT	Parameter	BAT-AEL (mg/Nm ³)
BAT 67	Total emissions of dust and fluoride to air from the electrolysis house (collected from the electrolytic cells and roof vents)	BAT-AELs for existing plants (kg/t Al)	≤ 0.6
		BAT-AELs for new plants (kg/t Al)	≤ 0.35

Notes:

AEL = associated emission level

Al = aluminium

BAT = best available technique

EU = European Union

HF = hydrofluoric acid

kg = kilogram

mg/Nm³ = milligrams per cubic metre at normal conditions

t = ton

To date, there is no detailed information at the European Union (EU) level instructing industry operators on fluoride compliance in emissions to water. It is expected that policy developments in Europe under the umbrella of the Green Deal, such as the Zero Pollution Action plan, may see increased regulatory pressure to develop a higher level of monitoring in substances to water beyond the existing quality controls.

Broader directives within the EU do not establish formalized limits for fluoride releases. European guidance on the release of fluoride from industrial facilities is variable across countries. Therefore, the discussion included herein is focused on general discussion on EU directives and information provided by stakeholders on BATs for managing fluoride releases to the aquatic environment.

Proposal for a Directive of the European Parliament and of the Council amending Directives (2000/60/EC and 2008/105/EC) as regard[ing] priority substances in the field of water policy, COM/2011/0876 final - 2011/0429, does not list fluoride as a priority substance. Directive 2006/11/EC of the European Parliament and of the Council of 15 February 2006 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (Codified version). Fluoride is listed as a List II compound with no emission limits defined.

Further to this, some member states such as France issue recommendations to industry when managing surface water fluoride releases using the French Article 32 Order of 2 February 1998 relating to emissions of all kinds from installations classified for the protection of the environment. Details specific to managing aluminium production facilities are provided below.

- The general water limit of fluoride for any installation for which a permit is required (for example secondary aluminium production) is F less than 15 mg/L if the discharge is more than 150 grams per day (g/day).
- The general water limit for aluminium smelter installation is F less than 15 mg/L or F less than 25 mg/L in the case of mixing of these effluents with rainwater (in particular from leaching of roofs).

In addition, the general water-specific limit for surface treatment installation is F less than 15 mg/L if the direct release with discharges exceeds 30 g/day.



3.4.1.3 Other Regions

In CNA the water *Pollutant Emission Standards for the Aluminium Industry* are governed by the GB 2546-2010 guidance published in 2010 and prepared by the General Administration of Quality, Supervision, Inspection and Quarantine (GB 2546-2010). The GB 2546-2010 stipulate fluoride emission standards for direct and indirect emissions of 5.0 mg/L. Direct emissions refer to the act of discharge directly into the environment and indirect emissions refer to the discharge by sewage units into public sewage treatment systems. More stringent discharge limits of 2.0 mg/L fluoride may be applied for sensitive receiving water bodies at the discretion of provincial government based on local environmental conditions. The precise basis of these criteria is unknown although it may be derived from the *Environmental Quality Standards for Surface Water* (GB 3838-2002), which set criteria for drinking water and drinking water sources of 1.0 mg/L.

In the United Arab Emirates, the fluoride suggested limit in treated industrial wastewater at the point of discharge into the sea is 20 mg/L.

3.4.2 *Considerations for Permitted Water Releases*

The review of regulatory frameworks and an assessment of discharge requirements specific to aluminium production facilities across the IAI focus regions informed this assessment of considerations for permitted water releases. **Figure 3-2** provides a conceptual representation of key factors that influence the conditions governing the release of surface water from a hypothetical aluminium production facility.

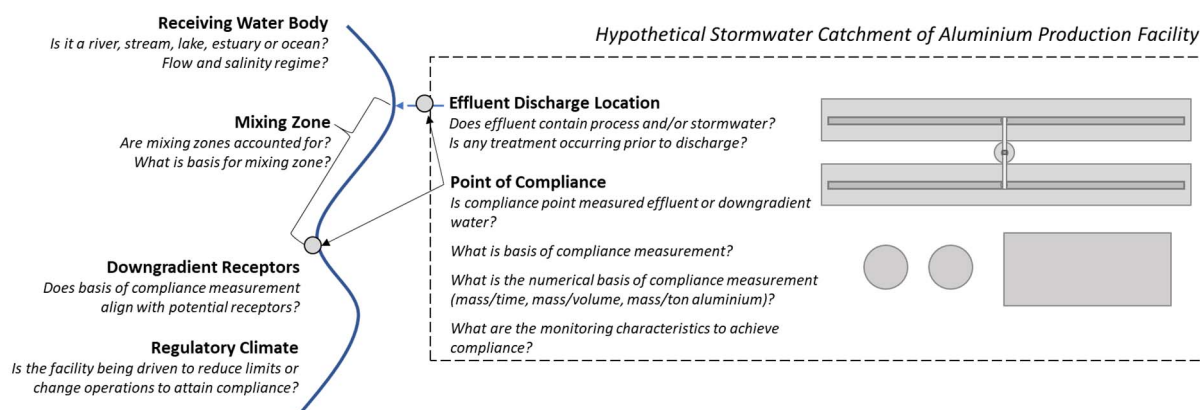


Figure 3-2 Conceptual schematic of factors influencing surface water permit compliance

3.4.2.1 Water Use at Aluminium Production Facilities

As discussed in **Section 1.4**, water use at aluminium production facilities is variable and largely dependent on the use of wet scrubber systems. Aluminium reduction does not require water – in fact, it is extremely hazardous to the smelting process. However, freshwater is used during several phases of production at relatively low quantities. Globally, freshwater input is approximately 1 m³, 6 m³ and 2 m³ per ton of aluminium for anode production, electrolysis and casting, respectively (IAI, 2017). However, seawater use is much higher in the electrolysis process, when available, because it can be beneficial in wet scrubber systems. The high ionic characteristics of seawater make it favourable to remove sulphur dioxide as well as other constituents, such as fluoride. Globally, approximately 39 m³ of seawater is used per tonne of aluminium produced.

Stormwater can also be a major component of the water released from aluminium production facilities in temperate regions with large precipitation volumes. Aluminium production facilities can easily occupy up to 50 hectares (ha) of impervious surfaces. During a 1-centimetre (cm) precipitation event, this area would generate roughly 5,000 m³ of stormwater runoff. Depending on the precipitation regime where the aluminium production facility is located, annual stormwater runoff may be orders of magnitude greater than process-related discharge. The regulation of stormwater runoff varies by region and may not be relevant in all regions where aluminium is produced.

Another consideration of the management of fluoride releases is the hydrological changes that may occur at a facility if it becomes idle, inactive or altogether removed. Legacy facilities or reduced capacity facilities may not have sufficient water volume to provide discharges to downgradient environments. Additionally, the removal of impervious surfaces may change the interaction between runoff volumes to the receiving environment and lead to greater infiltration.

A comprehensive understanding of process-related and stormwater dynamics is needed to effectively manage permitted water releases.

3.4.2.2 Characteristics of the Receiving Water Body Water

Understanding the characteristics of the receiving water body downgradient of a facility is as important as knowledge of site-specific hydrology. The receiving waterbody type, flow regime and water chemistry are all important.



Whether the permitted effluent is discharging into a river, stream, lake, estuary or open ocean are all important considerations. The hydrology and setting of the receiving water influence the rate and extent to which discharged waters will mix and attenuate. In addition, the water body type influences the aquatic receptor community that may be present and have complete exposure pathways.

The flow regime of the receiving water body is also important. Hydrologically closed systems, such as lakes or reservoirs with high surface water residence times pose the greatest challenge to managing aquatic fluoride releases. A sensitivity analysis of end-member mixing is provided in **Section 2.6.2**, which highlights how the magnitude of surface water and fluoride flux within a large river system from natural processes is difficult to modify. In addition, this section provides details for the important contrast between fresh and marine water chemistry.

3.4.2.3 Characteristics of the Compliance Point

The third consideration is the characteristics of the compliance point. This section discusses the technical basis of the compliance measurements, the location of the compliance measurement, its numerical basis and monitoring requirements.

Several examples of criteria are provided in **Section 3.2** and **Section 3.3**. The technical basis of the compliance measurement describes the rationale that contributes to the value in which the surface water or effluent must ultimately be below to attain permit compliance. For instance, a permit stipulates that fluoride concentration at an outfall cannot exceed a maximum concentration of 10 mg/L. The technical basis could be that the limit was established by taking known characteristics of the mixing zone (e.g., dilution by 5 times will occur in the chronic mixing zone) and a known aquatic life criteria of 2mg/L to establish the permit limit. The risk-based criteria and the nature of the mixing zone are the primary parameters influencing the compliance limit.

The numerical basis governing compliance of releases is also important to consider. Mass per volume (e.g., mg/L), mass per time (e.g., kg/month), or mass per ton of aluminium produced are among common metrics for compliance monitoring. Mass per time and mass per aluminium produced are both fixed points of attainment, which the total released mass cannot exceed. This approach is more rigid than concentration-based metrics that are subject to fluctuations in the volume of water. Monitoring characteristics contribute to each of these approaches. The frequency of sampling and statistical treatment of the analytical concentration detected all factor into the numerical basis.

3.5 Case Studies of Contrasting Permitting Conditions

A case study of two aluminium production facilities that discharge into freshwater is discussed below. **Figure 3-3** illustrates the contrasting characteristics of the two sites. Site A discharges into a freshwater river, whereas Site B discharges into a freshwater river that flows into a hydrologically closed freshwater lake system. The residence time in the receiving environment at Site B is much greater than Site A.

The point of compliance at Site A is situated downgradient of the facility where the Site B compliance point is at the effluent discharge location. The technical basis of compliance measurement is both chronic aquatic life criteria; however, the criteria at Site B is almost 10 times greater than Site A. The numerical approach to regulation at Site A is based on mass loading per unit time, which has been pro-rated based on aluminium production. Site B differs in that the



concentration criteria must maintain both a monthly average and daily maximum concentration to be in compliance. Monitoring requirements in Site A are continuous, with measurements of effluent and river discharge and fluoride, whereas Site B is comprised of a monthly composite measurement.

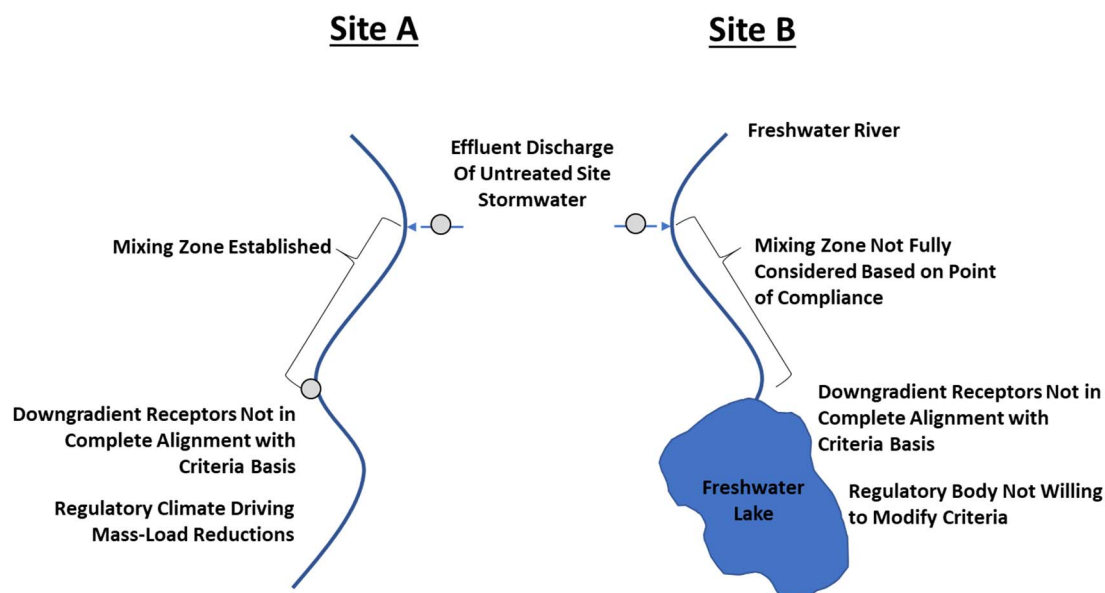


Figure 3-3 Contrasting regulatory frameworks and settings for two aluminium production sites

A dynamic stormwater management system is in place at Site A to help capture runoff and carefully control the timing of effluent releases to coincide with periods of least fluoride concentration in the receiving environment. The novel approach to capture and store stormwater minimizes water demands at Site A and enables the attainment of lower criteria concentrations at the downgradient point of compliance.

However, it is important to note that these sites are similar in the fact that the chronic aquatic life criteria informing the surface water fluoride releases are deficient and do not align with the environments where they are being used. Both aquatic life criteria rely on arbitrary ACRs and antiquated toxicity data. Taxa used to inform the acute tests were endemic to the region, but not necessarily to the habitats present within adjacent water bodies. Therefore, more comprehensive understanding of the fluoride aquatic ecotoxicity literature and localized habitat conditions are needed.

3.6 Summary of Review, Data Gaps and Recommendations

In summary, a high degree of contrast exists between the derivation and assumptions that contribute to existing drinking water quality guidelines, aquatic life criteria and the criteria established to manage the release of constituents to surface water.

Drinking water quality guidelines, particularly MACs, are largely informed by conditions that may result in increased risk for moderate dental fluorosis, whereas the United States MCLs are based on increased potential for more pronounced effects, such as the long-term risk for skeletal fluorosis. Among the values identified for the protection of drinking water, the concentration of 1.5 mg/L of fluoride had the greatest incidence of occurrence. Nevertheless, the existing guidelines all carry with them some level of conservatism based on large doses from ingestion of food or other non-drinking



water sources. In sources of drinking water these criteria are well suited to adequately protect the identified receptor populations. However, drinking water criteria are not always relevant points of comparison in surface waters and care should be taken to align the likely receptors most appropriately to the overarching management objective.

The aquatic life criteria information is either extremely antiquated or a paucity of information exists. In both fresh and marine waters, limited chronic toxicity information supports the derivation of guidelines. Rather, acute toxicity testing with somewhat arbitrary ACRs is routinely used to inform chronic criteria. In addition, there are multiple instances where freshwater criteria are at or below background concentrations of fluoride in surface water. **Section 2** describes the background conditions in greater detail. Hardness-specific guideline values in freshwater present the most technically robust approaches; however, the toxicological data supporting these studies are limited and dated. Marine water criteria rely heavily on background concentrations and a paucity of toxicological data was identified. Based on these conclusions and identified data gaps, **Section 4** provides a more up-to-date literature review of aquatic fluoride toxicity data and determines if sufficient data exists to establish more robust aquatic life criteria. Approaches, including the use of hardness-specific guidelines, are considered in accordance with the existing guideline derivation frameworks.

The review of factors influencing the regulation of surface water fluoride releases, as well as the case studies highlights the need for systematic understanding of the components contributing to effluent permits. Through the comparison of contrasting sites, it is apparent that certain geographic settings may be more favourable to the management of fluoride merely based on hydrological or geochemical characteristics of the receiving water body. Similarly, as was presented in the freshwater case study in Site A discussed above, the setting of facilities could be leveraged to maximize the resources available to manage surface water releases. Stormwater infrastructure systems may be expanded in temperate regions with high rainfall to provide a source of low fluoride, freshwater to help mitigate and dynamically manage effluent releases containing fluoride. More research is needed into alternative stormwater management approaches to best inform development at new aluminium production facilities or retrofit existing facilities facing challenges.



4 Fluoride Aquatic Ecotoxicity Literature Review

4.1 Introduction

A comprehensive understanding of aquatic ecotoxicity literature is needed to determine appropriate limits for managing surface water fluoride in the freshwater and marine environments. The preceding reviews have demonstrated that a high degree of variability exists in background conditions influencing surface water fluoride concentrations, and fluoride aquatic life guidance is often uncertain and variable across regulatory frameworks. In the context of the previous sections, the objectives of this aquatic fluoride ecotoxicity review are to 1) summarize the available peer-reviewed literature on toxicity to freshwater and marine organisms, 2) understand how certain factors, such as physical or chemical water quality conditions can ameliorate or modify the toxicity of fluoride, and 3) develop more robust fluoride aquatic life criteria using approved guidance on criteria derivation within the study focus area. In the absence of sufficient data to develop more robust criteria using approved approaches, the process itself will be used to identify information gaps or uncertainties where additional information is needed to derive more technically sound guideline values.

This aquatic ecotoxicity literature review will be organized in alignment with the recently promulgated United States *Final Aquatic Life Ambient Water Quality Criteria for Alumin[i]um* (USEPA, 2018). This approach has received widespread support from regulators within NAM and is easily transferable to other regulatory frameworks that rely upon SSD approaches. The review will include Problem Formulation and Effects Analyses sub-sections. The Problem Formulation details important background information on fluoride toxicity including, mode of action of toxicity, an ecological exposure model and specific assessment and measurements endpoints. The Problem Formulation also details the analysis plan used to derive preliminary criteria from acute or chronic toxicity data. The Effects Analysis summarizes available data for freshwater and marine environment for flora and fauna and describes potential effects of fluoride for acute and chronic tests in the freshwater and marine environment. The Effects Analysis also describes findings and discussion around preliminary criteria derived for acute and chronic freshwater and marine toxicity data. The availability of acceptable studies on fluoride toxicity will be particularly focused on leveraging multiple linear regression (MLR) approaches to normalize toxicity data to specific water quality conditions. In the absence of sufficient data to use MLR to normalize toxicity data to known water quality conditions, SSDs on unnormalized toxicity data are considered.

Background regulatory documents on water quality criteria derivation approach considered in this review include:

- USEPA – *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses* (Stephen et al., 1985).
- CCME. 2003. Canadian water quality guidelines for the protection of aquatic life: Guidance on the Site-Specific Application of Water Quality Guidelines in Canada: Procedures for Deriving Numerical Water Quality Objectives. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
- European Commission. 2018. Technical guidance for deriving environmental quality standards. Guidance Document No. 27.
- Warne, M., Batley, G., van Dam, R., Chapman, J., Fox, D., Hickey, C. and Stauber, J. 2018. Revised Method for Deriving Australian and New Zealand Water Quality Guideline Values for Toxicants – update of 2015 version. Prepared for the revision of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Governments and Australian state and territory governments, Canberra, 48 pp.



Across regions, regulatory bodies use the same building blocks of information to derive criteria. Although the specific details of the process may vary slightly the approach described below is applicable to most regions within the scope of this review. Inherently, the intent of guideline derivation is to reduce uncertainties. As a result, many approaches rely on highly conservative assumptions in the absence of information as discussed in detail in **Section 3**. Some of the specific toxicological or methodological constraints that contributed to the conservatism are explored.

4.1.1 Key Findings

The key findings provided below are intended to succinctly address the objectives and core questions of the review in the form of a question and answer format. Questions are presented in italicized text and the key findings are provided in normal text.

- *Does the detailed review of available peer-reviewed literature on toxicity to freshwater and marine organisms provide any new information that could support the development of more robust fluoride guidance?*
Generally, increased fluoride concentration, exposure time and water temperature enhance the toxic effects of fluoride on aquatic organisms. Above certain concentrations, water quality constituents, such as chloride and hardness, can ameliorate the toxic effects fluoride exerts on organisms. Many of the existing aquatic life guidelines have been derived several decades ago. Since the time of derivation, more research exists to support the ability to predict fluoride toxicity based on water quality conditions.
- *How do certain factors, such as physical or chemical water quality conditions, ameliorate or modify the toxicity of fluoride? Particularly, can the recently promulgated USEPA aluminium guidance that uses MLR approaches be used as a model for the development of more robust fluoride aquatic life criteria?*
Several studies have focused on the ameliorating effect of chloride and hardness on fluoride toxicity. However, these studies have relied on simple statistical approaches that examine one variable at a time. A metanalysis conducted as part of this review indicates that multiple water quality variables must be considered to predict fluoride toxicity. An MLR approach was employed to develop preliminary site-specific fluoride guidance. Expansion of this approach will ensure that the development of future aquatic life criteria appropriately considers site-specific water quality conditions.
- *Can more robust fluoride aquatic life criteria be derived using approved guidance on criteria derivation within the study focus area?*
Yes. This assessment successfully demonstrated that preliminary acute and chronic guidelines can be derived using approaches widely accepted by regulatory bodies across IAI regions. Preliminary chronic criteria ranged from 1.7 to 11.8 mg/L depending on the water quality conditions present. The **5- to 7-fold** increase in chronic criteria indicates that existing aquatic life guidelines are too conservative and more scientifically robust approaches need to be adopted.

4.2 Problem Formulation

This problem formulation section provides a strategic framework that will aid in the development of and/or identification of key data gaps that would need to be addressed to develop water quality criteria for fluoride. Fate and transport characteristics, as well as the distribution of fluoride from geogenic and anthropogenic sources, are discussed in detail in **Section 2**. A detailed review of



toxicological characteristics and factors affecting the toxicity of fluoride in the surface water environment are discussed herein. The synthesis of this information informs the development of a conceptual exposure model to best define the chemical properties that influence the toxicity of fluoride and endpoints for subsequent evaluation. The development of a sound ecological conceptual exposure model forms the foundation for assessments under multiple regulatory frameworks, including those that use predictive modelling to normalize toxicity data based on water quality conditions and those that leverage distribution fitting tools on unnormalized toxicity data to create species sensitivity distributions across all trophic levels.

The mode of action and toxicity of fluoride in the environment, conceptual exposure model, and analysis plan is provided in **Section 4.2.1**, **Section 4.2.2**, and **Section 4.2.3**, respectively.

4.2.1 Mode of Action and Toxicity

The mode of action and ecotoxicity of fluoride is discussed for aquatic and terrestrial receptors.

4.2.1.1 Aquatic Environment

Aquatic invertebrates and fish tend to take up fluoride directly from water, and, to a lesser extent, from the consumption of organisms that contain fluorides (Camargo, 2003). Fluorides can bioaccumulate within aquatic organisms, typically in exoskeletons for invertebrates and skeletal bones in fish. In aquatic flora, fluoride can accumulate in plant and root tissues. Similar to the discussion of biogeochemical factors controlling the fate and transport of fluoride in the aquatic environment discussed in **Section 2.3**, key factors are known to ameliorate or modify the toxicity of fluoride to aquatic flora and fauna. These factors are also discussed in detail.

The toxic action of fluoride is linked to the strong electronegative state of fluoride ions, which act as enzymatic poisons. Key enzymes, for which their activity can be compromised by the presence of fluoride ions, include phosphatase, hexokinases, enolase, succinic dehydrogenase, pyruvic oxidase and others (Camargo, 2003). The decreased enzymatic activity results in interruption of key metabolic processes, such as glycolysis and protein synthesis (Kessabi et al., 1984). The specific mechanism that causes the decoupling of metabolic processes due to enzymatic activity inhibition in aquatic flora and fauna is not fully understood.

In freshwaters, increased fluoride concentration, exposure time and water temperature enhance the toxic effects of fluoride on aquatic invertebrates (Camargo, 2003). Inorganic fluorides in a solution can be removed from the aquatic phase by precipitation in the presence of calcium carbonate, calcium phosphate, calcium fluoride and magnesium fluoride (Stumm and Morgan, 1996). Therefore, harder or more saline water tends to be less toxic to aquatic invertebrates. A review of available literature for freshwater acute and chronic effect endpoint data indicated that *Hyalomma azteca*, an amphipod, exhibits the greatest sensitivity to fluoride among the freshwater invertebrate species used for toxicological testing. The chronic 10 and 50 percent inhibition concentrations (IC₁₀ and IC₅₀) to growth were 1.8 and 4.1 mg F/L, respectively at a hardness of 90 mg/L CaCO₃ and chloride content of 2 mg Cl/L (Pearcy et al., 2015).

Increased fluoride concentration, exposure time and water temperature also increase the toxic effects of fluoride to fish (Camargo, 2003). However, increasing intraspecific fish size and increasing calcium and chloride concentrations in water tend to decrease the toxic effects of fluoride to fish. Based on recent work by Percy et al. (2015), it was noted that chloride concentration in surface water has a greater influence on the reduced toxicity of fluoride to freshwater organisms than



calcium carbonate. Chloride concentration in water reduces the toxic effects of fluoride to certain species; however, chloride does not mitigate toxic effects for all species. An evaluation of available literature for freshwater acute and chronic effect endpoint data indicated that *Oncorhynchus mykiss*, the rainbow trout, exhibits the greatest sensitivity to fluoride among the freshwater fish species used for toxicological testing. The chronic IC_{10} and IC_{50} to growth for *O. mykiss* were 6 mg/L and greater than 64.1 mg/L fluoride, respectively, at a hardness of 6 mg/L $CaCO_3$ and chloride content of 2 mg Cl/L (Pearcy et al., 2015). However, the sole consideration of chloride as an ameliorating factor does not account for the range of conditions that may present to ameliorate toxicity in natural systems. Additional discussion of possible mechanisms of action whereby water quality parameters influence toxicity is provided in the section below. Further assessment of the water quality conditions and acute toxicity testing of *H. azteca* and *C. mykiss* from Percy et al. (2015) are provided in **Section 4.2.3** to determine whether more robust statistical approaches can be used to predict toxicity ameliorating factors.

Depending upon concentration, exposure time, and species, fluoride can have inhibitory or enhancing effect on freshwater algal growth (Camargo, 2003). Like terrestrial plants, fluoride content in aquatic macrophyte tissue increases with increasing water concentration and exposure time. An evaluation of available literature for freshwater acute and chronic effect endpoint data for aquatic plants indicated that *Chlorella vulgaris*, a green algae, exhibits a sublethal and lethal response to fluoride exposure. The non-inhibitory concentration and lethal concentration in 50 percent of the test organisms (LC_{50}) were 66.5 and 380 mg/L fluoride, respectively, at a pH of 6.8 (Rai et al., 1998).

In marine waters, sublethal and lethal responses have been observed in aquatic organisms at greater fluoride exposure concentrations than in freshwater aquatic organisms. However, fewer studies using carefully controlled toxicity testing exist for marine waters and most marine toxicity studies are several decades old. Ladhar-Chaabouni et al. (2019) studied the effects of fluoride on cultured haemocytes (blood cells) from the marine gastropod *Haliotis tuberculata*. Acute studies (24-h) were conducted to assess cell viability, across a concentration gradient of fluoride from 0.9 to 566 mg/L. The marine snail haemocytes exhibited no acute effects on exposure concentrations up to 113 mg/L fluoride.

Other chronic (21-day) testing studies on marine invertebrates by Nell and Livanos (1988) indicated juvenile oysters, called spat, exhibited a 20 percent reduction in growth at exposure concentrations of 30.7 mg/L. The effect concentration was influenced by the salinity of the water, which ranged from 15 to 45 ppt. Growth conditions appeared to be optimized at 25 and 35 ppt salinity, regardless of fluoride treatments. Detailed examination of the effect of water quality characteristics on the toxicity of fluoride to marine invertebrates is not well documented. Similarly, the mode of toxicity is less understood given the natural adaptations of marine organisms to regulate saline water.

The toxicity of fluoride to marine fish has not been studied to a comparable extent as marine invertebrates and algae. Hemens and Warwick (1972) evaluated the effect of fluoride on estuarine organisms. Acute (96-h) testing was conducted on three species of fish (*Mugil cephalus*, *Ambassis safgha*, and *Therapon jarbua*). Acute exposure to fluoride concentrations up to 100 mg/L did not show lethal effects. Long-term mesocosm studies also conducted by Hemens and Warwick (1972) indicated non-lethal effects of fluoride at concentrations above 50 mg/L in *Mugil cephalus* (mullet), but the growth endpoint was not fully quantified.



Similarly, limited toxicity data exist for marine plants. Oliveira et al. (1978) studied chronic non-lethal effects of fluoride on 12 marine plankton species. No effects were observed at concentrations above 25 mg/L fluoride for any tested species.

Water Quality Parameters Affecting Toxicity

As mentioned above, water quality and other factors affecting the toxicity of fluoride have been evaluated in both the freshwater and marine environment. Water chemistry factors evaluated included pH, hardness, chloride and calcium concentrations. Physical conditions explored in the literature are limited to temperature.

As discussed in **Section 2.3**, pH affects the mobility of fluoride in the aquatic environment. Above pH of 6 standard units (s.u.) fluoride is most mobile, but increasing pH typically corresponds to a greater incidence of other constituents that may have an important role in ameliorating the toxicity of fluoride. Few studies have specifically examined the effect of pH on fluoride toxicity. Rai et al. (1998) conducted chronic (15-day) algal colony growth experiments under varying pH conditions. LC₅₀ values were pH-dependent in *C. vulgaris*, whereby increased pH decreased fluoride toxicity. LC₅₀ concentrations of 133, 266, and 380 mg/L corresponded with pH of 4.5, 6.0, and 6.8 s.u., respectively. The low pH treatment tested could have resulted in metal fluoride complexes which affected the overall sensitivity.

Multiple literature sources have studied the effect of hardness, alkalinity, and the presence of other ions, particularly chloride, on the toxicity of fluoride in the aquatic environment. These water quality parameters will be the primary focus of this review. A summary of potential mechanisms that drive the ameliorating effect of chloride, hardness and alkalinity on fluoride toxicity is discussed below.

Chloride is the most widely studied constituent thought to affect the toxicity of fluoride to aquatic organisms. For many taxa, increased chloride concentration results in decreased toxicity. The seminal work of Neuhold and Sigler (1962) was among the first on the topic of factors that affect the toxicity of fluoride in freshwater environments, particularly focusing on chloride. The experiment was designed to better understand how the presence of chlorides in surface water affect the toxicity of fluoride to *O. mykiss* (rainbow trout) and found that tempering fish in a chloride-rich environment prior to fluoride exposure reduced their response to fluoride exposure (Neuhold and Sigler, 1962).

In fish, the specific mechanism for this amelioration of fluoride toxicity by chloride is somewhat uncertain. Giguere and Campbell (2004) hypothesized that three mechanisms could explain the ameliorating effect of chloride: 1) the test organism is benefiting from the presence of hardness cations (Ca²⁺, Mg²⁺), either externally, at epithelial membranes, or internally; 2) complexation between fluoride ions and hardness cations, which reduces the free fluoride concentration; and 3) precipitation of calcium fluoride (CaF₂) in aquatic media, which also reduces the effective fluoride concentration.

Neuhold and Sigler (1962) attributed the ameliorating effect of chloride on fluoride toxicity to adaptations linked to fish salinity tolerance. Fish salinity tolerance is influenced by ontogenesis (the process of development from early life stages) and associated shifts in osmoregulatory capabilities (Varsamos et al., 2005). The ability of certain ontogenetical stages of fish to tolerate salinity through osmoregulation relies on integumental (skin) ionocytes, then digestive tract development and drinking rate, developing branchial chambers and urinary organ. Most teleost (ray finned-fish) prelarvae can osmoregulate at hatch, and their ability increases in later stages. Salinity tolerance often increases markedly at the metamorphic transition from larva to juvenile (Varsamos et al.,



2005). This may explain some differences observed in the role of chloride to ameliorate fluoride toxicity in fry versus adult fish. Regardless of the specific mechanism of action, the toxicity of fluoride to fish is influenced by surface water quality conditions (Neuhold and Sigler, 1962; Pimentel and Bulkley, 1983; Camargo, 2003).

In invertebrates, the mechanism responsible for the reduced fluoride toxicity caused by chloride is greater competition for the same binding sites of the cytosolic side of the cell membrane (Camargo, 2003). The presence of increased chloride inhibits the incorporation of fluoride into the cytosolic side of the cell membrane. Since the cell membrane has an affinity to chloride when fluoride is high and chloride is low, the fluoride can easily be transported into the cell. At increasing chloride concentrations, the likelihood that the cells incorporate chloride over fluoride increases, thus reducing the overall toxicity. Insects have specifically adapted chloride epithelia that transport ions to help facilitate osmoregulation (Komnick, 1977). Studies that have examined multiple sizes of invertebrates also note decreased toxicity to fluoride with increasing size, even in the presence of chloride. In invertebrates, this may also be attributed to greater osmoregulatory ability in more mature larval or adult invertebrate life stages. A similar mechanism has been described for the toxicity of nitrite (NO_2^-) in the presence of increased chloride (Alonso and Camargo, 2008).

Hardness is a measure of the two most prevalent divalent metal cations, calcium and magnesium. In toxicological assessments, water hardness is typically expressed in units of mg/CaCO_3 . In the absence of explicitly stated concentrations, hardness can be computed by calculation using Method 2340 B (APHA, 1995) as follows (**Equation 4-1**):

Equation 4-1 Hardness, $\text{mg equivalent CaCO}_3/\text{L} = 2.497 \times [\text{Ca, mg/L}] + 4.188 [\text{Mg, mg/L}]$

Where Ca and Mg are the soluble fractions of calcium and magnesium, respectively.

As water hardness increases, the presence of divalent metal cations in the water increases, which can form weak complexes with fluoride and reduce overall toxicity. It should be noted that other compounds, such as iron, aluminium, and manganese can also influence the total hardness of water. Fieser et al. (1986) found that fluoride forming complexes with polyvalent cations and several other factors can significantly affect the toxicity of fluoride to aquatic organisms. Similarly, Wright (1977) found the presence of calcium to have a pronounced effect at decreasing toxicity to *S. trutta*. Therefore, hardness is a metric of the presence of ions capable of forming complexes in the environment. As hardness increases, the toxicity of fluoride typically decreases.

Alkalinity is the acid-neutralizing capacity of water and represents the sum of all of the titratable bases present, such as carbonate, bicarbonate and hydroxide (Method 2320A; APHA, 1995). Presence of borates, phosphates, and other compounds also may contribute to the sum of bases present in surface water contributing to alkalinity. Although there has been limited work focusing specifically on the effect of alkalinity on fluoride toxicity, for other metals such as copper, the presence of increased hydroxyl groups (greater alkalinity) forms less toxic copper-base complexes (Stiff, 1971; Pagenkopf et al., 1974). It is unclear whether the mechanism driving decreased toxicity at increased alkalinity is attributed to the greater incidence of hydroxyl anions by a similar mechanism as the chloride anion or through complexation.

The prevalence of chloride, hardness and alkalinity have been linked to reduced fluoride toxicity; however, the ameliorating effect induced by other cations and anions has not been fully evaluated. This is attributed to the complexities and logistical constraints associated with large factorial experimental designs. Few toxicological studies evaluate the full suite of base cations and anions



needed to elucidate these interactions. The role of sulphate and nitrate are of interest because these compounds can comprise large proportions of the soluble compounds in receiving waters.

4.2.1.2 Terrestrial Environment

A summary of the mode of action and toxicity of fluoride in the terrestrial environment is provided below. The terrestrial environment is not the focus of this assessment, but this information is provided for reference purposes.

In terrestrial environments, fluoride can have effects on plant roots and aboveground vegetation depending on uptake mechanisms, as well as the age and source of fluoride. Plants can take up fluorides from soil and transfer them to foliar tissues through xylematic flows (Fornasiero, 2001). When taken up by roots, some residual fluoride is accumulated into root tissue; however, much of the fluoride is transported to shoot or leaf biomass (Jha et al., 2009).

In addition to potential uptake from the soil, gaseous fluorides can be absorbed through leaf stomata and transferred to foliar tissues through xylematic flows (Zouari et al., 2014). When exposure is predominately atmospheric, accumulation of fluoride in plant roots is much less than when exposure is predominately through soil sources (Baunthiyal et al., 2014). However, the uptake of fluoride into foliar tissue has been shown to decrease, coincident with decreasing atmospheric fluoride concentrations. For example, Horntvedt (1995) found no apparent long-term effects in spruce and pine needles from fluoride accumulation into foliar tissues over a period of approximately 25 years with coincidental decreases in atmospheric fluoride emissions. This suggests that both the age and source of fluoride in the environment may affect its uptake and toxicity within the terrestrial environment.

The most common visible symptom of fluoride toxicity in terrestrial plants is foliar damage (leaf necrosis). This occurs due to several morphological modifications to the upper and lower epidermis. The collapse of mesophyll results in cell distortion and sharpening (Fornasiero, 2001). Leaf necrosis can occur along the leaf margin (sides) or at the tip of the leaf (apical leaf necrosis).

High internal fluoride concentrations affect multiple physiological and metabolic plant processes (Yadu et al., 2016). Elevated fluoride can reduce growth and development, affect rates of photosynthesis and disrupt multiple enzymatic processes. However, the effects of fluoride on growth and development of terrestrial plants vary considerably between species (Baunthiyal et al., 2014). Coniferous trees have been identified as sensitive plant species for exposure to fluoride. Zwiazek and Shay (1988) reported a lowest observed effect concentration (LOEC) for *Pinus banksiana* (jack pine) seedlings for growth of 3 mg/kg dry weight (dw) of sand; effects were observed after 29 hours. However, experimental conditions may have influenced the apparent fluoride sensitivity of *P. banksiana*. Arnesen (1997) reported a LOEC for *Lolium multiflorum* (ryegrass) growth of 400 mg F/kg dw.

The effect of fluoride on terrestrial invertebrates is not as well studied as the effects on plants and higher trophic levels. Increased fluoride concentration and exposure time have been shown to increase fluoride body burden to the terrestrial invertebrate *Eisenia fetida* (Yu and Lawson, 2003). The accumulation of fluoride by numerous other invertebrates from fluoride contaminated soils has also been studied (Buse, 1986).

The fluorination of soils by the addition of super phosphate fertilizers (e.g., monocalcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$) has resulted in many studies which focus on the effects of fluorides on grazing animals



such as sheep and cows. Ingestion is the primary exposure route for fluoride in higher trophic level organisms. Fluoride compounds are absorbed in the stomach and small intestine, where acidic conditions can convert recalcitrant forms of fluoride into more bioavailable forms (Cronin et al., 2000). Threshold soil fluoride concentrations for cattle and sheep were between 326 and 1,085 mg/kg dw and 372 and 1,461 mg/kg dw, respectively. A more recent evaluation of terrestrial exposure by Pascoe et al. (2014) found that the lowest no observed adverse effects level (NOAEL) and lowest observed adverse effects level (LOAEL) risk-based concentrations were 149 mg F/kg soil dw and 659 mg F/kg soil dw, respectively. More information regarding the bioaccumulation factors (BAFs) between compartments of the terrestrial food web is needed to improve the ability to model the potential effect of total soil fluoride on flora and fauna.

One key consideration to the ecotoxicity of fluoride in soils is the degree to which fluoride is adsorbed to soil particles. Fluoride adsorption is greatest in acidic non-calcareous soils containing aluminium hydroxides, where fluorides occur predominantly as aluminium fluorosilicate complexes (Pascoe et al. 2014). In slightly alkaline soils with sufficient calcium carbonate (CaCO_3), soluble fluoride would be most likely completely fixed as CaF_2 (Brewer, 1966) and less bioavailable. However, an increasing electrostatic potential at even higher pH decreases the retention of fluoride on the soil and increases solubility. This is partially attributed to the displacement of adsorbed fluorine by the increased concentration of hydroxide ions (Larsen & Widdowson, 1971).

4.2.2 Conceptual Exposure Model

The conceptual exposure model identifies the relationships between human activities, stressors, and ecological effects on assessment endpoints. **Figure 4-1** illustrates the interactions between sources, stressors, ecological effects and assessment endpoints.

As discussed in **Section 2**, fluoride in the aquatic environment is sourced from both geogenic and anthropogenic sources. The weathering/erosion of minerals such as apatite or fluorapatite and volcanic activities are the primary geogenic sources. Several anthropogenic sources exist; however, the agricultural application of phosphate fertilizers, brick kiln industry, and coal and fossil fuel combustion are the largest sources (**Figure 4-1**). **Figure 1-3** focuses on fate and transport mechanism specific to a hypothetical aluminium production facility containing a smelter, whereas **Figure 4-1** highlights many of the same fate and transport mechanisms but in relation to exposure to aquatic organisms. Specific exposure processes are explained in greater detail below for surface water and sediment/pore water. Given the focus on the aquatic environment, riparian fluoride will not be discussed.

The surface water direct contact exposure pathway applies to both invertebrate and vertebrate taxa that are free-living within the water column, as well as epifaunal invertebrate communities in coarse substrate environments. Aquatic fauna can have a complete exposure pathway with surface water fluoride if uptake occurs at the surface of gills or integument (skin, shell or exoskeleton). Fish are an example of a vertebrate organism with a complete surface water exposure pathway. Surface water foliar uptake could also be a complete exposure pathway for phytoplankton, algae or the foliage of aquatic macrophytes above the sediment-surface water interface.

The sediment/pore water exposure media applies predominately to infaunal invertebrates, which are organisms without skeletons that live within sediments, and certain sediment-dwelling aquatic vertebrates, such as fish that inhabit and feed within the upper portion of the sediment. Root uptake of submerged aquatic vegetation would also be complete for the sediment/pore water exposure media; however, details pertaining to this exposure pathway are uncertain, due to a paucity of



literature on the topic. Metcalf-Smith et al. (2003) represents the most robust study that focused on fluoride sediment toxicity. Because insufficient data exists to understand fluoride risks associated with bulk sediment, application of surface water criteria to pore water or interstitial water measures of fluoride may be most appropriate.

Fluoride can accumulate in hard and soft tissues of flora and fauna as a result of direct contact exposure pathways. Insufficient evidence exists to support the presence of fluoride bioaccumulation through the aquatic food web (CCME, 2002). Therefore, the ingestion pathway is considered an uncertainty.

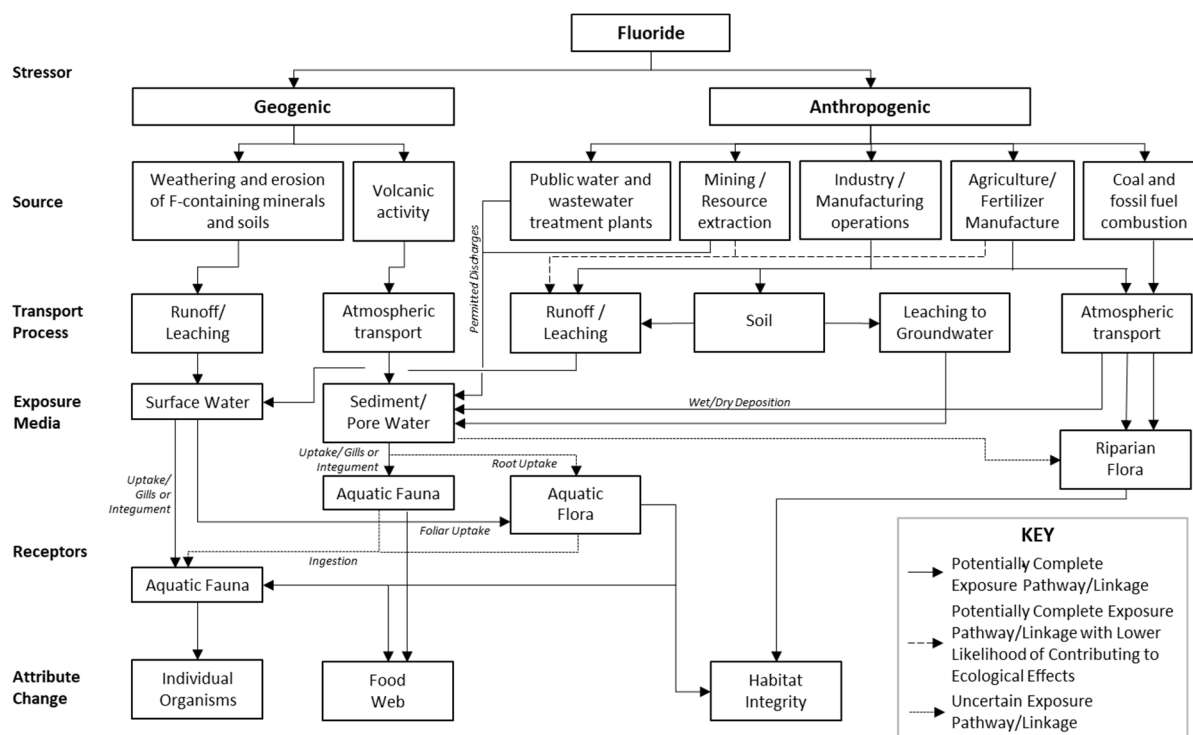


Figure 4-1 Fluoride conceptual ecological exposure model

4.2.2.1 Assessment and Measurement Endpoints

Assessment endpoints are explicit expressions of environmental values to be protected, and measurement endpoints are quantifiable metrics of an ecological effect that are used to determine changes to assessment endpoints (USEPA, 1998). **Table 4-1** illustrates the assessment and measurement endpoints that were reviewed. Assessment endpoints typically target lethal- or select sublethal characteristics that influence the overall fitness of the organism being protected. Under most regulatory frameworks, survival, growth and reproduction assessment endpoints are the primary focus for deriving guidelines/criteria.

Table 4-1 Summary of assessment and measurement endpoints considered

Target Receptor Group(s)	Aquatic Community Assessment Endpoint	Considered Measurements of Effect
Fish and Invertebrates	Survival, growth and reproduction of vertebrate and invertebrate fauna.	For acute effects: LC ₅₀ , EC ₅₀ For chronic effects: EC ₁₀ /IC ₁₀ and NOEC



Target Receptor Group(s)	Aquatic Community Assessment Endpoint	Considered Measurements of Effect
Plants (Phytoplankton and Algae)	Maintenance and growth of aquatic flora from standing crop or biomass.	NOEC, EC ₁₀ , EC ₅₀ , IC ₅₀ , reduced growth rate, cell viability, calculated MATC

Notes:

EC₅₀/EC₁₀ = Effect concentration to 50/10 percent of the test population

IC₅₀/IC₁₀ = Inhibitory concentration to 50/10 percent of the test population

LC₅₀ = Lethal concentration to 50 percent of the test population

LOEC = Lowest observed effect concentration

MATC = Maximum acceptable toxicant concentration (geometric mean of NOEC and LOEC)

NOEC = No observed effect concentration

The measures of effect for acute and chronic toxicity data are assessed below. Survival, growth, and reproduction endpoints were identified. Acute studies considered had exposure durations less than or equal to 4 days (96 hours). LC₅₀ values were preferably selected over non-lethal effect concentrations to 50 percent of the test population (EC₅₀) where both data were available. Chronic toxicity studies were equal to or greater than seven days in length; sub-chronic tests were also considered. Although, the bioaccumulation of fluoride in the food web presents an uncertainty, the 10 percent inhibitory/effect concentration was elected for chronic studies over the 20 percent concentration. The use of the lower percentile is also in line with the Canadian framework for deriving water quality guidelines (CCME, 2007). In the absence of stated IC₁₀/EC₁₀ concentrations, NOEC values were adopted. Only toxicity studies that were conducted using sodium fluoride (NaF) as the source of fluoride were considered to minimize the potential confounding effects from other cations.

The range of freshwater quality conditions included in the assessment are pH = 6.0 to 8.8 s.u., hardness = 3.8 to 385 mg CaCO₃/L, alkalinity = 3.0 to 397 mg CaCO₃/L and chloride = 0.0 to 98.4 mg/L. For the marine environment, salinities evaluated ranged from 15 to 35 ppt. Although detailed water quality conditions were not collected for most marine studies, marine and estuarine water from 15 to 35 ppt would have several orders of magnitude more chloride than freshwater. Chloride content of 15 to 35 ppt salinity corresponds to approximately 8,300 to 19,400 mg/L, respectively. Other important cations like magnesium and calcium would also be present in higher concentrations in marine waters.

Overview of Toxicity Data Requirements

Water quality guidelines typically have recommendations on the minimum required number of genera or specific taxonomic units needed to meet the appropriate diversity requirement for criteria derivation. In the United States, the 1985 guidelines require acceptable data be available for at least eight genera. The minimum data requirement (MDR) adopted by the USEPA is the most stringent among the IAI study regions and was used to evaluate acceptability. Variations in MDRs by fresh and marine environments are presented below for various guidance documents.

Summary of freshwater MDRs as reported in Stephan et al. (1985):

- Results of acceptable acute tests with at least one species of freshwater animal in at least eight different families such that all of the following are included:
 - Family Salmonidae in the class *Osteichthyes*
 - Second family in the class *Osteichthyes*, preferably a commercially or recreationally important warm-water species (e.g., bluegill, channel catfish)



- Third family in the phylum *Chordata* (may be in the class *Osteichthyes* or may be an amphibian, etc.)
- Planktonic crustacean (e.g., cladoceran, copepod)
- Benthic crustacean (e.g., ostracod, isopod, amphipod, crayfish)
- Insect (e.g., mayfly, dragonfly, damselfly, stonefly, caddisfly, mosquito, midge)
- Family in a phylum other than Arthropoda or Chordata (e.g., Rotifera, Annelida, Mollusca)
- Family in any order of insect or any phylum not already represented
- Acute-chronic ratios with species of aquatic animals in at least three different families provided that of the three species:
 - At least one is a fish
 - At least one is an invertebrate
 - At least one is an acutely sensitive freshwater species (the other two may be saltwater species)
- Results are available of at least one acceptable test with a freshwater alga or vascular plant. If plants are among the aquatic organisms that are most sensitive to the material, results of a test with a plant in another phylum (division) should also be available.
- At least one acceptable bioconcentration factor determined with an appropriate freshwater species.

Summary of marine water MDRs as reported in Stephen et al. (1985):

- Results of acceptable acute tests with at least one species of saltwater animal in at least eight different families such that all of the following are included:
 - Two families in the phylum Chordata
 - Family in a phylum other than Arthropoda or Chordata
 - Either the *Mysidae* or *Penaeidae* family
 - Three other families not in the phylum Chordata (may include *Mysidae* or *Penaeidae*, whichever was not used above)
 - Any other family
- Acute-chronic ratios with species of aquatic animals in at least three different families provided that of the three species:
 - At least one is a fish
 - At least one is an invertebrate
 - At least one is an acutely sensitive saltwater species (the other two may be freshwater species) if a maximum permissible tissue concentration is available
- Results of at least one acceptable test with a saltwater alga or vascular plant. If plants are among the aquatic organisms most sensitive to the material, results of a test with a plant in another phylum (division) should also be available.
- At least one acceptable bioconcentration factor determined with an appropriate saltwater species.

The Australian and New Zealand Guidance (Warne et al., 2018) differs from Stephan et al. (1985) in that the toxicity data requirements are slightly less specific. At least five species that belong to at least four different taxonomic groups are required by Warne et al. (2018). Vertebrates, invertebrates, plants and others that are from different phyla are considered taxonomic groups.

For the application of site-specific criteria derivation in Canada, minimum data requirements require at least six species of aquatic organisms be represented (CCME, 2007). Of the six species, a preference for three fish species, two invertebrate species, and one algae or aquatic vascular plant species is made.



The European Commission also adheres to the eight taxonomic group rule discussed by Stephan et al. (1985). In general, the approach is less prescriptive, but more detailed toxicological data on plants is recommended. The European Commission (2018) recommends the inclusion of the following taxonomic groups:

- Fish (species frequently tested include salmonids, minnows, bluegill sunfish, channel catfish, etc.)
- A second family in the phylum Chordata (e.g. fish, amphibian, etc.)
- A crustacean (e.g. cladoceran, copepod, ostracod, isopod, amphipod, crayfish)
- An insect (e.g. mayfly, dragonfly, damselfly, stonefly, caddisfly, mosquito, midge)
- A phylum other than Arthropoda or Chordata (e.g. Rotifera, Annelida, Mollusca)
- An order of insect or any phylum not already represented
- Algae or Cyanobacteria, and higher plants

4.2.3 Analysis Plan

Marine and freshwater fluoride toxicity data were sourced from primary literature sources, as well as the USEPA ECOTOX Ecotoxicity Database (USEPA, 2020a). Available fluoride toxicity information was reviewed for quality and to determine if acceptable data meets the MDRs discussed above. Literature quality was determined by the AQUIRE scoring system (USEPA, 2010) and by that described by Zhang et al. (2015). Only data meeting the acceptable quality in both scoring systems were retained for consideration. Data are organized by water type (freshwater vs. marine) and test duration (acute vs. chronic). For this evaluation, acute tests were less than or equal to 4 days in duration and chronic tests were greater than or equal to 7 days.

A matrix summarizing the reviewed acute toxicity literature can be found in **Appendix B**. Chronic toxicity literature is summarized in **Appendix C**. **Table 4-2** provides a summary of the toxicity data used to fulfil the MDRs as outlined in Stephan et al. (1985). In the case of acute and chronic tests, the MDRs were not met for both freshwater and marine study matrices.

Since the MLR approach was identified as a tool for the development of preliminary criteria for freshwater acute data, acceptable data required the presence of water quality parameters. The acute freshwater dataset with associated chloride, hardness and alkalinity measurements lacked two vertebrates and an invertebrate; however, this dataset had water quality parameters that were stated or inferred for the other five genera. Marine acute toxicity tests on fluoride represent the most limited group represented in the literature. No water quality parameters were available for the genera meeting the MDR.



Table 4-2 Summary of acceptable toxicity data for freshwater and marine water taxa

Family Minimum Data Requirement	Acute (Phylum / Family / Genus)	Chronic (Phylum / Family / Genus)
Freshwater		
Family Salmonidae in the class	Chordata / Salmonidae / Oncorhynchus	Chordata / Salmonidae / Oncorhynchus*
Second family in the class Osteichthyes	No acceptable data w WQPs	Chordata / Cyprinidae / Pimephales*
Third family in the phylum Chordata	No acceptable data w WQPs	Chordata / Acipenseridae / Acipenser*
Planktonic Crustacean	No acceptable data w WQPs	Arthropoda / Daphniidae / Ceriodaphnia*
Benthic Crustacean	Arthropoda / Hyalellidae / Hyalella	Arthropoda / Hyalellidae / Hyalella*
Insect	Arthropoda/ Hydropsychidae / Hydropsyche	Arthropoda / Chironomidae / Chironomus*
Family in a phylum other than Arthropoda or Chordata	Mollusca / Unionidae / Actinonaias	Mollusca / Tateidae / Potamopyrgus*
Family in any order of insect or any phylum not already represented	Chlorophyta / Selenastraceae / Raphidocelis	Annelida / Naididae / Branchiura*
Marine		
Family in the phylum Chordata	Chordata / Cyprinodontidae / Cyprinodon*	Chordata / Mugilidae / Mugil*
Family in the phylum Chordata	Chordata / Mugilidae / Mugil*	No acceptable data
Either the Mysidae or Penaeidae family	No acceptable data	Arthropoda / Penaeidae / Fenneropenaeus*
Family in a phylum other than Arthropoda or Chordata	No acceptable data	Mollusca / Mytilidae / Mytilus*
Family in a phylum other than Chordata	Arthropoda / Arthropoda / Artemia*	Arthropoda / Aoridae / Grandidierella*
Family in a phylum other than Chordata	Arthropoda / Crangonidae / Crangon*	Arthropoda / Cancridae / Cancer*
Family in a phylum other than Chordata	Arthropoda / Palaemonidae / Palaemo*	Arthropoda / Portunidae / Carcinus*
Any other family	Mollusca / Ostreidae / Magallana*	No acceptable data

Note:

*Fluoride toxicity data present, but it lacks water quality parameters or water quality parameter normalization

A greater number of MDR taxa were available for chronic freshwater and marine tests (Table 4-2). The eight genera requirement was met for the chronic freshwater group; however, species tested typically did not have measurements of water quality parameters to enable the application of MLR equations. Six of the eight genera had chronic marine toxicity data for fluoride. Species tested typically did not have measurements of water quality parameters to enable the application of MLR equations. As a result of the available data, preliminary acute freshwater criteria were estimated using the MLR approach used for aluminium (USEPA, 2018), as well as preliminary chronic freshwater criteria following an SSD approach. No preliminary criteria were derived for acute or chronic marine toxicity tests.

The approach used to normalize toxicity results to water quality conditions and preliminary criteria derivation approaches using acute and chronic toxicity data is discussed below.

4.2.3.1 Acute Toxicity Water Quality Parameter Normalization

As discussed in Section 4.2.1.1 several factors influence the toxicity of fluoride to aquatic organisms. Percy et al. (2015) evaluated the acute toxicity of fluoride on two receptor organisms (*O. mykiss* and *H. azteca*) to determine how chloride, hardness and alkalinity modified fluoride toxicity. The authors concluded that only chloride substantially modified the toxicity of fluoride, which was most obvious for *H. azteca*. However, Percy et al. (2015) lacked a detailed statistical assessment of potential synergistic or antagonistic effects among the other water quality parameters. The conclusions reached by Percy et al. (2015) did not fully explain the contribution of hardness and alkalinity on modifying fluoride toxicity in the presence of chloride. A more detailed assessment of the acute data collected by Percy et al. (2015) was conducted. This assessment demonstrates that a multivariate approach can be used to better predict fluoride toxicity and that consideration of multiple water quality parameters is needed to derive the most robust water quality benchmark for fluoride.



The data collected by Pearcy et al. (2015) were evaluated using the MLR approach applied in Deforest et al. (2018), which was the approach used to establish the final aquatic life ambient water quality criteria for aluminium by the USEPA (USEPA, 2018). Acute fluoride LC_{50} values were assessed separately for two receptor species, *H. azteca* and *O. mykiss*. Simple MLR models were constructed with LC_{50} as the response variable and chloride, hardness and alkalinity concentrations serving as potential main-effect predictor variables. The response and predictor variables were natural log transformed prior to assessment. Using the R statistical programming language and the glmulti package, the best model for predicting LC_{50} was selected from every possible linear model by leveraging the Bayesian information criteria (BIC) statistic. As this was an initial assessment of the value of MLR for the purpose of deriving preliminary criteria, predictor interaction terms, assumptions of linearity and methods for handling any potential non-linearity were not investigated in detail and not discussed herein.

The best models observed for predicting acute toxicity to *H. azteca* and *O. mykiss* are presented in **Equation 4-2** and **Equation 4-3** below, respectively.

Equation 4-2 *H. Azteca* $\ln(LC_{50}) = \ln(\text{Hardness}) \times -0.212 + \ln(\text{Chloride}) \times 0.545 + \ln(\text{Alkalinity}) \times 0.264 + 1.596$

Equation 4-3 *O. mykiss* $\ln(LC_{50}) = \ln(\text{Hardness}) \times 0.642 + \ln(\text{Alkalinity}) \times -0.447 + 3.012$

The best model identified using glmulti, a multivariate approach, was compared to chloride as a univariate predictor of the toxicity modifier. The relationship between observed LC_{50} concentrations and predicted LC_{50} by the multivariate and univariate models are illustrated in **Figure 4-2**. The best models are coloured black and the chloride-only univariate model is coloured grey. Each of the MLR models produced better predictions than chloride-only models. For *H. azteca*, the best MLR model explained 90 percent of the variance in LC_{50} , whereas the chloride-only model explained 80 percent. For *O. mykiss*, the best MLR model explained 39 percent of the variance in LC_{50} , whereas the chloride-only model explained 10 percent. It is also noteworthy that chloride is not included in the best model for predicting *O. mykiss* toxicity.

Some minor trends and outliers were observed in the residuals of each model, suggesting that some predictors may correlate non-linearly with toxicity; however, as previously noted, these characteristics were not investigated as part of this initial assessment but should be considered as part of future and more thorough analyses. Nevertheless, using the MLR approach improved the prediction of fluoride toxicity (**Table 4-3**).

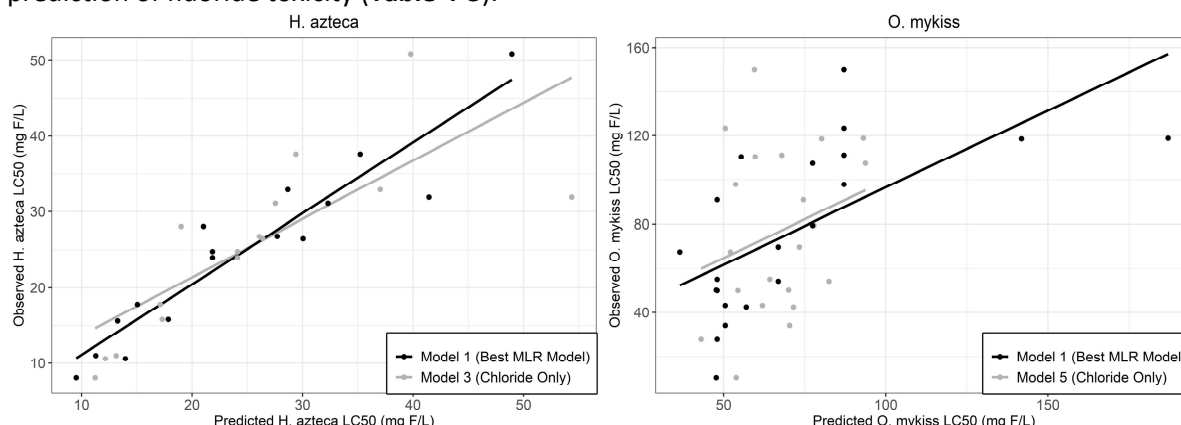


Figure 4-2 Predicted vs observed fluoride LC_{50} in *H. azteca* (left) and *O. mykiss* (right)



Table 4-3 Summary statistics from best model and chloride-only models

Model	R ²	Adjusted R ²	Residual Standard Error	F	Df1	Df2	p-value
<i>O. Mykiss Models Considered</i>							
1	0.39	0.33	0.51	6.33	2	20	0.007
5	0.10	0.06	0.60	2.37	1	21	0.139
<i>H. Azteca Models Considered</i>							
1	0.90	0.88	0.17	39.27	3	13	<0.001
3	0.80	0.79	0.23	59.61	1	15	<0.001

Notes:

Df1 = degrees of freedom for the number of treatment levels (parameters)

Df2 = degrees of freedom for the number of observations

F = F statistic

R² = coefficient of determination

4.2.3.2 Acute Criterion

Equation 4-2 and **Equation 4-3** establish a statistically significant relationship between acute toxicity and water quality parameters. The relationship is applied in the acute criteria derivation process by deriving equations to normalize literature-sourced toxicity results to targeted water quality conditions, where available. Using the reported toxicity information from the acceptable acute studies, normalized acute toxicity effects measures were calculated for *H. azteca* and *O. mykiss* using the linear models presented in **Equation 4-4** and **Equation 4-5**, respectively. **Appendix B** summarizes the reported and normalized toxicity values sourced from the acute toxicity literature. **Equation 4-4** was applied to invertebrate LC₅₀ values and **Equation 4-5** was used to normalize vertebrate LC₅₀ values.

Equation 4-4 $H. azteca$ $LC_{50, norm} = \exp[\ln(LC_{50, test}) + [\ln(Hard_{test}) - \ln(Hard_{target})] \times 0.212 - [\ln(Cl_{test}) - \ln(Cl_{target})] \times 0.545 - [\ln(Alk_{test}) - \ln(Alk_{target})] \times 0.264]$

Equation 4-5 $O. mykiss$ $LC_{50, norm} = \exp[\ln(LC_{50, test}) - [\ln(Hard_{test}) - \ln(Hard_{target})] \times 0.642 + [\ln(Alk_{test}) - \ln(Alk_{target})] \times 0.447]$

where:

LC _{50, norm}	=	normalized LC ₅₀ concentration in µg/L
LC _{50, test}	=	reported acute fluoride LC ₅₀ concentration in µg/L
Hard _{test}	=	reported test hardness concentration in mg/L
Cl _{test}	=	reported test chloride concentration in mg/L
Alk _{test}	=	reported test alkalinity concentration in mg/L
Hard _{target}	=	hardness concentration to normalize to in mg/L
Cl _{target}	=	chloride concentration to normalize to in mg/L
Alk _{target}	=	alkalinity concentration to normalize to in mg/L

Note that in **Equation 4-4** and **Equation 4-5** the intercepts are replaced with the reported LC₅₀ value from the study and the coefficient signs are opposite from **Equation 4-2** and **Equation 4-3**.

Normalization was conducted for two separate water quality condition scenarios, low ion water and high ion water. The low ion water was moderately hard and had low chloride (hardness = 66 mg/L, alkalinity = 58 mg/L, chloride = 1.5 mg/L). This water is typical of major rivers in the Northwest United States and Southwest Canada (**Figure 4-3**). The high ion water would be considered hard



water and is typical of large rivers in the Great Lakes and St. Lawrence watershed in North America (hardness = 124 mg/L, alkalinity = 92 mg/L, chloride = 25 mg/L) and in other more coastal regions or areas where winter conditions require the use of road salts.

Low and high ion water scenario toxicity normalization scenarios were used to calculate $LC_{50, \text{norm}}$. The normalized toxicity data was reduced further to species mean acute values (SMAVs) and genus mean acute values (GMAVs) by taking the geometric mean of the normalized acceptable toxicity data for a given species or genera, respectively. Preliminary FAVs were estimated for each water quality scenario by extrapolating the 5 percent hazard concentration (HC_5) of the GMAVs. The HC_5 is a statistical measure of the distribution of toxicity results that protects 95 percent of aquatic species tested. This was done in accordance with USEPA (2018) where linear interpolation or extrapolation of log transformed concentrations was done of the four most sensitive taxa. More robust distribution fitting approaches were explored for the preliminary chronic criterion estimation discussed below.

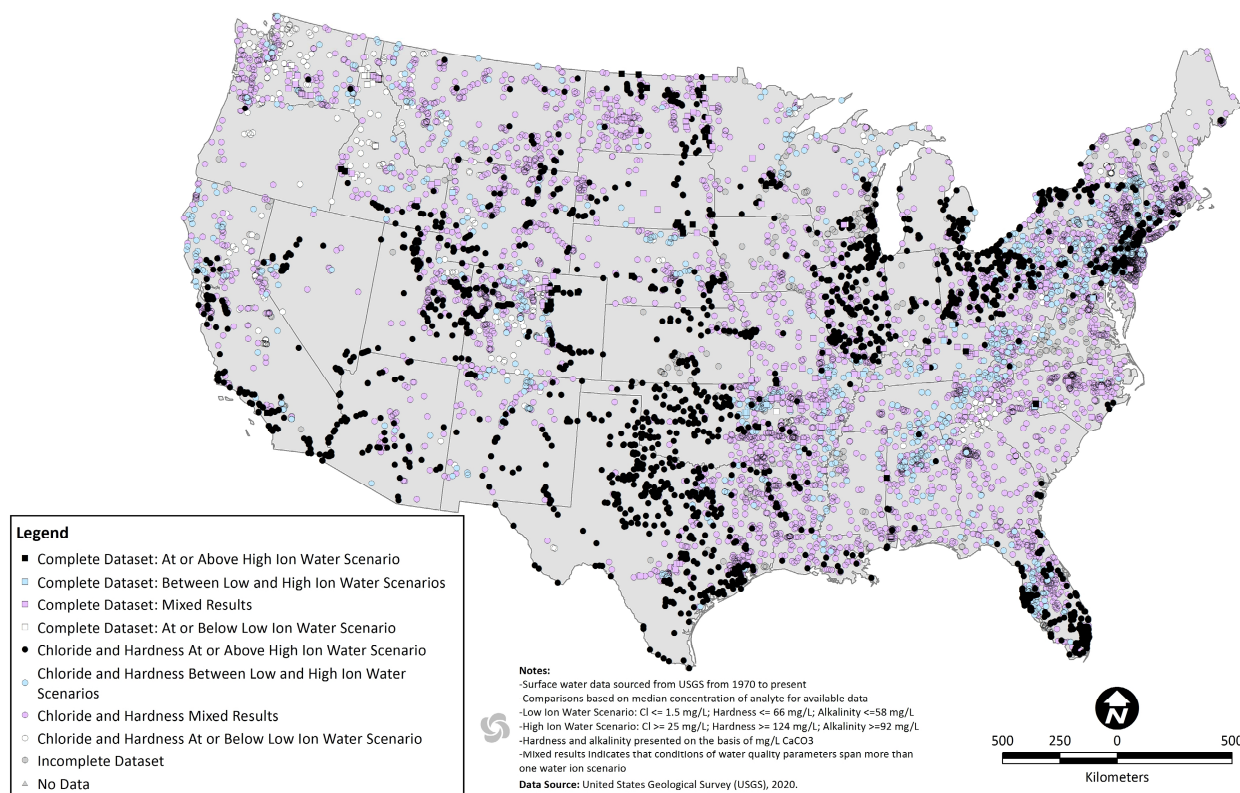


Figure 4-3 Distribution of ion water scenario types for preliminary criteria derivation across the United States

4.2.3.3 Chronic Criterion

Chronic toxicity data for freshwater and marine water was assessed to determine its suitability for deriving preliminary chronic criteria. The SSD approach elected the minimum EC₁₀, for a given species. If NOEC and EC₁₀ toxicity test results were available for a given species, EC₁₀ was used preferentially. No normalization approaches were applied in deriving the preliminary chronic criteria. A distribution fitting tool, SSD Toolbox, was employed to estimate the HC₅ for the compiled toxicological information. SSD toolbox (USEPA, 2020b) is a new computer software program designed to simplify the process of selecting appropriate cumulative probability functions to establish HC₅ or other limits appropriate for managing surface waters. The SSD Toolbox can test a variety of cumulative probability distribution functions including triangular, Weibull, normal, logistic, log-normal, Burr and Gumbel. The Akaike information criterion (AIC) and other metrics are provided to enable goodness-of-fit diagnostics to select the most parsimonious model.

4.3 Effects Analysis

The effects analysis provides a discussion of the available literature regarding fluoride toxicity to aquatic organisms. Acute and chronic freshwater studies are discussed in detail for freshwater and marine environments. The ability to normalize acute toxicity data for freshwater based on water quality conditions enabled a more detailed review regarding normalized SMAV and GMAVs, which contributed to the estimation of FAVs. In the absence of a robust framework to normalize chronic freshwater or marine data, the effects analysis discussion focuses on the available toxicity information. In addition, SSD models were fit to the chronic data to understand preliminary chronic



criteria for freshwater and marine waters. Recommendations are made based on the utility of the information available.

4.3.1 Freshwater

Dozens of studies were reviewed to describe the effects of fluoride toxicity on freshwater aquatic organisms. **Appendix B** provides a complete record of the toxicity data reviewed for acute data and **Appendix C** provides a complete record of the toxicity data reviewed for chronic data.

4.3.1.1 Acute Toxicity to Freshwater Fauna and Flora

A summary of key findings from notable studies on acute toxicity of fluoride to aquatic invertebrates, fish and plants is provided below based on the raw toxicity information reported. Additionally, the assessment of normalized toxicity data and associated use in estimating FAVs for fluoride under two surface water conditions are discussed.

Invertebrates

Aguirre-Sierra et al. (2013) examined both acute and chronic effects of fluoride on the survival and behaviour of the endangered white-clawed crayfish (*Austropotamobius pallipes*). Fluoride LC₅₀ concentrations for *A. pallipes* were estimated at 93.0, 55.3, 42.7, 36.5, 32.9, 30.6 and 28.9 mg/L for 48-, 72-, 96-, 120-, 144-, 168-, and 192-h exposure periods, respectively. The crayfish exoskeleton was found to accumulate more fluoride than the muscle and it was concluded that fluoride was not an important risk factor contributing to the decrease of *A. pallipes* in many European waterways.

Camargo et al. (1992) studied the relative sensitivity of caddisfly species (*Hydropsychid*) to fluoride in relation to a wastewater treatment plant situated on the Cache la Poudre River, Colorado, USA. Acute lethal concentrations were evaluated in soft water with an average hardness of 40.2 mg CaCO₃/L. LC₅₀ concentrations for *H. bronta* were estimated at 52.6, 25.8, 17.0, 13.4 and 11.5 mg/L for 48-, 72-, 96-, 120-, and 144-h exposure periods, respectively. LC₅₀ concentrations for *H. occidentalis* were estimated at 102.0, 53.5, 34.7, 27.0 and 27.0 mg/L for 48-, 72-, 96-, 120- and 144-h exposure periods, respectively. LC₅₀ concentrations for *Cheumatopsyche pettiti* were estimated at 128.0, 73.2, 42.5, 31.9 and 24.2 mg/L for 48-, 72-, 96-, 120- and 144-h exposure periods, respectively. *H. bronta* was the most sensitive of the *Hydropsychid* invertebrates studied. The sensitivity of *H. bronta* was linked to the potential for decreased abundances of the wastewater treatment facility.

Casellato et al. (2013) studied the tolerance of *Branchiura sowerbyi*, an aquatic oligochaete worm, to acute and chronic fluoride exposure. Acute (96-h) effects testing indicated that both temperature and presence of sediment influenced LC₅₀ fluoride concentrations. At 17±0.5 °C temperature, fluoride LC₅₀ with sediment present was 267.63 mg/L (95 percent CI = 257.75–277.51 mg/L) and 91.28 mg/L (95 percent CI = 84.50–98.05 mg/L) with sediment absent. At 22±0.5 °C temperature, fluoride LC₅₀ with sediment present was 80.07 mg/L (95 percent CI = 62.10–111.55 mg/L) and 61.68 mg/L (95 percent CI = 84.83–90.11 mg/L) with sediment absent.

Fieser et al. (1986) evaluated the effect of fluorides on the survival and reproduction of *Daphnia magna* over chronic and acute test durations in hard water. During acute tests, increasing temperature from 15 °C to 25 °C reduced the concentrations affecting *D. magna* survival. LC₅₀ calculated for 48-h exposure periods at 15 °C, 20 °C and 25 °C were 350, 247 and 180 mg/L fluoride, respectively.



Keller and Augspurger (2005) assessed the toxicity of fluoride to an endangered unionid mussel, the Appalachian elktoe (*Alasmidonta raveneliana*), and surrogate species in North Carolina. Acute tests were conducted on glochidia, which are larval mussel life stages, for 24 hours and juvenile mussels for 96 hours. Juvenile tests for one mussel species, *Actinonaias pectorosa* were also carried out across a range of hardness concentrations from 28 to 84 mg/L CaCO₃. Acute LC₅₀ for 96-h tests for juveniles were 172 mg/L, 234 mg/L and 303 mg/L, and ranged from 178 to 347 mg/L for *Lampsilis fasciola*, *Utterbackia imbecillis*, *A. raveneliana*, and *A. pectorosa*, respectively. LC₅₀ for *A. raveneliana* and *U. imbecillis* glochidia were 288 mg/L and 351 mg/L fluoride, respectively. NOECs were not dissimilar for the 24 h glochidia tests, with 250 mg/L indicating the presence of potential secondary factors contributing to mortality.

Metcalf-Smith et al. (2003) assessed sediment and surface water toxicity of fluoride to freshwater organisms. Acute toxicity to *D. Magna* (24-h), *H. Azteca* (24-h), *Hexagenia limbata* (96-h), and *Chironomus tentans* (96-h) was evaluated. LC₅₀ for fluoride (±95 percent CI) was 128 mg/L (90.5-181 mg/L), 6.6mg/L (5.7-11.3 mg/L), 14.6mg/L (4.7-23.3 mg/L) and 56.2mg/L (41.4-69.2 mg/L) for *D. Magna*, *H. Azteca*, *Hexagenia limbata* and *Chironomus tentans*, respectively.

The 2015 assessment of Pearcy et al. represents one of the most comprehensive evaluations of factors that modify the toxicity of fluoride to aquatic species. Acute testing (96-h) was carried out on *H. azteca* under varying conditions of water hardness, alkalinity and chloride to determine the effect of each at modifying fluoride toxicity. Chloride was concluded to be the major toxicity-modifying factor; however, these findings were not supported by an in-depth statistical evaluation. *H. azteca* had LC₅₀ test results that ranged from 8.1 to 50.9 mg/L fluoride across the studied water quality conditions. Despite the in-depth toxicity testing across a range of water quality conditions, the acute tests were ultimately very strongly catered to the assessment of chloride effects. A detailed multivariate approach on the acute toxicity data from Pearcy et al. (2015) is discussed in **Section 4.2.3**.

Fish

Metcalf-Smith et al. (2003) assessed sediment and surface water toxicity of fluoride to freshwater organisms. Acute toxicity to juvenile *P. promelas* (96-h) and the LC₅₀ (±95 percent CI) was 118.7 mg/L (90.5-181 mg/L).

The seminal work of Neuhold and Sigler (1962) was among the first on the topic of factors that affect the toxicity of fluoride in freshwater environments. The experiment was designed to better understand how the presence of chlorides in surface water affect the toxicity of fluoride to 4- to 7-inch rainbow trout (*Oncorhynchus mykiss*). Rainbow trout were manipulated by storing them in two, 300-gallon holding tanks for 48 hours. One tank had a chloride concentration of 34 mg/L chloride and the other had 0 mg/L chloride. Holding tank and toxicity testing water was soft (low hardness). The tempering of fish in chloride resulted in significant reductions in fluoride toxicity to rainbow trout. The 120-h LC₅₀ was 6 mg/L fluoride for non-tempered treatments, whereas the LC₅₀ of tempered treatments was 22 mg/L. Mortality occurred within the first 72 hours.

Acute testing (96-h) was carried out by Pearcy et al. (2015) on *O. mykiss* fry under varying conditions of water hardness, alkalinity and chloride to determine the effect of each at modifying fluoride toxicity. The acute LC₅₀ test results for *O. mykiss* varied by an order of magnitude across the studied water quality conditions (LC₅₀ 10.4 mg/L to 150.0 mg/L fluoride).



Wright (1977) studied the toxicity of fluoride to the brown trout (*Salmo trutta*). Trout fry were approximately 2 cm long and finished feeding. Water quality conditions were 29 mg/L calcium and pH was 6.8. A 96-h LC₅₀ was estimated to be around 18 mg/L. The higher LC₅₀ than in previous work by Neuhold and Sigler (1960) was attributed to the high calcium content in the water used.

Pimentel and Bulkley (1983) assessed the effect of water hardness on the toxicity of fluoride to *O. mykiss*. Acute, 96-h LC₅₀ tests were conducted and indicated that the exposure to fluoride was reduced at greater hardness concentrations with measured LC₅₀ of 51, 128, 140 and 193 mg/L fluoride at hardness concentrations of 17, 49, 182 and 385 mg/L CaCO₃, respectively.

Plants

Rai et al. (1998) assessed the pH-altered interaction of aluminium and fluoride on nutrient uptake and photosynthesis of the algae *Chlorella vulgaris*. Although numerous fluoride and aluminium-containing compounds were evaluated, the discussion herein will focus on NaF. Chronic (15-day) algal colony growth experiments were conducted under varying pH conditions. LC₅₀ exhibited pH dependence in the *C. vulgaris*, whereby increased pH decreased fluoride toxicity. LC₅₀ concentrations of 133, 266 and 380 mg/L corresponded with pH of 4.5, 6.0 and 6.8 s.u., respectively. Colony population growth rate NOECs of <9.5, <2.85 and <66.49 were observed at pH of 4.5, 6.0 and 6.8 s.u., respectively.

Freshwater FAV Estimation

Using the reported toxicity information from the acceptable acute studies and the linear models discussed in **Section 4.2.3.1**, normalized acute toxicity effects measures were calculated using **Equation 4-4** and **Equation 4-5**, respectively (**Table 4-4**). Normalization was conducted for two separate water quality condition scenarios, low ion water and high ion water. The low ion water was moderately hard and had low chloride (hardness = 66 mg/L, alkalinity = 58 mg/L, chloride = 1.5 mg/L). This water is typical of major rivers in the Northwest United States and Southwest Canada. The high ion water would be considered hard water and is typical of large rivers in the Great Lakes and St. Lawrence watershed in North America (hardness = 124 mg/L, alkalinity = 92 mg/L, chloride = 25 mg/L) and in other more coastal regions or areas where winter conditions require the use of road salts.

Table 4-4 Ranked freshwater genus mean acute values for low and high ion waters

Species	Normalized GMAV and SMAV to Low Ion Water Conditions (Hardness=66 mg/L, Alkalinity=58 mg/L, Chloride=1.5 mg/L)			Normalized GMAV and SMAV to High Ion Water Conditions (Hardness=124 mg/L, Alkalinity=92 mg/L, Chloride=25 mg/L)		
	Rank	GMAV (mg/L Fluoride)	SMAV (mg/L Fluoride)	Rank	GMAV (mg/L Fluoride)	SMAV (mg/L Fluoride)
<i>Scenedesmus subspicatus</i>	11	914.6	914.6	9	914.6	914.6
<i>Pseudokirchneriella subcapitata</i>	10	272.5	272.5	6	272.5	272.5
<i>Salmo trutta</i>	9	261.1	261.1	7	317.6	317.6
<i>Utterbackia imbecillis</i>	8	239.1	239.1	11	1079.0	1079.0



Species	Normalized GMAV and SMAV to Low Ion Water Conditions (Hardness=66 mg/L, Alkalinity=58 mg/L, Chloride=1.5 mg/L)			Normalized GMAV and SMAV to High Ion Water Conditions (Hardness=124 mg/L, Alkalinity=92 mg/L, Chloride=25 mg/L)		
	Rank	GMAV (mg/L Fluoride)	SMAV (mg/L Fluoride)	Rank	GMAV (mg/L Fluoride)	SMAV (mg/L Fluoride)
<i>Actinonaias pectorosa</i>	7	206.6	206.6	10	932.3	932.3
<i>Lampsilis fasciola</i>	6	157.4	157.4	8	710.3	710.3
<i>Chlorella vulgaris</i>	5	133.0	133.0	5	133.0	133.0
<i>Oncorhynchus mykiss</i>	4	57.6	57.6	3	70.0	70.0
<i>Chimarra marginata</i>	3	18.1	18.1	4	81.5	81.5
<i>Hydropsyche pellucidula</i>	2	12.6	17.7	2	56.7	79.7
<i>Hydropsyche lobata</i>			15.2			68.8
<i>Hydropsyche exocellata</i>			10.7			48.1
<i>Hydropsyche bulbifera</i>			8.7			39.2
<i>Hyaella azteca</i>	1	7.5	7.5	1	33.7	33.7

Notes:

GMAV = Genus mean acute value calculated using the geometric mean of normalized LC₅₀

SMAV = Species mean acute value calculated using the geometric mean of normalized LC₅₀

LC₅₀ = 50th percent lethal concentration

mg/L = milligrams per litre

Aquatic plants *S. subspicatus* and *C. vulgaris* were not normalized.

The effect of surface water quality conditions on the SMAV was substantial. For invertebrates, the high ion water scenario resulted in 4.5 times greater SMAVs than the low ion water scenario. For vertebrates, the high ion water scenario resulted in 1.2 times greater SMAVs than the low ion water scenario. Under both water quality scenarios, the normalized *H. azteca* GMAV/SMAV was the most sensitive taxon. Three out of the four most sensitive taxa were invertebrates when examining the GMAV and the most sensitive four taxa were invertebrates when examining the SMAV. Similarly, the GMAV for *Hydropsyche* was nearly twice of the GMAV for *Hyaella*. Although GMAVs were unable to be calculated, due to an absence of water quality parameters, the minimum LC₅₀ for *Ceriodaphnia* and *Daphnia* were 124.1 and 83.2 mg/L fluoride, respectively. These genera are generally comparable to that of *Hyaella* in water only toxicity tests (Environment Canada, 1997). Considering that the high ion water quality scenario resulted in a nearly 5-fold increase in the SMAVs for invertebrates, deriving guideline values using approaches that adequately consider water quality conditions is imperative. Similarly, it is recommended that a more thorough MLR assessment be conducted using additional toxicity data and more detailed statistical investigation. The initial results of the MLR suggest that hardness and alkalinity cannot be discounted in their effects on modifying fluoride toxicity.



The cumulative distribution of GMAVs by fluoride effect concentration is illustrated in **Figure 4-4**. The *O. mykiss* exhibited less sensitivity to fluoride than *S. trutta*. This is consistent with the findings discussed by Wright (1977). However, life stage likely influenced the rank of the two fish species evaluated. The *O. mykiss* were fry, whereas the *S. trutta* were more mature test organisms. Aquatic plants and molluscs generally showed the greatest tolerance to fluoride concentration.

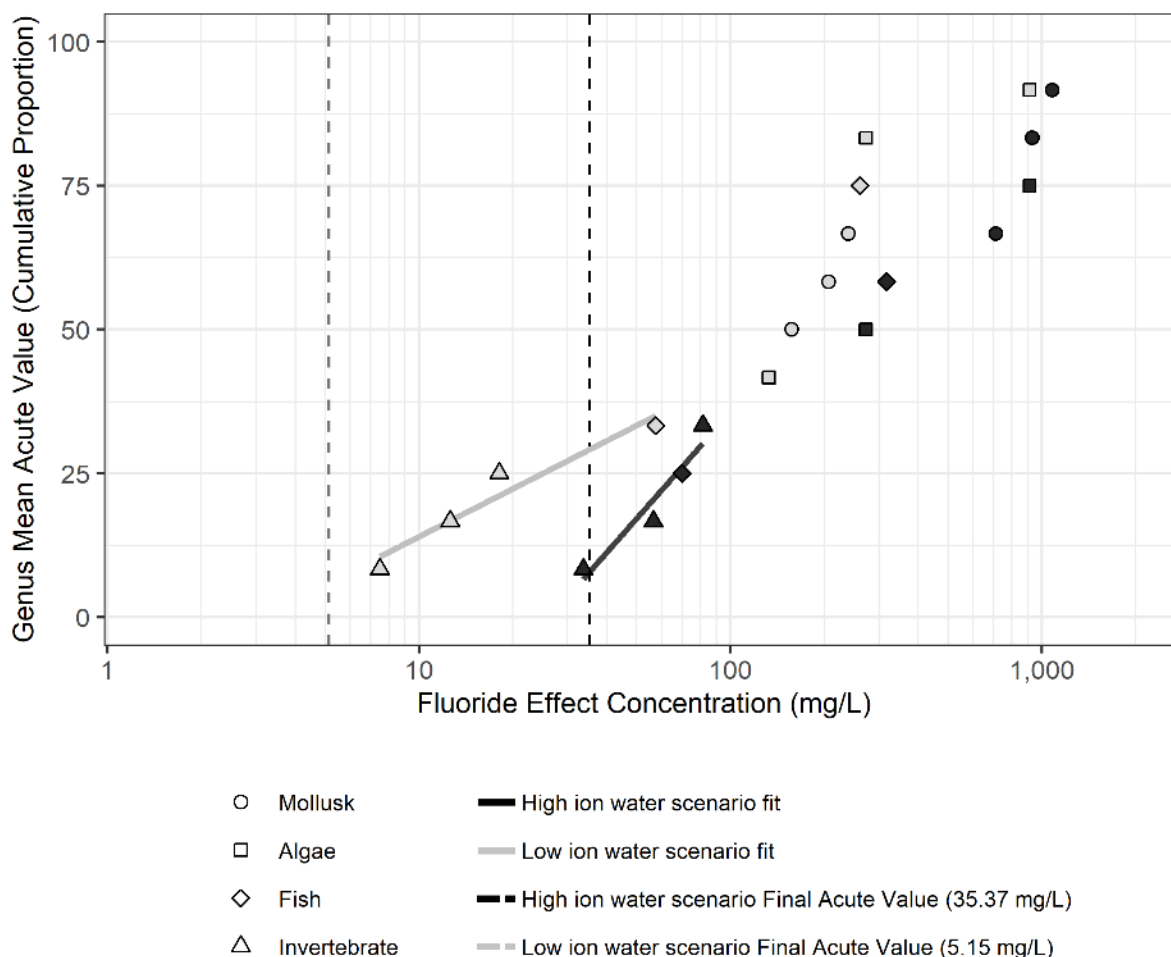


Figure 4-4 Cumulative proportion of GMAV and fluoride effect concentration with corresponding hard and soft water FAVs

FAVs are calculated by interpolating or extrapolating the 5th percentile of the cumulative probability distribution. The FAV from the low ion water scenario FAV_{LOW} was 5.2 mg/L fluoride. The FAV from the high ion water scenario FAV_{HIGH} was 35.4 mg/L fluoride. The FAV_{HIGH} was nearly 7 times greater than that of the FAV_{LOW} . The cumulative probability distribution of both water scenarios involved the same aquatic plant toxicity values. Given the high degree of tolerance of aquatic plants to fluoride, they are not considered in the evaluation of FAVs and likely do not warrant further evaluation.

One important nuance to the low and high ion water scenarios is that neither scenario fully controls for potential spurious conditions linked to the toxicity testing procedures. Some mortality in the control was noted for replicate tests of *H. Azteca* and the test procedure itself was being conducted as a *water only* test instead of the typical sediment toxicity test, which the method was designed to evaluate. The strong reliance on the *H. azteca* tests from Percy et al. (2015) and its sensitivity should be considered when evaluating these FAVs.



FAVs can be used to calculate criteria maximum concentrations (CMCs) by dividing by 2. Considering that the literature supporting the derivation of these values did not meet the acceptability requirements, no CMCs were derived. Similarly, FAVs can be used to derive chronic criteria using ACRs. A comparison of acute and chronic toxicity results from Percy et al. (2015) was reviewed to assess whether chloride or other water quality factors influenced the ACR (**Figure 4-5**). Generally, ACRs were consistent with mean \pm standard deviation ratios of 3.3 ± 1.5 and 2.8 ± 0.5 for *O. mykiss* and *H. azteca*, respectively. The derivation of chronic criteria using FAVs converted with ACRs presents an approach that captures the more robust MLR approach while leveraging the largest amount of available toxicity data.

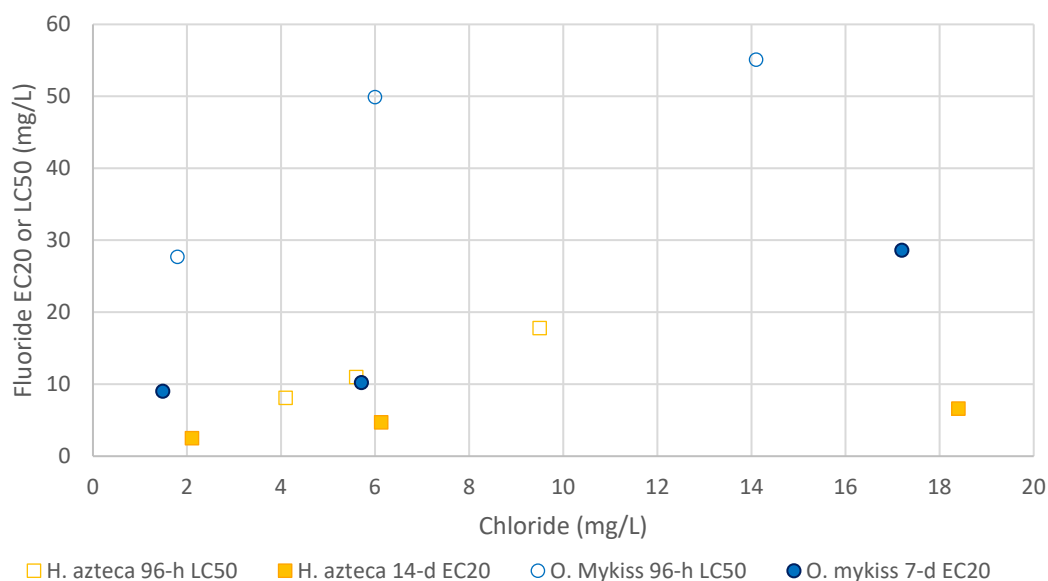


Figure 4-5 Pattern of acute and chronic *H. azteca* and *O. mykiss* toxicity data adopted from Percy et al (2015)

Estimated preliminary chronic criteria using the ACR approach ranged from 1.7 mg/L to 11.8 mg/L fluoride in low and high ion water scenarios, respectively. To place this estimate in context, the mean hardness-specific chronic criteria developed for the protection of aquatic life in Illinois, Michigan, and New York, USA and British Columbia, Canada would be 2.2 mg/L and 2.6 mg/L for the hardness concentrations in the low and high ion scenarios, respectively. The ACR derived chronic value is comparable for low ion regions but the current criteria likely significantly overestimate acceptable levels of fluoride risk in ion rich environments. This highlights the importance of thorough considerations of fluoride toxicity where alkalinity and chloride are elevated or increasing. Such patterns of increasing chloride and alkalinity are occurring in surface waters throughout the Northeast United States and other regions globally. **Figure 4-3** illustrates the distribution of high and low ion water scenarios across the United States. Roughly one-third of the surface water bodies where data exist would be at or below the low ion conditions, at or above the high ion conditions, or between the two. This suggests that greater than existing aquatic life guidance is overly conservative in at least two-thirds of the United States. Preliminary criteria derived using acute freshwater toxicity values highlight the strength of MLR approaches to adequately constrain estimates of toxicity and the utility of ACRs.



4.3.1.2 Chronic Toxicity to Freshwater Fauna and Flora

A summary of key findings from additional studies on the chronic toxicity of fluoride to aquatic invertebrates, fish and plants are provided below based on the raw toxicity information reported. No toxicity normalization was conducted; therefore, the discussed chronic toxicity data contributed to SSDs on reported IC₁₀ or NOEC for long-term studies that evaluated growth, reproduction or mortality endpoints.

Invertebrates

Alonso and Camargo (2011) examined sub-chronic (14-day) effects of fluoride on the survival and mobility of the aquatic snail *Potamopyrgus antipodarum*. Particularly, the study was interested in whether increasing fluoride would affect the speed of the organism. The study demonstrated that snail speed was a more sensitive endpoint than survival and mobility. Mortality and immobility NOEC and LOEC resulting from fluoride exposure was 17.5 mg/L and 37.0 mg/L, respectively.

Fieser et al. (1986) evaluated the effect of fluorides on the survival and reproduction of *Daphnia magna* over chronic and acute test durations in hard water. Chronic tests on *D. magna* occurred over 21 days and examined survival and reproduction. A reproduction NOEC was observed at a fluoride concentration of 26.1 mg/L and a LOEC was observed at 35.5 mg/L fluoride. Only a single mortality was observed at the highest chronic treatment of 158.0 mg/L fluoride.

Keller and Augspurger (2005) assessed the toxicity of fluoride to an endangered unionid mussel. Longer duration chronic tests on mortality were also conducted, 9-day (216-h) LC₅₀ tests on *A. raveneliana* and *L. fasciola* were 223 mg/L and 177 mg/L fluoride, respectively. Sub-chronic exposures during the 9-day test indicated that growth impairment occurs at a concentration of 31 mg/L fluoride, a concentration 17 times greater than the criteria permitted by the State of North Carolina.

Metcalf-Smith et al. (2003) was the only study in the literature that explicitly evaluated the toxicity of fluoride in bulk sediment. Long-term growth studies (10 to 28-d) and survival tests on *H. Azteca*, *C. tentans* and *H. limbata* were conducted. IC₂₅ for the growth endpoints were 290.2 mg/kg, 661.4 mg/kg and 1,221.3 mg/kg sediment fluoride for the three invertebrate taxa, respectively. LC₅₀ concentrations in sediment were 1,114.6 mg/kg, 1,652.2 mg/kg and 5,600 mg/kg for *H. azteca*, *H. limbata* and *C. tentans*, respectively.

Pearcy et al. (2015) also evaluated fluoride chronic toxicity tests on eight species for survival and growth endpoints. Test species included *H. azteca*, *Ceriodaphnia dubia*, *Chironomus dilutes*, *P. promelas*, *O. mykiss*, *Salvelinus namacush* (lake trout), *Lemna minor* (duckweed) and the algae *Pseudokirchneriella subcapitata*. The most sensitive species tested was *H. azteca*, which had a 14-day IC₁₀ of growth at 1.8 mg/L fluoride in water with chloride of 2.11 mg/L, hardness of 90 mg/L CaCO₃ and alkalinity of 58 mg/L CaCO₃. The chronic LC₅₀ for *H. azteca* was 4.8 mg/L to 12.9 mg/L fluoride. Replicate *C. dubia* tests were conducted for survival and reproduction. IC₁₀ ranged from 8.0 to 14.9 mg/L with no indication that chloride affected the concentration of fluoride growth inhibition. LC₅₀ for *C. dubia* ranged from 41.8 to 83.9 mg/L fluoride.

Fish

Camargo and Tarazona (1991) assessed the toxicity of fluoride in soft water to *O. mykiss* (rainbow trout) and *S. trutta* (brown trout) using chronic (8-day) static bioassays. Two-month-old fingerling



trout were used in the toxicity testing for lethal endpoints. LC₅₀ for *O. mykiss* corresponded to fluoride concentrations of 92.4, 85.1, 73.4 and 64.1 mg/L for exposure durations of 120, 144, 168 and 192 hours, respectively. LC₅₀ for *S. trutta* corresponded to fluoride concentrations of 135.6, 118.5, 105.1 and 97.5 mg/L for exposure durations of 120, 144, 168 and 192 hours, respectively. *S. trutta* was less sensitive to fluoride exposure than *O. mykiss*. Concurrent NaCl controls tests were also conducted using NaCl to rule out toxicity associated with sodium or chloride. Lethal 7-day NOECs and LOECs could be estimated for *O. mykiss* at concentrations of 22.3 and 34.3 mg/L fluoride, respectively. Lethal 7-day NOECs and LOECs could be estimated for *S. trutta* at concentrations of 0.08 and 34.5 mg/L fluoride, respectively. The variable dosing concentrations of fluoride between the study organisms likely influenced the estimated NOECs and LOECs.

Metcalf-Smith et al. (2003) assessed sediment and surface water toxicity of fluoride to freshwater organisms. Chronic, 7-day growth and survival tests were conducted on larval fathead minnows (*P. promelas*) across two treatments of water hardness (280 mg/L CaCO₃ and 160 mg/L CaCO₃). At a hardness of 160 mg/L CaCO₃, NOEC, LOEC and IC₂₅ concentrations for survival were 63 mg/L, 125 mg/L and 132 mg/L fluoride, respectively and NOEC, LOEC and IC₂₅ concentrations for growth were 63 mg/L, 125 mg/L and 72 mg/L fluoride, respectively. At a hardness of 280 mg/L CaCO₃, NOEC, LOEC and IC₂₅ concentrations for survival were 125 mg/L, 250 mg/L and 145 mg/L fluoride, respectively and NOEC, LOEC, and IC₂₅ concentrations for growth were 63 mg/L, 125 mg/L and 94 mg/L fluoride, respectively.

Metcalf-Smith et al. (2003) was the only study in the literature that explicitly evaluated the chronic toxicity of fluoride in bulk sediment. No growth or mortality effects were noted for sediment testing associated with juvenile *P. promelas* at concentrations up to 5,600 mg/kg.

Chronic toxicity testing of swim-stage *O. mykiss* was the most sensitive fish taxa evaluated by Pearcy et al. (2015). Results of 7-day chronic growth IC₁₀ under the lowest chloride treatment was 6.0 mg/L fluoride and the LC₅₀ was 11.5 mg/L fluoride. A 17-day embryo development test was conducted on *S. namaycush*. Both IC₁₀ and LC₅₀ toxicity tests did not affect the embryo viability at the greatest test concentration greater than 134 mg/L fluoride.

Shi et al. (2009) conducted a chronic (90-day) growth trial to determine the accumulation of fluoride in *Acipenser baerii* (Siberian sturgeon). Juvenile sturgeon (10.83 ± 0.05 cm body length, 8.55 ± 0.09 g wet body weight) were exposed to four fluoride treatments with nominal surface water concentrations of 4, 10, 25 and 62.5 mg/L. An unpublished acute toxicity (96-h) LC₅₀ of 125 mg/L fluoride for two-month-old *A. baerii* informed the nominal fluoride treatments. Growth parameters were assessed based on specific growth rate (SGR) and final body weight. SGR NOEC and LOEC occurred at a concentration of 18.7 mg/L and 51.8 mg/L fluoride, respectively. Final body weight NOEC and LOEC occurred at a concentration of 3.1 mg/L and 7.8 mg/L fluoride, respectively. A comprehensive dataset of fluoride concentration in tissue/organ groups is provided, which provides useful information for calculating species-specific BAFs, which is discussed in greater detail in **Section 4.3.1.3.**

Plants

Chronic plant toxicity testing by Pearcy et al. (2015) indicated that fluoride did not have a pronounced effect on the growth of *L. minor* or *P. subcapitata*. *L. minor* IC₁₀ concentrations for frond growth and dry weight endpoints were 125 and 215 mg/L fluoride, respectively. *P. subcapitata* algal cell growth IC₁₀ was 195 mg/L fluoride. No LC₅₀ concentrations were quantified.



Hekman et al. (1984) studied the responses (growth, photosynthesis, dark respiration, elonase activity and fluoride uptake) of six freshwater planktonic algae to fluoride concentrations up to 150 mg/L. The algal species evaluated included *Synechococcus leopoliensis*, *Oscillatoria limnetica*, *Ankistradesmus braunii*, *Scenedesmus quadricauda*, *Cyclotella meneghianiana* and *Stephanodiscus minatus*. Five of the six algal species showed no significant effect on growth at 50 mg/L fluoride and were considered NOECs. The NOEC for *S. leopoliensis* was 25 mg/L fluoride.

Freshwater Chronic Criterion Estimation

Using the acceptable minimum species toxicity value and the SSD Toolbox, preliminary freshwater chronic criterion were estimated for fluoride at the HC₅ (**Figure 4-6**). The triangular cumulative probability distribution exhibited the best model fit of the models tested.

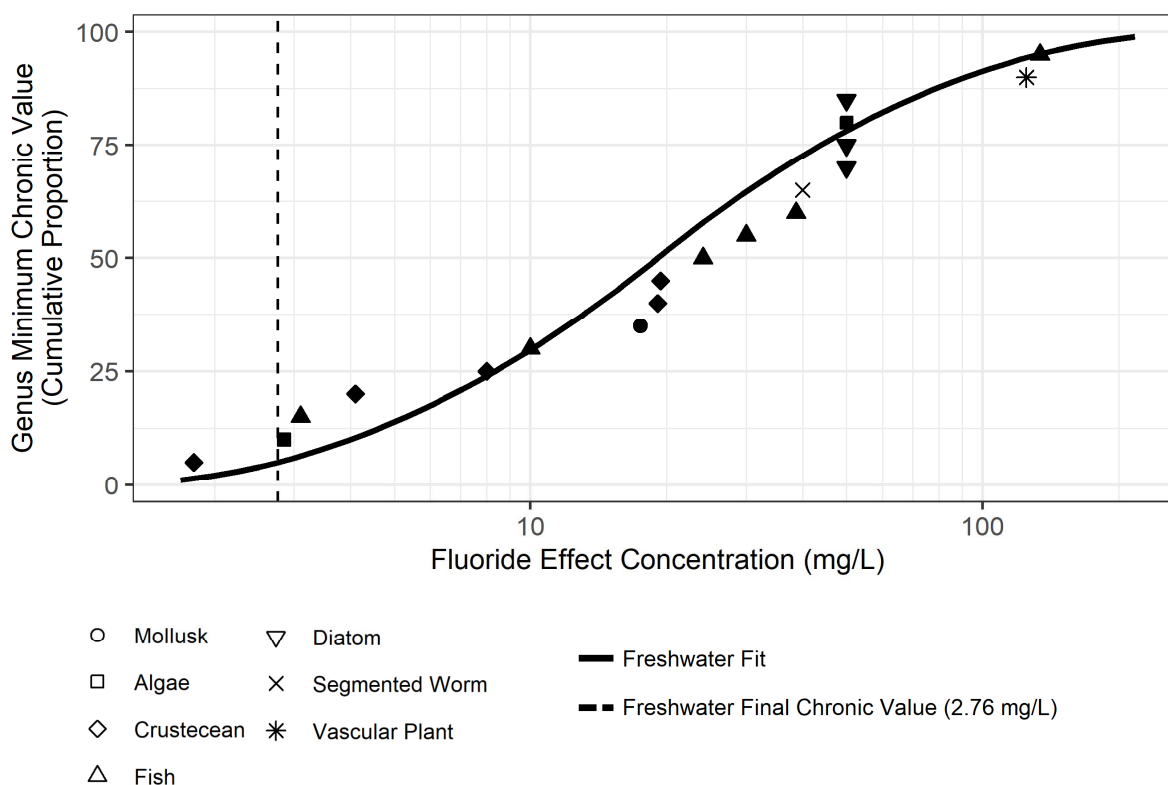


Figure 4-6 Cumulative proportion of genus minimum chronic value and fluoride effect concentration in freshwater

4.3.1.3 Bioaccumulation Potential and Other Considerations

As noted in **Section 4.2.1**, bioaccumulation of fluoride in aquatic invertebrates and fish are known to occur. Increasing fluoride exposure in water results in increasing fluoride concentration in aquatic organisms, particularly in the exoskeletons for invertebrates and bones or cartilage of vertebrates (Shi et al., 2009; Gonzalo and Camargo, 2012; Aguirre-Sierra et al., 2013). **Figure 4-7** summarizes the range of BAFs between surface water and tissue evaluated within the literature.

Bone and cartilage were the location of the greatest accumulated fluoride in the *A. baerii*, followed by gill and skin soft tissues at much lower concentrations (Shi et al., 2009). Muscle, liver, gut and pylorus did not tend to show an increasing concentration of fluoride tissue concentration with increased water concentrations. The whole-body concentration of fluoride in the *S. commercialis*



oyster increased with increasing concentration. Typical with most bioaccumulating compounds, fluoride BAFs decreased with greater exposure concentrations.

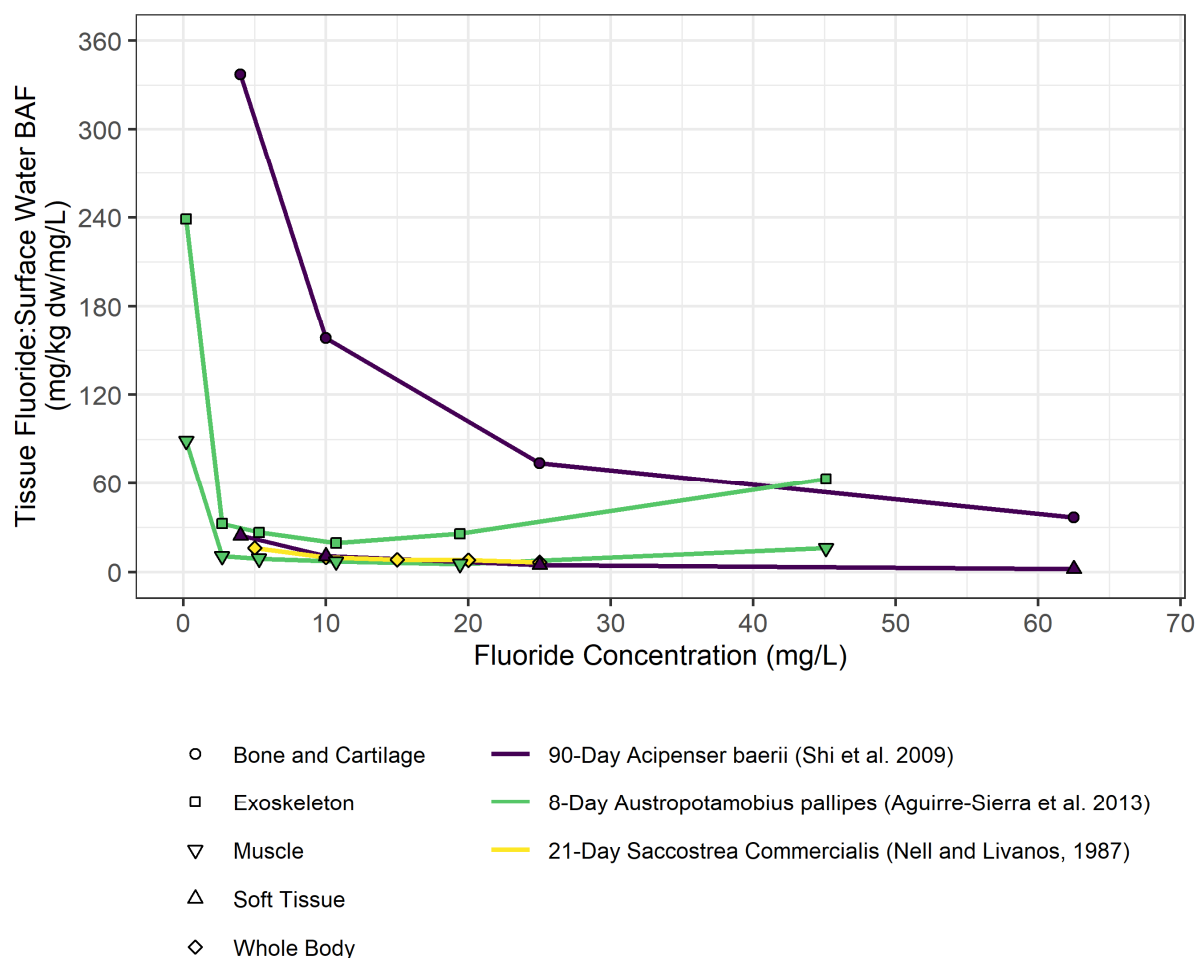


Figure 4-7 Summary of fluoride bioaccumulation factors (BAFs) by increasing fluoride concentration for surface water exposure conditions

Robust studies documenting the potential for fluoride to transfer or bioaccumulation from organism to organism in a freshwater food web have not been well documented. Rać et al. (2005) studied how the shell of a freshwater snail *Helix aspersa maxima* can act as a protection of bioaccumulation of sodium fluoride. Across a range of fluoride doses in food for a 40-day exposure period (control, 133, 665 and 1,330 mg/kg), the shell exhibited the greatest fluoride concentration (64.8, 638.2, 1,680.7 and 1,137.5 mg/kg) and the foot the least (7.9, 36.4, 182.5 and 145.9 mg/kg). BAFs, which are calculated by dividing tissue concentration by the concentration in the medium which in this case was food, were typically less than 1 for soft tissues and 0.9 to 4.8 for the shell. Only at a lower dose concentration and a longer duration did BAF increase in soft tissue. The low BAFs for food ingestion pathways provide support that surface water exposure is the predominant source of fluoride in aquatic organisms.

A single paper has been published that suggests that fluoride has the potential to biomagnify (Del Piero et al. 2012); however, no evidence of this was experimentally demonstrated. Moreover, no information was provided in Del Piero et al. (2012) as to the depuration procedures for purging the digestive tracks of test molluscs, which would be essential to demonstrate soft tissue concentrations observed were not the result of entrained particulate matter.



4.3.2 Marine

A summary of key findings from notable studies on the acute and chronic toxicity of fluoride to marine invertebrates, fish and plants is provided below based on the raw toxicity information reported.

4.3.2.1 Toxicity to Marine Fauna and Flora

Hemens and Warwick (1972) evaluated the effect of fluoride on estuarine organisms. Acute (96-h) testing was conducted on two species of prawns (*Penaeus indicus* and *Penaeus monodon*) and three species of fish (*Mugil cephalus*, *Ambassis safgha* and *Therapon jarbua*). Acute exposure to fluoride concentrations up to 100 mg/L did not show lethal effects. NOEC and LOEC estimated from the 5-day toxicity test on the *Perna* (brown mussel) were 1.2 and 7.2 mg/L, respectively.

Long-term (72-day) studies were also conducted in outdoor mesocosms on three species of invertebrates (*Penaeus indicus* [Indian prawn], *Palamon pacificus* [shrimp], *Tylodioplax blephariskios* [mud crab]) and one fish *Mugil cephalus* (mullet). Mesocosm fluoride concentrations were 1.05 mg/L in the control and 52.0 mg/L in the fluoride treated system. *T. blephariskios* and *P. pacificus* showed 61.4 and 22.8 percent reductions in survival from control to treatment. No apparent reductions in survival were noted for *P. indicus* and *M. cephalus* in the treated mesocosm. Non-lethal effects were noted particularly for *M. cephalus*; however, these effects were not quantified.

Oliveira et al. (1978) conducted culture studies to understand the effects of fluoride on the growth of marine phytoplankton. Chronic exposure conditions were studied ranging from 18 to 25 days. Eight species showed no effects on culture growth at the highest exposure concentration of 100 mg/L. Species with estimated NOECs of 100 mg/L fluoride include *Agmenellum quadruplicatum* (Marine Algae), *Dunaliella tertiolecta* (Marine Green Algae), *Nannochloris oculata* (Marine Algae), *Chroomonas salina* (Marine Algae), *Rhodomonas lens* (Marine Algae), *Bellerochea polymorpha* (Marine Diatom), *Chaetoceros gracilis* (Marine Diatom), and *Thalassiosira weissflogii* (Marine Diatom), *Pavlova lutheri* (Marine Haptophyte), *Prasinocladus marimus* (Marine Algae), and *Nitzschia angularis* var. *affinis* (Marine Diatom) had an estimated NOEC of 50 mg/L and a LOEC of 100 mg/L fluoride. *Amphidinium carteri* (Marine Dinoflagellate) was the most sensitive phytoplankton with an estimated NOEC and LOEC of 25 and 50 mg/L fluoride, respectively.

Nell and Livanos (1988) studied the effects of fluoride concentration in seawater on the growth and fluoride accumulation in spat oyster species; *Saccostrea commercialis* (Sydney rock oyster) and *Ostrea angasi* (flat oyster). Spat are an early life stage of an oyster that occurs after the mobile life stage establishes or sets onto a media. Over a 21-day study period *S. commercialis* exposed to 30.7 mg/L fluoride had a 20 percent reduction in biomass; therefore, the EC₂₀ was estimated to be 30.7 mg/L. Four salinity treatments (15, 25, 35 and 45 ppt) were tested under control and 30.7 mg/L fluoride exposure conditions. Growth was optimal at salinities of 25 and 35 ppt, but increased fluoride resulted in reduced growth for all treatments except the 25 ppt for the flat oyster.

Wright and Davison (1975) assessed the accumulation of fluoride by marine and intertidal invertebrates. Three species of crab (*Portunus depurator* [Swimming Crab], *Cancer pagurus* [Edible Crab], and *Carcinus maenas* [Shore Crab]) and *Mytilus edulis* (Edible Mussel) were studied in artificial seawater at a salinity of 34.38 ppt. Chronic tests of crab species showed no lethal effects after 90-day exposure to 30 mg/L fluoride (estimated NOEC = 30 mg/L). In a similar experiment with *M. edulis*, no mortality was observed at a concentration of 2.4 mg/L after 42 days and 100 percent



mortality was observed after 36 days exposed to 10 mg/L fluoride (estimated NOEC = 2.4 mg/L; estimated LOEC = 10 mg/L fluoride).

Connell and Airey (1982) studied the chronic effects of fluoride on the estuarine amphipods *Grandidierella lutosa* and *G. lignorum* using lifecycle bioassays. Duration of studies varied from 39 to 90 days (1 to 4 generations). Increase of mean fluoride level above background concentration of 1.3 to 1.7 mg/L in bioassays to 2.64 mg/L resulted in maximum amphipod population increases. MATC for population performance ranged between 5.0 and 6.2 mg/L fluoride. Reproduction data on female amphipod fecundity suggested that MATC may be as low as 4.15 mg/L fluoride.

4.3.2.2 Marine Chronic Criterion Estimation

Using the acceptable minimum species toxicity value and the SSD Toolbox, the preliminary marine chronic criterion could be estimated for fluoride at the HC₅ (**Figure 4-8**). The Burr cumulative probability distribution exhibited the best model fit among the models tested. However, given the uncertainty regarding the data gap between 3.8 and 30 mg/L fluoride the value was considered low confidence and not put forth.

Based on the data available the preliminary FCV is anticipated to be greater than many of the existing marine water aquatic life guidance summarized in **Section 3**, which indicates that most marine criteria adopted are overly conservative. This is likely attributed to the use of assessment factors or other tools to address data limitations at the time of derivation. The sensitivity of taxa to fluoride appears to be robust; however, the nature of the studies informing the SSD and the use of the NOECs provided some artefacts associated with bimodal toxicity values of similar fluoride concentration. Additional focused toxicological assessments in the marine environment could be considered; however, this may not be necessary given the known physiological adaptations of species to exist in a solute-rich environment.

The marine chronic SSD relied heavily on the use of NOECs rather than EC₁₀, which can introduce artefacts that make distribution fitting difficult. This effect is apparent in the clusters of minimum genus values at 30, 50 and 100 mg/L fluoride. Treatment concentrations in Oliveira et al., (1978), Nell and Livanos (1988), Wright and Davison (1975) and Hemens and Warwick (1972) all had concentrations that targeted this range.

Nevertheless, key themes are evident through the preliminary development of marine chronic criterion. First, marine organisms are generally less sensitive to chronic toxicity of fluoride than freshwater organisms. Second, invertebrates tend to be the most sensitive organisms to fluoride exposure while marine flora is most tolerant of surface water fluoride – leaving fish somewhat in the middle. These themes align well with the patterns observed in the freshwater dataset.

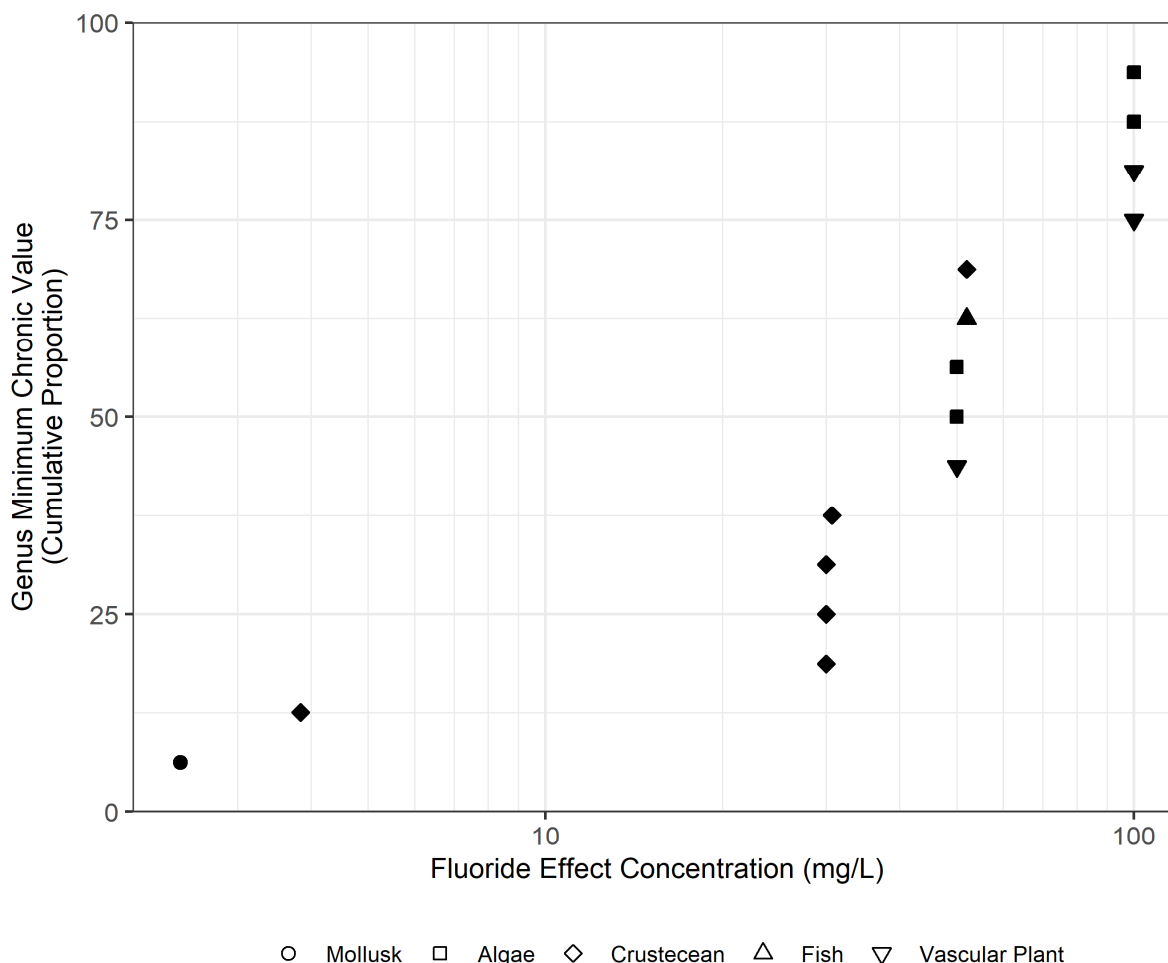


Figure 4-8 Cumulative proportion of genus minimum chronic value and fluoride effect concentration in marine water

4.3.2.3 Bioaccumulation Potential and Other Considerations

The bioaccumulation potential for fluoride in the marine environment is not fully understood; however, like the freshwater environment, the capacity for organisms to bioaccumulate fluoride from surface water does exist. As indicated in **Section 4.3.1.3**, organisms that grow calcium-rich shells or other hard tissues bioaccumulate fluoride. Tissue concentrations of fluoride after the 72-day incubation of marine mesocosms in studies conducted by Hemens and Warwick (1972) were two to three times greater in study organisms within the treatment versus the control. Similarly, Nell and Livanos (1988) observed greater fluoride accumulation in spat held in 15 ppt salinity water than in other treatments (**Figure 4-7**).

Given the increased concerns regarding the health of corals in marine environments, a brief review of the accumulation and potential for ecotoxicity of fluoride to corals is discussed below. Corals are known to accumulate the naturally occurring fluoride within marine waters.

Corals typically contain between 500 and 1,300 ppm F (Ramos et al., 2005; Tanaka and Ohde, 2010). The proposed mechanism for fluoride incorporation into the aragonite structure is a substitution reaction described in **Equation 4-6** where two fluoride ions exchange for a carbonate ion (Ichikuni, 1979).



Equation 4-6 $\text{CaCO}_3 + 2\text{F}^- = \text{CaF}_2 + \text{CO}_3^{2-}$

From this reaction, the fluoride content in CaCO_3 is dependent on seawater concentrations of the carbonate anion (CO_3^{2-}) and fluoride. As fluoride is a conservative constituent of seawater, the concentration of carbonate is thought to be the main factor controlling fluoride content in skeletal aragonite (Kendrick, 2018). Indeed, the ratio of F:Ca in corals has been demonstrated to increase linearly with increasing $[\text{F}^-]/[\text{CO}_3^{2-}]$ in seawater (Ramos et al., 2005; Tanaka and Ohde, 2010; Tanaka et al., 2013).

Tanaka and Ohde (2010) found that F:Ca ratios (milli mole per mole, mmol/mol) varied from 3 to 7 in corals collected from locations around the East Pacific and this variability was strongly proportional to the $[\text{F}^-]:[\text{CO}_3^{2-}]$ ratio in seawater. Carbonate concentrations in seawater increase with increasing temperature and decrease with increasing pCO_2 , which is the partial pressure of carbon dioxide, at the water surface. While scientific literature on fluoride toxicity to corals and other CaCO_3 skeletal organisms is sparse, increasing global temperatures and atmospheric CO_2 levels could have a profound impact on F mineralization in skeletal CaCO_3 and warrants further research. As biogenic precipitation of CaCO_3 is one of the major F sinks in the marine environment, the toxicity of F to organisms like corals and associated symbiotic algae is a key data gap in understanding F impacts on the marine environment.

The incorporation of F into CaCO_3 minerals represents one of the few F sinks present in the ocean. Of the various marine CaCO_3 mineralization pathways, the biogenic precipitation of aragonite is the most favourable pathway for fluoride incorporation into CaCO_3 structures. Aragonite and calcite are each polymorphs of calcium carbonate, sharing the same chemical formula but having different crystalline structures. Skeletal aragonite marine organisms have been found to contain greater F content than skeletal calcite organisms (Kitano and Okumura, 1973). Corals are one such organism that creates skeletons composed of aragonite and therefore incorporate relatively large amounts of F into their skeletal structures compared to other marine organisms. Kendrick (2018) found that coral, ooids (calcium carbonate-rich sedimentary grains) and marine algae that contain aragonite can contain between 500 and 1,700 mg/kg fluoride. Similarly, other calcareous algae can have up to 1,000 mg/kg fluoride.

While the lack of scientific literature on fluoride toxicity to coral species has been identified as a data gap in this assessment, it is unlikely that fluoride is toxic to corals in the normal range of natural seawater concentrations. There are, however, numerous external anthropogenic stressors that do pose a threat to coral species. Sedimentation, eutrophication and chemical pollution all negatively impact coral survivorship, particularly in the larval stage (Richmond et al. 2018). Pesticides, sewage outfalls and toxic anti-fouling agents used on ships have all been shown to decrease larval survival and settlement (Richmond et al. 2018). Additionally, these same stressors may have negative impacts on zooxanthellae— symbiotic algae that provide the majority of coral's energy needs through photosynthesis (Richmond et al., 2018). Thus, while limited information is available on the direct impacts of fluoride to coral livelihood, it is unlikely that fluoride alone is driving toxicity in these species, given the multitude of stressors that are currently contributing to coral die-offs.

4.4 Summary of Review, Data Gaps and Recommendations

This aquatic ecotoxicity review summarized the available peer-reviewed literature on toxicity to freshwater and marine organisms provided a detailed overview of how certain factors, such as physical or chemical water quality conditions, can ameliorate or modify the toxicity of fluoride, and developed preliminary fluoride aquatic life criteria using approved guidance that leverage more



technically robust assessment methodologies. Findings, data gaps and recommendations for the freshwater and marine assessment are presented below.

In freshwaters, increased fluoride concentration, exposure time and water temperature enhance the toxic effects of fluoride on aquatic invertebrates and fish. Invertebrates tended to be the most sensitive taxonomic group to fluoride concentration, followed by fish and algae. The literature review noted that chloride concentration in surface water had a greater influence on the reduced toxicity of fluoride to freshwater organisms than calcium carbonate; however, further assessment discussed below indicated that multiple factors can contribute to the amelioration of fluoride toxicity in freshwater. Although the MDRs were not met for the freshwater acute and freshwater chronic data reviewed, the datasets were able to be assessed in detail to provide important insight into criteria derivation approaches that are more technically sophisticated, and leverage the most recent scientific understanding.

The acute freshwater assessment leveraged both reported and supplemental materials from peer-reviewed studies to assess how hardness, alkalinity and chloride affect the toxicity of fluoride to aquatic organisms. Unlike key findings in the literature that emphasized the importance of chloride and hardness as univariate factors that influence aquatic toxicity, this assessment found that multiple water quality parameters must be evaluated together to best predict the ameliorating effect to aquatic toxicity. Invertebrate acute toxicity LC_{50} was best predicted for *H. azteca* by chloride, alkalinity and hardness. For *H. azteca*, the best MLR model explained 90 percent of the variance in LC_{50} , whereas the chloride-only model explained 80 percent. The best model to explain the ameliorating effect of water quality parameters on fluoride toxicity in *O. mykiss* included hardness and alkalinity. For *O. mykiss*, the best model explained 39 percent of the variance in LC_{50} , whereas the chloride-only model explained 10 percent. It is also noteworthy that chloride is not included in the best model for predicting *O. mykiss* toxicity. These findings provide support for more robust water quality criteria derivation that incorporate site-specific water quality conditions. Existing promulgated guidelines that use hardness-specific approaches are useful, but more widespread adoption of MLR-based approaches that consider multiple water quality parameters are needed.

The optimized model enabled the normalization of available acute freshwater ecotoxicity data for preliminary criteria derivation that is dependent on site-specific water quality conditions. FAVs were calculated under low ion and high ion freshwater scenarios. The low ion water scenario was similar to surface waters present in the Northwest United States and Southwest Canada. The high ion water was similar to surface water in the Great Lakes and St. Lawrence River basins. High and low ion water scenarios resulted in FAVs of 35.4 and 5.2 mg/L, respectively. Surface water quality characteristics exhibiting hard water (high ion) resulted in a 7-fold increase in FAVs. The acute toxicity of the most sensitive species used in FAV derivation, *H. azteca*, influenced the resulting FAV estimation. A more thorough review of the suitability of inclusion of sediment benthic crustaceans, *H. azteca*, in water-only toxicity testing is recommended.

Application of ACRs can be used to estimate preliminary chronic criteria from FAVs. Mean \pm 1 standard deviations (SD) ACR for *O. mykiss* and *H. azteca* were 3.3 ± 1.5 and 2.8 ± 0.5 , respectively. Estimated preliminary chronic criteria using the ACR approach ranged from 1.7 mg/L to 11.8 mg/L fluoride in low and high ion water scenarios, respectively. To place this estimate in context, the mean hardness-specific chronic criteria developed for the protection of aquatic life in Illinois, Michigan, and New York, USA and British Columbia, Canada would be 2.2 mg/L and 2.6 mg/L for the hardness concentrations in the low and high ion scenarios, respectively. The ACR derived chronic value is comparable for low ion regions but the current criteria likely significantly overestimate



acceptable levels of fluoride risk in ion rich environments. This highlights the importance of thorough considerations of fluoride toxicity where alkalinity and chloride are elevated or increasing. Such patterns of increasing chloride and alkalinity are occurring in surface waters throughout the Northeast United States and other regions globally. Preliminary criteria derived using acute freshwater toxicity values highlight the strength of MLR approaches to adequately constrain estimates of toxicity and the utility of ACRs.

The chronic freshwater assessment leveraged available EC_{10} and NOEC effects measurements in several genera to develop preliminary chronic criteria. Within the reviewed literature, insufficient information was available to provide an MLR-based approach using multiple water quality parameters to predict chronic toxicity. Unlike the FAV estimation process, which used linear interpolation to estimate HC_5 , the USEPA SSD Toolbox software was used to fit the cumulative probability distribution to the unnormalized chronic data. Genus minimum chronic values were used to construct the SSD and multiple models were fit to the data. The triangular model exhibited the strongest fit to the freshwater chronic dataset. HC_5 was used as a preliminary FCV, which corresponded to a concentration of 2.76 mg/L fluoride. The 95 percent confidence interval (CI) of the FCV was 1.6 to 4.7 mg/L. The range of FCVs within the 95 percent CI captures much of the variation in the existing freshwater aquatic life guidance summarized in **Section 3**.

Although a strong degree of alignment exists in employing the SSD approach, the influence of unnormalized toxicity data to account for water quality conditions was apparent. The lower tail of the distribution was sensitive to a few toxicological studies, most notably the toxicity testing of *H. azteca* at low chloride concentrations. Nevertheless, the chronic FCV would be considered an appropriate criterion for the protection of aquatic life under some regulatory frameworks that do not emphasize the importance of accounting for known ameliorating factors of toxicity. Moreover, the use of distribution fitting tools, such as the SSD Toolbox should be considered over more traditional approaches that rely on linear interpolation or extrapolation for identifying FAVs or FCVs.

In marine waters, increased fluoride concentration, exposure time and water temperature were reported to enhance the toxic effects of fluoride on aquatic invertebrates and fish. Invertebrates tended to be the most sensitive taxonomic group to fluoride concentration, followed by fish and algae. The literature review noted that few studies have explicitly examined the ameliorating effect of water quality parameters. However, given the elevated total dissolved solids present in seawater, optimal salinity ranges between 25 and 35 ppt appeared to have the greatest influence on ameliorating fluoride toxicity.

The MDRs were not met for the marine acute data reviewed and no further assessment was conducted. However, the marine chronic datasets were still able to be assessed as preliminary tools for understanding the effect of fluoride on marine water. This review provided important insight into more technically sophisticated criteria derivation approaches that leverage the most recent scientific understanding.

The chronic marine assessment leveraged available NOEC effects measurements in several genera to develop preliminary chronic criteria. Within the reviewed literature, insufficient information was available to provide an MLR-based approach using multiple water quality parameters to predict chronic toxicity. The optimal cumulative probability distribution to the unnormalized genus minimum chronic values was the Burr type distribution. HC_5 was not put forward as a preliminary FCV, due to a large data gap, which in the SSD is between 4 and 30 mg/L fluoride. The anticipated range of preliminary marine FCVs is likely greater than many of the existing marine water aquatic life guidance summarized in **Section 3**, which indicates that most marine criteria adopted are overly



conservative. This is likely attributed to the use of assessment factors or other tools to address data limitations at the time of derivation. The sensitivity of taxa to fluoride appears to be robust; however, the nature of the studies informing the SSD and the use of the NOECs provided some artefacts associated with bimodal toxicity values of similar fluoride concentration. Additional focused toxicological assessments in the marine environment could be considered; however, this may not be necessary given the known physiological adaptations of species to exist in a solute-rich environment.

This assessment critically demonstrated the importance of toxicity ameliorating factors in the form of water quality parameters chloride, alkalinity and hardness through the MLR assessment. However, the current evaluation was limited to the availability of concurrent water quality measurements in the literature; other water quality parameters may be important for understanding the ameliorating effect on fluoride toxicity. Additional review of the potential for sulphate or nitrate, important ions in certain surface waters, is recommended to determine their effect on aquatic fluoride toxicity.

Resulting preliminary chronic and acute criteria highlighted the conservatism that currently exists in the promulgated regulatory frameworks. This is true particularly for waters with water quality conditions similar to, or more ion rich than, the high ion scenario evaluated. Guidance derived with the application of assessment factors in freshwater that are less than 1 mg/L are likely far too conservative and should be updated to reflect more robust understanding. This approach provides support to constrain acceptable levels of fluoride, independent of other physical attenuation mechanisms, such as mixing zones, which should also be considered.



5 Conclusions

This assessment used a multi-faceted approach to provide a detailed summary of important factors that should be considered when managing surface water fluoride. The current regulations of inorganic fluoride in surface waters are highly variable across regions of aluminium production globally. To effectively manage acceptable levels of surface water fluoride risk to aquatic receptors, this review summarized the distribution of background fluoride conditions in the environment, regulatory frameworks in key regions of aluminium production and the available scientific aquatic ecotoxicity literature and guideline derivation approaches for aquatic life criteria. This information helps inform and guide stakeholders on best practices for managing and communicating acceptable levels of risk associated with fluoride in the aquatic environment.

The review of background conditions influencing surface water fluoride concentration found that natural mineral weathering is one of the largest sources of fluoride to the environment. Phosphate fertilizer application, brick kilns and coal combustion are presently among the largest anthropogenic sources of fluoride to the environment. Once entrained in surface waters, a variety of biogeochemical processes affect the fate and transport of fluoride. Bicarbonate, calcium, magnesium and pH exert strong controls over fluoride mobility. However, in most freshwaters that are circumneutral, fluorine exists as free fluoride, which is highly mobile. The mobility and electronegativity of fluoride contribute to the lack of cost-effective remedial options for surface water fluoride removal.

A detailed evaluation of publicly sourced background surface water fluoride data was conducted. Continental level analysis was undertaken to understand the distribution of fluoride across broad geographic regions. Median background fluoride concentrations in freshwaters range from 0.11 mg/L in Asia to 0.30 mg/L in Africa. Although freshwater fluoride concentrations were relatively constrained at the continental scale, the high variability of concentrations became more apparent at the national scale and within the more local scales for a detailed assessment conducted across the United States. This variability is predominantly a reflection of local geology, which was found to be a primary driver of surface water fluoride concentration. Regions with abundant fluorine-containing mineral deposits tend to have the highest fluoride concentrations in surface water. Therefore, knowledge of regional mineralogy or geology would greatly improve constraining estimates of background freshwater fluoride.

Based on the available data for large river systems in the United States, aluminium production facilities did not have any discernible effect on surface water fluoride concentrations. Due to the natural background levels of fluoride in major river systems within the United States and the high rate of flux, it is difficult to detect the influence of anthropogenic fluoride inputs considering the natural weathering rates. Even at sampling locations downstream of plausible sources of fluoride, little changes in concentration were noted. This assessment, in conjunction with the knowledge of the high degree of fluoride loading from phosphate fertilizer application and significant atmospheric releases of fluoride associated with coal-fired power plants, supports the conclusion that aluminium production facilities have minimal effects at broader scales.

In marine waters, fluoride is naturally more abundant and has an average concentration of approximately 1.3 mg/L, versus the global freshwater median of 0.2 mg/L. Certain, more isolated, coastal marine water bodies may have even greater fluoride concentrations due to limited exchange and high evaporation rates. Elevated levels of fluoride and other ions have been observed in coastal wetlands. While fluoride is a conservative constituent of seawater and concentrations can be reasonably estimated for the open ocean, anomalies exist near coastal regions, estuaries and



hydrologically isolated saltwater bodies that are not well captured in the scientific literature. The higher typical fluoride concentrations in marine waters, and the large capacity to physically mix with fresh surface waters, lends support to situating aluminium production facilities near marine systems, if possible.

The review of surface water fluoride regulatory frameworks found that a high degree of contrast exists between the derivation approaches and assumptions used to develop existing drinking water quality guidelines, aquatic life criteria and the criteria established to manage the release of constituents to surface water. Drinking water quality guidelines, particularly MACs, are largely informed by conditions that may result in increased risk for moderate dental fluorosis, whereas the United States MCLs are based on increased potential for more pronounced effects, such as the long-term risk for skeletal fluorosis. Among the values identified for the protection of drinking water, the concentration of 1.5 mg/L fluoride had the greatest incidence of occurrence. Nevertheless, the existing guidelines employ conservative assumptions based on large doses from ingestion of food or other non-drinking water sources. In sources of drinking water, these criteria are adequately protective of identified receptor populations. However, drinking water criteria are often irrelevant points of comparison in surface waters where aquatic life would be the primary receptor of interest. Care should be taken to align the receptors with the overarching management objective.

The information that has supported historical aquatic life criteria derivation is inadequate. Existing aquatic life guidance was developed using antiquated approaches or reflect the limited information that was available at the time of derivation. There are multiple instances where freshwater criteria are at or below background concentrations of fluoride in surface water. Four hardness-specific guideline values in freshwater represent the most technically robust approaches currently in use; however, the toxicological data supporting these studies is limited and outdated. Marine water criteria rely heavily on background concentrations and a paucity of toxicological in the marine environment data was identified.

The review of specific case studies and factors influencing the regulation of surface water fluoride releases highlights the need for systematic understanding of the components contributing to effluent permits. Through the comparison of contrasting sites, it is apparent that certain geographic settings may be more favourable to the management of fluoride based solely on hydrological or geochemical characteristics of the receiving water body. Stormwater infrastructure systems can be effective tools for managing fluoride discharges in temperate regions with high rainfall. Storage and strategic release of these stormwaters can provide a source of low fluoride, freshwater to help mitigate and dynamically manage effluent releases containing fluoride.

The aquatic ecotoxicity review summarized the available peer-reviewed literature on toxicity to freshwater and marine organisms, provided a detailed overview of how certain factors, such as physical or chemical water quality conditions, can ameliorate or modify the toxicity of fluoride, and developed preliminary fluoride aquatic life criteria using approved guidance that leverage more technically robust assessment methodologies.

In freshwaters, increased fluoride concentration, exposure time, and water temperature were found to be key factors that enhance the toxic effects of fluoride to aquatic invertebrates and fish. Invertebrates tended to be the most sensitive taxonomic group to fluoride, followed by fish and algae. Surface water chloride was shown to have a greater ability to reduce the toxicity of fluoride to freshwater organisms than calcium carbonate.; however, further assessment indicated that multiple factors contribute to the amelioration of fluoride toxicity in freshwater.



The acute freshwater assessment leveraged both reported and supplemental materials from peer-reviewed studies to assess how hardness, alkalinity and chloride affect the toxicity of fluoride to aquatic organisms. The assessment concluded that multiple water quality parameters must be evaluated together to best predict the ameliorating effect on aquatic toxicity. Developed models could predict up to 90 percent of the variability in acute toxicity (LC_{50}). This assessment demonstrated that site-specific water quality parameters should be critical components to the derivation of aquatic fluoride guidance. FAVs were calculated under low ion and high ion freshwater scenarios. High and low ion water scenarios resulted in FAVs of 35.4 and 5.2 mg/L, respectively. Surface water quality characteristics exhibiting hard water (high ion) resulted in a 7-fold increase in FAVs. The acute toxicity of the most sensitive species used in FAV derivation, *H. azteca*, influenced the resulting FAV estimation.

Application of ACRs was used to estimate preliminary chronic criteria from FAVs. Mean \pm standard deviation ACR for *O. mykiss* and *H. azteca* was 3.3 ± 1.5 and 2.8 ± 0.5 , respectively. Estimated preliminary chronic criteria, final chronic values (FCVs), calculated using the ACR ranged from 1.7 mg/L to 11.8 mg/L fluoride in low and high ion water scenarios, respectively. Using the hardness concentrations of the low and high ion scenarios for the hardness-specific chronic criteria developed for the protection of aquatic life in Illinois, Michigan, and New York, USA and British Columbia, Canada results in fluoride limits of 2.2 mg/L and 2.6 mg/L, respectively. Therefore, the ACR derived chronic value is comparable for low ion regions but highlights the importance of thorough considerations of fluoride toxicity where waters are heavily ionized. Moreover, increasing chloride and alkalinity is a common pattern in surface waters throughout the Northeast United States and other regions globally. Preliminary criteria derived using acute freshwater toxicity values highlight the strength of MLR approaches to adequately constrain estimates of toxicity and the utility of ACRs.

The assessment of chronic criteria leveraged available EC_{10} and NOEC effects measurements in several genera to develop preliminary chronic criteria for freshwater and marine environments. Within the reviewed literature, insufficient information was available to provide an MLR-based approach using multiple water quality parameters to predict chronic toxicity. Using an SSD approach, an FCV of 2.76 mg/L fluoride was estimated in freshwater and somewhere between 4 and 30 mg/L in marine water. The 95 percent confidence interval of the freshwater FCVs captures much of the variation that exists in current freshwater criteria for aquatic life. Additional work into the marine guideline value represents an important data gap.

Although a strong degree of alignment exists in employing the SSD approach, the influence of unnormalized toxicity data to account for water quality conditions was apparent. The lower tail of the distribution was sensitive to a few toxicological studies, in the case of freshwater, and data gaps for marine water. Nevertheless, the chronic FCVs could be considered appropriate criteria for the protection of aquatic life under some regulatory frameworks that do not emphasize the importance of accounting for known ameliorating factors of toxicity.

The tiered assessment framework employed in this review highlights the importance of geogenic sources, as well as major anthropogenic sources not attributed to smelting, that affects background fluoride conditions in the environment. The biogeochemical processes that affect the fate and transport of fluoride also have an important role in mediating or ameliorating the toxicity of fluoride to aquatic receptors. Existing regulatory frameworks are inconsistent between regions, and aquatic fluoride criteria are likely overly conservative, due to the absence of regulatory mechanisms to account for physical attenuation through mixing or the ameliorating effect of other water quality compounds on fluoride toxicity. The aquatic ecotoxicity review demonstrates that more scientifically robust approaches to derive criteria exist and can be employed for fluoride. These advances will



have a significant effect on the current regulatory drivers. This is particularly relevant for regions where freshwaters are ion rich or in marine environments where current criteria are overly conservative and do not reflect the current state of the science.



6 Data Gaps and Recommendations

The findings of this review identified multiple information gaps, where more detailed assessment may be warranted. Although collection of targeted toxicity data could facilitate guideline derivation and should be considered, many of the data gaps and recommendations are intended to address tractable tools for stakeholders in the context of implementing more robust near- and long-term management strategies for aquatic fluoride. Data gaps are provided in italicized text and recommendations follow in normal text.

Understanding the distribution of water quality parameters that are known to affect fluoride toxicity is a key component of appropriately managing acceptable levels of risk. Knowledge of how these parameters change with seasonality is another crucial consideration, as increased flows will drive increased dilution in freshwaters low flow conditions may cause increases in concentrations of water quality parameters capable of ameliorating fluoride toxicity. Additional information from stakeholders regarding bicarbonate, calcium, magnesium, and pH in receiving water bodies and how these conditions vary seasonally would help to constrain estimates of fluoride toxicity – particularly during low flow conditions.

Limited publicly available data exists to facilitate validation of estimated fluoride concentrations in coastal and estuarine systems. Having the means to validate these estimates would be valuable, as the high natural fluoride concentrations and large capacity to physically mix with fresh surface waters could make these locations favourable for aluminium production facilities. Additional information from stakeholders operating in marine environments is requested to confirm this assessment.

The background assessment has established the primary anthropogenic sources of fluoride as phosphate fertilizer application, coal combustion and brick kiln emissions. In alignment with the conceptual exposure model, the ability for these sources to affect the aquatic environment was not readily observable. However, the influence of these anthropogenic sources on the terrestrial environment presents an important data gap to the stakeholders, where managing acceptable levels of terrestrial fluoride risk can also be a priority. Further review into the pathways by which these sources can deliver fluoride to the terrestrial environment and to surface waters may be useful from a risk management perspective. In addition, the relative magnitude of risks posed by atmospheric fluoride deposition versus unintended application through fertilizer application is of interest.

Existing regulatory frameworks are highly variable by region and aquatic fluoride criteria are overly conservative due to the absence of regulatory mechanisms to account for physical attenuation through mixing or the ameliorating effect of other water quality compounds on fluoride toxicity. Additional review of stakeholder information to elucidate the underlying assumptions that contribute to permit limits at individual facilities is warranted to identify which IAI assessment regions could see improvements in the management of fluoride limits using more defensible, scientific methods.

The role of stormwater in transporting localized soil or ground surface fluoride was identified as an important migration pathway. In addition, in high precipitation regions stormwater can provide a source of low fluoride, freshwater to help mitigate and dynamically manage effluent releases containing fluoride. More research is needed into alternative stormwater management approaches to best inform development at new aluminium production facilities or retrofit existing facilities facing challenges.



The assessment demonstrated that multiple parameters influence the toxicity of fluoride in freshwater and that the use of MLR approaches to predict fluoride toxicity can be used to develop robust guideline values that are based on site-specific conditions. However, some limitations of the approach were identified. Particularly, that insufficient information exists that explicitly demonstrates how a full range of potential ameliorating water quality factors (beyond hardness, chloride and alkalinity) affect fluoride toxicity. Additional review of the potential for sulphate or nitrate and other base cations and anions is recommended to determine their effect on aquatic fluoride toxicity. One cost-effective solution to addressing this data gap may be through the implementation of focused water quality parameter measurements to accompany whole-effluent toxicity testing that is required under certain operational permits.

Additional toxicological studies are needed in order to meet the MDRs for many of the acute and chronic tests in the freshwater and marine environment. Prior to any recommendation on additional toxicological studies, site-specific information is requested. A large portion of the primary literature reviewed reflects work funded by the aluminium or similar industries. Therefore, any additional information from IAI stakeholders could easily be incorporated to supplement this analysis.



7 References

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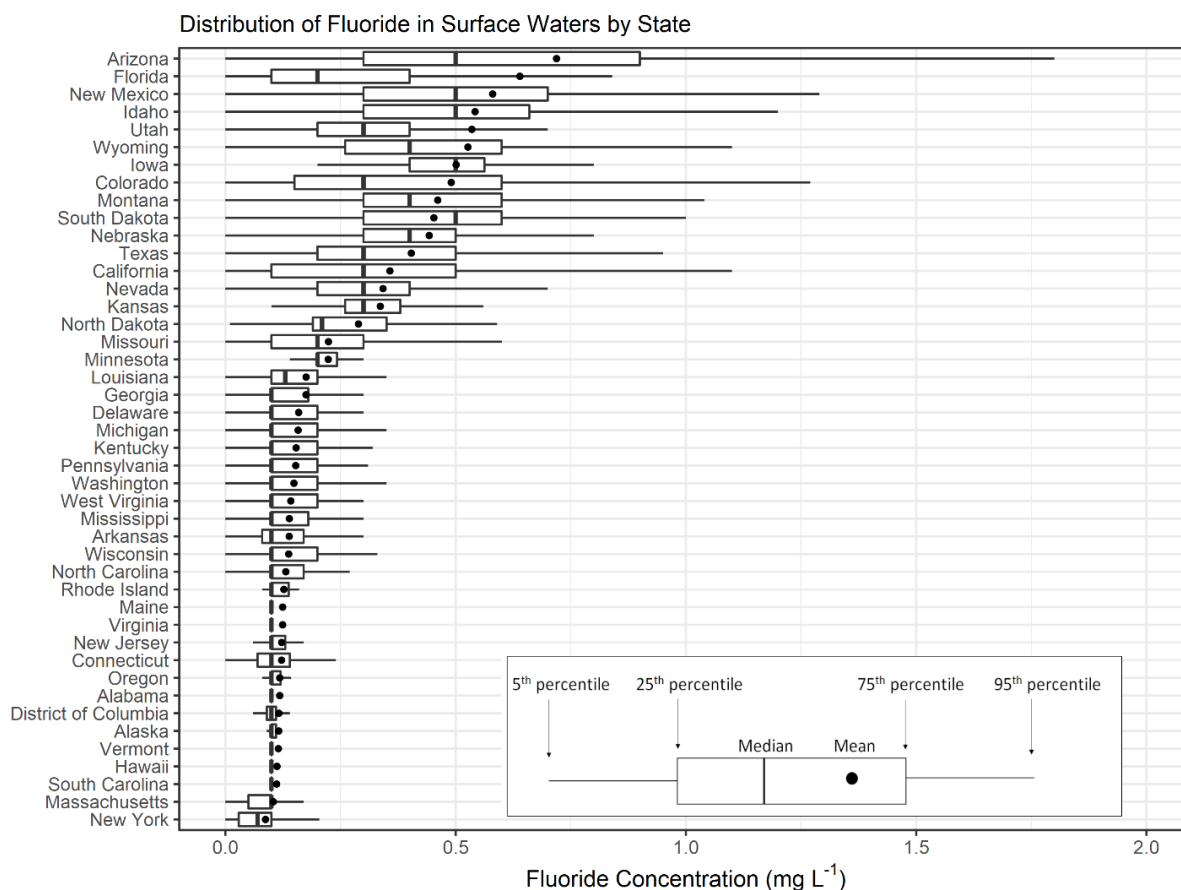
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Appendix A Supplemental Figures



Supplemental Figure A-1 **Surface water fluoride concentrations for all U.S. states with available data. This figure has been replaced in the body of the report with a version that only depicts states that contain primary or secondary aluminium smelters**



Appendix B Acute Toxicity Data Summary

Table B-1
Acceptable Acute Toxicity Data of Fluoride and Marine Aquatic Animals
Fluoride Regulatory Framework and Aquatic Toxicity Review - Appendix B

Family	Genus	Scientific Name	Common Name	Age, Size, Lifestage	Constituent	Endpoint(s) Type	Hardness (mg/L)	Alkalinity (mg/L)	Chloride (mg/L)	LC50/EC50 Value (mg/L)	Normalized LC50 Value (mg/L) (Hardness = 66 mg/L, Alkalinity = 58 mg/L, Chloride = 1.5 mg/L)	Normalized LC50 Value (mg/L) (Hardness = 124 mg/L, Alkalinity = 92 mg/L, Chloride = 25 mg/L)	Reference
Freshwater													
Kingdom: Animalia; Phylum: Annelida													
Naididae	Branchiura	Branchiura sowerbyi	Oligochaete	Gametes	NaF	Survival	--	--	--	80.07	--	--	Casellato et al. 2013
Kingdom: Animalia; Phylum: Arthropoda													
Chironomidae	Chironomus	Chironomus tentans	Midge	10--day old	NaF	Survival	145	--	--	32.3	--	--	Metcalfe-Smith et al. 2003
Daphniidae	Ceriodaphnia	Ceriodaphnia dubia	Daphnid	Neonate, <24h Post-Hatch	NaF	Mortality	250	--	--	157.9	--	--	Hickey 1989
		Ceriodaphnia pulchella	Water Flea	Neonate, <24h Post-Hatch	NaF	Mortality	250	--	--	83.2	--	--	Hickey 1989
	Daphnia	Daphnia carinata	Water Flea	Neonate, <24h Post-Hatch	NaF	Mortality	250	--	--	353.6	--	--	Hickey 1989
		Daphnia magna	Water Flea	Larvae <24h Post-Hatch	NaF	Mortality	173	--	--	340	--	--	LeBlanc 1980
				Larvae <24h Post-Hatch	NaF	Mortality	--	--	--	680	--	--	LeBlanc 1980
				Neonate, <24h Post-Hatch	NaF	Mortality	250	--	--	353.6	--	--	Hickey 1989
				1-7-day old	NaF	Survival	145	--	--	124.1	--	--	Metcalfe-Smith et al. 2003
				Neonate, <24h Post-Hatch	NaF	Mortality	250	--	--	201.5	--	--	Hickey 1989
Hyalellidae	Hyalella	Hyalella azteca	Amphipod	Obtained from Aquatic Biosystems	NaF	Mortality	10	4	1.8	--	--	--	Pearcy et al. 2015
							10	4	6	--	--	--	Pearcy et al. 2015
							10	4	14.1	--	--	--	Pearcy et al. 2015
							10	4	30.4	--	--	--	Pearcy et al. 2015
							24	26	4.8	10.6	5.6	25.4	Pearcy et al. 2015
							26	16	5.7	15.6	8.7	39.3	Pearcy et al. 2015
							26	16	22	26.8	7.2	32.6	Pearcy et al. 2015
							46	26	9.7	15.8	6.6	29.7	Pearcy et al. 2015
							48	34	11.7	28.1	10.0	44.9	Pearcy et al. 2015
							48	34	22.5	26.5	6.6	29.8	Pearcy et al. 2015
							86	60	24.5	31.1	7.2	32.5	Pearcy et al. 2015
							88	24	4.1	8.1	6.3	28.4	Pearcy et al. 2015
							88	24	5.6	11	7.2	32.6	Pearcy et al. 2015
							88	24	9.5	17.8	8.8	39.6	Pearcy et al. 2015
							88	24	18.8	24	8.2	36.9	Pearcy et al. 2015
							88	24	18.8	24.8	8.5	38.2	Pearcy et al. 2015
							154	18	44.2	32.9	8.6	38.7	Pearcy et al. 2015
							166	108	27.9	37.6	8.0	36.1	Pearcy et al. 2015
							166	108	51	50.9	7.8	35.3	Pearcy et al. 2015
							306	26	95	31.9	5.8	26.0	Pearcy et al. 2015
							316	196	37.8	--	--	--	Pearcy et al. 2015
							316	196	98.4	--	--	--	Pearcy et al. 2015
Hydropsychidae	Hydropsyche	Hydropsyche bulbifera	Caddisfly	Larva(e)	NaF	Mortality	16.94	28.955	9.59	26.3	8.7	39.2	Camargo and Tarazona 1990
		Hydropsyche exocellata	Caddisfly	Larva(e)	NaF	Mortality	12.61	22.56	6.705	26.5	10.7	48.1	Camargo and Tarazona 1990
		Hydropsyche lobata	Caddisfly	Larva(e)	NaF	Mortality	17.525	24.37	11.455	48.2	15.2	68.8	Camargo and Tarazona 1990
		Hydropsyche pellucidula	Caddisfly	Larva(e)	NaF	Mortality	18.185	28.655	5.405	38.5	17.7	79.7	Camargo and Tarazona 1990
Philopotamidae	Chimarra	Chimarra marginata	Caddisfly	Larva(e)	NaF	Mortality	12.61	22.56	6.705	44.9	18.1	81.5	Camargo and Tarazona 1990
Streptocephalidae	Streptocephalus	Streptocephalus proboscideus	Fairy Shrimp	--	NaF	Mortality	--	--	--	70.2926	--	--	Calleja et al. 1994
Ephemeridae	Hexagenia	Hexagenia limbata	Mayfly	3-4 Months old	NaF	Survival	145	--	--	282.8	--	--	Metcalfe-Smith et al. 2003
Kingdom: Animalia; Phylum: Chordata													
Acipenseridae	Acipenser	Acipenser baerii	Long-Nosed Siberian Sturgeon	Juvenile(s)	NaF	Mortality	--	--	--	125	--	--	Shi et al. 2009
Centrarchidae	Lepomis	Lepomis macrochirus	Bluegill	--	NaF	Mortality	--	--	--	>530	--	--	USEPA 1978
				Not coded	NaF	Mortality	--	--	--	830	--	--	USEPA 1992
										--	--	--	USEPA 1992
Channidae	Channa	Channa punctata	Snake-Head Catfish	--	NaF	Mortality	--	--	--	300	--	--	Saxena et al. 2001
Cyprinidae	Pimephales	Pimephales promelas	Fathead Minnow	--	NaF	Mortality	--	--	--	180	--	--	Smith et al. 1985
				10-day-old	NaF	Survival	145	--	--	262.4	--	--	Metcalfe-Smith et al. 2003
				--	NaF	Mortality	78	--	--	340	--	--	Smith et al. 1985
Gasterosteidae	Gasterosteus	Gasterosteus aculeatus	Threespine Stickleback				146	--	--	380	--	--	Smith et al. 1985
							300	--	--	460	--	--	Smith et al. 1985
Poeciliidae	Gambusia	Gambusia affinis	Western Mosquitofish	Female Adult(s)	NaF	Mortality	--	100	--	925	--	--	Wallen et al. 1957
										1240	--	--	Wallen et al. 1957

Table B-1
Acceptable Acute Toxicity Data of Fluoride to Freshwater and Marine Aquatic Animals
Fluoride Regulatory Framework and Aquatic Toxicity Review - Appendix B

Family	Genus	Scientific Name	Common Name	Age, Size, Lifestage	Constituent	Endpoint(s) Type	Hardness (mg/L)	Alkalinity (mg/L)	Chloride (mg/L)	LC50/EC50 Value (mg/L)	Normalized LC50 Value (mg/L) (Hardness = 66 mg/L, Alkalinity = 58 mg/L, Chloride = 1.5 mg/L)	Normalized LC50 Value (mg/L) (Hardness = 124 mg/L, Alkalinity = 92 mg/L, Chloride = 25 mg/L)	Reference
Salmonidae	Oncorhynchus	Oncorhynchus kisutch	Silver Salmon	172d	NaF	Mortality	--	47.5	--	--	--	--	Holland 1960
		Oncorhynchus mykiss	Rainbow Trout	--	NaF	Mortality	17	11	--	51	57.5	70.0	Pimentel and Bulkley 1983
							49	36	--	128	125.0	152.0	Pimentel and Bulkley 1983
							182	139	--	140	108.4	131.9	Pimentel and Bulkley 1983
							385	397	--	193	148.3	180.5	Pimentel and Bulkley 1983
							--	--	--	200	--	--	Smith et al. 1985
				Juvenile(s), 2 Months	NaF	Mortality	22.4	37.5	10	107.5	176.4	214.6	Camargo and Tarazona 1991
				Not coded	NaF	Mortality	--	--	--	317	--	--	USEPA 1992
										--	--	--	USEPA 1992
				Fry	NaF	Mortality	10	4	1.8	27.7	27.8	33.8	Pearcy et al. 2015
							10	4	6	49.9	50.1	61.0	Pearcy et al. 2015
							10	4	14.1	55.1	55.3	67.3	Pearcy et al. 2015
							10	4	30.4	90.9	91.3	111.1	Pearcy et al. 2015
							24	26	4.8	67.5	89.9	109.3	Pearcy et al. 2015
							26	16	5.7	10.4	10.6	12.9	Pearcy et al. 2015
							26	16	22	50.1	50.9	62.0	Pearcy et al. 2015
							46	26	9.7	110.4	96.9	117.9	Pearcy et al. 2015
							48	34	11.7	43.2	41.7	50.7	Pearcy et al. 2015
							48	34	22.5	34.1	32.9	40.0	Pearcy et al. 2015
							86	60	24.5	42.5	36.4	44.3	Pearcy et al. 2015
							88	24	4.1	123.4	69.0	84.0	Pearcy et al. 2015
							88	24	5.6	97.8	54.7	66.5	Pearcy et al. 2015
							88	24	9.5	150	83.9	102.0	Pearcy et al. 2015
							88	24	18.8	111.1	62.1	75.6	Pearcy et al. 2015
							154	18	44.2	118.5	40.7	49.5	Pearcy et al. 2015
							166	108	27.9	69.7	51.1	62.2	Pearcy et al. 2015
							166	108	51	54.2	39.7	48.3	Pearcy et al. 2015
		306	26				95	118.8	31.0	37.7	Pearcy et al. 2015		
		316	196	37.8	79.4	50.4	61.3	Pearcy et al. 2015					
	316	196	98.4	107.4	68.2	82.9	Pearcy et al. 2015						
	Salmo	Salmo trutta	Brown Trout	Juvenile(s), 2 Months	NaF	Mortality	21.2	32.2	10.8	164.5	261.1	317.6	Camargo and Tarazona 1991
				Organisms at different lifestages	Unknown	Mortality	--	--	--	125	--	--	Woodiwiss and Fretwell 1974
Kingdom: Animalia; Phylum: Mollusca													
Unionidae	Actinonaias	Actinonaias pectorosa	Pheasantshell Mussel	Juvenile	NaF	Survival	28	23	2	259	235.5	1062.8	Keller and Augspurger 2005
							30	47	2	178	136.4	615.4	Keller and Augspurger 2005
							68	108	2	347	254.3	1147.5	Keller and Augspurger 2005
							84	118	2	298	223.1	1006.8	Keller and Augspurger 2005
	Alasmidonta	Alasmidonta raveneliana	Appalachian Elktoe Mussel	glochidia	NaF	Survival	30	--	--	288	--	--	Keller and Augspurger 2005
				Juvenile	NaF	Survival	28	--	--	303	--	--	Keller and Augspurger 2005
				Lampsilis	Lampsilis fasciola	Wavy-Rayed Lampmussel	Juvenile	NaF	Survival	32	25	2	172
	Utterbackia	Utterbackia imbecillis	Paper Pondshell Mussel	glochidia	NaF	Survival	30	47	2	351	269.0	1213.5	Keller and Augspurger 2005
				Juvenile	NaF	Survival	34	27	2	234	212.6	959.3	Keller and Augspurger 2005
Kingdom: Animalia; Phylum: Rotifera													
Brachionidae	Brachionus	Brachionus calyciflorus	Rotifer	--	NaF	Mortality	--	--	--	183.3	--	--	Calleja et al. 1994
Kingdom: Plantae; Phylum: Chlorophyta													
Chlorellaceae	Chlorella	Chlorella vulgaris	Green Algae	Exponential growth phase (log)	NaF	Mortality	--	--	--	132.99			Rai et al. 1998
						Plant/Cell Growth	--	--	--	--			Rai et al. 1998
Scenedesmaceae	Scenedesmus	Scenedesmus subspicatus	Green Algae	Exponential growth phase (log)	NaF	Plant/Cell Growth	--	--	--	850			Kuhn and Pattard 1990
										900			Kuhn and Pattard 1990
										>1000			Kuhn and Pattard 1990
Selenastraceae	Raphidocelis	Pseudokirchneriella subcapitata	Green Algae	--	NaF	Plant/Cell Growth	--	--	--	272			USEPA 1978
				Exp. Growth Phase	NaF	Plant/Cell Growth	14	7	3.72	273			Pearcy et al. 2015

Table B-1
Acceptable Acute Toxicity Data of Fluoride to Freshwater and Marine Aquatic Animals
Fluoride Regulatory Framework and Aquatic Toxicity Review - Appendix B

Family	Genus	Scientific Name	Common Name	Age, Size, Lifestage	Constituent	Endpoint(s) Type	Hardness (mg/L)	Alkalinity (mg/L)	Chloride (mg/L)	LC50/EC50 Value (mg/L)	Normalized LC50 Value (mg/L) (Hardness = 66 mg/L, Alkalinity = 58 mg/L, Chloride = 1.5 mg/L)	Normalized LC50 Value (mg/L) (Hardness = 124 mg/L, Alkalinity = 92 mg/L, Chloride = 25 mg/L)	Reference
Marine Water													
Kingdom: Animalia; Phylum: Arthropoda													
Artemiidae	Artemia	Artemia salina	Brine Shrimp	--	NaF	Mortality	--	--	--	3040			Calleja 1994
Crangonidae	Crangon	Crangon crangon	Sand Shrimp	Adult(s)	NaF	Mortality	--	--	--	>300			Portmann and Wilson 1971
Palaemonidae	Palaemonetes	Palaemonetes pugio	Daggerblade Grass Shrimp	--	Unknown	Mortality	--	--	--	75.3			Curtis and Ward 1981
Penaeidae	Fenneropenaeus	Penaeus indicus	Indian Prawn	NR	NaF	Survival	--	--	--	--			Hemens and Warwick 1972
	Penaeus	Penaeus monodon	Prawn	NR	NaF	Survival	--	--	--	--			Hemens and Warwick 1972
Kingdom: Animalia; Phylum: Chordata													
Ambassidae	Ambassis	Ambassis safgha	(blank)	Adults	NaF	Survival	--	--	--	--			Hemens and Warwick 1972
Cyprinodontidae	Cyprinodon	Cyprinodon variegatus	Sheepshead Minnow	Juvenile(s)	NaF	Mortality	--	--	--	--			Heitmuller et al. 1981
										>500			Heitmuller et al. 1981
Mugilidae	Mugil	Mugil cephalus	Mullet	Juvenile	NaF	Survival	--	--	--	--			Hemens and Warwick 1972
Terapontidae	Terapon	Terapon jarbua	(blank)	Adults	NaF	Survival	--	--	--	--			Hemens and Warwick 1972
Kingdom: Animalia; Phylum: Mollusca													
Ostreidae	Magallana	Crassostrea gigas	Pacific Oyster	Larva(e)	NaF	Mortality	--	--	--	>100			Cardwell et al. 1979

Notes:

EC50 - Concentration that produces an effect in 50% of the test population
LC50 - Concentration that is lethal to 50% of the test population
mg/L - milligram per litre
NaF - Sodium fluoride
NR - Not reported

Family: Haliotidae
Genus: Haliotis



Appendix C Chronic Toxicity Data Summary

Table C-1
Acceptable Chronic Toxicity Data of Fluoride to Freshwater and Marine Organisms
Fluoride Regulatory Framework and Aquatic Toxicity Review - Appendix C

Family	Genus	Scientific Name	Common Name	Exposure Duration (days)	Age, Size, Lifestage	Constituent	Endpoint(s) Type	Hardness (mg/L)	Alkalinity (mg/L)	Chloride (mg/L)	EC10/IC10 Value (mg/L)	EC20/IC20 Value (mg/L)	NOEC Value (mg/L)	LOEC Value (mg/L)	Chronic Effect Measure	Chronic Value (mg/L)	SMCV (mg/L)	GMCV (mg/L)	Reference	
Freshwater																				
Kingdom: Animalia; Phylum: Annelida																				
Naididae	Branchiura	Branchiura sowerbyi	Oligochaete	18	Gametes	NaF	Survival	--	--	--	40	70	--	80	EC10	40	40	40	Casellato et al. 2013	
Kingdom: Animalia; Phylum: Arthropoda																				
Astacidae	Austropotamobius	Austropotamobiuse pallipes	White-Clawed Crayfish	8	6 months	NaF	Survival	189	--	--	--	--	19.4	45.1	NOEC	19.4	19.4	19.4	Aguirre-Sierra et al. 2013	
Chironomidae	Chironomus	Chironomus dilutus	Midge	10	3rd Instar	NaF	Survival and Growth	90	58	2.11	4.1	8.2	--	--	EC10	4.1	4.1	4.1	Pearcy et al. 2015	
Daphniidae	Ceriodaphnia	Ceriodaphnia dubia	Daphnid	7	<24h Neonate	NaF	Survival and Reproduction	82	62	2.11	12.5	16.5	--	--	EC10	12.5	8.0	8.0	Pearcy et al. 2015	
				7	<24h Neonate	NaF	Survival and Reproduction	82	62	6.27	9.5	11.5	--	--	EC10	9.5			Pearcy et al. 2015	
				7	<24h Neonate	NaF	Survival and Reproduction	88	56	18.8	14.9	16.6	--	--	EC10	14.9			Pearcy et al. 2015	
				7	<24h Neonate	NaF	Survival and Reproduction	88	64	18.5	8	10	--	--	EC10	8			Pearcy et al. 2015	
				7	<24h Neonate	NaF	Survival and Reproduction	90	56	6.21	9.3	13.9	--	--	EC10	9.3			Pearcy et al. 2015	
	Daphnia	Daphnia carinata	Water Flea	14	Neonate, <24h Post-Hatch	NaF	Reproduction	250	--	--	--	--	--	>50	--	--	--	--	Hickey 1989	
		Daphnia magna	Water Flea	21	Neonates (<24 h old)	NaF	Survival and Reproduction	145.2	135.4	3.8	--	--	26.1	35.5	NOEC	26.1	26.1	26.1	Fieser et al 1986	
				14	Neonate, <24h Post-Hatch	NaF	Reproduction	250	--	--	--	--	--	>50	--	--	--	--	Hickey 1989	
Hyalellidae	Hyalella	Hyalella azteca	Amphipod	21	Larvae <24h Post-Hatch	NaF	Reproduction	--	--	--	--	--	14	--	NOEC	14	14.0	14.0	Kuhn and Pattard 1989	
				14	Obtained from Aquatic Biosystems	NaF	Survival and Growth	88	58	18.4	5.2	6.6	--	--	EC10	5.2	1.8	1.8	Pearcy et al. 2015	
				14	Obtained from Aquatic Biosystems	NaF	Survival and Growth	88	60	6.13	3.8	4.7	--	--	EC10	3.8			Pearcy et al. 2015	
				14	Obtained from Aquatic Biosystems	NaF	Survival and Growth	90	58	2.11	1.8	2.5	--	--	EC10	1.8			Pearcy et al. 2015	
Kingdom: Animalia; Phylum: Chordata																				
Acipenseridae	Acipenser	Acipenser baerii	Long-Nosed Siberian Sturgeon	90	Juvenile (10.8+/- .05 cm tl, 8.55+/- .09 g ww)	NaF	Growth	22+/- 4	--	< 5.2	--	150	3.1	7.8	NOEC	3.1	3.1	3.1	Shi et al. 2009	
				90	Juvenile(s)	NaF	Growth	22	--	5.2	--	--	3.1	--	NOEC	3.1			Shi et al. 2009	
				90	Juvenile(s)	NaF	Growth	22	--	5.2	--	--	18.7	--	NOEC	18.7			Shi et al. 2009	
				90	Juvenile(s)	NaF	Growth	22	--	5.2	--	--	--	7.8	--	--			--	Shi et al. 2009
				90	Juvenile(s)	NaF	Growth	22	--	5.2	--	--	--	51.8	--	--			--	Shi et al. 2009
Channidae	Channa	Channa punctata	Snake-Head Catfish	90	--	NaF	Cell(s)	--	--	--	--	--	30	--	NOEC	30	30.0	30.0	Saxena et al. 2001	
				--	--	NaF	Cell(s)	--	--	--	--	--	60	--	NOEC	60			Saxena et al. 2001	
				--	--	NaF	Cell(s)	--	--	--	--	--	30	--	--	--			Saxena et al. 2001	
				--	--	NaF	Cell(s)	--	--	--	--	--	60	--	--	--			Saxena et al. 2001	
Cyprinidae	Cyprinus	Cyprinus carpio	Common Carp	7.2	--	NaF	Mortality	--	--	--	--	--	--	--	--	--	--	--	Neuhold and Sigler 1960	
				7	< 24 hrs	NaF	Growth	160	--	--	--	--	63	125	NOEC	63	63	63	Metcalfe-Smith et al. 2003	
	Pimephales	Pimephales promelas	Fathead Minnow	7	< 24 hrs	NaF	Growth	280	--	--	--	--	63	125	NOEC	63			Metcalfe-Smith et al. 2003	
				7	< 24 hrs	NaF	Survival	160	--	--	--	--	63	125	NOEC	63			Metcalfe-Smith et al. 2003	
				7	< 24 hrs	NaF	Survival	280	--	--	--	--	63	125	NOEC	63			Metcalfe-Smith et al. 2003	
				7	< 24h Posthatch	NaF	Survival and Growth	86	50	15.8	77.7	87.7	--	--	EC10	77.7			Pearcy et al. 2015	
				7	< 24h Posthatch	NaF	Survival and Growth	86	56	5.74	38.2	55.6	--	--	EC10	38.2			Pearcy et al. 2015	
				7	< 24h Posthatch	NaF	Survival and Growth	90	60	1.76	14.6	52.2	--	--	EC10	14.6			Pearcy et al. 2015	
Poeciliidae	Gambusia	Gambusia affinis	Western Mosquitofish	30	--	NaF	Cell(s)	178	--	44	--	--	10	--	NOEC	10	10	10	Sharma et al. 2012	
				60	--	NaF	Cell(s)	178	--	44	--	--	--	10	--	--	--	Sharma et al. 2012		
				90	--	NaF	Cell(s)	178	--	44	--	--	--	10	--	--	--	Sharma et al. 2012		
Salmonidae	Oncorhynchus	Oncorhynchus mykiss	Rainbow Trout	7	Fry, Swim Stage (2-6 d)	NaF	Survival and Growth	6	8	1.49	6	9	--	--	EC10	6	5.8	5.8	Pearcy et al. 2015	
				7	Fry, Swim Stage (2-6 d)	NaF	Survival and Growth	6	8	5.71	5.8	10.2	--	--	EC10	5.8			Pearcy et al. 2015	
				7	Fry, Swim Stage (2-6 d)	NaF	Survival and Growth	6	8	17.2	21.6	28.6	--	--	EC10	21.6			Pearcy et al. 2015	
				7	Juvenile(s), 2 Months	NaF	Mortality	22.4	37.5	10	--	--	--	--	--	--	--	Camargo and Tarazona 1991		
				8	Juvenile(s), 2 Months	NaF	Mortality	22.4	37.5	10	--	--	--	27.6	--	--	--	Camargo and Tarazona 1991		
				8.9167	Egg(s)	NaF	Mortality	--	--	--	--	--	--	--	--	--	--	Neuhold and Sigler 1960		
				17.6667	Egg(s)	NaF	Mortality	--	--	--	--	--	--	--	--	--	--	Neuhold and Sigler 1960		
				20	--	NaF	Mortality	--	--	--	--	--	--	--	--	--	--	Neuhold and Sigler 1960		
				28	Fingerling	NaF	Mortality	--	--	--	--	--	100	--	NOEC	100	100	100	Bowser et al. 1988	
				34.375	Embryo(s)	NaF	Mortality	--	--	--	--	--	--	--	--	--	--	Neuhold and Sigler 1960		
	Salmo	Salmo trutta	Brown Trout	7	Juvenile(s), 2 Months	NaF	Mortality	21.2	32.2	10.8	--	--	--	--	--	--	--	--	Camargo and Tarazona 1991	
				8	Juvenile(s), 2 Months	NaF	Mortality	21.2	32.2	10.8	--	--	--	--	--	--	--	Camargo and Tarazona 1991		
	Salvelinus	Salvelinus namaycush	Lake Trout	17	Embryo	NaF	Embryo Development	6	8	3.21	>134	>134	--	--	EC10	134	134	134	Pearcy et al. 2015	
Kingdom: Animalia; Phylum: Mollusca																				
Tateidae	Potamopyrgus	Potamopyrgus antipodarum	New Zealand Mud Snail	28	Adults	NaF	Reproduction	90.7+/- 7.5	--	<5	--	--	17.5	37	NOEC	17.5	17.5	17.5	Alonso and Camargo 2011	
Unionidae	Alasmidonta	Alasmidonta raveneliana	Appalachian Elktoe Mussel	7	Juvenile	NaF	Survival	28	--	--	--	--	--	--	--	--	--	--	Keller and Augspurger 2005	
				9	Juvenile	NaF	Survival and Growth	28	--	--	--	--	--	31	--	--	--	--	Keller and Augspurger 2005	
	Lampsilis	Lampsilis fasciola	Wavy-Rayed Lampmussel	7	Juvenile	NaF	Survival	32	25	2	--	--	--	--	--	--	--	--	Keller and Augspurger 2005	
				9	Juvenile	NaF	Survival	32	25	2	--	--	--	--	--	--	--	--	Keller and Augspurger 2005	
Kingdom: Chromista; Phylum: Bacillariophyta																				
Stephanodiscaceae	Stephanodiscus	Stephanodiscus minutus	Freshwater Diatom	7.3	Growth Cultures	NaF	Growth	--	--	--	--	--	50	--	NOEC	50	50	50	Hekman et al. 1984	
Kingdom: Chromista; Phylum: Ochrophyta																				
Stephanodiscaceae	Cyclotella	Cyclotella meneghiniana	Freshwater Diatom	7.3	Growth Cultures	NaF	Growth	--	--	--	--	--	50	--	NOEC	50	50	50	Hekman et al. 1984	
Kingdom: Plantae; Phylum: Chlorophyta																				
Chlorellaceae	Chlorella	Chlorella vulgaris	Green Algae	15	Exponential Growth Phase	NaF	Growth	--	--	--	--	--	66.5	--	NOEC	66.5	2.85	2.85	Rai et al. 1998	
				15	Exponential Growth Phase	NaF	Growth	--	--	--	--	--	2.85	--	NOEC	2.85			Rai et al. 1998	
				15	Exponential growth phase (log)	NaF	Growth	--	--	--	--	--	0.95*	--	NOEC	0.95*			Rai et al. 1998	
Kingdom: Plantae; Phylum: Tracheophytes																				
Araceae	Lemna	Lemna minor	Duck Weed	7	7-10d Culture	NaF	Dry Weight	206	90	73	215	335	--	--	EC10	215	125.0	125.0	Pearcy et al. 2015	
				7	7-10d Culture	NaF	Frond Growth	206	90	73	125	196	--	--	EC10	125			Pearcy et al. 2015	
Kingdom: Plantae; Phylum: Chlorophyta																				
Scenedesmaceae	Scenedesmus	Scenedesmus quadricauda	Green Algae	7.3	Growth Cultures	NaF	Growth	--	--	--	--	--	50	--	NOEC	50	50	50	Hekman et al. 1984	
Selenastraceae	Ankistrodesmus	Ankistrodesmus braunii	Freshwater Algae	7.3	Growth Cultures	NaF	Growth	--	--	--	--	--	50	--	NOEC	50	50	50	Hekman et al. 1984	

Table C-1
Acceptable Chronic Toxicity Data of Fluoride to Freshwater and Marine Organisms
Fluoride Regulatory Framework and Aquatic Toxicity Review - Appendix C

Family	Genus	Scientific Name	Common Name	Exposure Duration (days)	Age, Size, Lifestage	Constituent	Endpoint(s) Type	Hardness (mg/L)	Alkalinity (mg/L)	Chloride (mg/L)	EC10/IC10 Value (mg/L)	EC20/IC20 Value (mg/L)	NOEC Value (mg/L)	LOEC Value (mg/L)	Chronic Effect Measure	Chronic Value (mg/L)	SMCV (mg/L)	GMCV (mg/L)	Reference
Marine																			
Kingdom: Animalia; Phylum: Arthropoda																			
Aoridae	Grandidierella	Grandidierella lutosa and G. lignorum	Estuarine Amphipod	90	Ovigerous Females produced Juveniles	NaF	Survival and Reproduction	--	--	--	--	--	3.84	4.86	NOEC	3.84	3.84	3.84	Connell and Airey 1982
Camptandriidae	Tylodioplax	Tylodioplax blephariskios	Mud Crab	72	Small	NaF	Survival	--	--	--	--	--	--	52	--	--	--	--	Hemens and Warwick 1972
Cancridae	Cancer	Cancer pagurus	Edible Crab	90	From Cresswell	NaF	Survival	3733	--	18980	--	--	30	--	NOEC	30	30	30	Wright and Davison 1975
Palaemonidae	Palaemon	Palamon pacificus	Shrimp	72	Juvenile	NaF	Survival	--	--	--	--	--	--	52	--	--	--	--	Hemens and Warwick 1972
Penaeidae	Fenneropenaeus	Penaeus indicus	Indian Prawn	72	Juvenile	NaF	Survival	--	--	--	--	--	52	--	NOEC	52	52	52	Hemens and Warwick 1972
	Carcinus	Carcinus maenas	Shore Crab	90	From Cresswell	NaF	Survival	3733	--	18980	--	--	30	--	NOEC	30	30	30	Wright and Davison 1975
	Liocarcinus	Portunus depurator	Swimming Crab	90	From Cresswell	NaF	Survival	3733	--	18980	--	--	30	--	NOEC	30	30	30	Wright and Davison 1975
Kingdom: Animalia; Phylum: Chordata																			
Mugilidae	Mugil	Mugil cephalus	Mullet	72	Juvenile	NaF	Survival	--	--	--	--	--	52	--	NOEC	52	52	52	Hemens and Warwick 1972
Kingdom: Animalia; Phylum: Mollusca																			
Mytilidae	Mytilus	Mytilus edulis	Edible Mussel	42	Northumbrian coast	NaF	Survival	3733	--	18980	--	--	2.4	10	NOEC	2.4	2.4	2.4	Wright and Davison 1975
Ostreidae	Saccostrea	Saccostrea commercialis	Sydney Rock Oyster	21	Spat (Juvenile), Fed Algae (Isochrysis galbana and Pavlova lutheri)	NaF	Growth	--	--	--	--	30.7	30.7	--	NOEC	30.7	30.7	30.7	Nell and Livanos 1988
Kingdom: Chromista; Phylum: Bacillariophyta																			
Bacillariaceae	Nitzschia	Nitzschia angularis var. affinis	Marine Diatom	23	Growth Cultures	NaF	Growth	--	--	--	--	--	50	100	NOEC	50	50	50	Oliveira et al. 1978
Bellerocheaceae	Bellerochea	Bellerochea polymorpha	Marine Diatom	18	Growth Cultures	NaF	Growth	--	--	--	--	--	100	--	NOEC	100	100	100	Oliveira et al. 1978
Kingdom: Chromista; Phylum: Cryptophyta																			
Hemiselmidaceae	Chroomonas	Chroomonas salina	Marine Algae	18	Growth Cultures	NaF	Growth	--	--	--	--	--	100	--	NOEC	100	100	100	Oliveira et al. 1978
Kingdom: Chromista; Phylum: Haptophyta																			
Pavlovaceae	Pavlova	Pavlova lutheri	Marine Haptophyte	25	Growth Cultures	NaF	Growth	--	--	--	--	--	50	100	NOEC	50	50	50	Oliveira et al. 1978
Kingdom: Plantae; Phylum: Chlorophyta																			
Chlorellaceae	Nannochloris	Nannochloris oculata	Marine Algae	18	Growth Cultures	NaF	Growth	--	--	--	--	--	100	--	NOEC	100	100	100	Oliveira et al. 1978
Chlorodendraceae	Prasinocladus	Prasinocladus marimus	Marine Algae	18	Growth Cultures	NaF	Growth	--	--	--	--	--	50	100	NOEC	50	50	50	Oliveira et al. 1978
Dunaliellaceae	Dunaliella	Dunaliella tertiolecta	Marine Green Algae	18	Growth Cultures	NaF	Growth	--	--	--	--	--	100	--	NOEC	100	100	100	Oliveira et al. 1978

Notes:

EC10 - Concentration that produces an effect in 10% of the test population

EC20 - Concentration that produces an effect in 20% of the test population

GMCV - Genus minimum chronic value

IC10 - Concentration that produces an inhibitory effect in 10% of the test population

IC20 - Concentration that produces an inhibitory effect in 20% of the test population

LOEC - Lowest observable effect concentration

mg/L - milligrams per litre

NaF - Sodium fluoride

NOEC - No observable effect concentration

NR - Not reported

SMCV - Species minimum chronic value

*The 0.95 mg/L NOEC value from Rai et al. (1998) was not used because the pH was 4.8