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A REVIEW OF FLUORIDE TOXICITY IN AQUATIC ENVIRONMENT

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ABSTRACT
Fluoride is one of the common aquatic water pollutants presented from industrial effluents, agricultural runoff, and even municipal discharges. Although it plays a vital role in some biological processes at low concentration, fluoride can be highly toxic at high concentration and may cause adverse effects on aquatic organisms. This review compiles available knowledge on fluoride toxicity in different forms of aquatic organisms, including fish, invertebrates, and plants. We discuss the physiological, reproductive, and behavioral effects of fluoride, those factors that modulate its toxicity, and its movement through aquatic food webs. Finally, this review underscores the need for strict regulatory standards and further research on the long-term effects of fluoride exposure on aquatic biodiversity.

KEYWORDS: Fluoride toxicity, aquatic organisms, bioaccumulation, water pollution, fish, invertebrates, environmental contamination.

INTRODUCTION
Fluoride (F-) is a naturally occurring ion, which found its place in soils, waters, and air. Sources of fluoride ions entering fresh and marine aquatic environments include natural weathering of fluoride-containing minerals and effects of volcanic activity. The remaining sources are industrial wastes released by aluminium and phosphate fertiliser companies as well as various urban sewage effluents (**Camargo, 2003; WHO, 2020**). Although fluoride is essential to the development of bones and teeth in vertebrates at trace concentration, it can be very toxic at higher concentrations and impacts aquatic ecosystem health (Ghorai & Pant, 2021).

The primary aim of this paper is to provide a review on fluoride toxicity in aquatic systems, considering its effects on both fish and other invertebrates as well as the aquatic flora. This review synthesises studies regarding the physiological, reproductive, and behavioural impacts of fluoride on aquatic organisms and further spots out the environmental factors that may influence the toxic potential of fluoride. Additional implications for ecosystem health and bioaccumulation across trophic levels are also discussed.

Chemistry and Bioavailability of Fluoride in Aquatic Systems
Fluoride ions are very soluble in water and can readily dissolve in aquatic systems. The bioavailability and toxicity of fluoride to aquatic organisms depend on various factors, some of which include pH and temperature and water hardness. Typically, low pH or acidic conditions and soft water increase the solubility of fluoride, hence increasing its bioavailability and possible toxicity to aquatic organisms (**Camargo, 2003**). On the contrary, high calcium and alkaline water can reduce fluoride toxicity by increasing its precipitation in the form of insoluble calcium fluoride (CaF2) that reduces the availability of fluoride within the water column (**Hemens & Warwick, 2020**).

The susceptibility of aquatic organisms to fluoride toxicity is regulated through environmental parameters such as pH, water temperature, and hardness. Many studies have demonstrated that fluoride is more harmful to freshwater organisms than to marine organisms due to the formation of complexes between calcium and magnesium ions in seawater, thereby restricting its availability in biological environments (**Dey et al., 2021**). Furthermore, the co-presence of other toxicants, such as heavy metals, may also synergize the toxic effects of fluoride (**Mehdi et al., 2018**).

Effects of Fluoride on Aquatic Organisms
Fluoride can be toxic to aquatic organisms, causing a variety of effects including- growth impairment, lethargies, emaciation mitigation and even death also. These effects vary in intensity and symptoms in various aquatic organisms.

1. Fluoride Toxicity to Fish

Some of the best-studied organisms in terms of fluoride toxicity are fish. The physiological disorders in tissues of the gills, livers, and kidneys of fish start manifesting with high fluoride concentrations in water (**Sharma et al., 2020**). Exposed to fluoride, damage can also occur in the osmoregulation, further leading to an electrolyte imbalance, reducing their swimming performance (**Palaniappan et al., 2009**). Besides this, fluoride also inhibits the activity of acetylcholinesterase, thereby interfering with neural transmission, which could lead to behavioural changes, such as feeding reduction and erratic swimming behaviour (**Palaniappan et al., 2009**).

Fluoride exerts major impacts on the reproductive health of fish. Exposure to high levels of fluoride reduces fertility and embryonic development and may even trigger teratogenic effects in the offspring (**Manoj et al., 2019**). Delayed hatching, abnormalities in larvae, and decreased egg viability have also been recorded in zebrafish, Danio rerio, and other species subjected to fluoride-contaminated water (**Shi et al., 2018**).

2. Fluoride Toxicity to Invertebrates

Invertebrates like molluscs and crustaceans are also pretty sensitive to fluoride contamination. Fluoride has been proven to cause interference in the formation and growth rate of mollusks' soft tissues, which causes bioaccumulation (**Mota et al., 2020**). Flora and fauna species such as crustaceans like shrimp and crabs exposed to fluoride experience lower reproductive success, a decrease in their growth rates, and increase in the mortality rate. Studies on freshwater shrimp have shown that fluoride exposure causes disruptions in moulting patterns that eventually lead to reduced developmental outcomes (**Mehdi et al., 2018**).

3. Fluoride Toxicity to Algae and other Aquatic Plants

Fluoride affects aquatic primary producers also. The exposed algae and aquatic plants show efficiency in photosynthesis, stunted growth, and nutrient uptake performance (**Singh et al., 2019)**. The cascading influence on food web dynamics can trick down to higher trophic levels because of reduced primary productivity caused by fluoride exposure, respectively **(Camargo, 2003**).

Interspecies Comparison of Toxic Threshold Values of fluoride contamination

Exposure models can predict toxic effects of fluoride toxicity in aquatic environment. Simple spatial metrics can predict fluoride accumulation in a free-ranging organisms. The LC50 and EC50 values of fluoride for various aquatic organisms are highly diverse (Table-1). Spatially explicit exposure models offer a quantitative approach for evaluating and managing the potentially toxic effects of chronic fluoride exposure in aquatic ecosystem.

Table 1: Interspecies variability in fluoride toxicity.

S.N.	Species	LC50 (mg/L)	EC50 (mg/L)	Reference
1	*Oncorhynchus mykiss* (Rainbow trout)	7.5	3.5	Sharma et al., 2020
2	*Danio rerio* (Zebrafish)	10.0	5.0	Shi et al., 2018
3	*Penaeus monodon* (Shrimp)	15.0	7.5	Azevedo et al., 2021
4	*Mytilus galloprovincialis* (Mussel)	20.0	12.5	Mota et al., 2020
5	*Chlorella vulgaris* (Algae)	40.0	25.0	Singh et al., 2019

Mechanisms of Fluoride Toxicity

The exact mechanism of fluoride toxicity is unknown, but it's thought to involve a combination of factors, including the concentration of fluoride, how it's administered, and the surrounding environment of each cell. This includes oxidative stress, organelle damage, and apoptosis in single cells, and skeletal and soft tissue damage in multicellular organisms. The mechanism of fluoride toxicity can be broadly attributed to four mechanisms: inhibition of proteins, organelle disruption, altered pH, and electrolyte imbalance. At the cellular level, fluoride inhibits normal enzymatic activities related to energy metabolism and ion transport. It impacts ATPases, which is one of the most significant mechanisms in maintaining ionic homeostasis; consequently, this causes osmotic stress for aquatic organisms (**Dey et al., 2021**). Fluoride exposure results in oxidative stress caused by increased production of reactive oxygen species, thereby causing lipid peroxidation and DNA damage (**Sharma et al., 2020**).

Fluoride and biomineralization

Fluoride interaction with calcium affects the biomineralization process of vertebrates in aquatic animals. In fish, fluoride can alter mineral composition in bones and teeth, causing skeletal malformations and a lower density of bones (**Camargo, 2003**). In mollusks, fluoride interferes with the formation of calcium carbonate shells, creating shells less strong but rather brittle (**Mota et al., 2020**).

Fluoride contamination and regulation guideline standardisation

The World Health Organization (WHO) recommends that drinking water contain no more than 1.5 milligrams of fluoride per liter (mg/L). However, national standards may be lower depending on the overall amount of fluoride a person is exposed to. Adverse effects of fluoride on aquatic organisms have led to the development of water quality standards in many countries around the world. Countries have set limits on fluoride concentration in surface and drinking water to avoid damage to aquatic life (Table 2).

Table 2: Limits of fluoride contamination in various countries.

S.N.	Country	Fluoride Limit (mg/L)	Regulatory Body
4	India	1.0	Bureau of Indian Standards (BIS)
2	United States	1.5	Environmental Protection Agency (EPA)
3	European Union	1.0	European Commission
	Australia	1.2	Australian and New Zealand Environment Conservation Council (ANZECC)

The maximum allowed concentrations vary based upon regional environmental conditions like water hardness and prior level of fluoride in the background. However, these standards are not strict enough to protect sensitive species because the toxic effect has been observed at many concentrations below the acceptable levels (**Ghorai & Pant, 2021**).

Mitigation Strategies and Future Challenges

Fluoride pollution mitigation initiatives in the aquatic media include up-gradation of treatment processes for industrial effluent and promotion of fluoride-free alternatives in agriculture and industry sectors. Improved techniques for the removal of fluoride from industrial effluents may be achieved through better filtration and chemical precipitation methods before such effluents reach the water bodies (**Azevedo et al., 2021**). Public education on proper use of fluoride-containing products, like fertiliser and pesticide may also be improved.

Open knowledge gaps are still present in fluoride toxicity. Long-term studies are required to evaluate the chronic effects of low-dose exposure to fluoride, especially in ecosystems bearing multiple stresses. Fluoride effects on microbial communities and whether this substance can change nutrient cycling in aquatic ecosystems is a subject still under research (**Mehdi et al., 2018**). Future studies must establish the synergistic effect of fluoride with other pollutants such as heavy metals and endocrine-disrupting chemicals, **Dey et al. 2021.**

CONCLUSION

Fluoride can be toxic to aquatic life but some organisms are more sensitive to its effects than others. Its toxicity is very low for bacteria involved in wastewater treatment and appears to be low for algae. Aquatic organisms living in soft waters may be more adversely affected by fluoride pollution than those living in hard or seawaters because the bioavailability of fluoride ions is reduced with increasing water hardness.

This review brings to light the comprehensive implications of fluoride contamination towards aquatic organisms, such as fishes, invertebrates, and plants. Some of the environmental factors that may vary fluoride toxicity include pH and water hardness, and its effects also involve physiologic stress through reproductive failure. Although regulatory guidelines exist in setting bounds to fluoride pollution, it lacks wholeness in the sense that the vulnerable species are not protected. Therefore, the stringent regulations and further research are necessary to safeguard the aquatic biodiversity from fluoride contamination.

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