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# ARSENIC, SELENIUM AND FLUORIDE INDUCED TOXICITY ON FISH AND OTHER AQUATIC ORGANISMS – A REVIEW

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*The natural and manmade activities increase the concentration of various common chemicals including arsenic (As), selenium (Se) and fluoride ($F^-$) in the natural environment. The increase in the concentrations of As, Se and $F^-$ in the natural water bodies causes serious problems in aquatic ecosystem, especially to fish and other aquatic animals.The present review elucidates the different aspects of acute and chronic toxicities of As, Se and F-to fish and other organisms. Discussion on the abundance, source and toxicity of these pollutants are important from the ecotoxicological view point and biomonitoring perspectives.*

## *Introduction*

Progressive urbanization has led to intensified increasing exposure of living organisms to elemental pollution which in turn emerges interest in chemical compounds as environmental toxicants[1]. Pollution is an inherent output of casualty of all human activities as a result of advanced technologies. Ironically, all these developments have resulted in enhanced utilization of natural resources and production of thousands of by-products as wastes[2].The contamination of different chemicals in natural environment and especially in water bodies arising from natural and human activities has become a prime concern due to their toxic effects on aquatic organisms and human health. These chemicals include arsenic (As), selenium (Se) and fluoride ($F^-$)which are highly enriched in industrial effluents, sewage and trade wastes and create unexpected changes in the aquatic and non-aquatic equilibrium. This has emerged as a major environmental concern due to problems associated with its disposal in the water bodies[3]. When they are accumulated in the natural water resources, these chemical toxicants not only affectthe physicochemical properties such as pH, salinity, alkalinity, hardness, dissolved oxygen and buffering of the aquatic body but also it distorts the physiological parameters of the aquatic organisms[3].

Different human activities are the main causing factors for the release of enormous and diverse chemical substances in the aquatic environment leading to deterioration of freshwater biodiversity[4]. Different urban, agricultural and industrial activities are now increasing the probability of exploitation of natural water resources leading to the deterioration of the quality of water and living conditions. The treated and untreated effluents from different industries like thermal power plants, steel plants, tannery, battery industries, etc. and also the uncontrolled use of chemical fertilizers and pesticides containing heavy metals in agriculture cause serious environmental problems through the deterioration of water quality and poses threat on sustaining aquatic biodiversity[5].

Freshwater fishes are one of the most threatened taxonomic groups because of their high sensitivity to the qualitative and quantitative alteration of aquatic habitats. Consequently, they are often used as bioindicator for the assessment of water quality, metallic pollution [6]. As those

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chemicals are not eliminated from aquatic ecosystems by natural methods, they act as important pollutants for fish. Their effects vary with the types of fish, their age and other physiological factors. Different organs of fish are also affected by different chemicals. The metabolic processes of fish are altered by these chemicals changing the action of essential elements which leads to toxicity[7].

Monitoring of different toxic chemicals is of sheer necessity for safety assessment of the natural aquatic ecosystem and the health of the aquatic animals in particular. Different workers around the world are engaged to find out the hazardous effects of those chemicals and their possible remedial measures[8]. However, cursory reports are only available on the acute and chronic toxicity of different groups of chemicals on fish and fish food organisms and their bioremediation. The present review emphasizes on the acute and chronic toxicity of As, Se and $F^-$ on fish and fish food organisms.

### *Arsenic Contamination in the Environment*

The metalloid arsenic (As) with atomic number 33 is widely found in the environment as 0.00005% of the earth's crust with ranking 20$^{th}$ in natural abundance. The metalloid As is an important environmental threats to millions of people because of its carcinogenic activity[9]. As per WHO guideline the maximum permissible limit of arsenic in drinking water is 10 μg/l[10]. Estimated daily intake of inorganic As from drinking water is reported to be 1.83 μg/day which is low compared to As intake from rice consumption (45.1 μg/day) in China[11]. Earlier studies indicate that rice can accumulate arsenic up to 2.0 mg/kg in grains, the major part of which is inorganic arsenic. These values of inorganic arsenic for rice exceed the permissible limit as recommended by WHO (1.0 mg $kg^{-1}$), European Food Safety Authority (0.2 mg $kg^{-1}$) and Chinese Food Standards Agency (0.2 mg $kg^{-1}$). The inorganic As are 10-60 times more toxic than the organic As compounds, since most of the forms of organic arsenicals are metabolized in body system and eliminated through excretion. Additionally, inorganic forms of As are better absorbed by body than organic arsenic[12].

### *Arsenic Contamination in a Global and Indian Context*

The distribution pattern of arsenic in world and India is given in Fig. 1 and Fig. 2 respectively.

### *Route of Exposure of Arsenic*

The most common cause of arsenic (As) poisoning is through contaminated drinking water. The groundwater is most often contaminated by As through natural processes. However, contamination may also take place from mining or agriculture. Other routes of exposure include toxic waste sites and traditional medicines[13]. Arsenic may also be found in the soil and air[14]. Nowadays arsenic contamination is a serious health concern in many countries, especially in South-East Asia where its elevated concentration (up to 3200 μg/l) in drinking water far exceeds the WHO declared safe limit of 10 μg/l[15]. Arsenic contamination in drinking and cultivatable water poses serious issue on water quality and thus has great impact on crops and societal health. Anthropogenic sources such as industrial wastes and pesticides are other sources of As in the environment and thereby increase the probability of its contact with humans and animals through the food chain[16]. A huge variation in As concentration of natural groundwater is found in different countries[17]. Presence of high As concentrations in crops such as rice and specially in its straw arouses a potential threat since rice straw is used as cattle feed and thus As may ultimately find its way to humans via contaminated meat and milk[18].

### *Arsenic Induced Toxicity on Aquatic Organisms*

Generally, fish is used as a suitable model to determine the effects of environmental pollution on aquatic ecosystems[19]. Fish are continuously exposed to toxic environment by their skin, gills, and by the intake of As-contaminated food[20]. These are really good enough for toxicogenomics studies to establish as biomarkers of pollution. Fish appear to have evolved different mechanisms for biotransformation of As to less toxic forms, which are then readily excreted[21]. The high level of As concentration, more than permissible limit (10 ìg/l), in an aquatic ecosystem affects various physiological systems such as growth, reproduction, ion regulation, immune function, enzyme activities and histopathology of fish[22]. As-contaminated fish consumption could result in As exposure to humans and lead to adverse health effects[23]. Arsenic could evoke a series of molecular events involved in oxidative stress, iron homeostasis, lipid metabolism disorder and carcinogenesis[24]. Such findings show that further work is necessary for better understanding of As toxicity to fish and fish food organismsand its bioremediation for safe disposal.

### *Selenium Contamination in the Environment*

Selenium, the crystalline metalloid, with atomic number 34 occurs widely in the environment with ranking 67$^{th}$ in natural abundance. It is present as selenocysteine

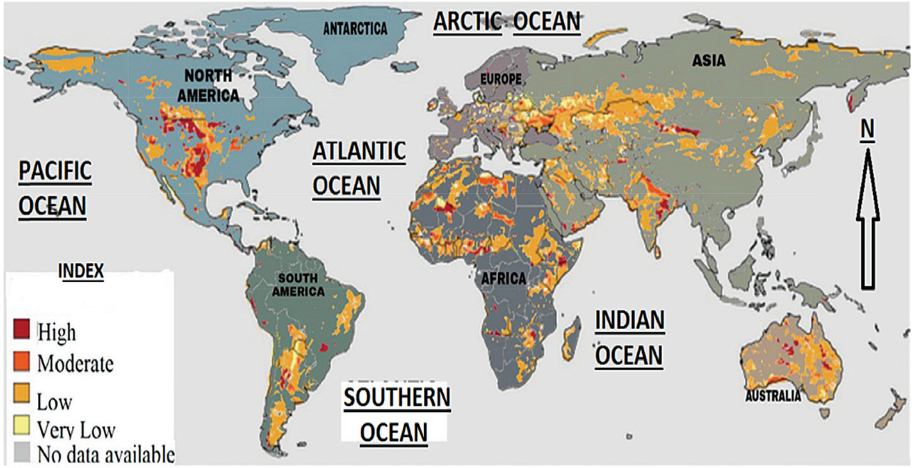


**Fig.1** Geographical Distribution Pattern of As in the World

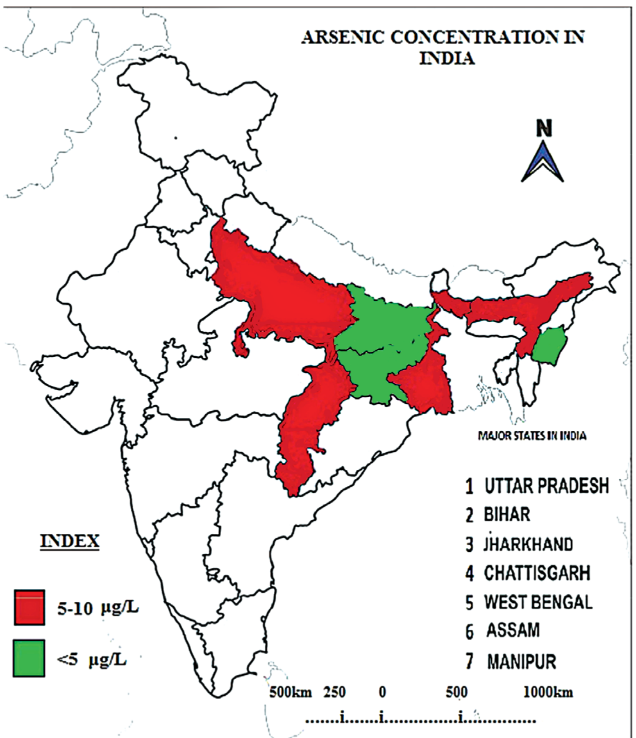


**Fig. 2** Geographical Distribution Pattern of As in India

and selenomethionine in body of animals and plants[25]. On the other hand, selenite ($Se^{+4}$) and selenate ($Se^{+6}$) are abundant in aqueous environment (Yu et al., 2018). Selenite ($Se^{+4}$) is more toxic than selenate ($Se^{+6}$)[26]. As per WHO guideline the maximum permissible limit of selenium in drinking water is 6000 µg/l. The Se content in drinking water is considerably low in natural conditions[27]. The volcanic explosion, marls, gypsum, aerosol particle from sea or sea spray, biological cycling methods including the weathering of Se containing rocks and soils are prevalent natural resources[28]. Besides natural sources, human interference including mining, oil refining, fuel combustion, pesticide use, photocells and glass manufacture are the important contributor of Se to the environment[29]. Some crops, vegetables and animal products are rich in sulfur and these possess a greater Se accumulating capability since the Se can replace sulfur in the proteins[30]. Se contamination becomes risky and shows toxicity for livestock when it exceeds 5 ppm[31]. It is important to note that an alteration of the tertiary structure of proteins occurs due to Se toxicity[32].

### *Selenium Contamination in a Global and Indian Context*

The distribution of Selenium in world and India is given in Fig. 3 and Fig.4 respectively.

### *Route of Exposure of Selenium*

Selenium may be taken up by organisms directly or through the food they eat. Some plants take up selenium from the soil, concentrating large amounts in their tissues[33]. Eating such plants or ordinary forages and feeds grown on seleniferous soils can be harmful to livestock. Selenium may have a greater impact in aquatic ecosystems where human activities have made it more available[34]. In aquatic systems, selenium is cycled predominantly through biological pathways, food chains and metabolic

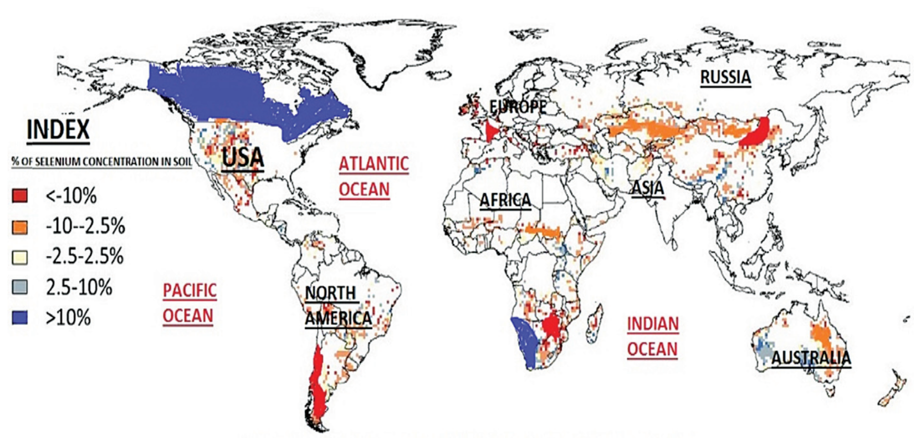


**Fig. 3.** Geographical Distribution of Se in World

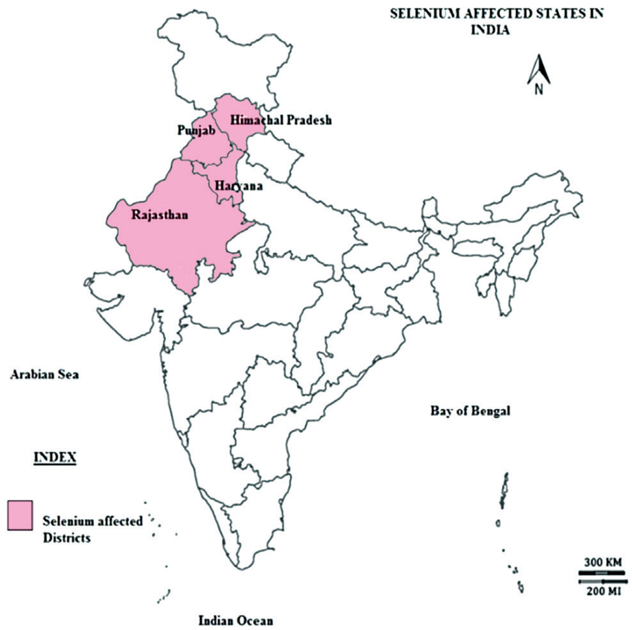


**Fig. 4.** Geographical Distribution of Se in India

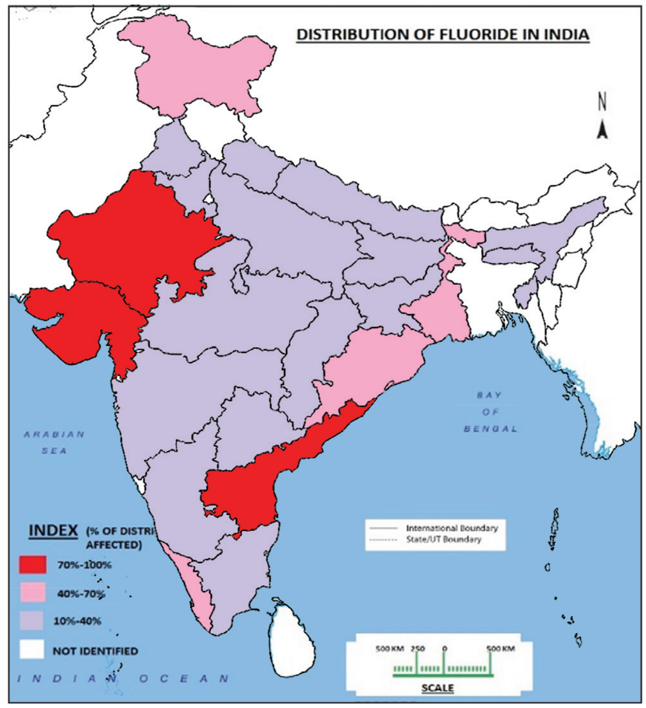


**Fig. 6** Geographical Distribution of Fluoride in India

processes[27].

## *Selenium Induced Toxicity on Aquatic Organisms*

A general mechanism of selenium toxicity involving oxidative stress or impaired organ structures of the exposed organisms leading to death is reported[35]. Moreover, the potential negative effects of selenium on different animals at the cellular, molecular and organism levels including pathological alterations in different organs like liver, heart, kidney, and ovary as well as reproductive failure and teratogenic deformities of different organs were also reported[36].

Se toxicity was due to an alteration of the tertiary structure of proteins when Se substituted for S, but a more general mechanism involving oxidative stress or impaired immune function has also been proposed[37]. The toxicity of Selenium and impact on haematological and/or biochemical parameters was evaluated in different fish species. Organic Selenium is highly toxic to carp. The 96h $LC_{50}$value of selenium for Striped bass is reported as 85.80 mg/l (USEPA, 1987); for Zebra danio is 35 mg/l[38]; for Coho salmon is 39 mg/l[39]; for Walleye is 11.7 mg/l [40] and for Red sea bream is 70.0 mg/l [41].

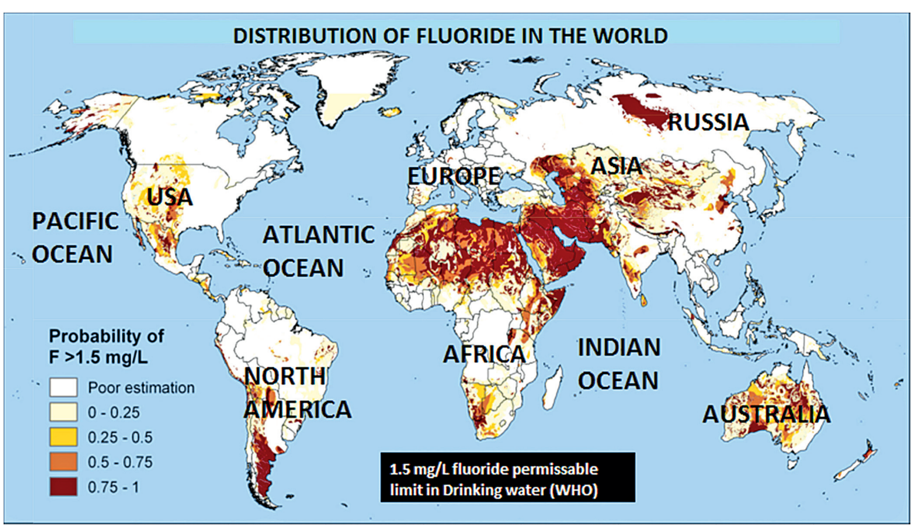


**Fig. 5** Geographical Distribution of Fluoride in World

But sufficient information is not available to link the acute and chronic toxicity of Se to fish and other aquatic organisms with the concentration of the toxicant in water. Such reports show that further work is of paramount importance for much better understanding of selenium poisoning in natural water bodies and its bioremediation for safe disposal.

## *Fluoride Contamination in the Environment*

Fluoride is an inorganic, monatomic anion and its chemical formula is $F^-$ (also written $[F]^-$). It is a naturally occurring strongest oxidizing element, found in air, water and soil. It occurs as a free anion, hydrofluoric acid and different fluoride complexes[42]. Fluoride comes to the ground water from rocks and soil of the earth's crust due to solvent and acts as an essential element for life. It is never found in nature in the form of element as it is highly electronegative in nature. Hydrofluoric acid is used as reactant in several industries such as phosphatic fertilizer industry, coal washing, semiconductor or metals manufacturing unit, etc[43]. Geological and anthropogenic factors are responsible for the contamination of groundwater with fluoride[44]. Random disposal of industrial wastewater into the environment affects both soil and groundwater quality[45]. Fluoride-contamination of groundwater is a serious problem in several countries of the world because of the intake of excessive fluoride caused by the drinking of the contaminated groundwater[46]. Fluoride levels may be as high as 96.8 mg/l in industrial wastewater, and in extreme cases, reach up to 3000–5000 mg/l[47].

### Fluoride Contamination in a Global and Indian Context

The distribution of fluoride in world and India is given in Fig. 5; and Fig.6 respectively.

### Fluoride Induced Toxicity on Aquatic Organisms

Reports indicate that fluoride is accumulated in the exoskeleton of invertebrates and bone of fish in aquatic ecosystem[48]. The combination of fluoride with calcium and phosphorous especially in the marine environment causes hardening of hard tissues through the formation of fluorapatite[49]. Many workers stated that fluoride has genotoxic, mutagenic and neurotoxic effects to aquatic organisms[50]. Fluoride ions inhibit enzyme activity and interrupt different metabolic processes including glycolysis and protein synthesis in aquatic organisms[51]. The toxicity of fluoride increases with increasing concentration of fluoride, water temperature and time of exposure. The toxicity decreases with water content of calcium and chloride and increasing body size[52].

Aquatic animals, such as fish and invertebrates, can take up fluoride ions directly from the water or to a much lesser extent through food chain. The uptake is basically a function of fluoride concentration in the aquatic medium, exposure time and physiological characteristics of the species[53]. The potential negative effects of fluoride in aquatic organisms, especially crabs and fish, and rats have been well documented at the molecular, cellular and organism levels[47]. Data on fluoride toxicity to aquatic organisms remain insufficient to set water quality criteria for aquatic organisms globally[47]. Liver, heart and kidney are the most susceptible soft tissues to fluoride toxicity[54]. All the three organs exhibit histopathological and functional changes if exposed to prolonged doses of fluoride[55]. Excess amounts of fluoride in potable water may cause irreversible demineralization of bone and tooth tissues and long-term damage to the brain, liver, thyroid and kidney[54]. Reports of the toxicity of $F^-$ to fish and other aquatic organisms are scanty which needs further work for much better understanding of fluoride poisoning in natural water bodies.

### Conclusion

The present review was designed to elucidate the sources, distribution, route of exposure and adverse effects of arsenic, selenium and fluoride to different aquatic organisms and aquatic ecosystem. It can be concluded from the present review that the reported data on the source, distribution, acute and chronic toxicity, bioaccumulation and biomonitoring of arsenic, selenium and fluoride may provide valuable inputs for the safe disposal of arsenic, selenium and fluoride to natural aquatic ecosystem. The findings will provide necessary information needed for sustainable fishery management, fish breeding programme in natural water bodies and conservation of different commercially important wild fish in their natural habitat. However, further studies are required to determine the changes in the ultrastructural and molecular levels due to arsenic, selenium and fluoride induced toxicity on aquatic organisms and the cost-effective bioremediation of these toxicants. ❒

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