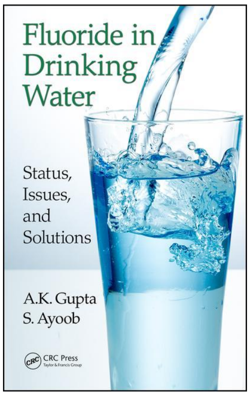

Fluoride in Drinking Water
Status, Issues, and Solutions

A.K. Gupta, S. Ayoob

Fluoride in Drinking Water: A Global Perspective

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Fluoride in Drinking Water: A Global Perspective

1.1 Introduction

Water is life as it aids in nurturing the lives of all biota. The availability of clean water has become obliquely central to the quality of human life. However, there are deep currents that affect the water dynamics of today's world. Currently, two-thirds of our planet is covered water; however, the unfortunate paradox is that in the next decade, bulk of the human population will lack access to safe drinking water. This acute shortage of drinking water may change our traditional perceptions about both the quality and usage of water in the future. Further, the presence of geogenic pollutants in groundwater makes this issue more complex. Of late, the presence of fluoride in drinking water has attracted much attention in the scientific world due to the impending issues associated with human health and well-being.

1.2 Drinking-Water Scenario

In 2014, it was reported by the World Health Organization that around 750 million people from the poor and socially deprived sections of society all over the world do not have access to improved drinking-water sources. Almost one-fourth of the people living in rural habitations use and drink untreated surface water. In 2015, it was estimated that around 550 million do not have access to improved drinking-water sources.[1] It is predicted that in 2035, there will be a one-third reduction in the per capita drinking-water availability. By 2025, around 34% of the global population will face acute drinking-water shortage.[1] This sorry state of affairs is reflected in the terribly short supply of good quality water in many parts of the world. As a result, the global water supply system is beleaguered at both the demand and supply ends. The acute scarcity of drinking-water sources and increased competition in the early periods of the twenty-first century, the traditional ways of using and valuing water have taken a dramatic turn. Thus, the scarcity of water and the limited access to safe drinking-water sources are predicted to be the most challenging and crucial environmental issues of the future in preserving and defining the quality of life on earth.[2,3]

Groundwater has been perceived to be the safest of all the drinking-water sources available on the surface of the earth. As a result, half of the global population blindly relies on groundwater sources for both drinking and survival. Apart from this, in many regions of the world, groundwater sources turn out to be the single largest source of supply for drinking. Further, in many communities, these sources appear to be the only economically viable option for drinking, as they supply reliable quality water and stable quantity water compared with water from surface sources. Since groundwater plays such a crucial role in the existence of the majority of the global human population, its availability, safety, and purity have become issues of critical concern for many habitations across the globe.[3,4]

Of late, due to rapid urbanization and industrialization, more xenobiotic substances are getting diffused into different spheres of the earth. A considerable portion of these substances rests with the biosphere, of which water sources occupy a considerable share. Water sources act as "sinks" for many of these pollutants, resulting in drinking-water pollution and water scarcity. This situation is more serious in developing countries, as they are grappling with acute issues related to both scarcity and contamination of drinking water. Intrinsically, the excessive groundwater pumping that is disproportionate to recharge will also lead to the depletion of water, thus posing challenges to drinking-water supply systems. Plenty of examples are available to validate this point. In many developing countries such as India, in urban groundwater sources cater to around one-half of the water requirements. In rural areas, groundwater sources alone cater to more than two-thirds of the total water demand, thus resulting in the situation appearing really critical. The indiscriminate tapping of groundwater created alarmingly low levels of the water table in many parts of the developing world.[3,5,6] Thus, inadequate access to safe drinking water, on the one hand, and its ever-increasing intimidation from abundant contaminants, on the other hand, make the global drinking-water scenario more complex. As a result, the world is heading toward a water crisis. This is a crisis affecting both the quantity and quality of water. In a little more than half a century, this global water crisis has evolved, mainly affecting the developing world in and around the arid and semi arid regions, especially areas where groundwater is the main source of drinking water. The drilling of tube wells for agricultural purposes is often unregulated, though it is supplemented by subsidized electricity for pumping. Much of the progress in food production, such as the Green Revolution in India and other countries, has taken place unsustainably at the expense of groundwater. This has triggered a severe drawdown of groundwater tables[7]; it has also had lasting and often irreversible impacts on groundwater, resulting in a synergy of water quality issues.

1.3 Geogenic Pollutants

Of late, the entry of geogenic pollutants such as fluoride and arsenic into groundwater aquifers has turned out to be a decisive environmental problem the world over. This situation is extremely critical in developing countries such as China and India. In India, fluoride has become endemic in approximately 37,000 habitations, whereas issues of arsenic are diffused into around 3,200 habitations, thus exhibiting the dominance of the issue. The presence of excess fluoride in drinking water raises a red flag of concern, as it initiates fluorosis in various proportions, thereby reducing the quality of human life. It was estimated that people from more than 35 nations across the globe are under the threat of fluoride attack. The number of people affected with the "risk of fluorosis" has probably crossed 200 million.[8–10] Therefore, fluoride in groundwater can be treated as a critical driver in defining the quality of groundwater in many parts of the world. The steady increase in the number of people falling prey to fluoride pollution, especially in the developing world, brings the issue under global focus. Thus, it would be interesting to have a brief overview on the pathways of fluoride into groundwater, the chemical profile and geo-chemistry of fluoride, and the status of global fluoride pollution while narrating its context and relevance.

1.3.1 Fluorine: The Chemical Profile

Fluorine is the ninth element in the periodic table, with an atomic weight of 18.9984. It belongs to the group VII A. It is rated thirteenth in abundance and is estimated to be widely distributed at 0.3 g/kg of the earth's crust. Elemental fluorine is the most electronegative and reactive of all elements; as a result, it rarely occurs naturally in the elemental state. Its electronegative nature demonstrates that it has a strong tendency to acquire a negative charge in solution, forming fluoride ion (F^-). Except inert gases, it can bond with every other element, thus forming stable electronegative bonds. "Fluorine reacts with other elements to produce ionic compounds like hydrogen fluoride and sodium fluoride in water and upon dissociation forms negatively charged fluoride ion."[3,6,11,12]

1.3.2 Sources of Fluoride

Fluoride is an abundant trace element that is found with an average concentration of 625 mg/kg of fluorine in the earth's crust. However, its occurrence is found to vary depending on the types of rocks (from 100 mg/kg in limestones to 2000 mg/kg in volcanic rocks).[13] The rich underlain presence of crystalline igneous and metamorphic rocks in regions of India, Sri Lanka, Senegal, Ghana, and South Africa along with areas of volcanic and associated hydrothermal activity contributes to fluoride. Since "fluorine has a higher affinity for silicate melts than solid phases it is progressively enriched in magmas and hydrothermal solutions with time due to magmatic differentiation."[3] As a result, the hydrothermal vein deposits and rocks that crystallize from highly evolved magmas often contain fluorite-, fluorapatite-, and fluoride-enriched micas and/or amphiboles. Based on the percentages of silica and calcium present in magma, cryolite, villiaumite, and/or topaz can also be formed. The highest fluoride levels were reported from regions that were predominately occupied by crystalline igneous and metamorphic rocks. These rocks are associated with syenites, granites, quartz monzonites, granodiorites, felsic and biotite gneisses, and alkaline volcanic types. It is suggested that the presence of biotite alone may produce dissolved fluoride concentrations in groundwater to a level of more than 4 mg/L.[13]

The parent rock serves as the most natural contributor of fluoride into drinking water. However, fluorite, the only principal mineral of fluorine, is regarded as an accessory mineral in granitic rocks. Granite rocks are reported to exhibit fluoride concentrations of 20–3600 mg/L. Apatite, muscovite, amphibole, hornblende, pegmatite, mica, biotite, villiaumite, and certain types of clays are also found to contain fluorine. The reported natural Indian sources include the following: the hard rock terrains (south of Ganges valley) in the arid north-western part; fluoride-rich rocks and canal-irrigated black cotton soils of Karnataka; the dark mineral fraction of gneisses of Tamil Nadu; granites, minerals such as sepiolite and palygorskite, acid volcanic and basic dikes of Rajasthan; soils and clays of Gujarat; granitic rocks of Andhra Pradesh; tourmaline-bearing pegmatites of Maharashtra; and sodic soils in irrigated areas of Haryana and Andhra Pradesh.[3,14–19] High fluoride concentrations can also result from "anion exchange (OH^- for F^-) on certain clay minerals, weathered micas and oxyhydroxides that are typically found in residual soils and sedimentary deposits."[3] Areas underlain by alkaline volcanic rocks and sedimentary formations that contain fluorapatite- and/or fluoride-enriched clay minerals may contribute to fluoride concentration. Crystalline basement rocks such as felsic intrusive rocks and their metamorphic forms are also prone to fluoride dissolution. Though fluoride is not readily leached from soils due to its strong associations with the soil components (only 5%–10% of the total fluoride in soil is water soluble), its concentration may increase with depth to the tune of 200–300 mg/L.[20] The rate of fluoride dissociation depends on the soil chemistry, chemical form, climate of the region, and deposition rates. It is reported that in acidic soils with a pH less than 6, fluorides can form complexes with iron and aluminum; they can also form a bonding with clay by replacing hydroxide from the clay surface. pH plays a crucial role in this adsorption process as it turns significant at a pH of 3–4, whereas it is reduced at a pH higher than 6.5. The application of fertilizers under intensive irrigation may result in releasing fluoride into groundwater. Alkalinization may enhance the concentration of fluoride content in irrigated lands and soils.[20,21]

1.4 Fluoride in Humans

It was estimated that 99% of the absorbed fluoride in humans gets deposited in bones and teeth. Though fluoride does not get accumulated in most soft tissues, such as hydrogen fluoride (HF), it can find its way into the intracellular fluid of soft tissues. It is plausible that within kidney tubules, fluoride may get concentrated at high levels, even at a higher concentration than plasma. Due to this relatively high fluoride-level exposure, kidneys are regarded as the most vulnerable sinks of fluoride, resulting in them becoming an impending target of acute and chronic fluoride toxicity.[21,22] Since the transportation of fluoride from plasma to milk is minimal, the observed fluoride levels in human milk are only to the tune of 5–10 µg/L.[20] The level of fluoride concentration in saliva reflects the plasma fluoride availability. Only low concentrations of fluoride are reported in sweat (around one-fifth of plasma levels). Renal excretion of fluoride may be 35%–70% of intake in adults. As a result, urine, plasma, or saliva could be used as biomarkers of fluoride exposure. The average per capita dietary intake range of fluoride will be 0.020–0.048 mg/kg for adults (living in regions with fluoride concentrations of 1.0 mg/L in water). Although a "no-observed-adverse-effect level (NOAEL) of 0.15 mg fluoride/kg/day and a lowest observed-adverse-effect level (LOAEL) of 0.25 mg fluoride/kg/day of fluoride in human" are suggested, these levels are still under scientific debate.[3,20,23–25]

1.5 Genesis of Fluoride in Groundwater

The origin of fluoride in groundwater is due to an interaction between groundwater and surface water with rocks containing fluoride-rich mineral. The presence and concentration of fluoride in groundwater are a reflection of the amount of concentration of fluoride-bearing minerals present in their parent rock types. The decomposition and dissolution activities of the rock types that are exhibited through rock–water interactions play a crucial role.[26] In the developing countries such as India, since the contribution from drinking water is the most significant source of fluoride entry into the human body, a thorough understanding of the geo-chemistry of fluoride in groundwater appears relevant. It is observed that the rainwater falling on the earth gets charged by different sources of CO_2 from the soil and the atmosphere, in addition to the biochemical reactions between bacteria and organic matter during its descent. Thus, the rainwater may turn slightly acidic due to the formation of carbonic acid. As a result, during percolation, the secondary salts present in the soil (mixture of varying content of $NaHCO_3$, NaCl, and Na_2SO_4) may get leached out. In phosphate fertilizer-applied lands, soils most likely contain different percentages and proportions of fluoride-rich materials and compounds. Simultaneously, an ion-exchange reaction takes place, with exchangeable cations present in the soil–clay complex as follows:[27]

$$CaX_2 + 2Na^+_{(aq)} \leftrightarrow 2NaX + Ca^{2+}_{(aq)} \quad (1.1)$$

where X is the clay mineral. As demonstrated by the equations cited, the hydrogen-ion concentration in groundwater is increased due to the dissolution of CO_2. The calcareous minerals, especially $CaCO_3$, also get dissolved as follows:[27–29]

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (1.2)$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \quad (1.3)$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \quad (1.4)$$

$$CaCO_3 + H^+ + 2F^- \rightarrow CaF_2 + HCO_3^- \quad (1.5)$$

$$CaF_2 \rightarrow Ca^{2+} + 2F^- \quad (1.6)$$

The groundwater charged with alkalinity may mobilize F^- from weathered rocks, soils, and CaF_2, resulting in the precipitation of $CaCO_3$ as follows:[29]

$$CaF_2 + 2HCO_3^- \rightarrow CaCO_3 + 2F^- + H_2O + CO_2 \quad (1.7)$$

The dissolutional and assimilating activity of fluoride gets enhanced with the excess presence of sodium bicarbonates in groundwater as follows:[29]

$$CaF_2 + 2NaHCO_3 \rightarrow CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2 \quad (1.8)$$

The CaF_2 has a solubility product (K_{sp}) as follows:[30]

$$K_{sp} = \left[F^-\right]^2\left[Ca^{2+}\right] = 4.0 \times 10^{-11} \quad (1.9)$$

The low-solubility product (Equation 1.9) suggests that high fluoride concentrations in groundwater are generally associated with low calcium content (with a negative correlation between the two ions) and high bicarbonate ions (in some cases with high nitrate ions).[3] Also, it was observed that groundwater is generally undersaturated with respect to fluorite (in some cases, it may be saturated with both calcite and fluorite).[3,27] It has been established that the pH of groundwater plays a significant role in defining the concentration of fluoride in groundwater. An alkaline environment (within a pH range 7.6–8.6) with a high bicarbonate concentration is said to be more conducive for fluoride dissolution. Thus, the weathering of primary minerals in rocks appears to be the main contributing factor of fluoride into groundwater. The weathering of rocks results in the leaching of fluoride-containing minerals into groundwater. Being the most predominant mineral, mainly the presence of fluorite clues in about the concentrations of fluoride in groundwater. As evidenced in Equation 1.9, the low-solubility product is an irrefutable proof that low levels of calcium result in high fluoride concentrations in water. Further, groundwater in the sodium bicarbonate and bicarbonate chloride types exhibits high fluoride concentrations. The ion-exchange mechanism, as suggested in Equation 1.1, turns significant in the context of reported excess fluoride in groundwater in regions of high sodicity of soil. This process and the mechanisms related to it turn relevant in issues pertaining to reported high fluoride concentrations near the major south Indian irrigation projects.[16,17,26,28,31–33] In 2012, the most recent research conducted in the rocks of Hangjinhouqi in a fluoride endemic area of China suggests that due to CaF_2 solubility control, Na-predominant water is favorable for fluoride enrichment with low total dissolved solid (TDS).[34] The elevated fluoride concentrations in the groundwaters of south-eastern Pakistan region (1.13–7.85 mg/L) are also attributed to the enhanced fluorite solubility due to Ca depletion, high ionic strength, and the release of fluoride from colloid surfaces under high pH conditions.[3,35] The excess fluoride concentration in the Kolar and Tumkur districts in Karnataka, India, is also attributed to the reduced levels of calcium-ion concentration in groundwater due to the calcite precipitation.[36] It is also reported that the dry and hot climate enhances fluoride levels in the groundwater nearer to the surface. In regions with high rainfall, the dilution effects in groundwater may outweigh the enrichment effects. In dry regions where precipitation rates are lower than evaporation, the fluoride generated from the dissolution of fluoride-bearing minerals may move toward the surface as a result of evaporation. This causes an increase in fluoride concentrations in groundwater. The hydrolysis (OH^- in water exchanges for F^-) of F-bearing silicates such as muscovites (Equation 1.10) and biotites (Equation 1.11) in alkaline soda water can be expressed as follows:[37,38]

$$KAl_2\left(AlSi_3O_{10}\right)F_2 + 2OH^- = KAl_2\left(AlSi_3O_{10}\right)\left(OH\right)_2 + 2F^- \tag{1.10}$$

$$KMg_3\left(AlSi_3O_{10}\right)F_2 + 2OH^- = KMg_3\left(AlSi_3O_{10}\right)\left(OH\right)_2 + 2F^- \tag{1.11}$$

Thus, it could be inferred that the enrichment of fluoride in groundwater results from water–rock interactions of F-bearing silicates. The dissolution of fluorite may get further triggered by its enrichment through evapo-transpiration.

1.6 Summary

- The average per capita water availability may get reduced by one-third over the next two decades. As a result, by 2025, one-third of humanity will be under the risk of severe water scarcity.
- Inadequate access to safe drinking water has become the most crucial challenge to the sustainable water supply systems of the world.
- The world is heading toward a water crisis. This global water crisis mainly affects the developing world in and around the arid and semi arid regions where groundwater is the main source of drinking water.
- The entry of geogenic pollutants such as fluoride and arsenic into groundwater aquifers has become an issue of global concern, especially in developing countries such as India and China.
- Around 200 million people from more than 35 nations the world over are "at risk" of fluorosis.
- The main source of fluoride in soil is obviously the parent rock itself. The origin of fluoride in groundwater is mainly due to the interaction between groundwater and surface water with rocks containing fluoride-rich minerals.
- The rate of fluoride dissociation depends on the chemical form, rate of deposition, soil chemistry, and climate.
- Around 99% of the absorbed fluoride in humans gets deposited in bones and teeth. The fluoride accumulation within kidney tubules may be very high compared with the plasma. As a result, the kidney could be considered an impending sink, site, and target of the acute fluoride toxicity.

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