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Fluoride in Groundwater- Sources, Geochemical Mobilization and Treatment Options



PJ Sajil Kumar*

Department of Hydrogeology, Freie Universitat, Germany

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*Corresponding author: PJ Sajil Kumar, Freie Universitat Berlin, Institute of Geological Sciences, Hydrogeology Group, Malteserstr. 74-100, 12249 Berlin, Germany Email: pjsajil@gmail.com

Abstract

The drinking water supply in many countries is affected by excess fluoride concentration. In India, several states are affected by high F^- groundwater. This paper presents a short review of the sources, geochemical mobilization and possible treatment options for high fluoride groundwater. Natural sources are large contributors to the F- enrichment in groundwater. The mobilization of fluoride from the from the aquifer to the aqueous solution is controlled mainly by the alkaline nature of the water, high concretion of HCO₃ and a high Na⁺ over Ca²⁺ concentration. Additionally, the possible treatment options such as adsorption - and membrane based techniques were also reviewed in this paper.

Introduction

Groundwater is the most common and important source of drinking water for India and the world Sajil Kumar [1], Belkhiri and Moumi [2]. This resource also serves other human purposes, such as domestic agriculture and industry Ramesh and Elango [3], Sajil Kumar et al. [4]. The availability of this resource is decreasing day by day due to problems in quality and quantity CGWB [5]. Overexploitation remains the major quantity issue whereas industrial, domestic, and agricultural pollutions and saline intrusions in coastal areas are examples of anthropogenic activates that deteriorate groundwater quality. Fluoride is a minor ion and its occurrence in groundwater is mostly attributed the natural sources, mainly of aquifer materials and rock formations in which groundwater is passing. The increase in the concentration of this ion is known as fluoride enrichment. The maximum permissible limit of fluoride in drinking water is 1.5mg/L WHO [6]. However, each country has their own standards based on the geo-environmental conditions and the per capita intake of water. In India, the permissible limit of fluoride is 1.2mg/L BIS [7]. Intake of fluoride rich groundwater can cause severe health problems such as dental and skeletal fluorosis. Andezhath and Gosh [8] reported that 62 million people in India are affected by health issues due to high fluoride consumption.

Discussion

In this section, the major sources of fluoride in groundwater, its controlling factors, geochemical mobilization and possible

treatment options will be discussed briefly. Factor influencing the F enrichment in the groundwater and the remedialtreatment possibilities is also addressed.

Sources and Fluoride in groundwater

Both natural and anthropogenic sources of fluoride in groundwater have been reported. However, it has been reported that the majority originate from the weathering and dissolution of fluoride rich minerals such as fluorite, apatite, mica, amphiboles, clay and villiaumite Apambire et al. [9]. Granitic rocks are having minerals rich in F⁻ with a range in concentration 500 – 1400 mg/kg. Gneissic and volcanic rocks can also act as an originating source. Volcanic and fly ash are also contributing fluoride to the groundwater Brindha and Elango [10]. Among the anthropogenic sources, industrialization and the agricultural operations are the primary sources. A high concentration of fluoride is reported from the coal combustion and brick kilning industries Agricultural fertilizers, especially rock phosphate fertilizers have very high concentration of fluoride.

Geochemistry of fluoride in groundwater

Geochemically, fluoride is a highly electronegative and reactive element it can combine with most of the elements to form ionic or covalent fluoride Saxena and Ahmend [11]. The major geochemical controls on fluoride are the presence F minerals, geology of the area, residence time, concentration of carbonate minerals pH, temperature, solubility, anion exchange capacity of the aquifer, groundwater age, depth of water occurrence, porosity of the aquifer and structure Apambire et al. [9]. Weathering of minerals such micas and amphiboles are one of the important factors that control the mobility of fluoride. In the presence of calcium, due to the high electro negativity of fluoride, it often forms CaF2 (Equation 1 and 2). A common ion effect can also be suggested, as in the presence of Ca2+, when the dissolution of fluorite is suppressed and causes decrease in the concentration of F in groundwater.

$$CaCO_{2}(s) + H^{+} - Ca^{2} + HCO_{2}(1)$$

 $CaF_{2} \rightarrow Ca^{2+} + 2F^{-}(2)$

According to Handa [12], these reactions can be combined and written as,

$$CaCO_{3}(s) + H^{+} + 2F^{-} -> CaF_{2}(s) + HCO_{3} - (3)$$

Alkaline pH is one of the triggering factors for the occurrence of fluoride in groundwater Jacks et al. [13]. Acidity in the water results in the absorption of F to the clay layers while alkaline water causes desorption from the aquifer and increases the concentration in groundwater Saxena and Ahamed [11], Sajil Kumar [14]. The resulting equation can be written as,

 $CaF_{2} + 2NaHCO_{3} = CaCO_{3} + 2Na^{+} + 2F_{-} + H_{2}O + CO_{2}$ (4)

Higher concentration of Na over Ca, along with alkalinity and bicarbonate ions also favors fluoride in groundwater.

Remedial measures and treatment options

Several methods have been in use and more are developing for the removal of fluoride from drinking water. Household techniques and low cost methods like lime softening, to highly sophisticated membrane techniques, are available. Mohapatra et al. [15] reported that fluoride removal techniques can generally be classified as adsorption based techniques and membrane based techniques. The most common adsorption techniques use alumina, clays and soils, calcium minerals, synthetic compounds and carbon materials, zeolite materials and ion exchange resins. The most common membrane techniques are nanofiltration, reverse osmosis and electro coagulation, and have also used in the treatment.

Conclusion

Fluoride concentration in groundwater mainly originates from natural sources, with a very less contribution from the anthropogenic activities. In most of the cases the fluoride enrichment occurs in groundwater by the dissolution of F-rich minerals such as amphiboles and micas present in the aquifers, mostly granitic rich rocks. The most favorable condition for increasing F⁻ concentration in groundwater is alkaline pH, high concentration of HCO_3 and high Na/Ca ratio. Consumption of F rich groundwater may cause serious health problems such as dental and skeletal fluorosis. Adsorption- and membrane based treatment methods are available techniques for the removal of F⁻ from groundwater.

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