Abstract

An area of around 100 square kilometers in the Nayagarh District of Orissa, India is reportedly affected by fluoride contamination in potable water particularly in and around Singhpur and Sagaragan villages.

Analyses of potable water indicate wide spatial variation of fluoride and other chemical species. About 20% of the total area, surrounding the hot spring has fluoride concentrations more than 1.5 ppm (the maximum permissible limit in potable water). Hydrogeochemically, majority of the potable water sampled belong to "no dominant type" in cation, and "bicarbonate" or "chloride type" in anion facies and those with high fluoride content are generally "sodium/potassium type" in cation facies and "chloride type" in anion facies. While the potable water with fluoride concentration above permissible limit is close to saturation and the normal water is undersaturated with respect to fluorite. On the other hand, all the water samples are in the range of near saturated to oversaturated condition with respect to calcite.

The thermal spring water in the area is alkaline in nature and characterized by high F^-, Na^+ and HCO_3^- with low Ca^{2+}, Mg^{2+}, Al^{3+} and Fe^{3+} concentrations. This water belongs to "sodium type" in cation facies and "bicarbonate type" in anion facies. The water is near to full equilibrium with respect to average crustal rock and is close to the fluorite saturation while saturated with respect to calcite. The temperature at the surface of this water body is around 55 ^{0}C and the subsurface reservoir temperature calculated from the concentrations of the aqueous species of Na^+, K^+ and Mg^{2+} (Giggenbach, 1988) varies from 100 to 125 ^{0}C.

Fluoride concentrations in water, irrespective of their sources of collection, show positive relations with pH, Na^+, Cl^- and HCO_3^- and negative with Al^{3+} and Fe^{3+}. Spatial distribution of fluoride shows higher values in the area surrounding the hot spring and decreases, sharply in the north and westerly directions and gently in the southeast direction. Principal component analysis on various parameters convincingly establishes mixing of thermal water with groundwater. Based on the fluoride concentrations in water, the area can be divided into high, moderate, mild and uncontaminated zone for management purposes.

Resistivity investigations in the vicinity of the hot spring show the presence of two to three litho-units, out of which the weathered and/or fractured layer mainly constitutes the unconfined aquifer. The sudden increase in the thickness of this formation close to the hot spring indicates the presence of buried structural discontinuities acting as possible conduits for venting the hot spring water. The inverse exponential relationship between the fluoride concentration and the apparent resistivity besides its spatial distribution also point towards likely mixing of potable water sources with thermal water. The low apparent resistivity zone overlaps with the high fluoride concentration zone in water.

Total and water-soluble fluoride measured in bulk and profile soils, collected from the vicinity of the hot spring, shows very high concentrations compared to the ones from the uncontaminated areas. Further, these parameters showed positive relations with OC, EC, Na and Si and negative with Al, Fe, Ca, Mg and K content only in the case of bulk soil in the vicinity of the hot spring. However, no such significant relations were observed in case of soils collected from areas more than 2 km away from the hot spring. In the profile soils, the increases in both total and water-soluble fluoride with depth are directly related to their clay content. The dominant clay minerals viz. smectite, kaolinite and illite, control the fluoride fixation in the soil.

Spatial distribution of both total and water-soluble fluoride indicated a point source i.e. the hot spring with highest concentrations, which gradually decreased away from it. The distribution patterns of both of them in soil matched with that of groundwater fluoride. Geostatistical analysis performed on the measured parameters in bulk soil identified three major factors likely controlling fluoride distribution. Based on these factors, the soil of the area has been divided into highly contaminated, moderately contaminated and uncontaminated zones.

The major rock types in the area are mafic granulites, khondalites and charnockites. Based on the biotite content in the charnockite, it is further grouped into biotite-rich and biotite-poor types. The biotite-rich charnockites and mafic granulites contain higher fluoride compared to the khondalites and biotite-poor charnockites. A comparative study on the modal percentages of major minerals and the respective fluoride contents, it is confirmed that the amount of biotite in rocks mainly controls the fluoride concentrations.

Water-rock interaction studies indicate that biotite-rich charnockites and mafic granulites release more fluoride into water irrespective of time and temperature as compared to khondalites and biotite-poor charnockites. The amount of fluoride leached from these rocks increases with increase in temperature. The ratios of F:(Fe+Mg+K) and F:(Fe+Mg) are low in khondalites and biotite-poor charnockites, their leachates, besides the water in contact and soil derived from them compared to those in the case of mafic granulites and biotite-rich charnockites. The variations in these ratios among rock types, water and the evidence of biotite breakdown along with apatite dissolution confirm the control of water-rock interaction on the composition of water and soil. Further, the presence of mylonitized bands provides easy channel for migration of fluid and increased surface area that enhance the intensity of water-rock interaction. The ratios, in water and soil collected from the vicinity of the hot spring, showed much higher values (>100 times) than from other areas. This, in turn confirms the effect of the thermal spring on water and soil characteristics in its vicinity.

The high fluoride content and higher values of F:(Fe+Mg+K) and F:(Fe+Mg) in the hot spring water are explained by assuming the interaction of equal proportions of all the rock types present in the area at rock-water ratio of 10 and at temperatures of about 100 ^{0}C. However, the depletion in the concentration of Ca, Mg, K and Fe in thermal water is probably due to their fixation on the wall rock in the course of water-rock interaction.

The present work confirms that the hot spring plays a major role in controlling the fluoride concentration and its distribution in both groundwater and soil in the area though the source of fluoride is entirely from the rocks through prolonged interaction with water at subsurface conditions. Abundance of biotite and mylonitization of litho units are responsible in the release of higher levels of fluoride from the rocks. The topography controls the water table and in turn has restricted the extent of mixing of thermal water with groundwater. Soils in the area have acted as sinks of fluoride by virtue of their clay contents as evident from the distribution pattern of fluoride in them.

Keywords : Fluoride, Hot spring, Water, Soil, Rock, Factor analysis, Resistivity, Water-rock interaction, Nayagarh