GROUNDWATER QUALITY STATUS WITH RESPECT TO FLUORIDE CONTAMINATION IN INDUSTRIAL AREA OF ANGUL DISTRICT ORISSA INDIA

*Rizwan Reza¹ and Gurdeep Singh²
¹Department of Civil, B. A. College of Engineering and Technology, Jamshedpur
²Department of Environmental Science and Engineering, Indian School of Mines, Dhanbad
*Author for Correspondence

ABSTRACT
The present study deals with the ground water quality with respect to F in Angul district of Orissa, India. Eighteen groundwater samples were collected from different locations covering open wells as well as tube wells for determining various parameters (pH, TDS, F, Cl, Na⁺, Ca²⁺ and Mg²⁺). The samples were collected during pre and post monsoon season. The study reflects the seasonal variation along with hydro-geochemical activities. Correlation matrix and factor analysis revealed that the hydro-geochemical condition was the main source for fluoride contamination whereas the run-off and atmospheric deposition was responsible for additional F⁻ concentration during post monsoon season. The obtained results were compared with the drinking water Standards to know the portability of water.

Key Words: Drinking Water Standard, Hydro-Geochemical, Al-Smelter, Correlation and Factor Analysis

INTRODUCTION
Among the water quality parameters, fluoride is one of the minor constituent in natural water. Fluoride has been classified as essential parameters in ascertaining the suitability of potable water (NRC, 1980; IS: 10500 and WHO, 1996). Fluoride content in groundwater is mainly due to natural contamination, but the process of dissolution is still not well understood (Handa, 1975; Saxena & Ahmed, 2001). Fluoride, an electronegative element, is highly reactive, therefore, almost never occurs in elemental state in natural water. It combines with most of the elements to form ionic or covalent fluorides. Areas with semi-arid climate, crystalline igneous rocks and alkaline soils are mostly affected (Handa, 1975). The origin of fluoride in groundwater is through weathering of alkali, igneous and sedimentary rocks. The common fluoride bearing minerals are Fluorspar (CaF₂), Cryolite (Na₃AlF₆), Fluorapatite (Ca₅ (PO₄)₃ F), Fluorite (CaF₂) is the principle bearer of fluoride and is found in granite, granite gneisses and pegmatite (Deshmukh et al., 1995 and Rao, 2009). Apart from natural sources, a considerable amount of fluoride may be contributed due to anthropogenic activities. Burning of coal, manufacturing process of aluminium, steel, bricks, Phosphatic fertilizers industries, often contain fluoride as an impurity and are being leached down to the ground water (Deshmukh et al., 1995; Anderson et al., 1991; Smith & Hodge, 1979; Tailor & Chandel, 2010).

Table 1: Range of fluoride concentration found in various parts of India

<table>
<thead>
<tr>
<th>Locations</th>
<th>Fluoride concentration (mg/l)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andhra Pradesh</td>
<td>0.38 – 4.0</td>
<td>Sreedevi et al., (2006)</td>
</tr>
<tr>
<td>Assam (Guwahati)</td>
<td>0.18 – 6.88</td>
<td>Dass et al., (2003)</td>
</tr>
<tr>
<td>Bihar (Rohtas)</td>
<td>0.1 – 2.5</td>
<td>Ray et al., (2000)</td>
</tr>
<tr>
<td>Delhi</td>
<td>0.11 – 32.5</td>
<td>Susheela et al., (2003)</td>
</tr>
<tr>
<td>Maharashtra (Yavatmal district)</td>
<td>0.30–13.41</td>
<td>Madhure et al., 2007</td>
</tr>
<tr>
<td>Gujarat (Mehsana)</td>
<td>0.1 – 40</td>
<td>Chinoy et al., (1992)</td>
</tr>
<tr>
<td>Karnataka</td>
<td>1.0 – 7.4</td>
<td>Sumalatha et al., (1999)</td>
</tr>
<tr>
<td>Kerala (Palghat district)</td>
<td>1.51 – 5.75</td>
<td>Shaji et al., (2007)</td>
</tr>
<tr>
<td>Madhya Pradesh (Shivpuri)</td>
<td>0.2 – 6.4</td>
<td>Nawlakhe et al., (1995)</td>
</tr>
<tr>
<td>Rajasthan (Dungapur)</td>
<td>0.1 – 10</td>
<td>Choubisa et al., (1996)</td>
</tr>
<tr>
<td>Tamil Nadu</td>
<td>0.51 – 4.0</td>
<td>Handa, (1975)</td>
</tr>
<tr>
<td>Uttar Pradesh (Agra)</td>
<td>0.1 – 12.8</td>
<td>Gupta et al., (1999)</td>
</tr>
<tr>
<td>West Bengal (Birbhum)</td>
<td>0.006 – 1.95</td>
<td>Gupta et al., (2006)</td>
</tr>
<tr>
<td>Rajasthan</td>
<td>1.0-5.2</td>
<td>Choubisa, (2007)</td>
</tr>
<tr>
<td>Uttar Pradesh (Sonbhadra)</td>
<td>0.48 – 6.7</td>
<td>Raju et al., (2009)</td>
</tr>
<tr>
<td>Andhra Pradesh (Visakhapatnam)</td>
<td>1.15-1.28</td>
<td>Rao, (2009)</td>
</tr>
<tr>
<td>Rajasthan (Malpara Tehsil)</td>
<td>0.08 -11.3</td>
<td>Tailor &amp; Chandel, (2010)</td>
</tr>
<tr>
<td>Angul-Talcher, Orissa</td>
<td>0.2 – 2.4</td>
<td>Present study</td>
</tr>
</tbody>
</table>
The high level of fluoride in drinking water beyond the permissible limit (IS: 10500 and WHO, 1996) has toxic effects, while its optimum level shows beneficial effects in reducing dental carries. The severity depends upon the amount ingested and the duration of intake Fawell et al., (2006). Though fluoride enters the body through water, food, industrial exposure, drugs, cosmetic etc., drinking water is the major source (75%) of daily intake Sarala and Rao, (1993). Major health problems caused by high level of fluoride are dental fluorosis (teeth mottling), skeletal fluorosis and deformation of the bones in children as well as adults (Ramaiah et al., 2006).

In the Indian context, the fluoride is dissolved in groundwater mainly from geological sources. Fluoride epidemic has been reported mostly in granite and gneissic geological formation of different states in India (Tripathy et al., 2005; Agrawal, 1997 and Raju et al., 2009). The high fluorides occur in top aquifer system and have reached to endemic level in most of the state’s (Agrawal, 1997). In early (1986), fluorosis was reported only in 13 states of India, in 1992 it was 15, in 2002 it was 17 and now it is more than 19, indicating that endemic fluorosis has emerged as one of the most alarming public health problem of the country. At present 62 million people, including 6 million children suffer from fluorosis because of consuming fluoride contaminated water (Raju et al., 2009). Fluoride concentration in drinking water in various places of India is illustrated in Table 1.

MATERIALS AND METHODS

Study area
The study area is bounded by latitudes 20° 37’ N to 21° 10’ N and longitudes 84° 53’ E to 85° 28’ E and situated at an average height of 139 m above mean sea level. The river catchment is characterized by Precambrian granites, gneisses and schists of Eastern Ghats with local intrusive and volcanic lithologies; lime stone, sand stone and shales of the Gondwanas (Konhauser et al., 1997; Panda et al., 2006 and Sundaray et al., 2006). The area comes under sub tropic monsoon climate with an average annual rainfall of 1370 mm and the temperature varies from 11.9° C to 44.4° C (Sundaray, 2009). Availability of raw materials and perennial water supply from Brahmani and its tributaries (Tikira, Singhara, Nandira and Kisinda) led to rapid growth of industrialization in the study area. At present, it accommodates several large and medium scale industries such as Nalco Smelter and its Captive Power Plant (CPP-960MW), Talcher Super Thermal Power Station, NTPC (TSTPS-3000MW), Talcher Thermal Power Station (TTP-460MW), Iron and Steel industries and various coal mines. These industrial activities affect various components of ecology and the environment including groundwater contamination.
Sampling and analysis
In order to estimate the fluoride contamination in groundwater at Angul district of Orissa, samples were collected from eighteen different locations (open well and tube well) during summer and post-monsoon seasons. The sampling sites are selected in order to have a fairly comprehensive picture of the fluoride intensity in groundwater. Care was taken to collect subsequent samples from same location in both seasons. The Samples were taken using acid washed plastic container to avoid unpredictable changes in characteristic as per standard procedures APHA, (1998). Average values of three replicates were taken for each determination. Details of sampling locations along with their latitude and longitude are illustrated in Table 2. pH and total dissolved solids (TDS) were measured by pH and TDS meter respectively. Cl by AgNO₃ titration, F by SPANDS method, while ions such as Ca²⁺, Mg²⁺ and Na⁺ by flame-photometer.

To evaluate the potential relationship between various physico-chemical parameters, Pearson correlation analysis was carried out by using “Statistical Package for Social Science (SPSS), version-16”. “Principal component analysis” was used to extract the driving factor of pollutants either by natural or anthropogenic activities.

RESULTS AND DISCUSSIONS
The results of chemical analysis of ground water samples of Angul district are illustrated in Table 2. The pH value of ground water in study area varied from 6.4 to 7.5 and 5.3 to 9.2 in summer and post-monsoon respectively. It indicates slightly alkaline condition in most of the cases, which favours the dissolution of fluoride bearing minerals in ground water (Saxena & Ahmed, 2001).

Total dissolved solids of the sample varied from 176 to 326 mg/l and 160 to 303 mg/l in summer and post-monsoon season respectively. In most of the cases the concentrations of TDS were higher in summer than the concentration found in post-monsoon season. It indicates the intense chemical weathering of the minerals bearing rocks. It may be due to stagnant or low flow of ground water and accumulation of dissolved salts during summer season (Reddy et al., 2009 and Manahan, 1993).

The maximum values of Ca²⁺ and Mg²⁺ ions in ground water were found 171 mg/l and 74.4 mg/l in summer season while in post-monsoon season the values were found to be 122.8 mg/l and 59 mg/l respectively. The higher concentration of these ions in summer season may be resulted from dissolution or weathering of respective minerals from rocks whereas in post-monsoon season the concentration of following ions become slightly low. It may be attributed to dilution effect of rain through seepage and percolation of surface or sub-surface water (Sengupta, 1993). Similarly the Cl⁻ ion concentration varied from 25.5 to 64 mg/l and 15 to 55 mg/l in summer and post-monsoon respectively. The higher value of Cl⁻ was found in summer as comparison of post-monsoon season. It may be due to accumulation of salt concentration (Cl⁻) especially from evaporation or loss of water in unsaturated zone during summer season. While in the case of Na⁺, the concentrations were found in the range of 6.2 to 39.5 mg/l in summer season whereas in post monsoon season it was 10.1 to 47.5 mg/l. The higher concentration of Na⁺ during post-monsoon season may be attributed to percolation or seepage of agricultural and domestic waste water (Saxena & Ahmed, 2001).

The fluoride concentrations were found in the range of 0.2 to 2.1 mg/l and 0.4 to 2.4 mg/l in summer and post monsoon seasons respectively. The higher fluoride concentration was found during post-monsoon season. It is to be supported with low calcium values and high sodium content in the ground waters along with high pH. Alkaline condition of ground water favours the solubility of fluorine- bearing minerals while in acidic medium (acidic pH), fluoride is adsorbed in clay. However, in alkaline medium, it is desorbed, and thus alkaline pH is more favourable for fluoride dissolution activity (Raju et al., 2009; Rango, 2008; Saxena & Ahmed 2003; Handa, 1975 and Meenakshi et al., 2004). Minerals which have the greatest effect on the hydro-geochemistry of fluoride are fluorite, apatite, mica, amphiboles, certain clays and villiamite (Raju et al., 2009 and Rango, 2008). Even taking into consideration aquifers containing fluorine bearing minerals, water rarely contain more than 8-10 mg/l, due to the very low solubility of F-bearing minerals (Rango, 2008). Although CaF₂ is one of the major sources of fluoride but its solubility in fresh water and its dissociation rate are very low (Rango, 2008 and Saxena & Ahmed, 2001).

The aqueous ionic concentrations of groundwater also influenced the fluoride solubility behaviour; for example, in the presence of excessive sodium bicarbonates in groundwater, the dissociational activity of fluoride will be high, and this can be expressed as in Equation 1 (Saxena & Ahmed, 2003). Equation 2 suggesting the fluoride concentration in natural waters is inversely related to Ca concentration. The lower Ca content permits free mobility of the fluoride ion into the solution (Rango, 2008).

\[
\text{CaF}_2 + 2\text{NaHCO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na} + 2\text{F} + \text{H}_2\text{O} + \text{CO}_2
\]  \hspace{1cm} (1)

\[
\text{CaF}_2 \rightarrow \text{Ca}^{2+} + 2\text{F}^-
\]  \hspace{1cm} (2)
Higher concentrations of fluoride in ground water during post-monsoon season also indicate the results of anthropogenic activities within the study area. Fluoride contamination to the ground water may be due to seepage, moving and percolation of fluoride contaminated effluents from nearby existing industries such as Aluminium smelter and Talcher Thermal Power Plants (Deshmukh et al., 1995 and Anderson et al., 1991). Leaching from ash pond after rain also contributes to the higher concentration of fluoride in ground water (Prasad, 2007). In present study the fluoride concentration in most of the ground water samples were found within permissible limit (IS: 10500 and WHO) during both seasons except a very few samples. The samples in which the higher concentration of fluoride in summer season were Banaropal Chowk, tube well water (GW14), Nuasaiki village, open well water (GW16), Tulipsyal village, open well water (GW17), Lonipeida village, tube well water (GW18) and Gadarkhai village, open well water (GW18) while in post-monsoon season two more samples were found as Gotamara village, tube well water (GW1) and Kandasaar, open well water (GW4). It is observed that the high fluoride concentration found in the samples which was collected from the nearby industrial complexes particularly aluminium smelter, thermal power plants and ash ponds etc. The effluents of following industrial activities are responsible for fluoride contamination in ground water through seepage and percolation of contamination (Konhauser, 1997; Deshmukh et al., 1995; Anderson et al., 1991; Prasad, 2007 and Sengupta, 1993).

Free circulation of water caused by rainfall and/or irrigation in the weathered products dissolves and leaches the minerals, contributing fluoride to the ground water (Rao 2009 and Shaji et al., 2007). Therefore, the concentration of fluoride in 27.8% and 38.9% of the total groundwater samples in summer and post-monsoon season which exceeds the desirable limits of fluoride (1.0 mg/l) prescribed for drinking purpose by Indian and WHO standard. Higher concentrations of fluoride were found in the seven out of eighteen ground water samples during post-monsoon season. It may be due to higher concentration of sodium ions as indicative of weathering of minerals. When the concentration of sodium in groundwater increases its solubility increases correspondingly and it diverts more fluoride into water (Raju et al., 2009).

Table 2: Statistical variation of obtained data various parameters during summer and post monsoon season

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH</th>
<th>TDS</th>
<th>F</th>
<th>Cl</th>
<th>Na+</th>
<th>Ca2+</th>
<th>Mg2+</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Summe</td>
<td>Post-</td>
<td>Summ</td>
<td>Post-</td>
<td>Summe</td>
<td>Post-</td>
<td>Summe</td>
</tr>
<tr>
<td>Min.</td>
<td>6.4</td>
<td>5.3</td>
<td>176.1</td>
<td>160.7</td>
<td>0.2</td>
<td>0.4</td>
<td>25.5</td>
</tr>
<tr>
<td>Max.</td>
<td>7.5</td>
<td>9.2</td>
<td>326.5</td>
<td>303.6</td>
<td>2.1</td>
<td>2.4</td>
<td>64.0</td>
</tr>
<tr>
<td>Mean</td>
<td>7.1</td>
<td>7.3</td>
<td>231.3</td>
<td>216.7</td>
<td>0.9</td>
<td>1.1</td>
<td>44.1</td>
</tr>
<tr>
<td>SD</td>
<td>0.27</td>
<td>0.73</td>
<td>51.51</td>
<td>43.32</td>
<td>0.62</td>
<td>0.65</td>
<td>12.89</td>
</tr>
</tbody>
</table>

Table 3: Details of samples exceeding the desirable limits of fluoride within study area

<table>
<thead>
<tr>
<th>Parameter</th>
<th>IS Standards</th>
<th>WHO Standards</th>
<th>No. of samples exceeding desirable limits</th>
<th>Percentage (%) of the total No. of samples exceeding limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>0.6-1.2 mg/l</td>
<td>0.5 mg/l</td>
<td>5*</td>
<td>27.8*</td>
</tr>
</tbody>
</table>

Statistical analysis

For understanding the controlling mechanism of fluoride concentration in the groundwater, the correlation coefficient (r) of fluoride with pH, calcium and sodium is illustrated in Figs. 2, 3 and 4. The relation between fluoride - pH and fluoride - sodium shows the significant positive trend in both seasons. This indicates that higher sodium along with the alkaline environment activates the leaching or weathering of fluoride from the source material and thus, affects the concentration of fluoride in the groundwater (Shaji et al., 2007; Handa, 1975 and Raju et al., 2009). Other side there is also a positive correlation among fluoride and calcium. But, this correlation is not as high as that for fluoride and sodium during post-monsoon. This indicates a greater affinity of fluoride with sodium rather than calcium. It also suggests that if there is more sodium in groundwater, the lesser would be the calcium contents (Shaji et al., 2007 and Handa, 1975). The occurrence of higher sodium content in the groundwater during post-monsoon season might have been released from the weathered soil and intrusion of agricultural and domestic waste water.
Figure 2: Correlation between fluoride and pH

Figure 3: Correlation between fluoride and calcium

Figure 4: Correlation between fluoride and sodium
Factor analysis (varimax rotated) of following data of ground water indicates three trends for both season. The total variability accounted by 3 factors is 85.5% in summer while in post-monsoon it is 80.7%. The number of significant factors within the data is established by considering only those with an Eigen value >1.0. The degree of association between each variable and each factor is given by its dependability on other factor.

In summer season (Table 4), factor 1 shows geo-chemical relationship between TDS, Ca\(^{2+}\) and Mg\(^{2+}\). It indicates soluble minerals from rocks-water interaction in low flow of groundwater. Factor 2 explains good relationship between pH and Cl\(^{-}\). It may be due to the presence of chloride containing rocks and accumulation of salt (Cl\(^{-}\)) due to loss of water during summer season. Factor 3 shows high score of Na\(^{+}\) with F. High value of Na\(^{+}\) increased the suitability of fluoride from rocks strata. In post-monsoon season factor 1 shows good relationship between TDS, Ca\(^{2+}\) and Mg\(^{2+}\). It indicates weathering of various minerals and rocks due to excess of water. Factor 2 accounted strong correlations between pH, F\(^{-}\) and Na\(^{+}\). It gives the favorable conditions for solubility of fluoride in ground water. Intrusion of agricultural and domestic waste may appreciate the favorable condition. Factor 3 explain the high concentration of Cl\(^{-}\), it may be due to seepage of contaminated water from agricultural field or domestic areas.

### Table 4: Factor analysis for various seasons

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Summer</th>
<th></th>
<th>Components</th>
<th>Post-monsoon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>pH</td>
<td>-.149</td>
<td>.869</td>
<td>.005</td>
<td>.009</td>
</tr>
<tr>
<td>TDS</td>
<td>.960</td>
<td>.230</td>
<td>.004</td>
<td>.946</td>
</tr>
<tr>
<td>F</td>
<td>-.571</td>
<td>.320</td>
<td>.635</td>
<td>-.788</td>
</tr>
<tr>
<td>Cl</td>
<td>.220</td>
<td>.836</td>
<td>.227</td>
<td>-.004</td>
</tr>
<tr>
<td>Na(^{+})</td>
<td>-.009</td>
<td>.123</td>
<td>.954</td>
<td>-.101</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>.913</td>
<td>-.001</td>
<td>-.281</td>
<td>.873</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>.887</td>
<td>-.114</td>
<td>-.157</td>
<td>.878</td>
</tr>
<tr>
<td>% variance</td>
<td>42.12</td>
<td>23.41</td>
<td>21.04</td>
<td>43.85</td>
</tr>
<tr>
<td>Cumulative % of variance</td>
<td>42.12</td>
<td>65.53</td>
<td>86.57</td>
<td>43.85</td>
</tr>
<tr>
<td>Eigen value</td>
<td>3.32</td>
<td>1.93</td>
<td>0.79</td>
<td>3.29</td>
</tr>
</tbody>
</table>

**CONCLUSION**

Most of the ground water samples in study area were found within the drinking water quality standard (IS: 10500 and WHO, 1996). The study revealed that rock-water interaction is the major source of fluoride in ground water and very much influenced by local lithology. But in post-monsoon season, besides the weathering processes, anthropogenic activities also play an significant role in the incidence of fluoride in ground water. The samples (Gotamara village, Nuasahi village, Tulsipal village, Longipeda village, Gadakhai village, Girang village water and Banarpal chowk) around the Aluminium smelter and thermal power plants are evidenced to excess fluoride concentration in ground water. We conclude the fluoride contamination to the ground water during the post-monsoon season is mainly due to the seepage, moving and percolation of fluoride contaminated water nearby industrial complexes.

**ACKNOWLEDGEMENT**

The authors are thankful to State Pollution Control Board Orissa, for sponsoring this study. Authors are also grateful to Director, ISM to providing research facilities. One of the authors (Rizwan Reza) is grateful to Indian School of Mines/MHRD/Govt. of India, for granting of fellowship.

**REFERENCES**


Choubisa SL (2007). Fluoridated ground water and its toxic effects on domesticated animals residing in rural tribal areas of Rajasthan, India. International Journal of Environmental Studies, 64(2) 151-159.


Handa BK (1975). Geochemistry and genesis of fluoride containing ground waters in India. Groundwater, 3(3) 275–281.


