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A Statistical Appraisal to Hydrogeochemistry of Fluoride Contaminated Ground Water in Nayagarh District, Odisha

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Abstract: Seasonal variation of ground water in Nayagarh district, Odisha is determined by analysing both pre and post monsoon water samples. The high fluoride content is an endemic problem in the area and special attention was attached to the point. The chemical compositions of the ground water of the area are dominated by CaCl, NaCl and mixed CaMgCl types in pre-monsoon and $CaHCO_3$-mixed CaMgCl type in post-monsoon. This is largely due to chemical weathering of Eastern Ghats Mobile Belt rock types. Increasing alkalinity vis-a-vis F concentration in pre-monsoon is associated with sodium-bicarbonate water types having high pH (>7) and low calcium and magnesium contents. The percentage of total high fluoride containing water samples is nearly double in pre-monsoon than in post-monsoon. During both the seasons, pH values indicate mildly alkaline to weakly acidic nature of the water samples. Fluoride concentration has good correlation with pH in pre-monsoon whereas in post-monsoon it shows good correlation with Fe. Facies analysis indicates that water is becoming predominantly Ca-Na cation and Cl-SO_4-HCO_3 anion type in pre-monsoon than Ca-Mg type and HCO_3- Cl-SO_4 type in post-monsoon. The seasonal variations in concentrations of anthropogenic components demonstrate that the groundwater system is very less liable to pollution by human activities.

Keywords: Hydrogeochemistry, Water analysis, Fluoride contamination, Facies analysis, Clusture analysis, PCA/FA, Odisha.

INTRODUCTION

Fluoride pollution of the environment can occur due to natural reasons and human activities. Fluoride in minerals can be leached out by rainwater resulting in contamination of ground and surface water. In groundwater, the natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the rocks, the temperature, the action of other chemical elements, and the depth of the aquifer. Fluoride contamination can also occur due to discharge of untreated industrial wastewater. Fluoride in drinking water within a certain limit is beneficial for healthy bones and teeth. But excessive intake of fluoride causes dental or skeletal fluorosis. According to WHO (2006) norms, the upper limit of fluoride concentration in drinking water is 0.5-1.0 mg/l. Although ground water is mostly presumed to be safe for drinking purpose, overexploitation may affect the quality of water. So a periodic assessment of ground water quality is very important. Estimates indicate that total availability for use in the country is around surface and ground water availability is around 1,869 billion cubic meters (BCM). Of this, 40% is not available for use due to geological and topographical reasons. Around 4,000 BCM of fresh water is available due to precipitation in the form of rain and snow, most of which returns to the sea via rivers. Eighty nine per cent of surface water is used in agricultural sector, nine per cent is used for domestic purposes and two per cent is used by industrial sector (Khurana and Sen, www.wateraid.org). The pressure of development is changing the distribution of water in the country and access to adequate water has been cited as the primary factor responsible for limiting development. The average availability of water remains more or less fixed according to the natural hydrological cycle, but per capita availability reduces steadily due to increasing population. In a recent study undertaken by CGWB, Bhubaneswar, net annual ground water availability in Nayagarh district is around 51430 ham of which 1898 ham is being used for domestic and industrial purposes (Pati, 2009). The present study area is in news for fluoride contamination of ground water and severe fluorosis of the inhabitants.

GEOLOGY AND GROUNDWATER CONDITIONS

Nayagarh district is a rugged and hilly terrains with thick forest cover. Hills and plateaus occupy around

66% (2507 sq. km) of the district. It covers an area of 3890 sq. km. The annual rainfall is around 1449 mm. The chief drainage is constituted by Mahanadi river and its tributaries. The study area ($20^0 08'39.9"$:$85^0 02'57.9"$) is located in the eastern part of Nayagarh district adjacent to Khurda district. The area comprises a small part of the Eastern Ghats Mobile Belt. This belt is a poly-deformed and poly-metamorphosed terrain with rock types varying in age from Archean to Recent (Mukherjee et al. 1999). The rock types are khondalites, quartzites, calc-silicate granulites, charnockites and gneisses with migmatised quartzo-feldspathic gneisses. Lithologically, the garnet-sillimanite gneiss is the predominant rock type, which is highly altered. The major minerals are plagioclase, orthoclase, biotite, hornblende, hypersthene and quartz. These rocks contain fluorapatite, a source of fluorine, in appreciable quantity. Regional structural control is demonstrated by Mahanadi boundary fault along Gondwana graben and Archaean geothermal lineament trending NNW-SSE. Thermal springs are present along these lineaments (Mezger and Cosca, 1999). There are more than 50 thermal springs along this lineament.

The Archaean weathered and crystalline rocks form the most predominant hydrogeological unit of the area with low to moderate development potential. The fluctuation in water table is due to seasonal recharge and discharge. Ground water development is through shallow dug wells tapping the meta-sedimentary and gneissic horizons. The ground water phreatic zone is variable according to the annual rainfall and seasonal recharge. Ground water development in Nayagarh district is around 15.52% and is limited to the pediment areas (Pati 2009).

The classical geology related to fluorine mineral-chemistry reveals that the hydroxyl ion gets substituted by fluoride ion, since fluorapatite is more stable than hydroxylapatite. The fluorine, which cannot be incorporated in crystalline phase during crystallization and differentiation of magmas, will be accumulated in hydrothermal solutions. These fluids may form hydrothermal fluorite deposits and veins. Fluorine transport in these aqueous solutions is controlled mainly by the solubility of CaF_2 (Allmann and Koritnig, 1974). In carbonate sedimentary rocks the fluorine is present as fluorite. Clastic sediments have higher fluorine concentrations as the fluorine is concentrated in mica and illite of the clay fractions. In metamorphosed rocks, the original minerals are enriched in fluorine by metasomatic processes (Frencken, 1992). The present study is focused on fluoride contamination of ground water and its relations with other physico-chemical parameters.

MATERIALS AND METHODS

Sampling was done during pre-monsoon and post-

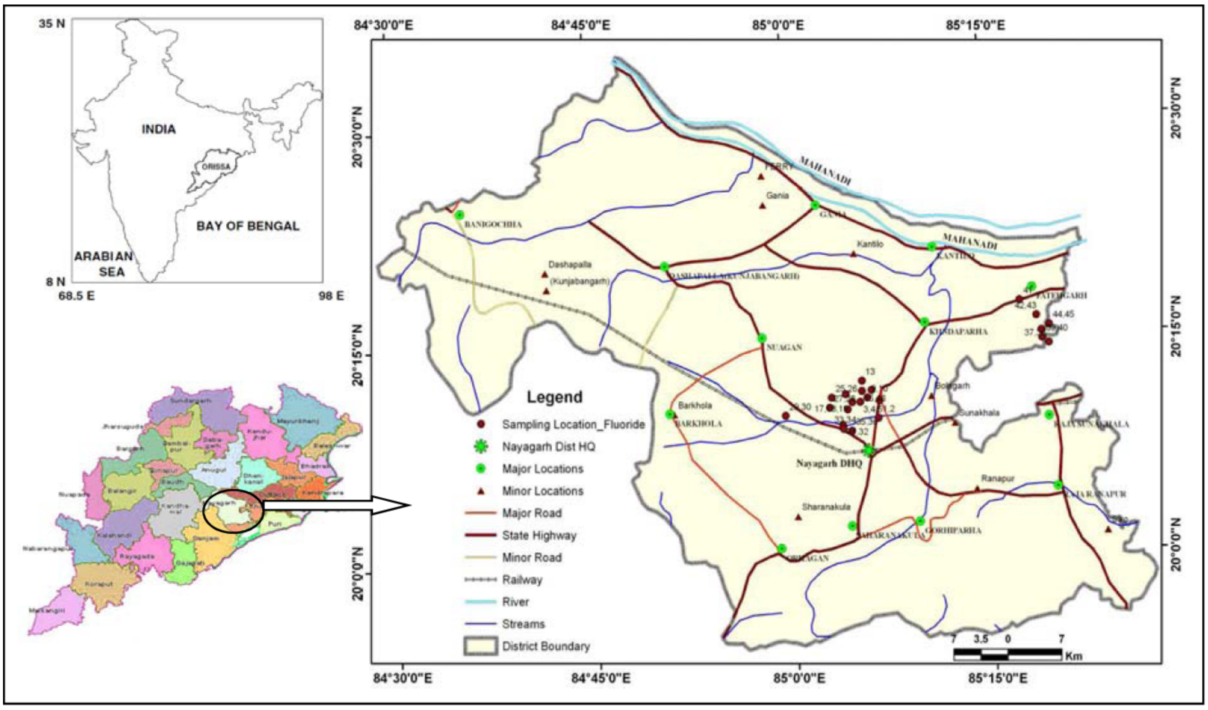


Fig.1. Map showing sampling points of Nayagarh district.

monsoon of 2010. For collection, preservation and analysis of the samples, the standard methods (APHA, 1995) were followed. The water samples were collected in pre-washed (with hydrochloric acid) and rinsed (3 to 4 times with distilled water) bottles. EC, pH, salinity and conductivity were measured in the field by water measurement kit. The chemical parameters like Cl, SO_4, Ca hardness, Mg hardness, Ca, Mg, HCO_3, and CO_3 were determined by standard titration methods in the laboratory. Phosphate was measured by spectrophotometer whereas Na and K were analysed by flame photometer. Al was determined by ICP-OES. Concentration of F was measured by Metrohm fluorometer. Heavy metals like Fe, Cu, Pb, Zn, Mn, Cd, Co, Cr and Ni were analysed by AAS. The sampled dug wells are up to 15 to 20 m and tube wells are up to 60 m deep depending upon topography of the area.

RESULT AND DISCUSSION

The various physico-chemical parameters of water samples were analysed and the descriptive statistics of the analyzed parameters are given in Table 1.

The observed pre and post monsoon samples exhibit much variation in concentration of several parameters. pH values indicate, the water is mildly alkaline to weakly acidic. High EC values are result of high level of mineralization in the phreatic zone due to the heavy leaching of Ca, Mg, Na, K, Cl, SO_4 , HCO_3, CO_3, NO_3, Fe and F (Hem, 1991). Max EC of 4.10 μS/cm was noted in pre-monsoon samples at Tarabalo village dug well. EC shows very good correlation with salinity during both the seasons. The total hardness values indicate moderately hard water type with maximum TH value of 1095.38 mg/l (as $CaCO_3$) in post-monsoon period. The chloride concentration exceeds the desirable limit, (ISI, 1991) in many stations.

Most of the chemical components show higher concentration in pre-monsoon than in post-monsoon. Ground water in the study area is generally alkaline in nature. pH values vary between 6.14–8.26 and 6.36 to 8.65 in post-monsoon and pre-monsoon with a mean of 6.8 and 6.9 respectively. TDS values range from 0.011 to 1.965 mg/L during the post-monsoon and 0.008 to 1.729 mg/L during the pre-monsoon indicating higher TDS values in post-monsoon. Chloride shows significantly higher concentrations in most of the pre-monsoon samples with a mean of 164.27 mg/l. Nitrate concentrations in the ground water samples are higher in the pre-monsoon as compared to post-monsoon. The concentration range of several parameters in two different seasons are represented in Box and Whisker diagram (Fig.2).

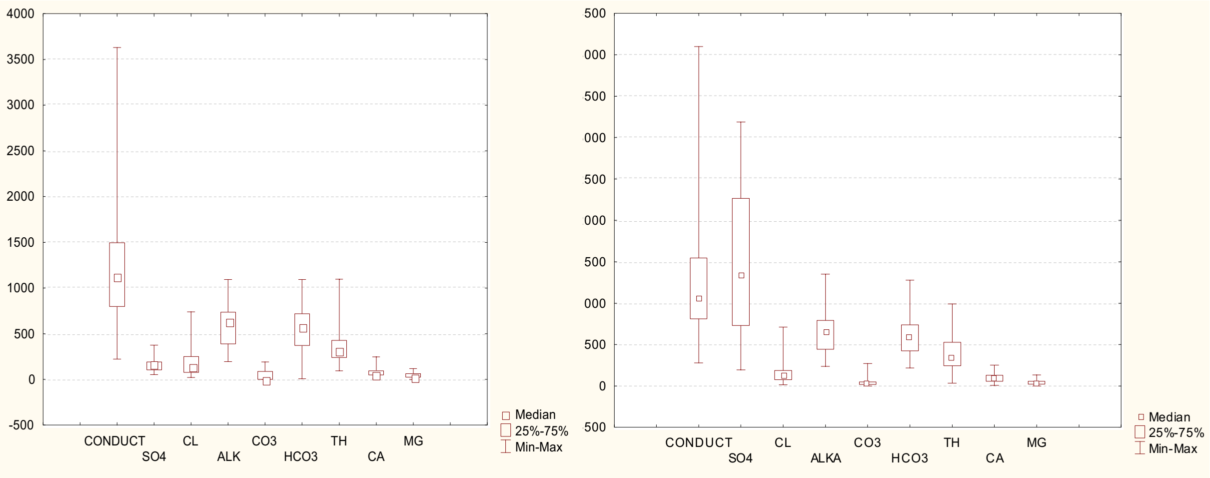
The notable feature of the plot is that some concentration values of certain parameters like Na, K, EC and F are beyond the plotting range indicating the diversity of water-aquifer rock interaction due to seasonal recharge.

Correlation Analysis

There are two ways to analyze the relationship between the fluoride concentration and hydrochemical parameter. One would be to define a single criterion for the considered hydrochemical parameter and to investigate whether the

Table 1. Descriptive Statistics of the analytical data

	Pre-monsoon					Post-monsoon				
	Min.	Max.	Mean	Std. Devn	Variance	Min.	Max.	Mean	Std. Devn	Variance
pH	6.14	8.65	6.9719	0.3668	0.135	6.14	7.53	6.882	0.306914	0.0942
EC	222.00	4100.0	1268.44	790.306	624584.29	222.0	3730.0	1291.16	837.44914	701321.07
Salinity	0.00	1.9	0.416	0.429	0.184	0.00	1.90	0.45	0.489206	0.239
F	0.01	14.0	1.04	1.9823	3.929	0.0056	6.775	0.73	1.031018	1.063
PO_4	0.02	3.356	0.3603	0.61069	0.373	0.0022	2.095	0.26	0.489209	0.239
Na	0.90	677.0	79.52	115.444	13327.4	0.90	22.2	5.15	4.273325	18.261
K	0.01	611.0	35.56	92.394	8536.68	0.01	16.2	2.01	3.543851	12.559
SO_4	53.76	3187.2	800.456	921.166	848546.7	53.76	376.32	153.31	61.8	3819.277
Cl	10.26	738.92	164.27	153.18	23465.07	10.263	738.92	169.21	162.029	26253.533
Alka	194.99	1350.0	604.538	228.009	51988.4	194.99	1090.79	594.01	220.189	48483.477
CO_3	0.00	270.0	41.699	53.813	2895.8	0.00	231.68	48.52	64.1987	4121.473
HCO_3	7.72	1278.0	563.28	229.706	52764.9	7.72	1090.79	546.69	244.77	59912.51
TH	32.03	1095.38	371.147	208.1	43307.4	49.244	1095.377	336.82	186.056	34616.98
Ca H	20.02	624.55	202.87	122.85	15091.39	27.625	614.1476	174.70	102.303	10465.88
Mg H	0.00	544.48	167.699	124.146	15412.19	0.00	481.229	161.66	108.056	11676.125
Ca	8.01	249.82	81.22	49.157	2416.39	11.072	246.15	70.02	41.003	1681.246
Mg	0.00	132.31	40.76	30.176	910.6	0.00	117.035	39.31	26.279	690.599
Fe	0.0029	3.2051	0.4499	0.672033	0.452	0.0029	3.205	0.2657	0.597014	0.356



(a) post-monsoon (b) pre-monsoon

Fig.2. Box and Whisker plot of different parameters in two seasons.

obtained values correlate significantly with each other. Another is performed as a simple correlation component analysis between the above said variables (Helena et al. 2000; Panagopoulos et al. 2004) described in factor analysis headers. Correlation coefficient study indicates, conductivity shows very good correlation with salinity in both the seasons (r=+0.926 in pre-monsoon and r=+0.996 in post monsoon). pH shows a positive relationship with fluoride concentration in post monsoon whereas a strong correlation (r=+0.931) is established between Fe and F in pre-monsoon. Correlation coefficient between Na and F is found to be a direct function of seasonal recharge. The coefficient values are 0.63 and 0.36 for post-monsoons and pre-monsoons respectively. In case of potassium, a negative correlation with fluoride was observed for both of the seasonal water samples.

HCO_3 is well correlated with Mg (pre-monsoon) and Na (post-monsoon) indicating weathering of feldspar and pyroxene from the host rocks (Lakshmanan et al. 2003; Madhavan and Subramanian, 2006) in pre-monsoon samples, whereas the post-monsoon samples are very poorly correlated indicating almost no or a very little weathering influence. The less contribution of K may be due to the greater resistance of K to weathering and its fixation in the clay minerals (Sarin et al. 1989).In both the seasons; high TH factors have good correlations with bicarbonate in contrast to carbonate indicating that Ca and Mg concentrations regulate the alkalinity character. Poor correlations of SO_4 and PO_4 with total alkalinity and other parameters indicate lesser influence of anthropogenic impact in both the seasons. F concentration is less in many samples, but higher values are also noticed at a few places (up to 14 mg/l at Tarabalo Hot Spring). The relations between parameters vary from highly competitive to noncompetitive type. This type of variation in correlation indicates complexity of the hydrochemical components of ground water (Aris et al. 2007). The degree of chemical activity of water regime on country rocks depends upon the mineralogy and other geological characteristics of the rocks. Proximity of cation concentration in the study area is variously controlled by other physico-chemical parameters. In pre-monsoon samples, the alkalies are regulated by the chloride ions. Fluoride is mostly regulated by iron concentrations in post-monsoon and pH in pre-monsoons times. This deviation may be due to the decreased level of water recharge and hence the less availability of transition metal ions along with alkalis ions for halogen ion-exchange process (Karbassi, 1996).

Hydrochemical Facies

The hydrochemical characteristics of groundwater can be understood by plotting the major cations and anions in the Piper trilinear diagram (1944) explaining hydrochemical evolution and identification of the dominant processes that control water chemistry.

The water samples are plotted in Piper trilinear diagram (Fig. 3a and b) and facies map (Back, 1961) (Fig. 4a and b) to find out their hydrochemical behaviour in two seasons. In pre-monsoon water samples, the water quality is more towards sodic and calcic fields (Fig.3a). The overall chlorinity increases as there is decrease in seasonal ground water recharge governing the increase in salinity. Moreover maximum number of samples belong to CaCl, NaCl and mixed CaMgCl fields. It is noted that, though the alkalinity of the water samples remain almost unchanged in both the seasons, the water regimes exibit increased salinity in pre-monsoon. Piper trilinear plotting in post-

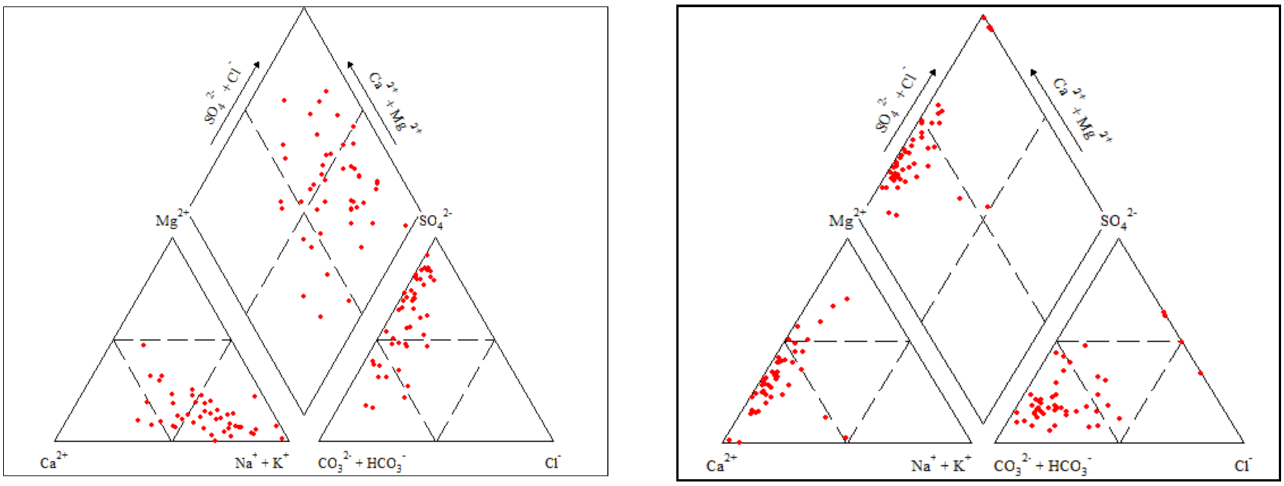


Fig.3a. Piper plot. **(a) P**re-monsoon. **(b)** Post-monsoon.

monsoon water samples (Fig.3 b) indicates that the chemical properties of the water are dominated by the alkaline earths and weak acids. A few samples are non carbonates exceeding 50%. The overall information is that most of the ground water samples fall in the field of $CaHCO_3$ where as a few samples fall in the fields of mixed CaMgCl type fields. These water types reflect the predominance of bicarbonate alkaline earth waters with higher alkali contents, but with a general tendency towards no-dominant water types' regime.

The facies analysis indicates Pre-monsoon ground water samples belong to Ca-Na to Na-Ca cation and Cl-SO_4-HCO_3 to HCO_3-Cl-SO_4 anion facies, whereas, post-monsoon water samples belong to calcium-magnesium cation and bicarbonate-chloride-sulphate anion facies (Fig.4a and b).

Mineralogical Evidences

Minerals which have greatest effect on hydrochemistry of fluoride are fluorite, apatite, micas, clay group of minerals, chlorites and chloritoids. The XRD pattern of sediment/soil samples from the area indicates the presence of fluorine bearing minerals (fluorite, fluoro-apatite, carbonate-apatite) along with secondary regoliths (Illite, montmorrilonite, mullite, chlorite). Fluorine in clay group of minerals is more susceptible to chemical leaching than those of micas and other fluorine bearing heavy minerals (Deer-Howie-Zussman, 1985), thus more F is evident in ground water of Nayagarh area as XRD-pattern indicates presence of more clayey proportions. Chemical analysis data reveal that the water is becoming more sodic in pre-monsoon indicating that more Na cation is added due to the leaching process

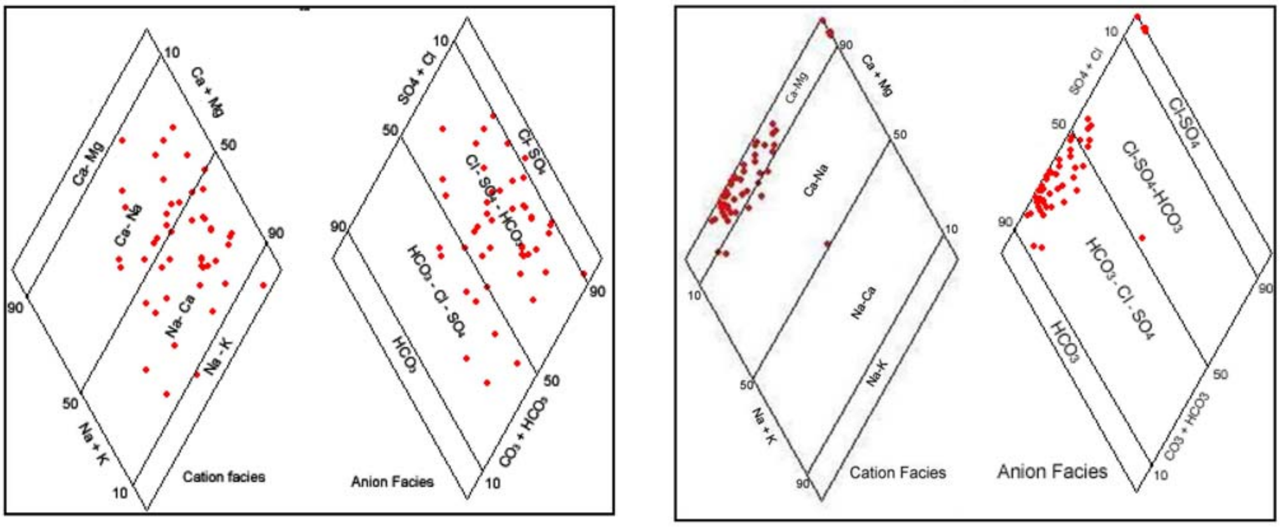


Fig.4. Water Facies map. **(a)** Pre-monsoon. **(b)** Post-monsoon.

through lateritization (Srivastava, 2005). Ultimately the $CaHCO_3$ and CaMgCl water types of post-monsoon are the byproduct of base-exchange process as Ca is being replaced by Na giving rise to NaCl and mixed CaMgCl type water in pre-monsoon samples. From the above hydrochemical monitoring it is evident that high fluoride is associated with sodium-bicarbonate water types having high pH (>7) and low calcium and magnesium. This demonstrates that fluoride in the terrain is due to the partial or complete alteration of gneissic country rocks and is associated with alkaline water types. Fluoride concentration in pre-monsoon is increased as an effect of increase in sodium and decreased level of calcium, which causes increase in fluoride concentration by prohibiting its mobility. Further in post-monsoon the above criterion is reversed facilitated by higher ionic strength of ground water.

Statistical Studies

Statistical analysis has been used as a major tool in the study of ground water geochemistry (Briz-Kishore and Murali, 1992; Ramesh Kumar and Riyazuddin, 2008). Each sampling site is characterized by a large number of chemical and physical variables, making the regional hydrogeochemical study a multivariate problem. The multivariate statistical analysis, a quantitative and independent approach of groundwater classification, allows to group of samples and correlations between chemical parameters and groundwater samples. An initial approach involved in cluster and principal component analysis requires normal distribution of variables. Prior to the analysis, skewness and kurtosis of all the variables were checked and it was found that except pH in post-monsoon samples, all variables are positively skewed with kurtosis co-efficient significantly greater than zero (95% confidence). After log-transformation, the variables are z-scale standardized to minimize the effect of differences in measurement units and variance. R-mode factor analysis has been used to interpret the data more scientifically. Hierarchical Clusture Analysis is applied on standardized log-transformed data for both of the seasons to depict temporal similarities and grouping water qualities. Factor analysis is applied to analyse data of all the ground water samples to extract the principal factors from the sources of variation in the hydrochemistry. Preparation of a correlation matrix of the data from which initial factor solutions were extracted is done by the principal component extraction method (Kaiser, 1958). Orthogonal rotation of these initial factors to terminal factor solutions is done with Kaiser's normalization scheme (Davis, 2002). Factor score coefficients are derived from the factor loadings. Factor scores are computed for each sample by a matrix multiplication of the factor score coefficient with the standardized data.

Spatial Variations and Grouping

Spatial distribution dendogram was produced by hierarchical CA using Ward's method with squared Euclidean distances to group 18 hydrological variables in to three clusters at $(D_{link} / D_{max}) \times 100 < 35$, and the difference between clusters is significant. All classifications varied with the significance level, because the monitoring sites in these groups had similar backgrounds and may have been affected by relatively similar sources. In post monsoon samples (Fig.5a) cluster 1 comprised all the water hardness parameters characterizing the water type of the aquifer regime. Cluster 2 depicts the salinity and alkalinity character of the water samples and cluster 3 solely describes the acidic property of the water and association of fluoride with iron.

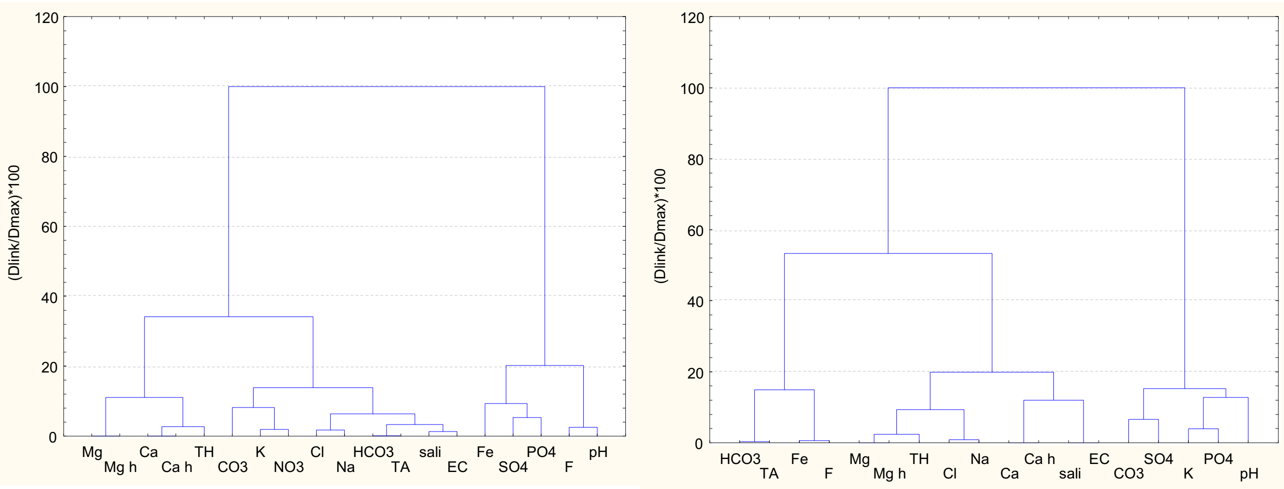


Fig.5. Dendogram showing temporal clustering of different parameters of water samples in different seasons.

Similarly for pre-monsoon water samples the spatial CA reveals three groups of clustering (Fig.5b). Unlike in pre-monsoon, the first cluster includes alkaline characters along with the fluoride-iron association. The next one demonstrates salinity and hardness character. The characteristic part is the association of SO_4 and PO_4 along with pH in both seasonal water types depicting the anthropogenic prospectus of water samples accompanied by K in pre-monsoon.

The variation indicates the movement of ground water with respect to recharge and discharge in the flow system. It gradually enriches its ionic content through the interaction with aquifer material such that the EC, total hardness and total alkaline character in the pre-monsoon time. On the basis of the observed chemical associations, cluster 3 represents anthropogenic impacts such as domestic waste, and agricultural chemicals. For cluster 3, the SO_4, and PO_4 ions are common constituents of domestic waste and agricultural chemicals such as fertilizers and pesticides being extensively used in the area. The characteristic part to fluoride contamination from CA study is that the contamination is chiefly facilitated by acidic property of water regime and associated with pH and iron concentration regulatory.

Principal Component and Factor Analysis

Correlation among 18 hydrochemical parameters is statistically examined. Varimax rotation is used to define the factor scores and percentage of variance in the hydrochemistry. The correlation matrix of analyzed parameters is presented in Table 2 and 3. The regression coefficients are calculated using linear regression analysis. The relations between parameters vary from highly competitive to noncompetitive type. This type of variation in correlation indicates complexity of the hydrochemical components of ground water (Aris et al. 2007). A six factor model is extracted for both of the seasonal hydrological variables.

Post-Monsoon samples: Six factors were extracted that explains 91.421% of total variability (Table 2).

Factor 1 was represented by conductivity and total hardness variables controls 22.408% of the total variance. Significant factor scores by Ca, Mg, Cl and Na represent solution activity on cations. Cl affinity demonstrates a moderate saline nature of the aquifer (Hem, 1991). This factor may be considered as either the salinity or the hardness factor or both TH-salinity factor due to the strong affinity of the squared data loading towards Ca, Mg and Cl. It is well known that TH is related to Ca and Mg content and is a function of the salinity of water (Hem, 1991). E.C. and Ca loadings on factor 1 can be explained by the dissolution of soils and minerals in sediments such as calcite ($CaCO_3$) and other calc-magnesian rocks and may be interpreted as a mineral weathering indication.

Factor 2 explains 20.466% of the total variance and shows high positive loadings towards E.C., salinity, PO_4, K

Table 2. Rotated Component Matrix of post-monsoon samples

	Component					
	1	2	3	4	5	6
pH	.209	.378	.178	.260	-.655	.193
EC	.541	.750	-6.057E-02	.196	.175	.140
Salinity	.517	.757	-7.105E-02	.193	.174	.167
F	.08015	-.114	.929	.247	-.123	.03283
PO_4	-.200	.867	.06765	-.231	.169	-6.497E-02
Na	.475	.398	.713	.174	-4.221E-03	.0503
K	.187	.893	-2.870E-03	.03959	-2.793E-02	.167
SO_4	-.135	.168	.05575	-.195	.09459	.921
Cl	.563	.397	.537	.139	.158	-2.936E-02
Alkalinity	.239	.139	.286	.870	-2.309E-02	-.160
CO_3	-9.653E-02	.563	.04307	-.611	-.226	-2.794E-02
HCO_3	.236	-6.578E-03	.254	.918	.03599	-.105
TH	.775	.173	.148	.203	.535	.02479
Ca H	.417	.245	.04301	.141	.813	.155
Mg H	.922	.05168	.213	.198	.120	-.113
Ca	.417	.245	.04301	.141	.813	.155
Mg	.922	.05168	.213	.198	.120	-.113
Fe	.127	-8.428E-02	.968	.09326	.06804	.01604
% of variance	22.408	20.466	16.162	13.814	12.568	6.003
Cumulative %	22.408	42.874	59.036	72.85	85.418	91.421

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization and CO_3 and moderate loading on Na and Cl. The high loading variables may indicate (i) domestic and/or agricultural practices due to PO_4 and K, (ii) dissolution of alkali feldspars. The halite input (Cl, PO_4) may be due to the reason cited above, but it should be noticed that the molar ratio could vary spatially and temporally as a result of cation exchange processes indicating the conductivity and salinity model of the aquifer (Barrow and Ellis, 1986; Karbassi, 1996). Furthermore, a few samples have excess Cl, which could be the result of a number of processes such as the exchange between sodium and potassium (Chidambaram et al. 2005).The higher factor scores of PO_4 and CO_3 indicates more possibility for anthropogenic contaminations.

The third factor explains 16.162% of the total variance and has very high positive loadings on Fluoride and Iron (> 0.9), high loading on Na and Cl. Such a high loading on Fe may demonstrate the acidic nature of the water regime. However, water acidity is affected not only by pH, iron and phosphate but also by the dissolution of oxygen (Lee et al. 2001; Romero et al. 2002). The factor can't be explained by the sulphide affinity as the loading gives a very poor output. The very strong affinity of fluoride towards iron may demonstrate the ion-exchange process of host rocks by the water regime. The lower loadings for Na and Cl are related to the country rock-water interaction and somewhat to anthropogenic practices.

Total Alkalinity and HCO_3 have high positive loadings on factor 4, which explains 13.814% of the total variance. The heavy loading of HCO_3 and alkalinity indicates the salinity conditions of the aquifer. Dissolution of soil and minerals in sediments/rock types may be the reason for HCO_3 concentration, but effects of other biotic and abiotic causes can't be ignored. Surface water charged with atmospheric and biogenic CO_2 infiltrates into the subsurface and aggressively attack aluminosilicates (feldspars and micas) present in the litho types bringing cations such as Ca and Mg into the water and leaving residues of clay minerals (Bartzokas and Metaxas, 1995; Chidambaram et al. 2007). Here the factor depends and explains mainly the origin of natural water and association of dissolved oxygen in the study area and hence the alkaline character (Lee et al. 2001; Romero et al. 2002). Very weak loading (< 0.2) on Ca, Mg and Na indicate the concentrations have been caused by abiotic processes.

The fifth factor represents the hardness affinity of the water regime and explains 12.568% of the total variance is known as hardness factor. High positive loading (>0.8) for Ca and low loading (<0.2) for Mg are observed. In general leaching of secondary minerals, weathering and anthropogenic impacts are the dominant controlling factors of the loadings. The sixth factor explains 6% of total variance and has a high positive loading on SO_4 (>0.9) and low loading (<0.2) on Ca and K. It has got a negative loading on PO_4. Such a high loading of sulphate demonstrates the sulphide affinity of the water regime (Hartmann et al. 2005; Hartmann and Levy, 2005). The sulphur compound association condition is best observed on field at Tarabalo

Table 3. Rotated Component Matrix of pre-monsoon samples

	Component					
	1	2	3	4	5	6
pH	-.253	.134	.104	.216	.769	.103
EC	.522	.667	.306	.284	.193	-4.035E-02
Salinity	.710	.285	.305	.248	.281	.07928
F	-.123	-.115	-7.927E-03	-.156	.914	-.135
PO_4	-1.218E-02	.130	-1.485E-03	-.238	-.115	.799
Na	.487	.478	-4.074E-02	.363	.538	-.146
K	-9.615E-02	.867	.09409	.143	-1.721E-02	.275
SO_4	-5.245E-02	-.242	-.244	.05137	.0258	.556
Cl	.526	.686	-.116	.0436	.191	-7.818E-02
Alkalinity	.336	.427	.279	.751	-.105	-8.682E-02
CO_3	.05766	-3.758E-03	.04032	.825	.164	-.122
HCO_3	.359	.470	.299	.666	-.147	-7.180E-02
TH	.661	.03762	.705	.127	-.143	-8.765E-02
Ca H	.909	-1.986E-02	.184	.109	-.280	-3.545E-02
Mg H	.179	.07984	.956	.09917	.04234	-.107
Ca	.909	-1.986E-02	.184	.109	-.280	-3.545E-02
Mg	.179	.07984	.956	.09917	.04234	-.107
Fe	-7.102E-02	-.218	.238	-.335	-.368	-.261
% of variance	19.92	17.311	15.309	12.087	11.92	6.676
Cumulative %	19.92	37.232	52.541	64.627	76.548	83.224

Table. 4. Different parameter concentration ranges according to ISI specification

ISI Spec.	Desirable	Maximum Permissible	Maximum Pre-monsoon Concentration	Maximum Post-monsoon Concentration
TDS, mg/l	500	2000	1729	1965
pH value	6.5-8.5	No Relaxation	8.65	7.53
Total hardness (as $CaCO_3$), mg/l	200	600	1095.38	1095.377
Iron (Fe)mg/l	0.3	No relaxation	3.2051	3.205
Aluminium (Al) mg/l	0.03	0.2	0.188	0.113
Copper (Cu)mg/l	0.05	1.5	0.113	0.034
Manganese (Mn) mg/l	0.1	0.3	0.525	0.291
Zinc (Zn) mg/l	5	15	0.387	0.61
Magnesium (Mg) mg/l	30	No Relaxation	132.31	117.035
Calcium (Ca) mg/l	75	200	249.82	246.15
Nitrate (NO_3) mg/l	45	No Relaxation	109.27	145.5
Sulphate (SO_4) mg/l	200	400	3187.2	376.32
Fluoride (F) mg/l	1	1.5	14.0	6.775
Chlorides (Cl) mg/l	250	1000	738.92	738.92
TA (as $CaCO_3$) mg/l	200	600	1350.0	1090.79

hot spring sediment types. Though iron and SO_4 loadings are poorly correlated, the pyritic association in a polymetamorphosed archean belt can't be discarded.

Pre-monsoon sample: A six factor model was extracted (Table 3) for pre-monsoon samples that explains 83.224% of the total variance. Factor 1 explains 19.92% of the total variance and is dominated by E.C., salinity, chlorinity and hardness variables. A very strong positive loading (>0.9) was observed for Ca. Na and alkalinity exhibit lower loadings. pH indicates a weak negative loading. Higher scores of E.C. and total hardness indicate continuous and prolonged chemical leaching of secondary minerals from the aquifer lithology (Prasanna et al. 2008b). High score for Cl along with moderate values for Na and alkalinity demonstrates the water becoming more saline than the post-monsoon (Lakshmanan et al. 2003; Panagopoulos et al. 2004). The high scores of several cations indicate the area is the densely populated and consequently witnesses higher groundwater extraction (Helena et al. 2000; Prasanna et al. 2008b; Prasanna et al. 2010). The salinity is increasing due to the decrease in the recharge potential of the water regime. Presence of HCO_3, Ca and Mg reflects signatures of natural water recharge and rock–water interaction. This indicates the chemical leaching of aluminosilicates (feldspars and micas) leaving a clay residuum and facilitating sites for fluoride accumulation by ion-exchange.

Factor 2 has high loading for E.C., Cl and K (>0.5 each) and accounts for 17.311% of the total variance. High E.C. and Cl scores along with HCO_3 demonstrate water hardness and higher salinity. Factor 3, describing 15.309% of the total variance solely specifies high hardness and Mg scores. These two loadings are weakly correlated with E.C., salinity and alkalinity. This relation indicates natural recharge of the aquifer and rock-water interaction. Factor 4 describing 12.087% of the total variance has a higher score for alkalinity i.e. CO_3 and HCO_3 values (>0.8). The alkalinity loading has a weak positive relation with pH, E.C. and Na scores indicating the secondary salt leaching activity and hence the increased salinity. The fifth factor represents the fluoride affinity of the water regime, explaining 11.92% of the total variance. The fluoride loading scores (>0.9) are well correlated with pH (>0.7) score. This indicate that the fluoride concentration is a function of pH and is largely dependable on it. Negative loadings with alkalinity and other cations except Na (>0.5), and fluoride score indicate the secondary ion-exchange activity with OH^-. From correlation coefficient value and factor loading scores it may be inferred that the alkaline nature of ground water in pre-monsoon favors more F concentration rather than acidic nature in post-monsoon. Around 12% of post-monsoon samples and 22.449% of pre-monsoon samples have fluoride concentration in excess of the permissible limit (ISI, 1991). The sixth factor explains 6.676% of the total variance and has the highest loadings for SO_4 (>0.5) and PO_4 (>0.7) scores. This is the indication of large anthropogenic impact mostly due to agricultural practices. However, the effect of algal and other microphytal/microbial activity inside the open wells can't be overruled (Ravichandran et al. 1996; Rajesh et al. 2002). Lower positive loading for K score adds to the concept as microphytal activity largely controls the K concentration (Weber et al. 1996).

CONCLUSION

The change in the water quality is due to the physical, chemical and biological environments through which it passes. Piper plotting indicates that the salinity of water regime is more in pre-monsoon than in post monsoon season. The bicarbonate factor gradually shifts towards more sodic and chlorinity character. pH of the ground water samples during both the seasons are within the permissible limit with a few exceptions.

The concentration range of different parameters are compared with ISI specifications (Table 4). The concentration of TDS are within the permissible limit. Pre-monsoon ground water samples have high concentrations of Na^+, K^+, NO_2^{3-} and Cl^- than the post-monsoon samples indicating that the ground water is susceptible to contamination resulting from low mobility of water in the pre-monsoon time (Barrow and Ellis, 1986). SO_4 concentration is much higher in pre-monsoon period than in post-monsoon due to dissociation of sulphate, evaporites and oxidation of sulphide minerals and organic sulphur. In post monsoon a total of 18% water samples contain SO_4 more than the desirable limit (ISI, 1991), which increases to 93.88% for desirable limit and 83.67% for max permissible limit in pre-monsoon samples. A total of 22% water samples in post-monsoon indicate Cl concentrations more than the desirable limit, which is 16.33% in pre-monsoon samples. As regards hardness, a total of 10% and 20.4% of samples are very hard water in post-monsoon and pre-monsoon seasons respectively. The concentrations of fluoride in the groundwater samples are found to be higher than the permissible limit (0.5-1.5 mg/l; ISI, 1991) in both the seasons but in pre-monsoon it is much higher than in post-monsoon. In post-monsoon period, more than 12% of samples contain fluoride concentration exceeding the permissible limit (ISI, 1991), whereas in case of pre-monsoon 22.449% of samples exceeds the limit. It is observed that high fluoride ground water is associated with high sodium-bicarbonate-iron affinity with elevated pH values (i.e.>7.0) and relatively low magnesium**.** High concentration of fluoride is due to temperature, pH, solubility of fluoride bearing minerals, ion exchange capacity of aquifer materials (OH^- & halogens), and the geological formations drained by water and accordingly the contact time of water with a particular formation.

CA plots helped to investigate the patterns of water quality and pollution sources in different seasons. It revealed different groups of parameters: cations, anoins, nutrients, alkaline and acidity parameters among which several showed the highest chemical pollution in pre-monsoon, highest nutrients in post-monsoon and highest solids in pre-monsoon. By comparing the correlation analysis and factor analysis results the water quality parameters that are most important for water quality variation in the Nayagarh district were identified. For fluoride contamination, pH and iron concentrations play a significant role in framing water pollution control strategy. Contribution of hydrologic processes and anthropogenic activities was also demonstrated by FA. The analytical results indicate that the surface water of the Nayagarh is a unique example of the compound impact of weathering, hydrologic and anthropogenic processes. Results of PCA/FA evinced that, a parameter that can be significant in contribution to water quality variations in aquifers for one season, may be less or may not be significant. Accordingly it is required that, when selecting water quality parameters for implementing environmental monitoring plans in underground water regimes, the seasonal variations of water quality must be consider.

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