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Advances in Applied Science Research, 2013, 4(6):187-196

ISSN: 0976-8610
CODEN (USA): AASRFC

Fluoride dynamics in the weathered mantle and the saprolitic zone of the Purulia district, West Bengal

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ABSTRACT

Present research work undertakes fluoride (F^-) hydrogeochemistry in the unconfined aquifer of Purulia (Block II) integrated with geospatial approach. Based on the geospatial analysis, it has been observed that high F^- in groundwater mainly occurs in the formation having a litho-assemblage of saprolitic zone between fractured granite gneiss and weathered mantle. Groundwater with high F^- concentration is mainly associated with Ca-Cl, Mixed Ca-Mg-Cl indicating dominance of evaporation effect. Positive correlation with pH, HCO_3^- and Na^+ indicates dissolution of fluoride bearing mineral such as fluorite is the main responsible mineral for F^- contamination. PHREEQCI geochemical modeling also indicates that F^- in groundwater can be increased as a result of precipitation of $CaCO_3$, $CaMg(CO_3)_2$ and $CaSO_4$, $2H_2O$ at high pH, which removes Ca^{2+} from solution allowing more fluorite to dissolve. Since the increase in Na^+ concentration increases the solubility of F^- bearing minerals, the geochemical processes leading to increase in Na^+ and decrease in Ca^{2+} concentrations play an important role in F^- enrichment in groundwater. Apart from fluorite dissolution cation exchange (Na^+ for Ca^{2+}) accompanied with anion exchange (OH^- for F^-) may also be the important processes by which muscovite and biotite minerals (containing fluorine at the OH^- sites) may contribute to F^- enrichment in groundwater.

Key words: Fluoride, Hydrogeochemistry, Weathered mantle, Purulia (Block II), West Bengal

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INTRODUCTION

Fluoride (F^-) is the 13th most abundant element on earth that does not occur in the elemental state in nature because of its high reactivity. The average crustal abundance of F^- is 300 mg/kg [1]. Fluoride is common in semi-arid climate with crystalline igneous rocks and alkaline soils [2]. In Indian continent, the higher concentration of fluoride in groundwater is associated with igneous and metamorphic rocks. The chief sources of fluoride in groundwater are the fluoride-bearing minerals, such as fluorite (fluorspar), fluorapatite, cryolite, biotite, muscovite, lepidolote, tourmaline and hornblende series minerals. In water, fluoride is strongly reactive or exists in free state, eventually precipitating as fluorite (main solid phase with the fluoroapatite, $Ca_5[PO_4]_3[F,Cl]$) [2,3]. Fluoride content in groundwater usually depends on rock type, interaction period with host rock, as well as the dissolution kinetics for fluorite, apatite or silicate minerals.

In recent times, there have been media reports that fluoride contamination is widespread in West Bengal. It has been highlighted that 60 blocks in eight districts, *viz*. Bankura, Bardhaman, Birbhum, Purulia, Midnapur, Malda and West Dinajpur are affected by fluoride [4, 5, 6]. Traditionally, fluorosis has been connected with higher intake of fluoride through drinking water. According to the recommendation of World Health Organization [7] (WHO 2004), the optimum range of fluoride in groundwater is fixed as 0.5–1.5 mg/l.

Study area: Block II of Purulia district (lies between 22°60'' and 23°50' latitudes and 85°75' and 86°65' longitudes), West Bengal is selected as a study area for the present research work **(Fig. 1)**. The study area is characterized by undulating topography with isolated mounts and hills, which comprises 70% of the total area of the district. The district has a dry tropical climate marked by a moderately cold winter and highly oppressive summer and normal annual rainfall in the district is about 1322 mm. The main source of rainfall in the district is the south west monsoon, which accounts for 80% of the total rainfall. Temperature ranges from 4°C (minimum) during winter to 48°C during summer (maximum). Humidity in the area varies between 70 to 85 %. Dry, hot wind in summer blows across the district with velocity ranging between 5-6 Km/hr.

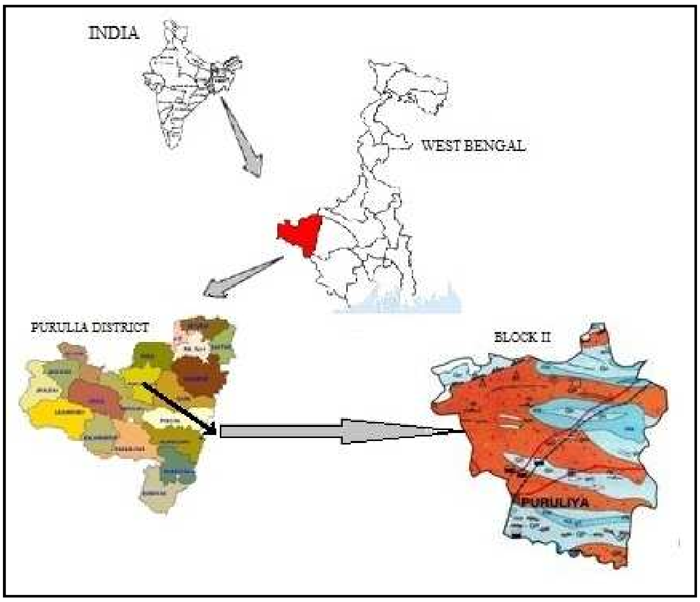


Fig. 1: Study area location

***Geology and Hydrogeology*:** Soil in the district is in general of the residual type derived from the weathering of the Archaen granites, gneisses and schists. Lateritic soil prevails in the uplands whereas in the valleys reddish clay loam or white to reddish clay are common. Many textural classes are met with, such as sandy loam, reddish loam, white or reddish stiff clay etc. Because of the undulating nature of the topography the soil cover is thin and the soil is generally gravelly. Almost in the entire district soil is acidic and the fertility is low.

The district is underlain by Pre-Cambrian metamorphics except in a small area in the northeastern part where sediments of Gondwana age predominate. Unconsolidated sediments of recent to sub-recent age are restricted to the narrow rivers channels and to the valleys. The most common rock of widespread occurrence in the district are granites and granite gneisses into which metabasics occurs as intrusive.

Groundwater in the district occurs mainly in (1) weathered mantle which varies in thickness and attains a maximum thickness of 25m. Groundwater occurs under water table condition and it is mostly developed by dug/open well. At some places these wells go dry during peak summer. These dug wells yield up to 2.75 lps.(2) Saprolitic zone is sandwiched between weathered mantle and fresh rock mass in granitic terrain. The depth of this zone varies between 10-30 mbgl, with an average thickness of 4m. Ground waters occurs under semi-confined condition and yield up to 2.5l lps (3) Fractured zones of hard rock and (4) narrow zone of unconsolidated sediments along the river valley are of limited thickness and fall within 5-13 mbgl with a real extent not exceeding 1-2 km across river valley. Saturated thickness of alluvial tract varies from 1m >5.5m.

MATERIALS AND METHODS

Sampling and analysis of groundwater: Water samples were collected from 38 different dug wells under Purulia Block- II in Purulia District **(Fig. 2).** The sampling bottles soaked in 1:1 HCl for 24 hour were rinsed with distilled water followed by deionized water. At the time of sampling, the sampling bottles were thoroughly rinsed two three times, using groundwater to be sampled. Samples were collected after pumping the well for at least 10 to 15 minutes. The chemical parameters *viz.* pH and electrical conductivity (EC) were measured, using portable instruments immediately after sampling. Sampling bottles were labelled, tightly packed, transported to the laboratory and stored at 4°C for chemical analysis such as total dissolved solid (TDS), total hardness (TH), total alkalinity (TA), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), total iron (Fe), chloride (Cl^-), sulphate (SO_4^{2-}), nitrate-N (NO_3^-), phosphate (PO_4^{3-}) and silica (SiO_2^{4-}) as per standard methods [8]. Fluoride (F^-) was analysed by ion-selective electrode (Orion).

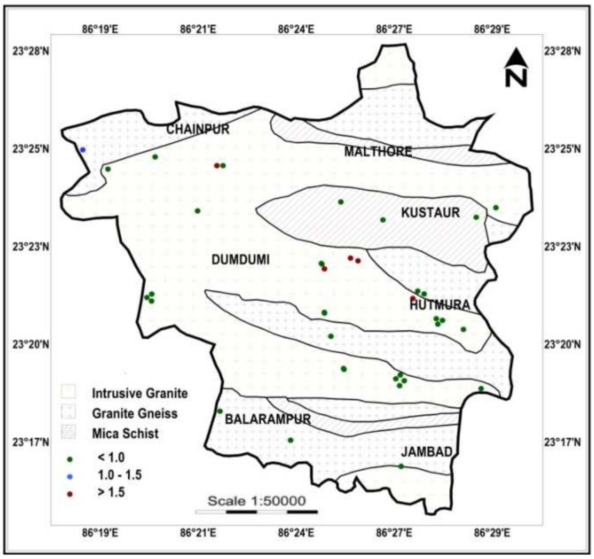


Fig. 2: Sampling points with respect to different rock types of Purulia Block-II

Statistical Analysis

Descriptive statistics: Parametric statistical methods were used to compute the central tendency (arithmetic mean) and dispersion (standard deviation) analysed parameters of 38 ground water samples by using XL STAT Version 10.0. This reflects a significant influence towards the hydrogeochemical conditions. Further the degree of association or the strength of a linear relationship among the chemical variables was evaluated by scatter diagram.

***Factor analysis*:** The obtained matrix of hydrogeochemical data was subjected to multivariate analytical technique. Factor analysis also known as principle component analysis (PCA), is an efficient ways of displaying complex relationships among many variables and their roles [9,10]. These analyses were performed using Exel Stat software package (Version 10.0). With the help of linear combinations, an originally large number of variables are reduced to a few factors. These factors can be interpreted in terms of new variables.

Spatial interpolation: Digital Elevation Model (DEM) is generated on the basis of sampling points, stored as a point layer along with attributes of fluoride. DEM is generated by using VEDIMINT algorithm in the Geomatica V.10.1 software. The output DEM is represented as a zonation map of the said parameter. The algorithm consist of three major steps plus and optical step for processing 2D features. In the first step, input vector points (F^- concentration with respect to different location) are re-projected to the raster coordinates and burned into the raster buffer, and the second step, the elevation at each DEM pixel is interpolated from the source elevation data. The interpolation process is based on an algorithm called Distance Transform. In step 3, a finite difference method is used to iteratively smooth the DEM grid. The algorithm uses over relaxation technique to accelerate the convergence. During the iterations, the source elevation values are never changed, while the interpolated values are updated based on the neighbourhood values.

RESULTS AND DISCUSSION

***Hydrogeochemistry*:** The analytical output along with descriptive statistics of collected groundwater samples is presented in **Table 1**. Most of the groundwater samples are neutral to alkaline in nature having a pH of 6.97 to 7.72 (mean 7.37). The electrical conductivity (EC) values are found to be within the range of 140 µmos/l – 610µmos/l with mean value of 351.84 µmos/l. Total dissolved solids (TDS) indicate the inorganic pollution load. The concentrations of TDS ranges from 90 mg/l to 1710 mg/l (mean 482 mg/l) with an exceedence of 34% of total samples with respect to WHO recommended limit of 500 mg/l. Very high standard deviation in EC value suggests the spatial variability of leaching and dilution with recharging rainfall water, which can be further, linked with the local variation in point sources, soil type, multiple aquifer system and other agriculture related activities in the area. The total hardness (TH) ranges from 57 mg/l to 1097 mg/l (mean of 330.64 mg/l). According to [11] Durfor and Becker, classification of water types based on TH, out of total 38 water samples examined, 24 samples are recognised as very hard, 7 samples are under 'hard' and 6 samples are of moderately hard categories (**Table 2**). Alkalinity of water is mainly due to the presence of CO_3^{2-} and HCO_3^{-}.The alkalinity in natural water systems may come from $H_3BO_3^{2-}$, HPO_4^{2-} and HS^-. These compounds result from dissolution of mineral substances in soil. Total alkalinity (TA) ranges from 35 mg/l to 345 mg/l with a mean of 162.37 mg/l.

Table 1: Hydrogeochemistry and descriptive statistics of groundwater samples of Purulia (Block – II)

Sample No.	Temp(^{0}C)	pH	EC(µs/cm)	TDS	TA	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	Fe^{2+}	$CO3^-$	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	PO_4^{3-}	SiO_2^{4-}	F^-
D1	28.4	7.01	280	230	85	93.60	35.09	1.47	34	121	0.29	0	103.70	90.92	20.81	7.81	0.55	4.98	0.07
D2	28.3	7.53	150	90	65	72.80	18.57	6.48	16	4	0.15	36	79.30	19.14	1.55	1.12	0.73	6.62	0.20
D3	28	7.36	530	773	285	480.48	134.16	35.41	75	13	0.25	24	274.50	296.71	78.93	1.24	0.64	5.08	0.33
D4	30.1	7.6	470	1206	285	982.80	258.01	82.38	118	7	0.12	0	298.90	435.50	86.93	2.53	0.20	5.55	2.20
D5	30.1	7.59	450	987	225	837.20	278.65	34.49	114	8	0.20	0	274.50	483.36	24.08	5.55	0.20	5.57	1.80
D6	28.7	7.22	380	490	85	314.08	105.26	12.49	56	16	0.14	0	103.70	138.78	43.31	6.21	17.64	5.94	2.27
D7	29.5	7.52	360	394	125	214.24	80.49	0.75	77	6	0.13	0	152.50	177.70	35.43	2.84	0.41	4.27	0.29
D8	28.5	7.36	280	228	125	151.84	51.60	5.61	39	5	0.19	12	152.50	43.70	24.16	4.53	0.38	3.86	0.25
D9	29.9	7.52	170	104	165	114.40	39.21	4.02	21	5	0.30	0	176.90	38.28	2.58	1.52	0.17	3.28	0.35
D10	28.6	7.36	430	738	115	483.60	167.19	16.14	86	37	0.45	0	140.30	272.78	81.34	6.34	0.78	4.65	0.20
D11	30	7.72	470	747	225	504.40	142.42	46.23	116	6	0.32	12	274.50	282.35	90.03	2.75	0.15	5.17	1.76
D12	29.9	7.61	280	236	35	244.40	72.24	15.58	55	5	0.22	0	18.30	57.42	37.58	4.80	0.26	3.49	0.56
D13	30.4	7.55	230	160	235	213.20	63.98	13.01	30	7	1.94	0	286.70	38.28	11.95	1.52	0.29	2.12	0.47
D14	29.9	7.58	160	98	85	67.60	14.44	7.66	27	4	0.26	0	103.70	33.50	7.91	1.24	0.06	4.99	0.25
D15	30	7.34	230	157	105	67.60	18.57	5.16	26	33	3.75	0	128.10	38.28	13.76	3.70	33.40	5.73	0.30
D16	29.1	7.35	370	344	165	161.20	47.47	10.38	49	64	0.28	0	201.30	76.57	27.69	5.60	23.65	5.33	0.41
D17	27.8	7.53	610	1258	345	691.60	237.37	24.14	147	78	0.55	0	420.90	540.78	150.56	4.42	0.09	4.63	0.23
D18	28.1	7.11	320	278	155	171.60	59.85	5.40	40	24	0.18	0	189.10	90.92	14.79	4.61	1.63	3.72	0.31
D19	28.3	7.31	290	249	105	202.80	51.60	17.99	41	12	0.24	0	128.10	76.57	21.15	1.81	4.35	3.85	0.20
D20	28.5	7.27	390	644	205	546.00	154.80	38.81	58	14	0.07	0	250.10	177.07	50.22	5.78	7.57	5.69	1.26
D21	27.3	7.35	450	627	245	410.80	117.65	28.49	103	18	0.09	0	298.90	272.78	77.21	2.30	0.87	5.04	0.53
D22	27.6	7.25	330	347	95	254.80	55.73	28.12	52	5	0.08	0	115.90	95.71	45.92	8.26	0.15	3.78	0.30
D23	27.7	7.17	310	290	95	213.20	59.85	15.51	45	7	0.12	0	115.90	119.64	17.28	6.26	0.26	2.43	0.26
D24	29.4	7.28	260	220	95	140.40	39.21	10.33	33	6	0.14	0	115.90	52.64	7.91	6.24	0.17	1.92	0.21
D25	28.7	7.45	280	244	135	161.20	51.60	7.88	48	5	0.06	0	164.70	76.57	16.94	3.85	5.66	4.74	0.66
D26	27.7	7.37	330	326	225	182.00	47.47	15.44	48	46	0.10	0	274.50	86.14	11.69	2.61	6.56	5.08	0.40
D27	28.3	6.97	420	547	55	296.40	88.75	18.21	79	32	0.09	0	67.10	210.57	38.44	9.05	0.93	4.89	0.47
D28	27	7.49	490	954	265	639.60	212.60	26.52	131	6	0.06	0	323.30	464.21	77.82	8.55	0.09	5.87	1.64
D29	27.4	7.51	280	232	105	171.60	63.98	2.90	33	9	0.08	0	128.10	57.42	34.31	7.77	0.06	3.15	0.12
D30	27.3	7.57	390	454	235	379.60	117.65	20.91	73	10	0.16	0	286.70	205.78	29.66	8.10	1.13	5.72	0.73
D31	27.5	7.16	140	104	55	57.20	10.32	7.64	13	7	0.09	0	67.10	38.28	5.93	7.25	0.15	2.91	0.16
D32	27.3	7.37	580	1710	305	1097.20	406.62	20.08	155	68	0.10	0	372.10	885.36	131.90	8.40	1.60	5.52	0.80
D33	27.2	7.13	390	467	185	348.40	92.88	28.34	58	25	0.10	0	225.70	134.00	41.27	8.26	8.07	5.73	0.96
D34	27.5	7.22	340	305	135	150.80	39.21	12.86	59	27	0.10	0	164.70	95.71	22.27	6.40	0.90	5.17	0.13
D35	27.8	7.04	170	118	65	78.00	22.70	5.18	24	4	0.09	0	79.30	52.64	4.39	2.83	0.12	5.42	0.19
D36	28.1	7.58	450	521	225	306.80	92.88	18.23	58	79	0.10	0	274.50	138.78	31.81	8.42	12.33	5.11	0.77
D37	27.2	7.4	380	442	225	504.40	171.32	18.69	64	8	0.08	0	274.50	157.92	17.34	8.64	0.09	5.28	0.52
D38	27.1	7.33	530	999	205	556.40	158.93	38.84	108	65	0.07	0	250.10	406.78	98.28	8.86	10.68	5.75	0.45
Descriptive statistics																			
Minimum	27.00	6.97	140.00	90.00	35.00	57.20	10.32	0.75	13.00	4.00	0.06	0.00	18.30	19.14	1.55	1.12	0.06	1.92	0.07
Maximum	30.40	7.72	610.00	1710.00	345.00	1097.20	406.62	82.38	155.00	121.00	3.75	36.00	420.90	885.36	150.56	9.05	33.40	6.62	2.27
Mean	28.43	7.37	351.84	482.05	162.37	330.64	102.11	18.63	63.39	23.58	0.31	2.21	193.59	183.15	40.40	5.21	3.76	4.68	0.61
SD	1.04	0.19	120.29	374.67	80.83	257.73	85.99	15.70	37.02	27.62	0.65	7.30	95.70	183.74	36.29	2.62	7.25	1.14	0.59
SE	0.17	0.03	19.51	60.78	13.11	41.81	13.95	2.55	6.00	4.48	0.11	1.18	15.53	29.81	5.89	0.43	1.18	0.19	0.10

[*All the parameters are expressed as mg/l except Temp, pH and EC*]

Among the cations the contribution of Ca^{2+} and Mg^{2+} to the total cations is approximately 49.16% and 8.97% respectively. The concentration of Na^{+} varies from 13 mg/l to 155 mg/l with a mean of 63.39 mg/l, which is the second dominant ion among the cations, contributing approximately 30.52% to the total cations. This is because of the silicate weathering and/or dissolution of soil salts stored by the influences of evaporation and anthropogenic activities [12, 13] . Low concentration of K^{+} is observed (mean 23.58 mg/l) in the study area, because the potash feldspars are more resistant to chemical weathering and is fixed on clay products. The contribution of K^{+} to the total cations is approximately 11.35%. The contribution of various cationic species indicated that 52.63% and 23.68% of the groundwater samples follow the sequence of $Ca^{2+}>Na^{+}>Mg^{2+}>K^{+}$ and $Ca^{2+}>Na^{+}>K^{+}>Mg^{2+}$ respectively. Bicarbonate (HCO_3^{-}) ion is the most dominant species constituting 46.41% of the total anions (TZ^{-}), where as concentration of Cl^{-} and SO_4^{2-} was found to be 43.91% and 9.68%, respectively. With respect to the abundance of anion , 63.16% of the groundwater samples follows a sequence of $HCO_3^{-}>Cl^{-}>SO_4^{2-}$ while 36.84% follows $Cl^{-}>HCO_3^{-}>SO_4^{2-}$.

Table 2 : Classification of the groundwater samples on the basis of hardness

Type of water	Hardness (mg/l)	Number of samples
Soft	0-60	1
Moderately hard	61-121	6
Hard	121-180	7
Very Hard	>180	24

Majority of the samples belong to the Ca^{2+} - Mg^{2+} - Cl^{-} - SO_4^{2-} and Ca^{2+} - Mg^{2+} - HCO_3^{-} type followed by the Na^{+} - K^{+} - HCO_3^{-}, Na^{+} - K^{+} - Cl^{-} - SO_4^{2-} types in the study area **(Fig. 3)**. **Table 3** shows that 57% of groundwater samples fall in Ca-Mg-Cl-SO_4 hydrofacies followed by Ca-Mg-HCO_3 facies (31%).

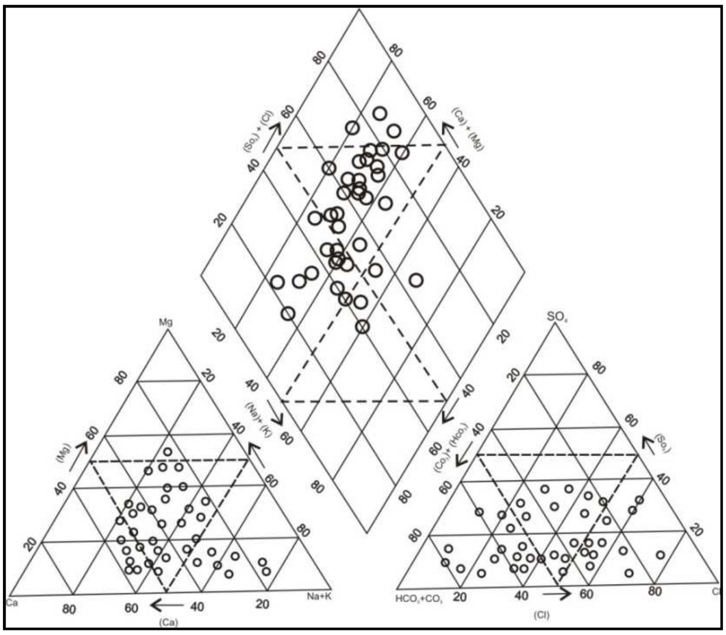
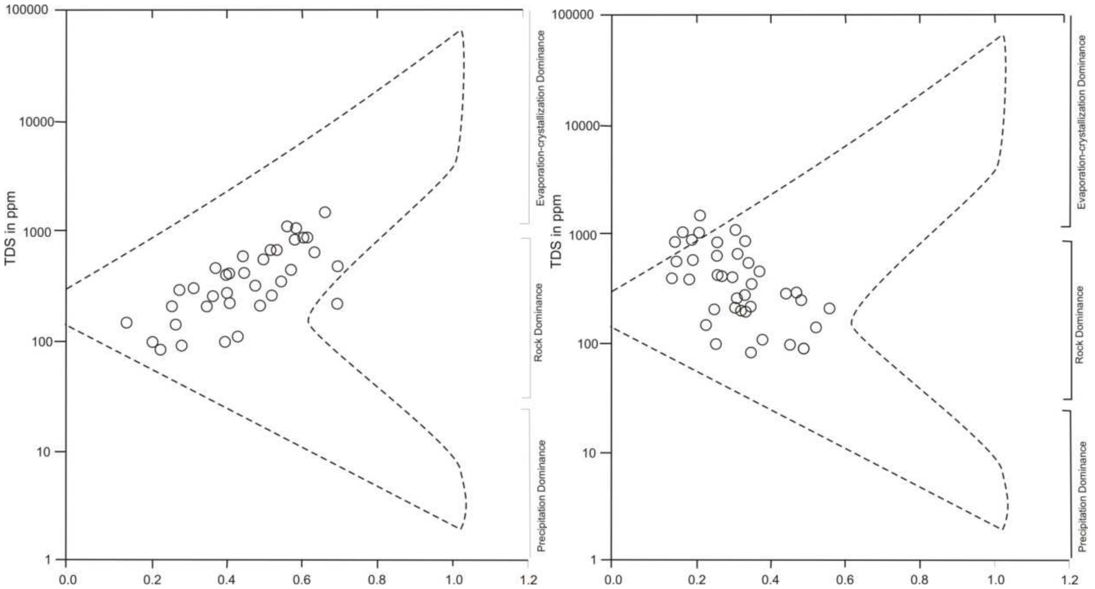


Fig. 3: Piper trilinear diagram showing water types

Table 3: Variation of hydrochemical facies in Purulia Block –II

Hydrochemical facies	Number of samples	Percentage of sample fall (%)
Ca, Mg, Cl, SO_4	22	57.89
Na, K,Cl, SO_4	1	2.63
Na, K,HCO_3	3	7.89
Ca, Mg, HCO_3	12	31.57

***Mechanism controlling groundwater chemistry*:** Gibbs diagram represents the ratio of [Cl /(Cl+HCO_3)] and [(Na +K)/(Na+ K+ Ca)] as a function of TDS which is widely used to assess the functional sources of dissolved chemical constituents such as, precipitation dominance, rock dominance, and evaporation dominance [14] **(Fig. 4)**. Ratio 1[Cl / (Cl + HCO_3)] of groundwater samples ranges from 0.2 to 0.8 and whereas ratio 2 [(Na +K)/ (Na+ K+ Ca)] ranges from 0.2 to 0.6. The chemistry of groundwater samples indicates that as per ratio 1 and 2, 87% and 98% of fall in the samples rock dominance domain respectively. So chemical weathering could be the main process contributing ions to the groundwater of the study area.



(a) **(b)**

Fig. 4: Mechanism controlling groundwater chemistry (a) Cl/(Cl+HCO$_3$) and (b) (Na+K)/(Na+K+Ca)

***Cation exchange*:** In the current study, a plot of Ca+Mg-SO_4-HCO_3 (meq/l) against Na+K-Cl (meq/l) **(Fig.5)** suggests that cation exchange processes probably do occur in the study area. The Ca+Mg-SO_4-HCO_3 (meq/l) and Na+K-Cl (meq/l) indices, respectively represent the concentrations of the alkaline earth elements and alkali elements after subtracting the contributions of their sulphate and carbonate minerals (for the alkaline earth elements), and chlorides (for the alkali elements). These indices provide a good way of determining how the concentrations of the alkaline earth elements vary with those of the alkali elements. If the two indices vary inversely with a slope close to -1, with the data plotting away from the origin, cation exchange activity is most probably significant in the hydrochemistry [15]. In **Fig. 5**, the slope of the line is -1 and near to -1 moreover the data is plotted away from the origin, suggesting that cation exchange plays an active role in the study area.

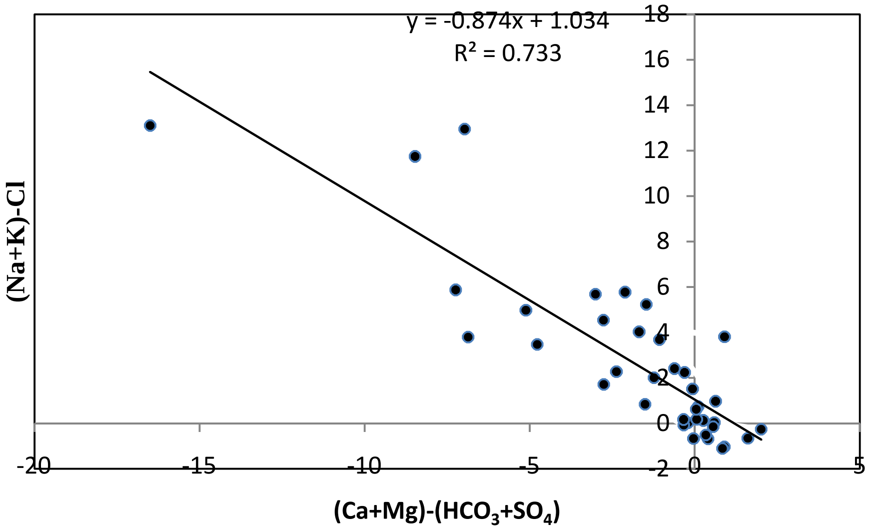


Fig. 5: Biplot suggesting the possibility of cation exchange in the study area

***Spatial distribution of fluoride in groundwater*:** The concentration of F^- in groundwater (N = 38) varies from 0.07 to 2.27 mg/l. With regard to the number of places where high F^- concentration is found, it is found that at five locations F^- values are consistently above the acceptable limit of 1.5 mg/l. On the basis of concentration of F^- prescribed for drinking water (WHO, 2004) [7], the area could be classified into three categories:

- Low fluoride with < 0.5 mg/l
- Moderate fluoride with 0.5 – 1.5 mg/l
- High fluoride with > 1.5 mg/l

The distribution of F^- concentration shows that about 63.15% and 23.68% of the total samples throughout the study area fall within the low to moderate F^- category.

The spatial distribution of fluoride in groundwater samples in the study area **(Fig. 6)** shows that lower concentrations are distributed along major parts of the study area. Higher concentrations (>1.5 mg/l) of F^- are noted in the north-eastern and central part of the study area where the weathered mantle and saprolitic zone produced from a parent rock of granite and granite gneiss. The lowest concentration is noted in the region dominated by the parent rock mica-schist.

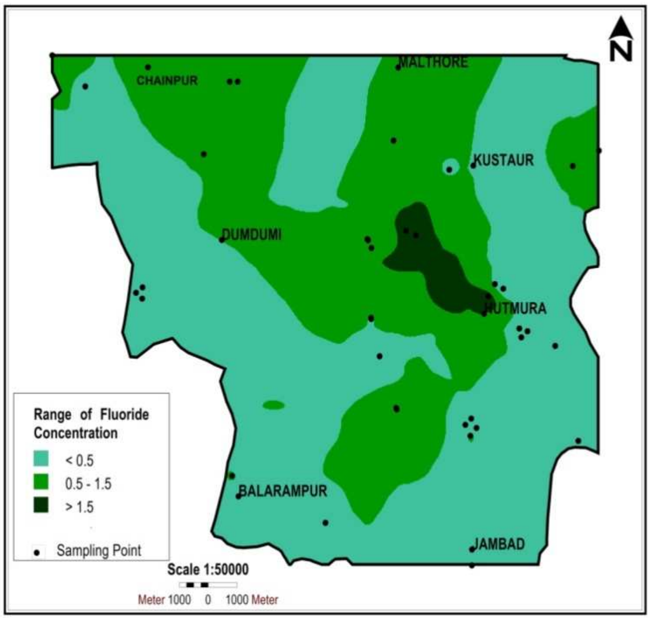
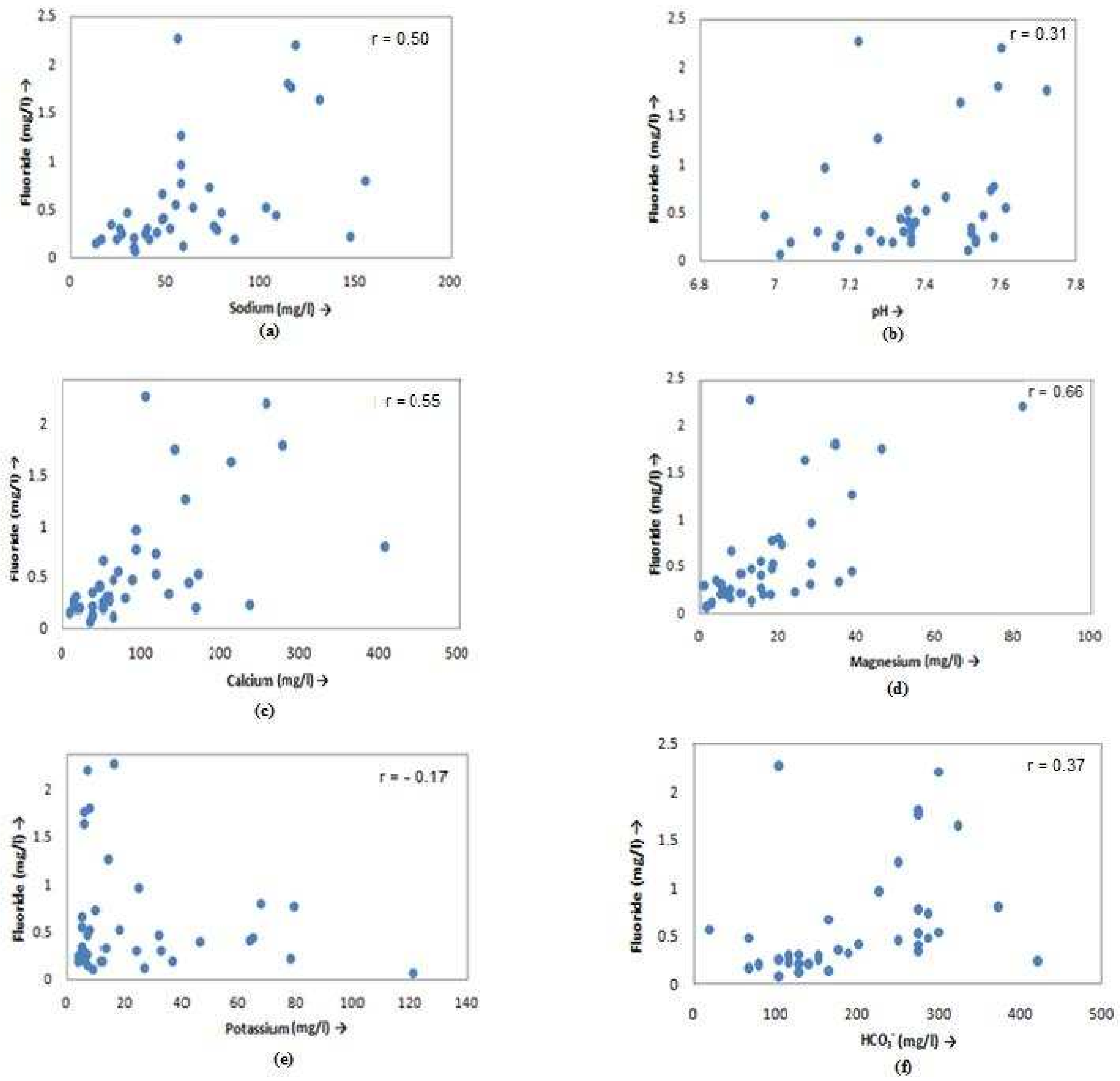


Fig. 6: Spatial interpolation of fluoride in the study area

***Scatter plots of F^- with other geochemical parameters*:** To examine the relationships of F^- with other geochemical parameters, scatter plots have been generated for derived parameters of groundwater samples. It is observed that the relation between F^- and pH is positive (r = 0. 31). Thus, higher alkalinity of groundwater activates the leaching of F^-, therefore, affects the concentration of F^- in the groundwater [4]. As HCO_3^- ion is the dominant species of carbon in the intermediate pH of water, so a positive correlation (r = 0.37) is also observed between F^- and HCO_3^-. The positive relation between $F^-$and HCO_3^- can be explained by considering the mass law equation relating to calcite and fluorite when both are in contact with water [2,16]. In the present study, F^- is observed to have positive correlation with Ca^{2+} (r = 0.55) and Mg^2+ (r = 0.66). Samples having high F^-concentration are also associated with the higher concentration of Na^+ ion (r = 0.50) **(Fig.7)**. This also favours that groundwater with high $HCO_3^-$and Na^+ is usually alkaline in nature with relatively high OH^-content. As OH^- and F^- have similar ionic size, so the OH^- can replaces F^- of fluoride bearing minerals such as biotite or muscovite thus increasing the F^-content in groundwater. On the basis of above observation, therefore, it can be safely presumed that the groundwater with high HCO_3^-, Na^+, and higher pH value under the control of water– rock interactions could be the important factor for the release of F^- from the aquatic matrix into the ground waters of the study area. Fluoride showed a statistically significant positive correlation with NO_3^-. Septic systems, animal waste and fertilizer are all potential sources of NO_3^- contamination. Nitrate is a chemical species that essentially originates from the land surface and is eventually removed from groundwater by denitrification with increased residence times [17,18].

***Factor analysis*:** The results of the factor analysis of hydro-geochemical data are summarized in **(Table 4)** respectively. Three factors were identified for respectively which control groundwater quality. Factor 1 account for 46% variance with the strong loading of variables like EC, TDS, TA, TH, Ca, Mg, Na, HCO3, Cl, SO4, SiO2 and F. This factor seems to be attributed to geogenic contribution of F in the study area. Factor 2 and 3 account for 13% and 10% variance in the data respectively. Factor 2 shows high negative loading for K^+ and $NO^{3-}$and high positive loading for pH, CO_3^-. Ion exchange mechanism and silicate weathering is the major contributing factor for this factor. Factor 3 shows a high loading of PO_4^{3-}, which may be attributed from anthropogenic activities such as domestic and industrial waste discharge, runoff from agriculture field. In summary, it seems that different hydro-geochemical processes like weathering and ion-exchange, and are the key factors in the season.



(a) (b) (c) (d) (e) (f)

Fig.7: Scatter plot of Fluoride versus (a) Sodium, (b) pH, (c) Calcium, (d) Magnesium, (e) Potassium, and (f) Bicarbonate

Source and geochemical processes for F^- enrichment in groundwater: For F^- in groundwater, fluorite may be a natural mineral source, and F^- is also abundant in some hydroxy- minerals such as muscovite, biotite, and apatite [19]. The weathering of these minerals is the source of F^- for the subsurface environment. However, the F^- in groundwater is mainly derived from the leachable or exchangeable F^- that only accounts for a small proportion of the total fluorine in aquifer materials [20, 21]. For the dissolution of fluorite in groundwater with high HCO_3^- contents, the reaction is as follows:

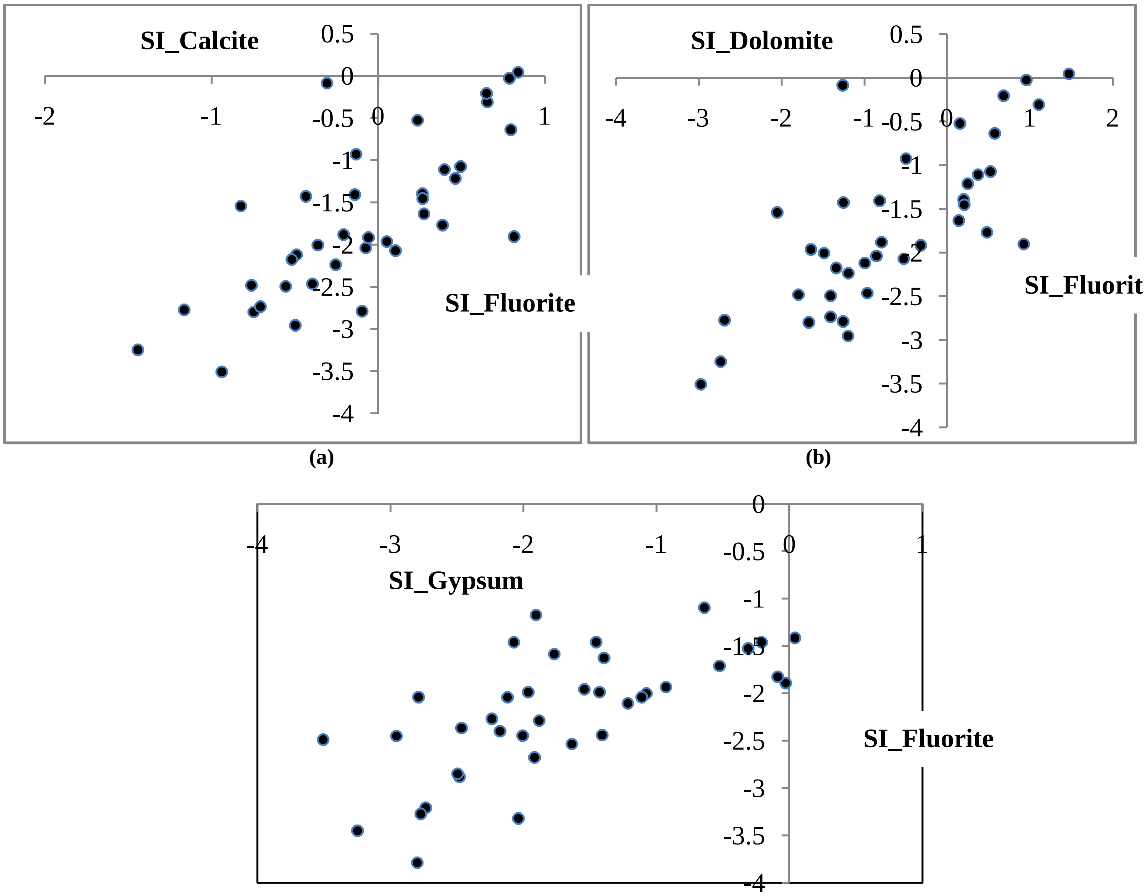
$$CaF_2 + 2HCO_3^- = CaCO_3 + 2F^- + H_2O + CO_2$$

Moreover, groundwaters with high HCO_3^- and Na^+ content are usually alkaline and have relative high OH^- content, so the OH^- can replace the exchangeable F^- of fluoride-bearing minerals, increasing the F^- content in groundwater. The reactions are basically as follows:

Muscovite: $KAl_2[AlSi_3O_{10}]F_2 + 2OH^- \longrightarrow KAl_2[AlSi_3O_{10}][OH]_2 + 2F^-$

Biotite: $KMg_3[AlSi_3O_{10}]F_2 + 2OH^- \longrightarrow KMg[AlSi_3O_{10}][OH]_2 + 2F^-$

Thus, as indicated by regional hydrochemical data, groundwater with high HCO_3^- and Na^+ contents occurs in the discharge areas at Purulia block II as a result of silicate mineral hydrolysis and cation exchange. So the occurrence of groundwater with high HCO_3^- and Na^+ contents and high pH value under the control of above water–rock interactions is the important reason for F^- release from the aquifer matrix into groundwater. In addition to interaction between groundwater and fluoride-rich minerals, evaporation is another important factor resulting in the occurrence of high F^- groundwater. As a result of evaporation, Ca^{2+} would precipitate out as $CaCO_3$, reducing Ca^{2+} concentration of the groundwater, and consequently the solubility control of CaF_2 on fluoride enrichment in the aqueous phase becomes weaker. In Purulia Block II, most water samples in the evaporation zone are over saturated with calcite due to evaporation and the calcite precipitation can reduce the Ca^{2+} content and promote the dissolution of CaF_2. The same relationship between evaporation and fluoride enrichment was noticed by Datta et al. [22] at Rajasthan, India, where strong evapotranspiration is also associated with the high F^- content in the groundwater.



(a) **(b)**

(c)

Fig. 8: Saturation indices (SI) of fluorite (CaF_2) versus (a) calcite ($CaCO_3$), (b) dolomite [CaMg $(CO_3)_2$] and (c) Gypsum ($CaSO_4$, $2H_2O$) in the groundwater

Thermodynamic approach: The saturation indices (SI) of fluorite (CaF_2) Vs calcite ($CaCO_3$), dolomite Ca$(MgCO_3)_2$ and Gypsum $CaSO_4$, $2H_2O$ in the groundwater samples were calculated using PHREEQCI version 2 [23] and are plotted in **(Fig. 8)** which shows that 42%, 36% and 2% of the samples is oversaturated with respect to calcite, dolomite and gypsum whereas, all sample except two have been found undersaturated with respect to fluorite. This situation of solubility control on the higher concentration of fluoride can be explained by the fact that fluoride ions in groundwater can be increased as a result of precipitation of $CaCO_3$, Ca $(MgCO_3)_2$ and $CaSO_4$, $2H_2O$ at high pH, which removes Ca^{2+} from solution allowing more fluorite to dissolve. Therefore, fluorite undersaturation in groundwater of area under study might be due to the calcite saturation, preventing it by reducing calcium activity and allowing more fluorite to dissolve thereby increasing the F/ Ca ratio of solution. The carbonate minerals are generally supersaturated - saturated in the system, whilst the sulfate minerals are undersaturated throughout the system. Several factors may have contributed to the saturation-supersaturation of the carbonate minerals: incongruent weathering of silicate minerals and carbonate mineral dissolution. In the study area, the aquifers are not known to contain appreciable quantities of carbonate minerals whose weathering could lead to the supersaturation of these minerals in the groundwater system. Incongruent silicate mineral weathering is therefore the most likely source of the enrichment of Ca^{2+} and HCO_3^- ions. Silicate mineral weathering is a slow process and will require several years of rock-water interaction to generate a couple of ions in solution. It is probably on account of this that the carbonate minerals are generally largely saturated. Although F^- concentrations at some locations in the study area are higher than the recommended maximum permissible in groundwater, fluorite is undersaturated. Undersaturation of fluorite suggests that it is being dissolved in the system.

Acknowledgement
The authors wish to thank Dr A. R. Ghosh (Associate Professor) Department of Environmental Science, The University of Burdwan, for his constant support and valuable suggestions during the course of the investigation. Sincere thanks are also due to all the anonymous reviewers of this manuscript.

REFERENCES

[1] T.H.Y. Tebutt, Principles of Quality Control, Pergamon, England, **1983,** 235.
[2] B.K. Handa, *Groundwater*, **1975, 13**, 275-81.
[3]Alveteg and M. Jonsson, Amendment of high fluoride groundwater, (Master of science degree project, Stockholm), **1991.**
[4]B.K. Wodeyar and G. Sreenivasan, *Curr.Sci.*, **1996**, 70, 71–73.
[5]B. Das , J. Talukdar, S. Sarma, B. Gohain, R.K. Dutta, H.B. Das and S.C. Das, *Curr. Sci.*, **2003,** 85(5), 657 -661**.**
[6]N. Subba Rao and D.J. Devdas , *Environ. Geol.*, **2003,** 45, 243-51 **.**
[7]World Health Organization (WHO), Guidelines for drinking water quality, 3rd edn. WHO, Geneva, 1 , **2004,** 515.
[8]APHA, Standard methods for the examination of water and wastewater, American Public Health Association, Washington D.C. **1998.**
[9]M.G. Dalton and S.B. Upchurch , *Groundwater*, **1978,** 16, 228–233**.**
[10] C. Guler, G.D. Thyne , J. E. McCray and A. K. Turner, *Hydrogeol. J.*, **2002,** 10, 455–474 **.**
[11] C.N. Durfor and E. Becker, Public *Geol. Surv. water supp. paper*, **1964,** 1812, 364**.**
[12] R. F. Stallard and J.M. Edmond , *J.Geophys. Res.*, **1987,** 92, 8292-8302**.**
[13] M. Meyback, *Am. J. Sci.*, **1987,** 287, 401-428**.**
[14] R. J. Gibbs, *Science,* **1970,** 170, 1088–1090 **.**
[15] M Jalali., *Environ. Monit. Assess.*, **2007,** 130, 347-364**.**
[16] T. Rafique, S. Naseem, M.I. Bhanger and T.H. Usmani, *Environ. Geol.*, **2008,** 56, 317–326**.**
[17] G. T. Chae, S. T. Yun, , K. Kim and B. Mayer, *J. Hydrol***, 2005,** 321,326-343**.**
[18] K. Kim and G. Y. Jeong, *Chemosphere*, **2005,** 58, 1399-1408 **.**
[19] G. Jacks, P. Bhattacharya, V. Chaudhary, and K.P. Singh, *Appl. Geochem.*, **2005,** 20, 221-228.
[20] J. Zhang, F. Zhu, R. Chen, X. Miao and S. Yao , *Geol. J. China Universities*, **1998,** 4 (2), 140–146 **.**
[21] L. Zhu and G.Yin, *J. Henan Polytech. University*, **2005,** 24 (5),366 -368 **.**
[22] P. S. Datta, D.L. Deb and S.K.Tyagi, *J. Contam. Hydrol*., **1996**,24, 85-96 .
[23] D.L. Parkhurst and C.A.J.Appelo, User's Guide to PHREEQC (Version 2)-A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. United States Geological Survey, Water Resources Investigations Report 99-4259, Washington, DC, USA. **1999,** p. 326**.**