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Geochemical provenance and spatial distribution of fluoride in Groundwater in parts of Raniganj coal field, West Bengal, India

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ABSTRACT

Present research work undertakes the hydro-geochemical characterization as well as demarcation of fluoride (F^-) contaminated area by means of GIS modeling. F^- concentration in the study area ranges from 0.20 mg/l to 1.67 mg/l with a mean of 0.72 mg/l. Among the twenty six (26) collected samples from water table sedimentary aquifer of study area 54% samples have F^- concentration <0.6 mg/l; and 8% of the samples have concentration >1.5 thereby unsuitable for drinking purpose. Majority of the water samples fall under the category of Ca-Mg-Cl followed by Ca- HCO_3^- type hydrofacies. Fluoride has a significant ($p<.05$) positive correlation with bicarbonate (HCO_3^-) ion and it also shows a positive correlation with sodium (Na^+) but higher negative correlation with calcium (Ca^{2+}). This may be attributed to ion-exchange process where Ca^{2+} ions in water may react with clay minerals (sodium-montmorillonite) to release Na^+ ion in groundwater. All the groundwater samples have $Ca^{2+} \ll HCO_3^-$ thereby reflects its precipitation as carbonate. Ion exchange between Ca^{2+} and Na^+ due to the movement of groundwater in the weathering zone may also result in high F^- associated with high Na^+ and low Ca^{2+} concentration. Gibb's ratio suggests that majority of high-fluoride groundwater samples are mainly attributed to weathering of rocks. Activity diagram between Ca^{2+} vs. F^- suggests that all the water samples are unsaturated with respect to fluoride. Raniganj sandstone, containing 248mg/kg of total F^- may be the major contributor of F^- in the water-table aquifer of the study area. Output of GIS based thematic map reveals that fluoride distribution may also structurally controlled.

Key words: Hydro geochemistry; Fluoride; Ion-exchange; GIS; Raniganj coal field; West Bengal.

INTRODUCTION

Most of the fluoride contaminated zones in the world have been identified in sedimentary aquifers that are made up of fluoride-bearing minerals derived from granite parent rocks [1] during chemical weathering, especially in arid and semi-arid environments [2,3]. The fluoride ion contributes over 95% of the total fluoride present in drinking water [4]. The occurrence of

fluoride in groundwater where human interference is almost negligible can be attributed to the weathering and leaching of amphiboles, fluorite, apatite and mica. Thus, the areas where such rock types are dominant high fluoride concentration can be suspected [5-9].

Fluoride concentration in Groundwater depends on various factors such as temperature, pH, carbonate and bicarbonate alkalinity, solubility of fluorine-bearing minerals, anion exchange capacity of aquifer materials (OH^- for F^-), and the nature of geological formations drained by water and contact time of water with a particular formation while carbonate and bicarbonate alkalinity, pH is detrimental when rock silica is dominant. The fluoride concentrations are found to be higher in water with high alkalinity whereas water contains maximum amount of calcium ions limits fluoride ion level is to about 8 mg/l. It is well known that regions with highest fluoride levels and having bedrock layer composition of igneous and metamorphic rocks are of geological composition of syenites, granites, quartz, monzonites, granodiorites, felsic and biotite gneisses, and alkaline volcanic. Although these rock types can contain a variety of fluoride-rich accessory minerals, laboratory experiments and field studies have shown that the presence of biotite alone is sufficient to produce dissolved fluoride concentrations above 4 mg/l.

Fluoride is a persistent and non-degradable poison that accumulates in soil, plants, wild life and in humans. Daily intake of 1 mg/l of fluoride is very much essential for healthy growth of teeth, but level higher than the permissible limit of 1.5 mg/l is dangerous to health. Severe chronic and cumulative over exposure can cause the incurable crippling of skeletal fluorosis. The dental and skeletal fluorosis is irreversible and no treatment exists. It is toxic at concentrations greater than 1.5 mg/l and is associated with dental fluorosis [10]. At fluoride levels between 3.0 mg/l to 6.0 mg/l in drinking water skeletal fluorosis may be observed and when a concentration of 10 mg/l is exceeded crippling fluorosis can take place.

More than 23 developed and developing nations are facing the problem of fluoride contamination in groundwater. India is one where fluoride contamination in groundwater creating health problems. Fluoride concentration in Groundwater of India varies widely ranging from 0.01 mg/l to 48 mg/l [11]. In India approximately 65 million people including 6 million children facing the problem of fluorosis due to consumption of water contaminated with fluoride. In recent times, there have been media reports that fluoride contamination is widespread in West Bengal. It has been highlighted that 60 blocks of the Bankura, Bardhaman, Birbhum, Purulia, Midnapur, Malda and West Dinajpur districts in West Bengal are affected by fluoride [5,12-16]. So far no work has been reported on fluoride contamination in Raniganj coal field area. With this backdrop the present research is undertaken to determine the fluoride hydrogeochemistry in this area.

The objective of the present study is to identify the probable source of fluoride contamination in the study area by means of geochemical signature and to locate the areal extent of fluoride contaminated area with the help of GIS modeling.

Study area:

Raniganj coalfield lies in West Bengal and partly in Jharkhand states at the easternmost part of the Damodar valley coalfields. It is the next only in importance to the Jharia coalfield. Raniganj coalfield is situated about 185 Km North-West of Kolkata. The Raniganj coalfield is the birth

place of coal mining in the India and mining operation in this coalfield started in the year 1774. The Raniganj coalfield area covers about 1530 km², spreading over Burdwan, Birbhum, Bankura and Purulia districts in West Bengal and Dhanbad district in Jharkhand. The area is surrounded on all the three sides by perennial rivers viz., Damodar, Ajoy and Barakar and plenty of rainfall, there appears to be substantial Groundwater potential in the area.

The present study area (part of the Raniganj Coalfield) shown in the (Fig 1) is situated between latitude 23°37' N and 23.62° N and longitude 87°08' E and 87.13° E with an average elevation of 91 meters (29 feet). Spatial variation of altitude (Fig 2) shows that the northern part of the study area represents a higher elevation with respect to the south-eastern part.

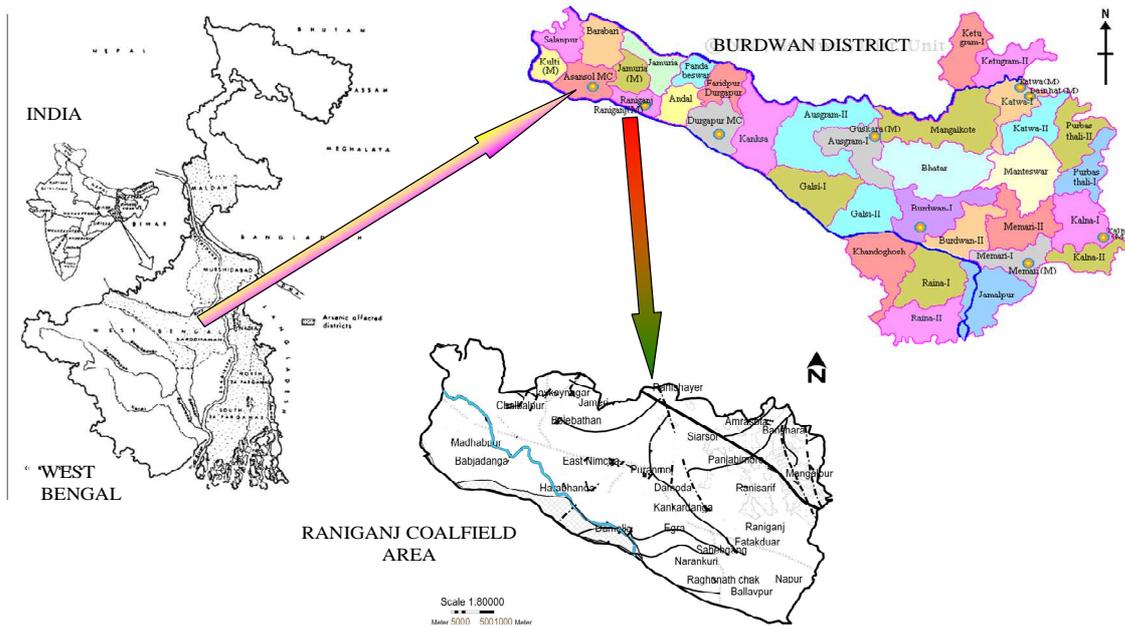


Fig 1: Location map of study area

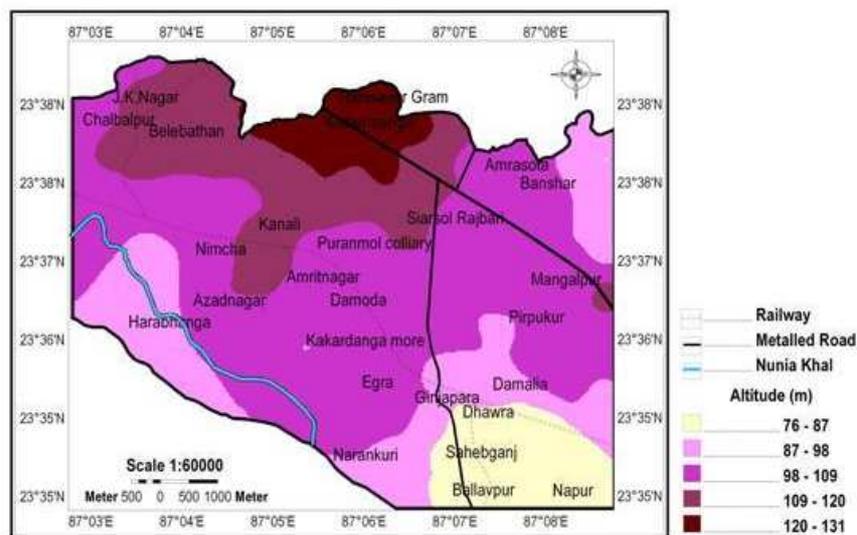


Fig 2: Spatial variation of altitude in Raniganj Coal field area

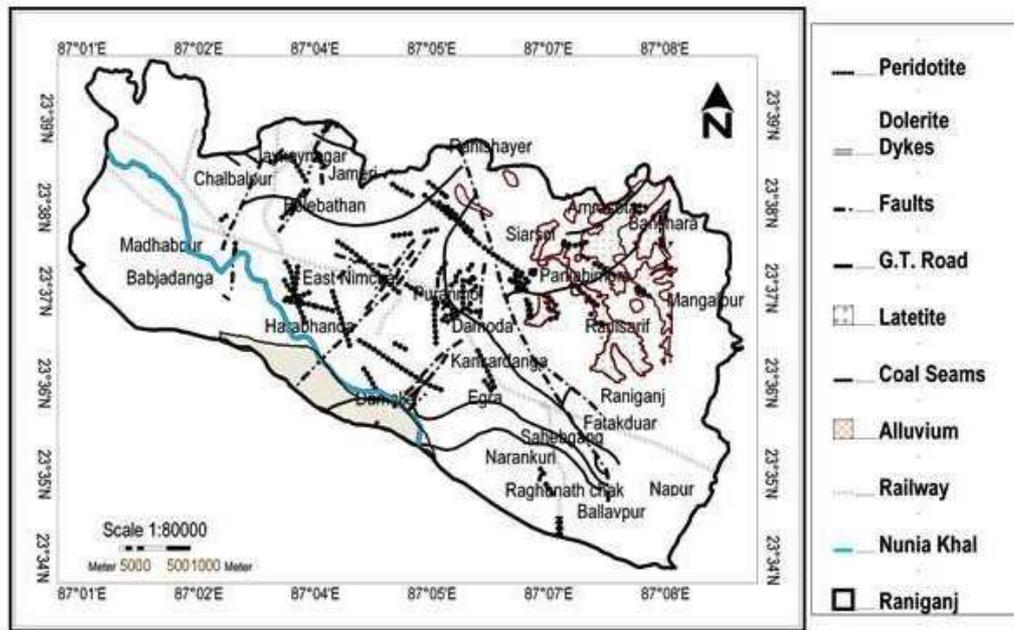


Fig 3: Geological map of Raniganj Coal field area

Table 1: Geological succession of Raniganj Coal field area

Geological area	Formation	Major lithology
Recent	River alluvium Unconformity	Sand, clay and lime stone
Jurassic to Cretaceous	Rajmahal Trap or Intrappeans	Dolerite, mice peridotite ,dykes and sills
Upper Triassic	Supra Panchet Unconformity	Sand stone and shales
Lower Triassic	Panchet series	Medium to coarse grained feldspathic sandstone and red clay
Upper Permian	Raniganj measures	Fine to medium grained sand stone, sandy/micaceous shale, coal seams, siltstone and carbonaceous shale
Middle Permian	Iron stone shale	Carbonaceous shales containing nodules of clays
Lower Permian	Barakar measures	Massive sand stones and grits with shale beds and coal seams
Upper Carboniferous	Talchir series Unconformity	Tillites to boulder conglomerate, yellowish green sandstone, etc.
Archaean	Metamorphic rocks with igneous intrusive	Granite, granite gneiss, hornblende schist, pegmatite and veins of quartz

Geology of the study area: The study area mainly comprised of Lower Gondwana group of rocks in the Permian era and underlain by Archaean metamorphic which are exposed in the North-Western part of the area. Two major faults traverse the area, one trending NNE-SSW in the Western part and other NNW-SSE direction in the eastern part (Fig 3). Geological formations (Table 1) of the area consist of dark grey and black micaceous shale, siltstone, and sandstone along with thin to moderately thick ironstone bands. The ironstone bands are bluish grey or brown to reddish brown in colour, hard and compact basaltic rocks. Lithology of the area is represented by course to medium grained sandstone with siltstone, carbonaceous and grey

shale and coal seam. Groundwater occurs under phreatic conditions in the weathered and fractured zones. The depth to water table ranges from 5.6 to 12.1 m below the ground surface.

MATERIALS AND METHODS

Sampling techniques and analytical details:

Water samples were collected from 26 different locations (Table 2) of well at Raniganj coalfield area for detail hydro geochemistry analysis of that water. pH, temperature and electrical conductance were measured immediately after collection of samples by portable meters. For analysis of the other hydrogeochemical parameter the groundwater samples were collected in polyethylene bottles. The bottles were rinsed before sampling and tightly sealed after collection and labeled in the field. Samples were collected after pumping the well for at least 10 to 15 minutes. Other than previously mentioned parameters Analysis was carried out for - total dissolved solid (TDS), total hardness (TH), 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-}), silica (SiO_2) and fluoride (F^-) as per standard methods [17].

Table 2: Sampling point with location details

Sample Number	Location Details	Latitude	Longitude
S1	Mangalpur	23d37'10.8"	87d08'45.8"
S2	Ronai (sporting club)	23d36'52.8"	87d08'01.7"
S3	Girijapara	23d36'07.1"	87d06'55.8"
S4	Sahebganj	23d35'30.6"	87d07'08.0"
S5	Ballavpur	23d35'01.1"	87d07'16.2"
S6	Egra(opposite shiksa sadan)	23d36'11.4"	87d06'16.5"
S7	Natun Egra	23d36'01.9"	87d06'12.3"
S8	Narankuri	23d35'29.1"	87d05'58.8"
S9	Siarsol Rajbari	23d37'46.8"	87d06'44.1"
S10	Ranisayer more	23d38'52.5"	87d05'58.9"
S11	Bijpur Shiksanikatan vidyapith	23d39'35.7"	87d05'53.5"
S12	Kadamdanga	23d38'42.6"	87d05'53.3"
S13	Puranmol colliery	23d37'29.1"	87d05'42.0"
S14	Damoda(colony no. 2)	23d37'05.8"	87d05'58.8"
S15	Kakardanga	23d36'35.7"	87d05'42.1"
S16	Amritnagar	23d37'10.9"	87d05'24.5"
S17	Harabhanga	23d36'46.5"	87d03'52.8"
S18	Damalia	23d36'10.2"	87d07'37.6"
S19	Nimcha	23d37'34.0"	87d04'34.8"
S20	Nimcha Gram	23d38'19.3"	87d05'28.9"
S21	Belebathan	23d38'37.5"	87d04'05.4"
S22	J.K.Nagar(Kamarpara)	23d38'52.0"	87d03'39.9"
S23	Chalbalpur	23d38'43.7"	87d03'18.4"
S24	Bogra	23d39'43.4"	87d03'57.1"
S25	Amrasota	23d38'22.5"	87d07'23.4"
S26	Banshara	23d38'07.1"	87d07'54.0"

Soil samples were collected from vertical surfaces of Bansra underground mine in a regular interval and were kept in a plastic zipper bag and were transported to laboratory for further

analysis of water soluble fluoride (F_{H_2O}), Calcium chloride extractable fluoride (F_{CaCl_2}) and Total fluoride (F_{Total}).

Statistical Analysis of the Experimental Data:

The Pearson correlation among F and other ions in irrigation water was calculated by using the following formula [18]:

$$r = \frac{\sum_{i=1}^n (X_i - \bar{X})(Y_i - \bar{Y})}{(n-1)S_X S_Y}$$

Where X and Y are two variables, with means \bar{X} and \bar{Y} respectively with standard deviations S_X and S_Y . Significance of observed correlation co-efficient (r) was tested by using student t-test.

GIS Methodology:

Digital Elevation Model (DEM)

DEM is generated on the basis of sampling points, stored as a point layer along with attribute such as F. 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, with the elevations generated due to different concentration of the said parameters interpolated linearly between vector nodes. 2D layers are ignored in this stage. If multiple elevation values are scanned into a single pixel, the maximum value is assigned the pixel, and the pixel is marked as a cliff. In 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. Interpolation is made between the source elevations and elevations at equal-distance points from source locations. If 2D vector layers are present, they are scan converted into a flag buffer during the optional step. The 2D features are also initialized to prepare for use in the smoothing stage. 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 neighborhood values.

Inverse Distance Interpolation (IDINT) technique

Inverse distance interpolation is used to read the gray level values for the arbitrary number of pixel locations in order to generate a raster image based upon interpolation between the specified gray levels. This method of interpolation combines the idea of Thiessen polygon with the gradual change of trend surface. It considers weighted moving average. Weights are computed from a linear function of distance between sets of points and the points to be predicted. In this method the size of the starting radius is specified, which defines the starting search area for interpolation points around grid point.

Table 3: Physico-chemical analysis of water samples (All the units are expressed in mg/l except pH, EC and WL)

Location	Tem(⁰ C)		EC(μ S/cm)	WL(m)				Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Fe ²⁺	CO ₃ ⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	PO ₄ ³⁻	SiO ₂ ⁴⁻	F ⁻
	pH			TDS	TA	TH														
S1	21.60	7.88	1360	10.2	810	420	730	84	126.88	132.26	17.64	0.233	180	240	139.957	79.35	0.795	0.011	2.551	1.02
S2	20.60	7.58	1540	6.6	912	160	830	294	23.18	136.8	21.62	0.107	80	80	299.907	110.488	0.404	0.018	4.025	0.202
S3	20.20	7.65	1380	5.87	785	330	670	176.4	55.876	145.08	23.46	0.236	ND	330	229.929	98.374	3.661	0.012	2.346	0.483
S4	20.10	7.74	1250	0.93	704	420	560	151.2	44.408	84.16	17.22	0.116	ND	420	129.96	81.545	0.254	0.018	2.044	1.67
S5	20.60	7.57	1250	6.25	700	280	430	100.8	43.432	154.3	28.72	0.094	ND	280	199.938	62.114	2.338	0.02	2.32	0.358
S6	24.20	8.12	740	7.8	399	330	440	92.4	50.996	140.78	16.24	0.133	ND	330	29.991	43.984	0.374	0.008	2.473	0.907
S7	25.20	7.72	1680	5.24	1018	310	760	285.6	11.224	116.88	4.7	0.1	ND	310	189.941	154.472	1.01	0.011	2.413	0.576
S8	27.10	7.62	860	2.89	470	250	320	84	26.84	102.46	5.74	0.223	ND	250	49.985	55.691	3.245	0.021	3.088	0.618
S9	22.3	7.51	1450	8.45	827	170	800	193.2	77.348	92.5	15.36	0.113	80	90	179.944	128.943	2.355	0.03	2.771	0.277
S10	26.5	7.44	1130	4.14	637	270	530	134.4	47.336	126.66	23.48	0.1	ND	220	129.96	61.626	3.468	0.018	2.298	1.19
S11	24.9	7.53	1480	5.75	857	220	720	159.6	78.324	111.14	36.56	0.107	60	270	249.923	138.211	2.798	0.02	2.618	0.526
S12	23.8	7.59	290	2.98	144	50	170	42	15.86	23.84	3.7	0.107	ND	50	9.997	33.902	0.082	0.035	1.966	0.225
S13	24.2	7.66	810	2.08	445	280	390	84	43.92	136.12	12.78	0.094	ND	280	19.994	63.333	3.141	0.022	2.048	0.616
S14	28.1	7.86	1420	3.38	825	410	630	100.8	92.232	120.3	8.96	0.097	80	330	139.957	139.35	2.866	0.024	2.842	1.3
S15	24.1	7.8	570	3.2	300	120	250	84	9.76	96.14	7.58	0.116	ND	120	29.991	36.911	1.856	0.041	2.943	1.01
S16	24.7	7.59	1100	2.71	612	280	470	142.8	27.572	114.48	20.4	0.149	ND	280	39.988	144.472	4.229	0.014	3.032	0.419
S17	25.4	7.45	520	8.87	275	80	240	84	7.32	128.58	6.88	0.097	ND	80	39.988	45.366	4.607	0.016	3.092	0.269
S18	26.4	7.63	1460	11.5	623	260	680	193.2	48.068	123.48	6.68	0.1	ND	100	99.969	95.772	2.024	0.018	3.379	0.388
S19	25.6	7.86	1200	5.79	695	210	500	109.2	55.388	142.84	10.72	0.091	ND	210	119.963	125.772	0.202	0.042	1.999	0.778
S20	26.7	7.51	920	3.46	500	170	310	58.8	39.772	154.98	20.24	0.97	ND	170	89.972	45.528	3.008	0.008	2.163	1.62
S21	25.6	7.77	1120	5.2	619	230	460	117.6	40.504	104.34	1.78	0.107	80	150	119.963	106.098	3.446	0.018	1.917	0.443
S22	25.9	7.38	1440	5.9	813	420	550	159.6	36.844	118.6	3.48	0.11	ND	420	169.947	76.911	3.507	0.014	2.432	1.277
S23	25.3	7.65	1120	6.1	625	260	510	176.4	16.836	94.38	5.34	0.126	ND	260	119.963	73.496	3.176	0.013	3.04	0.525
S24	25.6	7.59	770	0.65	414	260	330	75.6	34.404	82.1	5.94	0.116	ND	260	69.978	23.659	3.61	0.012	2.186	0.896
S25	20.5	7.4	1840	8.2	1070	180	810	176.4	90.036	123.52	28.6	0.11	ND	180	459.857	54.553	0.868	0.025	2.156	0.547
S26	19.3	8	1320	5.94	715	330	510	109.2	57.828	99.64	35.84	0.1	60	270	99.969	134.309	3.498	0.013	2.171	0.512

*N.D stands for not detected range

RESULTS AND DISCUSSION

The chemical constituents of the water samples are shown in (Table 3). The statistical parameters (maximum, minimum, mean, standard deviation and co-variation etc.) of various physico-chemical parameters that were analysed are given in (Table 4). F⁻ concentration in the water table aquifer of the Raniganj coal field area ranges from 0.20 to 1.67 mg/l with a mean of 0.72 mg/l. The desirable range of F⁻ concentration in drinking water is from 0.6 to 1.2 mg/l according to Indian standard specifications [19]. Thus if the concentration of F⁻ is below 0.6 and above 1.2 mg/l, the water is not suitable for drinking purposes. However, it is suggested that the maximum limit can be extended up to 1.5 mg/l (BIS 1992). It was observed that nearly 8% of the samples exceeded the maximum permissible limit of World Health Organisation [20] and BIS standards.

Table 4: Descriptive statistics of the analytical data

Parameter	Mean	Minimum	Maximum	SD	CV	WHO (1997)		BIS (2004)	
						Desirable	Permissible	Desirable	Permissible
Tem (°C)	24.00	19.30	28.10	2.52	951.59	—	—	—	—
pH (Unit)	7.66	7.38	8.12	0.18	4204.07	7.00	9.20	6.50	8.50
EC (µS/cm)	1154.62	290.00	1840.00	376.92	306.33	—	—	—	—
WL(m)	5.39	0.65	11.49	2.73	197.37	—	—	—	—
TDS	645.92	144.00	1070.00	228.53	282.65	—	—	500.00	2000.00
TA	257.69	50.00	420.00	100.29	256.94	—	120.00	—	—
TH	523.08	170.00	830.00	189.20	276.46	—	500.00	300.00	600.00
Ca ²⁺	133.43	42.00	294.00	62.65	212.98	75.00	200.00	75.00	200.00
Mg ²⁺	46.24	7.32	126.88	28.50	162.24	30.00	150.00	30.00	100.00
Na ⁺	115.63	23.84	154.98	27.83	415.53	50.00	200.00	—	—
K ⁺	14.99	1.78	36.56	10.16	147.47	10.00	12.00	—	—
Fe ²⁺	0.16	0.09	0.97	0.17	91.03	—	—	0.30	1.00
CO ₃ ⁻	23.85	0.00	180.00	44.91	53.10	—	—	—	—
HCO ₃ ⁻	230.00	50.00	420.00	102.10	225.27	—	—	—	—
Cl	133.04	10.00	459.86	100.20	132.77	250.00	600.00	250.00	1000.00
SO ₄ ²⁻	85.16	23.66	154.47	39.31	216.66	200.00	600.00	200.00	400.00
NO ₃ ⁻	2.34	0.08	4.61	1.39	167.70	50.00	—	45.00	—
PO ₄ ³⁻	0.02	0.01	0.04	0.01	212.31	—	—	—	0.10
SiO ₂	2.55	1.92	4.03	0.51	498.55	—	—	—	—
F ⁻	0.72	0.20	1.67	0.42	171.16	0.90	1.50	1.00	1.50

F⁻ is the most electronegative element and thus it reacts immediately to form fluoride compounds and therefore making presence of free F⁻ an obsolete possibility but under favorable physico-chemical conditions with long residence time it may occur as dissolved from groundwater [21,22]. At acidic pH the F⁻ is adsorbed on the surface of the clay. A higher value of pH favours the enrichment of F⁻ in groundwater. The OH⁻ in groundwater with high value of pH can replace the exchangeable F⁻ of fluoride containing minerals (muscovite) thus can increase the concentration of fluoride in groundwater.

The hydroxyl ions replace F⁻ from muscovite as shown below:



In sandstone dominant aquifers dissolution of F^- can be possible reason for presence of fluoride in groundwater. The hydrolysis of aluminosilicate minerals in the sandstone aquifers produces bicarbonate ion, which can enhance fluorite dissolution as below:



F^- concentration is generally independent of other water soluble components but a noticeable correlation exist between F^- and pH. The F^- solubility is lowest in the pH range of 5-6.5 [23]. At higher pH ionic exchange occurs between F^- and OH^- ions (Illite, mica and amphiboles) resulting in increase of F^- ion concentration in groundwater. The presence of high HCO_3^- , Na^+ and pH favours the release of F^- from aquifer matrix into groundwater. It is observed that groundwater pH in the study area varies from 7.38 – 8.12 with a mean of 7.66. The alkaline nature of the Groundwater favours the solubility of fluoride bearing minerals.

A statistical study of the inter-relationship between F^- and Ca^{2+} concentration ($r=-0.29$ at $p<.05$) showed a lack of significant correlation but data presented in (Fig 4) suggests that most of the water is unsaturated condition with respect to F^- . Similar were the results in the case of Ca^{2+} and HCO_3^- ions, where the correlation coefficient was found to be of low order. Here again the Groundwater appeared to be at or approaching equilibrium with calcite.

The waters are categorized according to their content of major cations and anions using a Piper diagram (Fig 5). Most of the high-fluoride groundwater samples contain Ca^{2+} , Mg^{2+} as the predominant cation. HCO_3^- and Cl^- are the predominant anions for the different kinds of high-fluoride groundwater samples, respectively. In the study area, the most common water types among the high-fluoride groundwater samples are mixed Ca-Mg-Cl type and Ca- HCO_3^- type (Table 6).

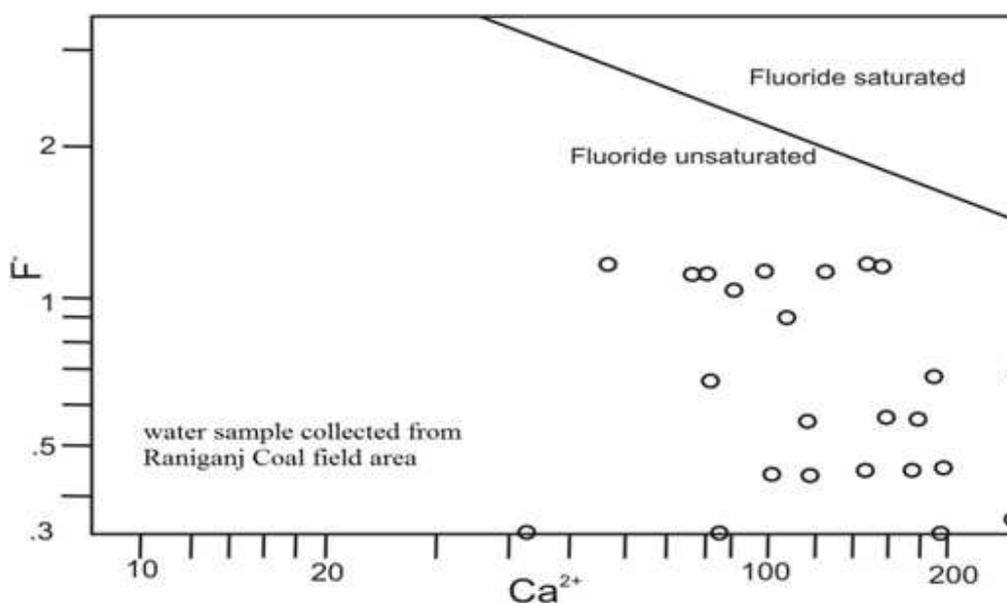


Fig 4: Plot activity of F^- (mg/l) against the activity of Ca^{2+} (mg/l)

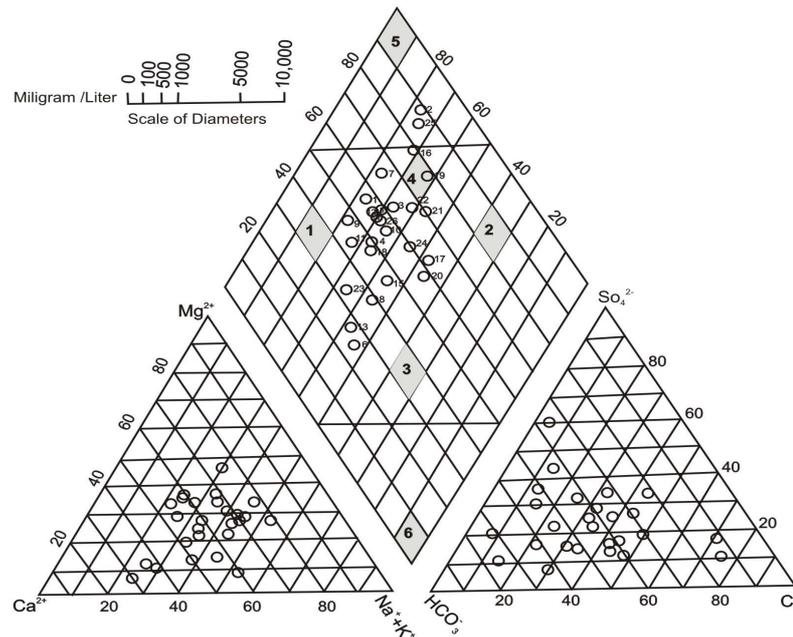


Fig 5: Trilinear diagram for representing the analysis of Groundwater quality (piper diagram)

The $\text{HCO}_3^-/\text{Ca}^{2+}$ ratio at all the places is found to be greater than 1, suggesting favorability of chemical conditions for the fluoride dissolution processes [24]. Further it is noticed that the ratio of $\text{Na}^+/\text{Ca}^{2+}$ at 42% of all sampling locations is greater than 1 indicating low calcium activity. A high concentration of sodium favours dissolution of fluoride bearing minerals at higher pH [25]. Samples with more than 1.5 mg/l F^- concentration present a negative correlation between F^- concentration and $\text{Na}^+(\text{Ca}^{2+} + \text{Mg}^{2+})$ or $\text{Cl}^-(\text{HCO}_3^- + \text{SO}_4^{2-})$ ratio, while the F^- concentration is approximately in direct proportion to $\text{Na}^+(\text{Ca}^{2+} + \text{Mg}^{2+})$ ratio for the majority of data points and negative proportion to $\text{Cl}^-(\text{HCO}_3^- + \text{SO}_4^{2-})$ ratio. It implies that the increases in F^- concentration of high-fluoride groundwater samples with more than 1.5 mg/l are mainly attributed to the dissolution of some fluorine minerals with respect to chemical weathering.

Gibbs [26] proposed a diagram to understand the relationship of chemical components of waters from their respective aquifer lithologies. Three distinct fields, namely precipitation dominance, evaporation dominance, and rock dominance areas are shown in the Gibbs diagram (**Fig 6**) Gibb's ratios are calculated with the formulae given below:

$$\text{Gibb's Ratio I (for anion)} = \text{Cl} / (\text{Cl} + \text{HCO}_3)$$

$$\text{Gibb's Ratio II (for cation)} = \text{Na} + \text{K} / (\text{Na} + \text{K} + \text{Ca})$$

where all ions are expressed in meq/l.

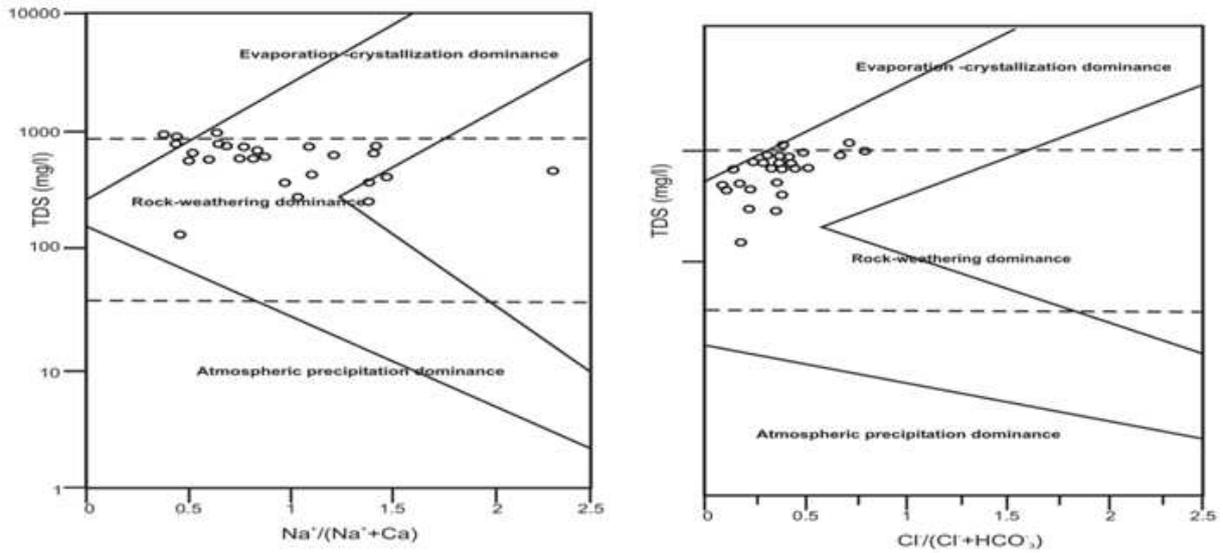


Fig 6: Mechanism controlling the chemistry of groundwater

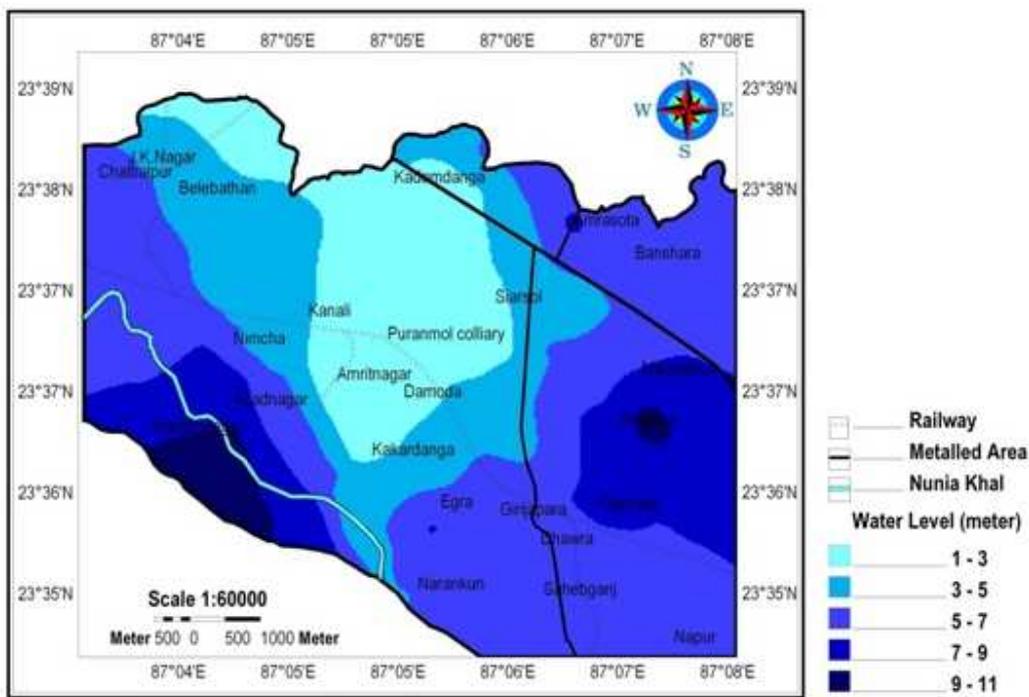


Fig 7: Spatial variation of water level in Raniganj Coal field area

Gibbs ratios for the study area samples are plotted against their respective total dissolved solids to know whether the Groundwater chemistry is due to rock dominance or evaporation dominance or precipitation dominance. Almost all the samples fall at the margin of rock-weathering and evaporation dominance area suggesting that majority of high-fluoride groundwater samples are mainly attributed to rock weathering with minor contribution by evaporation.

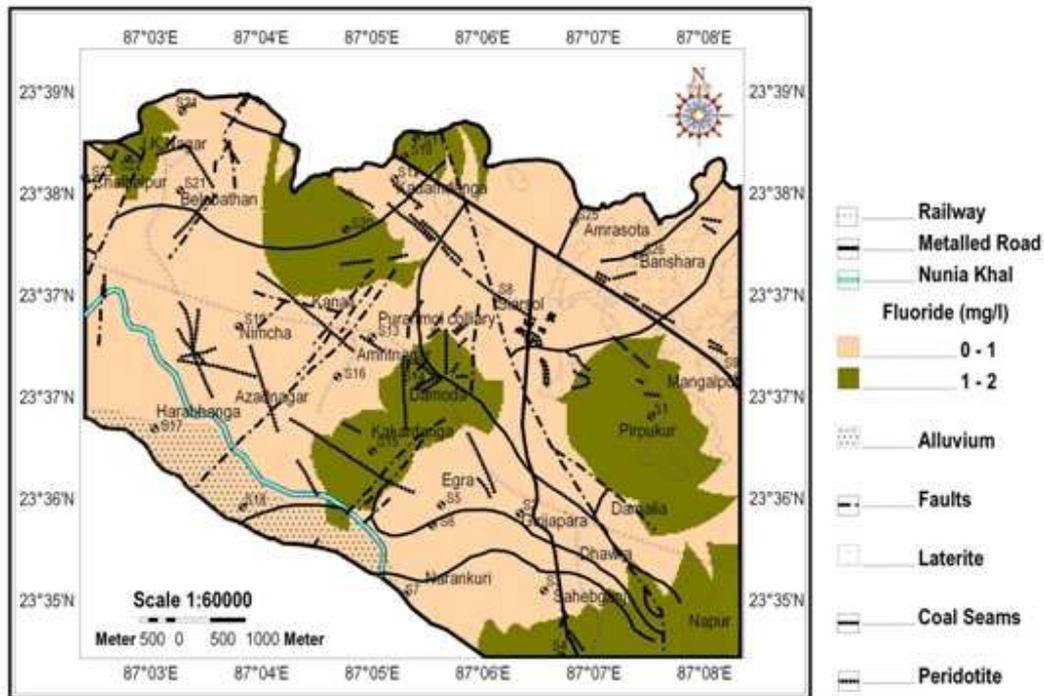


Fig 8: Fluoride zonation map of Raniganj Coal field area

The anthropogenic origin of fluoride in the study area can completely be ruled out as the area has neither industries nor much human settlements except very few in both the side of National Highway #2 so as to consider the discharge from these as potential source of fluoride input in groundwater as contaminant. Thus high concentration of fluoride is geogenic in origin, i.e. local hydro-geological conditions in the area are responsible for its higher concentration in groundwater. The F^- content of groundwater varies greatly depending on geological settings, type of rocks and climate. Another major possibility of F^- enrichment can be attributed to evaporation. Since the study area lies in semiarid environment and the temperature in summers is very high and rainfall is very less so due to evaporation the groundwater becomes oversaturated with calcite thus precipitating calcite which in turn reduces calcium content and thus promotes dissolution of fluorite. F^- ion is positively correlated with calcium ions before the water is saturated with fluorite. After over saturation the concentration of Ca^{2+} ions overrides the solubility limit of fluorite as fluorite dissolution is suppressed by common ion effect and the correlation between the two ions (Ca^{2+} and F^-) becomes negative [21].

An examination of the chemical analysis data highlights the following features in Groundwaters containing high fluoride content:

- 1.High fluoride Groundwaters are generally associated with low calcium content, there being a negative correlation between the two ions. This is reasonable in view of the low solubility of fluorite.
- 2.High fluoride Groundwater is generally associated with high bicarbonate ions ($r=0.52$, $p<.05$).
- 3.All most all the water samples are unsaturated with respect to fluorite.

From the GIS output it is seen that the water level follows the topography of the study area i.e., highest water level is found at topographically elevated portion of the northern region of the Raniganj coal field area (Fig 2). Groundwater flow direction can be predicted from the (Fig 7) as NNW to SSE. A distinct spatial distribution of F⁻ is predicted by applying Inverse Distance Interpolation technique (Fig 8). High fluoride concentration is mostly associated along a major fault trending from NE to SE. From the vertical profile of underground mine soil/rock exposure (Fig 9) it reveals that the yellow colour Raniganj sandstone which acts as a potential aquifer has water soluble F⁻ concentration of 4.51mg/kg and CaCl₂ extractable F⁻ 9.6mg/kg with a total F⁻ concentration of 248 mg/kg.

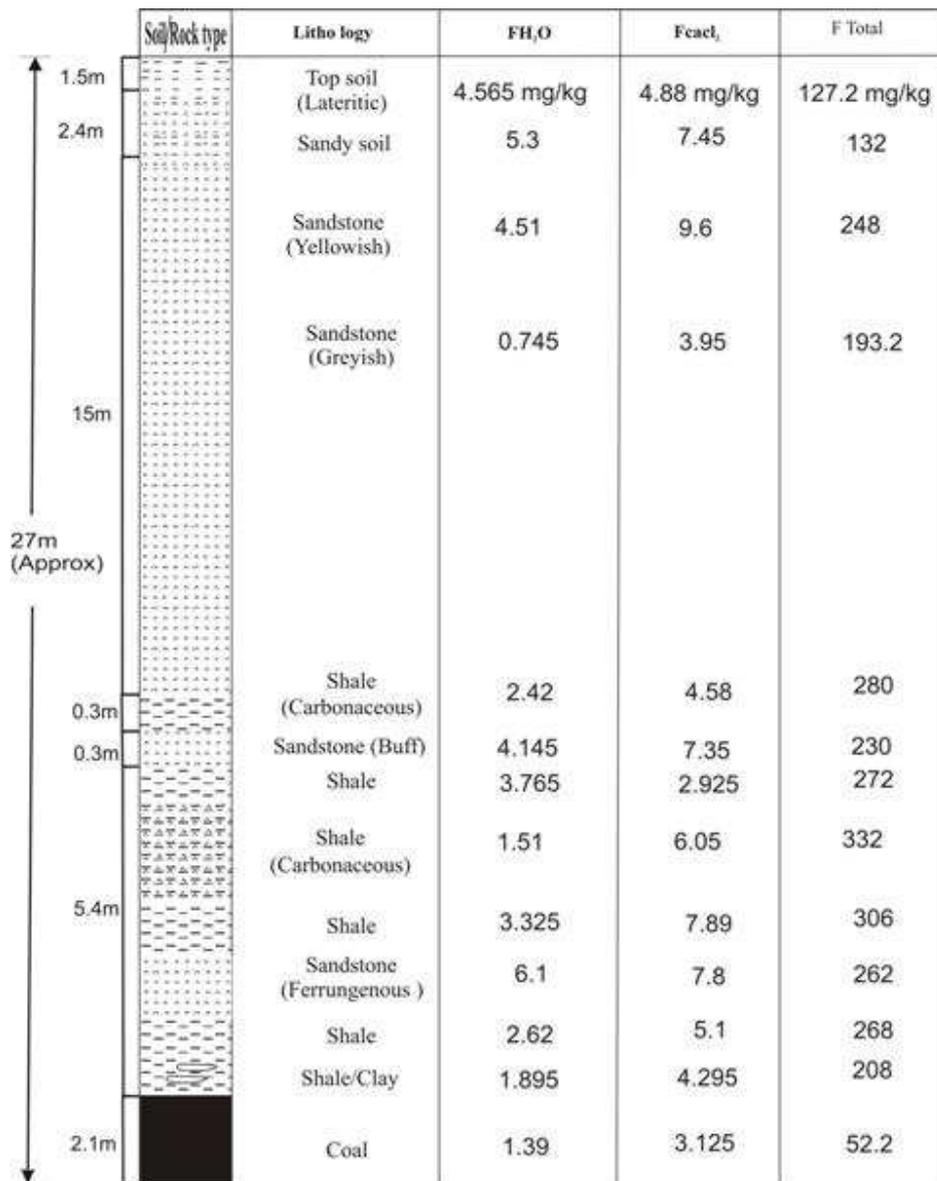


Fig 9: Vertical exposure of soil/rock in Bansara underground mines

CONCLUSION

Ion-exchange within Raniganj Sandstone and to some extent evaporation are the major contributing factors of fluoride contamination in the Raniganj coal field area. Activity of the F⁻ ion is also highly unsaturated with respect to fluorite. GIS modeling also shows that apart from geogenic source fluoride concentration in groundwater also controlled structurally.

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