Original Article

2023, Vol. 63 : 01-08
ISSN-0972-7434

Madhya Bharti Journal of Science

Fluoride (F^-) incidence in groundwater in Bundelkhand granitoids, parts of Chhatarpur District, central India

Anjali Renuka Dahanga and P. K. Kathal*

Department of Applied Geology, Dr. Harisingh Gour Vishwavidyalaya, Sagar-470003, India
Corresponding author email: kathalpk@rediffmail.com

(Received on 18/07/2022 Accepted on 21/10/2022)

Abstract

The present report is on the appraisal of fluoride (F^-) and its relation with physicochemical groundwater parameters, in Chhatarpur district. It aims to characterize concentration of F− pollution/contamination and its sources in groundwater besides evaluation of variability in physiochemical parameters like, pH, TDS, EC, Ca^{2+}, Mg^{2+}, K^+, Na^+, F^-, HCO_3^-, Cl^-, SO_4^{2-}, and NO_3^-. Seventy-one groundwater samples, collected in pre-monsoon season (June, 2018), were analyzed. F^- values have been found to be above/below the desirable permissible limits.

Since the area lacks industrialization; thus anthropogenic input may be considered negligible. Accordingly, F^- enrichment may be attributed to the occurrence of F^- in rocks and its chemical kinetic behavior with groundwater.

***Keyword:** Fluoride, Bundelkhand granitoids, rock-water interaction, alkalinity, Groundwater*

Introduction

Fluoride pollution/contamination in groundwater is hotly discussed for its associated adverse impacts on the health of living beings. According to reports of the United Nations International Children's Emergency Fund (UNICEF, 1999), fluorosis endemicity is an emerging problem in more than 62 million people in 23 states of India (Central Ground Water Board, CGWB, 2018) in the form of 'dental caries' ($F^- <$ 1ppm) and 'dental and skeletal fluorosis' ($F^- >$ 1.5ppm) as per the standard desirable limits defined by the World's Health Organization (WHO).

Groundwater movement through the weathered/fractured zones makes it rich in F^- due to weathering of fluorite, fluoroapatite, mica, amphibole, clays, and villianmite, etc. with pronounced hydrochemical effects that enhances concentrations of F^- further.

Study area

The area of 2800 km^2 (Lat. 24°45' – 25°00' N; Long. 79°15' – 79° 45' E) in central region of the Bundelkhand plateau, Madhya Pradesh, India falls in warm to humid climatic zone. Geologically, the rocks belong to the Bundelkhand-granitoids (with numbers of pegmatite dykes and quartz reefs), Bijawars Group and Vindhayan Supergroup, which are partially covered by the alluvium (Auden 1933). The region has 'poor to moderate' groundwater potential as it percolates only through weathered and fractured zones (Fig.1and 2).

Materials and Method

Based on a preliminary geochemical analyses of 15 samples, which indicated incidences of high/low F^- the area was demarcated and 71 tube/dug wells samples of groundwater were collected in the pre-monsoon period (June, 2018). The samples were taken in 1 lt. polyethylene bottles after rinsing with the same water. The co-ordinates of sampling sites were worked out suing Geographic Positioning System (GPS). Temperature and pH of water were recorded on the spots using litmus paper and thermometer.

The samples were filtered through 'Whatman filter paper 42' for physicochemical study of groundwater in the laboratory, which included Electric Conductivity (EC) and Total Dissolved Solids (TDS) measured by 'soil water analyzer kit'. However, further analysis was carried out at the National Environmental and Engineering Institute (NEERI) Nagpur, following American Public Health Association (APHA 2005) procedure for pH (using pH Meter), F^- (by Ion Selective Electrode Method), Total Hardness (TH), HCO_3^-, Ca^{2+}, Mg^{2+} and Cl^- (by Standard Titration Methods), Na^+ and K^+ (by Flame Photometer), and SO_4^{2-} and NO_3^- (by Ultraviolet, UV spectrophotometer). Correlation of analytical data is carried out using Scatter Plot, Gibbs Diagram and Piper Plots.

Result and Discussion

Hydrogeochemical analyses shows that TDS ranges from 244–1549 mg/l while EC ranges from 488–3080. The results reveal that the 'primary phenomenon' for high values of F^- in groundwater is due to prolonged 'rock-water interaction' coupled with 'ion exchange process' in mica and clay minerals in the alkaline medium. In 2008, 1.9 ppm F^- in groundwater was reported amidst pH varying from 7.2–8 (Ram Avtar *et al.*, 2013), which has been found enhanced up to 3 ppm in 2018 (present study) amidst pH ranging from 7.8 to 8.7 (Table 1).

The study attests that high values of F^- in granitoids (granites, granodiorites, tonalites, adamalites, trondhjemites) may be attributed to the geogenic processes i.e., presence of fluorite (Wenzel and Blum, 1992 and Bardsen *et al.*, 1996). Also that weathering of rocks and prolonged presence of groundwater in fractured zones in alkaline medium/over-exploitation of groundwater at deeper levels may enhance the concentration of F^- in the region..

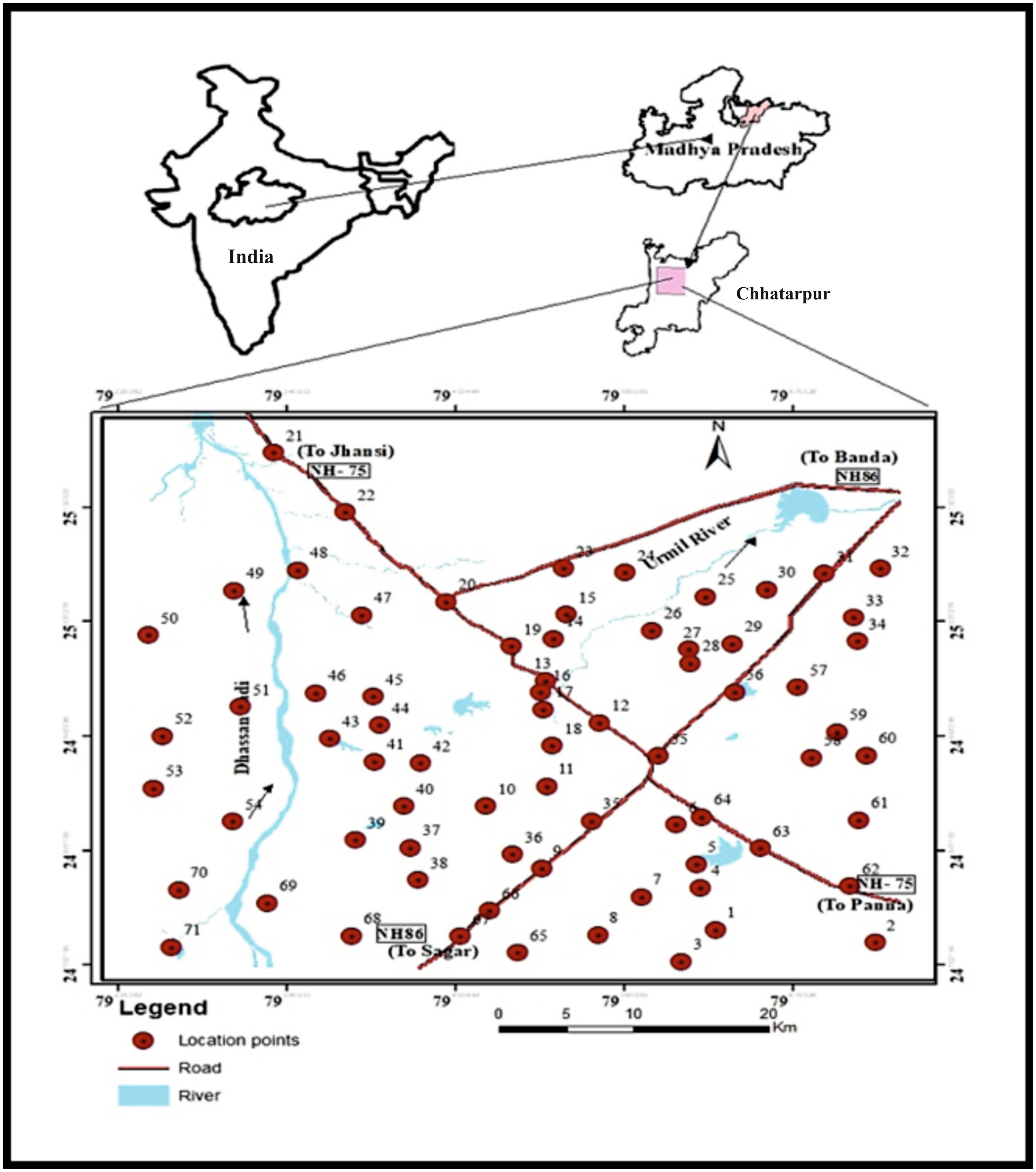


Figure 1: Location Map of the Study

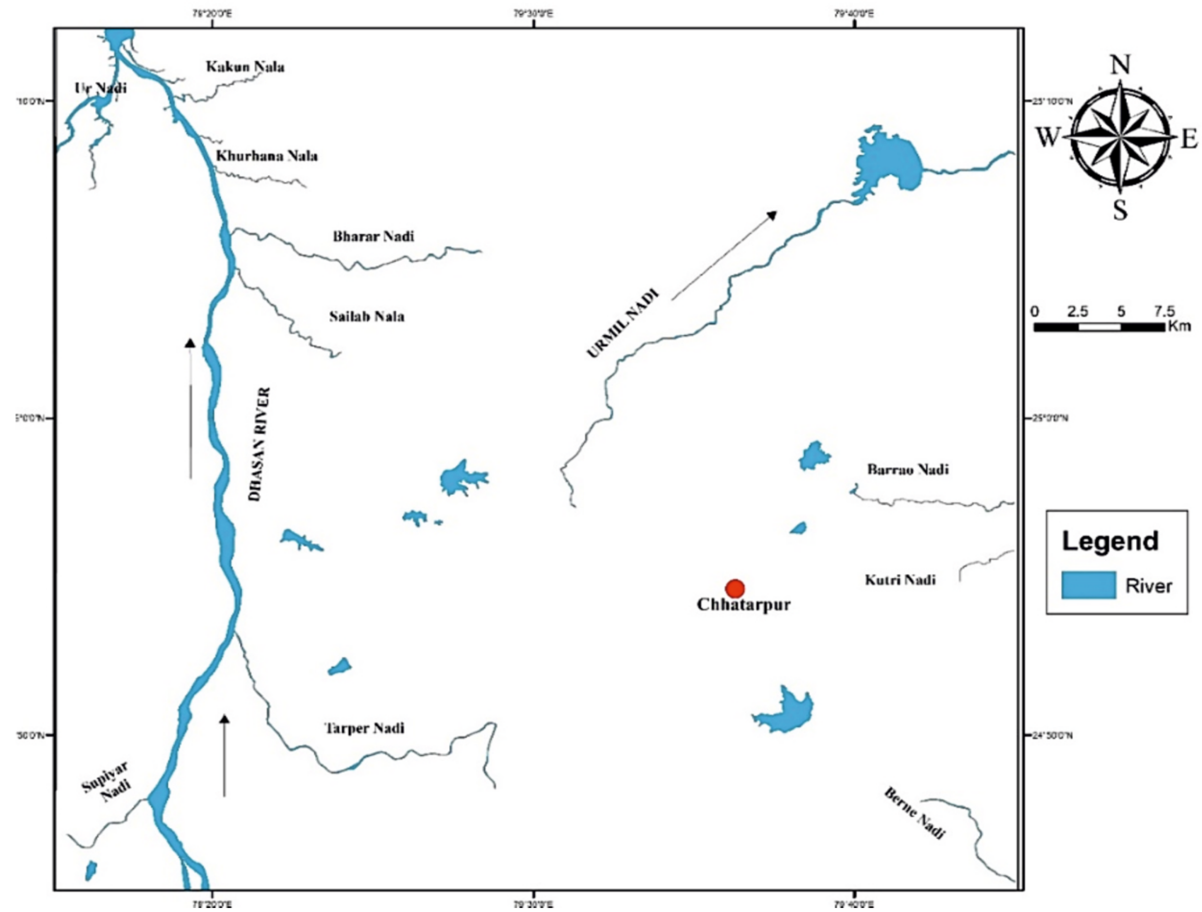


Figure. 2 Drainage map

Table 1: Statistical summary of physicochemical parameters of groundwater samples.

Parameter	Unit	WHO (2017) standards	BIS (2015) standards	Pre-monsoon (June, 2018)			
				Max	Min	Mean	SD
pH	-	6.5-8.5	7.0-8.5	**8.7**	**7.8**	8.22	0.21
TDS	mg/l	500 -1000	500-2000	**1549**	244	532.45	258.45
EC	µS/cm	400-2000	-	**3080**	488	1066.33	517.80
T.H	mg/l	-	200-600	**1280**	110	344.50	195.04
SO_4^{2-}	mg/l	25-250	200-400	281.8	0.61	61.81	57.34
F^-	mg/l	1.0-1.5	1.0-1.5	**3.0**	0.24	0.908	0.47
Cl^-	mg/l	250	250-1000	750	20	132.67	116.55
NO_3^-	mg/l			290.34	1.38	110.7	82.38
HCO_3^-	mg/l	-	300	**340**	40	67.10	152.81
K^+	mg/l	10-12	-	**105.2**	1.1	9.81	19.32
Ca^{2+}	mg/l	100-200	75-200	**512**	72	167.26	80.57
Na^+	mg/l	200	-	**343.5**	12.5	70.12	66.02
Mg^{2+}	mg/l	30	30	**187.2**	2.4	29.14	33.53
SD=Standard Deviation. Values abo ve the permissible limits are show in **bold** letters.							

Dominancy trend of cation: Cl> HCO_3>NO_3>SO_4>F and anions: Ca>Na>Mg>K

Table 2: Localities showing high F^- values in alkaline medium

S. No.	District	Pre-monsoon (June, 2018)		
		Name of locality	F^- values >1.5 mg/l	**pH value**
1	Chhatarpur	Hatna	2.0	8.7
2		Dharampura	1.9	8.2
3		Barduwaha	1.6	8.3
4		Bedar	1.6	8.1
5		Palera	3.0	8.6
6		Harrai	1.8	8.2
7		Gopalpura	2.2	8.5

Table 3: Study area zone Classification associated with Fluorosis vulnerability based on permissible range of F^- with as per WHO

Classification	F^- Conc. Ranges(ppm)	No. of Samples	% of the samples	Associated risk
Low Risk Zone	< 1	55	77.46	Dental Caries
Safe Zone	1-1.5	10	14.08	-
High Risk Zone	>1.5	06	8.45	Dental and/ Skeletal Fluorosis

Table 3, shows 8.45% exceeds the 'desirable limit' of F^- and therefore falls under the 'high risk zone' whereas 77.46% under the 'low risk zone' and 14.08% under the 'safe zone' (Fig. 3).

Fig. 3 and 4 represents concentric contours in mg/l, showing spatial variation in pH and F^- in Chhatarpur district.

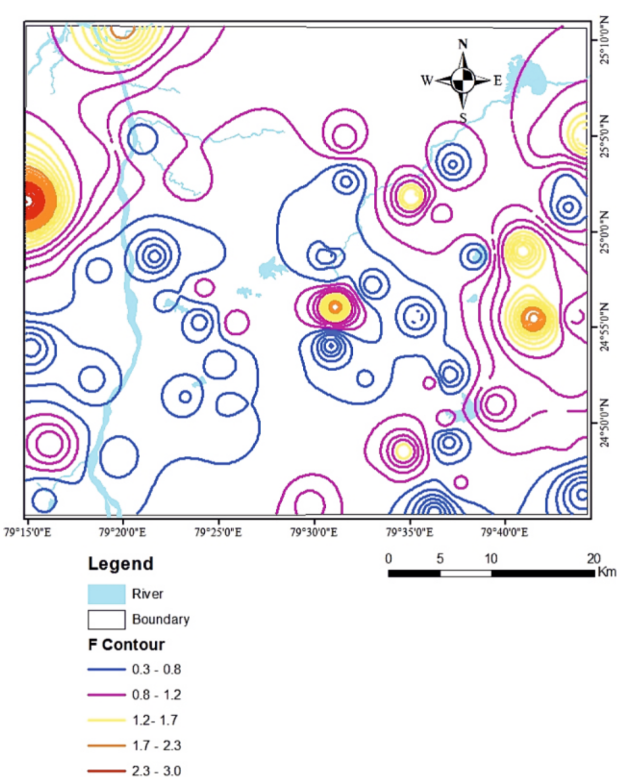


Figure 3: Spatial distribution of F^-

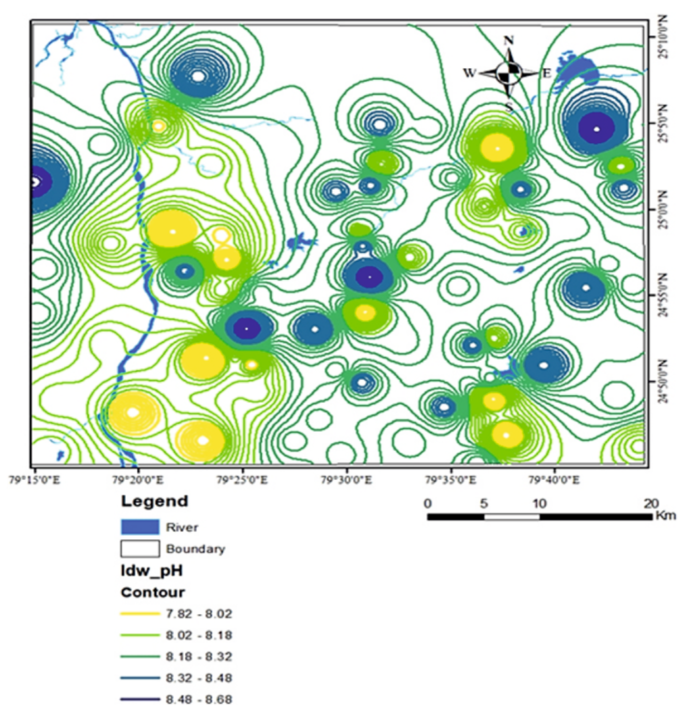


Figure 4: Spatial distribution of pH

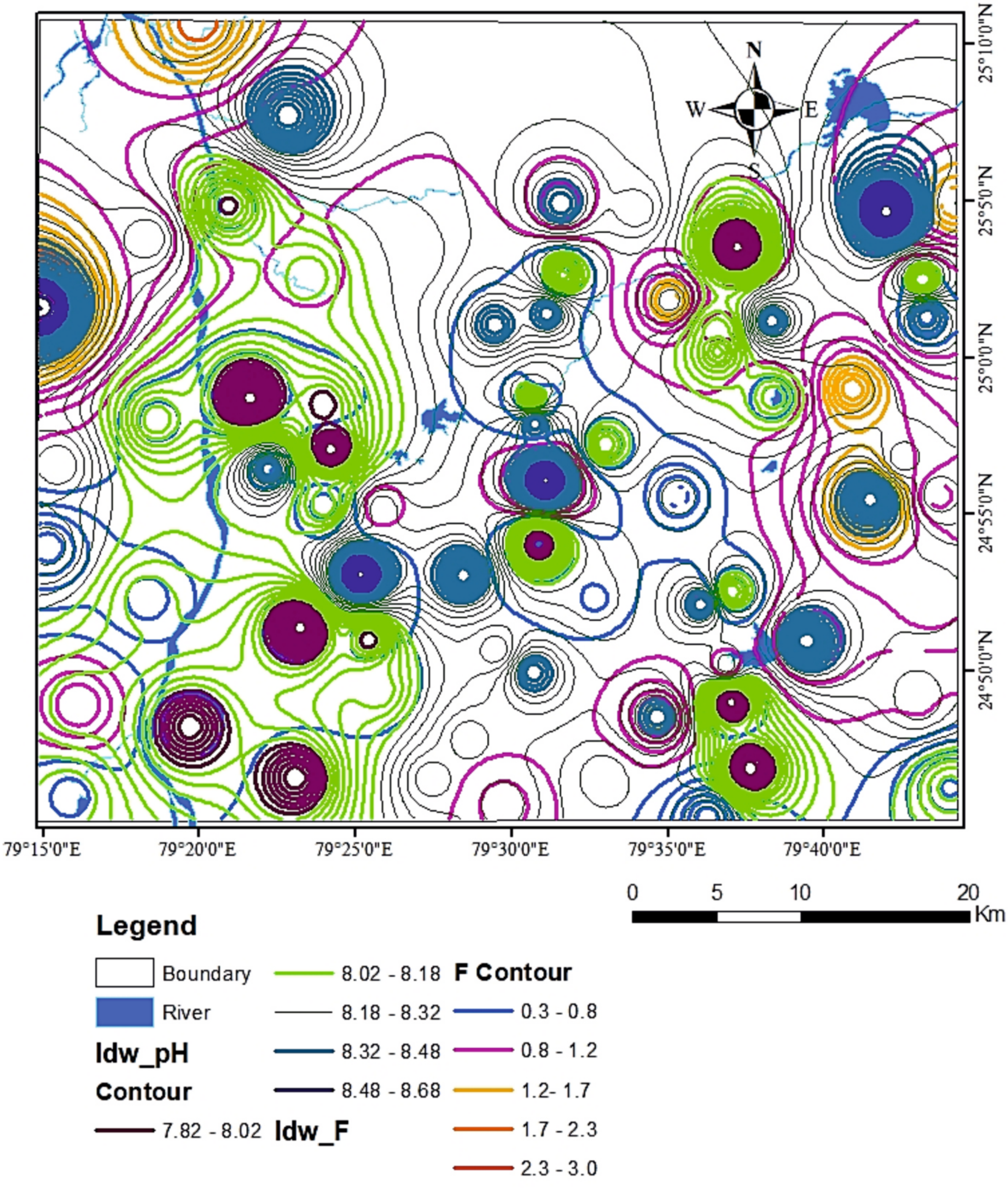
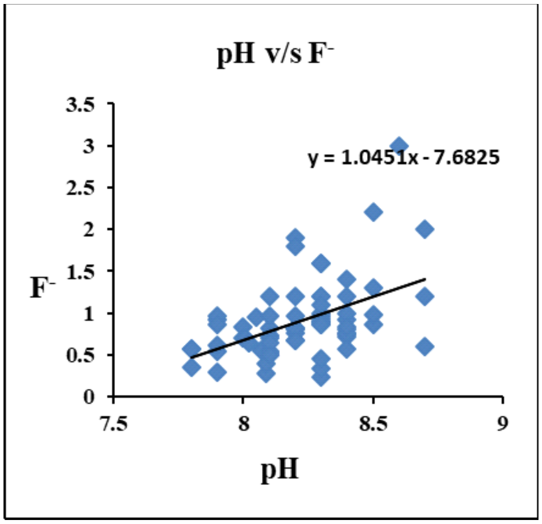
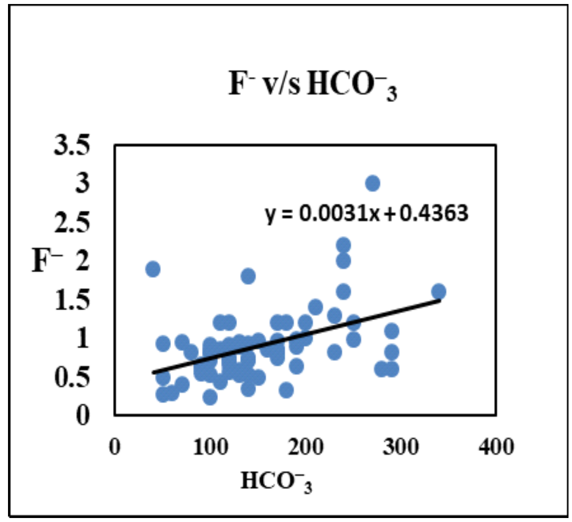


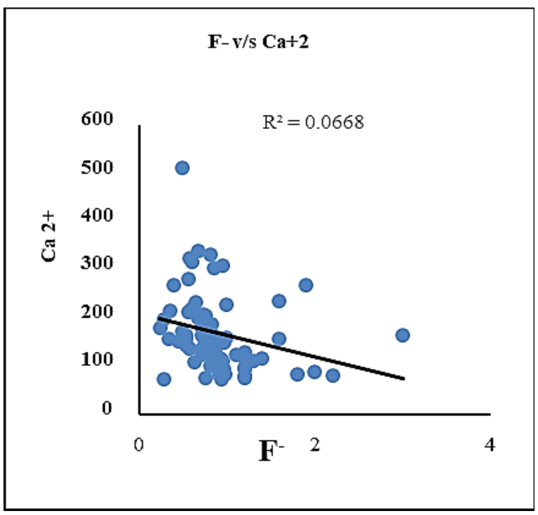
Figure 5: Correlation Spatial distribution of F^{-} with respect to pH



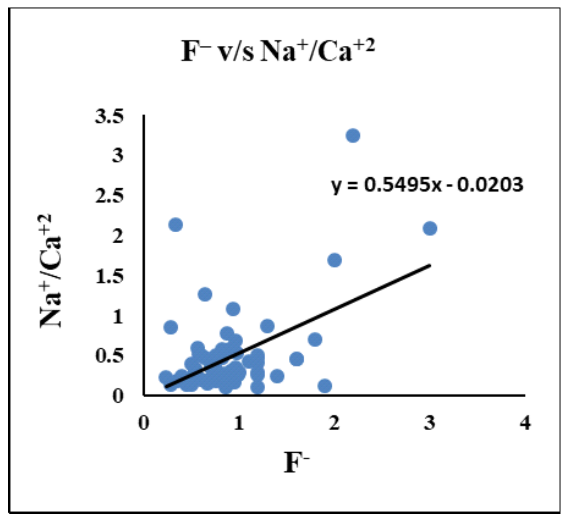
(a)



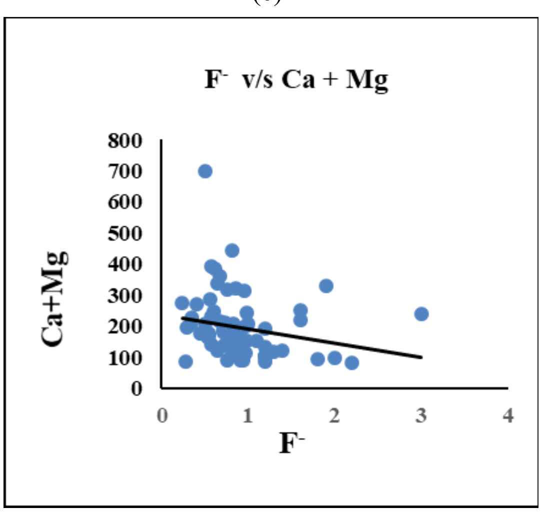
(b)



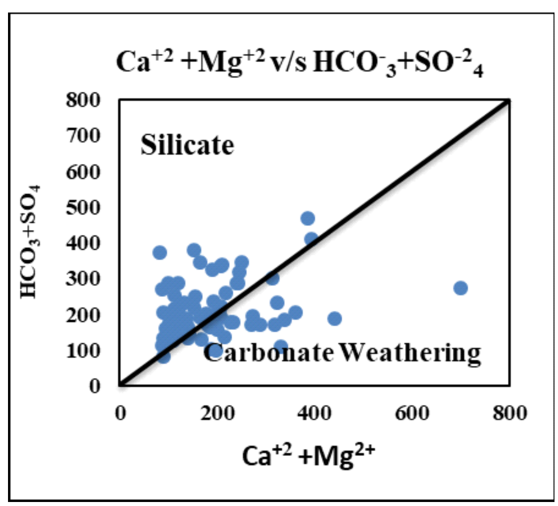
(c)



(d)



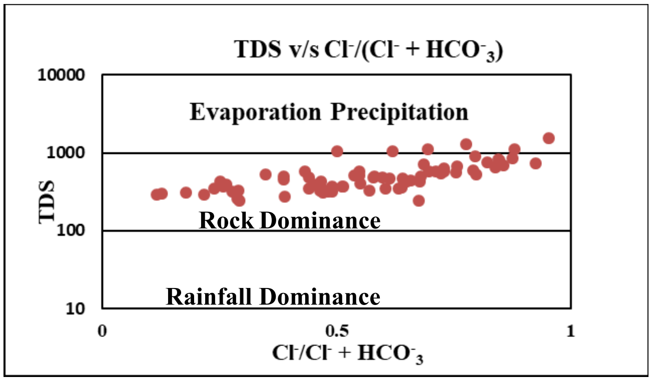
(e)



(f)

Figure 6: Correlation scatter plots of physicochemical data of groundwater samples of pre-monsoon period (a- f).

High F^- contents are prognostically related with 'moderate to high' pH, $HCO3^-$ (Fig. a and b) and antagonistically with Ca_{+2} (c). It signifies 'dissolution of minerals' due to prolonged 'rock weathering' under 'alkaline medium' and precipitation of $CaCO_3$ within solution causing liberation of F^- ions into the groundwater. Scatter plot of Na^+/Ca^{+2} ratio and F^- (Fig. c and d) reveals that depletion of Ca^{+2} ions occurs due to rapid increase in Na^+ and F^- ions in groundwater. It affirms that release of F^- ions *vis-à-vis* precipitation of $CaCO_3$, into the groundwater, under high-alkaline regime (pH 8.7 or above). Scatter plot of $Ca^{2+} + Mg^{2+}$ v/s $HCO_3^- + SO_4^-$ (Fig. e), shows that 90% of groundwater samples are clustered above the equiline (1:1) that signifies the progressive enrichment of Na^+, K^+, HCO_3^- ions due to weathering and dissolution of alkali silicates and fluoride minerals in alkaline medium.



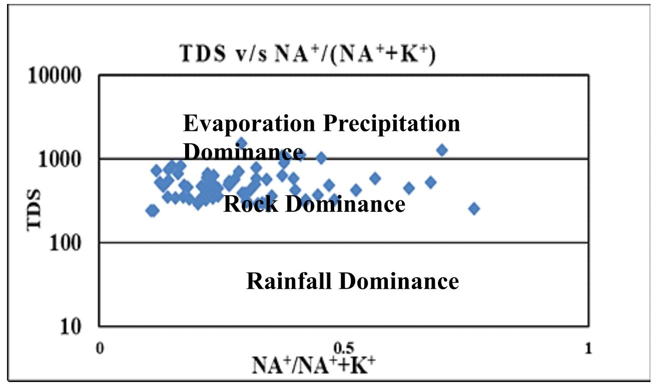


Figure 7: Gibbs plot representing the ratio of Na^+/Na^++Ca^{+2} and $Cl^-/Cl^-+HCO_3^-$

Gibbs (1970) recommended a diagram for evaluating the effects of rock weathering, precipitation and evaporation on water chemistry by simple plot of TDS against molar ratio of Na^+/Na^++Ca^{+2} and $Cl^-/Cl^-+HCO_3^-$. Gibbs plot of our samples (Fig. 7a and b) shows that the majority (>90%) of the groundwater samples lies in the 'rock dominance weathering regime' and the rest fall in the 'precipitation–crystallization dominance regime'. It explicitly signifies that the groundwater chemistry is controlled by rock types occurring in the 'weathered zones' as 'rock-water interaction' dominates over other processes in semi-humid region.

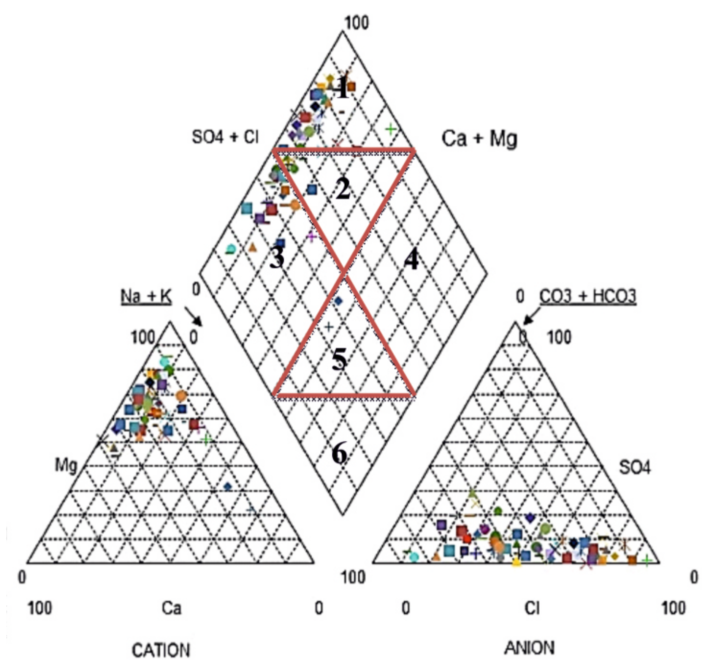


Figure 8: Piper-plot showing hydro-geochemical facies and character of groundwater

Most of the samples fall in the 'Class 1' and 'Class 3' (Ca-Mg-SO_4 and Ca-Mg-HCO_3) and rest in the 'Class 2' (Ca-Mg-Cl, mixed type) and 'Class 5' (Na-HCO_3-Cl, mixed) categories of waters (Fig.8).

Figure 9 (a)   Figure 9 (b)

Figure 9: Dental fluorosis recorded in juveniles (~12 years) at Gopalpura (Fig. a) and Palera (Fig. b)**.**

Conclusion

In absence of major industries in the area, F^- pollution/ contamination in groundwater may be attributed to geohydrochemical reasons. The Scatter Plot (Fig. 4) attest that the pollution/contamination, which is geogenic in nature, is primarily due to long 'rock-water interaction' accompanied with 'cationic exchange' phenomena. F^- increases where Ca^{+2} is low and Na^+ may be due to the presence of potash-feldspars in granites/granitoids as due to precipitation of calcium, soil becomes alkaline with high content of sodium. Evaporation plays an important role in enhancing F^-content in pre-monsoon periods. Increase in alkalinity cause more dissolution due to a long 'soil and rain water interaction'. High F^- occurs in alkaline environment as it favors replacement of exchangeable F^- from minerals by hydroxyl-ions of groundwater. Dental fluorosis is prevalent in Hatna, Dharampura, Bedar, Palera, Harrai, Gopalpura, Barduwaha and Rampura localities of Chhatarpur District.

Acknowledgement

Anjali Renuka Dahanga thanks to the Ministry of Tribal Affairs, Govt. of India, New Delhi for financial support, for the analysis of groundwater samples, the National Environmental and Engineering Institute (NEERI), Nagpur for allowing to analyze all the samples, Dr. Jemini Khatik for her helpful reviews and support for improvement of the manuscript and the Head, Department of Applied Geology for providing basic infrastructure facilities.

References

1. Auden, J. B., (1933) Vindhayans of Son valley. *Mem. Geol. Sur. Ind*, XII, pt. II**.**
2. Avtar, Ram., Kumar, P., Singh, K., Sahu, N., Verma R.L., Thakur, J.K., Mukherjee, S. (2013). Hydrochemical assessment of groundwater quality of Bundelkhand, India using statistical approach. In: Water Qual. Expo Health, 5: 105-115.
3. American Public Health Association (APHA, 2005). Standard methods for examination of water and wastewater (21st ed., Am. Water Works Assoc. Water Environ. Fed.).
4. BIS (2015). Drinking water specification, IS; 105000, Bureau of Indian Standards.
5. Bardsen, A., K, Bgorraton., Selving, K.A. (1996). Variability in fluoride content of subsurface water reservoirs. *Acta Odontol. Scand*., 54, pp. 343-347
6. Gibbs, R. J. (1970). Mechanism controlling world water chemistry. *Science* 170: 1088-1090.
7. Hem, J. D. (1985). Study and Interpretation of the chemical characteristic of natural water, Depp. Interior US Geol. Sur., 2254.
8. Khatik, J.*,* Kathal, P.K., Trivedi, R.K. (2012). Fluoride contamination in groundwater in a part of tribal belt Chhindwara District, Madhya Pradesh, *Ind. Bhujal News*., 27(1-4):42-60.
9. Piper, A. M. (1944). A graphic procedure in the geochemical interpretation of water analyses, *Eos*. *Trans. Am. Geophy. Union,* 25 (6), 914-928.
10. Report CGWB (2018). Groundwater quality in shallow aquifers in India. Central Groundwater Board.
11. Report UNICEF (1999). State of the art report on the extent of fluoride in drinking water and the resulting endemicity in India. Fluorosis Res. Rural Dev. Found., UNICEF.
12. WHO (2017). Guidelines of drinking water quality, 4th Edn., Incorporating the first and second addenda, vol. 1 recommendation. World Health Organization (WHO).
13. Wenzel, W. W. and Blum, W. E. H. (1992). Fluoride speciation and mobility in fluoride contaminated soils and minerals. *Soil Science*, 153, 357-364.