[Now published in full after initial publication as an Epub ahead of print on Sept 13, 2020 at www.fluorideresearch.online/epub/files/099.pdf]

GROUNDWATER QUALITY WITH SPECIAL REFERENCE TO FLUORIDE IN UNNAO DISTRICT, UTTAR PRADESH, INDIA: A HYDRO-GEOCHEMICAL AND MULTIVARIATE STATISTICAL APPROACH

SK Jha,[a,*] YK Sharma,[b] AK Nayak,[c] VK Mishra,[a] T Damodaran[a]

Lucknow, India

ABSTRACT: An assessment of groundwater quality with special reference to fluoride (F) contamination was carried out systematically on extensive basis using hydro-geochemical and multivariate statistical approach to delineate the factors governing the chemistry of groundwaters in Unnao district of Uttar Pradesh (India). The water samples (n=84) were collected randomly at a random intersection of 2.6 km $\times$ 2.6 km of a square grid from both shallow (n=42) and deep (n=42) hand-pumps from the study area. The results revealed higher concentration of F in shallow hand-pumps which ranged between 0.19 to 4.33 mg L^{-1}. The F level in the shallow hand-pumps exceeded the desirable limit of 1.0 mg L^{-1} in 28.57% of sampled water whereas it was only 7.14% in case of deep hand-pumps. The hydro-geochemical analysis revealed that, besides pH, weathering of silicates, carbonates, and ion exchange processes were responsible for the geochemistry of the groundwater. The F had a significant positive correlation with pH (r=+0.63, p<0.05) in shallow hand-pumps. The water type of majority of the samples of groundwater was found to be Na-HCO_3 type. The spatial distribution of F concentration in deep hand-pumps was determined by geo-statistical method using semi-variogram analysis and F map was generated by using Kriging. The inverse distance weighting method was applied for mapping of F in shallow hand-pumps, where no valid semi-variogram was obtained. The present study may be helpful for public health departments for carrying out epidemiological surveillance to reduce the F exposure risk in the delineated areas.

Keywords: Assessment; Geochemical; Groundwater; Kriging; Multivariate; Spatial.

INTRODUCTION

Fluoride (F) contamination in the groundwater is a worldwide health problem.[1] In India, out of 36 states and union territories, 23 including Andhra Pradesh, Arunachal Pradesh, Assam, Bihar, Chhattisgarh, Delhi, Gujarat, Haryana, Jammu and Kashmir, Jharkhand, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Manipur, Odisha (Orissa), Punjab, Rajasthan, Tamil Nadu, Telangana, Uttar Pradesh, Uttarakhand, and West Bengal, have F beyond the maximum permissible limit of 1.0 or 1.5 ppm in drinking groundwater due to presence of heavy deposition of F bearing minerals in the earth crust.[2,3] Prolonged exposure of such fluoridated water causes diverse health problems (fluorosis) in both humans[4-6] and domestic animals.[7-10]

In the state of Uttar Pradesh, F content with varying amount in the groundwater of Indo-Gangetic plains has been reported.[11-13] Although, in different regions of Unnao district of this state a high content of F in groundwater has also been reported,[14-16] no systematic attempts have been made so far for characterization and mapping of F in the district or identification of the factors responsible for high F occurrence in the groundwater. Therefore, the present study was aimed to interpret groundwater quality of both shallow and deep hand-pumps in Nawabganj block of Unnao district of Uttar

[a]ICAR-Central Soil Salinity Research Institute, Regional Research Station, Lucknow-226002, India; [b]Environmental Science Division, Department of Botany, University of Lucknow, Lucknow-226007, India; [c]ICAR-National Rice Research Institute, Cuttack-753006, India. *For correspondence: Dr SK Jha, Principal Scientist, ICAR-Central Soil Salinity Research Institute, Regional Research Station, Lucknow-226002, India; E-mail: jhask_01@yahoo.com

Pradesh, India, with special reference to F using both hydro-geochemical and multivariate analysis techniques and to determine the spatial distribution of F using geo-statistical method.

MATERIALS AND METHODS

The study area lies between 26º 32’ 33” N to 26º 41’ 42” N latitude and 80º 30’ 04” E to 80º 48’18” E longitude in the Central Indo-Gangetic plains of Unnao district, Uttar Pradesh, India which is a part of Ganga-Gomti drainage basin (Figure 1).

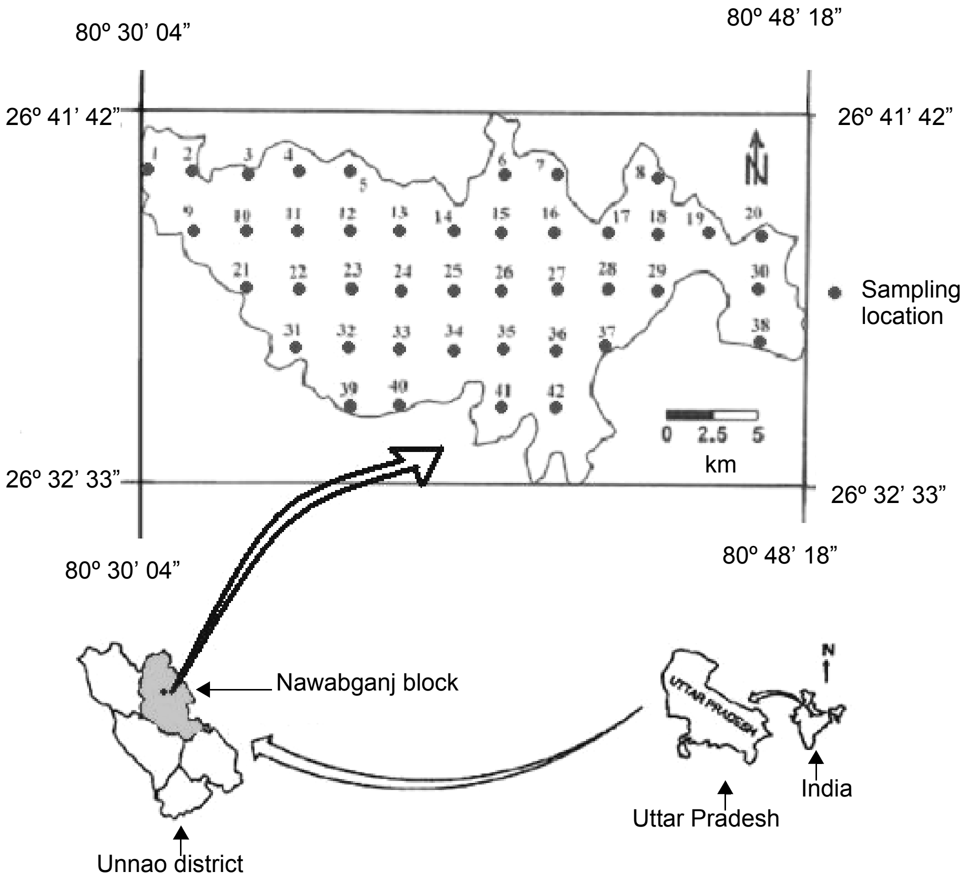


Figure 1. Map of study area showing location of sampling points.

Geologically, the area consists of quaternary sediments differentiated into older alluvium of middle to late Pleistocene age.[17] The water samples were collected from the study area in fresh and clean 500 mL polypropylene bottles separately at a random intersection of 2.6 km × 2.6 km of a square grid from both privately owned shallow hand-pumps (25–35 feet) and India MK-II deep hand-pumps (>150 feet) installed by Uttar Pradesh Jal Nigam, Government of Uttar Pradesh. The analysis of F and other water quality parameters were carried out as per APHA methods.[18] The hydro-geochemical characterization of groundwater was carried out using trilinear Piper diagram and 1:1 equiline scatter plots. The chemical data generated was subjected to principal component analysis (PCA).[19] The spatial distribution of F in shallow and deep hand-pumps was determined by geo-statistical method using semi-

[Now published in full after initial publication as an Epub ahead of print on Sept 13, 2020 at www.fluorideresearch.online/epub/files/099.pdf]

variogram analysis and Kriging.[20] Where no valid variogram could be drawn, the mapping was done using inverse distance weighting (IDW) method.[21]

RESULTS

The data showed that the pH value of shallow hand-pumps ranged from 7.39 to 8.97 with a mean of 7.96 (SD=0.38) whereas for deep hand-pumps it varied from 7.54 to 8.57 with a mean of 8.09 (Tables 1A and 1B). The dominance order of cations in the shallow and deep hand-pumps was Na>Mg>Ca>K while anions followed dominance as HCO_3>SO_4>Cl>CO_3 in shallow and HCO_3>Cl>CO_3>SO_4 in deep hand-pumps. The F concentration in the shallow hand-pumps was found higher (0.19 to 4.33 mg/ L) than the deep hand-pumps (0.21 to 1.48 mg/L) where 28.57% of the sampled water in shallow hand-pumps and 7.14% in deep hand-pumps were found to be contaminated with F exceeding the desirable limit of 1.0 mg/L.[3] The hydro-chemical analysis using trilinear piper diagram showed Na-HCO_3 type waters for both shallow and deep hand-pumps.

Table 1A. Classical statistics of water quality parameters of shallow hand-pumps in the study area (SAR= Sodium adsorption ratio)

Statistic	Parameter					
	pH	EC (dS/m)	F (mg/L)	CO_3 (mg/L)	HCO_3 (mg/L)	Cl (mg/L)
Mean	7.96	1.09	0.94	1.35	4.51	2.61
Median	7.91	1.00	0.63	1.10	4.30	1.75
SD	0.38	0.55	0.81	0.91	1.34	3.26
Minimum	7.39	0.38	0.19	0.00	2.10	0.30
Maximum	8.97	2.84	4.33	4.60	7.90	16.20
Lower quartile	7.65	0.75	0.51	0.80	3.80	1.10
Upper quartile	8.21	1.26	1.03	1.60	5.00	2.60
	SO_4 (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SAR
Mean	2.70	1.81	3.93	5.09	0.47	3.16
Median	2.00	1.40	3.35	5.20	0.20	2.85
SD	2.84	1.24	2.53	2.90	0.80	1.78
Minimum	0.10	0.60	1.20	0.80	0.10	0.61
Maximum	13.80	6.20	12.60	12.80	3.80	8.80
Lower quartile	0.60	0.90	2.50	3.10	0.14	1.79
Upper quartile	3.70	2.00	4.00	6.60	0.26	4.35

Table 1B. Classical statistics of water quality parameters of deep hand-pumps in the study area (SAR= Sodium adsorption ratio)

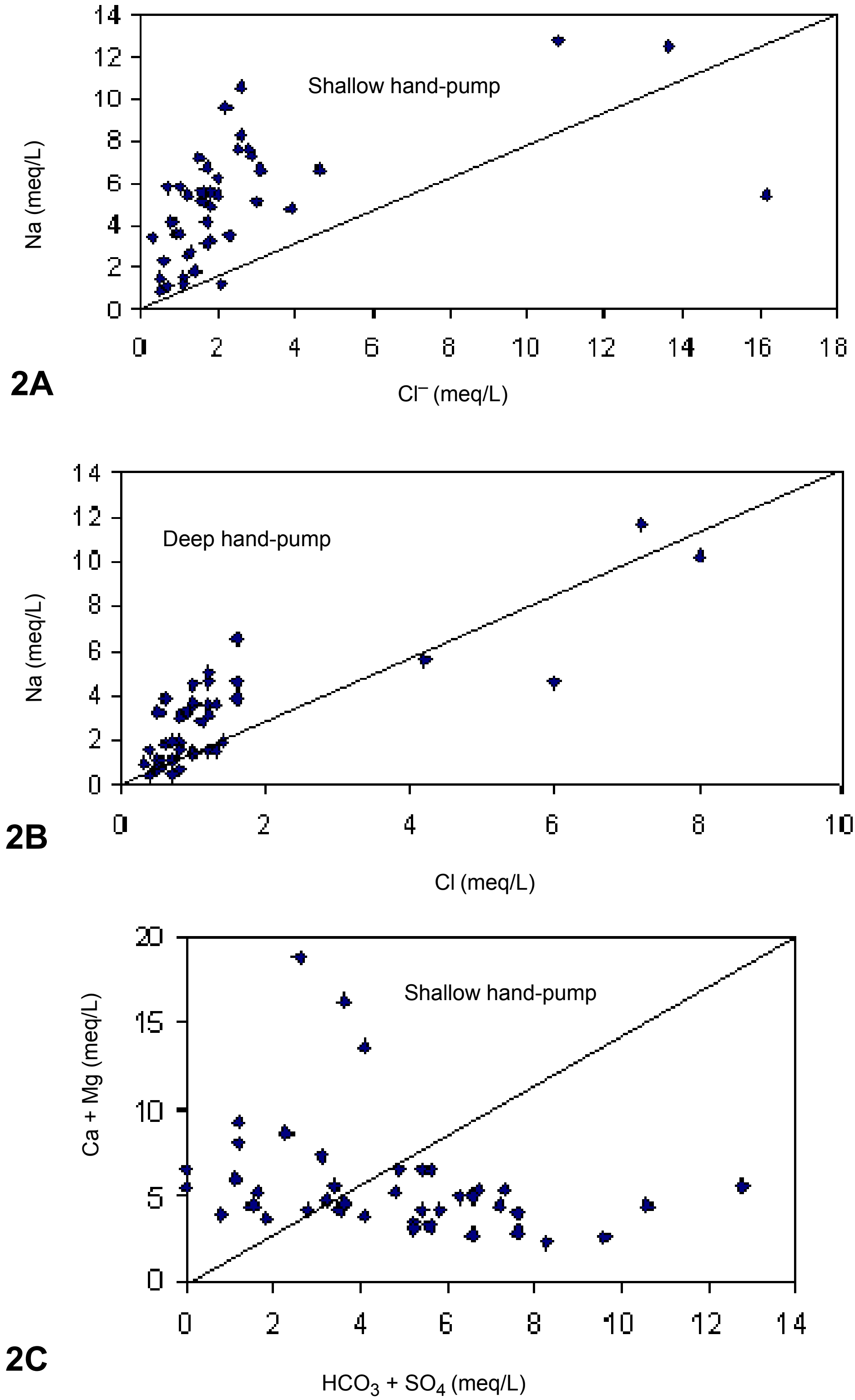
Statistic	Parameter					
	pH	EC (dS/m)	F (mg/L)	CO_3 (mg/L)	HCO_3 (mg/L)	Cl (mg/L)
Mean	8.09	0.75	0.58	1.22	3.99	1.43
Median	8.12	0.65	0.52	1.20	3.70	1.00
SD	0.27	0.37	0.29	0.62	1.48	1.71
Minimum	7.54	0.34	0.21	0.40	2.20	0.30
Maximum	8.57	2.03	1.48	3.90	9.10	8.00
Lower quartile	7.91	0.52	0.38	0.80	3.10	0.60
Upper quartile	8.31	0.88	0.68	1.50	4.50	1.20
	SO_4 (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SAR
Mean	1.09	1.53	2.91	3.00	0.35	1.92
Median	0.70	1.60	2.65	2.40	0.13	1.50
SD	1.17	0.59	1.11	2.43	0.76	1.55
Minimum	0.10	0.50	1.20	0.40	0.07	0.31
Maximum	4.10	2.80	6.00	11.70	3.50	7.55
Lower quartile	0.15	1.00	2.30	1.40	0.10	0.67
Upper quartile	1.50	1.90	3.50	3.90	0.18	2.82

The geo-chemical variations in the ionic concentration in the groundwater were studied using 1:1 equiline plot. The plot of Na vs Cl showed most of the water samples lying around or above the equiline in both shallow and deep hand-pumps (Figures 2A and 2B).

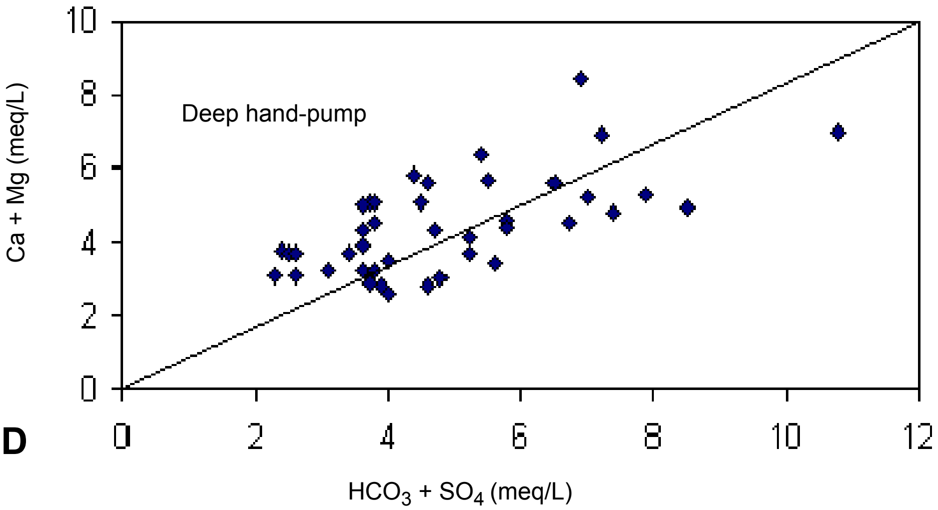
The graph of Ca+Mg vs HCO_3+SO_4 showed the points scattered almost equally between 1:1 equiline, indicating both silicate and carbonate weathering processes (Figures 2C and 2D). The graph also suggested ion exchange and reverse ion exchange processes.

The Ca+Mg vs TC (total cations) plot indicated Ca+Mg enrichment compared to alkali (Na+K) in waters of deep hand-pumps which was also explained by considering Ca+Mg/Na+K ratio (Figures 2E and 2F).

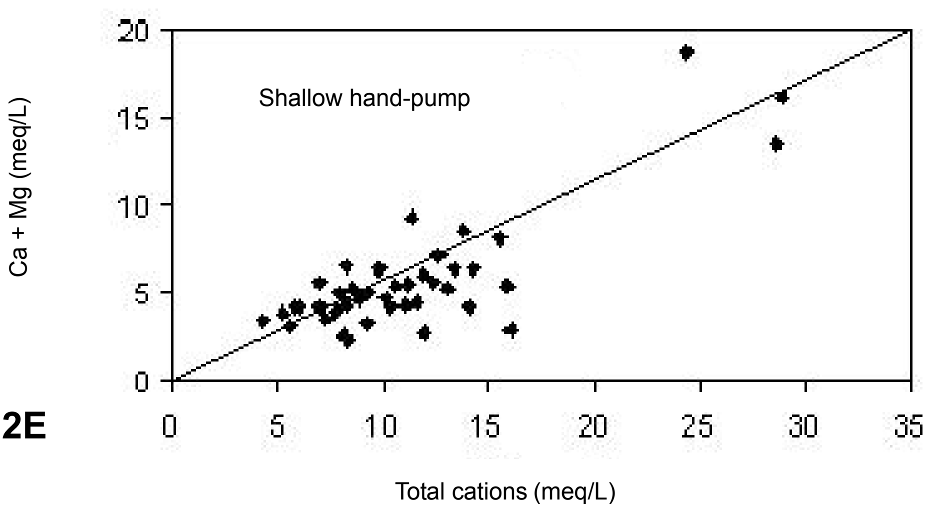
In shallow hand-pumps, Ca+Mg/Na+K was found to be 1.44 while in deep hand-pumps, it was 2.31. The relative contributions of the calcite or dolomite weathering processes were assessed using the Ca/Mg ratio and this suggested the dominance of calcite weathering, as most of the sample points were found to be below 1 (Figure 2G).



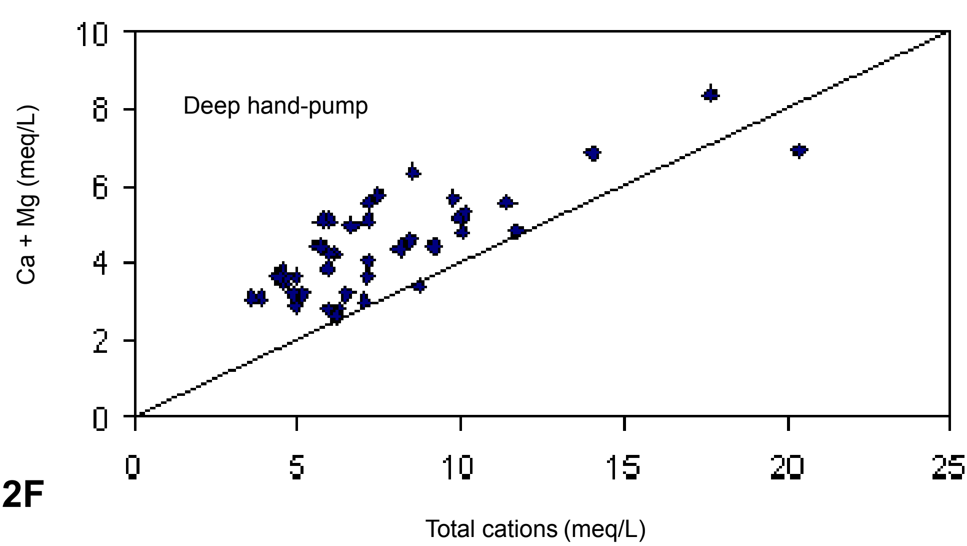
Figures 2A–2C. Scatter diagram for different parameters for the ground waters of shallow and deep hand-pumps depicting the hydro-geochemical processes.



2D

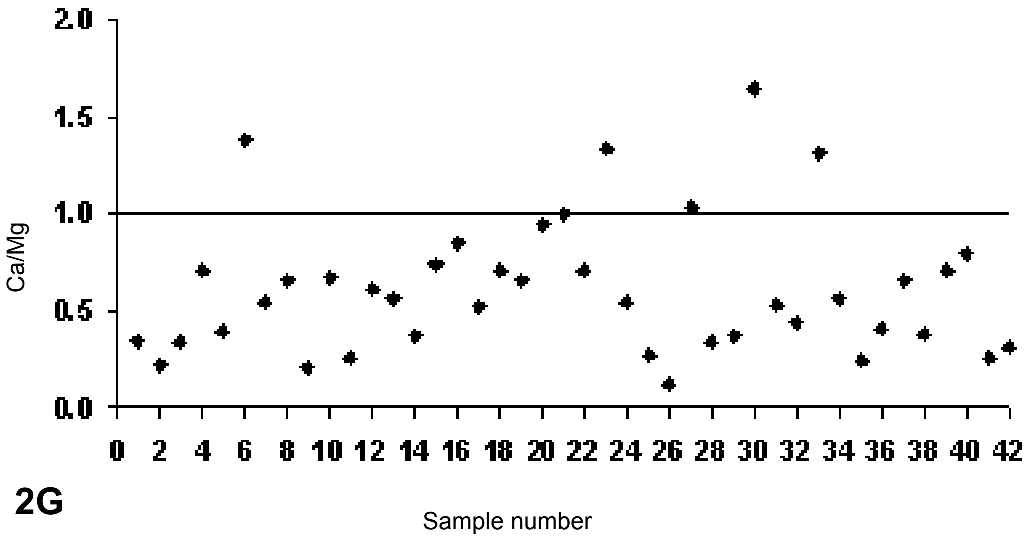


2E



2F

Figures 2D–2F. Scatter diagram for different parameters for the ground waters of shallow and deep hand-pumps depicting the hydro-geochemical processes.



2G

Figure 2G. Scatter diagram for different parameters for the ground waters of shallow and deep hand-pumps depicting the hydro-geochemical processes.

The Pearson's coefficient correlation analysis indicated that F had a significant positive correlation with pH (r=+0.63, p<0.05) and sodium adsorption ratio (SAR) (r = 0.41, p<0.05) in shallow hand-pumps and negatively correlated with Ca in both the sources of water. In the PCA analysis, only factors with eigen values greater than 1 were considered (Table 2). It revealed that factors 1, 2, and 3 accounted for 35.62%, 25.79%, and 13.15%, of the total variance, respectively, in the data pertaining to shallow hand-pumps. On the other hand, factors 1, 2, and 3 in the deep hand-pumps accounted for 46.13%, 18.39%, and 10.39% of total variance, respectively.

In shallow hand-pumps, the variogram analysis could not display an increase of semi-variance with increasing distance. Thus mapping of F in shallow hand-pumps was carried out by IDW interpolations technique. In the deep hand-pumps, a valid variogram was obtained that followed a linear model with slope, nugget, and R^2 as 0.065, 0.18, and 0.85, respectively. With the help of semi-variogram, geo-statistical interpolations by point Kriging were carried out for F concentrations in deep hand-pumps. The cross-validation result with respect to the mean absolute difference between the Kriged estimate and the measured value was found to be 0.010 (Table 3).

The high F concentration (F>1.5 mg/L) loops (Figure 3A) in the shallow hand-pumps was found to be scattered mostly towards north to south-west direction in the Nawabganj area. The interpolated map of F (Figure 3B) for deep hand-pumps was prepared using the Kriged values which indicated an apparent regional spatial variation pattern of F with distinct loops.

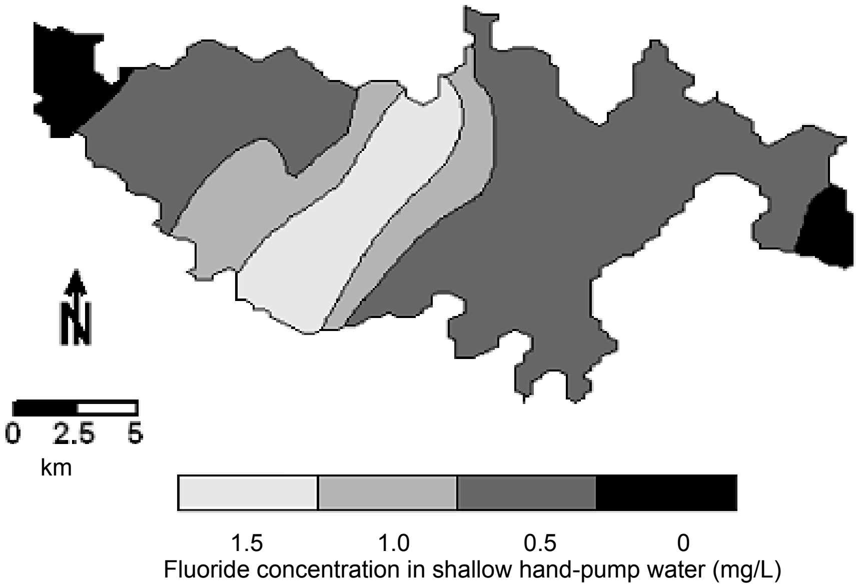
[Now published in full after initial publication as an Epub ahead of print on Sept 13, 2020 at www.fluorideresearch.online/epub/files/099.pdf]

Table 2. Eigen values and factor loadings in shallow hand-pumps and deep hand-pumps in the study area: Extraction method: Principal component analysis. Rotation method: varimax with Kaiser normalization (SAR= Sodium adsorption ratio)

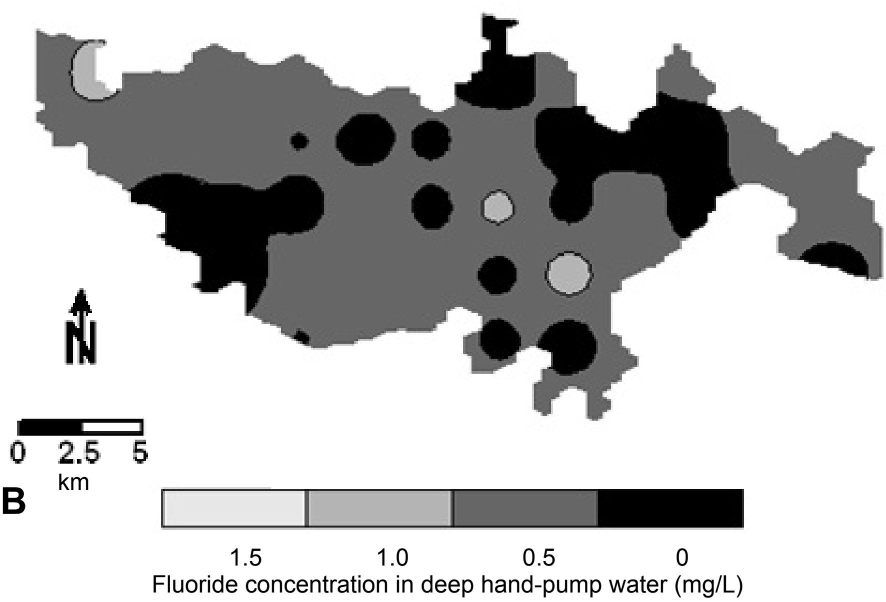
Variable	Rotated component matrix					
	Shallow hand-pumps			Deep hand-pumps		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
pH	–0.423	0.556	0.140	0.346	0.716	0.120
EC (dS/m)	0.840	0.079	0.532	0.904	0.176	0.175
F (mg/L)	–0.394	0.601	0.336	–0.077	0.880	–0.127
CO_3 (mEq/L)	0.017	0.799	–0.102	0.062	0.738	0.339
HCO_3 mEq/L)	0.058	0.647	0.221	0.682	0.424	0.242
Cl (mEq/L)	0.877	–0.034	0.278	0.894	–0.036	0.283
SO_4 (mEq/L)	0.600	–0.362	0.646	0.653	–0.288	–0.305
Ca (mEq/L)	0.836	0.232	–0.294	0.117	–0.067	0.732
Mg (mEq/L)	0.880	–0.215	0.186	0.277	0.170	0.108
Na (mEq/L)	0.395	0.106	0.882	0.948	0.224	–0.092
K (mEq/L)	0.139	0.593	0.486	0.849	–0.010	0.418
SAR	–0.086	0.219	0.925	0.918	0.216	–0.226
Eigen values	4.631	3.354	1.709	5.997	2.391	1.350
Variance (%)	35.621	25.797	13.146	46.133	18.395	10.388
Cumulative variance (%)	35.621	61.418	74.564	46.133	64.528	74.916

Table 3. Comparison of statistical parameters for the measured and Kriged values of fluoride in deep-hand pumps in the study area

Type of water source	Parameter	Measured value	Estimated value from point Kriging	Residual obtained from cross validation
Deep hand-pumps	Mean	0.937	0.948	0.010
	SD	0.805	0.537	0.888
	Variance	0.648	0.288	0.789



3A



3B

Figures 3A and 3B. Fluoride concentration (mg/L) map of the groundwater from hand pumps in the study area. 3A: water from shallow hand-pumps; (3B) water from deep hand-pumps.

DISCUSSION

The presence of higher F content in the water of shallow hand-pumps may be due to the presence of hard pan of $CaCO_3$ concretions at a shallower depth which acts as a potential source of F contamination[22] because during its formation, F gets embedded into it. During weathering of parent rocks, F/OH exchange-adsorption reactions also occur in the clay minerals[23] which could be responsible for higher concentration of F in the shallow aquifer water. The water type in the study area was Na-HCO_3 type which increases the solubility of CaF_2, [24,25]and thereby releases F into the groundwater as shown in Equation 1:

$$CaF_2 + 2NaHCO_3 = CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2 \text{ .... Equation 1}$$

In the geochemical evaluation of the ionic constituents, the source of Na excess in Na vs Cl 1:1 equiline was attributed to silicate weathering. Such findings have also been observed in the previous studies.[26,27] The points which are placed towards the Ca+Mg of 1:1 equiline plot of Ca+Mg vs HCO_3+SO_4 indicated dominance of carbonate weathering while those placed below 1:1 equiline are indicative of silicate weathering.[26,28] The plot for Ca+Mg versus HCO_3+SO_4 is also a major indicator to identify ion exchange process activated in the area. If ion exchange is the process, the points shift to right side of the plot due to HCO_3+SO_4 excess [29] whereas in reverse ion exchange, points shift left due to Ca+Mg in excess.[30] The ratio Ca+Mg/Na+K has also been used as an index to understand carbonate and silicate weathering.[31] The higher ratio signifies carbonate weathering. The dominance of calcite weathering was confirmed by Ca/Mg ratio being less than 1. This result also corroborates the earlier finding.[32]

The positive correlation between F and pH suggests that the pH is an important determining factor for F in the groundwater.[33] The alkaline pH favors the F dissolution activities.[34] The positive correlation of F with pH and SAR (sodium adsorption ratio) was also reported.[35] The contribution of a factor in PCA analysis is said to be significant when the corresponding eigen values is greater than unity.[36] The positive high loading on EC and Mg compared to Ca may be due to the fact that salinity is mainly caused by the salts of Mg.[37] In the present study area, the pedogenic calcite and dolomite were found at shallower depth[17] (upper 2 m of the horizon) and were the source of Ca and Mg. The association of high F concentrations with high EC or TDS, pH, Na, and SAR has also been reported earlier.[38] The strong loading on Na and K indicated natural weathering of rock minerals and various ion exchange processes in the groundwater system which agrees with the earlier findings.[39] The percentage abundance of these variables indicated that their sources of origin may be expected from silicate weathering. The silicate weathering processes releases Na and K ions to the groundwater.[26] The source of K may be mineral ‘illite’ which is prevalent in the area [15] and is a source of F. The high loadings on K might be due to weathering of illitic minerals in the present study area.[40] Such weathering reactions result in the release of bicarbonate ions and are responsible for the alkalinity of groundwater as shown in Equation 2:

$$2KAlSi_3O_8 + 2CO_2 + 11H_2O = Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2K^+ + 2HCO_3^- \text{...... Equation 2}$$

Such findings have also been reported from a large coal mine of Anhui China.[41] The deep hand-pumps showed no loops of F>1.5 mg/L, i.e., the F in waters of the deep hand-pumps was within the desirable or maximum permissible limit.[3] The findings of the present study may be helpful for public health departments for carrying out epidemiological surveillance to reduce the F exposure risk in the delineated areas.

CONCLUSIONS

As there were no major anthropogenic sources of F contamination in the groundwater of studied area, the occurrence of high F was attributed to natural or geogenic sources. The results of present study showed that combining factor analysis and water chemistry is an effective approach for studying geochemistry of F in the groundwater. The water types of majority of the samples in shallow and deep hand-pumps were found to be Na-HCO_3 type, which helps in increasing the solubility of CaF_2 and thereby releases F into the groundwater. The correlation studies indicated a significant positive correlation between F and pH whereas a negative correlation existed between F and Ca in both the sources of water. The natural weathering of carbonate, silicate minerals, and various ion-exchange processes contributed to the high F occurrence in the groundwater as well as the alkalinity. The study suggests, deep bore wells and hand-pumps should be provided in the area in order to reduce exposure risk from F, as F in waters of deep hand-pumps are within the safe limit.

REFERENCES

1 Adler P, Armstrong WD, Bell ME, Bhussry BR, Büttner W, Cremer H-D, et al. Fluorides and human health. World Health Organization Monograph Series No. 59. Geneva: World Health Organization, 1970.

2 Choubisa SL. A brief and critical review on hydrofluorosis in diverse species of domestic animals in India. Environ Geochem Hlth 2018;40(1):99-114.

3 Choubisa SL. A brief and critical review of endemic hydrofluorosis in Rajasthan, India. Fluoride 2018; 51(1):13-33.

4 Choubisa SL, Choubisa DK, Joshi SC, Choubisa L. Fluorosis in some tribal villages of Dungarpur district of Rajasthan, India. Fluoride 1997;30(4):223-8.

5 Choubisa SL. Endemic fluorosis in southern Rajasthan (India). Fluoride 2001;34(1):61-70.

6 Choubisa SL, Choubisa L, Choubisa DK. Endemic fluorosis in Rajasthan. Indian J Environ Hlth 2001;43(4):177-89.

7 Choubisa SL. Some observations on endemic fluorosis in domestic animals of southern Rajasthan (India). Vet Res Commun 1999;23(7):457-65.

8 Choubisa SL. Osteo-dental fluorosis in horses and donkeys of Rajasthan, India. Fluoride 2010;43(1):5-10.

9 Choubisa SL. Fluorosis in dromedary camels of Rajasthan, India. Fluoride 2010;43(3): 194-9.

10 Choubisa SL. Fluoride toxicosis in immature herbivorous domestic animals living in low fluoride water endemic areas of Rajasthan, India: an observational survey. Fluoride 2013;46(1):19-24.

11 Ray SK, Ghosh S, Tiwari IC, Kaur P, Reddy DCS, Nagchaudhuri J. Dental fluorosis in Ledhupur and Rustampur villages near Varanasi. Ind J Med Res 1993;77:112-8.

12 Chadha DK, Tamta SR. Occurrence and origin of groundwater fluoride in phreatic zone of Unnao district, Uttar Pradesh. J App Geochem 1999;1:21-6.

13 Misra AK, Mishra A, Premraj. Escalation of groundwater fluoride in the Ganga alluvial plain of India. Fluoride 2006;39:35-8.

14 Agarwal CS, Choudhary NK. Fluoride pollution in ground water and related ill effects with geomorphological mapping using IRS data in parts of Unnao district Uttar Pradesh. GSI Spl Pub 2001;65(II):187-9.

15 Kumar S, Rai D, Rai PK, Shukla AB, Saxena A. To study the causes of fluoridated water problem in Unnao district and its feasible measure to solve the problem. In: Tiwari VK, Pande RN, editors. Uttar Pradesh sodic land reclamation research, achievements. Lucknow, Uttar

Pradesh, India: Division of Natural Resource Management and Engineering, Utttar Pradesh Council of Agricultural Research (UPCAR); 2007. pp. 90-3.

16 Jha SK, Nayak AK, Sharma YK. Fluoride occurrence and assessment of exposure dose of fluoride in shallow aquifers of Makur, Unnao district Uttar Pradesh, India. Environ Monit Assess 2009:156:561-6.

17 GSI. District Resource Map, Unnao, Uttar Pradesh. Geological Survey of India, Northern Region; 2001.

18 APHA. DC, USA: American Public Health Association, American Water Works Association, Water Environment Federation; 2005.

19 Guler C, Thyne GD, McCray JE, Turner AK. Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. Hydrogeol J 2002;10:455-74.

20 Burgress TM, Webster R. Optimal interpolation and isarithmetic mapping of soil properties, The semi variogram and punctual krigging. J Soil Sci 1980;(31):315-31.

21 Fisher NS, Lewis T, Embleton BJJ. Statistical analysis of spherical data. Cambridge: Cambridge University Press;1987. pp 329.

22 Jha SK, Nayak AK, Sharma YK. Potential fluoride contamination in the drinking water of Marks Nagar, Unnao district, Uttar Pradesh, India. Environ Geochem Health 2010; 32:217-26**.**

23 Hubner M. Geochemische interpretation non fluoride/hydroxide Austauscheversuchen and Tonmineralen. Ber Dentsch. Geo. Geol. Wise. B. Miner. Lagerstatten-Forsch 1969;14:5. [in German].

24 Handa BK. Geochemistry and genesis of fluoride containing ground waters in India. Ground Water 1975;13(3):275-81.

25 Saxena VK, Ahmed S. Dissolution of fluoride in groundwater: a water reaction study. Environ Geol 2001;40:1084-7.

26 Stallard RF, Edmond JM. Geochemistry of Amazon River: the influence of the geology and weathering environment on the dissolved load. J Geophy Res 1983;88:9671-88.

27 Kumar M, Ramanathan AL, Rao MS, Kumar B. Identification and evaluation of hydro-geochemical process in the ground water environment of Delhi, India. Environ Geol 2006;50(7):1025-39.

28 Datta PS, Bhattacharya SK, Tyagi SK. ^{18}O studies on recharge of phreatic aquifers and ground water flow paths of mixing in Delhi area. J Hydrol 1996;76**:**26-36.

29 Cerling TE, Pederson BL, Damm KLV. Sodium calcium ion-exchange in weathering of shale; implication for global weathering. Budget 1989;17:552-54.

30 Srinivasamoorthy K, Chidambaram S, Prasanna MV, Vasanthavihar M, Peter J, Anandhan P. Identification of major sources controlling ground water chemistry from a hard terrain – A case study from Mettur, Salem district, TamilNadu, India. J Earth Sys Sci 2008;117(1):49-58.

31 Sarin MM, Krishnaswami S. Major ion chemistry of the Ganga–Brahmaputra river systems, India. Nature 1984;312:538–41.

32 Kumar M, Kumari K, Singh UK, Ramanathan AL. Hydro-geochemical processes in groundwater environment of Muktsar, Punjab: Conventional graphical and multivariate statistical approach. Environ Geol 2009;57:873-84.

33 Gupta S, Banerjee S, Saha R, Datta JK, Mondal N. Fluoride geochemistry of ground water in Nalhati-1 block of Birbhum district, West Bengal, India. Fluoride 2006;39(4):318-20.

34 Saxena VK, Ahmed S. Inferring the chemical parameters for the dissolution of fluoride in ground water. Environ Geol 2003;43:731-6.

[Now published in full after initial publication as an Epub ahead of print on Sept 13, 2020 at www.fluorideresearch.online/epub/files/099.pdf]

35 Nayak AK, Chinchmalatpure AR, Rao GG, Jha SK, Khandelwal MK. An assessment of fluoride in the coastal aquifer of the Bara tract in Bharuch district, Gujarat (India). Environ Monit Assess 2008;158:315-17.

36 Briz-Kishore BH, Murali G. Factor analysis for revealing hydro-geochemical characteristics of watersheds. Environ Geol 1992;19:3-9.

37 Mor S, Singh S, Yadav P, Rani V, Rani P, Sheoran M, et al. Appraisal of salinity and fluoride in a semi-arid region of India using statistical and multivariate techniques. Environ Geochem Hlth 2008;31(6):643-55.

38 Rafique T, Naseem S, Usmani TH, Bashir E, Khan FA, Bhanger M I. Geochemical factors controlling the occurrence of high fluoride groundwater in the Nagar Parkar area, Sindh, Pakistan.J Hazard Mat 2009;171(1-3):424-30.

39 Drever IJ. The geochemistry of natural water: surface and groundwater environments. 3rd ed. New Jersey, USA: Prentice Hall; 1997. pp. 436.

40 Smolders AJP, Hudson-Edwards KA, Van der Velde G, Roelofs JGM. Controls on water chemistry of the Pilcomayo river (Bolivia, South-America). App Geochem 2004;19:1745-58.

41 Qian J, Wang L, Ma L, Lu Y, Zhao W, Zhang Y. Multivariate statistical analysis of water chemistry in evaluating groundwater geochemical evolution and aquifer connectivity near a large coal mine, Anhui China. Environ Earth Sci 2016;75:747-56.