Geochemical appraisal of fluoride incidences in groundwater from granitic aquifers, parts of Jhansi and Tikamgarh districts (Bundelkhand region), central India: Lineament controls and human health

N Ranjan
Research Scholar, CAS in Geology, Department of Applied Geology, Dr. Harisingh Gour Central University, Sagar-470 003 (M.P.), India

Email: nranjangeo@rediffmail.com

Abstract. A geochemical investigation based on the analyses of a total of 41 groundwater samples collected during the pre-monsoon and post-monsoon periods from tube/bore-wells points to human health issues due to fluoride levels above and below the tolerance limits specified by the World Health Organization (WHO) and the Bureau of Indian Standards (BIS). The study shows that the fluoride (F) concentration in groundwater in the Bundelkhand granitoid varies from 0.13 to 2.55 mg/l and 0.17 to 2.2 mg/l in pre-monsoon, post-monsoon periods, respectively. The high F values (>1.5 mg/l) were found in 13 samples (pre-monsoon), and 06 samples (post-monsoon) periods collected from shallow aquifers (120-200 ft) are causing dental fluorosis in the area. The hydro-geochemical processes like ion-exchange reactions, depletion of Ca²⁺ under alkaline medium (high pH) have been found as a favorable environment for the liberation of F into groundwater. The weathering of rocks containing fluoride-minerals and evapotranspiration processes govern fluoride enrichment in groundwater. The principal F hosting minerals like apatite, biotite, muscovite, chlorite, sericite, hornblende, and kaolinite were the key geogenic sources of F in the area. The presence of weak/shear zones delineated as lineaments facilitated F- to the groundwater release due to prolonged rock-water interaction. Dental deformities are more ubiquitous in minor and old aged inhabitants than adults.

Keywords: Fluoride contamination, Groundwater, Dental fluorosis, Lineaments, Bundelkhand Granites.

1. Introduction
In recent days, water-born fluorosis is a very swiftly spreading ailment across the globe due to excessive ingestion of fluoride-rich water in the body. In India, hitherto, 23 states are infested with high fluoride in groundwater [1]. Fluoride (F) is lucrative for developing teeth and bones if it ranges between 1.0-1.5 mg/l in drinking water [2,3]. However, its prolonged intake beyond its permissible range causes fluorosis. Excess of fluoride (>1.5 mg/l) may cause dental and or skeletal deformities and its dearth (<1.0 mg/l) leads to dental-carries, mottled enamel etc. [4]. The fluoride bearing minerals like Fluorite, cryolite, fluor-apatite, micas, hornblende, apophyllite [5] often found associated with granites/granitoid and granite gneissic rocks as accessory minerals [6] and some clay minerals like Montmorillonite, Kaolinite, vermiculite, goethite, and allophane [7,8] are reckoned as the possible geogenic sources of fluoride in natural waters. The water-rock interaction process in an alkaline medium with long residence...
time supplements the process of ingestion of fluoride from fluoride bearing aquifers [9]. The precipitation of Ca under semi-arid climate due to evapotranspiration [10], and accumulation of weathered material of host rock, and low recharge conditions may trigger the high incidence of F into groundwater [11,12].

The present study has been conducted in the shallow-deep aquifers within Bundelkhand granites (granites/granitoids, granite gneisses, pegmatites etc.) in parts of Jhansi and Tikamgarh districts, central India which comprises a detailed account of geochemical assessment and lineament/structural controls on fluoride pollution/contamination in groundwater and which is further dovetailed with a human health check on the local habitats.

2. Study area

The investigation area falls in the parts of the Survey of India (SOI) topographic maps nos. 54K/15, 54K/16, 54O/3, and 54O/4 (1:50,000 scale), covers the parts of Jhansi district (U.P.) and intervening parts of Tikamgarh district (M.P.) in Bundelkhand region, bounded by the latitude 25°4’15” - 25°22’00” N and longitude 78°54’20” - 79°15’00” E that marks the area of 1150 sq. km and traversed by the rivers namely- Sukhnai, Saprar, Kurar and Ur (figure 1). The topographically concerned area is undulating and rugged comprised of dissected uplands, presenting a north-easterly sloping older eroded surface carved out of granitoid. The red (upland soils) and black (low land soils) are two kinds of soils found in the area [13,14]. The region's climate is ‘sub-humid to sub-arid’ and experienced mean precipitation of 972 mm/annum [15].

Figure 1. Compiled Geological Map of investigated area (modified after GSI 2001) showing well locations.
3. Geological setup
Geologically, figure 1 illustrates the study area mainly comprised of undifferentiated granitoids, metavolcanics, granites, granite gneisses, metabasites, pegmatites, and aplites, as the rock assemblage of Bundelkhand Gneissic Complex (BGC; Archaean to Proterozoic) and Newer Alluvium (Sand, Silt, and Clay) of Holocene [16,17,18,19]. The TTG (Tonalite-Trondhjemite-Granodiorite) suite near Kuraicha village (W-3, Fig.1) records the oldest date (3.3Ga) in the area [20]. The NE-SW trending long and narrow quartz reefs are emplaced within BCG seem to have been controlled by the granites’ pre-existing joints, which are moderately sheared and crushed at places [21]. However, the NW-SE trending swarms of basic doleritic dykes (younger than quartz reefs) are intruded along with two sets of joints in granites, which are at the right angle to the trend of major reefs. The ~E-W trending Babina-Mauranipur-Mahoba shear-stress zone passes through the area [22]. Its strain is evident in the Bundelkhand granites/ gneisses as localized joints, grain size reduction, S-C fabric, non-coaxial laminar flow etc. (figure 2a, b, and c). Including essential minerals of granites/granitoid like quartz, orthoclase, and plagioclase feldspar, the fluoride-minerals viz. biotite, muscovite, hornblende, and apatite have also been found associated with the granites/ granitoids as accessory minerals [17,23].

4. Hydro-geomorphology
In the studied area, phreatic-water occurs in the weathered (disintegrated and decomposed) and ruptured zones of Bundelkhand granites/ granitoid where the lattice of interconnected joints, fracture, and other deformational lineaments (secondary porosity) facilitate the hydraulic conductivity into groundwater system under unconfined to semi-confined conditions (in deep aquifers up to basement). The water level often varies from 25 to 300 ft deep below the ground surface.

5. Material and Methods
In the preliminary phase of field studies, the Zirconium Xylenol Orange method [24] was used to spot F in the water drafted from dug wells, tube/bore wells to bring out a bird-eye view of F values in the area. Thence, a total 41 locations (figure 1) (based on spotted anomalous values) were further sampled for detailed hydro-geochemical investigation. However, dug wells were found free from F contamination, so debarred from the study. The water samples were collected in clean HDPE bottles of one-liter capacity (previously rinsed thrice with the water to be sampled) from tube/bore-wells in pre-monsoon (June 2017) and post-monsoon (October 2017) seasons. Further, rock samples were collected
for the petrography to ascertain the association of fluoride-minerals in the rocks. Meanwhile, verbal-interface with local people was also carried out to victimize the people affected by fluorosis.

The physicochemical entities were determined based on specified guidelines of the American Public Health Association [25]. The determinants viz. pH, Electric Conductivity (EC) and Total Dissolved Solids (TDS) were determined by using soil/water analyzer kit; Total Hardness (TH), Ca$^{2+}$, Mg$^{2+}$ and HCO$_3^-$ were determined by titrimetric method (colorimetry); Na$^+$ and K$^+$ by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES); F$^-$ by ion-selective electrodes method, and SO$_4^{2-}$ by UV-Spectrophotometer. The analytical data were treated with specific statistical methods to deduce fruitful interpretations and conclusions. Photo Geology and Remote Sensing (PGRS) and GIS studies were carried out to delineate the lineaments based on relief and tonal variation on the landscape using Landsat-8 OLI satellite imagery SRTM & Aster DEM Data on ERDAS Imagine and ArcGIS platforms. The spatial-distribution maps of fluoride (F) were prepared through Inverse Distance Weighted (IDW) interpolation methods. The values of F were weighted as per the average values of surrounding sample locations.

### Table 1. Descriptive statistics of physicochemical entities of analyzed 41 groundwater samples.

| S. No. | WHO (2017) Standards | BIS (2015) Standards | Pre-monsoon Min. | Pre-monsoon Max. | Pre-monsoon Mean | Pre-monsoon SD | Post-monsoon Min. | Post-monsoon Max. | Post-monsoon Mean | Post-monsoon SD |
|--------|----------------------|----------------------|------------------|------------------|------------------|----------------|------------------|------------------|------------------|----------------|
| 1 | pH (6.5-8.5) | 7.0-8.5 | 6.5 | 8.8 | 7.35 | 0.52 | 6.3 | 8.8 | 7.85 | 0.57 |
| 2 | EC (µS/cm) (400-2000) | - | 257 | 4250 | 917.21 | 671.61 | 413 | 3010 | 1170.27 | 611.52 |
| 3 | TDS (500-1000) | 500-2000 | 129 | 2120 | 458.63 | 335.77 | 206 | 1498 | 583.95 | 303.65 |
| 4 | T.H. (200-600) | - | 48 | 924 | 177.75 | 151.87 | 20 | 740 | 144.48 | 172.05 |
| 5 | Ca$^{2+}$ (100-200) | 75-200 | 9.6 | 182.4 | 38.43 | 36.77 | 8 | 278.4 | 55.25 | 54.09 |
| 6 | Mg$^{2+}$ (30) | 30 | 1.92 | 112.32 | 19.59 | 17.93 | 0.96 | 94.08 | 15.66 | 18.36 |
| 7 | Na$^+$ (200) | - | 1.5 | 148 | 64.38 | 33.31 | 9 | 242 | 60.02 | 33.77 |
| 8 | K$^+$ (10-12) | - | 161 | 6.23 | 25.28 | 0.5 | 46 | 2.95 | 7.48 |
| 9 | Cl$^-$ (250) | 250-1000 | 12.6 | 865 | 129.34 | 157.96 | 25 | 475 | 124.87 | 120.82 |
| 10 | HCO$_3^{-}$ (300) | 262.3 | 835.7 | 539.18 | 156.43 | 91.5 | 622.2 | 220.19 | 95.55 |
| 11 | SO$_4^{2-}$ (25-250) | 200-400 | 6 | 303 | 48.51 | 54.10 | 2.83 | 220.93 | 47.64 | 45.19 |
| 12 | F (1.5) | 1.0-1.5 | 0.13 | 2.55 | 1.09 | 0.67 | 0.17 | 2.2 | 0.83 | 0.52 |

Note: SD=Standard Deviation; BDL= Below Detection Limit; Entities are in mg/l (except pH and EC)

### 6. Result and Discussion

#### 6.1. Chemical characterization of groundwater

The descriptive statistics of physicochemical entities (table 1) show that groundwater's pH is slightly acidic to alkaline in nature, as it ranges from 6.8 to 8.8 and 6.3 to 8.8 in pre-monsoon and post-monsoon periods, respectively. Electronic Conductivity (EC) varies from 257 to 4250 µS/cm and 413 to 3010 µS/cm in pre-monsoon and post-monsoon periods, respectively, whereas the Total Dissolved Solids (TDS) varies from 129 to 2120 mg/l, and 206 to 1498 mg/l in pre-monsoon and post-monsoon periods respectively. Therewithal, the mean spatial variations of various chemical entities in pre-monsoon and post-monsoon periods are: Ca$^{2+}$ 38.43 and 55.25 mg/l; Mg$^{2+}$ 19.59 and 15.66 mg/l; Na$^+$ 64.38 and 60.02 mg/l; K$^+$ 6.23 and 2.95 mg/l; HCO$_3^-$ 539.18 and 220.19 mg/l; SO$_4^{2-}$ 48.51 and 47.64 mg/l and Cl$^-$ 129.34 and 124.87 mg/l. The seasonal (in pre-monsoon and post-monsoon seasons) dominancy trends of cations and anions are Na$^+$$>$Ca$^{2+}$$>$Mg$^{2+}$$>$K$^+$ and HCO$_3^-$ $>$ Cl$^-$ $>$ SO$_4^{2-}$ in respectively. In groundwater, the alkali metals (Na$^+$ + K$^+$) exceeds alkali earth metals (Ca$^{2+}$ + Mg$^{2+}$), and weak acids (HCO$_3^-$) exceeds strong acids (SO$_4^{2-}$ + Cl$^-$) are perhaps due to the dominancy of silicate weathering (alkali feldspars) in the presence of carbonic acid in contrast with carbonate weathering (figure 3e, and 4e) [26].
6.2. Fluoride in groundwater and its endemcity

The analytical results show (Table 1) the fluoride ion (F-) spatially varies from 0.13 to 2.55 mg/l (mean 1.09 mg/l) in pre-monsoon with the Standard Deviation (SD) of 0.67, whilst in post-monsoon, it varies from 0.17 to 2.2 mg/l (mean 0.83 mg/l) with SD of 0.52. Table 2 shows the F- concentration beyond the upper tolerance limit (>1.5 mg/l) occur in 31.70% samples in the pre-monsoon from ~120-200 ft depth with the average pH of 7.66 and 14.63% samples from 06 villages in the post-monsoon periods from ~150-200 ft depth with the average pH of 8.15. The well W-2 (Basari village) in pre-monsoon and post-monsoon period and well W-1 (Harkanpura village) in post-monsoon were found infested with high F- content (>1.5 mg/l) as 2.55 mg/l and 2.20 mg/l, respectively. Therewithal, 48.78% of all the samples from 20 villages in pre-monsoon and 61.41% samples from 26 villages in post-monsoon are found below the desirable limit of F- (1.0 mg/l).

Table 2. Groundwater samples classification based on guideline values for F- specified by WHO (2017) and BIS (2015).

| S. No. | F- conc. (mg/l) | Pre-monsoon | Post-monsoon | Repercusion of fluorosis |
|-------|----------------|-------------|--------------|-------------------------|
|       |                | Out of 41 Samples | % of samples | Avg. pH | Out of 41 Samples | % of samples | Avg. pH | Dental Carries | Safe Zones | Dental and Skeletal Fluorosis |
| 1     | <1.0           | 20          | 48.78        | 7.27    | 26          | 63.41        | 7.78    |                |            |                              |
| 2     | 1.0-1.5        | 08          | 19.51        | 7.09    | 9           | 21.95        | 7.86    |                |            |                              |
| 3     | >1.5           | 13          | 31.70        | 7.66    | 6           | 14.63        | 8.15    |                |            |                              |

6.3. Correlation among Fluoride and other physicochemical entities

The correlation coefficients are used to establish relationships among two distinct variables [27]. The range of correlation coefficients from 0.70 to 1.00, 0.30 to 0.70, and 0.00 to 0.30 represent strong, moderate, and weak positive correlations, respectively, whereas the range from -0.70 to -1.00, -0.30 to -0.70, and -0.00 to -0.30 represent strong, moderate, and weak negative correlations respectively [28,29].

Table 3. Correlation matrix of physicochemical entities in pre-monsoon groundwater samples.

| Variables | pH  | EC  | TDS | T.H. | Ca2+ | Mg2+ | Na+ | K+ | Cl- | HCO3- | SO42- | F- |
|-----------|-----|-----|-----|------|------|------|-----|----|-----|-------|-------|----|
| pH        | 1   |     |     |      |      |      |     |    |     |       |       |    |
| EC        | -0.52 | 1   |     |      |      |      |     |    |     |       |       |    |
| TDS       | -0.52 | 1   | 1   |      |      |      |     |    |     |       |       |    |
| T.H.      | -0.45 | 0.95 | 0.95 | 1    |      |      |     |    |     |       |       |    |
| Ca2+      | 0.45  | 0.86 | 0.86 | 0.93 | 1    |      |     |    |     |       |       |    |
| Mg2+      | -0.36 | 0.88 | 0.88 | 0.89 | 0.66 | 1    |     |    |     |       |       |    |
| Na+       | -0.13 | 0.45 | 0.45 | 0.31 | 0.20 | 0.38 | 1   |    |     |       |       |    |
| K+        | 0.17  | -0.04 | -0.04 | -0.07 | -0.11 | -0.01 | 0.44 | 1  |     |       |       |    |
| Cl-       | -0.52 | 0.98 | 0.98 | 0.95 | 0.90 | 0.82 | 0.45 | -0.03 | 1  |       |       |    |
| HCO3-     | -0.12 | 0.15 | 0.15 | 0.02 | -0.11 | 0.17 | 0.24 | -0.10 | 0.01 | 1     |       |    |
| SO42-     | -0.47 | 0.96 | 0.96 | 0.92 | 0.85 | 0.82 | 0.45 | 0.02 | 0.96 | 0.01 | 1     |    |
| F-        | 0.34  | -0.26 | -0.26 | -0.34 | -0.51 | -0.08 | 0.15 | 0.22 | -0.31 | 0.24 | -0.26 | 1  |

In the current study, the different physicochemical entities are correlated by bivariate scatter plots. The correlation matrices of correlation coefficient (table 3, and 4) show that in pre-monsoon and post-monsoon water samples, F- exhibits the moderate positive correlation with pH (figure 3a and 4a) and weak positive correlation with HCO3-, and Na+ + K+ (figure 3 b-c and 4 b-c), whereas, it exhibits a moderate negative correlation with Ca2+ (figure 3d and 4d). However, F- exhibits a moderate positive correlation with HCO3- (figure 3b and 4b) and a weak positive correlation with pH and Na+ + K+ (figure 3 a, c and 4 a, c). Also, TDS shows moderate to strong correlation with major ions in pre-monsoon (table 2) except F-, HCO3-, and K+ ions. It indicates the fall in the water table escalates the ion contents into
groundwater [28]. The correlation analyses signify that the groundwater with high pH, HCO$_3^-$, and Na$^+$ + K$^+$ concentrations and low Ca$^{2+}$ concentration escalate the F$^-$ concentration into groundwater [6,30].

**Table 4.** Correlation matrix of physicochemical entities in post-monsoon groundwater samples.

| Variables | pH   | EC    | TDS  | T.H. | Ca$^{2+}$ | Mg$^{2+}$ | Na$^+$ | K$^+$ | Cl$^-$ | HCO$_3^-$ | SO$_4^{2-}$ | F$^-$ |
|-----------|------|-------|------|------|-----------|-----------|--------|-------|--------|-----------|------------|-------|
| pH        | 1    |       |      |      |           |           |        |       |        |           |            |       |
| EC        | 0.43 | 1     |      |      |           |           |        |       |        |           |            |       |
| TDS       | 0.43 | 1     | 1    |      |           |           |        |       |        |           |            |       |
| T.H.      | 0.29 | 0.91  | 0.91 | 1    |           |           |        |       |        |           |            |       |
| Ca$^{2+}$ | 0.11 | 0.65  | 0.64 | 0.81 | 1         |           |        |       |        |           |            |       |
| Mg$^{2+}$ | 0.06 | 0.39  | 0.39 | 0.45 | 0.59      | 1         |        |       |        |           |            |       |
| Na$^+$    | 0.37 | 0.59  | 0.59 | 0.32 | 0.09      | 0.09      | 1      |       |        |           |            |       |
| K$^+$     | 0.22 | 0.55  | 0.55 | 0.37 | 0.26      | 0.17      | 0.76   | 1     |        |           |            |       |
| Cl$^-$    | 0.36 | 0.97  | 0.97 | 0.95 | 0.74      | 0.41      | 0.51   | 0.54  | 1      |           |            |       |
| HCO$_3^-$ | 0.16 | -0.28 | -0.28| -0.37| -0.30     | -0.24     | 0.27   | -0.08 | -0.35  | 1         |            |       |
| SO$_4^{2-}$| 0.32 | 0.91  | 0.91 | 0.82 | 0.59      | 0.41      | 0.60   | 0.67  | 0.91   | -0.36     | 1          |       |
| F$^-$     | 0.22 | -0.30 | -0.30| -0.35| -0.43     | -0.27     | 0.15   | -0.08 | -0.34  | 0.43      | -0.28      | 1     |

**Figure 3.** Scatter plots of (a) F$^-$ Vs pH; (b) F$^-$ Vs HCO$_3^-$; (c) F$^-$ Vs Na$^+$ + K$^+$; (d) F$^-$ Vs Ca$^{2+}$; (e) Ca$^{2+}$ + Mg$^{2+}$ Vs HCO$_3^-$ + SO$_4^{2-}$, and (f) F$^-$ Vs Na/Ca$^{2+}$ are illustrating the dominant process and correlation among physico-chemical entities in pre-monsoon groundwater samples.
6.4. Hydro-geochemical origin of fluoride and rock-water interaction
The hydro-geochemistry of the area is chiefly controlled by the hydrological cycle, rate of groundwater flow, aquifer type, composition, and water interaction. Rainfall infiltrates the meteoric water into the subsurface, which is mostly charged with carbonic acid. It dissolves the aquifer material and liberates the ions into groundwater [31]. Thereby, such hydro-geochemical processes are responsible for the alteration of groundwater composition with respect to time and space.

Piper diagram [32] distributes the water composition in different hydro-geochemical facies (figure 5 a, and b). It reveals, the bulk of samples in pre-monsoon and post-monsoon seasons with ‘high F- values’ are associated with Na-K-HCO₃, Na-HCO₃, Ca-Mg-HCO₃, and Ca-Mg-Na-K- HCO₃ type of facies, which connotes the exchange of Ca²⁺ and Mg²⁺ ions by Na⁺ ion might be the result of longer retention time of groundwater in the aquifers aided by evapotranspiration process. However, the samples with ‘low F- values’ are associated with Ca-Mg-HCO₃, Ca-Mg-Cl, Na-K- HCO₃, Na-SO₄-Cl, and Ca-Cl type facies signify the input of atmospheric water in groundwater with a high rate of transmission within an aquifer.

![Figure 4](image1.png)

**Figure 4.** Scatter plots of (a) F Vs pH; (b) F Vs HCO₃⁻; (c) F Vs Na⁺ + K⁺; (d) F Vs Ca²⁺; (e) Ca²⁺ + Mg²⁺ Vs HCO₃⁻ + SO₄²⁻, and (f) F Vs Na⁺/Ca²⁺ illustrating the dominant process and correlation among physico-chemical entities in post monsoon groundwater samples.

Gibbs (1970) established a diagram that illustrates the partial chemical equilibrium between the two series of end members Ca²⁺- Na⁺ (Cation) and HCO₃⁻-Cl (anion) as a function of TDS. The Gibbs diagram mainly evinces the functional sources of dissolved solids and the dominant processes such as precipitation, rock weathering, and evaporation-crystallization that control the geochemical evolution of water [33,34,35]. Gibbs plots (figure 6 a, and b) show the majority of the groundwater samples
 (>90%) in pre-monsoon and post-monsoon periods are falling in the regime of ‘Rock Dominance Weathering’ and the rest samples falling in the regime of ‘Precipitation-Crystallization Dominance’. It explicitly signifies the geochemical interface controls between groundwater and weathered rocks rich in fluoride-minerals over fluoride enrichment into groundwater in partially evapotranspiration conditions under prevailing sub-humid climate in the study area.

In Ca\textsuperscript{2+} + Mg\textsuperscript{2+} vs HCO\textsubscript{3} - + SO\textsubscript{4} -2 plot, 100% of pre-monsoon (figure 3e) and 93% of post-monsoon samples (figure 4e) are clustered above the equiline (1:1) that signifies the progressive enrichment of Na\textsuperscript{+}, K\textsuperscript{+} along with HCO\textsubscript{3} - ions cause of the weathering and dissolution of alkali silicates and fluoride-minerals in the presence of carbonic acid [9,36,37]. A positive correlation exhibit by Na\textsuperscript{+}/Ca\textsuperscript{2+} ratio vs F\textsuperscript{-} plot (figure 3f, and 4f) illustrate the depletion of Ca\textsuperscript{2+} ions along with enrichment of Na\textsuperscript{+} and F\textsuperscript{-} ions. Consequently, this relation explains F\textsuperscript{-} ions’ release into groundwater with the precipitation of CaCO\textsubscript{3} under a higher alkaline medium [36,37,38].

![Figure 5. Piper-diagrams (1944), illustrating hydro-geochemical facies in (a) Pre-monsoon, and (b) Post-monsoon periods.](image)

6.5. Petrogenic sources of fluoride
The microscopic studies (figure 7) of rock samples (collected from pegmatitic and aplitic veins, sheared zones, altered zones, and deep dug well) revealed the occurrence of the Apatite, F\textsuperscript{-} replacing OH\textsuperscript{-} ions in minerals due to hydrothermal reactions like hornblende and micas (Biotite, Muscovite, Chlorite, and Sericite) in the aplites, pegmatites along week zones, granites/ granitoids of BGC are the principal fluoride hosting minerals polluting/ contaminating the groundwater in the area [6,31,36,37]. During prolonged rock-water interaction, the dissolution of biotite occurs (eq. 1), where OH\textsuperscript{-} replaces F\textsuperscript{-} sites at its octahedral sheets [39] and incessantly discharges the F\textsuperscript{-} ion into groundwater and pollute/ contaminate the aquifers.

\[
\text{KMg}_{3}\text{(AlSi}_{3}\text{O}_{10})\text{F}_{2} + 2\text{OH}^{-} \rightarrow \text{KMg}_{3}\text{(AlSi}_{3}\text{O}_{10})(\text{OH})_{2} + 2\text{F}^{-}
\]  

(1)

Besides, the occurrence of ‘Kaolinite’ (an altered product of alkali feldspars) in the crevices of weathered granites, vertical openings, and sheared/ fractured zones [40], sorbs the F\textsuperscript{-} ions on its surface and intermolecular spaces [8], identified as a secondary source of F\textsuperscript{-} enrichment in the groundwater.
Figure 6. Gibbs diagram illustrating the functional sources of dissolved solids during (a) Pre monsoon, and (b) Post monsoon periods.

Figure 7. Photomicrographs of rock-specimen depicting different mineral assemblages as inclusions of subhedral apatite (Apt) within cleavage of Biotite (Bt), Feebly altered Orthoclase (Or) with typical Carlsbad twinning, Muscovite (Mu), subhedral Hornblende (Hb), Chlorite (Chl) with berlin blue interference color, Sericite (Ser), and Quartz (Qtz).

6.6. Lineament/structural control on fluoride incidences
The present study points to the significant relation between fluoride incidences in groundwater and the prevailed geological structures in the study area. Structurally, the Bundelkhand Craton has suffered three to five phases of deformation. The imprints of deformation are very apparent in the TTG gneisses and meta supracrustals disposed of in the study area with steeply dipping foliations (60-70°) towards NE-SW. F1-F3 folding deformation can be seen in BIF, quartzite, calc-silicate rocks, and amphibolites in the area, where amphibolites show F2 generation folding. The aftermath of poly-phase deformations and stabilization of cratonic segment, emplacements Giant Quartz Veins (GQVs) and dyke swarms took
place along NE-SW and SE-NW trending weak zones, respectively. Besides, ~E-W trending archaean age crustal-scale sinistral shear zone (figure 1) is the younger phases of deformation, developed weak planes (major joints, fractures, foliations, flexure slips etc.), activated hydrothermal activities, injected hydrothermal fluid, filled the weak planes and dispersed fluorine within the Bundelkhand granites/granitoids [41]. Strained country-rock preserved two prominent sets of joints confined in the area striking roughly in NW-SE and NE-ENE to SW-WSW directions, including some subordinate set of joints. As per field observations, the trend of the crude foliation is N55°W-S55°E to N75°W-S75°E → 65°-75°NE, often found impressed on granitoid and granite gneisses. The GQVs have preserved the signature of younger phase ENE-NE to SWS-SW sinistral brittle-ductile deformation as flexure slips (figure 1; deformed Giant Quartz Reefs). These geological structures possess large scale lateral extension, and their orthogonally deep-seated roots are the open passages to the deep sub-surface.

Thus, to comprehend the structural controls on fluoride contamination in groundwater by using Geographic Information System (GIS), the conspicuous geological structures on the landscape such as joints, fractures, faults, shear zones etc. are delineated as lineaments and are superimposed on the spatial distribution maps of fluoride (figure 8 a, and b).

In figure 8 a and b show, the major high F- zones (NW-SE, and NNW-SSE) in pre-monsoon and post-monsoon periods are after the three prominent sets of lineaments viz. (i) NW-SE, (ii) WNE-ENE, and (iii) NNW-SSE, however, minor zones are along NE-SW trending lineaments. The lineaments trending NE-SW represent quartz reefs, whereas, NW-SE, WNW-ESE, and NNW-SSE lineaments correspond to joint sets, sheared/fractured zone, faults and dykes present in the area. Therefore, lineaments present in the area are playing a pivotal role in controlling the natural aquifer conditions for fluoride incidences in the groundwater by augmenting the rate of rock-weathering; steering the permeability of crustal rocks that leads to an influx of surface runoff into the subsurface, and controls the dilution and enrichment of fluoride as well as other elemental concentrations; hindering the flow of subsurface water in particular areas (mostly central parts of the study area), and amplifying the time and space for prolonged rock/soil-water interaction and leaching of fluoride ions from minerals under alkaline medium. Also, retained water in the reservoir (Kamla Sagar Dam; figure 1) across the course of the river and along the shear zone could also be an additional factor for hydro-geological conditions to be prone to high fluoride ingestion in the area.

Figure 8. Lineaments superimposed on the spatial distribution of fluoride ranges in groundwater during (a) Pre-monsoon, and (b) Post monsoon
Moreover, a comparative study of the spatial distribution of fluoride values in pre-monsoon and post-monsoon periods (figure 8) inferred that the high fluoride contents' dilution and reduction in the fluoride zonation had been noticed in the post-monsoon period than pre-monsoon period. In the pre-monsoon period, the high fluoride zones (>1.5 mg/l) in NW and the isolated patches in NE, SE, and central parts of the area along the course (from SW to NE) of Sukhnai and Kurar river found normalized (1.0-1.5 mg/l) in the post-monsoon period. The normalization of fluoride content in the post-monsoon period is may be due to the feeding of monsoonal water by the aquifers, raised the water table, a decrease of pH (alkaline to near natural), and a slight increase in dissolved solids at shallow depth (table 1) due to influx of surface runoff into groundwater loaded with significant charged particles by during monsoon.

6.7. Prevalence of fluorosis and impact on human health
As a purview of Medical Geology, a human health survey was accomplished and gathered 506 data samples of human beings to study endemicity of fluorosis in the study area distinguished for water scarcity and episodes of droughts due to very hot climate during pre-monsoon period. The manifestations of fluorosis from high/low fluoride affected villages Basari (W-2), Bagora (W-3), Harkanpura (W-1), Kalothara (W-9), Parsara (W-20), and Nuna (W-5) shown in Fig. 4. The ailment fluorosis (dental and crippling fluorosis) in human beings results from the intake of excessive fluoride through drinking water. Its severity and duration vary from person to person and depend on humans' age, food and nutritional structure, amount of fluoride ingested, climate, and environment [42].

Figure 9. Dental Fluorosis and carries - (a) 14 years old boy from Basari village (W-2), (b) 15 years old boy from Harkanpura village (W-1), and (e) 56 years old man From Bagora village (W-3) are showing early to progressive dental fluorosis (yellow to brown stains); (d) 18 years old boy from Kalothara village (W-9) is showing early dental fluorosis (yellow stains); (e) 13 years old boy from
The potential hazards of Dental Fluorosis (DF) based on different ranges of F concentrations in groundwater (figure 10a) and frequency of different stages of DF in the habitants of different age groups (figure 10b) were evaluated from the data gathered during field studies. Consequently, about 32% cases of dental carries (white scales on teeth; figure 9e, and f), 18% cases of early DF (yellow stains away from the tooth enamel; figure 9d), and 25% cases of progressive DF (brown stains away from the tooth enamel; figure 9 a-c) are victimized corresponding to the F contents in groundwater <1.0 mg/l, 1.5-2.0 mg/l and >2.0 mg/l respectively. The bodies of affected people sorb F ions due to regular and prolonged intake of fluoride-rich water and gradually replaces the OH ions from the molecular structure of teeth i.e. hydroxyl-apatite \([\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]\) and forms fluor-apatite \([\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{F})]\) under its high electronegativity and similar ionic radii with OH ions. This ionic reaction deteriorates the natural molecular structure of teeth; reducing the crystal volume and mineral solubility and increasing structural stability and aftermath leads to dental deformities [43]. Parsara village (W-20), and (f) 28 years old man from Nuna village (W5) are showing mild dental-carries. (White scales on teeth).

**Figure 10:** Histograms showing (a) Potential hazard of DF* (Dental Fluorosis) Vs Fluoride ranges and, (b) Frequency of DF* in different age groups.

**7. Conclusion**

The present study reveals the prevalence of fluoride contamination in groundwater seems to be geogenic and directly related to fluoride-minerals’ occurrence in Bundelkhand granites/ granitoid. The Zirconium Xylenol Orange method for spot testing of fluoride (F) for groundwater was found very effective and functional in the study area. The principal fluoride hosting-minerals are apatite, hornblende, and micas (biotite, muscovite, chlorite, and sericite); besides, kaolinite (clay minerals) is also found as contributing F into the groundwater. The high weathering of F bearing minerals in granitic rocks, depletion of
groundwater table, the evapotranspiration process could be the controlling factor of F\(^-\) contamination in the area. Dissolution of F\(^-\) containing minerals into groundwater is the result of high alkalinity (high pH). Hydro-geochemical studies indicate the hydro-geochemical facies viz. Na-K-HCO\(_3\), Na-HCO\(_3\) and Ca-Mg-HCO\(_3\) are dominant in the high F\(^-\) zones governing the ion-exchange reactions due to longer rock-water interaction causing F\(^-\) enrichment in groundwater. Besides, weathering of silicates mineral (alkali rich) supplying the Na\(^+\) & HCO\(_3\)\(^-\) ions into the water system and elevating the alkalinity of groundwater and depletion of Ca\(^{2+}\) with elevated Na\(^+\) ions leading to precipitation of calcite under high-alkaline medium escalating the F\(^-\) ingestion into groundwater. The study shows that the localized lineaments are after the high F-belts (NW-SE, NE-SW, WNW-ESE, NNW-SSE) that substantiate the structural/ lineament controls on fluoride contamination in groundwater and facilitating the time and space for prolonged rock/soil-water interaction in the area. The high fluoride zones could be extended along NW-SE in the adjoining regions for further investigations. The high fluoride zones are confined to the shallow depth aquifer (~120-200 ft), while the deep aquifers and the dug-wells (very shallow aquifers) are recognized as safe for drinking purposes. The human health survey reveals that dental deformities are more ubiquitous in minors and old aged inhabitants than adults. The prevalence of dental fluorosis in the area might be due to the consumption of more fluoridated water in summers due to the hot climate and thirst. Though skeletal fluorosis has not been reported from the studied area, the cases with pain and stiffness in joints (maybe early stage of skeletal fluorosis) have been observed in old aged inhabitants.

8. Recommendations

The implementation of the following recommendations to avoid the risk of fluorosis in the area should be ensured by the government administration on a priority basis, though the issue of fluorosis is not yet reached the alarming stage:

- The habitation dependent on F\(^-\) contaminated shallow depth aquifers to meet their daily drinking needs may be facilitated with safe water from non-fluoride affected areas, where the density of lineaments is significantly less (NE, SE, and S-Western parts of the area).
- The water drafted from tube/bore-wells with high F\(^-\) contents may be marked as prohibited for drinking purposes or treated with defluoridation techniques [43].
- State governments may appreciate the installation of rain-water harvesting units for recharging the aquifers and dilution of high F\(^-\) content.
- Optimum use of groundwater resources by minimizing its over-exploitation.
- The awareness program on groundwater management (to avoid overexploitation) and nutritional dieting may be imparted to the school and the local populace of the study area.

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