



Geochemical factors controlling the occurrence of high fluoride groundwater in the Nagar Parkar area, Sindh, Pakistan

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ABSTRACT

Fluoride concentrations in groundwater near Nagar Parkar in the Thar Desert of southeastern Pakistan range from 1.13 to 7.85 mg/l, and roughly 78% of the samples contain fluoride in concentrations that exceed the drinking water standard of 1.5 mg/l set by WHO. The groundwater is alkaline (pH 7.1–8.4), brackish (TDS 449–15,933 mg/l), and classified as Na–Cl type water. This prevailing chemical character reflects the influence of saltwater intrusion, high evaporation rates, and ion exchange. Groundwater is also supersaturated with respect to calcite, which promotes the removal of Ca^{2+} and HCO_3^- from solution. As a result, groundwater is generally undersaturated with respect to fluorite, the mineral that typically controls the upper limit of fluoride concentrations. This study examines a number of geochemical parameters in an effort to discover the controls on fluoride concentrations in groundwater. High fluoride concentrations are associated with high TDS, high pH, high Na concentrations, and high sodium absorption ratios (SAR). This suggests that elevated fluoride levels are the result of enhanced fluorite solubility due to Ca depletion and high ionic strength and the release of fluoride from colloid surfaces under high pH conditions. Contrary to what has been found in other studies, sample depth and water temperature do not appear to have a significant role in the distribution of fluoride within the groundwater.

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1. Introduction

The vast Thar Desert occupies the SE part of the Sindh province, Pakistan. The study area forms a small peninsula surrounded by the great Rann of Kutch, near the Indian border (Fig. 1). The area is enclosed by Indian Territory on three sides, forming an enclave of Pakistan within India. Groundwater in the region surrounding Nagar Parkar is known to contain fluoride concentrations that exceed the drinking water standard of 1.5 mg/l set by WHO [1].

Fluorine is an essential micronutrient for human beings, serving to strengthen the apatite matrix of skeletal tissues and teeth. In regions where the fluoride (F^-) content of water is naturally low (<0.5 mg/l), some communities have chosen to add this constituent to their drinking water to strengthen teeth and minimize cavities [2]. On the other hand, high F^- (>1.5 mg/l) results in dental and skeletal fluorosis; renal and neuronal disorders along with myopathy [3]. Endemic fluorosis develops widely in many areas of the world, such as China [4], India [5–7], Mexico [8] and Africa [9]. In

Pakistan, the occurrence of high F^- groundwater has been reported in Lahore [10], Karachi [11], Naranji, NE of Peshawar [12] and also in Thar Desert where many suffer from dental and skeletal fluorosis [13].

Fluorine is a lithophile element with atmophile affinities, and occurs in many common rock-forming minerals. Therefore, high F^- concentrations in groundwater are expected in areas where fluorine-bearing minerals are abundant in the geologic substrate [14,15]. The granite of the study area contains abundant F^- bearing minerals [16], and during weathering, F^- can be leached out and dissolved in groundwater.

The aim of this paper is to present a systematic approach to evaluate the distribution of fluoride in the groundwater of Nagar Parkar area. Water quality parameters (e.g. pH, Eh, TDS, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , SiO_2 , Li, and SAR) have been measured to assess their potential relationship with F^- .

2. Geology

In the extreme SE corner of Pakistan near the Indian border, a fascinating exposure of Nagar Parkar igneous complex occurs. Regionally it is the part of NW Indian craton that extends into Pak-

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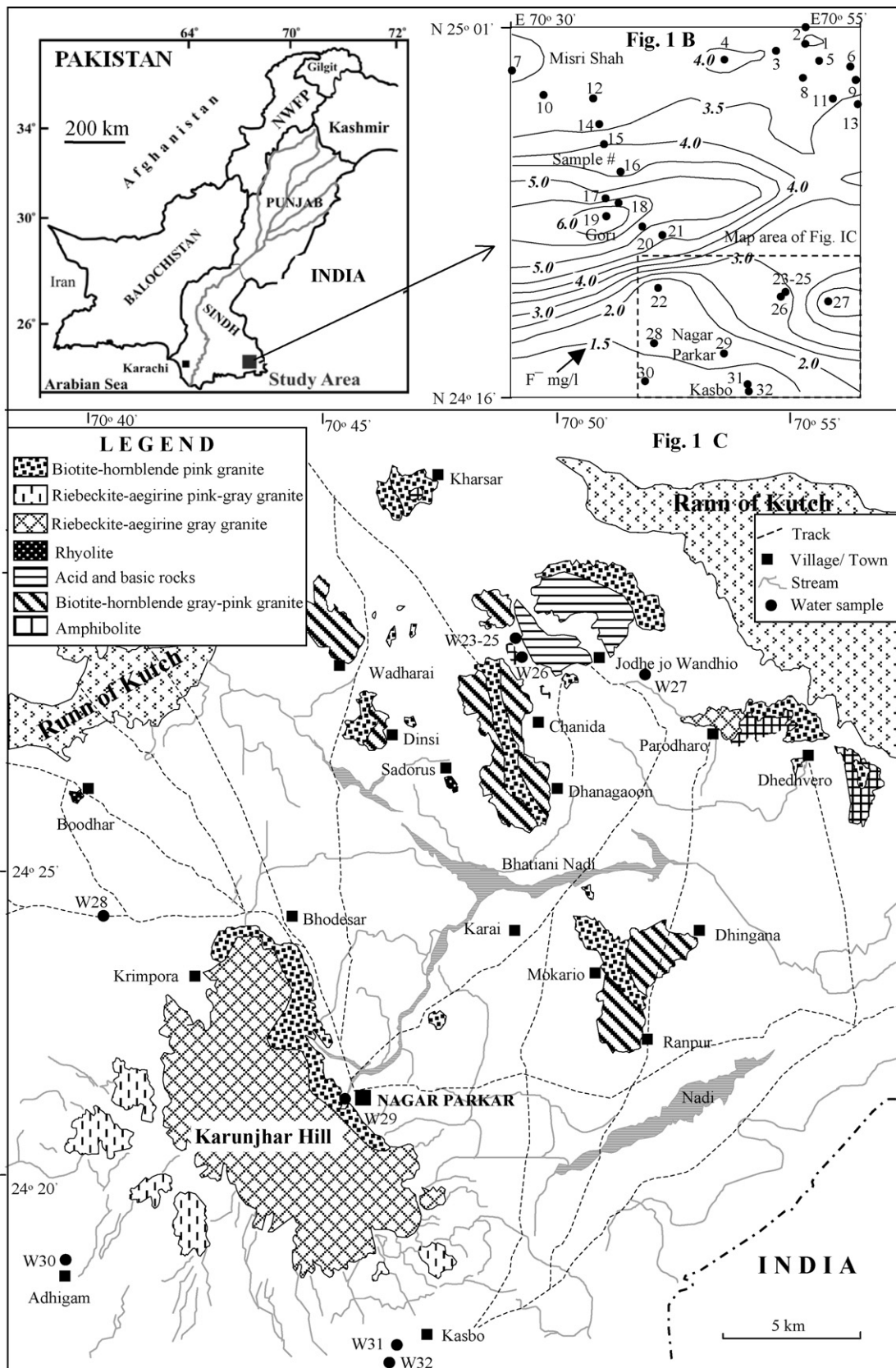


Fig. 1. (A) Map of Pakistan showing the study area. (B) Locations of wells used in the study and isoconcentration lines showing the distribution of F⁻. (C) Geological map of the Nagar Parkar area (simplified from Laghari et al. [16]) showing the locations of wells used in the study.

istan. The craton contains a mosaic of reworked Archean basement, Proterozoic fold belt (Aravalli–Delhi) and Late Proterozoic suites of Malani, Jalore and Siwana [17]. According to Roy and Jakhar [18], the Malani magmatism is related to Pan-African magmatic events (780–680 Ma). The associations of different groups of basic and ultramafic rocks are suggestive of different phases of igneous activity, viz. syn-rift stage, post-rift thermotectonic stage and inversion stage [19].

The granitic rocks of the Nagar Parkar area (Karunjhar Hill) may belong to the Late Proterozoic (720–745 Ma) Malani magmatism of Western Rajasthan, India. The basement rocks are comprised of an epidote-amphibolite facies of metamorphic rocks ranging from mafic to granodioritic composition. In the study area, amphibolite occurs in the NE of Nagar Parkar town. They appear as the product of crystallization differentiation of a calc-alkaline magma of island arc affinity. It is difficult to ascertain the exact age of the facies, however 2.83–3.5 Ga is assigned based on the isotopic work on Indian rocks [20]. Dykes of acid and mafic composition are also common in the area. Both are alkaline and show resemblance to continental alkaline basalts [21].

Kaolin deposits lie in a NE-E- and SW running belt of the Dedhvero complex in the Nagar Parkar area. These deposits are generally covered by a thin layer of sandy alluvium/lateritic clay. At some places the clay beds are exposed along stream cuttings. The dedhvero granite seems to show chemical weathering due to which feldspar has altered into kaolin in the tropical to subtropical climatic conditions in the geological past. The weathering products include laterite and ironstone as cap rock, grading downward into iron oxide-bearing kaolin to kaolin and finally, the unaltered granitic rock. The depth of the kaolin pockets is estimated to be 2–8 m below the surface [16].

3. Materials and methods

Extensive field work was carried out for the collection of groundwater samples and geological and hydrogeological information in the study area. A global positioning system (GPS), Garmin, Model eTrex Summit was used for location and elevation readings. This was supported by topographic sheets made available from the Survey of Pakistan. In situ measurements included temperature, pH, Eh (Redox potential), conductivity/TDS, and identification and recognition of the well characteristics such as name, depth, water level, condition and type.

Generally, one sample has been collected from each selected village from 5 to 10 km inter-distance between two sampling sites. Thirty-two groundwater samples were randomly collected from the dug-wells directly above the outlet after withdrawing the sampled water several times from the water table with a stainless steel container tightened with a fiber rope. This was done to remove groundwater stored in the well itself and to obtain representative samples. In all cases, pre-washed, nitric acid (1%) rinsed 1.5-l polyethylene bottles were used [22]. At the sampling sites these bottles were again rinsed with the groundwater to be sampled, completely filled, tightened with sealed caps and immediately transported to laboratory for analyses.

Standard methods were used for the determination of the chemical characteristics of the water samples [22]. Na⁺ and K⁺ were measured by flame photometry. Titrimetric methods were used for the determination of Ca²⁺, Mg²⁺, HCO₃⁻, and Cl⁻, whereas TDS was measured by evaporation and SO₄²⁻ was determined gravimetrically. Fluoride ion was determined by Ion Selective Electrode method using TISAB [22]. Trace elements (Li, SiO₂) were determined by AAS Hitachi-5000. Fluoride ion in some selected rock samples (*n* = 15) was determined by adopting the procedure of Johnson and Maxwell [23]. The analytical precision for the measurements of

Table 1

Statistical parameters of groundwater (*n* = 32) of Nagar Parkar area including concentrations of F⁻ in rock samples (*n* = 32).

Parameter	Range	Mean	Median
pH	7.14–8.36	8	7.98
Eh (mv)	-75 to +8.0	-52	-57
TDS (mg/l)	449–15933	3571	2505
EC (mS/cm)	0.674–23.9	23.900	3.758
Depth (ft.)	20–200	98	110
Temp. (°C)	23.4–34	30	30.75
Na ⁺ (mg/l)	70–5500	988	675
K ⁺ (mg/l)	3–395	39	21.75
Ca ²⁺ (mg/l)	14–782	106	57.5
Mg ²⁺ (mg/l)	5–414	91	53.5
Cl ⁻ (mg/l)	56–9111	1303	728
HCO ₃ ⁻ (mg/l)	203–773	434	404.5
SO ₄ ²⁻ (mg/l)	17–2568	330	206
F ⁻ (mg/l)	1.13–7.85	3.33	3.30
SiO ₂ (mg/l)	10.60–33.56	15.81	13.97
Li ⁺ (mg/l)	0.02–0.367	0.136	0.104
SAR	1.92–39.73	39.73	17.66
Fluoride concentrations in some selected rock samples (<i>n</i> = 15) of study area			
F ⁻ (mg/kg)	0.0–11975	1939	1070

cations (Ca²⁺, Mg²⁺, Na⁺, and K⁺) and anions (HCO₃⁻, Cl⁻, SO₄²⁻, and F⁻), indicated by the ionic balance error (IBE) was computed on the basis of ions expressed in meq/l. The value of IBE was observed to be within a limit of ±5% [24]. Solubility calculations were performed by using PHREEQC (Version 2) software package [25].

4. Result and discussions

4.1. Mobility

Fluorine has small ionic radii, maximum electro-negativity (4) and fairly high mobility. Probably one of the reasons for high F⁻ content in the groundwater samples is the high mobility of F⁻ ion. It can remain soluble in both oxidizing and reducing environments at variable pH [26]. Xu et al. [27] experimentally established the influence of rock-type on the mobility of F⁻ ions. A quantitative empirical estimate of relative mobility can be obtained by computing coexisting mobile and immobile phases. In particular, an approximation can be made by comparing the compositions of water and the rocks with which they are in contact. Perel'man [28] presents an expression to quantitatively estimate the mobility of an element.

$$\text{Coefficient of aqueous migration } K = \frac{(100 \cdot w)}{(t \cdot r)}$$

where *w* is the concentration of the element in water (mg/l); *t* is total dissolved solids (mg/l) and *r* is the concentration of the element in rock (%). Putting average values of the present study [Table 1 (*w* = 3.33, *t* = 3571 and *r* = 0.1939)] in the above equation, the coefficient of aqueous migration (*K*) is calculated as 0.481. According to Rose et al. [26], this value is in the limit of slightly mobile element (*K* 0.1–1) group. Probably due to large distance of sampling sites from granitic rocks (Fig. 1B and C), sorption by kaolinite and high TDS of water may hinder the mobility of F⁻ in the study area.

4.2. Ionic composition

A vector diagram provides a rapid visual method to express the composition of water (Fig. 2). The average composition of the groundwater of study area displays high Na–Cl and low but nearly equal proportions of Ca²⁺, Mg²⁺, HCO₃⁻ and SO₄²⁻ ions. A charge-balance error of 5% is generally considered acceptable, and the groundwater samples collected in this study had charge-balance

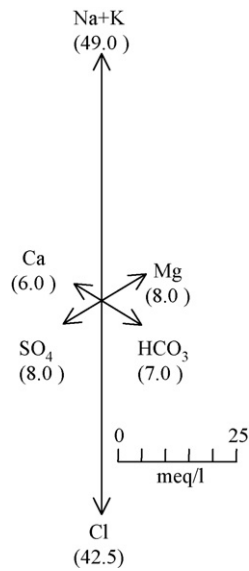


Fig. 2. Vector diagram showing average ($n=32$) major ion composition of groundwater of the study area.

errors ranging from 2.56 to -4.34% . The excess concentration of Na^+ and HCO_3^- is probably responsible for the occurrence of fluoride ions in the study area (Fig. 2). The presence of certain other trace elements such as Fe^{3+} , Al^{3+} , Si^{4+} and Mg^{2+} may modify the concentration level of F^- in the groundwater due to complex formation [29].

4.3. Hydrochemical facies

The concentration of F^- ions largely depends upon the chemical characteristics of the groundwater [30], and trilinear (Piper) diagrams [31] have sometimes been used to infer relationships between groundwater composition and fluoride distribution [4,32,33]. Fig. 3, which shows the 32 groundwater samples collected in this study plotted on a Piper diagram, reveals that most of the groundwater in the study area is classified as Na-Cl type water. Only three samples plot outside the Na-Cl field, and each of these samples contains relatively low (<1.5 mg/l) fluoride concentrations. Conversely, all but two of the samples within the Na-Cl field contain elevated (>1.5 mg/l) fluoride, and the highest fluoride concentrations are generally associated with those samples having the highest Na contents. A number of other studies have found a strong association between high fluoride and soft, alkaline (i.e., sodium-bicarbonate) groundwater that is depleted in calcium [33–36].

4.4. pH

A positive correlation between F^- concentration and pH is commonly observed in different parts of the world [29]. Fluoride is seldom detected in water having a pH value <7.0 [37]. This may be due to the similar ionic radii of F^- and OH^- , which often substitute for each other within minerals. Clay minerals, such as kaolin, are able to hold F^- ions on their surfaces, but at high pH OH^- ions can displace F^- ions, which are then released to groundwater [38]. This relationship might explain why the samples from the Nagar Parkar area with the highest fluoride concentrations are those with

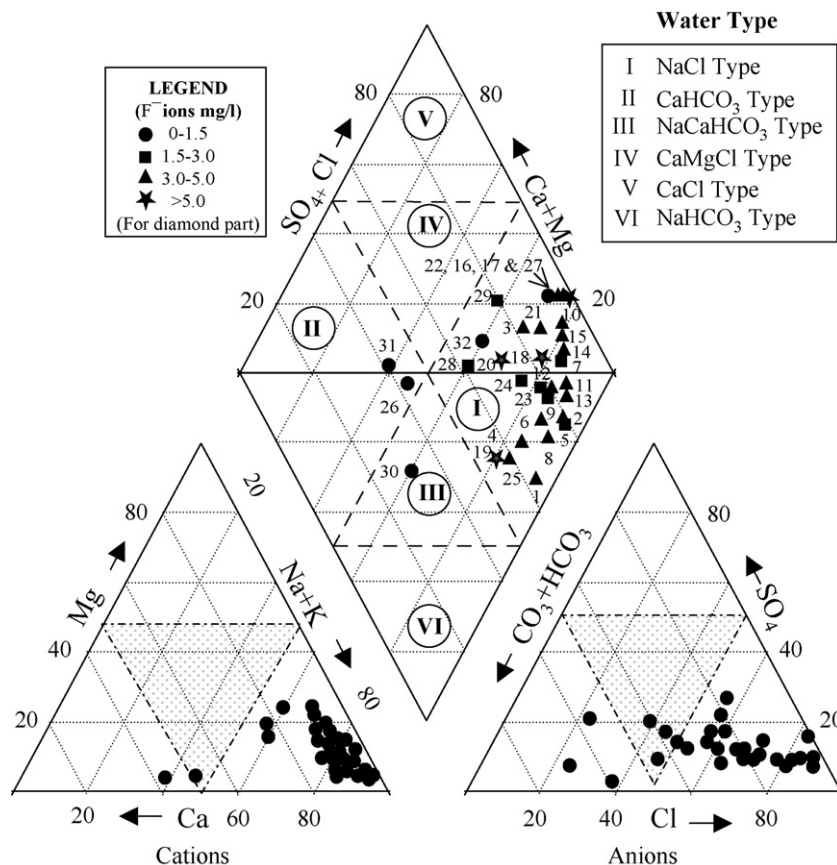


Fig. 3. Piper plots of the major ionic composition of groundwater in Nagar Parkar area. Sample no. and respective F^- ion concentration are marked in the diamond part of the diagram.

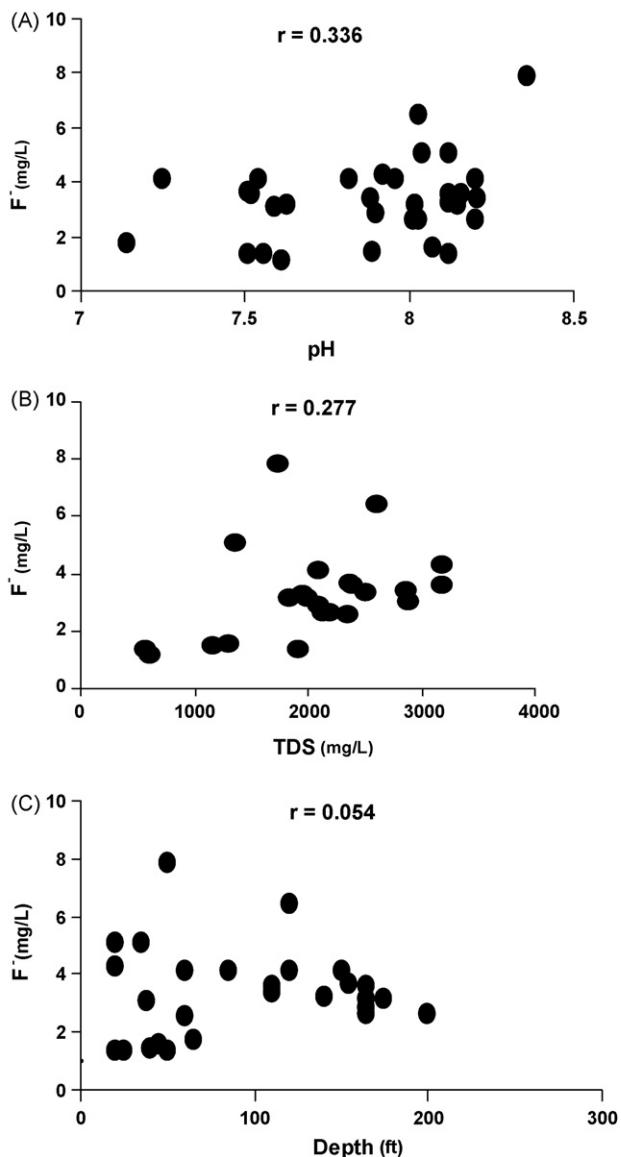


Fig. 4. Relationship between F^- content of groundwater and (A) pH, (B) TDS, (C) depth of well.

pH values above 7.5 (Fig. 4A). Saxena and Ahmed [30] found similar results for groundwater in parts of India.

4.5. Total dissolved solids (TDS)

Total dissolved solids in the study area range from 449 to 15,933 mg/l, with a mean value of 3571 mg/l (Table 1). The high TDS is mainly related to salt water intrusion and the dry climate. Subba [39] and Sreedevi et al. [38] have correlated high F^- with high salinities (TDS). A higher concentration of TDS enhances the ionic strength, leading to an increase in the solubility of F^- ions in the groundwater [40]. In the study area, low fluoride concentrations (<1.5 mg/l) are associated with samples that have relatively lower TDS values (<2000 mg/l). The concentration of F^- increases from 2 to 7.85 mg/l with the increase in TDS in whole data set. The average correlation matrix ($n = 32$) of F^- and TDS is 0.285, indicating that a relationship exists between these two variables (Fig. 4B). Thus, in addition to its direct effects on human health, the elevated TDS in the Nagar Parkar area also affects inhabitants indirectly through its influence on F^- concentrations.

4.6. Depth of well

Generally good quality of groundwater is lacking in the area; however, the quality of groundwater found in the south of Nagar Parkar in Kasbo locality is exceptionally good. A number of brackish to saline open dug-wells are present in low lying inter dune playa flats. The depth of the wells range between 20 and 200 ft. (mean 98 ft.) from the surface. Well depth increases along a northwest trend from Kasbo to Misri Shah (Fig. 1B). The relationship between F^- ion concentration and depth of well is important. Apambire et al. [41] have shown that F^- in groundwater increases with depth. In the study area, all of the wells greater than 100 ft. in depth have elevated (>2 mg/l) F^- concentrations; however, several of the shallower wells also have elevated F^- levels (Fig. 4C). The shallow wells with high F^- are those located within geologic materials that contain kaolin, which is a likely source of the F^- (see Sections 4.4 and 4.7).

4.7. Sodium absorption ratio (SAR) and ion exchange

The sodium hazard is expressed in terms of sodium absorption ratio (SAR) and can be calculated by the formula:

$$SAR = \frac{[Na^+]}{\sqrt{[(Ca^{2+} + Mg^{2+})/2]}}$$

The calculated values of SAR in the study area range from 1.92 to 39.73 (with a mean value of 17.66), which signify very high Na^+ and low Ca^{2+} concentrations in the groundwater. The high Na^+ in groundwater may reflect both the dissolution of lithogenic Na and the exchange of dissolved Ca for Na by clay minerals in the aquifer [4,42]. This assumption is also signified from high Na/Ca ratios (8.89), which show ion exchange between Na adsorbed on the surface of clay minerals and Ca in the groundwater [42]. The higher Na groundwater is associated with the pH conditions which favor the base-exchange softening of groundwater (Ca^{2+} and/or Mg^{2+} for Na^+). Laboratory studies have shown that aluminum-hydroxides have an especially high fluoride exchange capacity [43] and the release of F^- from clay minerals is favored by and/or produces high pH values (usually above 8.0) under conditions that can lead to the base-exchange softening of groundwater [41,44].

A plot of log TDS versus $Na/(Na + Cl)$ suggests that the process of ion exchange is occurring within the study area (Fig. 5A). Nearly 28% of the samples plot within the ion exchange field, and a majority of these samples also contain high (>3 mg/l) F^- concentrations. The low $SiO_2/(Na + K - Cl)$ ratio (average of 0.932) and low $Ca/(Ca + SO_4)$ ratio (average of 0.240) provide additional support for the process of ion exchange [45].

4.8. The saturation indices (SI)

Calcite ($CaCO_3$) and fluorite (CaF_2) both contain Ca^{2+} , their solubilities are interdependent [46]. As a result, conditions that lead to low calcite solubility can also lead to high F^- concentrations in groundwater [13]. For example, high pH conditions promote calcite precipitation and the removal of Ca^{2+} from solution, which then allows additional fluorite to dissolve [33–36,41,47–49], causing the F/Ca ratio in groundwater to increase [50,51].

The saturation indices for fluorite and calcite in groundwater samples collected within the study area were calculated [25] and plotted on Fig. 5B. A majority of these samples are undersaturated with respect to fluorite, and all of them are supersaturated with respect to calcite. This suggests that fluorite dissolution in the Nagar Parkar area is enhanced by the ongoing process of calcite precipitation.

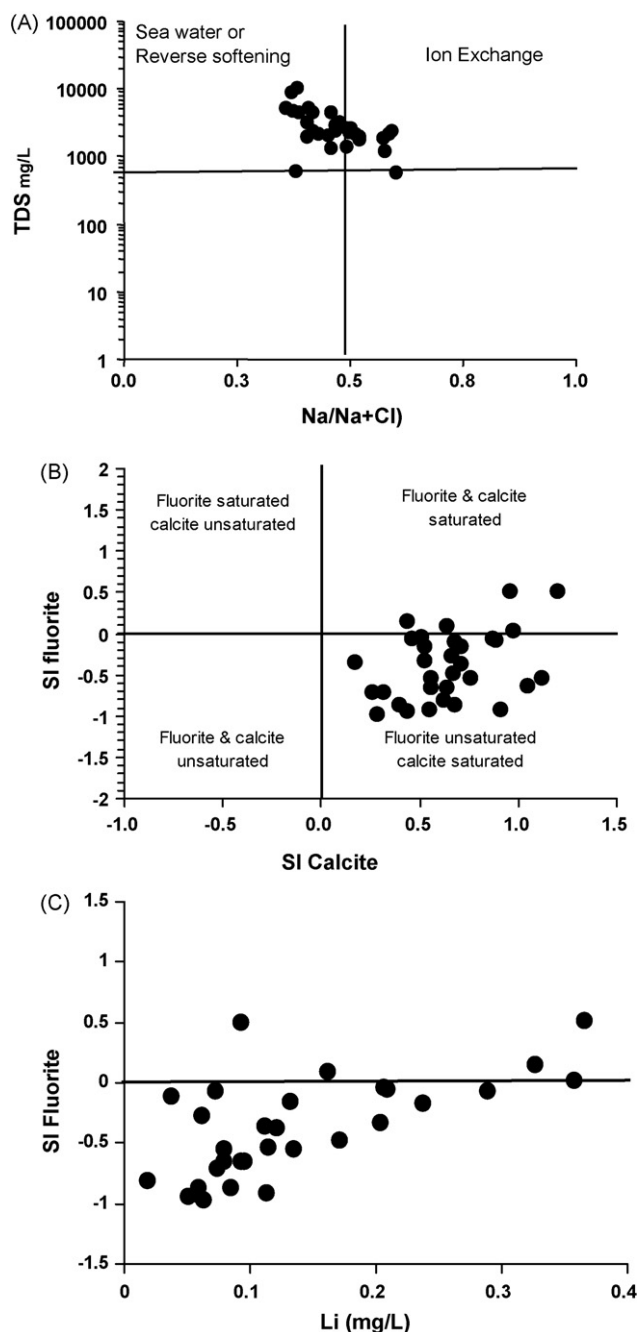


Fig. 5. (A) Plot of Log TDS versus $\text{Na}/(\text{Na}+\text{Cl})$ of the study area, (B) calcite saturation index versus fluorite saturation index, (C) fluorite saturation index versus Li concentration.

4.9. Temperature

Vasquez et al. [29] have shown that a positive correlation exists between F^- concentrations and temperature in the groundwater of Mexico City. The present study does not show any significant relationship between these two variables ($r=0.143$). Carrillo-Rivera et al. [8] have used saturation indices of fluorite and lithium concentrations to delineate temperature regimes in the groundwater of Mexico. They have found strong linear relationship between these two parameters, emphasizing the role of temperature in the mobilization of Li and F^- , suggesting a common origin for both species. A plot of fluorite saturation index versus Li concentration for groundwater in the Nagar Parkar area also shows a positive correlation

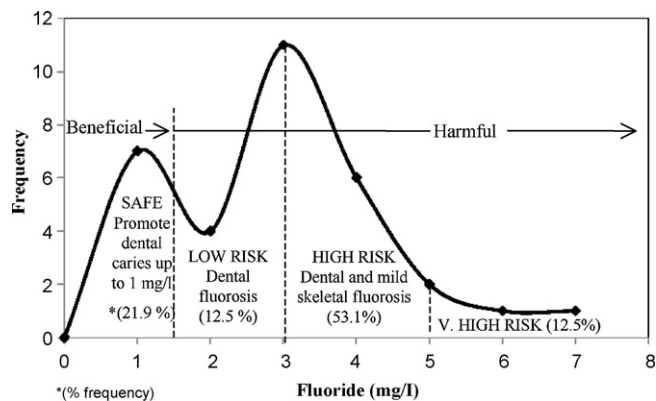


Fig. 6. Fluoride concentration zones of study area and associated fluorosis risk (fields are after Maithani et al. [2]).

(Fig. 5C). It designates that with increasing temperature, both Li and F^- ions are incorporated in the groundwater through the dissolution of granitic rocks of the study area.

5. Distribution and fluorosis risk

The distribution of fluoride ion in and around Nagar Parkar town shows two distinct zones on an isoconcentration map of the area (Fig. 1B). The areas of high F^- are observed in NNW of Nagar Parkar town, near the Temple of Gori, while the southern part has low F^- content. A small zone of higher concentration of F^- is present in the NE corner of the study area. The F^- concentration in groundwater ranges between 1.13 and 7.85 with mean and median values of 3.33 and 3.30 mg/l respectively (Table 1). Out of 32 analyzed samples, only 21.9% were found in the safe range, 12.5% in 1.5–3.0, 53.1% in 3.0–5.0 and 12.5% above 5.0 mg/l (Fig. 6). Nearly 78.1% samples of study area are above the prescribed limits of 1.5 mg/l for drinking water [52]. Maithani et al. [2] have elaborated the effects of F^- on human health. Fig. 6 illustrates the ranges of F^- concentration in groundwater of the study area and the possible associated dental and skeletal fluorosis risk.

6. Conclusions

Groundwater in the Nagar Parkar area is high in fluoride, with concentrations ranging from 1.13 to 7.85 mg/l. The median concentration in this study was 3.3 mg/l, and 78% of the samples contained fluoride concentrations that exceeded the drinking water standard of 1.5 mg/l set by WHO.

Groundwater in the study area is also high in TDS, ranging between 449 and 15,993 mg/l and having a mean value of 3571 mg/l. The prevalent chemical character is Na–Cl, which reflects the influence of saltwater intrusion, high evaporation rates, and ion exchange. Although Ca^{2+} concentrations are only about 10% of the Na^+ values, pH and HCO_3^- are high enough so that everywhere the groundwater is supersaturated with respect to calcite.

The same geochemical processes that control the overall groundwater chemistry also promote high fluoride concentrations. Fluorite solubility is enhanced by high ionic strength and the removal of calcium from solution by calcite precipitation and base-exchange softening. The pH conditions allow OH^- to displace fluoride attached to colloid surfaces, releasing it to groundwater. However, the role of depth and temperature does not have much influence on fluoride concentrations.

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