



Fluoride prevalence in groundwater around a fluorite mining area in the flood plain of the River Swat, Pakistan

Abdur Rashid ^{a,b,*}, Dong-Xing Guan ^{c,**}, Abida Farooqi ^b, Sardar Khan ^{a,**}, Salman Zahir ^{a,b}, Shah Jehan ^{a,d}, Seema Anjum Khattak ^d, Muhammad Sufaid Khan ^e, Raees Khan ^b

^a Department of Environmental Sciences, University of Peshawar, Peshawar 25120, Pakistan

^b Hydrogeochemistry Laboratory, Department of Environmental Sciences, Faculty of Biological Sciences, Quaid-i-Azam University, Islamabad, PO 45320, Pakistan

^c Key Laboratory of Surficial Geochemistry, Ministry of Education, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China

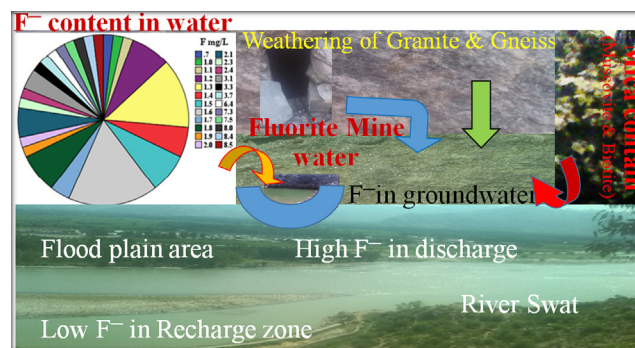
^d National Centre of Excellence in Geology, University of Peshawar, 25130, Pakistan

^e Departamento de Físico-Química, de Instituto Química, Universidade Estadual Paulista (UNESP), Araraquara 14800-900, SP, Brazil

HIGHLIGHTS

- Groundwater of flood plain area of river Swat, Pakistan was analysed for F⁻.
- Groundwater samples (62.2%) exceeded the WHO safe limit of F⁻ (1.5 mg/L).
- Fluoride enrichment was due to weathering of rocks and ion exchange processes.
- Minerals phases suggested both saturated (55%) and unsaturated (38%) groundwater.
- Health risk via (CFI) identified that groundwater is unfit for drinking purposes.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the fluoride (F⁻) concentrations and physicochemical parameters of the groundwater in a fluorite mining area of the flood plain region of the River Swat, with particular emphasis on the fate and distribution of F⁻ and the hydrogeochemistry. To better understand the groundwater hydrochemical profile and F⁻ enrichment, groundwater samples ($n = 53$) were collected from shallow (24–40 m), mid-depth (48–65 m) and deep (85–120 m) aquifers, and then analysed using an ion-selective electrode. The lowest F⁻ concentration (0.7 mg/L) was recorded in the deep-aquifer groundwater, while the highest (6.4 mg/L) was recorded in shallow groundwater. Most groundwater samples (62.2%) exceeded the guideline (1.5 mg/L) set by the World Health Organization (WHO); while for individual sources, 73% of shallow-groundwater samples (F⁻ concentration up to 6.4 mg/L), 42% of mid-depth-groundwater samples, and 17% of deep-groundwater samples had F⁻ concentrations that exceeded this permissible limit. Assessment of the overall quality of the groundwater revealed influences of the weathering of granite and gneisses rocks, along with silicate minerals and ion exchange processes. Hydrogeochemical analysis of the groundwater showed that Na⁺ is the dominant cation and HCO₃⁻ the major anion. The anionic and cationic concentrations across the entire study area increased in the following order: HCO₃⁻ > SO₄²⁻ > Cl⁻ > NO₃⁻ > F⁻ > PO₄³⁻ and Na > Ca > Mg > K, respectively. Relatively higher F⁻ toxicity levels were associated with the NaHCO₃ water type, and the chemical facies were found to change from the CaHCO₃ to

* Correspondence to: A. Rashid, Hydrogeochemistry Laboratory, Department of Environmental Sciences, Faculty of Biological Sciences, Quaid-i-Azam University, Islamabad, PO 45320, Pakistan.

** Corresponding authors.

E-mail addresses: abdur.rashid@bs.qau.edu.pk (A. Rashid), dxguan@nju.edu.cn (D.-X. Guan), sardar@uop.edu.pk (S. Khan).

(Na–HCO₃) type in calcium-poor aquifers. Thermodynamic considerations of saturation indices indicated that fluorite minerals play a vital role in the prevalence of fluorosis, while under-saturation revealed that – besides fluorite minerals – other F[−] minerals that are also present in the region further increase the F[−] concentrations in the groundwater. Finally, a health risk assessment via Dean's classification method identified that the groundwater with relatively higher F[−] concentrations is unfit for drinking purposes.

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1. Introduction

Fluoride (F[−]) is an essential micronutrient for human beings, strengthening both teeth and skeletal tissue (Nielsen, 2009; Rafique et al., 2009). It is the main inorganic toxicant of fluorine, predominantly promoted by alkaline pH, high concentrations of sodium cations (Na⁺) and bicarbonate (HCO₃[−]), and low concentrations of calcium ions (Ca⁺⁺) (Guo et al., 2007; Rafique et al., 2009). Fluoride enrichment mostly occurs in groundwater, soil, rocks, food, air, flora, fauna, and the human body (Rakshit, 2004; Raju et al., 2012; Varol et al., 2013; Raju et al., 2014; Singh et al., 2015; Xiao et al., 2015a, 2015b; Patel et al., 2016). Groundwater is the principal source of F[−] for human ingestion, potentially recognized and controlled by the regional chemistry of the host rock, hydrogeology, anthropogenic activities, and climatic factors (Frengstad et al., 2001; Saxena and Ahmed, 2003; Edmunds and Smedley, 2005; Chae et al., 2007; Khaliq et al., 2007; Rafique et al., 2009; Singh et al., 2015). Soil contributes 0.3 g/kg of the total F[−] content of the Earth's crust (Rakshit, 2004; Meenakshi and Maheshwari, 2006; Ghosh et al., 2013), making it the 13th most important source in terms of its natural abundance (Meenakshi and Maheshwari, 2006; Ghosh et al., 2013). Regions with relatively higher groundwater F[−] concentrations are mainly situated in discharge zones, particularly where average or shallower depths of groundwater occur.

Several minerals contain F[−], such as fluorite, fluorapatite, topaz, hornblende, tourmaline, villianmite, amphiboles, mica, biotite, and muscovite. Besides these minerals, some weathering silicates, igneous and sedimentary rocks also contribute a significant amount of F[−] to groundwater (Frengstad et al., 2001; Kim and Jeong, 2005; Antipin et al., 2006; Sreedevi et al., 2006; Msonda et al., 2007; Rafique et al., 2008; Feng et al., 2012; Doherty et al., 2014). Normally, F[−] enters into environment and human beings through food, water, industrial exposure, drugs, cosmetics, or mining activities (Hiyama, 2000). Elevated concentrations of F[−] in groundwater are regarded as a major health concern (Eby, 2004; WHO, 2004; Hudak, 2009). The prevalence of fluorosis is a widespread endemic disease of geological origin. Indeed, the link between the severity of fluorosis and concentrations of F[−] in groundwater is well recognized (Nayak et al., 2009). The recommendation from the World Health Organization (WHO) in terms of an acceptable concentration of F[−] in groundwater is 1.5 mg/L (WHO, 2004, 2006).

Endemic fluorosis afflicts >260 million individuals worldwide in 25 different nations, and >100 million people in southeast Asia, including India, Pakistan and Sri Lanka (Farooqi et al., 2007a, 2007b; Amini et al., 2008; Ravenscroft et al., 2009; Rafique et al., 2009; Kim et al., 2012). Both dental and skeletal fluorosis is a global problem, occurring in various countries, such as Ethiopia, Kenya and Tunisia (Rango et al., 2010, 2013; Olaka et al., 2016; Guissouma et al., 2017), India (Jacks et al., 2005; Vikas et al., 2013), China (Smedley et al., 2003; Guo and Wang, 2005; Guo et al., 2007; Amini et al., 2008; Wang et al., 2009; Currell et al., 2011), Brazil (Souza et al., 2013), and Pakistan (Farooqi et al., 2007a, 2007b; Rafique et al., 2015).

In Pakistan, the overuse and continuous consumption of groundwater for domestic purposes takes place mostly in semiarid and remote areas, potentially causing a deterioration in groundwater quality (Azizullah et al., 2011). Meanwhile, rapid industrialization, mining and

urbanization are major environmental issues in developing countries of the world, including Pakistan, India and China. Residents in some local communities even use mine-water for domestic purposes.

In the above context, we studied the contamination of groundwater with F[−] in a fluorite mining area in the flood plain of the River Swat, Pakistan. Specifically, we compared the chemistry of fluorite mine-water and surrounding groundwater, with the aim to: (1) identify the hydrogeochemical features responsible for the enrichment of groundwater with F[−], as compared with the depth profile of the aquifer; and (2) evaluate the health risk via Dean's classification (Dean and Elvove, 1935; Dean, 1942) for community fluorosis.

2. Study area

2.1. Profile of the study area

The selected flood plain area (Adenzai, Pakistan) is located at (34°–39°N, 71°–72°E) within a steep plain of the west-flowing River Swat and northwest-flowing River Panjkora. The rivers reach a confluence at Japan Bridge, near Matkhany. The area is located at the northern edge of Khyber Pakhtunkhwa (Fig. 1) and covers 120 km². The total population of the study area is 130,000. Topographically, the northeastern and southwestern portion is occupied by the foothills of Hindukush ranges. The study area included five fluorite mining zones and one control area in the flood plain of the River Swat, Adenzai (Fig. 1). The fluorite mines were previously drilled in the premises of Badwan, Chatpat, Ramial, Shamlie, Warsak and Osaky (Khaliq et al., 2007).

2.2. Climate, hydrology and hydrogeological settings

The region of Adenzai is situated in the northern part of Khyber Pakhtunkhwa and is characterised by semiarid climatic conditions of sultry summers and severely cold winters. The average annual maximum and minimum temperature recorded during summer and winter is 35 °C and −8 °C, respectively. Precipitation is bimodal, with peaks during the monsoons. The annual precipitation amount ranges from 254 to 1469 mm, falling mostly during the monsoon season (GOP, 1998). The mean rainfall in 2016 (the year of this study) was 19% lower than usual, although each monsoon still delivered large quantities of precipitation.

The regional hydrology reflects how residents in the various local areas consume groundwater sources differently, all of which are recharged mostly from precipitation. Shallow aquifers of groundwater have mostly low water tables and are used for drinking, domestic activities, agriculture, and industrial purposes. Inhabitants consume groundwater obtained from different sources, such as tube wells, hand pumps, dug wells, bore wells, and springs. Water from the municipal community tube well in the study area is delivered to residents through supply lines. The regional geological setting includes different formations (Fig. 2), such as Chilas complex, Indus suture melange, Khashala nokanai ghar and Saidu formations, Dir meta sediments, Quaternary alluvium, Kamila amphibolite, Kohistan batholith, Peshmal schist, Marghuzar and Duma formations, river beds, Shao formation and Utror volcanics, Swat and Mansehra granite complex. The complex geological setting of the study area includes different fluoride minerals present in the Kamila, Peshmal schist, Dir meta sediment and Swat

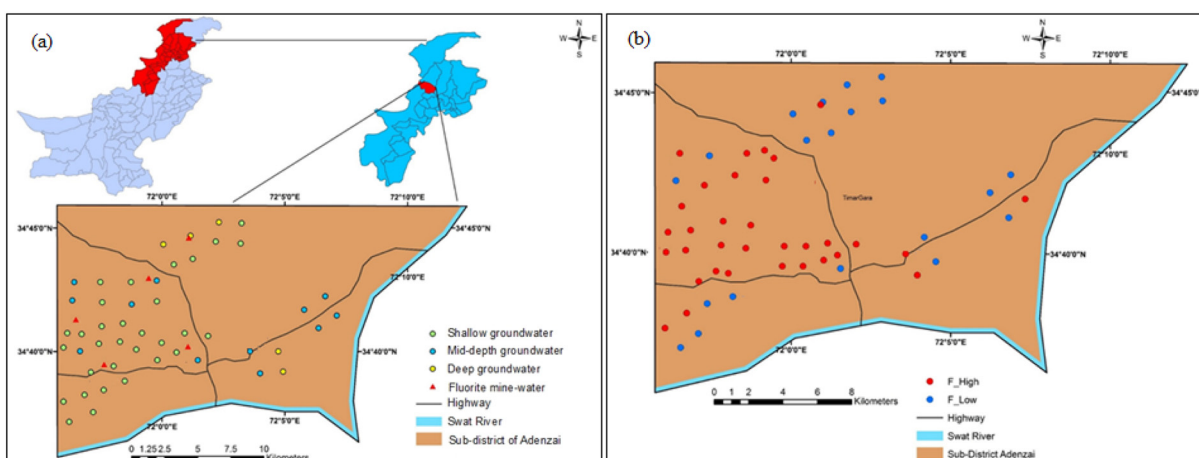


Fig. 1. (a) Map showing the locations of the groundwater samples in the flood plain area of the River Swat (Adenzai region, Pakistan). (b) Iso-concentration map of groundwater F^- .

granite formation. An understanding of the underlying geology and hydrogeochemical features is necessary to control groundwater properties and the chemical composition. It is also necessary, for minimizing the health risk due to fluoride exposure, to incorporate developmental approaches to the sustainable use of water (Fendorf et al., 2010).

3. Materials and methods

3.1. Collection and analysis of groundwater samples

Detailed hydrogeochemical investigations were carried out in the flood plain area of the River Swat (Adenzai), Pakistan. Specifically, groundwater ($n = 48$) and fluorite mine-water ($n = 5$) samples (covering high and low F^- concentrations) were collected from six villages during June 2016 (Fig. 1). Samples were obtained from various sources

(hand pump, open dug wells, bore wells, community tube well and fluorite mines). Among them, 30 groundwater samples were collected from shallow wells (24–40 m depth), 12 samples from mid-depth aquifers (48–65 m depth), and 6 samples from deep wells (85–120 m depth), with 5 samples from fluorite mine-water at shallow depth (29–36 m). A systematic grid sampling strategy was adopted for the collection of groundwater samples. Two systematic grids were designed in the form of a square grid at each location. The length of one side of the grid was 1000 m and each sample was collected from the middle of the grid (500 m), covering all four sides of the grid. Nearly all the grids were installed in densely populated areas of Adenzai (US EPA, 2002). Before sampling, a handheld GPS (HC Garmin) was used to determine the geographical coordinates of each individual sampling point (Fig. 1). At each source, the water wells were pumped for >5 min. The groundwater samples collected for determining the major

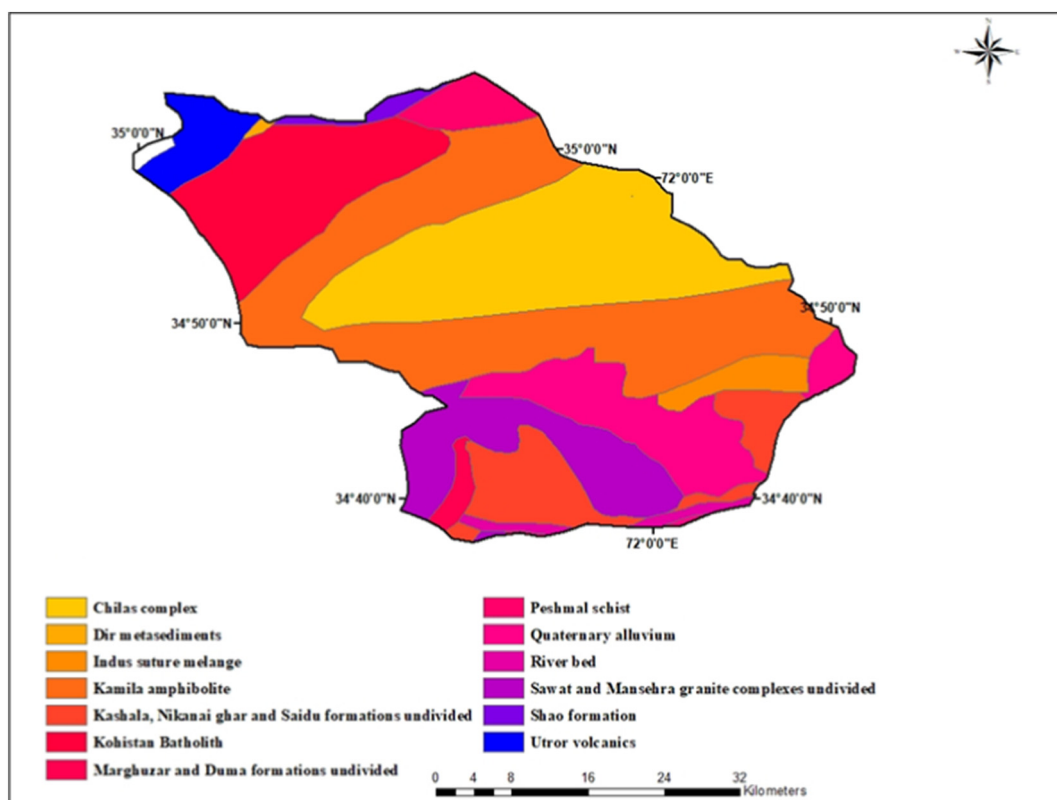


Fig. 2. Map showing the geology of the study area. Kamila amphibolite and Pashmal schist, as well as Swat and Mansehra granite complexes, contain plentiful fluoride minerals.

cations were filtered through Whatman filter paper (No. 0.42 μm), to protect not only the atomic absorption spectrophotometer (APHA, 1998) but also to ensure its accuracy. Samples were stored in 250 mL polyethylene bottles, which were properly rinsed and soaked twice with double deionized water. A duplicate sampling strategy was adopted for the collection of groundwater samples. Collected samples were preserved for cation analysis, by adding 2 to 3 drops of HNO_3 (65% purity) to bring the pH of the water samples down to <2.

The groundwater values of pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured in-situ using a portable Hanna instrument that was calibrated before use. The alkalinity was calculated via the titrimetric method, after immediate transportation of samples to the Hydrogeochemistry Laboratory of Environmental Sciences, University of Peshawar. The concentrations of sulphate (SO_4^{2-}), nitrate (NO_3^-) and phosphate (PO_4^{3-}) were measured using a UV visible spectrophotometer (DR 5000) following a standard turbid metric method, at wavelengths of 420, 410 and 690 nm, respectively (APHA, 1998 and 2005). Chloride (Cl^-) and F^- concentrations were measured through "Mohr's method and Fluoride Analyzer" ISE (ion-selective electrode), (HANNA Instruments manufactured by Japan, Model No. HI 5222 and HI 4110, type Solid-state; Combination). Several routine checks on standards were made according to Mandel and Shifan (1981) and Lloyd and Heathcote (1985). The ionic charge balance of cation and anion errors (ICBE) was calculated to check the analytical precision and accuracy of the groundwater data. The ICBE calculation was found to be within $\pm 5\%$, which defines the accuracy and validity of the water quality. Thus, the accuracy of the chemical analyses was satisfactory. The major cations, such as those of Ca^{++} , magnesium (Mg^{++}), sodium (Na^+) and potassium (K^+), in the groundwater samples, were analysed using a flame atomic absorption spectrophotometer (Varian Spectra AA-240, Australia) under standard operating conditions.

3.2. Statistical analysis

The variables were expressed as a range and mean with standard deviation. Statistical comparisons of F^- with groundwater variables and northing were designed in order to attain the degree of correlation, while linearity was assessed through the correlation coefficient (r) and coefficient of determination (R^2). The groundwater data were analysed statistically using SPSS software (version 20), XLSTAT software (2014 version), GIS (version 10.2.2), and PHREEQC interactive 2.11.

3.3. Principal component analysis

Principal component analysis (PCA) was used to infer the sources of groundwater pollution in terms of percentage contribution. The pollution load was calculated in an Excel spreadsheet by calculating the overall sum of water variables. The concentrations of each variable were divided by the overall sum, and then the overall sample results of individual variables were summed to obtain a pollution index (PI). The PCA was then determined by Varimax rotation via dimension reduction (rotation method: with Kaiser normalization). The three components, i.e., F1, F2 and F3, were extracted and interpreted with the PI. Then, the sheet was plotted in SPSS (version 20). The PI values were taken as dependent, while factors were loaded as independent values, to obtain the R^2 values. Similarly, the R^2 values for F1, F2 and F3 were obtained by leaving two factors as independent values. For simplicity, F1 was calculated by the sum of F2 and F3, while F2 was calculated by combining F1 and F3. Similarly, F3 was calculated by adding F1 and F2. The corresponding R^2 values were obtained from the model summary. Then, the individual differences for each component were calculated by subtracting the R^2 values of F1, F2 and F3 from the overall R^2 , followed by summation of all the differences to obtain the percentage contribution. The individual percentage contributions were obtained by

computing the individual component difference, multiplying by 100, and then dividing by the sum of the differences.

3.4. Saturation indices

To measure the equilibrium status of mineral phases and possibly control the dissolved chemical constituents of groundwater, saturation indices were calculated via the internet-based USGS package, PHREEQC (Parkhurst, 1995; Parkhurst and Appelo, 1999).

3.5. Health risk assessment and community fluorosis index

Clinical investigations were carried out among individuals of different gender and ages living together in the F^- endemic region of the target area. Community fluorosis index (CFI) values were calculated by examining the dental fluorosis symptoms. Seven categories were applied, according to Dean's classification (Dean and Elvove, 1935; Dean, 1942): normal, questionable, very mild, mild, moderate, moderately severe, and severe. Each class was given a numerical weighting from 0, 0.5, 1, 1.5, 2, 3 and ended on 4, as shown in (Fig. S2). Different individuals were examined and classified into various classes, and then the number of individuals in each class was multiplied by the Dean's classification numerical weight. The results calculated for different categories were added and their sum was divided by the total number of individuals examined:

$$\text{CFI} = \frac{\sum (\text{Number of individuals} \times \text{Dean's numericle weight})}{\text{Total number of individual examined.}}$$

when the CFI value exceeds 0.6, there is a public health issue in the study area.

The percentage prevalence of dental fluorosis was calculated by the ratio of the number of individuals afflicted with fluorosis to the total number of individuals surveyed. Higher secondary schools for both males and females in the F^- endemic region were visited in order to examine different age groups. A total of 285 male and 205 female students aged between 8 and 14 years, as well as 240 male and 145 female students aged between 15 and 30 years, were surveyed. Overall, the visit covered a total of 1005 men and 660 women aged from 25 to 60 years. People with dental fluorosis were examined and categorized with the assistance of a practicing dentist and a lady health worker. The investigating team recorded the water source consumption, eating, bathing and smoking habits, as well as the migration status, of the local residents. The water source choices in the survey included deep, mid-depth and shallow aquifers, community water supply, and mineral/bottled water.

4. Results and discussion

4.1. Major groundwater chemistry of hydrological settings

Table 1 lists the results on the hydrogeochemistry of groundwater and its assessment according to the specification of WHO (2004, 2011). For convenience of discussion, the groundwater samples were classified into three groups according to their depth: shallow (24–40 m), mid-depth (48–65 m), and deep (85–120 m). The charge balance of total cationic and anionic strength was calculated (meq/L) and found to be $\pm < 5\%$. However, overall, the hydrogeochemistry indicated widespread fluctuation.

The shallow groundwater was slightly alkaline, with pH values ranging from 7.2–8.3 (Jordana and Batista, 2004). The pH variability of groundwater causes alteration in the chemical composition of groundwater, and such alteration is mostly dependent on the lithology. The pH values of most groundwater samples were found to be within the WHO's guideline values. The depth, EC and TDS values of shallow groundwater ranged from 24 to 40 m, 210–1275 $\mu\text{s}/\text{cm}$, and

Table 1
Descriptive statistics of the groundwater chemistry of shallow, mid-depth and deep aquifers in the flood plain of the River Swat, Adenzai, Pakistan (n = 53).

Statistic	WHO	Shallow groundwater (n = 30); depth 24–40 m		Mid-depth groundwater (n = 12); depth 48–65 m		Deep groundwater (n = 6); depth 85–120 m		Fluorite Mine-water (n = 5); depth 29–36 m	
		Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD
pH	6.5–9.2	7.2–8.3	8 ± 0.3	7.2–7.8	7.52 ± 0.2	7.0–7.7	7.3 ± 0.3	8.1–8.3	8.2 ± 0.1
Depth m	–	240–40.0	35.0 ± 4.3	48.0–65.0	58.0 ± 10.0	85.0–120	94.2 ± 13.2	29.0–36.0	32.0 ± 3.0
EC µS/cm	400	210–1275	704 ± 259	330–930	728 ± 165	465–1110	687 ± 238	1785–1830	1805 ± 18.0
TDS mg/L	1000	126–765	423 ± 156	198–558	437 ± 99.0	279–666	412 ± 143	1071–1098	1083 ± 11.0
F mg/L	1.50	1.20–6.40	2.00 ± 1.00	1.00–2.30	2.00 ± 0.10	0.70–1.60	1.22 ± 0.30	7.30–8.50	7.90 ± 0.50
Cl mg/L	250	75.0–175	112 ± 24.0	35.0–112.0	87.0 ± 21.0	90.0–120.0	102.8 ± 12.8	80.0–95.0	87.0 ± 6.0
HCO ₃ mg/L	–	160.0–950.0	294.0 ± 135.0	185.0–330.0	261.0 ± 42.0	160.0–300.0	220.0 ± 48.6	600.0–640.0	626 ± 17.0
SO ₄ mg/L	500	85.0–230	157 ± 35.0	105–165	130 ± 21.0	75.0–145	119 ± 26.3	310–325	317 ± 6.00
NO ₃ mg/L	50	7.00–55.0	22.0 ± 12.0	5.00–28.0	18.0 ± 7.00	12.0–31.0	23.2 ± 6.2	11.0–15.0	12.8 ± 2.0
PO ₄ mg/L	0.1	0.10–20	0.30 ± 0.40	0.10–0.20	0.20 ± 0.03	0.10–0.20	0.14 ± 0.02	0.40–3.80	1.60 ± 2.00
Na mg/L	200	65.0–396	162 ± 74.0	50.0–180	103 ± 46	50.0–170	99.2 ± 54.7	350–390	371 ± 16.0
K mg/L	12	5.00–21.0	10.0 ± 3.00	0.10–12.00	7.00 ± 3.00	2.00–12.00	7.50 ± 4.20	2.00–6.00	4.00 ± 2.00
Ca mg/L	100	16.0–105	44.0 ± 24.0	31.0–95.0	58.0 ± 21.0	31.0–110	60.8 ± 30.7	14.0–25.0	20.2 ± 5.00
Mg mg/L	50	4.00–31.0	19.0 ± 8.00	10.0–30.0	22.0 ± 6.0	12.0–31.0	18.5 ± 7.0	8.0–15.0	11.6 ± 3.00

Note: SD, standard deviation.

126–765 mg/L, respectively. The considerable spatial variability in EC and TDS concentrations suggested that the groundwater chemistry was not homogeneous and controlled by different processes (Nagarajan et al., 2010). Bicarbonate and SO₄²⁻ were the most dominant anions, with their concentrations ranging from 160 to 950 mg/L and 85–230 mg/L, respectively (Table 1, Figs. 3 and S1). The dominant cation was Na⁺, with concentrations ranging from 65 to 396 mg/L. The halite dissociation is accountable for Na; if the molar ratio of Na⁺/Cl⁻ is ≥1, then the Na⁺ is the result of the weathering of silicate minerals (Meybeck, 1987). Here, the Na⁺/Cl⁻ ratio for the shallow groundwater

was 0.55–5.28 mg/L, indicating geogenic inputs of both halite and silicate minerals. The ionic concentrations in the shallow groundwater increased in the following order: HCO₃⁻ > SO₄²⁻ > Cl⁻ > NO₃⁻ > F⁻ > PO₄³⁻, and Na > Ca > Mg > K.

The mid-depth groundwater (n = 12) was slightly alkaline, with pH ranging from 7.2–7.8. The depth, EC and TDS, meanwhile, ranged from 48 to 65 m, 330–930 µS/cm and 198–558 mg/L, respectively. The dominant anion was HCO₃⁻, with concentrations ranging from 185 to 330 mg/L (Table 1, Figs. 3 and S1). The mid-depth groundwater had anionic and cationic concentrations in the following order: HCO₃⁻ > SO₄²⁻ > Cl⁻

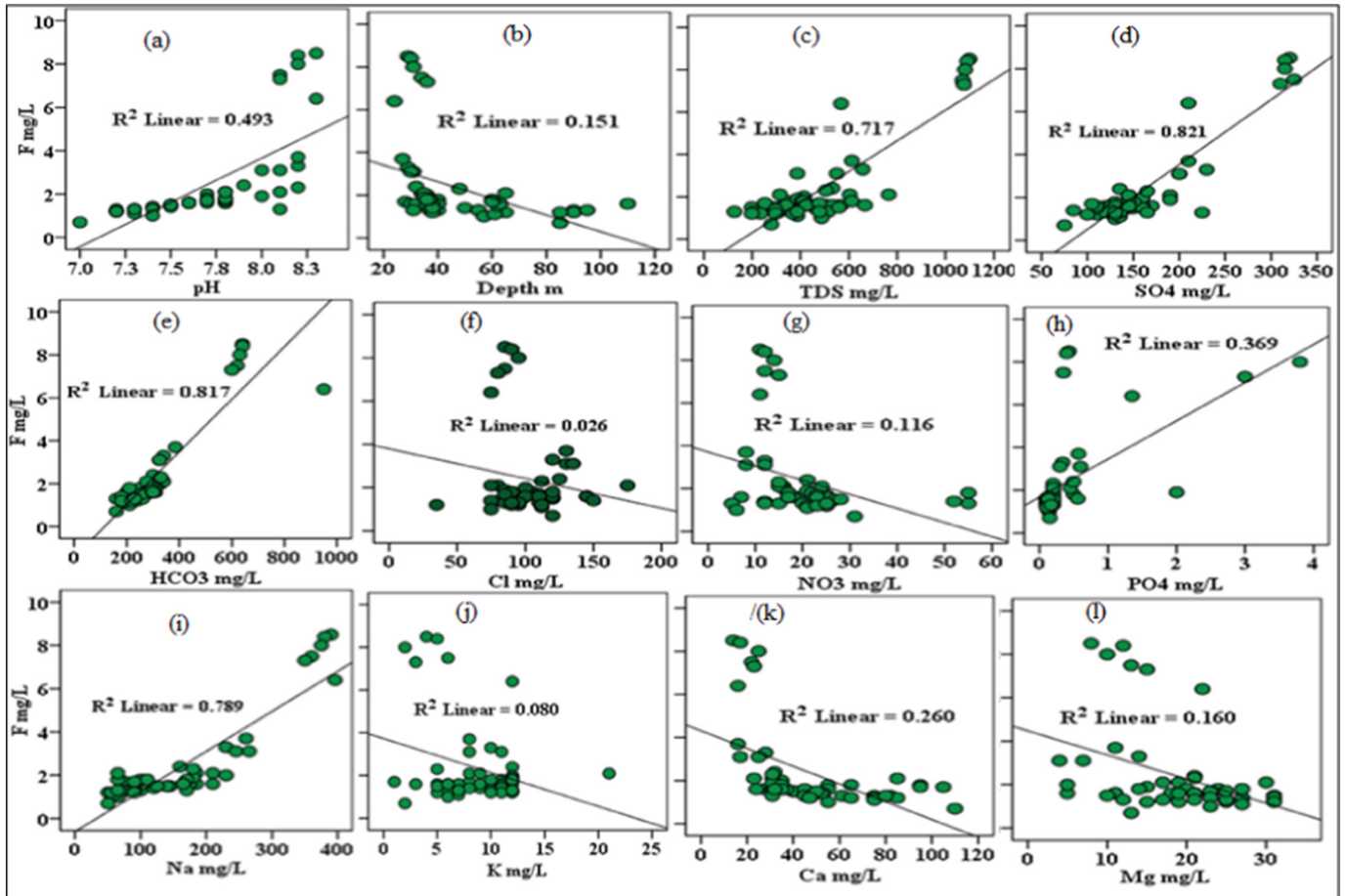


Fig. 3. Concentration profiles of F vs pH, depth, TDS, SO₄, HCO₃, Cl, NO₃, PO₄, Na, K, Ca and Mg, and the R² values of each variable.

$> \text{NO}_3 > \text{F} > \text{PO}_4$, and $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$, respectively. The anionic concentrations were within the WHO's guideline values, except F^- and PO_4^{3-} . The Na^+/Cl^- ratio for this depth of groundwater ranged from 0.54–1.89 mg/L, indicating that the Na^+ was triggered by the weathering of both halite and silicate minerals.

The deep groundwater samples showed narrow ranges of analytical data compared with the shallow groundwater. The pH was neutral to alkaline, ranging from 7.0–7.7. The depth, EC and TDS values ranged from 85 to 120 m, 465–1110 $\mu\text{S}/\text{cm}$ and 279–666 mg/L, respectively. The dominant anions were HCO_3^- and Na^+ , whose concentrations ranged from 160 to 300 mg/L and 50–170 mg/L, respectively. Whereas, the concentrations of Ca^{++} , Mg^{++} and K^+ were found to fall within the guideline values set by the WHO. The concentrations of Na^+ ranged from 170 to 200 mg/L and released F^- into the groundwater (Table 1, Figs. 3 and S1). Deep groundwater showed similar increasing ionic and cationic trends.

4.2. Fluorite mine-water chemistry

The fluorite mine-water was alkaline, with pH values ranging from 8.1–8.3. The depth, EC and TDS concentrations ranged from 29 to 36 m, 1785–1830 $\mu\text{S}/\text{cm}$ and 1071–1098 mg/L, respectively. The EC and TDS values exceeded the WHO's guideline values. The dominant ions were HCO_3^- and Na^+ , with their concentrations ranging from 600 to 640 mg/L and 350–390 mg/L, respectively. The concentrations of anions and cations in the fluorite mine-water increased in the following order: $\text{HCO}_3 > \text{SO}_4 > \text{Cl} > \text{NO}_3 > \text{F} > \text{PO}_4$, and $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$, respectively. The EC, TDS, Na^+ , PO_4^{3-} and F^- values exceeded the WHO's guidelines. The percentage contribution of each variable was 9.4% overall and 100% individually. The TDS values were mostly used to identify the different categories of groundwater (Table 1, Figs. 3 and S1). The overall hydrogeochemistry of the mine-water represented homogenous results and suggested that all the mine-water originated from the same source. The Na^+/Cl^- ratios, meanwhile, indicated the weathering of silicate and halite minerals, and their concentrations ranged from 3.95–4.59 mg/L.

4.3. Fluoride geochemistry

The F^- concentrations varied from 0.7–6.4 mg/L in groundwater and 7.3–8.5 mg/L in the fluorite mine-water. The shallow groundwater showed higher F^- concentrations, with a mean value of 2.0 ± 1.0 mg/L. Overall, the shallow groundwater wells (41.5%) had F^- concentrations that exceeded the WHO's guideline value. The F^- contamination in shallow aquifers is mostly the result of dissolution of fluorite minerals and other F^- -containing minerals in the host granite and gneissic rocks. Individually, the shallow groundwater aquifers contributed 73.3% $\text{F}^- > 1.5$ mg/L, at depths from 24 to 40 m (Table 1, Fig. 3 and S1). However, the presence of granitic rocks integrated with fluorite

minerals, and the weathering of silicate minerals, determined the elevation of F^- in groundwater (Fig. 4). The mid-depth and deep groundwater had low F^- concentrations: values ranged from 1.0–2.3 mg/L, with mean values of 2.0 ± 0.1 mg/L, in the mid-depth sources; and from 0.7–1.6 mg/L, with mean values of 1.2 ± 0.3 mg/L, in the deep groundwater sources. The groundwater well samples collected from shallow aquifers with depths < 40 m had F^- concentrations above the WHO's guideline value.

As the distance from the River Swat increased towards the fluorite mining areas, the F^- concentrations also increased. Therefore, 62.3% of all groundwater samples in the study area were heavily contaminated with F^- (Fig. 1b). The adjacent fluorite mine-water showed higher F^- concentrations. The range, mean and standard deviation were 7.3–8.5 mg/L, 7.9 mg/L and ± 0.5 mg/L, respectively. However, five mid-depth and one deep groundwater source (W1, W4, C4, C7, C8 and R7) had F^- concentrations > 1.5 mg/L. The individual percentage contribution of the mid-depth and deep groundwater was 33.3%, and the overall contributions were 9.4% and 1.8%, respectively.

Spatially and physico-geographically, the concentration of F^- in groundwater increased in the following order: Badwan $>$ Chatpat $>$ Ramaiyal $>$ Warsak $>$ Osakay $>$ Rambora (control area). Similar F^- trends were observed depth-wise, as follows: shallow $>$ mid-depth $>$ deep (Fig. 1). In such cases, the groundwater flow rate generally plays a key role in the formation of higher F^- concentrations in groundwater (Kim and Jeong, 2005). Also, foothills and mountain-front, less residence time of rock mineral and water, water regime, and insignificant contact time between water and minerals are factors that tend to reduce dissolved concentrations of the groundwater (Kim and Jeong, 2005). In our study, those regions located relatively farther away from the flow path of the River Swat were more F^- -enriched, due to the long distance and high residence time (HRT). The F^- enrichment in far most regions from River Swat is progressively increases due to (HRT). Thus, the prevalence of fluorosis in the study area was attributed to F^- -bearing minerals in the host granite, gneiss rocks and the presence of fluorite mines. Na^+ contributed 68% of all cations, while HCO_3^- contributed 67% of all anions (Fig. S3).

The occurrence of F^- in the deep and mid-depth aquifers results from mixing with shallow groundwater in the vadose zone. Furthermore, the weathering of rocks and ion exchange processes promote the dissolution of F^- in the study area. The source water, along with the introduction of F^- -containing minerals, determines the chemistry of the groundwater. It is the main factor controlling the dissolution rate of toxic ingredients during the formation of contaminated water. Variables like pH, Na^+ , HCO_3^- , OH^- and Ca^{++} play a significant role in the formation of F^- -contaminated water (Fordyce et al., 2007; Guo et al., 2010; Young et al., 2011). The dissolution of biotite and muscovite contains F^- at the OH^- sites (see reactions (4), (8) and (9)). OH^- displaces the F^- ion owing to similar ionic radii and, as a result, exchange takes place in the structure of the mineral matrix. The interaction

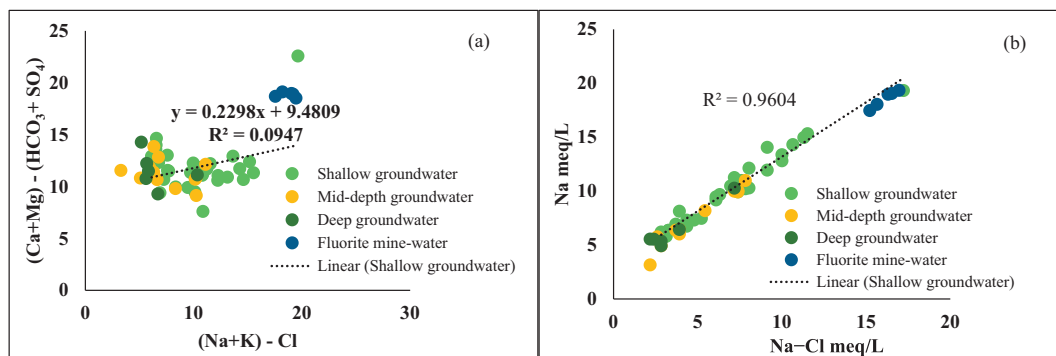
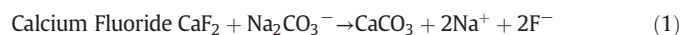


Fig. 4. Ion exchange processes describing the exchange behavior of Na^+ with Ca^{++} as a result the Na^+ released into the groundwater. (b) Na^+ to Na-Cl meq/L ratio and the contribution of Na^+ from meteoric water origin, balanced by meq concentrations of Cl^- .

between water and rock triggers the release of F^- into the water body, and hence the quality of the water deteriorates (Chidambaram et al., 2003; Jacks et al., 2005; Guo et al., 2007; Dar et al., 2011). Generally, examination of TDS and Na^+ concentrations in groundwater can reveal the effects of geogenic influence (Naseem et al., 2010).

The geology of the study area, as defined by Khaliq et al. (2007), includes hard rocks, like granite gneiss, quartzite, albite, quartz, hematite, pegmatites, sericite, fluorite and hornblende apatite, and the long-term interactions of these rocks with water has produced F^- -rich groundwater. The dissolution of fluorite minerals contaminates the groundwater as follows:



when the Ca^{++} concentrations are too high, the F^- precipitates as CaF_2 :



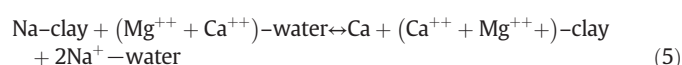
Reactions (1)–(4) represent the geochemical processes in which Ca^{++} are precipitated, while Na^+ and F^- are triggered into the groundwater aquifer.

4.4. Controlling role of major chemistry in fluoride behaviour

In most parts of the world with arid and semiarid climatic conditions, groundwater F^- concentrations are promoted by evaporation and evapotranspiration (Jacks et al., 2005). This mechanism explains the little portion of our study area. The concentrations of F^- correlated strongly or moderately with pH (0.70), EC (0.85), TDS (0.82), HCO_3^- (0.90), SO_4^{2-} (0.90), PO_4^{3-} (0.60) and Na^+ (0.89), while there was an inverse relationship with Ca^{++} (−0.51) (Table S1). Similarly, the values of the coefficients of F^- with other hydrogeochemical variables, like pH, TDS, SO_4 , HCO_3 , Na^+ and Ca^{++} , were 0.49, 0.71, 0.82, 0.81, 0.78 and 0.30 (Fig. 3), respectively. Thus, the higher values of the above-mentioned observations can be explained by the different sources in the study area. The pH variability will cause an alteration in the chemical composition of the groundwater. Sometimes, anthropogenic pollution also changes the pH of groundwater, which plays an important role in the mobility and dissolution of mineral matrices. Carbonate-enriched sedimentary rock is an important geogenic source of HCO_3^- in groundwater (BIS, 2004). Meanwhile, a common source for SO_4 will be gypsum dissolution and agriculture fertilizer (Guo and Wang, 2005). Sodium ions in the study area are extremely mobile and soluble owing to cation exchange processes and the weathering of halite and silicate minerals. The mobility of F^- in igneous geography is clearly understood (Edmunds and Smedley, 2005; Shaji et al., 2007; Reddy et al., 2010), in association with alluvial aquifers (Guo et al., 2010; Kim et al., 2012). Numerous dynamic factors control the movement of F^- in groundwater, such as CaF_2 dissolutions and $CaCO_3$ precipitation, which have been shown to be triggers for F^- entering the natural water system (Currell et al., 2011). Fluoride is also released into groundwater via adsorption/desorption and sorption mechanisms, which are mostly controlled by the environmental conditions being neutral to acidic (Kim et al., 2012).

Cation exchange is an important process that triggers the movement of F^- from F^- -bearing minerals into groundwater. The F^- minerals in sedimentary, metamorphic and igneous granitic terrain are of prime importance in base ion exchange processes (Apambire et al., 1997; WHO, 2004, 2011; Fawell et al., 2006). These processes involve the exchange of Na^+ with Ca^{++} during water circulation in the weathering zone. The values of $Ca^{++} + Mg^{++}$ and $HCO_3^- - SO_4^{2-}$ were plotted against $Na^+ - Cl^-$ to understand the ion exchange processes (Mondal et al., 2014), (Fig. 4a). These processes occur when the condition is alkaline,

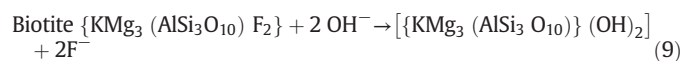
allowing Na^+ and Ca^{++} to exchange positions in the mineral matrix and, as a result, the Na^+ is released into the water and Ca^{++} is precipitated. This ion exchange process ultimately triggers the movement F^- into the surrounding groundwater aquifer. The solubility of calcite and dolomite is determined from the difference of (HCO_3^- and SO_4^{2-}) – (Ca^{++} and Mg^{++}). Similarly, Na^+ contribution from meteoric genesis will be balanced by meq concentrations of Cl^- . Thus, Cl^- concentrations were obtained by subtracting Cl^- from Na^+ . Therefore, cation exchange processes controlled the ionic composition of groundwater samples. The relationships among hydrogeochemical parameters should be linear. The R^2 between ($Ca^{++} + Mg^{++} - HCO_3^- - SO_4^{2-}$) and ($Na^+ + K^+ - Cl^-$) was 0.96 (Fig. 4b), suggesting the participation of Ca^{++} and Mg^{++} during the ion-exchange reaction. The Na^+ will be absorbed on the surface of the clay mineral matrix, and the Ca^{++} in the water will trigger Na^+ , further resulting in the mobilization of F^- into the aquifer. This hypothesis is confirmed by the high Na:Ca ratios (average value: 5.6) of the water samples analysed in this study, and further supported by the work of Xiao et al. (2015a, b). The ion exchange equation takes place as follows:



Alkaline pH values and low Ca^{++} concentrations will promote the release of F^- into the groundwater (Jacks et al., 2005). Therefore, the dependency of fluorite (CaF_2) dissolution is mostly related to high HCO_3^- concentrations (Guo et al., 2007; Saxena and Ahmed, 2003). During water circulation, the enrichment of Na^+ and precipitation of Ca^{++} occurs. The reaction of F^- -bearing minerals with different chemical species like fluorite, biotite, and muscovite in the groundwater aquifer in our study area can be summarised as follows:



Eqs. (1) and (2) (Section 4.3) describe the mechanisms triggering the movement of F^- into groundwater. Scientists have reported that OH^- and F^- exchange places owing to similar ionic radii. Reactions (8) and (9) describe this mechanism:



The fluorite dissolution reactions in groundwater with relatively higher HCO_3^- concentrations are thermodynamically supported by Eq. (2) (Section 3.3). Our findings are also supported by earlier geochemical investigations by Chinese, Indian and Pakistani researchers (Farooqi et al., 2007a, b; Rafique et al., 2009; Guo et al., 2010; Xiao et al., 2015a, b). Relatively high concentrations of both HCO_3^- and Na^+ in groundwater can significantly promote the dissolution of F^- in an alkaline environment. The interaction of groundwater with underlying geological setting of the aquifer helps in triggering of F^- (Li et al., 2011). These observations are further supported the PCA-MLR analysis results, which identified the F^- pollution sources. We believe that a ratio of $Ca:HCO_3 > 1$ suggests geochemical conditions conducive to the dissolution of F^- (Saxena and Ahmed, 2003).

4.5. Geochemical modeling of mineral phases

The most important F^- enrichment mechanism in groundwater is attributed to saturation indices, i.e., the thermodynamic trend of minerals to dissolve or precipitate, by computing the mineralogical data of

the underlying groundwater (Deutsch, 1997). Under-saturation illustrates either a short contact time or an insufficient volume of mineral concentrations in the groundwater. Over-saturation, on the other hand, indicates groundwater enriched with dissolved substances in the aquifer, because of the longer contact time with the internal geological setting, thus releasing the chemical constituents into the groundwater to reach equilibrium. Higher temperatures, reduced rainfall and rate of evaporation in semiarid climatic condition are the factors that exceed the calcite precipitation in the groundwater. The saturation indices calculated for 53 groundwater samples and their mineralogical results for calcite and fluorite, as well as fluorite and dolomite, are shown in (Fig. 5). The saturation indices (SI), relationship with respect to calcite and fluorite indicated that the upper-left quadrant contained 29 groundwater samples, which contributed 54.7% of the total, thus indicating saturation of fluorite and under-saturation of calcite (Fig. 5a). This relationship probably reflects the greater kinetics of calcite precipitation, as compared with fluorite dissolution (Edmunds and Smedley, 2005). Conversely, 20 groundwater samples in the lower-left quadrant constituting 37.7% of the total groundwater indicated that both calcite and fluorite were saturated (Fig. 5a).

Four fluorite mine-water samples were supersaturated with both fluorite and calcite, which contributed 80% individually and 7.5% overall. Although groundwater is commonly under-saturated in terms of fluorite, it can be supersaturated with both fluorite and calcite in many regions of the world (Handa, 1975). In our study, the solubility of fluorite was low, and F^- enrichment was frequently associated with relatively lower R^2 values (e.g., $R^2 = 0.3$) of Ca^{++} (Table S1, Fig. 3). The F^- concentrations in groundwater are predominantly controlled by the oversaturation of calcite – specifically, in granite gneiss rock – because of cation exchange process and water–rock interactions. The likely major controlling processes in our study area are cation exchange and water–rock interaction. Both CaF_2 and $CaCO_3$ provide Ca^{++} , which controls the composition of the groundwater. Hydrogeochemical studies have previously revealed that Ca^{++} , CO_3^- and F^- are interdependent (Rafique et al., 2008, 2009). Here, the relatively low solubility of calcite indicated relatively higher concentrations of F^- in the groundwater.

The saturation indices of CaF_2 and $CaCO_3$ ranged from -1.21 to -0.29 and from 0.33 to 0.79 for fluorite and calcite in groundwater, respectively; whereas, they ranged from -0.06 to 0.14 and 0.55 to 0.71 for fluorite and calcite in the fluorite mine-water. The mean concentrations ranged from -0.87 to 0.15 in the groundwater and from 0.03 to 0.58 in the mine-water. Similarly, the saturation indices for both CaF_2 and dolomite ranged from -1.21 to -0.29 and from -1.14 to 2.08 for fluorite and dolomite in groundwater; whereas, they ranged from -0.06 to 0.14 and from 1.2 to 1.36 for fluorite and dolomite in the fluorite mine-water (5b). The mean concentrations ranged from -0.87 to 0.27 for groundwater and from 0.03 to 1.27 for mine-water. Moreover, cation exchange processes will increase the level of $CaCO_3$ precipitation under

alkaline conditions by removing Ca^{++} from the groundwater. Therefore, a Ca^{++} -deficient environment will be created owing to CaF_2 dissolution. The released Ca^{++} will combine with CO_3^{2-} to form $CaCO_3$, which is a precipitant in the groundwater. Therefore, CaF_2 under-saturation might result from $CaCO_3$ precipitation, and thereafter the Ca^{++} actively allows more CaF_2 to dissolve. Thus, both supersaturation and under-saturation regarding CaF_2 and $CaCO_3$ dissolution were found in the groundwater samples (Fig. 5a). Meanwhile, NaF and MgF_2 were also under-saturated, and their dissolution predominantly contributed to the F^- in the associated groundwater samples.

4.6. Mechanisms controlling the groundwater chemistry

A Gibbs scatter diagram (Gibbs, 1970) can be used to estimate the influences of different mechanisms, such as (in this case) evaporation, precipitation and rock weathering. Factors like bedrock mineralogy, groundwater movement and climatic conditions control the groundwater composition; hence, to evaluate the influence of hydrogeological interactions on the groundwater data, a Gibbs diagram was designed. It established the association between water composition and aquifer geology, and allowed us to discuss the three controlling processes of rock dominance, evaporation and atmospheric precipitation. To understand the controlling mechanism, the groundwater data were arranged by plotting the TDS concentrations versus the weight ratios of the cations ($Na^+/Na^+ + Ca^{++}$) and anions ($Cl^-/Cl^- + HCO_3^-$) (Fig. 6). Almost all the groundwater samples, including the fluorite mine-water, fall into the rock dominant region. The diagram indicates the local hydrogeological setting and weathering phenomena play a leading role in the composition of the groundwater chemistry. Alongside rock dominance, cation exchange is another reasonable mechanism dictating the composition of the water chemistry in the study area. The Na^+ and Ca^{++} concentrations, both in the groundwater and fluorite mine-water exceeded, along the groundwater flow path of surrounding areas (Fig. 6). Although, the Na^+ concentrations were more evident than the Ca^{++} concentrations (Table 1).

4.7. Identification of potential pollution sources

Identification of the potential pollution sources helps in minimizing the number of variables with a relatively high loading and facilitates the interpretation of the PCA–MLR results. These results, based on 14 hydrogeochemical observations of 53 groundwater samples, are presented in Table S2. The PCA results indicate that the variations among groundwater and fluorite mine-water were minor (Table 1), when both were analysed together. The assessment of groundwater revealed three major eigenvalues and 14 loading factors (Fig. 7a). The three factors, F1, F2 and F3, were obtained with an eigenvalue >10 and described 71.3% of the total variance. The first factor (F1) contributed the

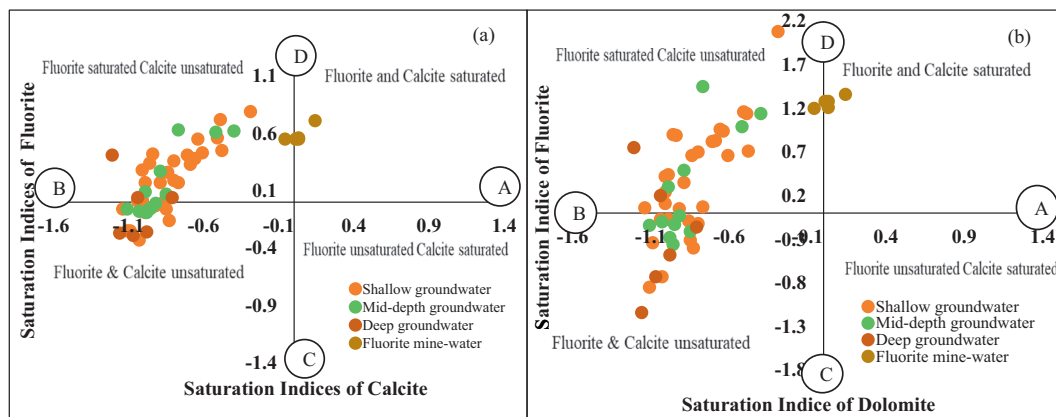


Fig. 5. Saturation indices of the mineral phases between (a) fluorite and calcite, and (b) fluorite and dolomite, of the flood plain area of the River Swat (Adenzai region, Pakistan).

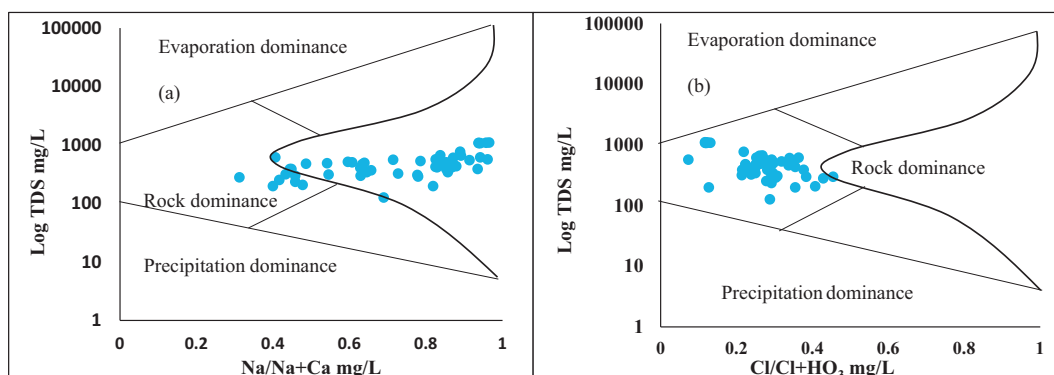


Fig. 6. Schematic diagram of the major ion chemistry and mechanisms controlling the groundwater of the flood plain area of the River Swat (Adenzai region, Pakistan): (a) Na/Na + Ca mg/L versus Log TDS; (b) Cl/Cl + HCO₃ mg/L versus Log TDS.

maximum variability (52.4%) with an eigenvalue of 7.34. In terms of the percentage contribution, PCA–MLR plays a leading role in defining the pollution source. The PCA results represent different groups in the form of factors like F1, F2 and F3, while the different factors of the PCA and their source apportionment are described as follows:

Component F1 is predominantly weighted by F^- and other hydrogeochemical variables like pH, EC, TDS, Na^+ , SO_4^{2-} , HCO_3^- , PO_4^{3-} , Ca^{++} and Mg^{++} , and their correlation coefficients were calculated to be 0.83, 0.85, 0.75, 0.93, 0.88, 0.90, 0.63, 0.96, -0.70 and -0.55 , respectively (Table S2). These components describe the ionic strength, i.e., the major cations and anions resulting from water–rock interaction and mineral weathering (Fig. 8), (Purushotham et al., 2011). Therefore, natural processes play a major role in the existence of F^- in the flood plain area of the River Swat in the Adenzai region of Pakistan. The substantial contribution of component F1 mostly resulted from natural processes, including carbonate ($CaCO_3$) weathering and the dissolution of aluminosilicate minerals, like feldspar, biotite, fluorite, muscovite, calcite and dolomite, significantly controlling the groundwater chemistry. The origin of HCO_3^- includes carbonate dissolution and the biological degradation of organic matter. The correlation efficacy of Na^+ and HCO_3^- was 0.77. Therefore, alkaline climatic conditions promote the dissolution of F^- . Overall, the percentage contribution of component F1 was 75.4%, due to mineral weathering, water–rock interaction and ion exchange processes (Ayoob and Gupta, 2006; Latha et al., 1999; Young et al., 2011) (Table S2, Fig. 8).

The second component, F2, contributed 10.9% of the total variance, with an eigenvalue of 1.53. Strong loading for Cl^- and K^+ was apparent, with correlation coefficients of 0.59 and 0.64, respectively. The variables identified in the first two principal components are plotted, as small and large ellipses, respectively, in (Fig. 7b). The percentage contribution of component F2 was 11.2% (Fig. 8), which identified anthropogenic

pollution in the study area in terms of mining activities, agricultural practices, domestic activity, and septic tanks. The origin of K^+ and Cl^- includes chemical fertilizers used in agricultural practices, industrial and sewage effluents, and septic tanks (Bohlke and Horan, 2000; Petelet-Giraud et al., 2003; Edmunds et al., 2003), as well as solid waste generated from household activities. In contrast, K^+ can be attributed to muscovite feldspar, orthoclase and plagioclase minerals, which are mostly found in granite rock and salt deposits containing syvite (KCl). Moreover, agricultural practices and domestic waste also lead to pollution in the study area.

The third component, F3, accounted for 8.01% of the total variability, with an eigenvalue of 1.12. A high loading of NO_3^- and Mg was indicated, with correlation coefficients of 0.39 and 0.57, respectively (Table S2). The percentage contribution for component F3 was 13.5%, which revealed a mix of pollution, i.e., natural and anthropogenic. The NO_3^- contamination resulted from agricultural practices including NO_3^- fertilizers in the form of KNO_3 , urea, animal manure and sewage effluent (Fig. 8) (Edmunds et al., 2003). Whereas, Mg^{++} originated from dolomite dissolution present in the underlying geological setting of the study area. The PCA–MLR results support the hydrogeochemical processes, as described in Sections 4.2, 4.3 and 4.4.

4.8. Hydrochemical facies of the study area

Groundwater F^- concentrations mostly depend on various chemical features (Chadha and Tamta, 1999). Chadha diagrams can be used to summarize the relationship between the distribution of F^- and the groundwater composition (Fig. 9) (Chae et al., 2007; Gao et al., 2007; Rafique et al., 2015). Chadha and Tamta (1999) recommended a hydrogeochemical pattern for the classification of groundwater by plotting the difference between anions and cations in terms of $\{HCO_3^-$ and Cl

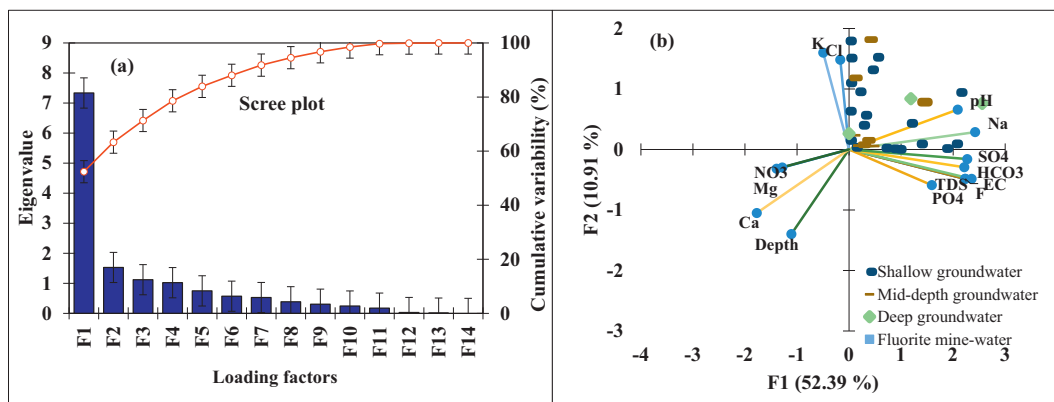


Fig. 7. (a) Loading factors of the PCA–MLR results. (b) Relationship between the first two loading factors (F1 and F2), after Varimax rotation.

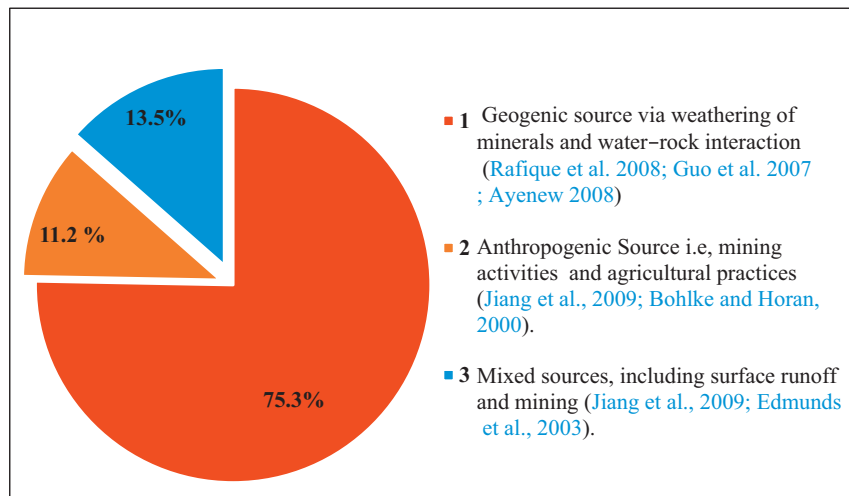


Fig. 8. Contributions of pollution sources (%) in the groundwater of the study area.

+ SO₄) concentrations, in meq/L, represented as percentage versus {(Ca + Mg) and (Na + K)} concentrations, in meq/L, also expressed as a percentage (Chadha and Tamta, 1999). The Chadha diagram is an expanded version of the Durov diagram (Durov, 1948; Piper, 1944). The resulting figure has four fields, which describe different types of hydrogeochemical processes responsible for water-type formations (Fig. 9). More than half ($n = 29$) of the samples had an NaHCO₃ water type, and $n = 17$ groundwater samples were of CaHCO₃ water type; whereas, $n = 2$ mid-depth groundwater samples were Ca-Mg-Cl in type, and all fluorite mine-water samples ($n = 5$) fell into the category of NaCl type (Tables 3 and 4; Fig. 9). The classification of these major ions was based on the well depth. However, Na⁺ tended to be the dominant cation in the shallow groundwater, whereas Ca⁺⁺ and Mg⁺⁺ tended to be higher in the mid-depth and deep groundwater sources.

Our hydrogeological investigations indicate that the groundwater of the flood plain area of the River Swat is predominantly NaHCO₃ in water type. The hydrogeochemical profile shows a decline in Ca⁺⁺ and an increase in Na⁺ concentrations. The anions remain dominated by HCO₃⁻. Thus, the groundwater from shallow origins comprises relatively higher concentrations of dissolved species. The facies classification indicated

the following water-type pattern: NaHCO₃ < CaHCO₃ < NaCl < Ca-Mg-Cl. Our observations are supported by the findings of Chae et al. (2007), who reported higher F⁻ associated with the NaHCO₃ water type in the underlying geological setting of Korea. During base ion exchange processes, both Ca⁺⁺ and Mg⁺⁺ species react with clay minerals, such as Na⁺ montmorillonite, which releases Na⁺ to form the NaHCO₃ water type (Hounslow, 1995). This process often gives rise to higher F⁻ (Boyle 1992).

Both recharge and the weathering of silicate and carbonate minerals are responsible for the formation of the CaHCO₃ water type (Mamatha and Rao, 2010). Reverse ion exchange processes are responsible for the Ca-Mg-Cl water type, while the NaCl water type identifies evaporation processes. Rafique et al. (2009) documented the formation of the NaCl water type in the study area. The Chadha diagram classified the anion composition (Table 4, Fig. 9) by providing the linear correlation for the anion formation between HCO₃⁻ and (Cl⁻ + SO₄²⁻), suggesting they have common origins as major contaminants, e.g., household waste and agricultural practices.

4.9. Community fluorosis prevalence

The CFI and prevalence of dental fluorosis and their percentage incidences are given in Table 2. To judge the health risk, Dean's formula was used to calculate the CFI. Specifically, five fluoride endemic areas and one control site were selected from the flood plain area of the River Swat. These endemic regions were present within the fluorite mining zone. People of all ages from the study area were at high risk of fluorosis. The CFI values were similar to those reported by Viswanathan et al. (2009). All sites showed high concentrations, except the control area. The CFI and percentage prevalence of fluorosis in all endemic regions were as follows (in boys and girls, respectively): Badwan, (1.85, 1.87) and (54, 53)%; Chatpat, (2.01, 1.93) and (58, 63)%; Ramial, (1.75, 1.63) and (50, 49)%; Osaky, (1.26, 1.73) and (29, 50)%; and Warsak, (2.08, 1.59) and (67, 51)%. For male and female adults, meanwhile, the results were: Badwan, (1.57, 1.69) and (46, 46)%; Chatpat, (1.53, 1.42) and (41, 40)%; Ramial (1.5, 1.47) and (42, 46)%; Osaky (1.5, 1.43) and (37, 42)%; Warsak (1.6, 1.63) and (43, 45)% (Table 2). The CFI and percentage prevalence indicated that teenage males and females (particularly the latter) are at high risk. The likely reason is that females tend to be household managers, performing much of their work in their homes on a daily basis. They have little chance or need to leave their home town; therefore, the younger generation is mostly affected by fluorosis.

A well-structured interview was designed to gather valuable information on people's choices of drinking-water sources, such as deep, mid-depth or shallow groundwater; mineral/treated bottled water; or

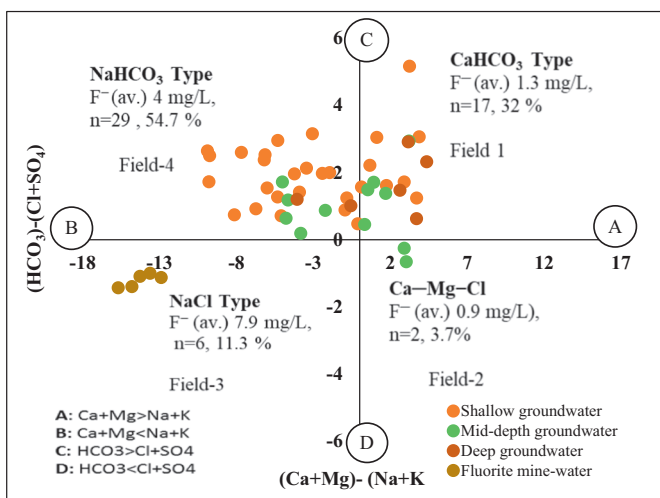


Fig. 9. Chadha diagram identifying the different water type formations in the groundwater of the flood plain of the River Swat (Adenzai region, Pakistan). Field 1: Ca-HCO₃ type water, representing both recharge and weathering processes. Field 2: Ca-Mg-Cl type water, reflecting reverse ion-exchange processes. Field 3: Na-Cl type water, indicating evaporation is the principle mechanism. Field 4: Na-HCO₃ type water, reflecting cationic and ionic exchange processes.

Table 2

Community fluorosis index and percentage prevalence of dental fluorosis in the flood plain area of the River Swat, Pakistan.

Location	Group	No. of individuals examined according to Dean's classification							Total individuals	Community fluorosis index	Percentage of fluorosis incidence
		0	0.5	1	1.5	2	3	4			
Badwan	Boys	5	7	8	10	18	10	7	65	1.85	54
	Girls	3	7	4	7	11	8	5	45	1.87	53
	Male	35	27	33	40	75	25	15	250	1.57	46
	Female	12	21	25	17	30	25	10	140	1.69	46
Chatpat	Boys	2	4	6	5	7	13	3	40	2.01	58
	Girls	2	5	2	3	11	5	3	30	1.93	63
	Male	27	13	25	15	25	18	12	135	1.53	41
Ramial	Female	25	10	15	10	18	17	5	100	1.42	40
	Boys	2	8	4	6	10	7	3	40	1.75	50
	Girls	5	3	7	3	9	6	2	35	1.63	49
Osaky	Male	31	14	25	20	35	20	10	155	1.50	42
	Female	28	15	15	7	30	17	8	120	1.47	46
	Boys	8	6	5	6	5	3	2	35	1.26	29
	Girls	4	3	5	3	7	5	3	30	1.73	50
Warsak	Male	25	30	30	25	30	20	15	175	1.50	37
	Female	16	15	13	8	23	10	5	90	1.43	42
	Boys	5	2	10	3	18	15	7	60	2.08	67
	Girls	7	5	3	2	10	5	3	35	1.59	51
Control	Male	25	20	23	17	28	22	15	150	1.6	43
	Female	17	13	10	15	20	16	9	100	1.63	45
	Boys	0	0	0	0	0	0	0	65	0	0
	Girls	0	0	0	0	0	0	0	45	0	0
Control	Male	0	0	0	0	0	0	0	140	0	0
	Female	0	0	0	0	0	0	0	110	0	0

municipal community water. The variation in the degree of fluorosis with respect to the source of drinking water followed an increasing pattern as follows: shallow > mid-depth > deep > municipal community water > mineral/bottled water. Generally, most people consumed shallow groundwater. People in different age groups, such as children between the ages of 8 and 14, and adults between 15 and 62, were investigated. The daily intake of water for adults was eight to ten cups, whereas children drank less than three cups (the storage capacity per cup was 500 mL, approximately). Most adults were involved in agricultural activities on a daily basis, and thus needed to drink more water. People in the study area used shallow groundwater for the following two reasons: (1) high electricity load shedding; and (2) lack of municipal water supply. People were compelled to use traditional methods to draw water from shallow aquifers, which was then mostly used for drinking, cooking, bathing, and washing clothes. Recalling that our results indicated the shallow groundwater in this region contains high F^- concentrations (Table 1), the reason why most people – and specifically the younger generation – suffer from dental fluorosis becomes clear (Fig. S2). If people have a chance to use relatively deeper groundwater sources, this would be beneficial, as the chemistry of such sources in terms of fluoride status means it is much safer for domestic use.

The survey also gathered data on the nutritional status of local inhabitants, which indicated a main diet of food plants and vegetables such as wheat, maize, rice, spinach, onion, garlic, pumpkin and pea. Wheat was predominantly used as a food supplement, while some people consume rice once a day. Vegetables are the predominant food of the people in the study area. All inhabitants consume foods grown in their fields, and these food sources are irrigated using shallow groundwater, which ultimately contaminates the agricultural soil, reduces the quality of the food, and increases the health risk via nutrient uptake.

Table 3Distribution of F^- in the groundwater of the flood plain area of the River Swat, Pakistan.

Range of F^-	No. of samples (n)	Percentage distribution
<1.5	17	32%
1.5–3.0	26	49%
3.0–5.0	4	7.5%
> 5.0	6	11.3%

Furthermore, weathering, erosion and surface runoff may also contaminate the fields and surrounding shallow aquifers. Plus, mining activities along with the exploration and installation of new bore wells will have enhanced the level of groundwater pollution in the study area. The prevalence of fluorosis was found to increase progressively with greater use of shallow groundwater (Fig. S2). Nearly 62.2% individuals were afflicted with more than a mild degree of fluorosis, and therefore the CFI values were greater than normal.

5. Conclusion

To the best of our knowledge, this study represents the first attempt to investigate the occurrence and prevalence of F^- in the groundwater of the flood plain of the River Swat, Pakistan. Shallow groundwater has been found to be unfit for drinking purposes, due to its relatively high F^- concentrations. Long-term water–rock interactions and the occurrence of fluorite minerals in the granite gneissic terrain releases F^- into the groundwater of an area clustered at the distal end (northwest) of the Adenzai region. The under-saturation of fluorite minerals suggests that, besides fluorite minerals, other F^- -bearing minerals, e.g., biotite and muscovite, are present, which invariably contribute F^- to the groundwater system. The concentrations of F^- in the groundwater aquifers increase in the following pattern: shallow > mid-depth > deep. Analysis of the hydrogeochemical facies (water types) indicates that 54.7% of samples are $NaHCO_3$ in type, 36% are $CaHCO_3$, and 9.4% are $NaCl$. A Gibbs diagram indicated that the weathering of rocks containing silicate minerals has potentially increased the concentrations of F^- . The concentrations of F^- showed positive correlation with pH, HCO_3^- and Na^+ , but an inverse relationship with Ca^{++} . Therefore, alkaline pH, enriched HCO_3^- and Na^+ and poor Ca^{++} concentrations were found to

Table 4

Water types of the flood plain area of the River Swat, Pakistan.

Field	Water type	No. of samples	Mean F^-	Contribution (%)
Field 1	$CaHCO_3$	17	1.3	32
Field 2	$CaMgCl$	2	0.9	3.7
Field 3	$NaCl$	5	7.9	9.4
Field 4	$NaHCO_3$	29	2.3	55

contribute significantly to F⁻ enrichment. It is recommended that groundwater F⁻ endemic regions should be mapped in order to encourage the government to design policies aimed at defluoridation. It is also recommended that local inhabitants use deep groundwater for drinking and domestic purposes.

Conflict of interest

The authors confirm that there is no conflict of interest to disclose.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.04.064>.

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