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RESEARCH ARTICLE

Co-occurrence of arsenic and fluoride in the groundwater of Punjab, Pakistan: source discrimination and health risk assessment

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Abstract The present study discusses elevated groundwater arsenic (As) and fluoride (F⁻) concentrations in Mailsi, Punjab, Pakistan, and links these elevated concentrations to health risks for the local residents. The results indicate that groundwater samples of two areas of Mailsi, Punjab were severely contaminated with As (5.9–507 ppb) and F⁻ (5.5–29.6 ppm), as these values exceeded the permissible limits of World Health Organization (10 ppb for As and 1.5 ppm for F⁻). The groundwater samples were categorized by redox state. The major process controlling the As levels in groundwater was the adsorption of As onto PO_4^{3-} at high pH. High alkalinity and low Ca^{2+} and Mg^{2+} concentrations promoted the higher F⁻ and As concentrations in the groundwater. A positive correlation was observed between F⁻ and As concentrations ($r=0.37$; $n=52$) and other major ions found in the groundwater of the studied area. The mineral saturation indices calculated by PHREEQC 2.1 suggested that a majority of samples were oversaturated with calcite and fluorite, leading to the dissolution of fluoride minerals at alkaline pH. Local inhabitants exhibited arsenicosis and fluorosis after exposure to environmental concentration doses of As and F⁻. Estimated daily intake (EDI) and target hazard quotient (THQ) highlighted the risk factors borne by local residents. Multivariate statistical analysis further revealed that both geologic origins and anthropogenic activities contributed to As and F⁻ contamination in the groundwater. We propose that pollutants originate, in part, from coal combusted at brick factories, and agricultural activities. Once generated, these pollutants were mobilized by the alkaline nature of the groundwater.

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Highlights • Elevated concentrations of arsenic (As) and fluoride (F⁻) in the groundwater of Tehsil Mailsi, Punjab, Pakistan are responsible for contamination.
• Simultaneous occurrence of As and F⁻ in ground water is common in arid and semi-arid regions.
• Estimated daily intake and associating human health risk were pronounced under the simultaneous occurrence of As and F⁻ in groundwater. Further, their health implications have been discussed with global perspectives.

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Abbreviations

As	Arsenic
DO	Dissolved oxygen
EDI	Estimated daily intake
F⁻	Flouride
SAR	Sodium adsorption ratio
TDS	Total dissolved solids
THQ	Target hazard quotient

Introduction

Both As and F⁻ contribute to the global water crisis by contaminating the drinking water. This also brings significant health problems (Naseem et al. 2010). Groundwater is the major source of drinking water around the world and is also used as an alternative water source for agricultural production and industrial processing (Mishra and Bhatt 2008). The contamination of these water resources, therefore, has important repercussion for the environment and human health (Emmanuel et al. 2009; Muhammad et al. 2011). Arsenic and F⁻ in drinking water are a serious challenge for every nation, as they are recognized worldwide as the most dangerous inorganic pollutants (Smedley and Kinniburgh 2002; Ng et al. 2003). Arsenic in water poses health hazards to humans, creates non-cancerous effects such as keratosis, skin pigmentation problems, black foot diseases, diabetes and in some serious cases, cancers of the skin, lung, and bladder (Wang et al. 1998).

The drinking water of about 70 nations has been affected by As. Most of these nations are found in Southeast Asia, suggesting that 150 million people are affected by the consumption of As-contaminated water (Ravenscroft et al. 2009). The As-affected nations include Bangladesh, India, China, Hungary, Thailand, Argentina, Germany, Canada, Chile, Mexico, Taiwan, USA, Romania, Ohio, Finland, Vietnam and Pakistan (Smedley et al. 2002; Nickson et al. 2005; Berg et al. 2007; Baig et al. 2009b). Although F⁻ in small amounts is an essential component for normal mineralization of bones and formation of dental enamel (Wood 1974), excessive F⁻ intake causes skeletal and dental fluorosis (Chen et al. 1997), cancer, arthritis, renal and neuronal disorders, and sympathy (Chen et al. 1997; Ayoob and Gupta 2006). Around 200 million people from 25 nations, of which 23 are developing nations, are affected by F⁻. These nations include China, India, Pakistan, Sri Lanka, Ghana, Germany, Senegal, Turkey, Algeria, Kenya, Uganda, Tanzania, Japan, Ethiopia, South Africa, Mexico, New Zealand, Thailand, and Argentina (Rafiq et al. 2009). Arsenic and F⁻ in groundwater are common in arid and semi-arid regions of the world (Farooqi et al. 2007; Currell et al. 2011; Brahman et al. 2013a, 2014). Higher As and F⁻ concentrations in water are characterized by a high redox potential and exhibit Na^+–HCO_3-groundwater type (Semedley and Kinniburgh 2002; Pauwels and Ahmad 2007; Kim et al. 2012). In particular, As and F⁻ groundwater contamination in unconsolidated sedimentary aquifers has been detected in Argentina, China, Mexico, Vietnam, and Cambodia (Smedley and Kinniburgh 2002; Kim et al. 2012).

The untreated, harmful run-off from agricultural, industrial, and unconsolidated sediments, and coal combustion and domestic sewage into natural water reservoirs has resulted in drinking water pollution that greatly affects public health (Tariq et al. 2008; Majidano et al. 2010; Muhammad et al. 2010; Azizullah et al. 2011; Brahman et al. 2013a). In Pakistan, As

and F⁻ affected areas include Jamshoro, Sindh (Baig et al. 2009a), Manchar Lake, Sindh (Arain et al. 2008, 2009), Lahore and Kasur, Punjab (Farooqi et al. 2007a, b), Muzaffargarh, Punjab (Nickson et al. 2005), Dera Ghazi Khan, Punjab (Malana and Khosa 2011) and Tharparkar, Sindh (Brahman et al. 2013a, b). In 2004, more than 40 people died in Hyderabad City from ingesting water contaminated with high levels of As and other toxic metals (Arain et al. 2008).

To evaluate the potential problems caused by As and F⁻ in drinking water, multivariate statistical analyses such as cluster analysis (CA), inter-metal correlation matrices (CM) and principal component analyses (PCA) have been employed for the source discrimination and ecological status of As and F⁻ in water (Zhang et al. 2011; Muhammad et al. 2011). Moreover, the public health engineering department of Pakistan, in collaboration with the United Nations Children's Fund (UNICEF) recently has revealed that trace metal-enriched groundwater occurs in the Indus alluvial basin of Pakistan (Nickson et al. 2005). The Pakistan Council for Research in Water Resources (PCRWR) has declared six cities as the most affected areas of Punjab in terms of As and F⁻ levels. These include Multan, Bahawalpur, Sheikhopura, Gujranwala, Kasur, and Lahore (PCRWR 2005).

In an earlier study, we reported As contamination in the groundwater of two different sites at Tehsil Mailsi, Punjab. Here, we report the As and F⁻ groundwater contamination in two other sites in the study area. This area is also of serious concern to researchers, because As and F⁻ in the groundwater are affecting the local populations. To our knowledge, this is first report evaluating: (1) the As and F⁻ distribution in groundwater of Tehsil Mailsi along with an assessment of their associated health risks, (2) the bio-geochemical indicators and potential mechanisms producing the high As and F⁻ in the groundwater, (3) the hydro-geochemical factors and processes controlling the high F⁻ in the groundwater, and (4) the development of a direct relationship between As and F⁻ in the groundwater. These findings will provide new insights into the behavior of As and F⁻ in the local groundwater at Tehsil Mailsi and associated human health risks, both locally and globally.

Materials and methods

Description of the study area

Tehsil Mailsi, southern Punjab, Pakistan, is located between 72° 11′–72° 19′E and 29°52′–29° 92′N, at an altitude of 132 m. The estimated population of the selected area is 704, 878 with an area of 14.88 km² (Fig. 1). Farming is the major economic activity in the two study areas, Jallah Jeem and Dur Pur. Jallah Jeem is situated in an active flood plain almost 3 km away from the Sutlej River. The study area has a semi-arid climate with long and extremely hot summers, and dry
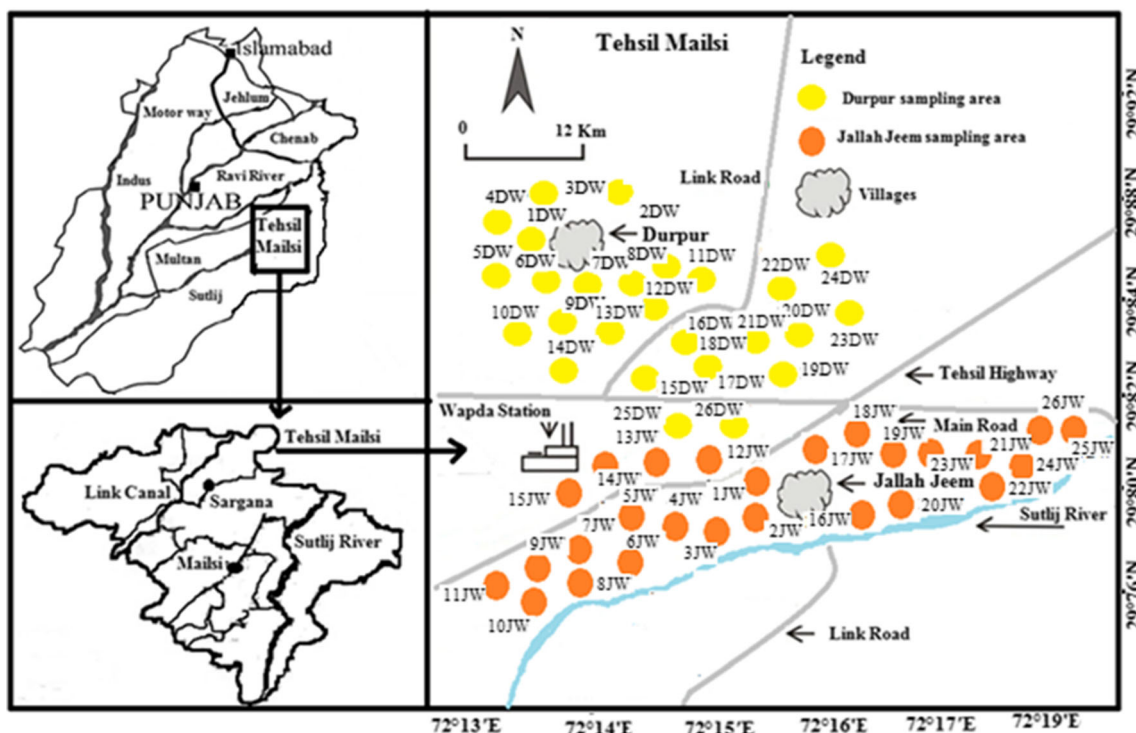
Fig. 1 Location maps showing the groundwater sampling stations from the Dur Pur and Jallah Jeem study areas

and warm winters, monsoons and dust storms. The highest recorded temperature was 51.7 °C and lowest temperature 5.8 °C (DCR 1998). The main water sources for irrigation are Link Canal, Siphon Lake, and Sutlej River along with tube wells. Drinking water supplies are also accessed by electric and hand pumps from the groundwater. The regional hydrology of Punjab has been previously described (Greenman et al. 1967). The aquifer sediments are comprised of alluvial plains, where >340 m thick Holocene and Pleistocene sediments are transported from the Sutlej River. These sediments contain a high percentage of fine coarse sand, silt, and clay with low organic matter. Quaternary alluvium is deposited on semi-consolidated secondary rocks that are directly overlain by the metamorphic, sedimentary, and igneous rocks of Precambrian age (Farooqi et al. 2007). The study area is towards the southwestern part of Bari Doab (the area between the two rivers, Sutlej and Chenab) which contains relatively older alluvial deposits that tend to coincide with zones of highly mineralized groundwater (Greenman et al. 1967). The geologic factors that influence permeability and transmissibility are lateral litho-logical changes, variation in sand thickness, and grain size distribution.

Water sampling and analysis

The two sampling sites (Fig. 1) were selected because they were potentially exposed to severe agricultural and anthropogenic activities. Water sampling was carried out in August 2011 using the methods outlined by Khan et al. (2012). A total of 52 groundwater samples, 26 from Dur Pur and 26 from Jallah Jeem were collected (Fig. 1). These samples were further divided into deep groundwater (>37 m) and shallow groundwater (6–30 m). All the water for geochemical analysis was filtered on site using Millipore Sterivex syringe capsules containing 0.45 μm cellulose acetate filters. Two filtered sub-samples were sealed in pre-cleaned 60 ml of Nalgene™ bottles, of which one sample was used for anion and the other for cation analysis (preserved using 10 % ultra-pure HNO_3^-, to acidify the sample pH to 2.0 or lower). A field duplicate was collected at every 10th sampling site for laboratory analysis precision. The temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO) in groundwater samples were measured in the field. The latitudes and longitudes were recorded via global positioning system (GPS) at the time of sample collection. All the samples either in the field or in the laboratory were preserved at 4 °C before analysis. Standard procedures were followed for the determination of As, F^-, and all the other drinking water quality parameters (APHA 1998). The pH, EC, and TDS in all water samples were determined by pH/EC meter (W2015, Sino well Company, Shanghai, China). The DO meter was also used for the determination of DO in all water samples. The cations including As, Na^+, K^+ Ca^{2+}, Mg^{2+}, Fe^{2+} and Mn^{2+} were determined using atomic absorption spectrophotometer (Spectra AA 220 FS, Varian, New Jersey, USA) and anions including SO_4^{2-}, PO_4^{3-}, NO_3^-, and F^- were determined spectro-photometrically using UV/VIS-Spectrophotometer

(Shimadzu model UV 1601) at a wavelength of 220 nm. The standard titration method was followed for the determination of anions including Cl^- and HCO_3^- (APHA 1998). Reproducibility of the analytical data was within 4 % and the systematic error was estimated at <10 %.

Human health risk assessment

Estimated daily intake

The US-EPA (1998) model was applied to assess health risk in individuals exposed to As and F^- groundwater contamination in terms of estimated daily intake (EDI). The estimated daily intake was compared with the current provisionally acceptable daily intake limit outlined by a Joint FAO/WHO expert committee on food and water additive online database (JECFA 2000; FAO 2006). EDI for As and F^- were calculated using the following equation;

$$EDI = C \cdot IR \cdot ED \cdot EF \cdot BW^{-1} \cdot AT \qquad (1)$$

where EDI is the estimated daily intake (mg kg^{-1} day^{-1}), C represents the concentration of As or F^- in water (mg L^{-1}), IR is the ingestion rate (2 L day^{-1}), ED is the exposure time in years (considered here to be 67 years), EF is the exposure frequency (365 days year^{-1}), BW is the average body weight (72 kg), and AT is the average life time (24,455 days), respectively (US-EPA 1989, 1997)

Target hazard quotient

The As and F^- exposure dose was calculated by determining the target hazard quotient (THQ), which is defined as the ratio of cumulative EDI to the reference dose (RfD) (US-EPA 2000). In the study area, carcinogenic health risks associated with the consumption of groundwater by the local residents were based on the THQ and calculations were made using the standard assumptions used in US-EPA risk analysis. The THQs was calculated by the following formula

$$THQ_s = EDI \cdot RfD^{-1} \qquad (2)$$

where THQ_s is considered to be the health risk (Khan et al. 2008), RfD is the reference dose (oral toxicity reference value) of both As and F^- which were 0.0003 and 0.06 mg kg^{-1} day^{-1}, respectively (US-EPA 2010).

Sodium adsorption ratio

Sodium adsorption ratio (SAR) in groundwater samples was calculated according to the equation by Patherson (1994).

$$SAR = Na \cdot \{Ca + 0.5 \cdot Mg\}^{-.5} \qquad (3)$$

where the concentrations of all ions were expressed in milliequivalents per liter.

Multivariate statistical analysis and maps

MVSP and SPSS (Statistics Software Version 19) were used for PCA, CM, and hierarchical cluster analysis (HCA). Arc-GIS Version 10 was used to make study area and distribution maps of As and F^-. Hydro-chemical facies was determined by the Piper diagram (Piper 1994), and the major ion composition of ground water samples was determined by Stiff diagram (Howie 1987).

Results and discussion

Hydrogeochemistry of the studied area as influenced by As and F^- contamination

The depth of the groundwater table varied significantly from 6 to 60 m resulting in variations in groundwater quality (Table 1). The charge balance of total cations and anions (meq L^{-1}) was determined to be 2.44 %, and the observed ion balance was better than ±5 %. The pH of the groundwater in Jallah Jeem and Dur Pur ranged from 6.84 to 9.24 and 6.74 to 9.15, respectively. DO values ranged from 6.23 to 8.24 and 6.45 to 8.23 mgL^{-1}, respectively (Table 1). The EC values ranged from 615 to 1950 and 620 to 1740 μS^{-1} cm in Jallah Jeem and Dur Pur, respectively (Table 1), and 27 % of the Jallah Jeem samples and 4 % of those samples at the Dur Pur site exceeded the WHO permissible limit of 1500 μScm^{-1} (WHO 2011). The TDS values ranged from 418.2 to 1326 and 421.6 to 1183.2 mg L^{-1} in Jallah Jeem and Dur Pur, respectively (Table 1), with 27 % of the measured groundwater samples of Jallah Jeem and 4 % of the samples at the Dur Pur site exceeding the WHO permissible limit of 1000 mg L^{-1} (WHO 2011). The samples collected from near the Sutlej River had higher EC and TDS values compared to samples collected far from River Sutlej. This trend countered that reported in a previous study conducted in southern Punjab (Malana and Khosa 2011).

A Piper plot of the major elements separated the groundwater types (Fig. 2a). This plot indicated that K^+ and Na^+ were the major cations, whereas SO_4^{2-} and HCO_3^- dominated the anionic species. Two major water types were identified in the study area; one was Na^+–HCO_3^- type, the other one was K^+–HCO_3^- with elevated bicarbonate concentrations. Anions in groundwater showed the following trend: $NO_3^- < PO_4^{3-} < SO_4^{2-} < Cl^- < HCO_3^-$, whereas the cations followed another: $K^+ < Mg^{2+} < Ca^{2+} < Na^+$. The predominant anion was HCO_3^-, which ranged from 300 to 980 and 210 to 905 ppm, while the predominant cation was Na^+, which ranged from 18 to 86 and 17 to 79 ppm in Jallah Jeem and Dur Pur, respectively. The

Table 1 Concentrations of major ions and field parameters of groundwater in the Tehsil Mailsi area ($n=52$)

Sample Id	pH	EC (uS cm^{-1})	TDS (mg L^{-1})	DO (mg L^{-1})	Cl$^-$ (mg L^{-1})	HCO$_3^-$ (mg L^{-1})	NO$_3^-$ (mg L^{-1})	SO$_4^{2-}$ (mg L^{-1})	PO$_4^{3-}$ (mg L^{-1})	Na$^+$ (mg L^{-1})	K$^+$ (mg L^{-1})	Ca^{2+} (mg L^{-1})	Mg^{2+} (mg L^{-1})	F$^-$ (mg/L)	As (μg/L)	Mn (mg/L)	Fe (mg/L)
Shallow groundwater of H.P.																	
JW1	8.83	1353	920.5	6.83	67	800	39.2	119.8	61.9	67.6	16.8	96.6	56.2	6.7	18.09	0.021	0.09
JW2	8.61	1320	897.6	6.78	35	785	28.2	134.14	48	21.7	11.1	43.4	19.7	8.9	17.6	0.013	0.05
JW3	7.97	1052	715.36	7.64	28	550	27.1	89	37.5	41.3	12.3	39	15.5	9.3	124.9	0.012	0.095
JW4	8.76	1075	731	7.42	125	580	38.5	42.3	64	35.3	14.5	47.8	14.8	17.8	91.9	0.0011	0.26
JW5	8.43	1100	748	7.25	211.9	600	37.4	143	65.4	54.7	16.4	87.3	28.6	9.3	21.2	0.018	0.07
JW6	8.52	1950	1326	7.63	110	980	28.6	83	58.2	56	47.9	33.5	83.8	16.2	14.3	0.021	0.05
JW7	8.43	1947	1323.96	7.55	125	900	26.2	342.6	55.5	45.9	53	38.3	89.1	13.2	8.5	0.018	0.29
JW8	8.21	1870	1271.6	7.16	175	850	24.5	143	49	45.8	13.7	42.5	97.5	6.5	9.5	0.017	0.07
JW9	8.32	1940	1319.2	7.65	100	930	27	110.6	42	86	57	43.2	26.6	6.9	9	0.008	0.06
JW10	8.31	1350	918	7.47	224.9	900	13.9	114.6	58.9	58.8	17.6	37.4	26.1	8.6	14.9	0.02	0.05
JW11	8.76	1502	1021.36	7.58	344.9	600	14.5	190	57	58.7	27.4	28.2	35.4	17	11.9	0.017	0.17
JW12	8.23	1200	816	6.23	145	550	25.8	98.13	47.1	65.4	26.1	29.1	21.5	8.7	23.9	0.019	0.24
JW13	6.84	975	663	6.33	140	370	15.8	130	48	60.2	15.6	34.8	31.6	8.9	10.8	0.004	0.14
JW14	8.53	702	447.36	6.55	85	300	27.8	29.3	56.6	65.5	17.4	53.4	24.1	8.5	15.2	0.008	0.14
Deep groundwater of TW.																	
JW15	8.74	700	476	7.55	45	400	26.1	45.7	44.8	28.9	21.1	26.9	14.2	8.4	507	0.011	0.09
JW16	8.51	720	489.6	8.24	178.9	420	23.2	133	56.9	59.7	18.1	24.6	26.7	6.9	23.5	0.011	0.09
JW17	8.65	804	546.7	8.18	110	300	18	55.5	38.5	23	12.5	21.4	14.9	29.6	223.3	0.022	0.295
JW18	8.98	800	544	8.23	75	500	21.3	38.7	42	24.5	13.8	61.4	18	6.7	85.8	0.012	0.26
Shallow groundwater of HP.																	
JW19	8.72	939	638.5	7.81	95	485	23	18	27.4	66.6	23.9	40.6	44.2	7.2	130.7	0.009	0.03
JW20	8.84	890	605.2	7.84	135	460	19.7	56	25.4	38.3	38.7	33.5	17.2	16.1	235.5	0.006	0.05
JW21	8.73	631	429	7.72	50	335	27	132.01	43.4	65.7	10.3	21.5	25.7	9.2	260.9	0.012	0.31
JW22	9.43	703	478	7.54	62	365	28.9	33.12	28.8	58.7	38.7	24.4	28.6	24.3	91.7	0.012	0.21
JW23	8.63	615	418.2	7.82	110	315	27.6	120.3	34	70.2	24.6	34.8	17.7	7.2	21.2	0.005	0.18
JW24	9.24	928	631	7.67	15	427	32.5	31.2	37	70.5	30	38.8	12.3	8.4	17.3	0.005	0.034
JW25	8.6`2	1505	1023.4	7.63	564.8	540	23.3	111	51.1	18.8	15.9	86.5	14.4	19	219.3	0.034	0.04
JW26	8.7	1620	1101.6	7.67	50	723	30.3	121	53	30.6	23.8	45.3	12.7	8.7	310.2	0.023	0.014
DW1	8.65	1050	714	7.53	75	560	27.4	102	45	24.5	22.5	26.6	10.5	8.7	124.5	0.005	0.02
DW2	8.54	1200	816	7.37	160	485	28	103.6	50.7	70.6	34.7	27.7	11.2	7.5	120.2	0.032	0.23
DW3	8.73	1150	782	7.56	55	602	21	118	56	30.8	13.5	32.7	21	17.5	86.1	0.011	0.14
DW4	8.86	1020	693.6	7.52	115	530	29	117	53	24.1	19.7	37.5	23.2	7.7	45.7	0.003	0.16
DW5	8.61	750	510	6.71	299.9	210	24.8	114.6	54	58.8	27	24.7	3.2	6.5	29.2	0.016	0.21
DW6	8.93	620	421.6	6.53	90	357	32	98.9	52	37.7	13.7	85.2	21	6.8	36.5	0.001	0.275
DW7	9.15	650	442	6.45	125	223	33	196.7	53.6	79	23.4	70.3	19.2	6.8	219	0.021	0.271
DW8	8.74	670	455.6	7.78	75	375	24.5	143	41.9	25.4	21.3	35.6	2.1	5.6	215.3	0.034	0.02
DW9	6.91	904	614.7	6.42	35	550	25.5	38.6	45	46.2	34.8	49.7	10.3	16.3	11.9	0.018	0.023
DW10	8.95	860	584.8	7.65	85	490	26.7	28.7	47	49.8	32.7	25.4	10.2	8.8	68.2	0.054	0.04
DW11	8.66	1400	952	7.51	29	810	30.9	65	46	60	20.1	26.2	11.2	6.9	110.7	0.005	0.23
DW12	8.52	1380	938.4	7.45	100	570	29.5	58	40.2	19.5	12.3	15.2	21.3	5.9	14.4	0.004	0.08
DW13	8.83	1740	1183.2	8.23	112	905	28.7	160	31	68.7	35.9	18.2	10.1	5.5	8.9	0.011	0.02
DW14	8.66	1420	965.6	7.61	125	844	34.7	69.4	43	33	13.4	32.1	10.3	6.6	8.8	0.021	0.002
Deep groundwater of TW.																	
DW15	8.56	1400	952	7.53	125	815	40.7	168.6	58	58.6	18.4	22.4	20.5	7.7	107.2	0.011	0.002
DW16	8.32	950	646	7.51	50	410	13.7	108.13	35	65.4	13.2	29.3	31.3	7.2	89.1	0.013	0.12
DW17	8.66	916	622.8	8.12	229.9	350	13.2	78.5	40.1	39.5	16.7	68.5	18	26.4	319.3	0.013	0.11
DW18	8.44	1000	680	6.56	50	380	27.5	34.6	29	17.4	19.3	16.8	11.9	20.4	32.5	0.011	0.17
Shallow groundwater of HP.																	
DW19	8.81	1150	782	7.43	95	385	28.3	29.8	57	57.3	17.9	17.1	10.26	9.4	5.91	0.002	0.29
DW20	8.87	1180	802.4	7.56	90	610	26.3	94.3	55.6	44.8	35	57.2	10.2	8.2	67.4	0.019	0.24
DW21	6.74	1050	714	7.53	179.9	540	31	124	43.7	36.7	18	35.2	13.2	8.7	12.27	0.003	0.27

Table 1 (continued)

Sample Id	pH	EC (uS cm⁻¹)	TDS (mg L⁻¹)	DO (mg L⁻¹)	Cl⁻ (mg L⁻¹)	HCO₃⁻ (mg L⁻¹)	NO₃⁻ (mg L⁻¹)	SO₄²⁻ (mg L⁻¹)	PO₄³⁻ (mg L⁻¹)	Na⁺ (mg L⁻¹)	K⁺ (mg L⁻¹)	Ca²⁺ (mg L⁻¹)	Mg²⁺ (mg L⁻¹)	F⁻ (mg/L)	As (µg/L)	Mn (mg/L)	Fe (mg/L)
DW22	8.53	1380	938.4	6.66	40	661	25	46	48.9	27	13.4	23.3	11.2	7.3	13.43	0.005	0.05
DW23	8.38	1362	926.12	6.47	62	650	24.8	32	56.9	20.3	29.6	27.6	14.3	8.8	16.07	0.031	0.288
DW24	8.57	950	646	8.17	95	475	33	25	60	23.3	13	17.1	15.4	7.9	8	0.011	0.296
DW25	8.53	880	598.4	6.54	100	490	27	34	56.8	38.1	13.9	18.6	15.9	5.9	13.9	0.002	0.13
DW26	8.61	976	663.68	8.14	98	493	29.7	102.1	59.9	45.2	17.6	23.5	18.8	9.8	34.5	0.042	0.234
WHO (mg/L)		1.5	1000		250	500	10	250		200	12	100	50	1.5	0.01	0.1	0.3

JW groundwater from Jallah Jeem and *DW* groundwater from Dur Pur, *n* number of samples, *HP* Hand pump, *TW* Tube well

concentration of Cl⁻ and SO₄²⁻ differed significantly throughout the area and ranged between 15 to 564 and 29 to 299.9 ppm, and 18 to 342.6 and 25 to 195.7 ppm in Jallah

Fig. 2 (**a**) Piper plot showing the major groundwater types (**b**) spatial variations by Stiff diagram in groundwater samples from the study area

Jeem and Dur Pur, respectively. Higher concentrations of NO₃⁻, PO₄³⁻, and K⁺ in the groundwater resulted from various anthropogenic activities, including agricultural and industrial activities and excessive use of various fertilizers. In the sampling areas, urea, diammonium phosphate (DAP) and other fertilizers have been widely applied on various cash crops including maize, cotton, wheat, rice, and sugarcane. In Pakistan, the fertilizer application has increased threefold over the past 30 years. This is especially true in the Punjab province which has the largest agricultural area (FAO 2004).

In order to sort out potentially hazardous hydrogeochemical anomalies, the measured concentrations of major ions and selected metals in all the groundwater samples were compared with the prevailing drinking water standards, recommended by the authorities (WHO 2006; US-EPA 2003). Chloride crossed the permissible limit in 8 % of the samples; NO₃⁻ crossed in 100 % of samples; K⁺ in 96 % of samples; Mg²⁺ in 7.6 % of samples. The remaining elements were within safe limits. The elements such as SO₄²⁻, Na⁺, K⁺, Ca²⁺, Cl⁻, and Mg²⁺ might have a role in producing a bad taste, but are below the permissible limits (US-EPA 2003).

A Stiff diagram displays graphically the major ion composition of different waters in the study area. Comparisons between numerous samples of irrigation water quality constituents were easily carried out by comparing the shapes of the Stiff diagrams (Fig. 2b). These results highlighted the dominance of Na⁺–Cl⁻, over Mg²⁺–SO₄²⁻, and K⁺–HCO₃⁻. A polygonal shape was drawn from the four parallel horizontal axes extending to the sides of a vertical zero axes. Sodium, K⁺, Ca²⁺, and Mg²⁺ are plotted in milliequivalents per liter on the left side of the zero axes where Na⁺ and K⁺ were dominant, while HCO₃⁻, SO₄²⁻, and Cl⁻ were plotted on the right side, where SO₄²⁻ remained dominant in ground water samples.

The classification of groundwater at the two sites, Jallah Jeem and Dur Pur, with respect to the SAR is given in Table 2. This ratio determines the suitability of the groundwater for use in irrigation. Water quality is compared on the basis of total salt concentration (as measured by EC), the relative proportion
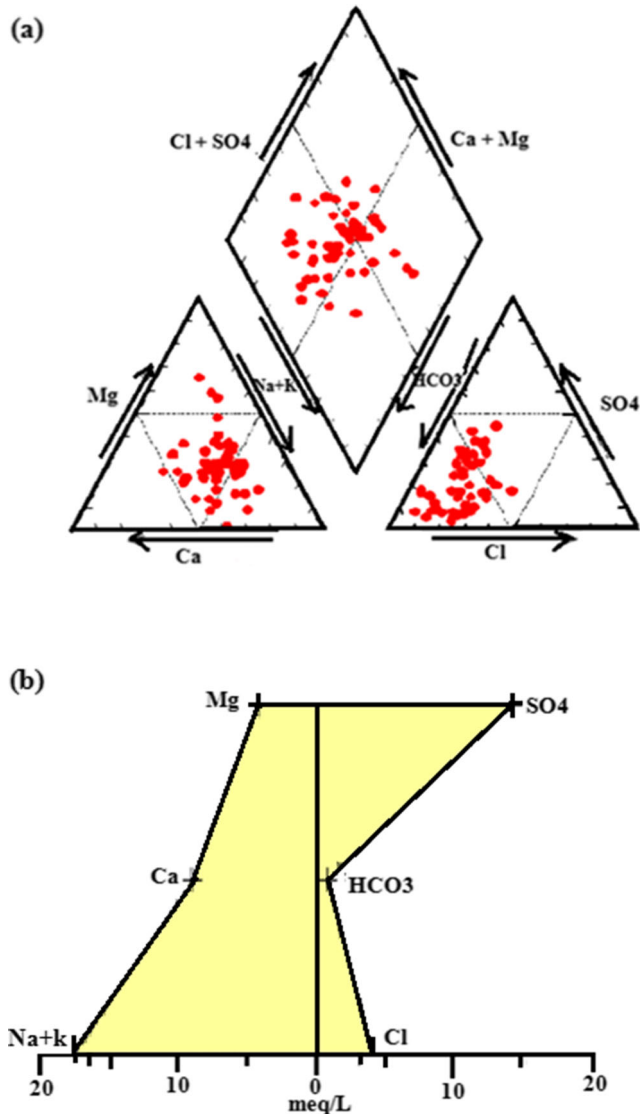
Table 2 Relative frequency distribution of ground water for irrigation quality characteristic (SAR) in the study area ($n=52$)

Parameter	Status	Richards, 1954	Muhammad, 1996	Malik et al. 1984	Jallah Jeem		Dur Pur	
					Ground water $n=26$		Ground water $n=26$	
	Range				0.48–2.6		0.77–3.1	
					No. of sample	(%)	No. of sample	(%)
SAR	Fit	<10	<7.5	<6	26	100	26	100
	Marginal	>10<18	7.5-15	>6<10	0	0	0	0
	Unfit	>18	>15	>10	0	0	0	0

of sodium to the other principal cations, the residual sodium carbonate index (RSC), and the % Na (Ciaccio 1971). The relative frequency distribution of SAR was less than 10 (Table 2), suggesting that the groundwater is fit for irrigation (Richard 1954; Malik et al. 1984; Muhammad 1996).

The spatial distribution of As in the groundwater samples of the Tehsil Mailsi is given in Fig. 3a. Arsenic concentrations exceeded permissible limits (WHO 2011; 10 ppb) in 86.6 % of the groundwater samples in the study area. The As in the Jallah Jeem had a mean value of 96.8 ppb and with a range of 8.5 to 507 ppb (Table 1). The sample JW15 (tube well having depth of 50 m) produced the highest As concentration, whereas JW7 (hand pump having depth of 22 m) showed the lowest As concentration. Overall, the deep groundwater samples were more contaminated with As than the shallow groundwater samples. This trend was opposite to the trend shown in previous studies conducted in Bangladesh (BGS 2001), East Punjab (Farooqi et al. 2007), and India (Chauhan et al. 2009). This might be due to variations in the groundwater table, leaching, and geography of the studied area. Unlike Jallah Jeem, the DurPur site exhibited a mean As concentration of 69.9 ppb and with a range of 5.9–319.3 ppb (Table 1). The highest As concentration was observed in the sample DW17 (tube well having depth of 52 m), whereas the lowest As concentration was observed in DW19 (hand pump having depth of 21 m). The As concentrations in Dur Pur were much lower than those found by studies conducted in East Punjab (Farooq et al. 2007) and Muzaffargarh (Nickson et al. 2005), but higher than those revealed in a previous study conducted in Dera Ghazi Khan (Malana and Khosa 2011). The results of the current study showed that the As concentration was higher in the regions located near to the Sutlej River compared to the areas located far from it. Nickson et al. (2005) also observed similar results in Muzaffargarh and Multan.

There are four basic geochemical mechanisms responsible for the release of As into the groundwater. These mechanisms include oxidative and reductive dissolution (Nickson et al. 1998; McArthur et al. 2001), desorption (Smedley et al. 2005), and concentration by evaporative enrichment, especially in arid environments (Welch et al. 2000). To determine which mechanism is responsible for As contamination in our samples, we analyzed the data for correlations. We observed a significant positive correlation for As with depth ($r=0.49$, $n=52$) and SO_4^{2-} ($r=0.48$, $n=52$) as shown in (Fig. 4a, b). Our results did not support the reductive dissolution mechanism because we did not observe a positive correlation between As and Fe (Fig. 4c), however, our data did somewhat support oxidative dissolution. The majority of the water samples were characterized by higher HCO_3^- (>500 ppm), high pH (>7.5), and low sulfates (250 ppm). Hence, our current study better supports the mechanism of desorption of As from PO_4^{3-} (Fig. 4d) at high pH. This suggests that in the arid environment of the study area, As in the groundwater is probably due to a combination of the oxidative and evaporative mechanisms.

The fluoride concentration crossed permissible values (1.5 ppm; WHO 2011) in all of the groundwater samples and its spatial distribution is shown in Fig. 3b. The Jallah Jeem samples had a mean F^- value of 11.5 ppm which ranged between 6.5 and 29.6 ppm (Table 1). JW17 (tube well at 60 m) had the largest value of F^- and JW8 (hand pump at 21 m) had the lowest concentration of F^-. The Jallah Jeem shallow groundwater samples were less contaminated than the deeper groundwater samples. This trend was opposite to the trend described in previous studies conducted in Lahore and Kasur districts and East Punjab (Farooqi et al. 2007a, b); but showed a similar pattern to a study conducted in China (Liu et al. 2012). The Dur Pur samples had a mean F^- concentration of 9.4 ppm and a range of 5.5–26.4 ppm (Table 1). The highest and lowest values were reported in DW17 (tube well at 52 m) and DW13 (hand pump at 23 m), respectively. The groundwater samples of the Jallah Jeem area had higher fluoride concentrations, being located near to the Sutlej River. Those samples taken from the Dur Pur area located far from the river had lower F^- concentrations. The fluoride concentrations in the study area were much higher than those found in previous studies conducted in Sialkot (Ullah et al. 2009), Dera Ghazi Khan (Malana and Khosa 2011), and North Jordan (Rukah and Alsokhny 2004).

The relationship of F^- with various parameters and major ions is shown in Fig. 5. Farooqi et al. (2007) reported that the

Fig. 3 Spatial distribution of (**a**–**b**) As and F⁻ in the study area groundwater
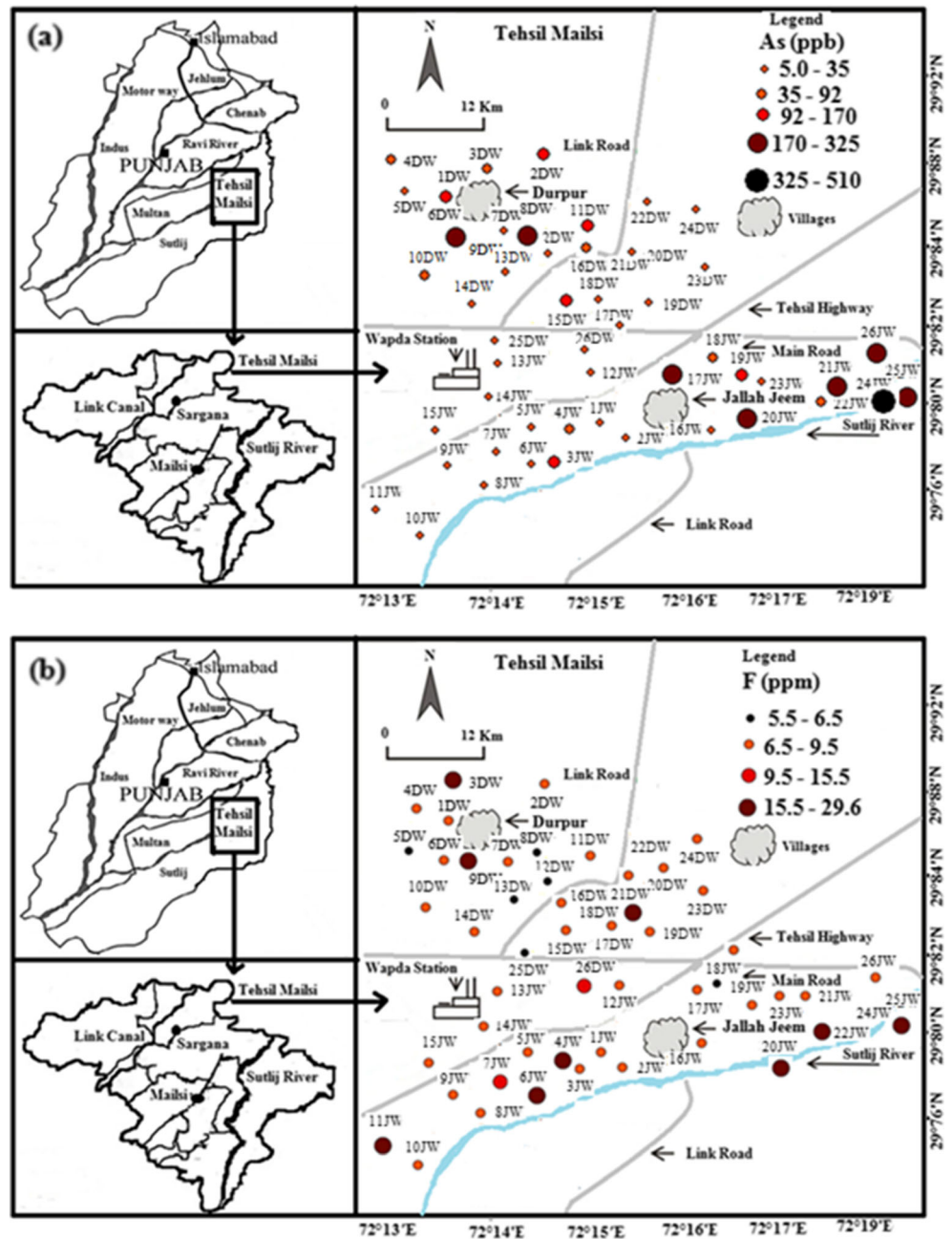
occurrence of high F⁻ levels in the groundwater is characterized by high concentrations of Na^+ and low concentrations of Ca^{2+} and Mg^{2+}. The penetrating cation exchange reaction between Ca^{2+} and Na^+ decreases the Ca^{2+} levels in the groundwater (Sarma and Rao 1997). High HCO_3^- concentrations and alkaline pH also promote the precipitation of Ca^{2+} as calcite (Sarma and Rao 1997) and Mg^{2+} as dolomite. Fluoride ions are absorbed by clays in acidic solution, but desorbed in alkaline solution. Thus, an alkaline pH is favorable for F⁻ dissolution (Sexena and Ahmed 2003). In our study, all of the groundwater samples were characterized by high levels of fluoride, HCO_3^-, Na^+, and low levels of Ca^{2+} at alkaline

pHs. In the current study, F⁻ showed a very weak negative correlation with Ca^{2+} and Mg^{2+} (Fig. 5b, c). These low Ca^{2+} and Mg^{2+} levels might have resulted from the precipitation of calcium as calcite and magnesium as dolomite at alkaline pHs. The alkaline pH also supported the dissolution of F⁻ (Fig. 5a), resulting in high F⁻ levels in all of the groundwater samples. Thus, the findings of the current study are consistent with previous studies conducted in East Punjab, Lahore, and Kasur districts (Farooq et al. 2007; Farooqi et al. 2007a). There are two important mechanisms used to explain the possible reasons for high F⁻ levels in ground waters throughout the world, and these processes include the dissolution of F⁻ bearing

Fig. 4 Relationship of As with (**a**) depth (**b**) SO_4^{2-} (**c**) Fe and (**d**) PO_4^{3-}
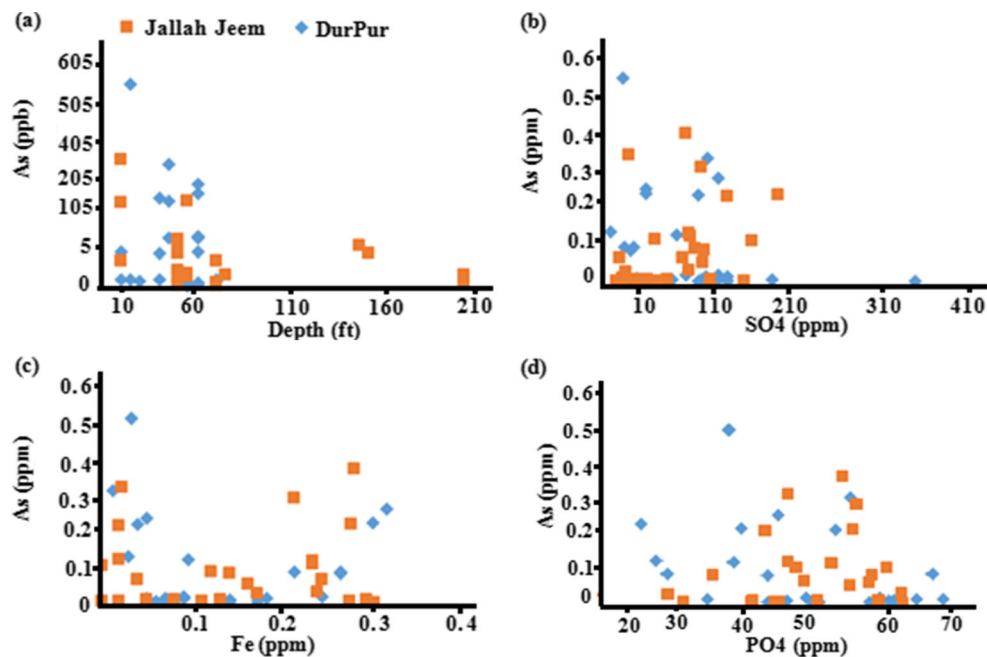
minerals, ion exchange, and evaporative concentration (Agrawal et al. 1997; Apambire et al. 1997; Saxena and Ahmed 2003). One of the mechanisms for high F^- concentrations in groundwater in arid and semi-arid regions is the condensation of soluble components due to evaporation and evapo-transpiration (Jacks et al. 2005). However, this mechanism is not supported by our results, since no positive correlation was observed between F^- and Cl^- (Fig. 5d). Fluoride in the study area groundwater could have originated from the dissolution of F^- bearing minerals including fluorite, granite, biotites, and topaz (Shah and Danishwar 2003). The negative correlation between F^- and Ca^{2+} (Fig. 5b) is in line with the findings of Jain and Ali (2000) and Chae et al. (2007). It also

suggests that fluorite solubility may enhance the F^- concentration ($K_{fluorite}=10^{-10.6}$ from Parkhurst and Appelo 1999) and dissolution of fluorite (Eq. (4)) in high HCO_3^- groundwater (Guo et al. 2007):

$$CaF_2 + 2HCO_3^- = CaCO_3 + 2\ F^- + CO_2 \qquad (4)$$
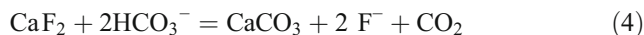
Mineral saturation indices calculated by PHREEQC 2.1 (Parkhurst and Appelo 1999) showed that all the groundwater samples were saturated with respect to fluorite, suggesting the dissolution of fluoride in groundwater (Fig. 6a). Figure 6b shows the relationship between the fluorite Saturation Index (SI) and Ca^{2+}. Thus, the SI of fluorite >0 for 81.4 % of the samples; <0 for 23.6 % of the samples, and >1 for only 0.03 %

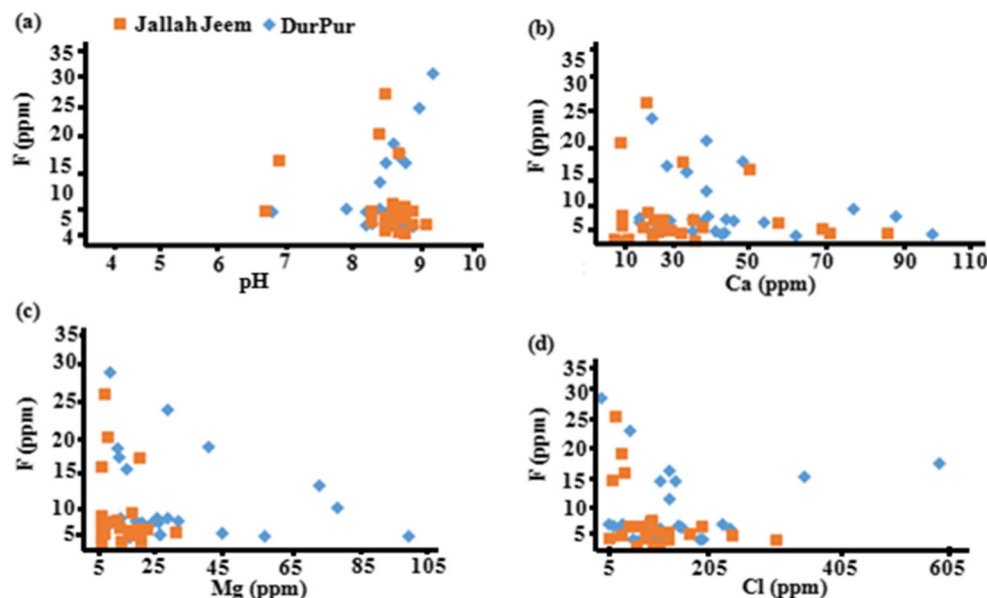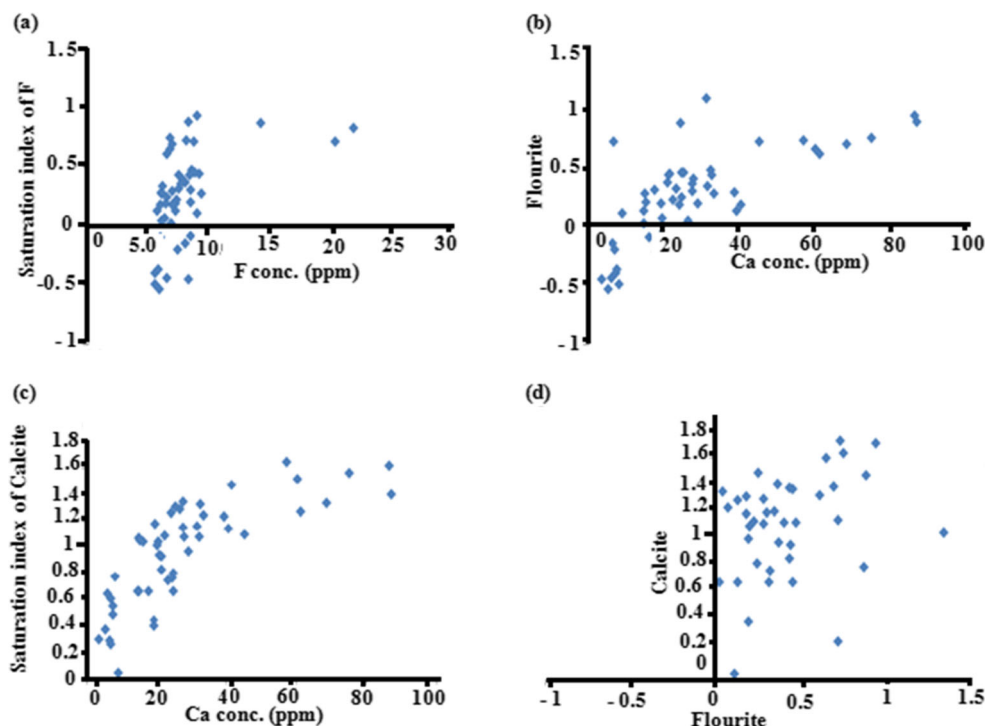**Fig. 5** Relationship of F^- with (a) pH (b) Ca^{2+} (c) Mg^{2+} (d) Cl^-

Fig. 6 Relationships between various concentrations and Saturation Indices from groundwater samples :(**a**) Fluorite SI vs. F^- concentration (**b**) Fluorite SI vs. Ca^{2+} concentration (**c**) Calcite SI vs. Ca^{2+} concentration and (**d**) Calcite SI vs. Fluorite SI

of the samples. However, the mineral saturation indices calculated by PHREEQC (Parkhurst and Appelo 1999) also showed that all groundwater samples were oversaturated with respect to calcite (SI of calcite >0), suggesting its precipitation. Precipitation of calcite would lower the dissolved Ca^{2+} concentration (Fig. 6c) and favor the dissolution of fluorite (Fig. 6d) in groundwater samples. The alkaline environment further sustains high F^- and encourages the replacement of OH^- with F^- in the groundwater of study area. The weathering of mica and granite in the study area produces abundant F^- bearing minerals that are easily leached out and dissolved in groundwater. Thus, another source of high F^- levels in groundwater includes leaching from fluoride-bearing minerals (Shah and Danishwar 2003; Naseem et al. 2010; Brahman et al. 2014). Weathering, industrial wastes (Siddique et al. 2006), agricultural fertilizers, brick production, organic landfills, and the combustion of coal all release fluoride into the air which later reaches the soil with rain (Farooqi et al. 2007b; Brahman et al. 2013a).

Identification of pollution sources using statistical techniques

Multivariate analysis was performed to differentiate groups of selected experimental parameters as tracers of natural or anthropogenic sources. CA, correlation matrices, and PCA have been effective for the identification of As and F^- sources and physicochemical parameters (Reghunath et al. 2002; Mico et al. 2006; Muhammad et al. 2011). Correlation matrices of all the parameters measured in ground water samples are

shown in Table 3. In groundwater samples, the correlation matrices show that several physicochemical parameter pairs have a significant positive correlation [EC–TDS ($r=0.988$; $n=52$), EC–HCO_3^- ($r=0.888$; $n=52$), EC–SO_4^{2-} ($r=0.365$; $n=52$), EC–Mg^{2+} ($r=0.499$; $n=52$), pH–DO ($r=0.305$; $n=52$), TDS–HCO_3^- ($r=0.906$; $n=52$), TDS–SO_4^{2-} ($r=0.334$; $n=52$), TDS–K^+ ($r=0.374$; $n=52$), TDS–Mg^{2+}($r=0.483$; $n=52$), Cl^-–Ca^{2+} ($r=0.287$; $n=52$), HCO_3^-–SO_4^{2-} ($r=0.298$; $n=52$), HCO_3^-–K^+ ($r=0.307$; $n=52$), HCO_3^--Mg^{2+} ($r=0.439$; $n=52$), NO_3^-–PO_4^{3-} ($r=0.298$; $n=52$), SO_4^{2-}–Mg^{2+}($r=0.429$; $n=52$), PO_4^{3-}–Ca^{2+} ($r=0.254$; $n=52$), Na^+–K^+ ($r=0.387$; $n=52$), K^+–Mg^{2+} ($r=0.252$; $n=52$), F^-–As ($r=0.37$; $n=52$)]. Similarly, some pairs show a significant negative correlation [EC–Fe^{2+} ($r=-0.279$; $n=52$), DO–PO_4^{3-} ($r=-0.236$; $n=52$), HCO_3^-–As ($r=-0.243$; $n=52$), HCO_3^-–Fe^{2+} ($r=-0.380$; $n=52$), PO_4^{3-}–As ($r=-0.286$; $n=52$), Mg^{2+}–As ($r=-0.251$; $n=52$)].

Analysis of the correlation matrix showed that both As and F^- had similar sources of contamination, such as agricultural activities, industrial activities, landfill, and household wastes in the study area. The co-relationship between F^- and As and physicochemical parameters was further supported by a CA dendrogram of ground waters from both sites (Fig. 7). In cluster analysis, similar objects fall closer together, and dissimilar groups fall further apart (Danielsson et al. 1999). The results of the CA agreed well with the PCA results, and helped to interpret the data. Levels of similarity at which observations merge are used to construct a dendrogram (Chen et al. 2007). Three groups of elements were identified in the groundwater samples. The linkage and clustering behavior of the

Table 3 Pearson correlation coefficient matrix of selected physicochemical parameters with F^- and As in the groundwater of the study area ($n=52$)

Parameters	pH	EC	TDS	DO	Cl^-	HCO_3^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	F^-	As	Mn	Fe
pH	1																
EC	−0.093	1															
TDS	−0.045	0.988	1														
DO	0.305	0.041	0.075	1													
Cl^-	−0.053	0.176	0.145	0.085	1												
HCO_3^-	−0.081	0.888	0.906	0.092	−0.024	1											
NO_3^-	0.18	0.083	0.118	−0.119	−0.253	0.204	1										
SO_4^{2-}	−0.072	0.365	0.334	0.034	0.292	0.298	−0.008	1									
PO_4^{3-}	0.001	0.21	0.2	−0.236	0.235	0.227	0.298	0.248	1								
Na^+	0.023	0.029	0.006	−0.047	0.009	0.019	0.054	0.233	−0.013	1							
K^+	0.04	0.379	0.374	0.07	−0.014	0.307	−0.011	0.213	−0.141	0.387	1						
Ca^{2+}	0.071	−0.013	−0.011	−0.172	0.287	0.023	0.168	0.173	0.254	0.066	−0.076	1					
Mg^{2+}	−0.066	0.499	0.483	−0.015	0.074	0.439	−0.049	0.429	0.17	0.221	0.252	0.169	1				
F^-	0.083	0.062	0.075	−0.09	0.01	−0.02	−0.011	−0.192	−0.133	−0.103	0.195	−0.051	0.013	1			
As	0.139	−0.235	−0.229	0.126	−0.133	−0.243	0.041	−0.11	−0.286	0.039	0.068	0.101	−0.251	0.37	1		
Mn	0.114	0.105	0.101	0.088	0.233	0.079	−0.07	0.114	0.187	−0.035	0.185	0.093	0.012	−0.09	0.108	1	
Fe	0.021	−0.279	−0.296	−0.087	−0.039	−0.38	0.02	0.038	0.205	0.006	−0.071	−0.07	−0.033	−0.099	−0.165	−0.087	1

Values in italics represent correlations that are significant at the 0.05 level
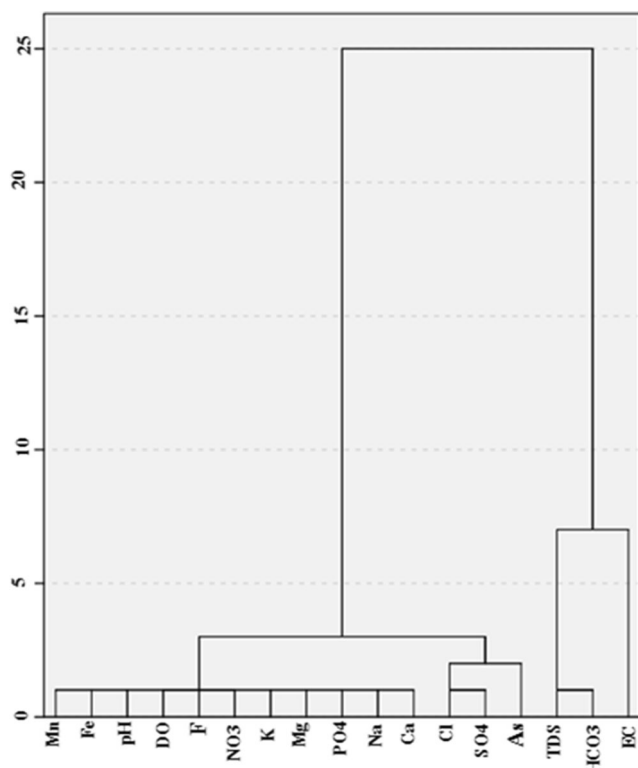
n=number of samples

Fig. 7 Dendrogram showing the clustering of selected sampling sites of groundwater according to distribution of F^-, As and other physicochemical parameters (Ward's linkage method, Euclidean distance measure percent chaining=85.6)

physicochemical parameters in the dendrogram showed one large and two small clusters. The first group included Mn, Fe, pH, PO_4^{3-}, DO, F^-, Na^+, Ca^{2+}, K^+, NO_3^-, and Mg^{2+} (Fig. 7), suggesting that all these parameters came from the same source, mainly anthropogenic (industrial) and natural activities. The second group included SO_4^{2-}, As, and Cl^- (Fig. 7). It is possible that all of the ions in this second group may have originated from the parent rock material. Elevated SO_4^{2-}, As, and Cl^- concentrations have been shown to be caused by the interaction of groundwater with aquifer sediments rich in carbonate (Ahmed et al. 2004). The third group includes TDS, EC, and HCO_3^- (Fig. 7). The elements of this group may also have originated from anthropogenic, natural, and parent rock materials. Similar results have been reported previously (Simeonov et al. 2003; Kim et al. 2005; Arain et al. 2009). Qualitative information about the clustering behavior was extracted using PCA (Table 4). PCA grouping produced seven factors having a total variance 74.3 % (Table 4). Factor-1 contributed 22.8 % of the total variance with highest loading of EC ($r=0.28$), TDS ($r=0.286$) and HCO_3^- ($r=0.273$). The sources of EC, TDS, and HCO_3^- could either be anthropogenic due to fertilizer and household wastes or geogenic activities due to weathering of the sulfide-bearing minerals and acidic rocks (Farooqi et al. 2007a, b). Factor-2 contributed 11.6 % of the total variance with high loadings of Cl^- ($r=0.52$) and Mn

($r=0.343$), suggesting the involvement of geogenic processes. Factor-3 contributed 9.3 % of the total variance with high loadings of SO_4^{2-} ($r=0.272$), Na^+ ($r=0.589$), K^+ ($r=0.356$), and Mg^{2+} ($r=0.222$) which was probably due to the local geochemistry of the area, as influenced by weathering of mafic and ultramafic rocks, manure, fertilizer, and industrial activities (Shah 2000). Factor-4 contributed 8.7 % of the total variance with high loadings of NO_3^- ($r=0.524$) and Ca^{2+} ($r=0.38$), signifying contamination from the both natural and anthropogenic sources such as fertilizer, animal farm, and the weathering of calcite rocks (Khan et al. 2012). Factor-5 contributed 8.3 % of the total variance with high loadings of As ($r=0.32$) and F^- ($r=0.681$). Higher As and F^- levels suggested that weathering of local mafic and ultramafic rocks, coal combustion, traffic activity, acid rain, pesticide use, fertilizer, and erosion of arseno-pyrite greatly influenced their release (Khan et al. 2012; Brahman et al. 2013a). Factor-6 contributed 7.5 % of the total variance with high loadings of pH ($r=0.546$) and DO ($r=0.531$) that might have been influenced by weathering of mafic and ultramafic rocks. Factor-7 contributed 5.9 % of the total variance with high loadings of PO_4^{3-} ($r=0.313$) and Fe^{2+} ($r=0.683$), suggesting that this factor might have been influenced by industrial and agricultural activity in the study area (Liu et al. 2005).

Co-occurrence of As and F^- in groundwater

Table 1 shows the As and F^- concentrations in the groundwater of Tehsil Mailsi, Punjab, Pakistan. The existence of As and F^- in groundwater samples suggested that both the elements have a common source or pathway of contamination, as a moderately positive correlation was observed between As and F^-. However, both of the elements were higher in deep groundwater samples and showed a significant positive correlation with water depth. Moreover, SO_4^{2-} showed a significant, positive correlation with As and water depth. Sulfate levels were within the permissible limits in all of the groundwater samples, but contributed synergistically to contamination with As and F^- in all of the samples. The occurrence of high F^-, As, and SO_4^{2-} in the groundwater suggests that their source might be air pollutants originating from coal combustion (Finkelman et al. 2002), specifically at brick factories, which are common in the study area (Farooqi et al. 2007; Brahman et al. 2013a).

Health risk assessment

The EDI of As and F^- have been summarized in Table 5. The results showed that EDI of As-contaminated groundwater in the local residents of Jallah Jeem and Dur Pur sites ranged from $2.4 \cdot 10^{-4}$ to $1.4 \cdot 10^{-2}$ and $1.6 \cdot 10^{-4}$ to $8.9 \cdot 10^{-3}$ mg kg^{-1} day^{-1}, respectively. Similarly, the EDI of F^- contaminated groundwater in the people of Jallah Jeem and Dur Pur ranged from 0.18 to 0.82 and 0.15 to 0.73 mg kg^{-1} day^{-1}, respectively

Table 4 Factor responsible for loadings in the experimental variables in groundwater samples ($n=52$)

Parameters	F1	F2	F3	F4	F5	F6	F7
pH	−0.024	−0.003	0.007	0.186	0.057	*0.546*	0.12
EC	*0.28*	0.007	−0.058	−0.028	0.055	−0.007	0.008
TDS	*0.286*	−0.012	−0.076	−0.009	0.054	0.027	0
DO	0.028	0.031	−0.026	−0.208	−0.21	*0.513*	−0.085
Cl^-	−0.025	*0.52*	−0.065	−0.112	0.035	−0.046	0.006
HCO_3^-	*0.273*	−0.099	−0.071	0.066	−0.062	0.027	−0.117
NO_3^-	0.04	−0.261	0.003	*0.524*	0	0.135	−0.002
SO_4^{2-}	0.022	0.185	*0.272*	0	−0.143	−0.004	0.032
PO_4^{3-}	0.06	0.171	−0.126	0.321	0.008	−0.005	*0.313*
Na^+	−0.107	−0.098	*0.589*	0.049	−0.086	−0.023	−0.072
K^+	0.074	−0.039	*0.356*	−0.122	0.272	0.096	0.141
Ca^{2+}	−0.113	0.273	0.102	*0.38*	−0.035	−0.126	−0.322
Mg^{2+}	0.112	0.033	*0.222*	−0.026	−0.015	−0.101	0.079
F^-	0.058	0.058	−0.091	−0.018	*0.681*	−0.107	0.15
As	−0.12	0.061	0.101	0.105	*0.32*	0.088	−0.288
Mn	0	*0.343*	−0.056	0.003	0.092	0.263	0.056
Fe	−0.066	−0.007	0.073	−0.028	0.098	0.067	*0.683*
Eigen values	3.882	1.983	1.587	1.481	1.412	1.284	1.003
Variability (%)	22.834	11.665	9.334	8.714	8.308	7.55	5.901
Cumulative (%)	22.834	34.499	43.832	52.547	60.854	68.405	74.306

Significant differences have been marked in italics for Tehsil Mailsi

(Table 5). In Jallah Jeem and Dur Pur locations, the THQ of As and F^- in groundwater ranged from 0.82 to 46.63 and 0.55 to 28.6, 3 to 13.6 and 2.5 to 12.1, respectively (Table 5).

Human health risk assessment quantification from the groundwater is of major importance in countries like Pakistan, where groundwater monitoring is limited, and health hazards elevated. Heavy metals are acquired through direct ingestion, inhalation, and dermal absorption; however, ingestion and dermal absorption are the common pathways (US-EPA 2004; Wu et al. 2009, 2010). High EDI values for As and F^- might be attributed to Pb–Zn sulfide mineralization, agricultural activities, industrial effluents, and mafic and ultramafic bed rocks hosting chromite deposits (Shah 2000). The data in Table 5 demonstrated that the THQ values in the study area were not within safe limits (THQ<1), suggesting that

ingestion of groundwater may be a health risk (Muhammad et al. 2011). About 80 % of the people in Jallah Jeem and Dur Pur use the water for drinking and household purposes and, thus, are considered to be at high risk due to As and F^- contamination (US-EPA 1999). This is alarming, and needs immediate attention and remediation.

Global perspectives

The As and F^- contamination in groundwater in different countries of the world, such as Bangladesh, India, China, Germany, Pakistan, Thailand, Argentina, Chile, Hungry, Nepal, USA, Mexico, Vietnam, Finland, Romania, Turkey, Kenya, Ethiopia, South Africa, Tanzania, and the USA, has been summarized in Table 6. According to the WHO (2006)

Table 5 As and F^- concentrations in ground water samples along with EDI and THQ values in the study area ($n=52$)

Parameters	Jallah Jeem Ground water $n=26$		Dur Pur Ground water $n=26$	
	Range	Mean	Range	Mean
As (mg L^{-1})	0.0085–0.507	0.0968	0.0059–0.319	0.0699
EDI (mg $kg^{-1}day^{-1}$)	2.4E−04–1.4E−02	2.7E−03	1.6E−04–8.9E−03	1.9E−03
THQ	0.82–46.63	9.00	0.55–28.6	6.3E+00
F^- (mg/L)	6.5–29.6	11.5	5.5–26.4	9.4
EDI (mg $kg^{-1}day^{-1}$)	0.18–0.82	0.32	0.15–0.73	0.26
THQ	3–13.6	5.3	2.5–12.1	4.4

Table 6 Global examples of elevated As and F⁻ in ground water

Countries	Arsenic conc. (ppb)	Fluoride conc. (ppm)	Sources	Reference(s)
Tehsil Mailsi (Punjab, Pakistan)	5.9–507	5.5–29.6	Groundwater	Present study
Lahore and Kasure districts (Punjab, Pakistan)	32–1900	2.47–21.1	Groundwater	Farooqi et al. 2007
District Tharparkar (Sindh, Pakistan)	100–3830	13.8–49.3	Underground water	Brahman et al. 2013a
Kohistan region (KPK, Pakistan)	0.13–16.69	–	Drinking water	Muhammad et al. 2010
Bangladesh	<10–>1000	–	Well waters	Dahar et al. 1997
North- West India	–	<19	Groundwater	Agarwal et al. 1997
Calcutta, India	<50–23,080	–	Arsenic-rich sediments	Mandal et al. 1996
Inner Magnolia, China	1–2400	–	Drinking water, bores	Guo et al. 2001
Jilin Province, China	–	>2–<10	Groundwater	Zhang et al. 2003
Ronpibool, Thailand	1–5000	–	Mining waste water contamination	Choprapwon and Porapakkham, 2001
Nakhon Si Thammarat Province, Thailand	1.25–5114	–	Shallow (alluvial) groundwater, mining	Williams et al. 1996
Argentina, Pampa, Cordoba	100–3810	–	Groundwater	Nicolli et al. 1989
Muenster region, Germany	–	<8.8	Wells water	Queste et al. 2001
Southeast regions, Argentina	–	3.8–182	Wells water	Paoloni et al. 2003
Chile	470–770	–		United Nations, 2001
Hungary	1–174	–	Deep groundwater	Sancha and Castro, 2001
Nepal	8–2660	–	Drinking water	Shrestha et al. 2003
Ethiopia	–	10–68	wells water	Rango et al. 2012
North eastern Ohio	<1–100	–	Natural origin	Matisoff et al. 1982
Lagunera region, Mexico	8–624	–	Well waters	Razo et al. 1990
Mexico	–	3.7	Groundwater	Carrillo-Rivera et al. 1996
Middle and eastern parts, Turkey	–	<13.7	Drinking water	Azbar and Turkman, 2000
Hanoi, Vietnam	1– 3050	–	Arsenic-rich sediments	Berg et al. 2001
Southwest Finland	17–980	–	Well waters; natural origin	Kurttio et al. 1998
Arusha Region, Tanzania	–	<330	Groundwater	Ghiglieri et al. 2012
South Africa	–	<40	Groundwater	Muller et al. 1998
Romania	1–176	–	Drinking water bores	Gurzau and Gurzau, 2001
USA	–	<4.3	Groundwater	Segreto et al. 1984
Western USA	1–48,000	–	Drinking water	Welch et al. 1988

provisional guidelines (10 ppb and 1.5 ppm for As and F⁻ in drinking water), more than 100 million people are at risk globally, with about 45 million of those belonging to developing countries (Ravenscroft et al. 2009). The situation is worse in Pakistan, where many of the regions exceed WHO As and F⁻ limits. Ashraf et al. (1990) reported elevated concentrations of As in the water reservoirs of Pakistan, i.e., Tarbela (620 ppb), Chashma (750 ppb), and Lloyd (620 ppb). Fluoride concentrations of 35.4 ppm have been reported previously in Nagar Parkar, near the Thar Desert of Pakistan (Naseem et al. 2010),13.5 ppm in Khyber Pakhtunkhwa (Shah and Danishwar 2003), and 21.1 ppm in Khalanwala, East Punjab (Farooqi et al. 2007a).

Excessive and long-term (6–10 years) human intake of toxic As above the 0.05 ppm level, leads to arsenicosis, which is the term used for arsenic health effects including skin problems, skin cancer, internal cancers (bladder, kidney, lung), and diseases of the blood vessels of the legs and feet (Karim 1999; WHO 2011). However, a recent report, (Smith et al. 2000), revealed that, despite the daily consumption of good nutritious food, some people have developed arsenic poisoning, such as the small populations of Chiu village (Chile) and, Eruani village of Laksam (Bangladesh), where drinking water contains As levels of 750 to 800 ppb and 250 to 260 ppb, respectively.

Chronic intake of fluoride at high doses leads to a wide diversity of adverse effects such as dental fluorosis, crippling skeletal fluorosis, revealed by dappled teeth in mild cases, brittle bones and neurological complications in severe cases (Fawell et al. 2006; Bhatnagar et al. 2011). The majority of studies carried out in China, India, Pakistan, and Tibet show increased instances of skeletal fluorosis and dental fluorosis, as a result of excessive fluoride consumption through water (Cao et al. 2005). Fluorosis is a widespread problem in the Yuncheng Basin, China, with almost 20 % of the people living in the basin

being affected by the disease in the last two decades (Gao 2005). Worldwide, elevated As and F^- concentrations are usually associated with calcareous minerals, or high alkaline and carbonaceous conditions where sodium ions instead of calcium ions dominate (Amini et al. 2008). In addition to natural dissolution of minerals, industrial operations such as fertilizer plants, metallurgical industries, semiconductor production generate effluents with high F^- and As. In the case of phosphate production, F^- in effluents can reach up to 3000 ppm (Ndiaye et al. 2005; Dolar et al. 2011). The sources of As in Pakistan include natural processes such as the dissolution of As compounds adsorbed onto pyrite ores. Fluorides are naturally released into the groundwater by the dissolution of fluoride-containing rocks and anthropogenic production of phosphate fertilizer, insecticides, herbicides, semi-conductors, timber preservatives, mining and smelting, and coal combustion (Mondal et al. 2006; Bundschuh et al. 2011; Brahman et al. 2013a, 2014).

Conclusions

Our study reveals that the groundwater of Jallah Jeem and Dur Pur areas of Punjab province are heavily contaminated with HCO_3^-, NO_3^-, As, and F^-. The water chemistry of both sites is dominated by Na^+-HCO_3^- and K^+-HCO_3^-. Groundwater from tube wells (60–65 m depth) has F^- concentrations up to 29.6 ppm with low Ca^{2+} and SO_4^{2-} concentrations. The highest As and F^- concentrations (507 ppb and 29.6 ppm) were recorded in the study areas of Jallah Jeem and Tehsil Mailsi. In these arid regions, the evaporative concentration of phosphate (and phosphate analog, As) in surface sediments, due to shallow water tables, plays a major role in the As contamination of the groundwater. The preferential adsorption of phosphate on sediments enhances the release of As. Our data demonstrate clearly that the co-occurrence of As and F^- is recognizable in study area groundwater especially in oxidized and alkaline environments. With a THQ less than 1, both As and F^- are a clear health risk to local inhabitants, based on US-EPA standards. Various anthropogenic, climatic and geologic factors contributed to contaminating the groundwater. We further conclude that the groundwater of Jallah Jeem and Dur Pur sites is not suitable for drinking or domestic use, but SAR values suggest that it is suitable for irrigation purpose. Therefore, we strongly recommend that water from the contaminated sites of Tehsil Mailsi must not be used for drinking purposes. The government of Pakistan should provide drinking water alternatives to these areas in recognition of the potential health risks associated with As and F^- poisoning. Further, the sources of high F^- and As in the groundwater should be traced using isotopes of environmentally stable molecules. Experiments are underway to further explore the As and F^- uptake of different crop species grown in the studied area. Different crop rotations will be the prime focus of future investigations.

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