Distribution of highly arsenic and fluoride contaminated groundwater from east Punjab, Pakistan, and the controlling role of anthropogenic pollutants in the natural hydrological cycle

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This paper reports the extended study from a previously-described study on As and F contaminated groundwater from a small village, Kalalanwala, in east Punjab, Pakistan (Farooqi *et al.*, 2007). Of the 147 groundwater samples investigated, 91% exceeded the WHO standard (10 $\mu\text{g/L}$) for As and 75% exceeded the WHO standard (1.5 mg/L) for F⁻. The highly contaminated As (max. 2400 $\mu\text{g/L}$) and F⁻ (max. 22.8 mg/L) groundwaters were found from shallow depths down to 30 m from the surface. The contaminated groundwaters are characterized by high pH (max. 8.8), alkalinity (HCO₃⁻ up to 1281 mg/L), SO₄²⁻ (max. 960 mg/L), Na⁺ (max. 1058 mg/L) and maximum electric conductivity >4.6 mS/cm.

Fluoride concentrations showed positive correlations with those of Na⁺ and HCO₃⁻ and negative ones with Ca²⁺ and Mg²⁺. The alkaline waters were saturated with calcite in spite of the low Ca²⁺ concentrations. Fluoride concentration is governed by fluorite solubility. Speciation analysis showed As is mostly in the form of As^V. There was a positive correlation between As and pH, while there is no relationship between As vs. Fe and F⁻. Thus, the fluoride and As contamination occurred in the oxidizing and alkaline conditions of the groundwater. However, F⁻ and As are derived from two or more sources. Suspected contaminant sources in the study area contained considerable amounts of F⁻ and As; fertilizers (DAP, *n* = 5) contained leachable F⁻ ranging from 53–255 mg/kg, and As 5–10 mg/kg, and coals (*n* = 8) contained F⁻ ranging from 5–20 mg/kg.

Sulfur isotopic ratios indicated that the high SO₄²⁻ in groundwater (3.2–7.0‰, CDT) is mainly derived from coal combusted atmospheric pollutants, fertilizers and household wastes. Nitrogen isotope data (8–30‰, Air) showed that NO₃⁻-N is attributed to animal waste distributed in the study area. The major chemical characteristics of the groundwaters are related with anthropogenic activities on the ground surface. The resultant major chemistry, especially highly alkaline and low Ca²⁺ and Mg²⁺ concentrations, must promote the high concentrations of F⁻ and As in the studied groundwaters.

Keywords: environmental pollution, phosphorus, semiarid climate, Indus Basin nitrogen and sulfur isotopes

INTRODUCTION

Natural and anthropogenic pollutants threaten the quality of life through the environmental pollution. From the point of view of groundwater contamination, As and F⁻ have received the most attention due to their toxicity (e.g., Smedley *et al.*, 2002). The release of soluble As species into groundwater is a serious problem in many areas of the world (e.g., Varsanyi *et al.*, 1991; Lepkowski, 1998; Welch *et al.*, 2000; Tian *et al.*, 2001; Bhattacharya *et al.*, 2004; Nickson *et al.*, 2005). The World Health Organiza-

tion (WHO) guideline of As concentration in drinking water was reduced from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ in 1993 (WHO, 1993). According to the WHO recommendation many developed countries changed the maximum admissible concentrations to 10 $\mu\text{g/L}$, however the developing countries, where arsenicosis is more widespread, are still using the previous guideline value (50 $\mu\text{g/L}$) due to the lack of facilities to analyze smaller concentrations precisely (Nickson *et al.*, 2005).

High F⁻ groundwater causes fluorosis in several regions of the world; East Africa (Nanyaro *et al.*, 1984), India (Rao *et al.*, 1993), and Inner Mongolia in China (Wang *et al.*, 1999). The drinking water limit (DWL) for F⁻ is 1.5 mg/L (WHO, 1994). Fluoride in drinking water has a narrow optimum concentration range in relation to human health. It prevents dental caries in the range of 0.7–1.2 mg/L, but is responsible for dental and skeletal

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Fig. 1. Index map showing the Punjab, study area, and location of brick kilns. Flood plain is shaded. The abbreviations for description of villages are the same as those in Table 1. The hatched area with abbreviations is the residential area.

fluorosis, if it is higher than 1.5 mg/L (CDCP, 1999).

The Pakistan Council for Research and Water Resources (PCRWR) and UNICEF have undertaken the assessment of drinking water quality since 1999 following the As crisis in Bangladesh and other neighboring countries. Consequently, the presence of As contaminated groundwaters (10–200 $\mu\text{g/L}$) has been recognized in many areas of Pakistan (www.pcrwr.gov.pk/Arsenic).

We reported As and F^- contamination of groundwater in a small village Kalalanwala, 30–35 km south of La-

hore, where >400 residents, mostly less than 15 years old, were diagnosed with bone deformity disease and molted teeth (Farooqi *et al.*, 2007). The maximum concentration of As was 1,900 $\mu\text{g/L}$ and that of F^- 21.1 mg/L. In addition to the high As and F^- , the groundwater contained high concentrations sulfate and was highly alkaline. Although As and F^- contaminated groundwater is distributed throughout the whole country, the situation of our reported area is more serious than in other areas where the maximum concentration of total As reported by

PCRWR was 200 $\mu\text{g/L}$, and that of F^- was $<2.0 \text{ mg/L}$ (www.pcrwr.gov.pk/Arsenic), and As in groundwater from Muzaffargarh area (south western edge of the Punjab) was 960 $\mu\text{g/L}$ (Nickson *et al.*, 2005).

On the basis of the previous report (Farooqi *et al.*, 2007), this study has been extended to 17 villages surrounding Kalalanwala, in order to reveal the extent and degree of groundwater pollution and to estimate the principal controlling geochemical factors concerned with the As and F^- pollution. This is based on the water chemistry including H, O, S and N isotopic ratios.

GEOGRAPHY, GEOLOGY AND CLIMATE OF THE STUDY AREA

The Punjab province, Pakistan, is located between 24–37°N and 62–75°E within an alluvial plain of the south-flowing Indus River and its five major tributaries. The districts of Lahore and Kasur are located in the central Pakistan at the eastern edge of the Punjab Province occupying an area of 3,995 and 1,772 km^2 and total population of 2.31 and 6.31 million, respectively. The present study area covers 1/5th of the Kasur and 1/6th of the Lahore districts. The area is located along the eastern bank of River Ravi (Fig. 1) and includes 17 villages between Chung, 15–20 km south from main Lahore and Zahirabad near to the district Chunian (Fig. 1). For daily water use, including drinking water, most of the residents use groundwater extracted from tube wells drilled up to 30 m in depth from the ground surface within individual dwellings.

Hydrology, hydrogeology, and aquifer sediments of the Punjab were first described in detail by Greenman *et al.* (1967); the Punjab Province is in an alluvial plain comprising >350 m thick Holocene and Pleistocene sediments transported by the Ravi and Satluj rivers. The sediments are mostly sand, containing high percentage of fine to very fine sand and silt and low organic matter content. The area is mainly recharged by the Ravi and Satluj rivers during monsoon season; however, the recharge from the rivers has diminished since canal irrigation started in the 17th century.

The Punjab province has a semiarid and subtropical continental climate characterized by sultry summers and cold winters. The mean annual maximum temperature recorded from May to June is 41°C and the mean annual minimum temperature from December to January is 4°C (Ali *et al.*, 1968).

Quaternary sediments, mainly of alluvial and deltaic origin, occur over large parts of the Indus Plain of Pakistan, predominantly in Punjab Province, (WAPDA-EUAD, 1989). The sediments there have some similarities to those of the As affected aquifers in Bangladesh and West Bengal, being Quaternary alluvial-deltaic

sediments derived from Himalayan source rocks. However, the Indus basin is climatically arid, and comprises older Pleistocene deposits including eolian sediments and is dominated by aerobic conditions of unconfined groundwater aquifers (Mahmood *et al.*, 1998; Tasneem, 1999; Cook, 1987).

SAMPLING AND ANALYSIS

The wells are installed into three different depths in the ca. 800 km^2 study area, and 147 groundwater samples were collected from those different depths: these comprise 123 samples from the shallow hand tube wells installed at 27–30 m in depth, 14 from 40–80 m in depth and 8 from deep wells 80–200 m in depth. In addition, two samples were collected from a canal drawn from Chenab River which originates from Indian Territory (Fig. 1).

Water temperature, pH, ORP, electric conductivity (EC) and alkalinity (quoted as HCO_3^-) were measured *in situ*. The ORP values were transformed to standard hydrogen electrode (SHE) readings (Eh) because the Ag/AgCl reference electrode had a difference of +200 mV with respect to SHE (Szogi *et al.*, 2004). At each site, water samples were collected for the laboratory analysis. After filtering the sample water using a 0.45 μm membrane filter, the water was transferred to two polyethylene bottles; one was acidified to 0.06 N HCl for the quantitative analysis of cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}), total As, and sulfur isotopes. The other aliquot was not acidified and used for anion analysis (Br^- , Cl^- , F^- , PO_4^{3-} , and SO_4^{2-}) and hydrogen and oxygen isotope analyses. For As^{III} and nitrogen isotope analysis 50 mL of water acidified to be 0.09 N H_2SO_4 solution was tightly sealed in a glass bottle. Sodium and K^+ were determined by atomic absorption spectrometry (SAS 7500, Seiko). Calcium and Mg^{2+} were analyzed by volumetric titration with ethylenediaminetetraacetic acid (EDTA 0.05N) with an analytical error $<\pm 2\%$. Chloride, Br^- , PO_4^{3-} , SO_4^{2-} and F^- were determined by Ion chromatograph (DX-120, Dionex) with a precision $<\pm 2\%$, estimated using duplicated standard solutions. Silica and Fe were determined with ICP-AES.

Water soluble fluoride in fertilizers was extracted to determine the concentration. Five grams of fertilizer sample and 25 mL distilled water were placed in polyethylene bottles, shaken for 0.5 hour on a shaker, centrifuged and the resultant water was used for the analysis by ion selective electrode (Orion) and ion meter (Metro Ohm). Total F^- in coal samples was analyzed by ion chromatography after the coal was alkali fused and dissolved in water (Shimizu *et al.*, 2006; Crossley, 1944). The reproducibility of analytical data was $<10\%$ for the duplicated samples. For total As in coal samples, acid digestion was used

Table 1. Concentration ranges of major anions, cations and isotopic ratios of groundwater in east Punjab, Pakistan

Locality	Abbr.	HCO ₃ ⁻ [mg/L]			Cl ⁻ [mg/L]			SO ₄ ²⁻ [mg/L]			NO ₃ ⁻ -N [mg/L]		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Chung	CNG	550	980	600	51	131	74	120	192	125	bdl	7.00	2.33
Sundar	SUN	732	1040	884	21	180	117	120	432	303	bdl	4.48	2.60
Shamkey	SKB	366	854	616	5	96	26	35	290	77	bdl	4.20	1.22
Manga Mandi	MM	201	610	430	11	262	79	14	440	250	bdl	46.0	6.50
Waran Piranwala	WP	440	616	520	13	129	71	72	341	200	bdl	5.90	1.20
Kot Asad Ullah	KAD	165	1037	537	5	241	212	30	672	461	bdl	2.00	0.3
Kalalanwala	KLW	244	1280	836	16	344	106	48	912	312	bdl	10.64	1.26
Muffat Pura	MPU	610	1160	915	62	213	138	211	960	581	bdl	bdl	bdl
Araian Da Khu	ARK	147	370	244	4	71	25	24	144	77	bdl	7.84	1.30
Deena Nath	DN	610	915	702	12	140	83	96	240	144	bdl	19.00	4.60
Nathe Khalsa	NK	490	915	732	14	70	46	96	240	163	bdl	0.70	0.40
Kot Ashraf	KA	610	671	630	54	121	83	192	290	231	0.14	11.50	0.90
Bahi Pheru	BP	213	550	427	41	52	46	67	170	127	bdl	2.52	1.30
Jamber Klan	JK	980	980	980	224	390	320	580	640	600	10.90	10.50	9.80
Rehman Pura	RPNA	494	494	494	107	144	125	355	500	432	2.60	10.00	6.20
Cantt Colony	CCO	370	430	400	10	15	12	39	72	54	bdl	bdl	bdl
Zaheer Abad	ZAB	480	793	610	213	415	304	480	960	672	7.00	14.00	9.52

Locality	Abbr.	Ca ²⁺ [mg/L]			Mg ²⁺ [mg/L]			Na ⁺ [mg/L]			K ⁺ [mg/L]		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Chung	CNG	28	48	36	5	18	11	46	460	276	3.90	8.97	5.70
Sundar	SUN	8	51	35	4	35	15	370	575	480	3.12	11.7	7.50
Shamkey	SKB	2	71	20	2	46	13	69	368	238	1.95	9.75	7.80
Manga Mandi	MM	5	93	54	2	61	27	46	460	210	2.73	39.00	12.00
Waran Piranwala	WP	4	54	23	2	16	10	115	437	315	2.73	7.80	5.12
Kot Asad Ullah	KAD	13	80	34	8	40	17	28	782	470	6.24	9.00	8.20
Kalalanwala	KLW	5	75	21	2	36	12	207	1060	483	3.90	12.10	7.05
Muffat Pura	MPU	34	57	47	11	23	17	300	805	600	6.24	11.70	9.08
Araian Da Khu	ARK	19	140	80	6	26	13	16	51	28	3.90	27.30	11.00
Deena Nath	DN	27	64	50	2	28	15	276	506	334	7.80	11.70	9.01
Nathe Khalsa	NK	11	66	40	6	35	20	230	391	300	7.80	15.60	11.04
Kot Ashraf	KA	6	47	30	3	28	17	253	370	330	3.90	11.70	9.00
Bahi Pheru	BP	10	39	24	4	17	10	69	300	215	4.29	5.07	5.00
Jamber Klan	JK	12	54	8	11	45	7	851	874	863	12.87	46.80	30.00
Rehman Pura	RPNA	4	23	53	5	14	40	240	44	345	11.70	23.40	18.00
Cantt Colony	CCO	60	66	63	31	47	24	12	19	16	19.50	27.30	24.00
Zaheer Abad	ZAB	6	15	12	2	13	9	575	900	713	9.75	19.50	15.00

(Aruscavage, 1977). A 0.1 g sample was taken into 125 mL Erlenmeyer flask; 20 mL HNO₃ and 2 mL H₂SO₄ were added and left overnight. 3 mL of HClO₄ was added into the flask, which was then heated at 175°C with a refluxer. After heating for 30 min., the refluxer was removed and the flask was heated continually till dense fumes came out. Finally, the flask was cooled down and 25 mL 6N HCl was added. The obtained sample solution was analyzed by hydride generation atomic absorption spectrometry (HGAAS, SAS 7500, Seiko Instruments).

For total As analysis, 2 mL of 12M HCl was added to 15 mL of sample water together with 0.25 mL of a solution containing 10% KI and 10% ascorbic acid. Hydride generation atomic absorption spectrometry (HGAAS,

SAS 7500, Seiko Instruments) was employed to measure the total As produced as the gaseous form (AsH₃) by reduction using sodium borohydride as reductant. Reproducibility of the analytical data was within 5%, and the analytical error estimated to be <10%, based on the analytical results of standard stock solutions independently prepared from the commercially distributed standard solution using a standard calibration line. The lower limit of quantification of As was 1 ppb.

Arsenite (As^{III}) concentrations were determined by the Voltammetry introduced by Holak (1980). The Voltammetry applied for natural waters has an advantage to reduce interference by dissolved salts. The lower detection limit of arsenite was 5 ppb, and the relative stand-

Table 1. (continued)

Locality	Abbr.	EC [mS/cm]			Eh [mV]			pH			SiO ₂ [mg/L]		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Chung	CNG	0.38	1.95	1.24	257	320	298	7.3	8.3	7.8	12	27	23
Sundar	SUN	1.30	2.60	2.10	273	363	328	7.2	8.1	7.8	21	25	23
Shamkey	SKB	0.70	1.70	1.12	218	358	312	7.2	8.8	8.0	15	29	23
Manga Mandi	MM	0.55	1.90	1.20	265	362	332	7.2	8.7	8.2	15	34	27
Waran Piranwala	WP	0.82	2.00	1.61	291	360	313	7.8	8.6	8.0	12	27	21
Kot Asad Ullah	KAD	0.34	3.70	2.20	222	316	287	7.6	8.3	7.7	7	20	14
Kalalanwala	KLW	0.45	4.60	2.19	225	343	276	7.6	8.7	8.1	16	27	22
Muffat Pura	MPU	1.40	4.10	2.90	315	324	323	7.7	8.0	7.5	18	26	23
Araiyan Da Khu	ARK	0.20	1.00	0.56	273	385	306	7.2	7.6	7.5	10	20	16
Deena Nath	DN	1.10	2.10	1.50	220	775	361	7.3	8.0	7.9	15	37	26
Nathe Khalsa	NK	1.24	1.70	1.40	276	346	314	7.3	7.9	7.7	12	32	24
Kot Ashraf	KA	1.20	1.38	1.50	288	320	304	8.2	8.6	8.1	19	27	23
Bahi Pheru	BP	0.64	1.50	1.11	310	337	325	7.5	8.1	8.0	12	29	21
Jamber Klan	JK	3.40	3.60	3.50	322	329	324	8.1	8.3	8.0	18	21	20
Rehman Pura	RPNA	1.82	2.10	1.90	258	264	261	7.5	7.8	7.6	19	22	21
Cantt Colony	CCO	0.50	0.70	0.60	243	258	254	7.2	7.3	7.6	25	29	27
Zaheer Abad	ZAB	2.20	4.40	3.20	218	343	283	7.4	8.5	8.2	15	30	25

Locality	Abbr.	Fe [mg/L]			$\delta^{18}\text{O}$ [‰]			δD [‰]			$\delta^{34}\text{S}$ [‰]		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Chung	CNG	bdl	0.17	0.05	-8.37	-7.5	-8.19	-53.8	-46.9	-52.4	5.1	5.4	5.3
Sundar	SUN	bdl	0.10	0.03	-8.50	-7.30	-7.68	-53.25	-45.9	-53.18	5.7	5.7	5.7
Shamkey	SKB	bdl	0.24	0.09	-9.30	7.79	-8.66	-61.91	-48.81	-55.39	5.6	7.0	5.8
Manga Mandi	MM	bdl	0.56	0.07	-8.70	-7.20	-7.80	-56.35	-42.54	-48.37	5.0	5.7	5.4
Waran Piranwala	WP	bdl	0.16	0.05	-8.30	-7.44	-8.01	-52.92	-43.68	-47.91	4.9	5.8	5.4
Kot Asad Ullah	KAD	bdl	2.42	0.70	-8.17	-7.25	-8.64	-52.92	-43.68	-47.91	5.3	5.6	5.5
Kalalanwala	KLW	bdl	0.50	0.12	-8.70	-7.65	-8.27	-60.68	-47.0	-52.85	5.2	5.8	5.5
Muffat Pura	MPU	0.14	0.25	0.18	-8.10	-7.90	-8.01	-51.0	-50.35	-50.6	5.7	5.7	5.7
Araiyan Da Khu	ARK	bdl	0.50	0.13	-7.87	-7.22	-7.57	-56.0	-44.42	-48.9	5.0	5.6	5.3
Deena Nath	DN	bdl	0.23	0.07	-8.13	-7.20	-7.75	-52.0	-46.48	-49.25	5.0	5.5	5.3
Nathe Khalsa	NK	bdl	2.80	0.60	-8.37	-8.20	-8.27	-54.79	-45.29	-51.81	5.8	6.3	6.0
Kot Ashraf	KA	bdl	0.03	0.01	-8.70	-7.50	-8.10	-48.76	-45.71	-47.5	5.6	5.7	5.6
Bahi Pheru	BP	0.02	0.04	0.03	-8.55	-7.91	-8.46	-56.35	-50.47	-52.6	5.3	5.6	5.4
Jamber Klan	JK	bdl	0.60	0.30	-7.80	-7.70	-7.75	-57.0	-46.48	-49.25	3.7	3.9	3.8
Rehman Pura	RPNA	0.01	0.03	0.02	-8.28	-7.30	-7.79	-50.59	-49.91	-50.25	3.7	3.8	3.7
Cantt Colony	CCO	0.15	0.22	0.20	-9.60	-9.32	-9.18	-48.47	-47.09	-47.78	5.5	5.6	5.5
Zaheer Abad	ZAB	0.03	0.03	0.03	-7.84	-7.00	-7.58	-59.83	-52.43	-54.79	4.3	4.7	4.5

“bdl” means below detection limit.

Detection limits for NO_3^- -N, and Fe are 0.05 and 0.01, respectively.

ard deviation was 8.5% for 20 ppb of the solution in this method. As^{V} is calculated from the concentration difference between the total As and As^{III} . The detection limit was determined from the lowest concentration of the standard solution giving the optical peak.

Sulfate was extracted as BaSO_4 by adding 10% BaCl_2 solution in water samples for sulfur isotope analysis. The precipitated BaSO_4 was collected on a $0.45\ \mu\text{m}$ membrane filter paper, dried, and ground together with SiO_2 and V_2O_5 . The sample powder was reduced to produce SO_2

gas by heating at 1120°C following the method by Yanagisawa and Sakai (1983). To analyze the sulfur isotopes of coal, the sample was processed according to the procedure modified from Nakai and Jensen (1967), and Ohizumi *et al.*, (1997). Two grams of coal was accurately weighed and combusted at 900°C in a vacuum line. The resulting gases were oxidized in 3% H_2O_2 solution to produce sulfate ions. The obtained solution was passed through a $0.45\ \mu\text{m}$ membrane filter and the dissolved sulfates were recovered via BaSO_4 precipitation using the

Table 2. Ranges of analytical data of groundwaters classified by the well depth and canal water

	Unit	Shallow (n = 123)			Middle (n = 14)			Deep (n = 8)			Canal water (n = 2)		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
EC	mS/cm	0.4	4.6	2.6	0.2	2.2	0.8	0.5	1.9	1.10	0.5	0.7	0.6
pH		7.3	8.8	8.0	7.1	8.7	8.0	6.9	8.7	7.9	7.5	7.6	7.6
Temperaure	°C	26	28	27	24	27	26	23	24	23	27	27	27
HCO ₃ ⁻	mg/L	195	1280	652	153	732	371	146	671	360	366	430	400
SO ₄ ²⁻	mg/L	38.0	960	257	24.0	480	125	32.0	341	150	36.0	72.0	54.0
Cl ⁻	mg/L	2.00	415	175	4.00	250	58.0	10.0	160	63.0	10.0	15.0	12.0
PO ₄ ³⁻	mg/L	bdl	2.18	0.30	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Br ⁻	mg/L	bdl	1.12	0.40	bdl	0.54	0.20	0.40	0.32	0.24	bdl	bdl	bdl
NO ₃ -N	mg/L	bdl	46.00	9.00	bdl	0.70	0.20	bdl	0.84	0.30	bdl	bdl	bdl
F ⁻	mg/L	0.11	22.8	6.30	0.25	4.20	1.50	0.50	3.10	1.10	1.70	2.28	2.00
Ca ²⁺	mg/L	2.0	138	32.0	19.0	73.0	45.0	6.0	86.0	53.0	60.0	66.0	63.0
Mg ²⁺	mg/L	1.44	65.0	14.7	5.5	39.6	18.0	5.0	35.0	18.0	2.0	49.0	24.0
Na ⁺	mg/L	12.0	1060	630	16.0	322	150	23.0	306	150	12.0	19.0	16.0
K ⁺	mg/L	2.7	46.8	5.2	2.0	8.6	5.4	4.0	8.6	6.0	20	28	24
SiO ₂	mg/L	7.4	37	22.3	10	28.6	22	11	30	20.5	26	29	27
As	µg/L	1.0	2400	123	14	392	72	8.0	611	139	1.0	1.0	1.0

"bdl" means below detection limit.

Detection limits for Br⁻, NO₃⁻-N and PO₄³⁻ are 0.02, 0.05 and 0.025, respectively.

same procedure as that for groundwater. The sulfur isotope ratio was measured using a mass spectrometer VG SIRA 10. The obtained isotope ratios are expressed in the familiar delta notation $\delta^{34}\text{S}$, referring to the CDT (Canyon Diablo Troilite) scale and defined by Eq. (1). The analytical precision for $\delta^{34}\text{S}$ was $<\pm 0.2\text{‰}$.

$$\delta^{34}\text{S} = \left[\frac{\left(\frac{{}^{34}\text{S}_{\text{sample}}}{{}^{32}\text{S}_{\text{sample}}} \right)}{\left(\frac{{}^{34}\text{S}_{\text{standard}}}{{}^{32}\text{S}_{\text{standard}}} \right)} - 1 \right] \times 1000. \quad (1)$$

Oxygen isotope ratios ($^{18}\text{O}/^{16}\text{O}$) were measured by H₂O–CO₂ equilibration method originally developed by Epstein and Mayeda (1953), using an online vacuum system attached to a mass spectrometer (VG-PRISM, Micromass). The analytical error was within 0.1‰. Hydrogen isotope ratios (D/H) were determined by the online Cr reduction method (Itai and Kusakabe, 2004) attached with a mass spectrometer (VG-SIRA10, Micromass). The analytical error was within 0.5‰.

The Devarda's alloy/ammonia protocol, developed by Sigma *et al.* (1997), was used for pretreatment of NO₃⁻-N isotope analysis. Nitrogen isotope analysis was carried out using an online elemental analyzer interfaced with an isotope ratio mass spectrometer (EA-IRMS). Based on the multiple analyses of laboratory standards (KNO₃, (NH₄)₂SO₄, and DL-alanine), the precision of the analytical data was $<0.20\text{‰}$.

To estimate the equilibrium condition of the minerals possibly controlling the soluble chemical species, saturation indices were calculated using an internet-based version of the USGS program PHREEQ (Parkhurst, 1995).

RESULTS

Analytical results of all water samples are listed in Appendix. Groundwater samples were categorized into three groups for convenience according to the well depth; shallow (20–27 m), middle (40–80 m) and deep (80–200 m). Geochemical characteristics of the groundwater are described in the following.

Major constituents

Analytical results of major and stable isotope ratios are summarized according to location in Table 1. The chemistry is summarized according to well depth in Table 2. Chemistry of the groundwater showed large variation in the concentration ranges, however, many of those contained high salinity. As described below, the ranges of each ion overlapped among the groundwaters from the different depths; the highest concentration of major anions and Na⁺ were almost twice as high in the shallow groundwaters than in the middle and deep groundwaters.

The shallow groundwaters gave the widest range of EC within 0.4 and 4.6 mS/cm, and most of those have EC >2.0 mS/cm. The alkalinity calculated as HCO₃⁻, was 195–1280 mg/L and sulfate ranged from 38.0 to 960 mg/L, such that 35% of the analyzed groundwaters exceeded the WHO guideline value (250 mg/L). Sulfate and bicarbonate were the most abundant anions. The Cl⁻ ranged from 2.0 to 415 mg/L. Sodium, the most dominant cation, was up to 1,060 mg/L, while Ca²⁺ concentrations were low, ranging from 2.0 to 140 mg/L with a mean value of 32.0 mg/L.

Electric conductivity of the middle groundwaters was 0.2–2.2 mS/cm, SO₄²⁻ 24.0–480 mg/L, alkalinity (as

HCO_3^- 153–732 mg/L, Na^+ up to 322 mg/L, Ca^{2+} 19–73 mg/L with a mean value of 45 mg/L, and Cl^- up to 250 mg/L. Groundwater from the deep aquifers showed narrow ranges of analytical data compared with those of shallow and middle groundwaters; EC 0.5–1.9 mS/cm, SO_4^{2-} 32.0–341 mg/L, alkalinity 146–671 mg/L, Na^+ up to 306

mg/L, Ca^{2+} 6.0–86 mg/L, and Cl^- up to 160 mg/L. The high EC and high concentration of the above dissolved species in shallow groundwater show that the shallow groundwater could be easily affected by the human activities.

More than half of the samples had $\text{Na}^+\text{--HCO}_3^-$ dominant type chemistry (Fig. 2). The classification based on major ions does not depend on the well depth. However, Ca^{2+} and Mg^{2+} tend to be slightly higher in the middle and deep groundwaters than in the shallow groundwater. Despite this, the groundwaters containing high amounts of dissolved species appear mostly from the shallow wells. The trilinear diagram showing anion composition in Fig. 2 gives the linear relationship for the anion composition between HCO_3^- and $\text{Cl}^- + \text{SO}_4^{2-}$, suggesting that the latter two have common origins as major contaminants, e.g., household waste and fertilizers. The waters were in neutral to alkaline pH of 7.1–8.7.

The two canal water samples had EC 0.5–0.7 mS/cm, pH 7.3, and SO_4^{2-} 36.0–72.0 mg/L, alkalinity 427 mg/L, Na^+ 12.0–19.0 mg/L, Ca^{2+} 60.0–66.0 mg/L and Cl^- 10.0–15.0 mg/L. The concentrations of the soluble components were much lower than the average values of the studied groundwaters with the exception of Ca^{2+} .

High NO_3^- -N concentrations were observed in shallow groundwaters, which can easily be affected by land

Fig. 2. Piper diagram showing the chemical compositions of groundwater samples. Solid triangles are symbols for shallow, diamond for middle, and square for deep groundwaters.

Fig. 3. Relationships of Cl^- vs. SO_4 (a), Na^+ (b), HCO_3^- (c), As (d), F^- (e) and $\text{NO}_3\text{--N}$ (f). Circles are symbols for canal water and the rest of the symbols are the same as those in Fig. 2.

Table 3. Summary statistical data for fluoride and arsenic in study area

Locality	As(V) [$\mu\text{g/L}$]					As(III) [$\mu\text{g/L}$]					F ⁻ [mg/L]				
	Min	Max	Mean	n	>10 $\mu\text{g/L}$	Min	Max	Mean	n	>10 $\mu\text{g/L}$	Min	Max	Mean	n	>1.5 $\mu\text{g/L}$
Chung															
All samples	5	67	27	5	4	nd	nd	nd	5	0	0.24	8.4	4.40	5	4
Only Shallow	3	8	6	4	3	nd	nd	nd	5	0	2.67	8.4	5.50	4	4
Sundar															
All samples	1	93	51	5	4	nd	nd	nd	5	0	1.52	10.1	5.80	5	5
Only Shallow	1	93	51	5	4	nd	nd	nd	5	0	1.52	10.1	5.80	5	5
Shamkey Bhatain															
All samples	3	883	132	25	24	nd	nd	nd	25	0	2.00	17.1	4.70	25	25
Only Shallow	3	443	105	21	20	nd	nd	nd	25	0	0.95	17.1	5.09	21	19
Manga Mandi															
All samples	3	672	121	17	13	nd	nd	nd	17	0	0.45	4.2	1.33	17	10
Only Shallow	4	424	68	14	10	nd	nd	nd	17	0	0.45	4.2	1.33	14	10
Waran Piran Wala															
All samples	36	681	197	11	11	nd	nd	nd	11	0	0.95	11.0	5.50	11	10
Only Shallow	33	677	171	7	7	nd	nd	nd	11	0	2.09	11.0	6.50	7	7
Kot Asad Ullah															
All samples	8	168	65	12	11	nd	nd	nd	12	0	0.40	19.0	8.10	12	9
Only Shallow	10	171	83	8	8	nd	nd	nd	12	0	7.60	19.0	11.23	8	8
Kalalnwala															
All samples	23	2400	291	29	29	nd	nd	nd	27	0	2.70	22.8	11.20	27	25
Only Shallow	23	2400	291	25	25	nd	nd	nd	27	0	2.70	22.8	11.20	25	25
Muffat Pura															
All samples	50	62	57	3	3	nd	nd	nd	3	0	0.11	0.6	0.30	3	0
Only Shallow	50	62	57	3	3	nd	nd	nd	3	0	0.11	0.6	0.30	3	0
Arian Da Khu															
All samples	1	74	37	10	6	10	23	16	9	3	0.30	0.6	0.50	9	0
Only Shallow	1	74	37	6	3	12	23	11	6	2	0.30	0.6	0.50	6	0
Deena Nath															
All samples	7	39	25	6	4	nd	nd	nd	6	0	0.76	15.4	6.20	6	4
Only Shallow	7	39	25	6	4	nd	nd	nd	6	0	0.76	15.4	6.20	6	4
Nathy Khalsa															
All samples	37	96	58	6	6	nd	nd	nd	6	0	0.50	11.4	4.10	6	4
Only Shallow	37	96	58	6	6	nd	nd	nd	6	0	0.50	11.4	4.10	6	4
Kot Ashraf															
All samples	173	624	398	3	3	nd	nd	nd	3	0	1.14	4.4	2.50	3	3
Only Shallow	173	624	398	3	3	nd	nd	nd	3	0	1.14	4.4	2.50	3	3
Bhai Pheru															
All samples	39	112	70	3	3	nd	nd	nd	3	0	1.00	12.0	5.70	3	3
Only Shallow	39	112	70	3	3	nd	nd	nd	3	0	1.00	12.0	5.70	3	3
Jambar Kalan															
All samples	5	100	53	2	1	nd	nd	nd	2	0	9.50	13.3	11.4	2	2
Only Shallow	5	100	53	2	1	nd	nd	nd	2	0	9.50	13.3	11.4	2	2
Rehman Pura															
All samples	21	69	45	2	2	nd	nd	nd	2	0	1.70	4.6	3.10	2	2
Only Shallow	21	69	45	2	2	nd	nd	nd	2	0	1.70	4.6	3.10	2	2
Camt Colony															
All samples	1	1	1	2	0	nd	nd	nd	2	0	1.71	2.28	2.00	2	2
Only Shallow	1	1	1	2	0	nd	nd	nd	2	0	1.71	2.28	2.00	2	2
Zahir Abad															
All samples	13	55	29	5	5	nd	nd	nd	5	0	3.80	8.4	5.80	5	5
Only Shallow	13	55	29	5	5	nd	nd	nd	5	0	3.80	8.4	5.80	5	5

“nd” means not detected.

Detection limit for As(III) is 5 ppb.

Fig. 4. Distribution map of As and F⁻ in the study area with their minimum, maximum and mean concentrations.

use. Six of them contained NO_3^- -N in excess of the WHO standard (10 mg/L) for drinking water. The highest concentration of NO_3^- -N was 46 mg/L. Middle and deep waters had NO_3^- -N of <10 mg/L (WHO standard), with the exception of two samples from the middle depth. The absence of NO_3^- -N in the deep waters would not be related to NO_3^- reduction as the groundwaters showed Eh values, up to 775 mV (Table 1). It is more likely due to the lack of nitrogen pollution at depths >30 m.

Fe concentration was low in the studied groundwaters in accordance with the highly positive Eh, indicating the oxidizing conditions prohibit high Fe dissolution. Most of the studied groundwater showed Fe concentrations below the detection limit, 0.01 mg/L. Only twelve samples had higher Fe, i.e., more than the WHO standard of 0.3 mg/L, and the maximum concentration was 2.8 mg/L at depth of 20–27 m.

The relationships between Cl^- vs. SO_4^{2-} , Na^+ , NO_3^- -N, and HCO_3^- , are given in Figs. 3a to 3f. Sulfate, Na^+ , HCO_3^- and NO_3^- -N concentrations show positive correlations with Cl^- (Figs. 3a, 3b, 3c, and 3f). Thus, among these elements the pollutant source(s) are either identical or the courses are similar.

Arsenic

Arsenic concentrations in the groundwater samples widely range from 1 to 2400 $\mu\text{g/L}$. The concentration of this element in the two canal water samples was 1 $\mu\text{g/L}$. Of 123 shallow groundwaters, 11 (ARK-1, 2, MM-4, 5, 8, 9, DN-1, 3, SKB-12, JK-2, and CNG-1, Appendix) contained <10 $\mu\text{g/L}$ of As. One common feature among these groundwater samples was that they contain high NO_3^- -N, e.g., MM-5 was amongst the highest containing NO_3^- -N. In the middle groundwaters, As ranged from 22 to 91 $\mu\text{g/L}$ ($n = 14$) with one exception, ARK-8, which contains 881 $\mu\text{g/L}$ As and has an exceptionally low SO_4^{2-} concentration (29 mg/L). The deep groundwaters ($n = 8$) had a 8–80 $\mu\text{g/L}$ range of As concentration with the exception of two samples, KLV-2 and MM-13, having As concentrations 242 and 611 $\mu\text{g/L}$ respectively.

Enormously high concentrations of As were found from shallow-well waters in four villages from the western and eastern part of the study area; 2400 $\mu\text{g/L}$ in Kalalanwala and Kot Asad Ullah (KLV and KAD have different names but share residential areas), 883 $\mu\text{g/L}$ in Shamkey Bhatian (SKB), 672 $\mu\text{g/L}$ in Manga Mandi (MM), and 681 $\mu\text{g/L}$ in Waran Piran Wala (WP) (Table 3 and Fig. 4a). These four villages are located near the area where brick kilns are concentrated. The maximum As concentrations of groundwaters in the villages distributed toward west to southwest from the kiln area are between 50 and 112 $\mu\text{g/L}$ except in Kot Ashraf (KA) where the maximum concentration is 625 $\mu\text{g/L}$. At Chung (CNG), 15 km away from the main Lahore City, the groundwaters

Table 4. Nitrogen isotope data

Sr No.	Sample ID	NO_3^- -N (mg/L)	$\delta^{15}\text{N}$ (‰, air)
1	MM-2	8.68	30.0
2	MM-3	7.42	14.0
3	MM-4	5.60	13.0
4	MM-5	46.00	25.0
5	MM-8	6.72	12.5
6	KLV-16	10.64	15.0
7	DN-3	18.90	12.5
8	DN-5	3.36	9.4
9	KA-3	11.48	8.1
10	ZAB-1	7.00	5.7
11	ZAB-2	7.56	5.0
12	ZAB-3	5.60	5.0
13	ZAB-4	14.00	5.0
14	ZAB-5	10.50	3.5
15	ARK-5	7.84	11.0
16	SKB-6	4.20	10.0
17	SKB-14	3.50	12.5
18	SKB-22	3.08	11.9
19	JK-1	10.50	15.0
20	JK-2	10.00	14.5
21	RPNA-2	10.00	7.2
22	Urea-1	na	1.4
23	Urea-2	na	0.9
24	Urea-3	na	1.6

“na” means not analyzed.

had As concentrations up to 67 $\mu\text{g/L}$, while those in Sundar (SUN) had 90 $\mu\text{g/L}$ As. Such a distribution of As concentrated groundwaters can support the previously proposed hypothesis that wet and dry deposition of As derived from combusted coals in the brick kilns is one of the contributing factors to high As and F^- in the study area (Farooqi *et al.*, 2007). On the other hand, canal waters (Cantt Colony, CCO) had As values <1 $\mu\text{g/L}$, implying that the surface running water is not seriously contaminated by As.

Voltammetry demonstrated that 97.3% of the 147 samples did not contain detectable amounts of As^{III} . Only the remaining 4 groundwaters contained detectable As^{III} . Those were found in the groundwater from the village ARK (Arain Da Khu), where the maximum concentration of As^{III} was 23 $\mu\text{g/L}$ in 56 $\mu\text{g/L}$ total As. Two of the four samples were from the shallow wells (ARK-1, 3), while the other two were from the middle (ARK-6) and deep (ARK-9) wells. The chemical compositions of these waters were mostly similar to those of the other waters collected from this village, where the EC value is 0.2–1.0 mS/cm and pH is neutral to alkaline. This village is the only one located in the flood plain among the studied villages, thus, its geographical location is probably related to the appearance of As^{III} .

Water soluble As in fertilizers (DAP) is estimated to

Table 5. Fluoride and As concentrations in coals and fertilizers

	Coals			Fertilizers	
	F (Total)	As (Total)		F (Leachable)	As (Leachable)
Coal-1	9.32	12	DAP-1	180	5
Coal-2	5.12	8	DAP-2	250	7
Coal-3	10.2	4	DAP-3	255	8
Coal-4	20.1	5	DAP-4	120	10
Coal-5	8.03	4	DAP-5	60	7
Coal-6	9.04	6			
Coal-7	8.11	8			
Coal-8	10.4	9			

All values are in mg/kg.

be 5–10 mg/kg with an average value of 7.4 mg/kg. The coal samples contain this element ranging from 4 to 12 mg/kg with an average value of 8 mg/kg (Table 5). Such a high concentration of As in fertilizers would be a potentially large pollutant source of surface soil and underlying groundwater associated with cultivation in the study area. The major anthropogenic introduction of As into the environment occurs by the use of pesticides in the form of calcium arsenate, arsenic acid, lead arsenate and sodium arsenate (Alloway, 1970; Woolson *et al.*, 1971). We have not analyzed pesticides in this study; however the use of pesticides must be responsible for the high As concentrations in the local groundwater.

Fluoride

Fluoride concentrations were high in the shallow-well waters that showed the high EC values >2.0 mS/cm. The 75% of water samples exceeded the WHO standard (1.5 mg/L), the maximum F⁻ content was 22.8 mg/L found in K LW. Twenty seven groundwater samples contained <1.5 mg/L F⁻ and nine of them were from MM, and six from ARK (Appendix), both of which are close to the kiln concentrated area. One of the F⁻ source(s) was suggested to be from air pollutants since the local rainwater contained a certain amount of F⁻ (Farooqi *et al.*, 2007). However less contaminated groundwaters in MM (Manga Mandi) imply that other larger source(s) of F⁻ must be present in this area.

Of the middle groundwaters, 63% had F⁻ content <1.5 and 37% have >1.5 mg/L. The maximum concentration was up to 4.2 mg/L found in KAD. The groundwater samples from the deep wells were <1.5 mg/L with the only exception of one sample K LW-2 that contained F⁻ 3.1 mg/L. The canal waters had F⁻ content 1.7–2.3 mg/L. Such an occurrence implies that the F⁻ is derived from the surface, and this ion decreases with increasing well depth.

Figures 4a and 4b, show that the highly As contaminated areas were also contaminated by high F⁻, e.g., in K LW, KAD, SKB and WP, but not the same well waters.

Figure 5 shows that F⁻ and As had a negative correlation. These facts suggest that not only one but rather more than two mechanisms and/or pollutant sources are responsible for the formation of the highly As and F⁻ contaminated groundwaters in the study area.

From Figs. 5b, 5c, 5d and 5e, weakly positive correlations are observed between F⁻ vs. HCO₃²⁻ and Na⁺ (Figs. 5b and 5c), while negative correlations exist between F⁻ vs. Ca²⁺ and Mg²⁺ (Figs. 5d and 5e). Such negative correlations suggest that the low Ca²⁺ and Mg²⁺ concentrations lead to occurrence of highly F⁻ containing groundwaters. Low Ca²⁺ and high Na⁺ concentrations could be explained by the cation exchange reaction in which Ca²⁺ originally in the water has been exchanged by Na⁺, or removed due to precipitation of carbonate minerals under high alkalinity (e.g., Nickson *et al.*, 2005). Fluoride did not show good relationship with pH (Fig. 5f).

Air pollutants from coal combustion and phosphate fertilizers are common sources of F⁻ in the environment (Pickering, 1985). The fertilizers contained soluble F⁻ ranging from 60 to 255 mg/kg with an average value of 175 mg/kg, while, coal samples contained total F⁻ ranging 5.12 to 20.1 mg/kg with an average value of 10.2 mg/kg (Table 5).

Stable isotopic compositions

Oxygen and hydrogen isotopes The ranges of stable isotopic ratios of hydrogen and oxygen of the groundwater samples are summarized in Table 1. The relationship between $\delta^{18}\text{O}$ and δD of groundwaters is plotted in Fig. 6, along with those values of local rainwaters.

Oxygen isotopic ratios of the groundwater ranged within –9.6 and –7.0‰, while δD within –61.9 to –42.5‰. The compositions did not show any distinctive relationship to well locations or depth. The $\delta^{18}\text{O}$ of canal waters ranged from –9.6 to –9.3‰ and δD from –59.8 to –52.4‰. The $\delta^{18}\text{O}$ and δD of all studied groundwater samples fell between those of the rain and canal waters, indicating

Fig. 5. Relationships of F^- with As (a), HCO_3^- (b), Na^+ (c), Ca^{2+} (d), Mg^{2+} (e), and pH (f). Symbols are identical to those in Fig. 3.

mixing between local meteoric water and the water from the river, which is mainly recharged at higher altitudes in Indian territory. The waters plot on a slope parallel to that of global meteoric water line (GMWL, $\delta D = 8 \times \delta^{18}O + 10$, Fig. 6), indicating that evaporation was not significant in the local groundwaters.

Sulfur isotopes Sulfur isotopic composition is an efficient tool for tracing and identifying the SO_4^{2-} pollutant sources. The $\delta^{34}S$ values of the studied groundwaters range from +3.7 to +7.0‰, and three groups can be identified from the data (Fig. 7a); groundwaters having constant $\delta^{34}S$ values (5.5–5.7‰) irrespective to the SO_4^{2-} concentration (A), those with high $\delta^{34}S$ values (6.3–7.0‰) and low SO_4^{2-} (B), those with low $\delta^{34}S$ values (3.7–4.8‰) and high SO_4^{2-} (C). The $\delta^{34}S$ values of rainwater ($n = 3$) range from 5.0 to 7.0‰. The $\delta^{34}S$ values of coal collected from the study area ($n = 8$) range within 3.5–10‰ with an average value of 6.0‰. The $\delta^{34}S$ values of fertilizer (DAP, $n = 5$) ranged within 3.4–7.6‰ with the mean value of 5.7‰.

In group A, all samples had $\delta^{34}S$ values around 5.5–5.7‰ with widely varying SO_4^{2-} concentrations. One of the SO_4^{2-} sources must be atmospheric pollution, since rainwater and coal samples also showed average $\delta^{34}S$ value around 6.0‰ and SO_4^{2-} concentration in the rain was 14 mg/L. The range is also concordant with the aver-

age $\delta^{34}S$ value of the fertilizers. In conjunction with the fact that considerable evaporation-condensation does not occur following recharge, high SO_4^{2-} concentration in the groundwaters of this group must be caused by the fertilizers distributed in the study area, although the recharging water was already contaminated by airborne sulfur.

Group B is characterized by the $\delta^{34}S$ values >6‰ with low SO_4^{2-} concentrations <250 mg/L. The maximum $\delta^{34}S$ value is +7.0‰, which is close to that of household detergents (+8.5 to +13.6‰; Laura *et al.*, 2004).

Group C groundwaters had low $\delta^{34}S$ and high SO_4^{2-} concentrations. All waters of this group were obtained from the villages RPNA, JK and ZAB, located at southwest of the study area in Fig. 7b, away from the brick kiln area. The effect of atmospheric pollution and fertilizers would be smaller in this area compared to other locations in the study.

The sulfur source cannot be elucidated, since $\delta^{34}S$ values of fertilizers and air pollutants overlap. However, the SO_4^{2-} in the groundwaters of the study area appears generally to have originated from fertilizers, air pollutants and household waste water including detergent used in the area.

Nitrogen isotopes Nitrate $\delta^{15}N$ was analyzed for 21 groundwaters to identify the sources of nitrogen contaminants (Table 4). Most of the groundwater samples give

Fig. 6. Oxygen versus Hydrogen isotope ratios. Symbols are identical to those in Fig. 3.

$\delta^{15}\text{N}_{\text{NO}_3} > 5\text{‰}$, with the maximum value 30‰ and the mean one 10‰ . The $\delta^{15}\text{N}_{\text{NO}_3}$ of the groundwater samples are in the same range of those of animal waste: for example, nitrate originating from animal excrement displays $\delta^{15}\text{N}_{\text{NO}_3}$ values typically in the range within $+10$ to 20‰ (Heaton, 1986; Widory *et al.*, 2004), and $+8$ to 25‰ (Fogg *et al.*, 1998). Volatilization and denitrification by microbial activities fractionate N isotopes such that ^{15}N becomes enriched in soil, although those two processes cannot increase $\delta^{15}\text{N}$ by more than 10‰ (Gormly and Spalding, 1979). Thus, the $\delta^{15}\text{N}_{\text{NO}_3}$ indicates human and animal waste distributed inside the villages as the major nitrate source.

The groundwaters from Zahir Abad (ZAB), the southwesternmost village among the studied villages, showed a narrow range of $\delta^{15}\text{N}$ from 3.5 – 5.7‰ . The $\delta^{15}\text{N}$ of fertilizer samples (urea, $n = 3$) were also analyzed, and those values were $< 2\text{‰}$, close to that of air. The range of $\delta^{15}\text{N}$ of ZAB groundwaters is in concordant with that of soil organic nitrogen (e.g., Chapella 2001) and chemical fertilizers used in China (Li *et al.*, 2007) but slightly larger than those used in this area. Since the concentration of NO_3^- -N is not very low in the analyzed waters, the soil organic nitrogen would not be the only source for this component. Denitrification of urea in the fertilizers would promote to enrich in ^{15}N in those waters.

DISCUSSIONS

Pollutant sources

Although As and F^- rich groundwaters are well known to occur naturally in many parts of world, anthropogenic

Fig. 7. The relationship between sulfur isotope ratios and sulfate concentrations (a), and the sulfur isotope ratios of groundwater samples corresponding to the sampling villages, coal, fertilizers and rainwater samples (b). In (a), solid triangles are symbols for shallow, diamond for middle and square for deep groundwaters and stars are for rainwaters.

contamination cannot be excluded in the studied area.

Arsenic in ambient air in the Lahore district is 230 – 2230 ng/m^3 (JICA and Pakistan EPA, 2000), which is much higher than those reported in the other areas in the world; e.g., 91 – 512 ng/m^3 in Calcutta, India (Chakraborti *et al.*, 1992), 25 ng/m^3 in Wuhan City, China (Waldman *et al.*, 1991), and 1.2 – 44 ng/m^3 in Los Angeles, USA (Rabano *et al.*, 1989). The SO_2 in the ambient air was 133 – $212 \text{ } \mu\text{g/m}^3/\text{hr}$ in Lahore (Punjab EPD, 1998–99), which is lower than the WHO guideline value for SO_2 in air, i.e., $350 \text{ } \mu\text{g/m}^3/\text{hr}$. We also reported high concentra-

Fig. 8. Relationships between calcite saturation index (SI_c) and Ca^{2+} (a), dolomite saturation index and Mg^{2+} (b), fluorite saturation index (SI_f) and F^- (c), fluorite saturation index (SI_f) and Ca^{2+} (d). Symbols are the same as those in Fig. 2.

tion of As ($<10\text{--}90\text{ }\mu\text{g/L}$), with SO_4^{2-} ($5\text{--}14\text{ mg/L}$) in the local rain (Farooqi *et al.*, 2007). Although the concentration of SO_2 in ambient air is lower than the WHO standard, the presence of As in the air and rainwater support that those elements in the studied groundwater are partly derived via ambient air.

Fluoride can be released in the environment from phosphate fertilizers, which include fluorine as an impurity (Pickering, 1985; Skjelkvale, 1994). Phosphate fertilizers commonly contain from 1.3 to 3.0% fluorine (McLaughlin *et al.*, 1996), much higher than those analyzed here. The annual consumption of fertilizers in 1999 was 2,824 thousand metric tonnes with 129 kg/ha cropland in Pakistan and mostly in Punjab (<http://earthtrends.wri.org>). The presence of leachable F^- and As in fertilizer and coal samples also shows anthropogenic

contribution of fertilizers being used in the study area and combusted coal in the brick factories. Local rainwater contained $0.16\text{--}0.23\text{ mg/L } F^-$, and we presumed that the F^- was partly derived from combusted coal in the studied area (Farooqi *et al.*, 2007). The presence of F^- and As in coal samples (though not so high) substantiates our hypothesis of the contribution of combusted coal; however, fertilizers (DAP) consumed in the surroundings would be more important as an anthropogenic source of F^- in the study area.

Controlling role of major chemistry on As and F^- behavior

High concentrations of As were found in groundwaters from shallow depths. The highly As contaminated waters were characterized by high EC values $>2\text{ mS/cm}$, $Na\text{--}HCO_3^-$ dominant major chemistry and have $pH > 8$. As

Fig. 9. Relationship between As and Fe (a) and pH (b). Symbols are the same as those in Fig. 2.

noted before, the As concentration increases with increasing pH (Fig. 9b) and As^{V} is the dominant As species in the studied groundwaters. Naturally As contaminated groundwater is mainly caused by two different processes: oxidation of arsenic-bearing sulfide minerals (Schreiber *et al.*, 2000) and desorption from and/or following reduction of FeOOH adsorbing As (Matisoff *et al.*, 1982; Robertson, 1989; Nimick, 1998; Nickson *et al.*, 1998, 2005; McArthur *et al.*, 2001) in response to the increase of pH and decrease of redox potential of the groundwater.

Based on laboratory experiments of As adsorption on the metal oxides, such as Fe, Mn and Al oxyhydroxide/oxides (Anderson *et al.*, 1976; Pierce and Moore, 1982; Dzombak and Morel, 1990; Gustafsson and Jacks, 1995;

Lindberg *et al.*, 1997) and clay fractions (Jacobs *et al.*, 1970; Manning and Goldberg, 1997), As^{V} is most effectively adsorbed on Fe-oxyhydroxide/oxide at weakly acidic to neutral pH conditions, and it is released into solution with increasing pH to alkaline conditions. Regardless of whether the As originates from anthropogenic source(s) or from natural substances, we can say that alkaline conditions promote the dissolution of As into the studied groundwaters.

Figure 9a shows that As and Fe have a negative correlation, and the groundwater containing $<0.2 \text{ mg/L}$ Fe, contains $>400 \mu\text{g/L}$ As. Thus, FeOOH , if it controls the As concentration in the studied groundwater, would fix the As to prohibit the dissolution of this element into the groundwater. As shown in Fig. 9b a positive correlation is observed between As and pH which has a dominant role on the As mobilization. Arsenate is desorbed from Fe oxides at alkaline pH (Dzombak, and Morel, 1990). Many researchers have pointed out that desorption of As from mineral oxides is responsible for the highly As-containing groundwater in Quaternary sedimentary aquifers, e.g., As release into the groundwater can occur without apparent reduction in the arid basins of Argentina (Smedley *et al.*, 2002).

Fluoride concentration in groundwater in arid and semiarid regions is promoted by evaporation and evapotranspiration (Jacks *et al.*, 2005). However, we pointed out that this mechanism cannot explain the case of our studied area, since F^- concentrations did not have the linear relationship with Cl^- (Fig. 3e), which is the most conservative component in the hydrosphere. Also, as shown in Fig. 6, plots of δD and $\delta^{18}\text{O}$ were parallel to the global meteoric water line (GMWL, Fig. 6), confirming that the studied waters were not affected by evaporation and condensation. Thus, the high concentrations of Cl^- , F^- and also SO_4^{2-} would be explained by one or more sources distributed on the land surface or intruded directly into the aquifer. Directly supplied pollutants and wet and dry deposition must be condensed on the land surface.

High F^- concentrations were found in alkaline water, although the F^- and pH did not show a clear correlation (Fig. 5b). As described above, F^- concentration increased with decreasing Ca^{2+} and Mg^{2+} and increasing Na^+ concentrations under alkaline conditions. Calcium and Mg^{2+} concentrations were low and controlled mainly by the solubilities of calcite and dolomite due to high HCO_3^- concentrations. As shown in Figs. 8a and 8b, most of the studied groundwaters were saturated with those minerals. The saturation index of fluorite (SI_f) increased with increasing F^- concentration (Fig. 8c), while Ca^{2+} did not show a clear relationship with SI_f (Fig. 8d). Therefore, the low concentrations of Ca^{2+} (and probably Mg^{2+}) must promote high concentrations of F^- in the studied groundwater, and that the upper limit of F^- concentrations is

controlled by fluorite solubility as seen in Fig. 8c. Low Ca^{2+} would also result from the intense cation exchange reaction between Ca^{2+} and Na^+ (Sarma and Rao, 1997). In the study area, the source water not only introduces As and F^- , but also determine the chemistry of the groundwater. It controls the dissolution rates of the toxic substances and must play an important role in the formation of polluted groundwater.

Topographic constraints

Highly As and F^- polluted groundwaters were concentrated in eastern and western part of the study area, e.g., K LW, KAD, SKB, and MM. The altitude of these villages is slightly lower than the other villages of the study area. Villages where the groundwater contains less amounts of As, are located in the surrounding area of K LW, KAD, SKB, and MM: CNG and SUN at northeast, BP at south and JK, ZAB, and RPNA at southwest. These villages are located at slightly higher altitudes (>220 m) than the higher polluted villages (K LW, KAD, SKB, and MM), which are situated at about 200 m. If the surface topography was concordant with the structure of the aquifer, groundwater would flow toward topographic low. The highly As and F^- polluted groundwaters are very alkaline and of $\text{Na}^+\text{--HCO}_3^-$ dominant type, indicating typical characteristics of groundwater chemistry in stagnant aquifers (e.g., Hinkle, 1997). Thus, it is probable that the As and F^- are coincidentally dissolved into the stagnant groundwater. Although we must wait evaluation of the relationship between aquifer structure and polluted groundwater formation to obtain geological profiles, the groundwater flow system, including flowing rate and direction, would deeply affect the groundwater chemistry and formation of the studied highly polluted groundwater.

CONCLUSIONS

This study demonstrates that As and F^- contamination of groundwater is not limited to a small area comprising two adjacent villages, K LW and KAD, but widely extends to the surrounding areas. In the studied 17 villages, a population of more than 2.0 million are directly exposed to As and F^- through air, surface soils and groundwater. In particular, the levels of As and F^- in the groundwater are much higher than the WHO standards. The studied groundwaters are not only polluted by high concentrations of As and F^- but also by SO_4^{2-} , NO_3^- , alkalinity and other anthropogenic pollutants. Ca^{2+} and Mg^{2+} are generally low due to the precipitation of carbonate minerals and cation exchange reactions with Na^+ . Low Ca^{2+} concentration promotes the dissolution of F^- , with F^- concentration being controlled by the solubility of fluorite. Speciation analysis shows that As is in the form of As^{V} . Given low Fe^{2+} concentration under positive Eh values,

As is dissolved into groundwater mainly under alkaline pH, at which As cannot be effectively adsorbed onto Fe and other metal oxyhydroxide/oxides and/or clay minerals.

Our present results indicate that the main anthropogenic source of As is air pollutants derived from kiln factories, with fertilizers being a possible secondary source. Minor amounts of F^- and SO_4^{2-} are also derived from air pollutants; however, major sources of these components must be fertilizers. Household waste water also contributes to the high SO_4^{2-} , although waste water lacks F^- and As. These pollutants can remain under alkaline conditions in our studied groundwaters, where major chemical composition would be controlled by the stagnant condition of the aquifer. Groundwater pollution is most serious in shallow sections of the aquifer between 20 and 30 m depth; however, highly polluted groundwater, especially by As occasionally occurs in the deep aquifers >40 m. Thus, whilst the groundwaters are grouped into three depths by convenience, are in reality probably connected, and the pollutants could migrate into the deeper part of the same aquifer. To evaluate this possibility, we should clarify the structure of the aquifers in this area, and we should plan to protect the groundwater quality in at least the deeper parts of the aquifer in this area.

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APPENDIX

(see p. 231–234).

Appendix. Chemistry and stable isotope data of groundwaters in east Punjab, Pakistan

Sample ID	Depth m	Tem. °C	EC mS/cm	pH	Eh mV	F ⁻	Cl ⁻	Br ⁻	NO ₃ -N mg/L	PO ₄ ³⁻	SO ₄ ²⁻	HCO ₃ ⁻	Tan	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Tca	As(V)	As(III)	Fe	SiO ₂	δ ¹⁸ O*	δD*	δ ¹⁵ N	δ ³⁴ S
													meq/L		mg/L	mg/L	mg/L	meq/L	μg/L	μg/L	mg/L	mg/L	‰	‰	‰	‰
CNG-1	20-27	27	2.00	7.3	257	4.94	131	0.33	7.00	bd	192	976	24.79	460	9.00	48	13	23.65	6	nd	0.17	18.81	-8.00	-50.32	na	5.4
CNG-2	20-27	27	1.36	8.1	297	2.67	78	0.23	bd	bd	120	549	14.06	230	4.76	39	18	13.582	71	nd	0.05	27.00	-7.50	-46.89	na	na
CNG-4	20-27	26	1.70	7.7	301	8.36	96	0.30	bd	bd	165	671	17.88	322	5.07	34	15	17.09	23	nd	0.05	19.50	-8.20	-52.66	na	5.1
CNG-5	20-27	27	1.25	7.3	320	6.08	51	0.14	bd	bd	116	610	14.33	299	3.90	42	14	14.90	14	nd	<0.00	12.00	-8.37	-53.82	na	na
SUNI	20-27	29	1.30	8.1	273	10.13	21	bd	bd	bd	120	884	18.13	380	4.68	8	4	17.32	92	nd	0.10	22.50	-8.50	-53.25	na	5.7
SUN2	20-27	29	1.61	8.0	289	8.36	60	0.16	0.98	bd	192	732	18.37	368	3.12	20	8	18.12	57	nd	0.10	21.30	-8.00	-52.34	na	5.7
SUN3	20-27	27	2.56	8.0	363	4.75	178	0.36	4.20	bd	432	854	28.91	575	7.80	31	18	28.28	85	nd	<0.00	24.80	-7.65	-48.61	na	5.7
SUN4	20-27	27	2.26	7.4	333	4.18	142	0.34	1.68	0.70	336	915	26.69	483	8.58	51	24	26.22	19	nd	<0.00	23.24	-7.30	-46.59	na	na
SUN5	20-27	28	2.60	7.2	337	1.52	177	0.45	4.48	bd	432	1040	31.85	575	11.7	37	35	30.80	1	nd	0.01	22.44	-7.30	-45.91	na	na
SKB-2	20-27	30	1.23	8.3	289	3.80	28	bd	bd	bd	106	671	14.20	299	3.90	6	3	13.62	91	nd	0.06	17.01	-8.74	-59.11	na	na
SKB-3	20-27	28	1.25	8.4	279	1.14	41	0.16	bd	bd	105	610	13.57	207	5.46	40	23	13.08	70	nd	0.24	27.66	-8.28	-51.40	na	5.9
SKB-4	20-27	28	1.49	8.5	310	5.70	19	bd	bd	bd	96	854	16.84	345	5.07	12	7	16.33	92	nd	0.01	24.00	-8.20	-51.42	na	na
SKB-5	20-27	29	1.13	8.5	312	10.14	10	0.04	0.42	0.60	50	732	13.93	276	3.90	3	13	13.38	443	nd	0.04	23.98	-8.89	-57.02	na	5.7
SKB-6	20-27	28	1.22	8.4	324	3.04	10	bd	4.20	2.90	38	732	13.57	288	1.95	3	6	13.19	283	nd	0.05	16.11	-9.03	-56.43	10.0	na
SKB-8	20-27	28	1.21	8.6	314	5.70	9	bd	2.24	0.80	35	636	11.87	276	3.90	2	3	12.46	195	nd	0.12	15.00	-9.03	-59.83	na	5.6
SKB-9	20-27	27	1.06	8.6	325	5.32	11	bd	0.70	1.4	48	549	10.65	230	3.90	4	2	10.42	231	nd	0.05	16.10	-9.20	-61.17	na	na
SKB-10	20-27	30	0.66	7.2	334	4.56	6	bd	bd	bd	43	366	7.31	115	4.30	16	13	6.97	223	nd	0.04	22.03	-9.06	-59.32	na	na
SKB-12	20-27	30	0.84	8.0	218	0.95	13	bd	2.38	bd	44	550	10.49	69	9.75	71	46	10.38	3	nd	<0.00	16.56	-8.26	-51.03	na	na
SKB-13	20-27	27	0.93	8.0	306	3.42	21	0.06	0.84	bd	58	490	10.41	184	6.24	23	12	10.32	56	nd	0.05	25.25	-8.98	-55.25	na	na
SKB-14	20-27	27	1.44	7.2	309	3.04	50	0.15	3.50	bd	110	732	16.27	322	6.80	25	11	16.17	15	nd	0.04	25.53	-8.27	-52.75	12.5	5.7
SKB-15	20-27	28	1.14	7.8	271	4.56	14	0.06	0.56	bd	91	732	14.64	299	4.70	11	4	13.96	43	nd	0.05	21.10	-8.67	-52.43	na	5.6
SKB-16	20-27	27	0.85	7.2	349	1.90	7	bd	1.54	bd	48	427	8.39	138	6.24	27	14	8.72	12	nd	0.07	26.36	-8.64	-55.95	na	7.0
SKB-17	20-27	26	0.83	7.8	338	5.32	8	bd	0.14	bd	44	457	8.94	161	4.00	15	10	8.68	41	nd	0.08	20.76	-9.20	-56.13	na	6.2
SKB-18	20-27	26	1.67	8.2	343	17.1	49	0.16	0.84	bd	110	854	18.8	368	7.80	8	3	16.88	63	nd	0.23	24.38	-8.30	-53.88	na	5.8
SKB-19	20-27	27	1.13	8.2	293	8.55	29	0.13	bd	bd	86	427	10.2	207	4.70	14	6	10.32	79	nd	0.13	21.84	-8.44	-55.09	na	5.7
SKB-20	20-27	26	1.04	7.8	300	5.70	13	0.05	bd	bd	72	550	11.22	207	5.85	22	11	11.13	30	nd	0.11	22.73	-8.52	-54.17	na	na
SKB-21	20-27	26	1.31	7.3	316	7.03	24	0.09	bd	bd	87	702	14.44	276	7.80	18	13	14.14	155	nd	0.12	16.70	-8.71	-56.03	na	5.6
SKB-22	20-27	27	1.13	7.4	352	2.09	14	0.06	3.08	bd	88	671	13.59	207	8.20	42	24	13.25	27	nd	0.02	17.00	-7.79	-48.81	11.9	na
SKB-23	20-27	27	0.86	7.6	279	4.94	5	bd	1.12	bd	43	490	9.38	161	5.10	22	14	9.39	33	nd	0.20	25.25	-8.50	-54.11	na	5.7
SKB-24	20-27	27	0.70	7.7	290	3.04	5	bd	4.20	0.20	48	550	10.61	230	3.90	9	5	11.00	38	nd	0.10	18.43	-9.30	-61.91	na	na
MM-2	20-27	28	1.37	7.5	351	1.14	106	0.30	8.68	bd	217	445	15.80	170	11.70	93	50	16.48	36	nd	<0.00	34.00	-7.52	-46.78	30.0	na
MM-3	20-27	28	1.44	7.3	314	1.33	80	0.21	7.42	bd	165	457	14.01	161	15.60	84	36	14.62	10	nd	0.31	30.00	-7.50	-46.39	14.0	na
MM-4	20-27	29	1.01	7.2	265	0.86	68	0.20	5.60	bd	149	323	10.97	124	8.80	68	26	11.23	4	nd	0.00	26.00	-7.70	-47.66	13.0	5.0
MM-5	20-27	28	1.43	7.3	364	2.28	262	0.76	46.00	bd	499	550	30.97	460	39.00	84	55	29.80	8	nd	<0.00	32.00	-7.20	-42.54	25.0	na
MM-6	20-27	29	1.82	8.3	316	3.04	124	0.40	bd	2.00	480	427	21.08	414	13.00	27	15	20.91	46	nd	0.01	30.00	-7.40	-44.98	na	5.6
MM-7	20-27	28	1.16	8.0	313	1.33	50	0.20	0.84	bd	259	610	17.13	253	19.50	73	33	17.80	23	nd	0.06	15.10	-7.70	-46.53	na	na
MM-8	20-27	27	1.40	7.7	347	1.14	67	0.23	6.72	bd	113	490	13.03	230	8.19	44	11	13.35	4	nd	<0.00	26.30	-7.50	-44.29	12.5	na
MM-9	20-27	27	1.57	7.4	350	1.90	110	0.30	7.56	bd	207	460	15.87	253	9.40	51	26	15.98	5	nd	0.03	30.00	-7.52	-46.20	na	5.7
MM-11	20-27	27	1.17	8.3	333	0.76	62	0.23	bd	bd	187	370	11.92	138	9.36	68	25	11.68	68	nd	0.04	28.33	-8.09	-49.42	na	5.3
MM-12	20-27	28	0.55	8.3	362	0.46	28	0.10	1.26	bd	82	213	6.22	46	5.85	56	19	6.53	42	nd	0.07	24.60	-8.12	-51.66	na	na
MM-14	20-27	27	0.58	8.6	328	0.57	23	0.06	bd	bd	75	201	5.62	46	5.46	36	18	5.46	134	nd	0.04	21.72	-8.47	-53.79	na	na
MM-15	20-27	26	1.90	8.5	332	0.57	99	0.63	bd	bd	336	550	19.47	368	9.00	29	12	18.67	70	nd	0.37	23.51	-8.32	-52.02	na	na
MM-16	20-27	27	1.83	8.7	324	0.60	117	0.37	bd	bd	355	506	19.41	299	7.80	38	61	20.28	75	nd	0.56	27.75	-7.80	-48.62	na	na
MM-17	20-27	26	1.18	8.4	303	4.18	11	bd	0.84	0.60	65	610	11.94	276	2.73	5	2	12.45	424	nd	0.01	18.43	-8.70	-56.35	na	5.6

Appendix. (continued)

Sample ID	Depth m	Tem. °C	EC mS/cm	pH	Eh mV	F ⁻	Cl ⁻	Br ⁻	NO ₃ -N mg/L	PO ₄ ³⁻	SO ₄ ²⁻	HCO ₃ ⁻	Tan	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Tca	As(V)	As(III)	Fe	SiO ₂	δ ¹⁸ O*	δD*	δ ¹⁵ N	δ ³⁴ S
WP-1	20-27	29	0.82	8.3	291	6.08	13	bd	bd	bd	72	520	10.69	220	3.90	13	7	10.82	33	nd	0.16	16.44	-8.30	-51.77	na	5.1
WP-3	20-27	26	1.90	8.5	320	5.70	113	0.22	5.88	bd	241	610	19.17	391	7.80	30	16	19.98	166	nd	0.13	17.33	-7.84	-46.48	na	4.9
WP-4	20-27	27	1.30	8.2	308	3.80	42	bd	2.52	bd	98	520	12.10	276	3.90	5	2	12.52	242	nd	0.00	12.18	-8.13	-52.02	na	5.1
WP-5	20-27	29	2.02	7.8	298	6.65	129	0.66	2.38	bd	240	616	19.93	437	5.10	15	7	20.45	153	nd	<0.0	20.00	-8.24	-51.55	na	5.6
WP-7	20-27	27	1.86	8.0	324	7.03	96	0.26	bd	bd	288	550	18.36	391	5.46	16	10	18.80	69	nd	0.02	24.50	-7.44	-45.97	na	5.7
WP-8	20-27	28	1.90	8.0	307	7.98	103	0.24	bd	bd	254	520	17.36	368	5.46	26	10	18.26	86	nd	0.02	21.35	-7.66	-47.45	na	na
WP-9	20-27	27	1.77	8.1	333	8.36	66	0.17	bd	0.52	221	610	17.08	368	4.70	14	7	17.42	46	nd	<0.00	20.00	-7.76	-48.47	na	5.8
WP-10	20-27	28	1.80	8.6	315	11.02	71	0.18	bd	bd	206	610	17.06	363	5.10	19	12	17.78	70	nd	0.12	21.60	-8.07	-49.74	na	na
WP-11	20-27	27	1.02	8.4	360	2.09	16	bd	bd	2.00	72	490	10.07	230	2.73	4	2	10.41	677	nd	0.02	26.11	-8.27	-51.32	na	5.7
KAD-1	20-27	27	2.82	8.2	290	7.60	241	0.60	bd	bd	624	550	29.81	621	7.80	17	9	28.96	42	nd	0.04	15.02	-7.55	-47.39	na	5.5
KAD-2	20-27	26	0.81	8.1	311	7.80	216	0.55	1.96	bd	624	550	29.21	621	7.80	13	8	28.52	142	nd	0.04	19.27	-7.85	-49.90	na	5.5
KAD-6	20-27	27	2.74	7.8	222	11.0	250	0.57	bd	bd	576	550	29.19	600	6.63	22	12	28.25	42	nd	0.02	19.64	-7.45	-45.32	na	5.4
KAD-7	20-27	27	2.04	8.0	258	9.50	213	0.53	bd	bd	528	540	29.99	621	7.80	17	10	28.90	158	nd	0.06	19.60	-7.25	-43.68	na	5.3
KAD-8	20-27	27	2.04	8.0	258	9.50	213	0.53	bd	bd	528	540	29.99	621	7.80	14	9	28.64	10	nd	0.00	19.27	-7.41	-45.79	na	5.6
KAD-10	20-27	26	2.55	7.7	267	19.0	184	0.50	bd	bd	528	793	30.71	621	6.24	26	9	29.18	62	nd	2.42	11.14	-7.60	-47.50	na	5.5
KAD-11	20-27	26	3.7	7.6	316	13.3	238	bd	bd	bd	624	1040	37.40	782	9.00	30	16	37.09	34	nd	2.40	7.35	-7.70	-48.45	na	5.3
KAD-12	20-27	27	2.50	8.3	281	9.50	177	0.50	bd	bd	480	915	31.01	621	7.80	25	14	29.58	171	nd	0.01	24.40	-8.17	-52.92	na	5.6
KLW1	20-27	27	3.38	8.0	246	3.23	43	0.17	bd	bd	192	805	18.76	345	7.80	35	13	18.26	38	nd	0.31	23.36	-8.45	-54.35	na	5.5
KLW3	20-27	28	1.60	8.5	301	9.50	32	bd	bd	0.50	178	854	19.12	414	4.30	8	3	18.91	615	nd	0.00	17.06	-8.23	-52.68	na	na
KLW4	20-27	27	1.70	8.0	298	2.70	42	bd	bd	bd	192	793	18.34	345	4.70	22	15	17.64	90	nd	0.18	24.72	-8.40	-53.41	na	5.7
KLW5	20-27	27	1.63	8.2	299	7.60	36	bd	0.84	bd	144	793	17.46	345	7.80	16	6	16.70	82	nd	0.06	23.5	-8.16	-51.41	na	5.6
KLW6	20-27	28	2.21	8.4	295	19.0	50	0.15	bd	bd	264	854	22.05	460	5.85	21	2	21.41	131	nd	0.22	27.11	-8.53	-56.82	na	5.5
KLW7	20-27	28	1.60	8.4	257	11.4	34	bd	0.70	bd	168	671	16.11	334	5.85	16	6	15.93	159	nd	0.07	26.00	-8.30	-46.98	na	5.7
KLW8	20-27	28	3.25	8.5	302	17.9	200	0.50	2.52	bd	576	915	33.76	713	7.80	26	11	33.50	217	nd	0.03	26.70	-7.69	-46.98	na	5.3
KLW9	20-27	26	2.61	8.5	329	19.0	163	0.35	bd	bd	432	701	26.45	552	11.70	19	2	25.42	213	nd	0.09	24.10	-8.40	-54.76	na	5.6
KLW10	20-27	28	1.86	8.6	295	17.7	62	bd	bd	bd	192	976	22.68	460	3.90	12	16	22.00	234	nd	0.03	21.44	-8.70	-58.86	na	5.5
KLW11	20-27	27	2.66	8.4	276	19.0	167	0.40	0.14	bd	408	841	28.42	575	5.85	23	14	27.11	157	nd	0.25	19.20	-8.49	-52.00	na	5.6
KLW12	20-27	26	3.01	8.2	326	17.7	217	0.45	bd	1.20	576	915	34.57	736	5.85	23	12	33.75	103	nd	0.05	23.68	-8.48	-53.40	na	na
KLW13	20-27	26	4.38	8.3	280	16.0	344	0.83	1.12	bd	912	1280	51.46	1060	12.10	27	30	49.47	111	nd	<0.00	23.92	-8.30	-53.48	na	5.4
KLW14	20-27	29	3.17	8.0	255	14.1	220	0.45	bd	bd	624	1280	49.76	736	7.80	30	17	34.42	79	nd	0.25	22.27	-7.65	-47.73	na	5.7
KLW15	20-27	28	4.60	8.3	247	10.1	328	0.71	3.92	bd	864	1280	49.76	1012	11.70	32	22	48.30	185	nd	<0.00	20.42	-7.90	-49.91	na	5.7
KLW16	20-27	27	2.22	8.4	296	3.99	160	0.43	10.64	bd	384	549	22.91	483	5.46	13	9	22.50	250	nd	<0.00	22.33	-7.80	-49.32	15.0	5.6
KLW17	20-27	29	3.27	8.2	261	7.98	249	0.53	2.38	bd	672	1100	39.60	805	8.58	27	22	38.02	137	nd	<0.00	22.33	-8.00	-51.96	na	5.5
KLW18	20-27	28	1.22	8.8	287	3.99	18	bd	bd	1.20	48	732	13.72	300	3.90	5	3	13.64	2400	nd	0.10	18.45	-8.21	-50.53	na	5.6
KLW19	20-27	29	2.26	8.3	273	8.93	107	0.27	2.24	0.80	336	1040	27.91	575	6.63	14	10	26.85	460	nd	0.22	21.63	-8.01	-51.22	na	5.7
KLW20	20-27	28	1.72	8.5	264	14.13	51	bd	2.80	bd	192	915	21.38	460	4.68	5	3	20.60	634	nd	0.18	18.53	-8.10	-53.25	na	5.8
KLW21	20-27	29	1.13	7.8	313	6.46	34	bd	bd	bd	96	702	14.80	311	3.90	7	6	14.52	23	nd	0.06	16.11	-8.40	-54.72	na	5.5
KLW22	20-27	29	1.28	8.5	296	21.10	17	bd	0.42	bd	96	671	14.62	300	4.68	12	9	14.00	120	nd	0.51	22.80	-8.60	-52.40	na	na
KLW23	20-27	28	1.58	8.0	250	10.31	39	0.12	bd	bd	187	793	18.66	391	5.10	16	7	18.75	30	nd	0.03	21.76	-8.20	-51.46	na	5.6
KLW24	20-27	29	1.25	8.6	267	6.08	21	0.07	bd	bd	96	671	13.99	280	5.46	24	8	14.02	639	nd	0.07	24.66	-8.70	-60.68	na	5.2
KLW26	20-27	28	1.06	8.0	225	8.36	16	bd	bd	bd	82	610	12.59	253	3.90	13	5	12.18	52	nd	0.07	22.40	-8.50	-56.68	na	5.4
KLW27	20-27	29	1.51	8.5	284	22.8	18	bd	bd	0.50	126	793	17.33	370	3.90	6	2	16.58	124	nd	0.21	18.60	-8.55	-54.26	na	5.5
MPU-1	20-27	27	3.12	8.0	324	0.12	213	0.63	bd	bd	605	915	33.64	670	7.80	50	11	32.70	64	nd	0.14	23.28	-8.10	-50.47	na	5.7
MPU-2	20-27	27	1.34	7.9	317	0.57	62	0.20	bd	bd	211	610	16.38	300	6.24	34	14	16.02	59	nd	0.16	26.00	-8.05	-50.35	na	na
MPU-3	20-27	26	4.10	7.9	315	0.19	200	0.70	bd	bd	960	1160	39.72	805	11.70	57	23	40.08	52	nd	0.25	18.50	-7.90	-50.98	na	5.6

Sample ID	Depth	Tem.	EC	pH	Eh	F ⁻	Cl ⁻	Br ⁻	NO ₃ -N	PO ₄ ³⁻	SO ₄ ²⁻	HCO ₃ ⁻	Tan	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Tca	As(V)	As(III)	Fe	SiO ₂	δ ¹⁸ O*	δD*	δ ¹⁵ N	δ ³⁴ S
	m	°C	mS/cm		mV				mg/L	mg/L	mg/L	mg/L	meq/L	mg/L	mg/L	mg/L	meq/L	meq/L	μg/L	μg/L	mg/L	mg/L	‰	‰	‰	‰
ARK-2	20-27	28	0.60	7.2	289	0.38	4	bd	bd	bd	48	335	6.640	23	7.80	99	10	6.96	8	nd	<0.00	14.30	-7.46	-45.71	na	5.1
ARK-3	20-27	29	0.40	7.3	296	0.65	5	0.04	0.42	bd	38	195	4.250	23	4.68	54	7	4.37	56	23	0.07	18.80	-7.23	-48.76	na	5.0
ARK-4	20-27	28	0.53	7.2	293	0.61	6	0.04	0.42	bd	72	244	5.780	30	4.68	69	14	6.02	2	nd	0.00	10.42	-7.70	-48.03	na	5.4
ARK-5	20-27	29	1.04	7.2	290	0.31	61	0.09	7.84	bd	144	366	11.39	51	23.4	138	20	11.40	1	nd	0.16	16.00	-7.82	-52.59	11.0	5.5
ARK-6	20-27	29	0.49	7.4	273	0.38	25	0.05	0.42	bd	67.2	274	6.71	23	5.85	91	14	6.88	40	12	0.51	20.00	-7.87	-54.79	na	5.4
ARK-7	20-27	28	0.68	7.6	292	0.59	39	0.09	bd	bd	110	305	8.52	46	27.30	104	9	8.62	73	nd	0.14	16.00	-7.22	-45.26	na	5.6
DN-1	20-27	28	1.22	8.0	315	0.76	122	0.33	2.52	bd	192	610	17.99	300	7.80	52	28	18.22	8	nd	0.10	29.00	-7.70	-47.90	na	na
DN-2	20-27	28	1.50	7.4	294	2.85	81	1.80	1.26	bd	240	640	19.84	345	7.80	46	22	19.34	31	nd	0.05	27.47	-7.88	-48.47	na	5.5
DN-3	20-27	26	2.10	7.5	775	6.08	136	0.30	18.9	bd	240	915	25.81	506	11.70	27	18	25.16	8	nd	0.02	32.00	-7.70	-47.09	12.5	5.0
DN-4	20-27	28	1.10	7.3	303	2.47	36	bd	1.40	bd	144	671	15.23	300	7.80	27	18	15.80	33	nd	<0.00	15.00	-7.90	-47.47	na	na
DN-5	20-27	27	1.60	7.5	220	5.13	110	0.33	3.36	bd	144	610	16.94	276	11.70	48	2	16.20	37	nd	0.02	17.00	-7.20	-46.00	9.40	5.4
DN-6	20-27	26	1.35	8.0	256	1.542	12	bd	bd	bd	96	732	15.15	276	7.80	64	8	15.80	38	nd	0.23	15.00	-8.13	-51.03	na	na
NK-1	20-27	29	1.24	7.7	276	1.71	56	0.15	0.70	bd	192	610	15.86	276	7.80	43	15	15.64	61	nd	0.03	24.30	-8.30	-49.91	na	5.8
NK-2	20-27	29	1.70	7.3	291	0.61	14	bd	0.42	bd	96	793	15.46	230	15.60	66	35	16.20	39	nd	0.02	12.22	-8.30	-51.66	na	na
NK-3	20-27	29	1.40	7.5	313	0.57	64	0.16	0.42	bd	194	671	17.04	253	11.70	60	26	16.50	65	nd	2.80	25.00	-8.20	-50.59	na	5.8
NK-4	20-27	27	1.41	7.4	334	1.33	70	0.18	bd	bd	240	488	15.22	253	11.70	44	25	15.62	41	nd	0.14	24.50	-8.20	-49.17	na	6.2
NK-5	20-27	27	1.33	7.4	346	11.4	20	bd	bd	bd	96	915	18.17	370	15.60	11	6	17.50	46	nd	<0.00	25.50	-8.30	-55.03	na	na
NK-6	20-27	28	1.42	7.9	317	8.40	57	0.14	0.70	bd	168	854	19.74	391	11.70	17	8	18.90	94	nd	<0.00	18.50	-8.37	-51.17	na	6.3
KA-1	20-27	28	1.38	8.2	288	1.14	75	0.20	0.14	bd	192	610	16.37	253	8.97	47	28	15.75	177	nd	0.03	26.6	-8.70	-53.86	na	5.6
KA-2	20-27	29	1.38	8.6	313	2.09	54	0.17	1.54	0.70	216	671	17.42	370	3.90	6	3	16.68	621	nd	0.00	23.00	-7.50	-45.81	na	5.7
KA-3	20-27	28	1.20	8.6	320	4.37	121	0.30	11.48	bd	288	610	20.76	370	11.70	37	21	19.96	392	nd	<0.00	32.00	-7.98	-48.06	8.1	5.6
BP-1	20-27	29	1.48	8.1	310	3.99	52	0.14	1.96	bd	170	550	14.50	300	5.07	21	6	14.71	109	nd	0.04	29.33	-8.37	-52.37	na	5.6
BP-2	20-27	28	1.23	7.8	337	12.03	41	0.11	2.52	bd	145	500	12.90	276	4.29	10	4	12.97	40	nd	0.02	31.26	-8.55	-54.13	na	5.3
BP-3	20-27	29	0.64	7.5	318	1.01	43	0.12	0.42	bd	67	213	6.30	70	4.68	39	17	6.52	54	nd	0.04	27.15	-7.91	-49.63	na	na
JK-1	20-27	26	3.40	8.3	322	13.32	224	bd	10.5	bd	638	1020	37.20	851	12.87	12	11	38.89	103	nd	<0.00	21.70	-7.70	-48.14	15.0	3.7
JK-2	20-27	27	3.60	8.1	329	9.50	390	1.02	10.0	bd	576	980	41.18	874	46.80	54	45	39.70	6	nd	0.60	37.00	-7.80	-49.94	14.5	3.9
RPNA1	20-27	26	2.10	7.5	264	4.56	107	0.25	2.59	bd	500	494	22.22	445	11.7	23	14	21.97	23	nd	0.03	18.60	-8.28	-56.36	na	3.8
RPNA2	20-27	27	1.82	7.8	258	1.71	144	0.27	10.00	bd	355	495	20.35	240	23.4	4	5	20.56	70	nd	0.01	25.24	-7.30	-44.28	7.2	3.7
CCO1	20-27	28	0.73	7.2	251	2.28	15	bd	bd	bd	72	430	9.04	19	19.5	66	47	8.64	1	nd	0.22	29.30	-9.60	-60.15	na	5.5
CCO2	20-27	29	0.52	7.3	243	1.71	10	bd	bd	bd	36	366	7.11	12	27.3	60	31	6.81	1	nd	0.15	26.30	-9.32	-58.05	na	5.6
ZAB-1	20-27	26	2.17	8.1	218	3.80	213	bd	7.00	bd	480	671	27.70	600	9.75	6	2	26.71	56	nd	0.03	25.00	-7.30	-46.26	5.7	4.5
ZAB-2	20-27	29	2.80	8.0	266	8.36	252	bd	7.56	bd	480	590	27.75	575	15.60	14	8	26.78	27	nd	0.03	30.00	-7.60	-46.56	5.0	4.3
ZAB-3	20-27	28	2.78	8.1	277	7.60	295	bd	5.60	bd	532	488	28.20	600	9.75	8	7	27.21	32	nd	0.03	23.15	-7.00	-41.08	5.0	4.6
ZAB-4	20-27	27	3.80	8.0	343	3.80	415	0.64	14.00	bd	960	520	42.05	874	19.50	14	12	40.18	22	nd	0.03	30.00	-7.84	-48.75	5.0	4.4
ZAB-5	20-27	29	4.40	7.4	312	5.70	355	bd	10.50	bd	821	793	41.15	900	15.60	15	13	41.28	14	nd	0.021	26.32	-7.03	-45.83	3.5	4.7

Appendix. (continued)

Sample ID	Depth m	Tem. °C	EC mS/cm	pH	Eh mV	F ⁻	Cl ⁻	Br ⁻	mg/L				meq/L				μg/L		Fe	SiO ₂	‰					
									Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Tan	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Tca			As(V)	As(III)	δ ¹⁸ O*	δD*	δ ¹⁵ N	δ ³⁴ S
KLW25	40-80	25	1.18	8.5	371	2.28	7	bdl	bdl	bdl	96	732	14.33	207	7.80	53	21	14.20	80	nd	0.18	26.20	-8.58	-56.29	na	5.3
ARK-1	40-80	24	0.20	8.1	380	0.30	4	bdl	bdl	bdl	24	153	3.125	16	3.90	39	6	3.26	53	16	<0.00	17.44	-7.48	-48.06	na	4.4
ARK-8	40-80	24	0.34	8.6	385	0.38	4	bdl	bdl	bdl	29	183	3.74	16	3.90	45	7	3.60	881	nd	0.04	23.23	-7.69	-46.18	na	5.4
WP-6	40-80	24	0.94	8.1	321	0.95	67	0.14	bdl	bdl	148	244	9.18	115	5.85	55	14	9.07	68	nd	0.10	22.70	-8.15	-51.64	na	5.7
SKB-1	40-80	26	1.70	8.3	273	2.28	96	0.30	bdl	bdl	288	732	21.13	322	8.58	58	37	20.26	91	nd	0.23	28.55	-8.39	-52.62	na	5.6
SKB-11	40-80	26	1.01	7.7	221	2.66	9	0.04	0.70	bdl	62	610	11.79	184	7.80	29	21	11.38	34	nd	0.04	25.34	-8.79	-54.88	na	5.7
MM-10	40-80	24	0.41	8.4	339	0.57	14	0.06	0.28	bdl	48	366	7.51	92	3.90	46	12	7.39	52	nd	0.10	26.62	-8.06	-49.81	na	5.7
KAD-3	40-80	26	0.81	7.5	301	0.44	57	0.15	0.28	bdl	134	213	8.09	70	5.85	55	28	8.19	24	nd	0.37	23.50	-8.01	-50.59	na	5.6
KAD-4	40-80	27	0.34	7.4	349	0.44	5	bdl	0.28	bdl	30	165	3.50	28	3.12	30	8	3.50	25	nd	0.14	23.60	-8.22	-52.67	na	5.6
KAD-5	40-80	24	1.10	7.3	286	4.20	117	0.28	0.56	bdl	225	213	12.04	115	7.80	72	40	12.10	22	nd	0.07	25.00	-8.37	-53.09	na	5.5
KAD-9	40-80	25	2.19	8.3	241	2.09	249	0.54	bdl	bdl	480	244	21.7	322	6.63	73	33	21.17	64	nd	2.18	9.86	-8.48	-53.75	na	5.6
KLW-29	40-80	25	2.50	8.7	409	2.32	36	bdl	bdl	bdl	96	550	12.12	276	3.90	28	9	13.10	672	nd	<0.00	15.03	-8.74	-57.26	na	na
CNG-3	40-80	24	0.38	8.3	293	0.25	12	0.04	bdl	bdl	29	183	3.98	46	1.95	28	6	3.91	45	nd	0.03	20.67	-8.10	-50.69	na	na
SKB-7	40-80	25	1.01	8.1	350	0.95	134	bdl	bdl	bdl	62	610	15.13	299	4.68	19	14	15.28	61	nd	0.12	24.14	-8.76	-57.08	na	5.7
WP-2	80-200	23	1.84	8.3	336	1.03	100	0.25	0.70	bdl	341	440	17.47	306	6.24	54	18	17.60	60	nd	0.06	21.00	-8.17	-52.07	na	na
SKB25	80-200	24	1.07	8.6	358	3.10	10	bdl	0.84	3.30	73	671	13.05	276	4.00	6	4	12.72	242	nd	0.06	17.34	-8.94	-58.90	na	5.6
MM-1	80-200	21	1.07	8.4	364	1.33	78	0.30	0.70	bdl	215	262	11.4	124	8.58	76	21	11.16	80	nd	0.30	30.00	-7.94	-48.51	na	6.2
MM-13	80-200	23	0.89	8.7	367	0.57	45	0.14	0.14	bdl	120	263	8.25	92	4.68	50	21	8.38	611	nd	0.04	26.18	-7.32	-45.22	na	5.6
KLW2	80-200	22	1.94	8.0	343	0.78	159	0.40	bdl	bdl	240	610	19.95	283	7.80	75	36	19.22	38	nd	0.41	26.71	-8.28	-51.10	na	5.6
KLW-28	80-200	20	0.45	7.6	343	0.95	25	bdl	bdl	bdl	77	244	6.36	62	4.00	60	5	6.22	43	nd	0.06	19.24	-8.25	-51.55	na	na
ARK-9	80-200	24	0.74	7.5	318	0.59	71	0.18	bdl	bdl	144	146	7.61	23	7.80	86	26	7.70	50	10	0.11	12.40	-7.67	-47.23	na	5.5
ARK-10	80-200	23	0.56	7.5	365	0.50	19	bdl	bdl	bdl	32	244	4.00	92	6.63	19	19	4.17	8	nd	<0.00	11.00	-8.15	-52.28	na	na

Abbreviations for villages are the same as those in Table 1.

"na" represents "not analyzed".

"bdll" stands for below detection limit.

Detection limits are the same as those in Table 1.

"nd" stands "for not detected". Detection limit for As(III) is 5 ppb.

*SMOW (Standard Mean Oceanic Water) is the standard used for determining δ¹⁸O and δ²H in water.