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Trace Element Contamination of Groundwater Around Kirana Hills, District Chiniot, Punjab, Pakistan

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Abstract: Thirteen groundwater samples and one river water samples were collected from wells and water sources in Chenab Nagar (Rabwah) area, district Chiniot, Punjab in July 2017, in order to analyze trace elements composition of water. The water samples were directly analyzed using an inductively coupled plasma mass spectrometry (ICP-MS). Judging from the Maximum Contaminant Level (MCL), Secondary Maximum Contaminant Level (SMCL) and Maximum Contaminant Level Goal (MCLG) as defined by USEPA and WHO Guidelines for Drinking-water Quality, the concentration of 5 elements, As, Mn, Cl, Br and S, in groundwater samples exceeded the standards. In particular, the concentration of As (max. 25.1 μg/l) and Mn (max. 443 μg/l) showed high level, which may cause negative effect if the contaminated water is continuously consumed. High concentrations of As (max. 161 mg/kg) and Mn (max. 355 mg/kg) were also detected in the Precambrian meta-volcano sedimentary rock samples collected from the Kirana hills, according to the aqua regia digestion ICP-ES/MS analysis. Arsenopyrite (FeAsS) and cryptomelane ($K(Mn^{4+}, Mn^{2+})_8O_{16}$) were identified in the rock samples using X-ray diffraction (XRD) and petrographic observation and those minerals are considered to be the main sources of As and Mn contamination. The groundwater contamination by As and Mn is caused by a water rock interaction in the subsurface zone, where basement rocks of Kirana hills and their debris are exposed with groundwater. High salinity of groundwater is inherent in the area, but shallower parts of the contamination by Cl, Br, and S is probably accelerated by anthropogenic origins such as septic tank and wastewater.

Keywords: Groundwater contamination, trace elements, rock-water interaction, XRD, ICP-MS

Introduction

Punjab is the most populous province in Pakistan, as its population reaches more than 100 million. The area is characterized by a semi-arid climate, and in most area, drinking water and agricultural water are obtained from water wells. Due to rapid population growth and expansion of agricultural fields, there has been a drastic increase in groundwater exploitation resulting in lowering of water tables and deterioration of water quality (Khan et al., 2008). Various types of groundwater contamination have been reported so far in the Punjab province (Azizullah, 2011; Farooqi et al., 2007a,b), and high salinity of groundwater is also known over the province (Qureshi et al., 2008; Geological Survey of Pakistan, 2000; Greenman et al.,1967). These groundwater contaminants are derived from natural and/or anthropogenic origins, however, pollution sources and detailed contamination mechanisms are considered to vary depending on local conditions.

The Kirana hills are located in the northern central part of Punjab, which exhibit a peculiar terrain of a series of rock masses, sporadically exposed on the Punjab plain. The rocks consist of Precambrian basement rocks intercalating the Hachi Volcanics with hydrothermal mineralization zones (Khan et al., 2009). Ahmad et al. (2016) reported that groundwater distributed around the Kirana hills showed very high electric conductivity (EC), total dissolved solids (TDS), hardness and concentration of Cl and Ca. They also pointed that there is a possible ‘barrier effect’ of the Kirana hills that traps lateral migration of groundwater. Actually there is a possibility that the existence and exposure of rock masses of the Kirana hills affect the groundwater quality. The composition of groundwater is not only controlled by a physical barrier effect, it is largely controlled by the chemical reaction of water and rocks, a water-rock interaction (Brantley et al., 2008).

Present study mainly focused on the water quality of groundwater distributed around the basement rocks exposures of Kirana hills in district Chiniot and examined the influence of basement rocks to groundwater quality as a water-rock interaction. The concentration of potentially toxic trace elements was also investigated for assessing groundwater quality as a source of drinking water.

Methods and Minerals

Samples of groundwater and rocks were taken from in and around the Kirana hills in Chenab Nagar (Rabwah) area, district Chiniot, in July 2017. One water sample was also collected from Chenab river, near the Chenab bridge as a reference. The location map is shown in

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Figure 1, and the sample list with on-site information is summarized in Table 1.

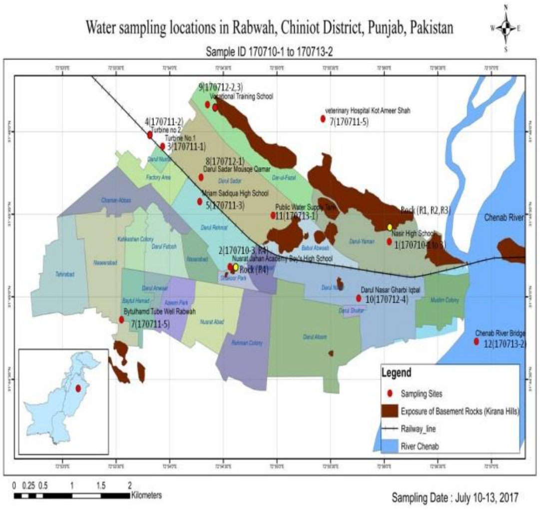


Fig. 1 Sampling location map (July 10-13, 2017) with local administrative boundary. Red circles show the location of water samples, and yellow circles show the location of rock samples. The exposures of Precambrian basement rocks (Kirana hills) are shown by dark brown and other parts are covered by Quaternary flood plain deposits.

Trace Elements Analysis for Water Samples

Trace elements in the groundwater samples were analyzed using a Parkin Elmer ICP-MS, Acme laboratory, Vancouver. If water sample contains high total dissolved solids (TDS) (>%), it was diluted 10 times by deionized water for minimizing a mask effect. The sample collected from Chenab river was filtered by Millipore paper filter because of being highly contaminated by suspended particles, while other samples were directly analyzed. The following 70 elements were analyzed: Ag, Al, As, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, S, Sb, Sc, Se, S, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr. Fluorine (F) was not analyzed. The lower detection limit (LDL) for each element is shown in Table 2. The precision of the analysis was verified by multiple measurements of the reference material as well as a blank test.

Trace Elements Analysis for Rock Samples

Four rock samples were collected from the exposures of Precambrian meta-volcano sedimentary rocks in

Table 1. List of collected samples and on-site description.

	Sample ID	Description	Sample
Nasir High School (close to an outcrop of basement rock , two small pumps)			
	170710-1	Well No.1 (nearby gate) pH=7.2 EC=3.54mS Temp=30.6C Turbidity=1.07NTU	water
	170710-2	Well No.2 (nearby administration bloc) pH=7.6 EC=4.00mS/cm Temp=31.3C Turbidity=15NTU	water
	170710R1	sandy metasediment	rock
	170710R2	greenish grey siliceous metasediment	rock
	170710R3	iron red metasediment	rock
Nusrat Jahan Academy Boy's High School (Outcrop of basement rok in the compound, small pump)			
	170710-3	Well pH=7.1 EC=5.36mS/cm Tep=30.6C Turbidity=0.2NTU	water
	170710R4	iron red metasediments	rock
Well Turbine No,2 (distribution to agricultural/drinking water) -250ft depth			
	170711-1	Well pH=7.6 EC=1.00mS/cm Temp=29.8C Turbidity=0.00NTU	water
Well Turbine No.1 (distribution to agricultural/drinking water) -250ft depth			
	170711-2	Well pH=7.3 EC=1.61mS/cm Temp=29.3C Turbidity=0.56NTU	water
Mriam Sadiqua High School			
	170711-3	Well (small pump) pH=7.2 EC=6.30mS/cm Temp=30.2C Turbidity=0.44NTU	water
Bytulhamd tube well Rabwah 200ft depth			
	170711-4	Well pH=7.5 EC=1.29mS/cm Temp=28.8C Turbidity=2.24NTU	water
Wetnary hospital kot ameer shah (hand pump)100ft depth			
	170711-5	Public well Ph=7.2 EC=0.88mS/cm Tmp=27.7C Turbidity=0.00	water
Darul sadar mousqe qamar 200ft depth			
	170712-1	Well pH=7.4 EC=2.78mS/cm Temp=29.2C Turbidity=0.65NTU	water
Vocational training school 120ft depth			
	170712-2	Well pH=7.2 EC=2.48mS/cm Temp=30.4C Turbidity=0.00NTU	water
	170712-3	house 65ft Well pH=7.0 EC=5.07 temp=29.1C Turbidity=1.56NTU	water
Darul nasar gharbi iqbal			
	170712-4	public well pH=7.5 EC=1.57mS/cm Temp=29.2C Turbidity=0.22NTU	water
Rabwah public water supply tank			
	170713-1	public water supply tap water pH=7.7 EC=0.46mS/cm Temp=26.7C Trbidity=0.21NTU	water
Chenab river bridge			
	170713-2	river water pH=8.3 EC=0.11mS/cm Temp=26.9C Tudbidity=350NTU	water

Kirana hills, the 170710-R1, R2, R3, and R4 (Fig. 1). The rock samples were firstly crushed, homogenized, pulverized, and sieved under 200 mesh (75 μm), secondly extracted by a strong acid of 1:1:1 HCl-HNO_3-H_2O (aqua regia), and then analyzed trace elements using a Parkin Elmer ICP-ES (Inductively coupled plasma - emission spectrometry) and ICP-MS system, Acme laboratory, Vancouver. The aqua regia extraction does not perfectly dissolve trace elements in rock forming minerals, but the results are acceptable for environmental interpretation. The following 36 elements were analyzed: Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Te, Th, Ti, Tl, V, W, and Zn. The lower detection limit (LDL) for each element is given in Table 3. The precision of the analysis was verified by multiple measurements of the reference material as well as a blank test.

Mineralogical Analysis Method for Rock Samples

Two samples showing remarkably high concentration of As (170710-1-R1) and Mn (170710-2-R4) were analyzed by an X-ray powder diffraction (XRD) method in order to identify the mineral composition, using a Shimadzu XRD, Laboratory of Sogo Kaihatsu Co., Ltd., Tokyo. The XRD analytical condition is: Voltage = 30 kV, Current = 15 mA, Target = Cu, Filter = Ni, Scanning speed = 0.5 degree/min., and Sampling (step) = 0.02 degree.

Mineral composition of these two samples was also examined with a petrographic observation of polished thin sections.

Results and Discussion

Trace Elements Composition of Groundwater and River Water

The results of ICP-MS trace element analysis of groundwater and river water are summarized as follows:

Table 2 Result of trace elements analysis of water by ICP-MS method. LDL: Lower Detection Limit, MCL: Maximum Contaminant Level, SMCL: Secondary Contaminant Level, MCLG: Maximum Contaminant Level Goal, WHO4: WHO Guidelines for Drinking-water Quality.

Element	Ag	Al	As	B	Ba	Be	Br	Cd	Cl	Cr	Cu	Fe	Hg	Mn	Ni	Pb	S	Sb	Se	Ti	U	Zn
Unit	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPM	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPM	PPB	PPB	PPB	PPB	PPB
LDL	0.05	1	0.5	5	0.05	0.05	5	0.05	1	0.5	0.1	10	0.1	0.05	0.2	0.2	1	0.05	0.5	10	0.02	0.5
170710-1	<100	<600	<3000	417	*	*	*	<700	*	<300	<80	<10000	*	121	<300	<4000	333	<2000	*	<100	<3000	<300
170710-2	<100	<600	<3000	682	*	*	*	<700	*	<300	<80	<10000	*	86	<300	<4000	321	<2000	*	<100	<3000	<300
170710-3	<100	<600	<3000	1269	*	*	*	<700	*	<300	<80	<10000	*	443	<300	<4000	674	<2000	*	<100	<3000	<300
170711-1	<0.05	<1	4.9	86	67.9	<0.05	180	0.13	150	11.9	2.4	<10	<0.1	2.47	<0.2	0.2	63	0.05	0.8	<10	7.48	1.9
170711-2	<0.05	<1	6.6	140	65.7	<0.05	338	<0.05	337	10.6	3.8	<10	<0.1	16.03	<0.2	<0.2	108	<0.05	2.3	<10	7.21	4.1
170711-3	<100	<600	<3000	1339	*	*	*	<700	*	<300	<80	<10000	*	150	<300	<4000	739	<2000	*	<100	<3000	<300
170711-4	0.1	<1	25.1	192	34.8	<0.05	151	<0.05	128	12.2	4.5	<10	<0.1	5.69	<0.2	<0.2	110	0.06	3	<10	9.78	3.2
170711-5	<0.05	<1	5.7	114	26.5	<0.05	120	<0.05	59	17.3	7.5	<10	<0.1	73.64	<0.2	<0.2	76	0.12	0.6	<10	2.19	86.8
170712-1	<100	<600	<3000	<400	*	*	*	<700	*	<300	<80	<10000	*	94	<300	<4000	206	<2000	*	<100	<3000	<300
170712-2	<0.05	<1	18.3	113	35.7	<0.05	540	<0.05	495	9.8	7.8	<10	<0.1	85.54	<0.2	<0.2	231	<0.05	2.6	<10	0.68	5.5
170712-3	<100	<600	<3000	689	*	*	*	<700	*	<300	<80	<10000	*	400	<300	<4000	536	<2000	*	<100	<3000	<300
170712-4	<0.05	<1	4.8	95	104	<0.05	334	<0.05	386	8.2	3.5	<10	<0.1	130.39	<0.2	<0.2	89	<0.05	1.6	<10	4.53	55.6
170713-1	<0.05	<1	3	41	187	<0.05	45	<0.05	16	8.9	2.6	<10	<0.1	4.35	<0.2	<0.2	21	<0.05	<0.5	<10	5.57	1.3
170713-2	2.13	109	2.3	14	26.8	<0.05	64	0.19	4	2.7	24.7	47	<0.1	8.67	2	12.5	8	0.24	0.5	<10	0.69	21.2
MCL			10	2000	2000	4		5		100	1300		2			15.0		6	50	2	30	
SMCL	100	50-200							250		1000	300		50			250					5000
MCLG			0		2000	4		5		100	1300		2			0		6	50	0.5	0	
WHO4			10	2400	700		10**	3	5	50	2000		6		70	10.0		20	40		30	

* analytical result could not be determined due to unusually high levels of interference from other elements. ** Bromate (BrO_3^-)

Six samples, 170710-1, 2, 3; 170711-; and 170712-1, 3, show very high concentration of TDS, and 10 times diluted specimen was analyzed. The result of ICP-MS analysis for 70 elements indicated that 9 elements (Na, Mn, Mg, Ca, K, Sr, Si, Cl, and S) show generally high concentrations in ppm or % order, 7 elements (Zn, Li, Cr, Ba, As Br, and B) show generally lower concentration in 10 to 100 ppb order, 11 elements (W, V, U, Se, Rb, Pb, P, Mo, Fe, Cu, and Al) show trace concentration in 1 to 10 ppb order. and 19 elements (Zr, Y, Tl, Sn, Sb, Rh, Re, Pd, Ni, Nd, Nb, La, Ge, Ga, Cs, Co, Ce, Cd, and Ag) show ultra-trace concentration in ppt order. Meanwhile, the concentration of following 23 elements, Au, Be, Bi, Dy, Er, Eu, Gd, Hf, Hg, Ho, In, Lu, Pr, Pt, Ru, Sm, Ta, Tb, Te, Th, Ti, Tm, and Yb, show below the detection limits (BDLs) in any water sample. The trace element composition of Chenab river water shows distinct composition in comparison with that of groundwater samples, i.e. lower salinity and relatively rich in base metals (Al, Cu, Fe, and Zn). The results are summarized in Table 2.

The concentration of trace elements is examined based on four criteria, USEPA’s three standard values (Maximum Contaminant Level (MCL), Secondary

Maximum Contaminant Level (SMCL) and Maximum Contaminant Level Goal (MCLG)) and guideline values of WHO Guideline for Drinking-water Quality (WHO, 2011). MCL is the maximum permissible concentration of a contaminant in drinking water which is delivered to the public. SMCL is legally non-mandatory water quality standards but they were proposed as guideline values to supply a better quality drinking water to the public. MCLG indicates the concentration of policy target for safety and are non-enforceable quality of drinking water. WHO Guideline values indicate the recommendations of World Health Organization (WHO) for avoiding the risk from hazards caused by low quality drinking-water derived from anthropogenic or natural origins, which are internationally accepted threshold values for protecting the environment and public health.

Total 22 trace elements in the water samples were assessed based on above-mentioned four criteria, and concentrations of the following seven elements are abnormally high according to one or more criteria:

Aluminum (Al)

Aluminum concentration above the SMCL was detected at 710713-2 (109 ppb), in the stream water of Chenab river, which is supposed to be a naturally derived Al. In all the samples collected from water wells, the Al concentration was below the detection limit (BDL). In present study, the diluted groundwater samples due to high TDS increased the detection limit to 600 ppb, which means there is a possibility to present Al contaminated groundwater above the SMCL.

Presence of aluminum concentrations in excess of 100 to 200 ppb often leads a precipitation of aluminum hydroxide, which influences water-treatment processes (WHO, 2011).

Arsenic (As)

Total As contamination above the MCL and the WHO guideline value (10 ppb) could be observed at 170711-4 (25.1 ppb) and 170712-2 (18.3 ppb), which is supposed to be a naturally derived As. In present study, the diluted groundwater samples due to high TDS increased the detection limit up to 3 ppm, which means there is a possibility for As contaminated groundwater to occur above the MCL and the WHO guideline value. As is widely known as a persistent contaminant in groundwater in countries such as Bangladesh, India, Cambodia, and Vietnam (Podgorski et al., 2017; Farooqi et al., 2007; Nickson et al., 2005). The Bengal Delta is the most prominent region because some 43 million people have been drinking As-contaminated groundwater for 20-30 years. Health problems are reported to occur after 10-15 years of chronic exposure to high As levels more than 50 ppb (Mandal and Suzuki, 2002).

Bromine (Br)

Total bromine concentration ranges from 45 to 540 ppb. The WHO guideline value is 10 ppb in the case of bromate (BrO_3^-), an oxyanion of Br. In present study, concentration of total bromine was only analyzed and it cannot be concluded whether bromate concentration exceeds the WHO guideline value or not. The bromine can easily produce bromate through various ways in the supplying process of municipal drinking water, but one of the most common ways is the reaction of ozone and bromide as follows:

$Br^- + O_3 \rightarrow BrO_3^-$

It suggests that ozone treatment method is risky for disinfection of groundwater in present area.

Chlorine (Cl)

Total chlorine concentration shows from 16 to 495 ppm which is apparently above the WHO guideline value and partly above the SMCL. High TDS groundwater contains much Cl, and groundwater in studied area is highly contaminated by Cl as reported by Ahmad et al. (2016). Cl/Br ratio is known as an indicator for assessing possible septic tank influence with the range of 400–1,100 (Katz et al., 2011). In present case, the Cl/Br ratio ranges from 492 to 1,156 except the sample from the public water supply (Cl/Br = 356).

Manganese (Mn)

Manganese concentration in groundwater varies from 4.35 to 443 ppb, where high concentration above SMCL (50 ppb) were observed around 70% of water well, which indicates Mn contamination widely spread over the area. Manganese is an essential element for a human body, but it is also toxic when ingested or inhaled in large amounts over time (Ljung and Vahter, 2007). A large amount of uptake of manganese causes a depletion of brain dopamine and a syndrome of motor dysfunction and memory loss resembling Parkinson disease (Woolf et. al., 2002). It has been reported that in drinking water, manganese is a potential threat to children's health due to its associations with a wide range of outcomes including cognitive, behavioral, and neuropsychological effects (Khan et al., 2012).

Lead (Pb)

High concentration of lead (Pb) above WHO guideline value was detected only in the sample 170713-2, Chenab river water. No high concentration of Pb was observed from groundwater samples.

Sulfur (S)

Concentration of sulfur (S) varies from 8 to 739 ppm, and high TDS groundwater often shows high concentration of sulfur. High concentration of sulfur is observed in both deep and shallow wells but frequently appears at shallow wells around 50 ft in depth (Fig. 2).

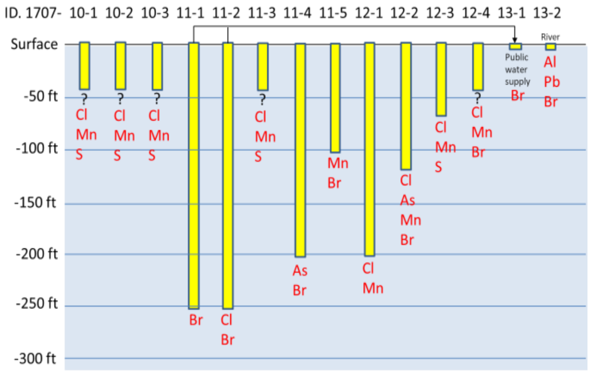


Fig. 2 Groundwater contamination according to the depth of aquifer. The vertical axis shows the depth of water well, and the elements described are those of which concentration is above MCL or SMCL. The wells 170711-1 and 170711-2 are combined with the local public water supply 170713-1.

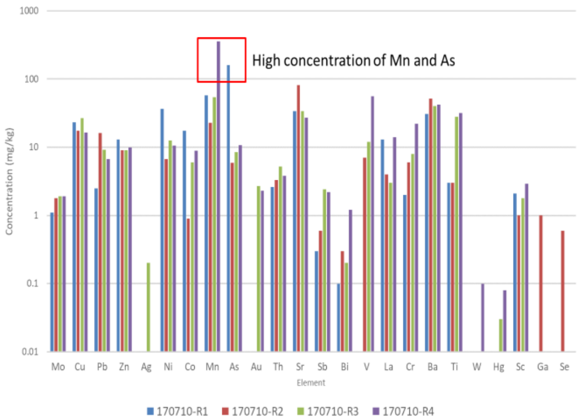


Fig. 3 Result of whole rock trace element analysis using aqua regia extraction and ICP-ES/MS method. The bar graph shows each trace element concentration of each sample. The vertical axis is shown in a logarithmic scale. Results of the 24 trace elements are shown but major elements (S, Fe, Ca, P, Mg, Al, Na, K) are excluded. Tl, Te, B, and Cd were not detected from all rock samples.

Trace Element Composition of Rock Samples

Groundwater chemistry is largely related to chemical composition of the aquifers as well as mineral composition of surrounding hydrological basement. Evaporation and concentration, dilution due to an infiltration of rain water also change the chemical composition of groundwater but water rock interaction is considered to be the major process because solid phases are the primary sources and sinks of dissolved constituents in groundwater (Elango and Kannan, 2007).

The result of whole rock trace element analysis using ICP-ES/MS is in Table 3. Four meta-volcano sedimentary rocks exposed in Kirana hills show similar composition of trace elements except for two trace elements, As and Mn. The and Mn show distinct high concentration level (>100 mg/kg) at 170710-R1 and 170710-R4, respectively.

Table 3. Result of analysis using 1:1:1 aqua regia extraction and ICP-ES/MS method.

	Mo	Cu	Pb	Zn	Ag	Ni	Co	Mn	Fe	As	Au	Th	Sr	Cd	Sb	Bi	V	Ca
Unit	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	%	PPM	PPB	PPM	PPM	PPM	PPM	PPM	PPM	%
LDL	0.1	0.1	0.1	1	0.1	0.1	0.1	1	0.01	0.5	0.5	0.1	1	0.1	0.1	0.1	2	0.01
170710-R1	1.1	23.2	2.5	13	<0.1	36.4	17.6	58	1.71	161.3	<0.5	2.6	34	<0.1	0.3	0.1	<2	0.61
170710-R2	1.8	17.4	16.1	9	<0.1	6.7	0.9	23	2.24	5.9	<0.5	3.3	81	<0.1	0.6	0.3	7	0.05
170710-R3	1.9	26.6	9.2	9	0.2	12.6	6	54	5.73	8.5	2.7	5.2	34	<0.1	2.4	0.2	12	0.56
170710-R4	1.9	16.5	6.7	10	<0.1	10.6	8.9	355	10.4	10.8	2.3	3.8	27	<0.1	2.2	1.2	56	0.13

	P	La	Cr	Mg	Ba	Ti	B	Al	Na	K	W	Hg	Sc	Tl	S	Ga	Se	Te
Unit	%	PPM	PPM	%	PPM	%	PPM	%	%	%	PPM	PPM	PPM	PPM	%	PPM	PPM	PPM
LDL	0.001	1	1	0.01	1	0.001	20	0.01	0.001	0.01	0.1	0.01	0.1	0.1	0.05	1	0.5	0.2
170710-R1	0.156	13	2	0.07	31	0.003	<20	0.59	0.131	0.3	<0.1	0.01	2.1	<0.1	<0.05	<1	<0.5	<0.2
170710-R2	0.014	4	6	0.01	52	0.003	<20	0.52	0.021	0.33	<0.1	0.01	1	<0.1	<0.05	1	0.6	<0.2
170710-R3	0.118	3	8	0.03	40	0.028	<20	0.36	0.063	0.22	<0.1	0.03	1.8	<0.1	0.18	<1	<0.5	<0.2
170710-R4	0.009	14	22	0.02	42	0.032	<20	0.29	0.036	0.16	0.1	0.08	2.9	<0.1	<0.05	<1	<0.5	<0.2

Parato charts of trace element pattern also indicate significant concentration of As and Mn in these two samples (Fig. 4). Other potentially toxic elements (PTEs), Cu, Pb, Ni, Co, Sr, V and Ba were also detected in the samples.

Mineral Composition of Rock Samples

The XRD charts for 710710-R1 and 710710-R4 are shown in Figures 5a and 5b.

The mineral composition of two rock samples is summarized as follows:

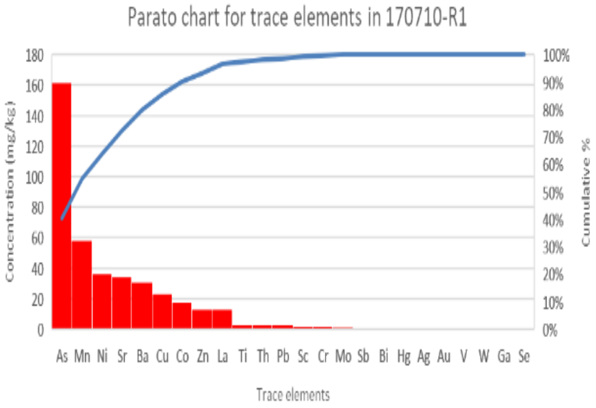
1) Mineral composition of 170710-R1 (High concentration of As)

Quartz > Mica group, Chlorite, Plagioclase > Hematite, Pyrite, Arsenopyrite

2) Mineral composition of 170710-R4 (High concentration of Mn)

Quartz > Mica group > Cryptomelane

The petrographic observation of polished thin sections of these two samples confirmed the occurrence of quartz, mica group, chlorite, plagioclase, hematite, pyrite, and arsenopyrite (FeAsS) in the sample 170710-R1 and quartz, mica group, and cryptomelane ($(K(Mn^{4+},Mn^{2+})_8O_{16})$ in the sample 170710-R4 as rock forming minerals (Figs. 6a, b).



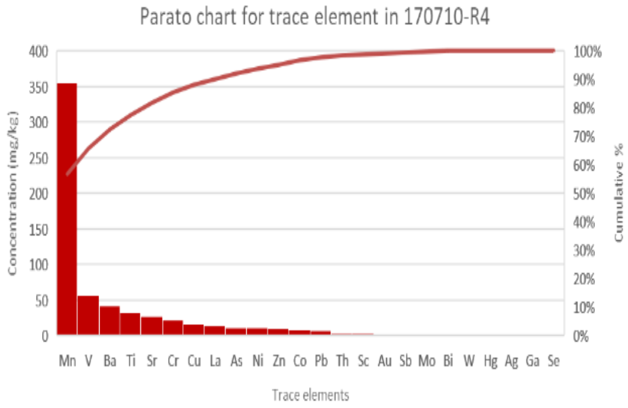


Fig. 4 Parato charts of concentration of trace elements for 170710-R1 (Top) and R4 (Bottom). Individual concentration values (mg/kg) are represented in descending order by bars, and the cumulative total (%) is represented by the line.

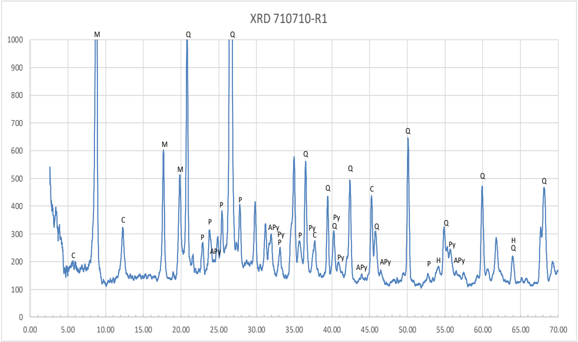


Fig. 5a XRD chart for 710710-R1. Q: quartz, P: plagioclase, C: chlorite, H: hematite, M: mica group, Py: pyrite, Apy: arsenopyrite.

Possible Causes of Groundwater Contamination by Trace Elements

High concentration of As in the sample 170710-R1 is caused by arsenopyrite and high concentration of Mn in the sample 170710-R4 is caused by cryptomelane. Based on a study on groundwater contamination in Lahore and Kasur districts. According to Farooqi (2007a) the presence of high levels of As in the surface soil and groundwater implies the contribution of air pollutants derived from coal combustion and the use of fertilizers. However, the groundwater contamination by As and Mn is caused by a water rock interaction (Elango and Kannan, 2007) in the subsurface zone.

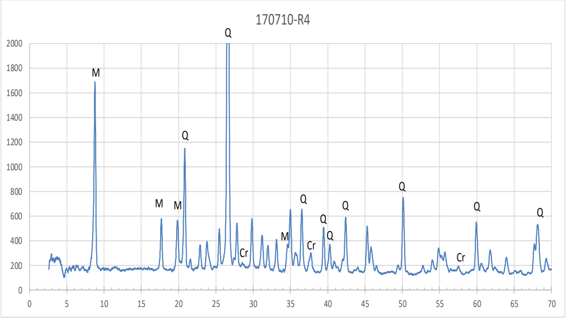


Fig. 5b XRD charts for 170710-R4. Q: quartz, M: mica group, Cr: cryptomelane.

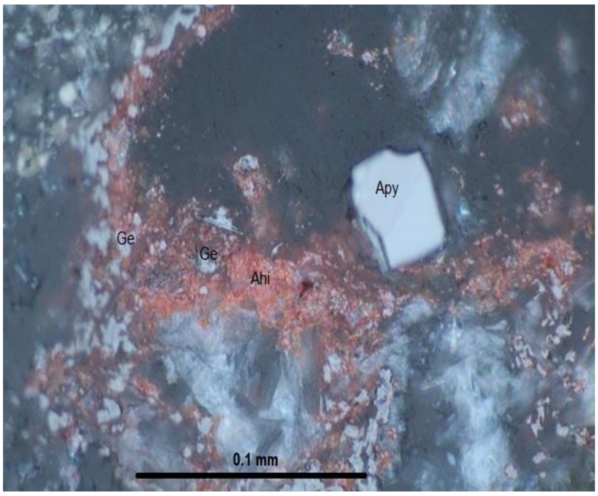


Fig. 6a Microscopic image of the sample 170710-R1. Observed by polarized reflective light with parallel nicols. Apy: arsenopyrite, Ahi: amorphous iron hydroxide, Ge: goethite.

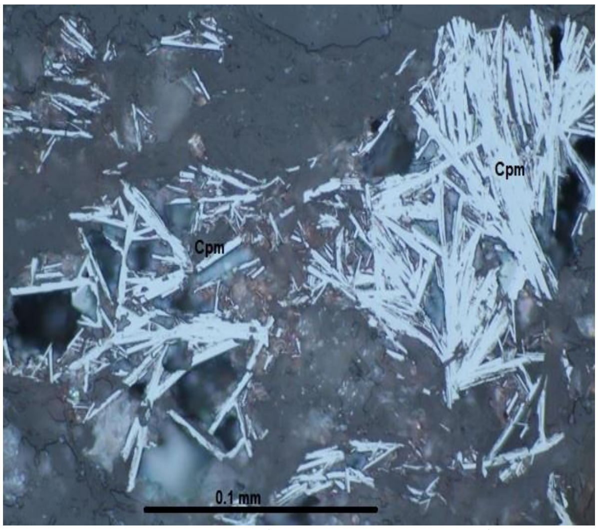


Fig. 6b Microscopic image of polished thin section of the sample 170710-R4. Observed by polarized reflective light with parallel nicols. Cpm: cryptomelane.

On the contrary, the contamination by Cl and Br cannot correspond directly to the chemical composition of basement rocks exposed in the Kirana hills, but high salinity is inherent in the area mainly due to underlying saline water (Greenman et al., 1967; Qureshi et al., 2008), and these two elements are considered to be of natural origin. Moreover, Cl/Br ratio suggests that groundwater from shallow wells is probably affected by septic tank and wastewater.

The S contamination is probably caused by both natural and anthropogenic origins. It has been reported that there are hydrothermal alteration zones in the Kirana hills basement rocks (Khan et al., 2009), and S contamination is possibly caused by the basement geologic system. However, for shallower parts of the groundwater aquifer, S contamination may be accelerated by man-made inputs from land surface, such as a contamination of solid waste leachate, a migration of wastewater and an infiltration from septic tanks.

Conclusion

Trace elements contamination was studied for groundwater collected around Kirana hills, Chiniot, Punjab, in order to assess the quality of groundwater, which is widely used for drinking water by local people. The concentration of five elements, As, Mn, Cl, Br, and S, in groundwater exceeds drinking water quality standards, USEPA MCL/SMCL/MCLG and WHO Guideline. As rich and Mn rich rocks were found in the basement rocks in Kirana hills, which suggest that the groundwater contamination is derived from a water-rock interaction. High salinity of groundwater is inherent in the area, but the contamination by Cl and Br is probably accelerated by anthropogenic origins such as septic tank or wastewater. S contamination is also considered to be natural and artificial in origins. In the area, only one public water supply tank (170713-1) is free from contaminations and safety for drinking, but other wells indicate more or less cautious level. Further survey, sampling, analysis, petrological and mineralogical observations and geochemical study are required for detailed discussion on groundwater contamination mechanism and rock-water interaction process in the area.

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References

Ahmad, M. N., Sultana, R., Salahuddin, M., Ahmad, J. S. (2016). Assessment of groundwater resources in Kirana hills region, Rabwah, district Chiniot, Pakistan. *Int. J. Econ. Environ. Geol.*, **7** (2), 46-50.

Azizullah, A., Khattak, M.N.K., Richter, P., Häder, D. P. (2011). Water pollution in Pakistan and its impact on public health - A review. *Environment International*, **37**, 479-497.

Brantley, S. L., Kubicki, J. D., White, A. F. (2008). Kinetics of water-rock interaction. Springer Science, New York.

Brian, G., Katz, B.G., Eberts, S.M., Kauffman, L.J. (2011). Using Cl/Br ratios and other indicators to assess potential impacts on groundwater quality from septic systems: A review and examples from principal aquifers in the United States. *Journal of Hydrology*, **397**, 151–166.

Elango L., Kannan, R. (2007). Rock-water interaction and its control on chemical composition of groundwater. *Developments in Environmental Science*, **5**, 229-243.

Farooqi, A., Masuda H., Firdous, N. (2007a) Toxic fluoride and arsenic contaminated groundwater in the Lahore and Kasur districts, Punjab, Pakistan and possible contaminant sources. *Environmental Pollution*, **145**, 839-849.

Farooqi, A., Masuda, H., Kusakabe, M., Naseem, M., Firdous, N. (2007b). Distribution of highly arsenic and fluoride contaminated groundwater from east Punjab, Pakistan, and the controlling role of anthropogenic pollutants in the natural hydrological cycle. *Geochemical Journal*, **41**, 213-234 pages.

Geological Survey of Pakistan (2000). Hydrogeology map of Pakistan. Geological Survey of Pakistan, Quetta.

Greenman, D. W., Swarzenski, W. V., Bennett, G. D. (1967). Ground-water hydrology of the Punjab, west Pakistan with emphasis on problems caused by canal irrigation. *U S Geological Survey Water-Supply Paper*, 1608-H.

Khan, K., Wasserman, G.A., Liu, X., Ahmed, E., Parvez, F., Slavkovich, V., Levy, D., Mey, J., van Geen, A., Graziano, J.H., Factor-Litvak, P. (2012). Manganese exposure from drinking water and children’s academic achievement. *Neurotoxicology*, **33** (1), 91–97.

Khan, S., Rana, T., Gabriel, H. F., Ullah, M. K. (2008). Hydrogeologic assessment of escalating groundwater exploitation in the Indus Basin, Pakistan. *Hydrogeol. Jour.*, **16** (8), 1635-1654.

Khan, Z. K., Ahsan, N., Mateen, A., Chaudhry, M.N. (2009). Petrography and mineralogy of dolerites of Hachi Volcanics, Kirana hills area, Pakistan. *Geol. Bull. Punjab Univ.*, **44**, 55-67.

Ljung, K., Vahter, M. (2007). Time to Re-evaluate the guideline value for manganese in drinking water? *Environmental Health Perspectives*, **115**(11), 1533-1538.

Mandal, B. K., Suzuki, K. T. (2002). Arsenic round the world: A review. *Talanta*, **58**, 201–235.

Nickson, R.T., McArthur, J.M., Shrestha, B., Kyaw-Myint, T.O., Lowry, D. (2005). Arsenic and other drinking water quality issues, Muzaffargarh district, Pakistan. *Applied Geochemistry,* **20**, 55-68.

Podgorski, J. E., Eqani, S.A.M.A.S., Khanam, T., Ullah, R., Shen, H., Berg, M. (2017). Extensive arsenic contamination in high-pH unconfined aquifers in the Indus valley. *Science Advances*, **3** (8), 1-10.

Qureshi, A.S., McCornick, P.G., Qadir, M., Aslam, Z. (2008). Managing salinity and waterlogging in the Indus Basin of Pakistan. *Agricultural Water Management*, **95**, 1-10.

WHO (2011). Guidelines for drinking-water Quality 4th Edition. World Health Organization, 541 pages.

Woolf, A., Wright, R., Amarasiriwardena, C., Bellinger, D. (2002). A child with chronic manganese exposure from drinking water. *Environmental Health Perspectives*, **110**(6), 1-4.