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Trace element geochemistry of groundwater from Quetta Valley, western Pakistan

Shuhab D. Khan · Khalid Mahmood ·
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Abstract This manuscript presents major, minor and trace elements data for groundwater samples collected from wells, tube wells, springs and karezes from Quetta Valley. Quetta Valley in Pakistan has frequently experienced shortage of groundwater. In recent years, the water quality has had a sharp decline at many locations. The study of groundwater resources in this valley is an attempt to understand the causes of and sources of contamination. At several locations, nitrate, sulfate, arsenic, selenium, chromium and nickel contamination has been determined. The preliminary results indicate that these contaminations apparently result from a combination of rock alteration and mining activity in the area. Different water sources could have also contributed to the deterioration of the water quality of Quetta Valley. This research provides the basis for future work, which will involve detailed hydrological modeling and water quality studies.

Keywords Groundwater chemistry · Trace elements · ICP-MS · Arsenic · Ultramafic rocks

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Introduction

The contamination of groundwater with trace elements is a risk to the health of millions of people. There are no direct means for identifying high-risk areas without conducting detailed geochemical work. An attempt has been made to relate high content of few trace elements to the bedrock geology in Quetta Valley in western Pakistan. This association could be used for indicating potential high-risk areas in other parts of the world.

Quetta is the capital of Balochistan, which is the largest province in Pakistan, yet it has the smallest number of people per unit area. This is largely due to the paucity of water resources related to its arid to semi-arid conditions. The climate in this province is typical of deserts; low rainfall (~ 100 mm/year) and extreme variations in temperature are observed. The indiscriminate and unplanned use of groundwater resources to meet water requirements in Balochistan, in general, and in Quetta, in particular, has led in the recent years to unsustainable overexploitation of groundwater. This has resulted in a progressively increasing decline in groundwater levels in Quetta (Khan and Mian 2000). This phenomenon has had socio-economic impacts exemplified in the migration of the population from rural to urban areas and Quetta is bearing the brunt of this migration.

Quetta Valley is bounded by limestone slopes of Chiltan, Takhatu, Zarghoun and Murdar ranges (Fig. 1). The drainage of the Quetta Valley flows through the gaps between these mountains and joins the Pasin Lora Basin in the north. The valley itself is covered by alluvium and loess deposits. The main sources of groundwater in Quetta Valley are springs, karezes, open wells and tube wells. Kareze systems are underground channels; the tunnels are laid on natural gradient for draining water with minimum
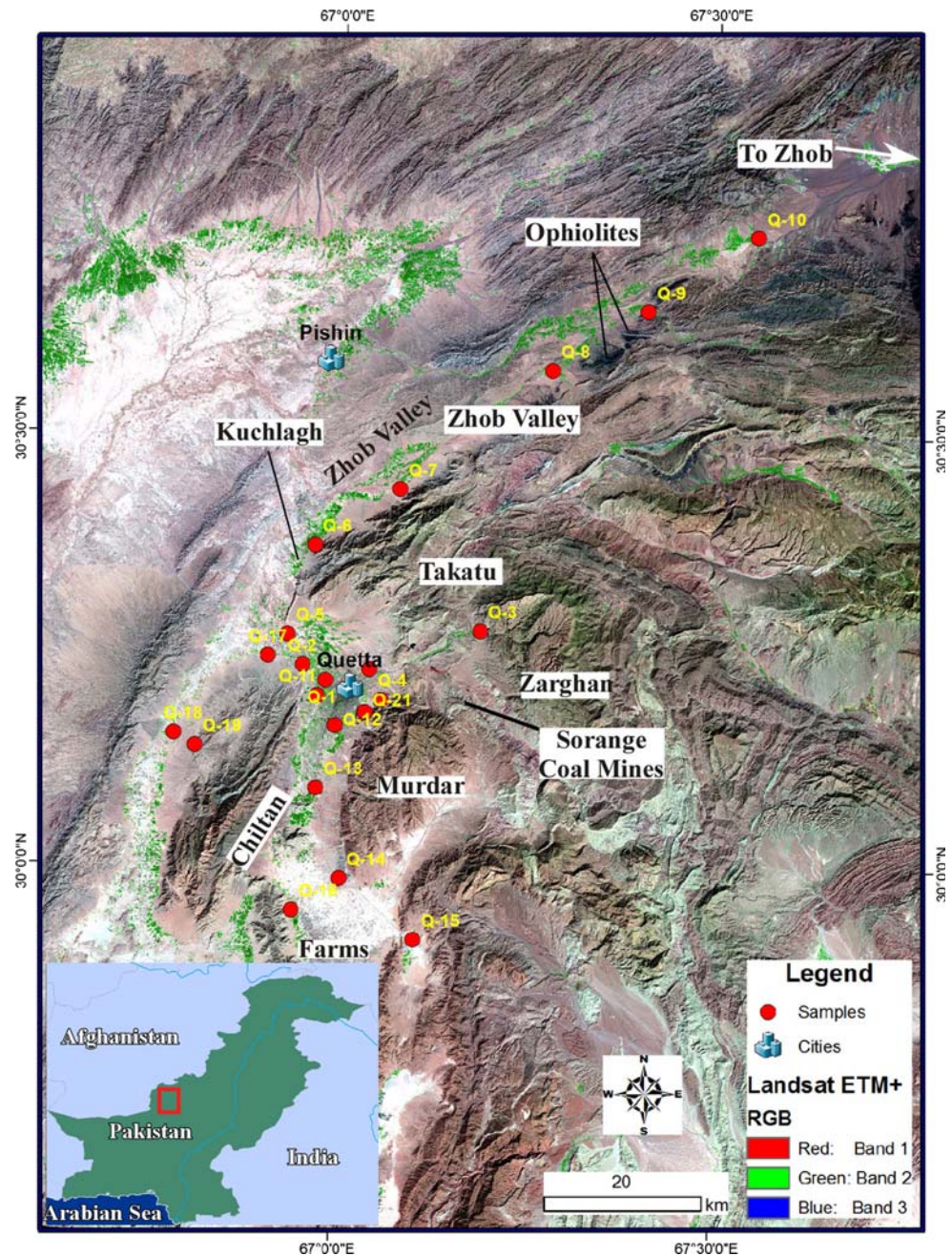
evaporation loss and without pumping. The water is
drained from a source well situated at higher elevation
from where the water flows through kareze and finally
water is distributed through open channels for domestic
and agricultural purposes. The kareze system was a com-
mon water system in the past; however, lately this system
is diminishing. The groundwater in the Quetta area flows
from the higher elevation areas in the foothills to the
central part of the valley and finally the groundwater drains
into an effluent stream (Sariab Lora; Kazmi et al. 2005).

Kazmi et al. (2005) identified two aquifers in Quetta
Valley: unconsolidated alluvial aquifer and bedrock

aquifer. The alluvial aquifer is the main aquifer and con-
sists of gravel, sand and silt deposits. This aquifer is
recharged from infiltration of precipitation, runoff and
inflow from the bedrock aquifer in the foothill areas. The
bedrock aquifer consists of limestone of Shirinab and
Chiltan formations and conglomerates of Urak Formation.
This aquifer is recharged in the surrounding mountain areas
where these formations are exposed. In the Zhob Valley, a
third type of aquifer, the ophiolitic aquifer, is recognized.
This aquifer consists of serpentinized ultramafic rocks; the
rocks are highly faulted, fractured and shared due to
intense weathering, alteration and solution activity. This

Table 1 Analytical results for minor and trace elements in groundwater samples of Quetta Valley

Samples	Q-1	Q-2	Q-3	Q-4	Q-5	Q-6	Q-7	Q-8	Q-9	Q-10	Q-11	Q-12	Q-13	Q-14	Q-15	Q-16	Q-17	Q-18	Q-19	Q-20	Q-21
Latitude	30.21537	30.2329	30.2741	30.2285	30.26861	30.37175	30.43746	30.57646	30.64578	30.73258	30.19771	30.16346	30.09062	29.9871	29.91733	29.9493	30.24361	30.15262	30.1387	30.19348	30.17917
Longitude	66.98519	66.9542	67.1897	67.04357	66.93371	66.9683	67.08042	67.28116	67.40758	67.55381	66.97425	66.99871	66.97452	67.00688	67.10656	66.9448	66.90823	66.78511	66.81334	67.05884	67.03793
Cl	84.2	87.3	6.9	10.4	91.4	80.4	67	66.4	86.6	27.6	97.7	71.6	157.6	354.8	103.1	127	207.3	83	83.3	26.5	29.4
SO$_4$	81.1	169.9	7.7	26.6	104.7	67.1	268.8	155.9	492.1	60	108	123.8	137	442.8	101.2	104.9	427.2	212.4	229.2	45.6	37.4
NO$_3$	50.4	13.8	4	4.4	13.5	6	12.4	16.6	49.2	16.4	0.6	23.5	16.8	50.2	158.8	60.3	23.3	22.9	21.2	6.4	19
Fe	<10	<10	<10	<10	29.9	10.6	57.4	<10	<10	4.8	6.7	4.4	<10	3.2	3.7	8.6	4.1	<10	25.7	<10	<10
Mn	<0.005	<0.005	<0.005	<0.005	0.0037	<0.005	0.0251	<0.005	<0.005	<0.005	0.0006	<0.005	<0.005	0.0031	0.0007	0.0007	0.0009	<0.005	0.0014	0.006	<0.005
Si	6.5	5.6	2.2	3	6	4.4	8.3	6.5	5.1	6.7	4.4	7.7	6.6	4.8	4.9	4.9	5.8	5.5	5.1	9.8	4.3
K	2.1	2.2	0.75	1.7	2.8	1.8	4	2.7	6.2	1.2	1.5	2	2.6	2.6	2	1.6	4.4	3.2	3.5	1.4	1.4
Na	73	73	8.5	15	66	53	154	78	164	41	157	87	145	420	99	97	270	141	127	58	29
Mg	38	43	6.4	7.5	32	32	46	76	105	47	13	33	37	57	38	44	94	70	75	15	22
Ca	85	62	45	50	67	49	50	30	130	60	19	60	43	76	50	68	72	44	50	28	51
Li	13.214	11.336	2.388	3.794	13.674	10.117	25.609	14.872	50.347	16.487	7.096	10.281	12.890	22.407	13.977	9.142	22.810	27.692	28.722	6.296	5.912
B	151.475	99.763	18.490	46.263	136.362	116.507	378.078	175.202	434.926	152.554	286.098	136.898	209.403	377.553	198.210	123.186	445.224	255.421	227.415	62.502	79.199
V	1.619	1.904	0.689	0.806	2.077	2.620	5.242	5.194	2.424	3.922	5.683	3.048	6.823	0.872	3.331	2.413	3.426	1.140	1.331	6.103	0.734
Cr	4.211	2.769	0.074	–	3.992	3.112	11.748	55.297	11.348	14.671	9.256	2.976	7.141	–	37.354	10.264	5.059	0.514	0.394	11.814	–
Mn	0.059	0.132	0.228	0.364	0.341	0.306	0.347	6.677	0.956	0.745	0.376	0.115	0.129	0.088	0.138	0.128	0.132	0.127	0.075	0.120	0.104
Co	0.108	0.026	0.031	0.077	0.021	0.072	0.020	0.547	0.115	0.055	0.023	0.023	0.021	0.038	0.034	0.026	0.042	0.031	0.037	0.011	0.019
Ni	0.778	0.505	1.313	0.697	0.707	0.700	0.957	71.581	1.796	1.073	1.362	0.450	0.329	0.685	0.527	0.593	0.654	0.523	0.431	0.928	0.474
Cu	–	–	1.291	–	–	–	–	1.200	0.067	0.244	3.588	–	–	–	0.073	–	–	–	–	–	10.326
Zn	–	–	–	77.092	19.637	165.183	1.337	43.602	49.988	7.272	17.138	–	24.446	99.002	3.299	9.598	9.632	–	0.341	–	3.581
Ga	0.003	0.005	0.003	0.042	0.060	0.062	0.025	0.028	0.033	0.030	0.046	0.008	0.005	0.003	0.007	0.007	0.005	0.002	0.001	0.013	0.004
As	0.918	1.138	0.784	50.390	18.207	59.411	21.856	15.585	64.535	19.437	14.015	0.943	1.523	0.783	1.591	0.877	1.106	0.496	0.382	2.119	0.381
Se	2.868	8.680	1.520	17.811	43.876	131.306	128.798	42.104	128.830	89.603	67.422	2.854	2.387	9.492	3.966	2.336	7.499	2.971	2.436	1.162	0.861
Rb	0.772	0.702	0.265	5.355	2.580	6.082	3.653	1.943	7.416	1.555	1.719	0.741	0.551	1.010	0.582	0.681	0.631	1.312	1.000	0.370	0.619
Sr	1324.026	1651.221	353.409	360.916	1335.989	1166.275	1724.342	1213.091	3793.976	834.231	525.439	1248.137	1815.076	1959.226	1408.510	1115.390	2727.485	1877.599	1705.018	567.281	648.531
Y	8.361	7.957	9.909	27.840	–	58.323	89.334	120.781	27.166	134.566	131.612	8.787	7.654	7.513	8.575	9.184	5.577	6.845	7.276	10.269	10.512
Ag	0.029	0.008	0.041	3.102	0.892	3.160	0.914	0.481	3.360	0.928	0.512	0.009	0.005	0.002	0.030	0.009	0.004	0.003	0.002	0.028	0.008
Cs	0.003	0.003	0.001	0.048	0.018	0.055	0.024	0.014	0.073	0.019	0.018	0.002	0.004	0.013	0.003	0.007	0.004	0.010	0.003	0.002	0.008
Ba	85.360	43.921	41.966	45.601	83.000	60.235	24.433	36.708	39.588	28.610	34.263	28.963	36.193	24.634	55.810	39.356	26.811	20.616	0.797	41.477	29.025
Tl	0.035	0.141	20.531	–	0.119	463.531	501.718	385.535	1383.127	257.298	180.808	225.620	350.982	480.002	405.439	181.678	1024.218	182.915	178.553	85.369	86.193
Pb	0.002	–	0.001	0.431	0.125	0.406	0.126	0.069	0.398	0.111	0.072	0.000	0.000	0.000	0.002	0.007	–	–	–	0.001	0.020
Th	6.325	8.555	8.056	124.196	869.282	–	–	–	184.227	–	1842.263	3.963	6.812	9.632	8.917	9.545	10.161	9.506	6.672	10.192	9.686
U	0.003	–	0.003	0.396	0.082	0.379	0.097	0.046	0.408	0.089	0.056	–	–	–	0.004	–	–	–	–	0.003	–
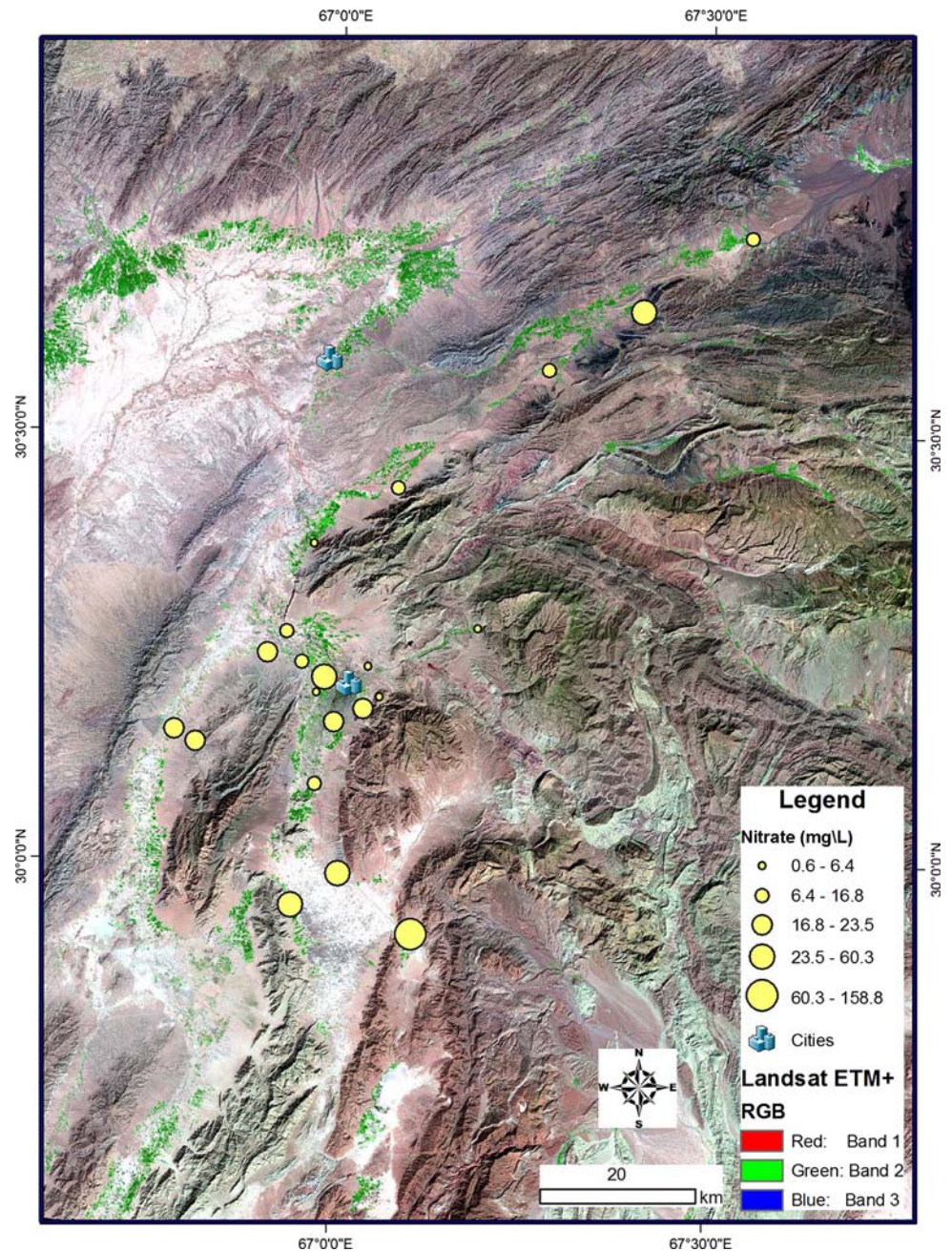
aquifer is a significant source of groundwater in this arid
region.

Geological formations ranging in age from Early
Jurassic to Quaternary are exposed in the Quetta Valley.
The Jurassic (Shirnab and Chiltan formations) are com-
posed of shales and limestones (Kazmi et al. 2005). The
Cretaceous rocks are shale, siltstones and limestone of the
Parh Group. The Tertiary rocks are thick sequence of shale,
siltstones, sandstones and conglomerates of the Urak
Group (Kazmi et al. 2005). The quaternary deposits com-
prising alluvial deposits are present in stream beds and
alluvial fans. The Zhob Valley ophiloite bodies are exposed

in the east–northeast of Quetta (Fig. 1). The Zhob Valley
starts from Kuchlagh and extends up to Zhob. These
ophiolite bodies are considered to be late Cretaceous in age
(Khan et al. 2007); ophiolites in the study area are com-
posed of highly fractured serpentinized ultramafic rocks,
which are rich in chromite and other sulfide minerals (Khan
and Mahmood 2008).

An integrated interdisciplinary approach for groundwa-
ter exploration is applied in the Quetta Valley, Balochistan
Province, Pakistan, in which inferences from remote
sensing data are integrated with information obtained
from other relevant data sources such as geochemistry,

Fig. 3 Concentration of sulfate (SO$_4$) is plotted at sampling sites. The *diameter* of the *circle* shows relative concentration. Most of the samples show high sulfate content, few samples show sulfate contamination and a couple of samples from the bedrock aquifer show minimum sulfate
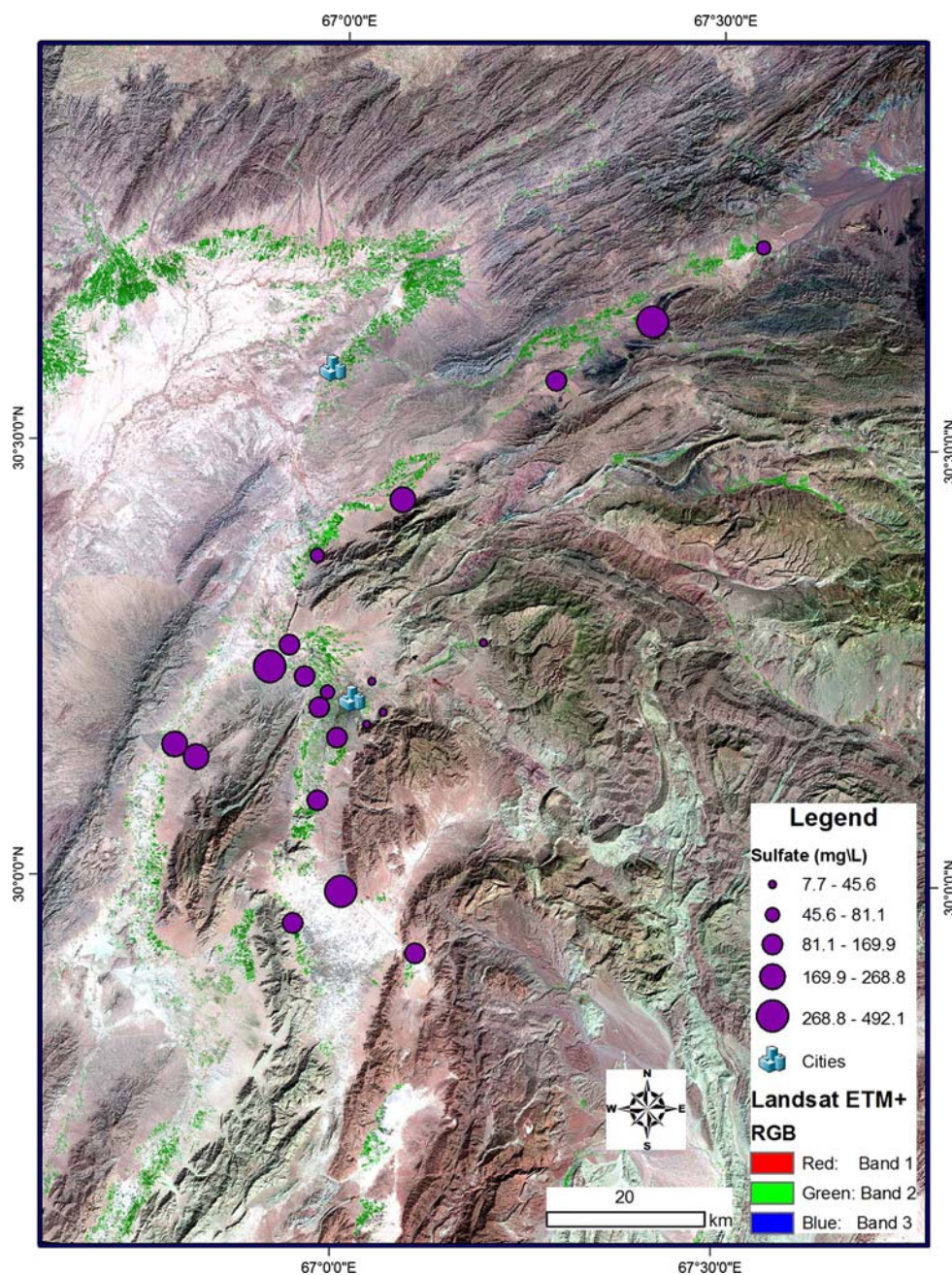
field geology, geophysics and surface runoff and groundwater flow modeling for a better understanding of the hydrological setting and the groundwater availability, and for identifying potential locations for productive wells. This paper focuses on the water quality aspect of this project.

Methodology

A total of 21 sampling sites in Quetta Valley were chosen for the collection of groundwater samples to be analyzed for their contents of major, minor and trace elements (Fig. 1). These sites included wells, tube wells, springs and karezes. Samplings were carried out in December 2007. Special care was taken in the collection and analysis of these samples and the procedures were followed as outlined in Eaton et al. (2005) and Stetzenbach et al. (1994).

Water samples were first filtered with Fisher brand Q2 filter paper. Then, 10 ml filtered water samples were dried down on a hot plate under a closed hood (with only filtered air drawn in), acidified with ultra-purified nitric acid and diluted to its former volume with milli-Q water (for

Fig. 4 Concentration of arsenic (As) is plotted at sampling sites. The *diameter* of the *circle* shows the relative concentration. With the exception of two samples in the west, most of the samples show high arsenic content and many samples show contamination. All the samples collected from the Zhob Valley show contamination in selenium too. Zhob Valley is characterized by the presence of serpentinized ultramafic rocks, which host chromite deposits and may be the source of arsenic in this area
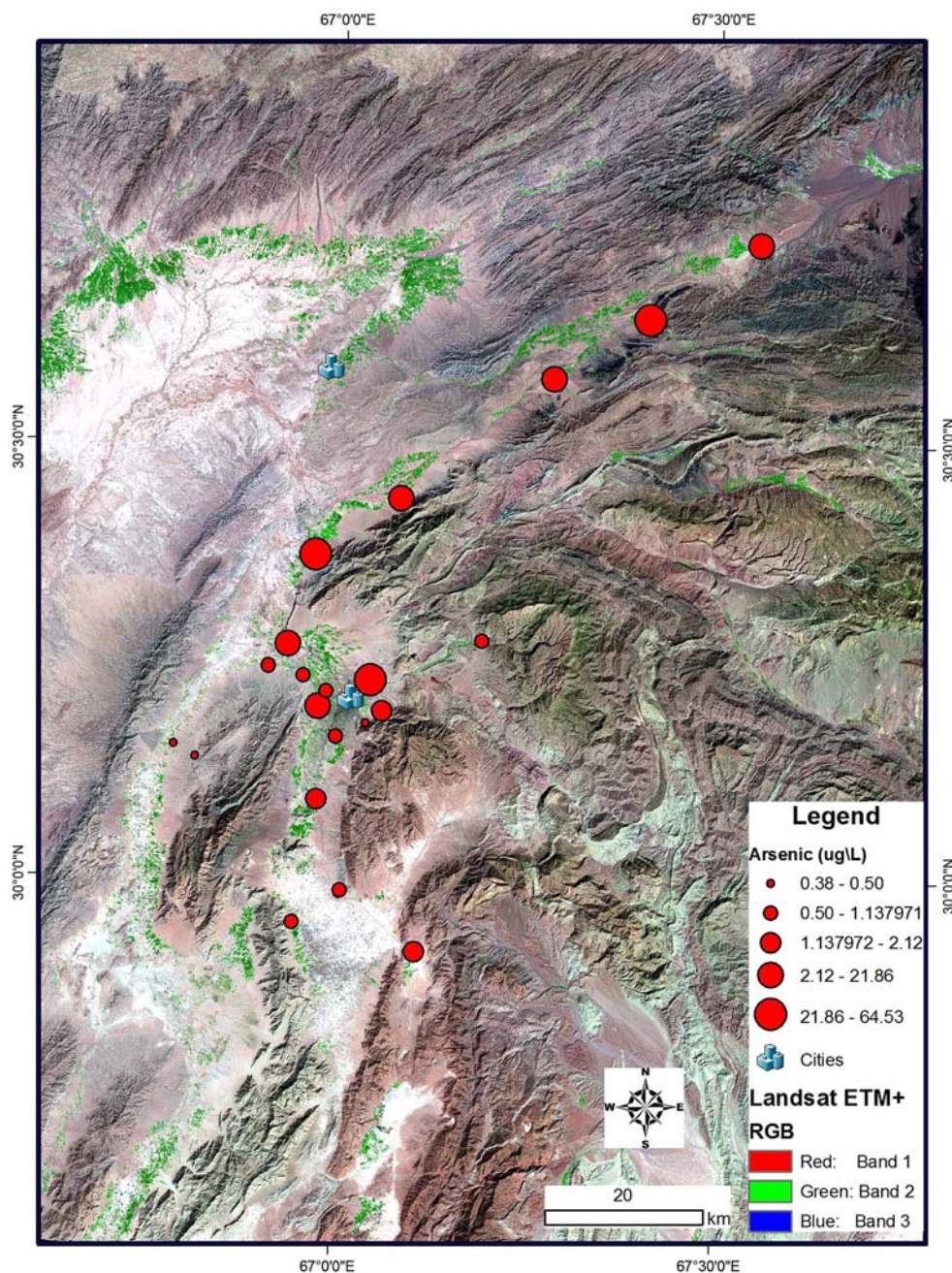
comparison, ten water samples were repeated with 1 ml and diluted to 10 ml), and then analyzed with inductively coupled plasma-mass spectrometry (ICP-MS) in the Department of Earth and Atmospheric Sciences, University of Houston. Standard sample 71A (diluted with ultra-purified acid to 10 ppb) was used as the external calibration sample. Measurements were repeated five times and most of the RSD were less than 5% with a majority less than 3%. The differences between the ten (10) repeated water samples were less than 5%, with the value of diluted ones lower than those without dilution. All the above indicate that the data are of high quality.

Results and discussions

Collected samples were quantitatively analyzed using ICP (AES) and ICP (MS) for the determination of major (Ca, K, Mg, Na, Si, Cl^- and SO_4), minor and trace elements (Fe, Mn, B, Ba, Li, Sr, Li, Be, B, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Ag, Cd, Cs, Ba, La, Ce, Pr, Nd_{145}, Nd_{146}, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Tl, Pb, Th, U). The results are given in Table 1. Some of these elements were analyzed to determine the water quality and source of contamination, whereas other trace elements were used as tracers to find water–rock interactions.

Fig. 5 Concentration of selenium (Se) is plotted at sampling sites. The *diameter* of the *circle* shows the relative concentration. All the samples, which have high selenium also show high arsenic suggesting similar source for both elements
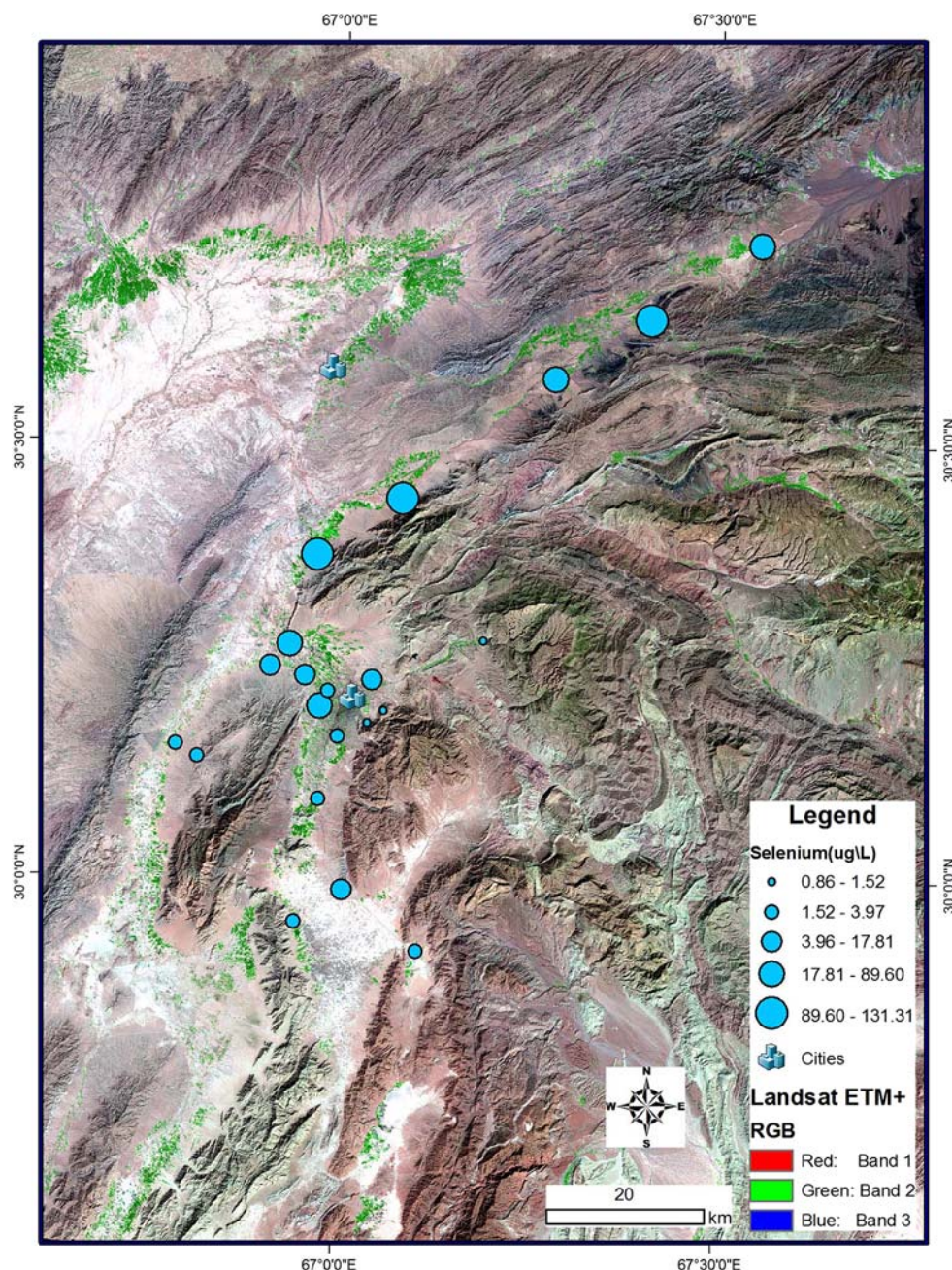
Water from all the sites from which samples were collected are used for drinking purposes, therefore, it is important to know the quality of water. Results were compared with the World Health Organization's (WHO) Maximum Contaminant Level (MCL) data (World Health Organization 2003, 2006). The data show elevated levels for nitrate (NO_3) and sulfate (SO_4) and some trace elements: arsenic (As), selenium (Se), chromium (Cr), Nickel (Ni) and thallium (Tl) (World Health Organization 2003, 2006).

Figure 2 shows spatial variation of nitrate concentration. Sample Q14, Q15, and Q16 show maximum concentration.

Sample (Q1) also shows concentration values more than the WHO guideline values (World Health Organization 2006). Sample Q15 shows nitrate content more than triple when compared with the WHO guideline value (World Health Organization 2003). High content of nitrate in drinking water can cause blue-baby syndrome, which is a disease in infants where the color of an infant's skin changes because of oxygen deficiency in the blood (World Health Organization 2003; Knobeloch et al. 2000, Bouchard et al. 1992). Field observations suggest that most of the samples with nitrate contaminations are located in

Fig. 6 Concentration of chromium (Cr) is plotted at sampling sites. The *diameter* of the *circle* shows the relative concentration. Chromium shows similar pattern as arsenic and selenium, and is of the highest content in the Zhob Valley, supporting the source in ultramafic rocks
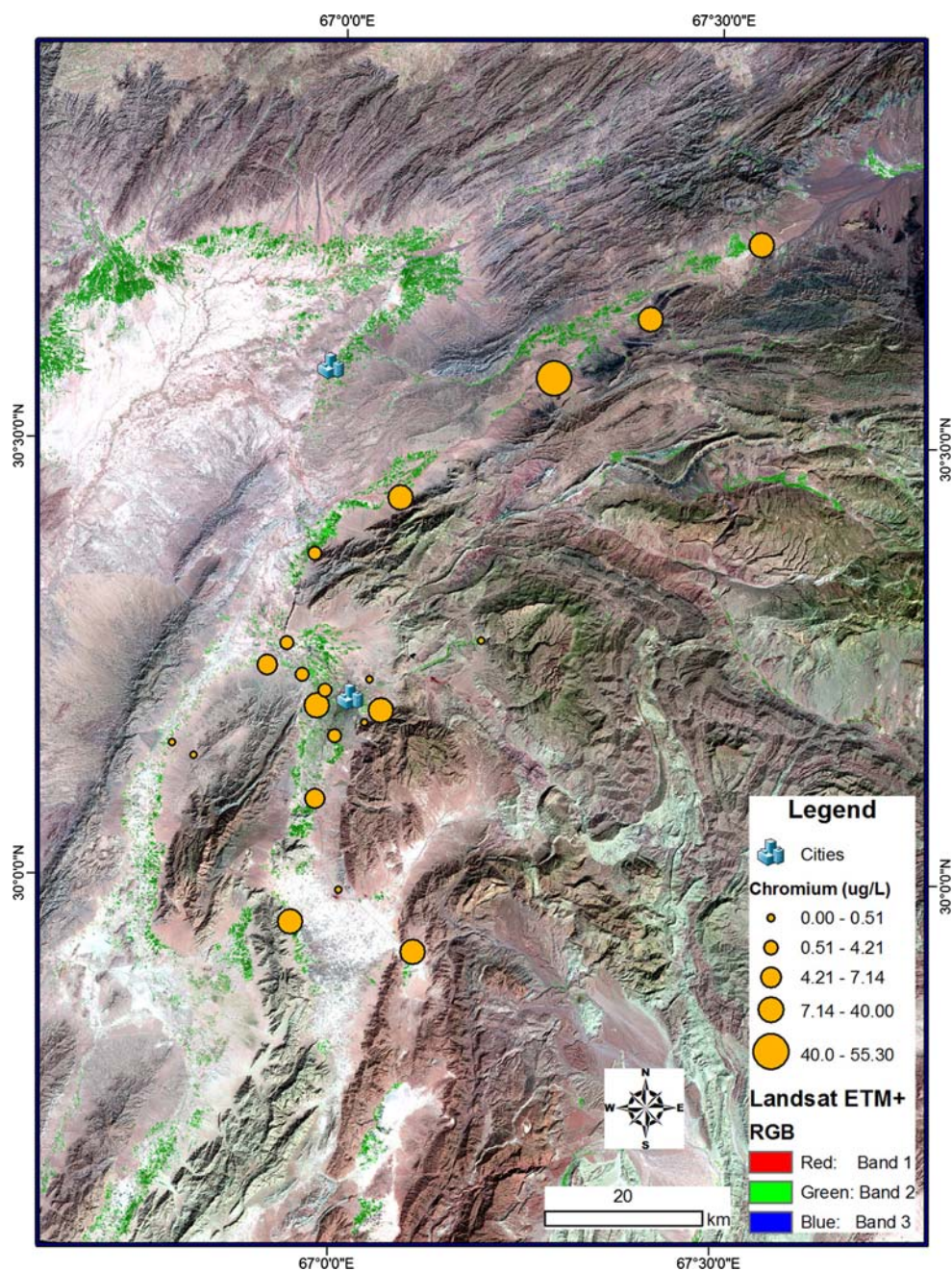
agricultural areas with animal farms (see Fig. 1); we consider this to be the main source of contamination.

Several samples from the study area show high concentration of sulfate (Fig. 3). Though sulfate is not considered to be a major contaminant, gastrointestinal effects can be caused by the ingestion of water with a high content of sulfate. Some authors have reported that drinking water with sulfate ranging from 500 to 700 mg/L can cause diarrhea (Heizer et al. 1997). The presence of gypsum in the surrounding rocks of Quetta Valley could be contributing to the sulfate in the groundwater of Quetta Valley.

Eight samples (Q4, Q5, Q6, Q7, Q8, Q9, Q10 and Q11) show arsenic and selenium contamination (Figs. 4, 5). All the samples collected in Zhob Valley (Q6, Q7, Q8, Q9, and Q10) show high concentration of arsenic and selenium. In addition, a few more samples (Q4, Q5, Q11) show values higher than the WHO guidelines (WHO 2006). The highest value comes from the sample Q9, which shows 6 times higher arsenic and almost 13 times higher selenium content when compared with WHO guideline values (World Health Organization 2006). Sample Q9 was collected from Kareze. In kareze, water flows for long distances and may dissolve contaminants from the rocks through which it flows.

Arsenic in very high concentrations is poisonous; low-level, long-term exposure to arsenic may lead to increased risk of cancer (National Research Council 1999). Arsenic is derived from anthropogenic sources, such as drainage from mines and mine tailings, pesticides, and biocides, and from natural sources such as hydrothermal leaching of arsenic containing minerals or rocks. Millions of people are affected by toxic levels of arsenic in many parts of the world (e.g., Bangladesh). There is considerable evidence for skin cancer caused by the presence of arsenic in drinking water, which also increases the mortality risk for internal cancers in several human organs (Morales et al., 2000). There are many examples of arsenic causing cancer from various parts of the world; for example, bladder and lung cancer mortality from Chile (Smith et al. 1998), and Argentina (Hopenhayn-Rich et al. 1996). Chen et al. (1985) observed increased mortality in Taiwan due to lung, liver, skin, kidney and bladder cancer, caused by arsenic in drinking water. The most severe cases of arsenic contamination are reported from Bangladesh, where some reports suggest that 35–77 million people are at risk of drinking contaminated water (Chowdhury et al. 2000, Smith et al. 1992). Elevated levels of selenium are toxic and could develop cancer, malformation of nails and hair, depression, nervousness and other symptoms in humans (Feder 1985).

Presence of elevated levels of arsenic and selenium in Quetta Valley poses a problem in this region and requires detailed study. The samples that show high concentration of arsenic and selenium in Zhob Valley also contain higher levels of chromium (Fig. 6) and nickel. This probably suggests that the alteration of ultramafic rocks may be contributing to the elevated levels of these metals in the Zhob Valley. This argument is supported by the occurrence of arsenic in groundwater and ultramfic rocks in other areas, for example Vermont, USA (Bright, 2006). The source of high content of arsenic and selenium in samples Q4, Q5 and Q11 may be from the coal mines in the Sorange area.

Conclusions

Geochemical analysis of drinking groundwater samples from Quetta Valley show high concentration of nitrate, sulfate, arsenic, selenium, chromium and nickel. Some of these samples show concentration levels higher than the WHO guideline values for drinking water. Continuous use of water with contaminants like arsenic and selenium may cause health problems. Alteration of ultramafic rocks and coal mining appear to be the potential sources. Detailed water quality study in this area, looking for the potential source of these contaminants is warranted.

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