

Role of mafic and ultramafic rocks in drinking water quality and its potential health risk assessment, Northern Pakistan

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ABSTRACT

This study investigates the drinking water (groundwater and surface water) quality and potential risk assessment along mafic and ultramafic rocks in the Swat district of Khyber Pakhtunkhwa Province, Pakistan. For this purpose, 82 groundwater and 33 surface water samples were collected and analyzed for physico-chemical parameters. Results showed that the majority of the physico-chemical parameters were found to be within the drinking water guidelines set by the World Health Organization. However, major cationic metals such as magnesium (Mg), and trace metals (TM) including iron (Fe), manganese (Mn), nickel (Ni), chromium (Cr) and cobalt (Co) showed exceeded concentrations in 13%, 4%, 2%, 20%, 20% and 55% of water samples, respectively. Health risk assessment revealed that the non-carcinogenic effects or hazard quotient values through the oral ingestion pathway of water consumption for the TM (viz., Fe, Cr and Mn) were found to be greater than 1, could result in chronic risk to the exposed population. Results of statistical analyses revealed that mafic and ultramafic rocks are the main sources of metal contamination in drinking water, especially Ni and Cr. Both Ni and Cr have toxic health effects and therefore this study suggests that contaminated sites should be avoided or treated for drinking and domestic purposes.

Key words | average daily intake, chronic risk, groundwater, statistical analyses, surface water, Swat district

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INTRODUCTION

Water is vital to human life and therefore, an adequate supply of clean and safe water is a determining factor for the health status of exposed population (Shah *et al.* 2012; Khan *et al.* 2013a, c, 2015; Chappells *et al.* 2014; Lotter *et al.* 2014; Singh *et al.* 2014). Unfortunately, the water can become contaminated with metals from natural (weathering of rocks and ore deposits) and anthropogenic (mining, agriculture, industry and domestic wastewater) sources (Khan *et al.* 2011, 2013a, c, 2014). Some metals are essential for normal human body function, including calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), cobalt (Co), copper (Cu) and zinc (Zn). However, high intake of these metals may produce toxicity. Whereas other trace metals

(TM), e.g., lead (Pb), chromium (Cr), nickel (Ni), arsenic (As) and cadmium (Cd), are extremely toxic even in very low concentrations to human health and the environment (Khan *et al.* 2013b, 2014, 2015; Hussain *et al.* 2014; Shah *et al.* 2014; Gul *et al.* 2015). Metal contaminated drinking water and food is the most direct route for human exposure (Shah *et al.* 2012; Khan *et al.* 2013b, 2014) and intake of such contaminated water may produce chronic and carcinogenic effects in the exposed human population (Muhammad *et al.* 2010, 2011; Khan *et al.* 2013c).

Contamination not only spoils water quality, but also threaten ecosystems, human health, social prosperity and economic development (Arsovski *et al.* 1991). Users are

dependent on the quality of water; if the quality is poor, the exposed population must pay an additional cost for treatment or incur the property damage or health risk (Koc 2010). Therefore, water quality monitoring and assessment has one of the highest priorities in environmental protection policy (Simeonov *et al.* 2002; Khan *et al.* 2015). Regular water quality monitoring provides helpful information about the status of drinking water (Rode & Suhr 2007; Muhammad *et al.* 2011; Shah *et al.* 2012).

Statistical analyses have proven useful for comparing and interpreting environmental data such as water quality. These analyses allow the identification of the possible contamination sources that influence the water system. These analyses also provide a valuable tool for reliable management of water resources and rapid solution to contamination problems (Krishna *et al.* 2009; Khan *et al.* 2013a; Kelepertzis 2014). The study area is dominantly composed of mafic and ultramafic rocks and could be the potential source of TM contamination into the water and environment (Shah *et al.* 2010; Muhammad *et al.* 2011; Khan *et al.* 2013a). Therefore, this study has been carried

out to assess the drinking water and evaluate the potential human health risk assessment. Further, using statistical analyses the study will identify the contamination sources of drinking water in the Swat district.

MATERIAL AND METHODS

Study area

This study was conducted in the Swat district, at the entry point to a major tourist area in the northern areas of Pakistan, between latitude $34^{\circ}45' - 35^{\circ}55'$ North and longitude $72^{\circ}08' - 72^{\circ}50'$ East and altitude range from 500 to 6,500 m above sea level (Figure 1) (Qasim *et al.* 2011). Mingora and Kabal areas of the district were selected for water quality assessment as the mafic and ultramafic rocks of the mélangé zone are mainly exposed in the area (Afridi *et al.* 1995; Shah *et al.* 2010). The mélangé zone rocks are chaotic assemblages of serpentinite, green schist, talc-carbonate schist and metabasalts (Kazmi *et al.* 1984; Jan & Jabeen 1990; Arif & Jan

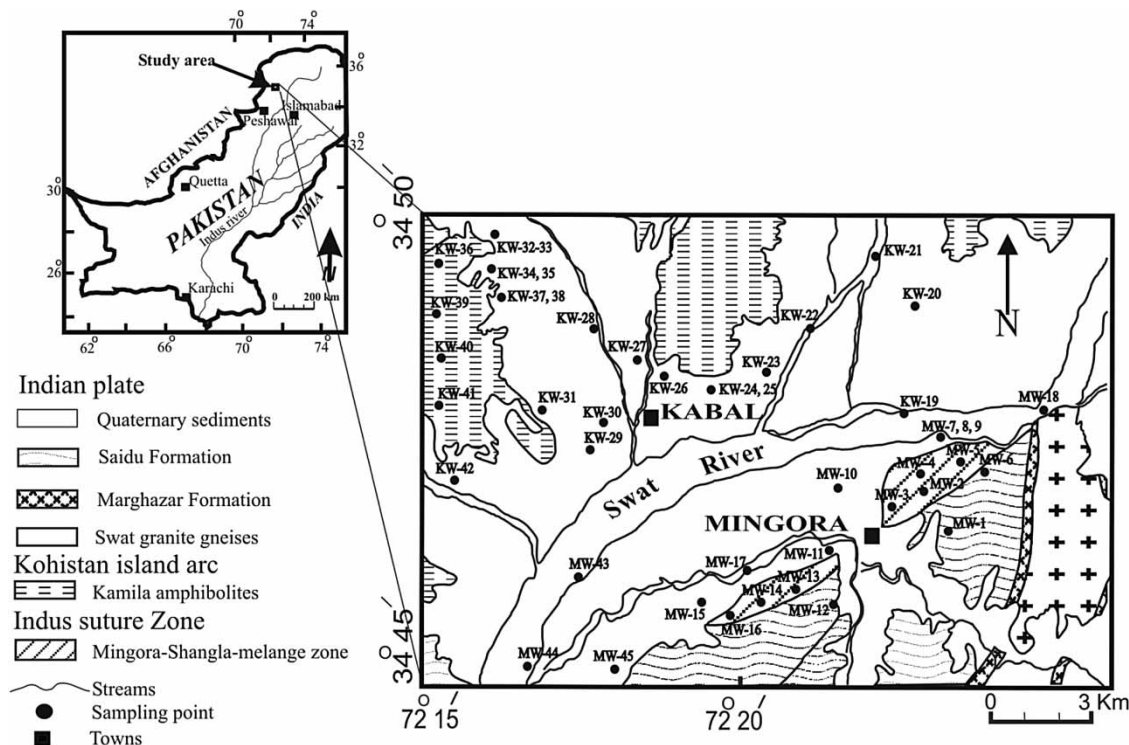


Figure 1 | Geological and sample location map for Mingora and Kabal areas (modified after Afridi *et al.* (1995)).

1993). These mafic and ultramafic rocks contain mainly mafic minerals such as olivine, pyroxene, serpentine and amphibole, etc., which are rich in magnesium, calcium, iron, chromium and nickel. Mingora and Kabal are densely populated areas, where the inhabitants and tourists obtain water for drinking, domestic use and agricultural purposes from groundwater and surface water sources. Swat River is the main source of irrigation flowing through the area. Agriculture is the largest sector of the economy and livelihood of the rural population. This zone hosts the emerald mines in Mingora, Swat. Tourism, business and government employment are also sources of income. Food is mostly produced and consumed locally and often subject to irrigation. Climatically, the area falls within the subtropical and moist temperate zone, with heavy rain and snowfall, severe winters (-10°C) and pleasant summers. Summer season is short and moderate. It is warm (35°C) in the lower Swat valley, including Kabal and Mingora, but cool in the upper northern part such as Bahrain and Kalam (DCR 1998; Khan *et al.* 2013a).

Water sampling and chemical analyses

Groundwater (dug wells $n=42$, tube-wells $n=21$ and springs $n=21$) and surface water (streams $n=15$ and Swat River $n=18$) samples were randomly collected in autumn season from selected sites of the Mingora and Kabal areas in the Swat district. From each site, clean polyethylene bottles (1 L) were filled in triplicates (Figure 1). Samples were properly marked and transported to the laboratory and stored in refrigerator at 4°C for major cationic metals (MCC) and TM analyses.

Basic parameters including pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured on the spot using a Consort C931 electrochemical analyzer. Water was filtered through Whatman ($0.45\ \mu\text{m}$) filter paper and acidified with nitric acid (HNO_3) from each sampling site. This acidification with HNO_3 preserves the TM in water samples due to a reduction in microbial activity, precipitation and sorption losses to container walls (APHA 2005). All filtered and acidified water samples were analyzed for MCC (Na, K, Ca and Mg) and TM (Fe, Cu, Pb, Zn, Ni, Cr, Co and Mn) under standard optimum conditions on a Perkin Elmer 700 atomic absorption spectrophotometer

equipped with a heated graphite atomizer. All samples were analyzed in triplicates and the reproducibility was accepted at a 95% confidence level. However, the average value was used for data interpretation. Chemicals and reagents used were of analytical grade (MERCK). These analyses were performed in the Geochemistry Laboratory of National Centre of Excellence in Geology, University of Peshawar, Pakistan.

Risk assessment

Exposure assessment

In the study area, average daily intake (ADI) of metal through consumption of drinking water for exposure assessment was calculated according to the equation adopted from USEPA (1998) and Shah *et al.* (2012):

$$\text{ADI} = \frac{\text{CW} \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (1)$$

where CW is concentration of metal in water (mg/L), IR is ingestion rate of water (2 L/day), ED is exposure duration (30 years), EF is exposure frequency (365 days/year), BW is body weight (70 kg) and AT is averaging time, i.e., 365 days/year \times ED for non-carcinogens and 365 days/year \times 70 years for carcinogens (Shah *et al.* 2012; Khan *et al.* 2013a).

Chronic risk assessment

Chronic non-carcinogenic risk level or hazard quotient (HQ) was calculated using the following equation adopted from USEPA (1998) and Muhammad *et al.* (2011):

$$\text{HQ} = \frac{\text{ADI}}{\text{RfD}} \quad (2)$$

where the oral toxicity reference dose (RfD) values for Cd, Cr, Cu, Mn, Ni, Pb and Zn are $5 \times 10^{-1}\ \mu\text{g}/(\text{kg}\cdot\text{day})$, $1.5 \times 10^3\ \mu\text{g}/(\text{kg}\cdot\text{day})$, $3.7 \times 10^1\ \mu\text{g}/(\text{kg}\cdot\text{day})$, $1.4 \times 10^2\ \mu\text{g}/(\text{kg}\cdot\text{day})$, $2 \times 10^1\ \mu\text{g}/(\text{kg}\cdot\text{day})$, $3.6 \times 10^1\ \mu\text{g}/(\text{kg}\cdot\text{day})$ and $3 \times 10^2\ \mu\text{g}/(\text{kg}\cdot\text{day})$, respectively (USEPA 2005; Muhammad *et al.* 2010; Shah *et al.* 2012). An HQ value less than one is considered to be safe for consumers (Muhammad *et al.* 2011).

Statistical analyses

Statistical manipulations including range, mean and standard deviation were calculated using Excel 2007 (Microsoft Office). Univariate and multivariate statistical analyses (one-way analysis of variance (ANOVA) procedure, correlation analysis and principal component analysis (PCA)) were performed using the SPSS 21 (SPSS Inc., Chicago, IL, USA).

RESULTS AND DISCUSSION

Physico-chemical parameters

Water pH naturally depends on CO₂, carbonate and bicarbonate equilibrium (APHA 1998). The usual range of pH in drinking water has no direct effects on human health but may exert indirect effects by changing the solubility of metals and pathogen survival. A bitter taste of drinking water may be associated with high pH (Muhammad *et al.* 2010). In the study area, pH values were circum-neutral ranging from 6.95 to 7.10 and 6.92 to 7.20 in groundwater and surface water, respectively (Table 1). All sources of water have nearly equal mean pH values. Drinking water pH in the study area was found to be lower than those reported by Khan *et al.* (2013a) for water in the upper Swat. EC reflects the amount of TDS in water and depends on the geology of the area, size and type of watershed and other sources of ions including contaminants (APHA 1998). EC values ranged from 189 to 1,515 $\mu\text{S}/\text{cm}$ in groundwater and from 71 to 465 $\mu\text{S}/\text{cm}$ in surface water (Table 1). The TDS values depend on the concentrations of carbonates, bicarbonates, chloride, sulfate, nitrate, Na, K, Ca and Mg (Muhammad *et al.* 2010). In the study area, TDS values were in the ranges 78–808 mg/L and 37–248 mg/L for groundwater and surface water, respectively (Table 1). Groundwater revealed higher TDS values as compared with surface water. These higher values in groundwater may be attributed to residence time and underground geology of the area (Shah *et al.* 2012). The TDS mean values in groundwater of the study area were found to be lower than those reported by Shah *et al.* (2012) in groundwater or subsurface water. Water pH, EC and TDS values were within the permissible limit of the

World Health Organization (WHO 2011), except for 7% of samples collected from dug wells in the Mingora area which showed higher EC values.

Calcium is needed for normal body functions including blood clotting, transmission of nerve impulses and regulation of heart rhythm (Muhammad *et al.* 2010). Magnesium and Ca deficiency in drinking water may be associated with cardiovascular diseases (Yang *et al.* 2006). The concentrations of Ca were in the ranges 1–126 mg/L and 2–58 mg/L in groundwater and surface water, respectively (Table 1). Higher concentrations of Ca are generally released to water from deposits of limestone, dolomite, gypsum and gypsiferous shale (APHA 1998).

Similarly, Mg concentrations were in the ranges 1–99 mg/L and 5–13 mg/L in groundwater and surface water, respectively (Table 1). In the study, groundwater showed multifold higher Mg concentrations as compared with surface water. These multifold higher concentrations may be attributed to the dissolution of Mg rich mafic and ultramafic bed rocks (Shah *et al.* 2010, 2012). The concentrations of Ca and Mg were within the permissible limits set by WHO (2011), except for 13% of instances where Mg concentrations (50 mg/L) exceeded these limits. These higher concentrations of Mg can be attributed to the percolation of water through Mg rich ultramafic rocks of the *mélange* zone.

The concentrations of Na were in the ranges 3–223 mg/L and 2–13 mg/L in groundwater and surface water, respectively (Table 1). This could be a localized phenomenon with input from the granitic rock which has higher amounts of sodium feldspar. However, most of the water samples from the area have quite low concentrations of Na, but not low enough to cause health problems, such as mental apathy, low blood pressure, fatigue, depression, and dehydration (Robert & Mari 2003). Latorre & Toro (1997) reported that on average, the adult daily intake is <0.1% of K through water ingestion. Like other MCC, K is also necessary for normal body functions. Similarly, K concentrations were in the ranges 1–28 mg/L and 1–26 mg/L in groundwater and surface water, respectively (Table 1). This could be attributed to the presence of schistose rocks containing greater amounts of minerals like muscovite and potash-feldspar. However, most of the water samples contained quite low concentrations (<4 mg/L) of K, but not low enough to cause heart problems, hypertension, muscle weakness,

Table 1 | Concentration of physico-chemical parameters of water samples of the study area

Parameters	Groundwater						Surface water				WHO	p-value
	Dug well (n = 42)		Tube well (n = 21)		Spring water (n = 21)		Swat River (n = 15)		Stream water (n = 18)			
	Range	Stand dev	Range	Stand dev	Range	Stand dev	Range	Stand dev	Range	Stand dev		
pH	6.95–7.02	(6.98) ± 0.06	6.99–7.10	(7.04) ± 0.04	6.97–7.02	(7.00) ± 0.02	6.95–7.02	(6.98) ± 0.03	6.92–7.20	(7.04) ± 11	6.5–8.5	0.794
EC µS/cm	189–1,515	(747) ± 434	218–1,160	(451) ± 327	390–798	(562) ± 133	71–102	(79) ± 6	256–465	(332) ± 79	1,400	0.001
TDS mg/L	78–808	(395) ± 235	116–618	(241) ± 174	208–425	(300) ± 71	37–54	(42) ± 8	162–248	(187) ± 36	1,000	0.001
Ca mg/L	19–126	(46) ± 29	17–48	(31) ± 11	1–56	(31) ± 23	2–13	(7) ± 5	31–58	(38) ± 11	100	0.078
Mg mg/L	5–59	(23) ± 17	1–34	(15) ± 11	9–99	(39) ± 35	8–12	(10) ± 23	5–13	(8) ± 4	50	0.005
Na mg/L	3–223	(32) ± 58	3–7	(6) ± 1	3–11	(7) ± 3	2–3	(4) ± 2	6–13	(9) ± 3	200	0.192
K mg/L	1–28	(6) ± 8	1–2	(1) ± 1	1–3	(2) ± 1	1–2	(1) ± 1	1–26	(7) ± 11	12	0.990
Fe µg/L	57–800	(165) ± 151	29–175	(99) ± 44	68–188	(126) ± 41	73–97	(87) ± 11	87–479	(193) ± 165	300	0.512
Cu µg/L	17–79	(34) ± 11	29–129	(62) ± 34	24–35	(30) ± 5	33–42	(37) ± 4	26–113	(50) ± 36	3,000	0.067
Pb µg/L	2–9	(5) ± 2	4–9	(6) ± 2	2–8	(5) ± 2	4–8	(6) ± 2	3–6	(4) ± 1	10	0.610
Zn µg/L	47–447	(112) ± 91	56–1,913	(485) ± 681	52–72	(57) ± 7	58–73	(65) ± 6	57–890	(227) ± 371	5,000	0.806
Ni µg/L	6–199	(38) ± 61	8–15	(11) ± 2	12–124	(57) ± 53	8–18	(15) ± 5	16–19	(18) ± 1	20	0.029
Cr µg/L	14–340	(72) ± 110	17–31	(26) ± 6	20–396	(170) ± 178	32–45	(38) ± 6	31–45	(38) ± 5	50	0.007
Co µg/L	30–74	(43) ± 11	34–61	(46) ± 9	34–54	(44) ± 7	35–45	(41) ± 5	32–48	(41) ± 7	40	0.246
Mn µg/L	20–2,198	(139) ± 472	25–82	(43) ± 19	30–100	(42) ± 26	63–80	(70) ± 7	31–87	(46) ± 23	400	0.020

Bold p-values significant at a level of 0.05.
Values in parentheses indicate mean values.

bladder weakness, kidney diseases and asthma (Marijic & Toro 2000; Aparna 2001a). The concentrations Na and K were within the permissible limits set by WHO (2011) except for 2% of the samples that showed higher (12 mg/L) K concentrations.

TMs are pollutants that may be harmful to human health owing to their toxicity, persistence and bioaccumulative nature in the environment (Khan *et al.* 2013b, 2014). Iron is one of the essential elements for human body and needed in hemoglobin, myoglobin and a number of enzymes. However, in excess Fe is also toxic and can cause human health issues including diarrhea, vomiting, liver, kidney and blood problems, with subsequent effects on the cardiovascular and central nervous systems (Goldhaber 2003). Among TM, Fe concentrations were in the ranges 29–800 µg/L and 73–479 µg/L in groundwater and surface water, respectively (Table 1).

High intake of Mn can cause toxicity in the nervous system, muscle tremors, dizziness, liver disease, cancer, oedema, fibroid tumors and colitis, while its deficiency may cause hypoglycemia, joint discolorations, asthma, migraine, osteoporosis and gastrointestinal disorder (Mergler 1999a, b). Mn concentrations were in the ranges 20–2,198 µg/L and 31–87 µg/L in groundwater and surface water, respectively (Table 1). The abnormally high Mn concentration (2,198 µg/L) in one sample of a dug well could be due to contamination from a huge solid waste dump site in the vicinity. In the study area, Mn concentrations were found to be higher than those reported by Muhammad *et al.* (2011). Therefore, the solid waste should be removed and the dug well water regularly monitored.

Excessive intake of Cu in drinking water can lead to several health problems, while its normal concentration is necessary for health including the immune system and artery strength (Kidd 2003). In this study, Cu concentrations were in the ranges 17–129 µg/L and 26–113 µg/L in groundwater and surface water, respectively (Table 1).

Pb concentrations were in the ranges 2–9 µg/L and 3–8 µg/L in groundwater and surface water, respectively (Table 1), and Zn concentrations were in the ranges 47–1,913 µg/L and 57–890 µg/L in groundwater and surface water, respectively (Table 1). Concentrations of Fe, Mn, Cu, Pb and Zn were within the permissible limits set by the WHO (2011). However, 4% and 2% of the water samples

showed higher concentration than their limits for Fe (300 µg/L) and Mn (400 µg/L), respectively.

Generally, Ni works as a factor in hormone, lipid and cell membrane metabolism, but in excess, Ni may cause itching, burning and redness of skin, and asthma in human beings (Knight *et al.* 1997). Ni concentrations were in the ranges 6–199 µg/L and 8–19 µg/L in groundwater and surface water, respectively (Table 1). Figure 2 shows that high concentrations of Ni were associated with very low Ca/Mg ratios, confirming the geogenic (mafic and ultramafic rocks) origins. For normal body functions, a specific amount of Cr is needed. However, its high concentrations may cause kidney and liver problems and it is a genotoxic carcinogen (Muhammad *et al.* 2011; Shah *et al.* 2012). The concentrations of Cr were in the ranges 14–396 µg/L and 31–45 µg/L in groundwater and surface water, respectively (Table 1). Like Cr, Co is also needed for normal body functions. However, its high concentrations may cause over-production of red blood cells (RBCs), polycythemia, abnormal thyroid artery and right coronary artery problems (Robert & Mari 2003). Cobalt concentrations ranged from 30 to 74 µg/L and 32 to 48 µg/L in groundwater and surface water, respectively (Table 1). Mean Ni, Cr and Co concentrations were lower than those reported by Shah *et al.* (2012) in drinking water from the Mohmand Agency (Pakistan). The concentrations of Ni, Cr and Co were generally within the permissible limits set by WHO (2011). However 20%, 20% and 55% of water samples showed higher concentration than the permissible limits for Ni (20 mg/L), Cr (50 mg/L) and Co (40 µg/L), respectively.

Results of the study revealed that groundwater samples collected from sampling sites (MW3, MW6, MW13, MW14, MW2, MW4 and MW5) in the Mingora-Shangla mélange zone horizon (Figure 1) are enriched in Mg, Cr and Ni, while all the other TM are within safe limits (WHO 2011). This enrichment of Mg, Cr and Ni can be attributed to the percolation of water and scavenging of Mg, Cr and Ni from ultramafic rocks enriched in Mg, Cr and Ni (Arif & Jan 1995; Shah *et al.* 2012).

Risk assessment

Information about sex, age, literacy rate, livelihood, health and drinking water of local people was collected in the

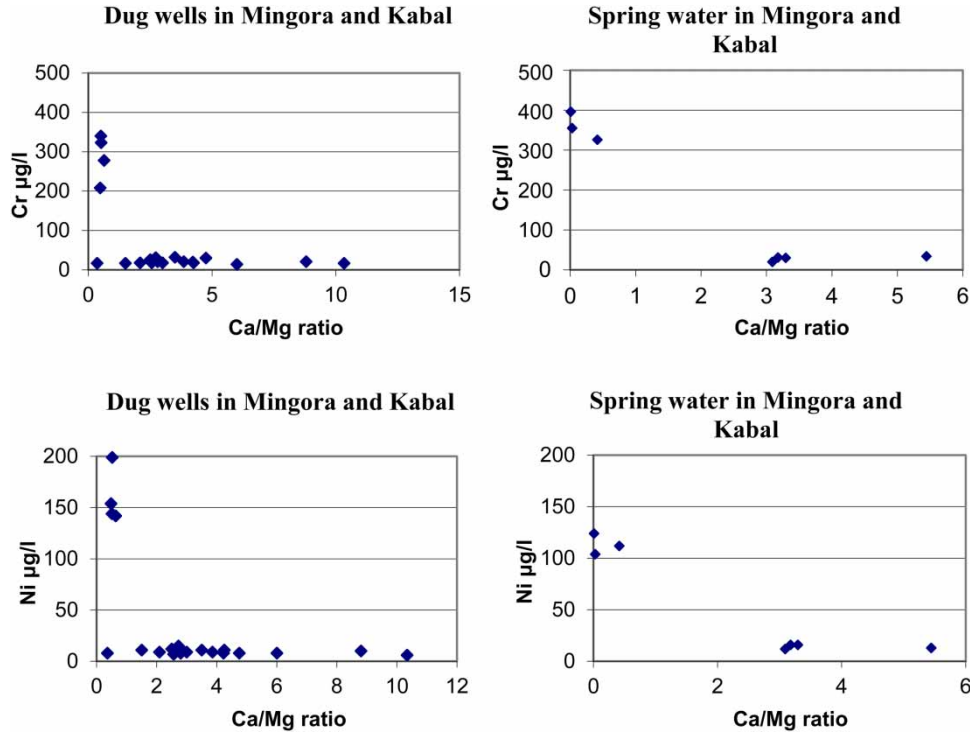


Figure 2 | Relationships between concentrations of Cr (upper plots) or Ni (lower plots) and Ca/Mg ratios in water samples for dug wells (left) and spring water (right) in the Mingora and Kabal area.

field. The study population is dependent on groundwater (bore well, dug well, hand pump and tube well) and surface water (stream) sources for drinking purpose. Therefore, samples from these sources were collected and evaluated for exposure assessment (viz., ADI) and chronic risk assessment (viz., HQ).

Exposure assessment

Average daily intake (ADI) values of the study area revealed the highest ($6.28 \times 10^1 \mu\text{g}/\text{kg}\text{-day}$) for Mn, with the lowest ($1.70 \times 10^{-1} \mu\text{g}/\text{kg}\text{-day}$) for Ni in groundwater (Table 2). Other TM ADI values were found in between the two

Table 2 | Risk assessment through drinking water consumption in the study area^a

Metals	Groundwater		Surface water	
	ADI ($\mu\text{g}/\text{kg}\text{-day}$)	HQ	ADI ($\mu\text{g}/\text{kg}\text{-day}$)	HQ
Fe	8.29×10^{-1} – 2.29×10^1	0.09–1.54	2.09×10^0 – 1.37×10^1	0.23–1.12
Cu	4.86×10^{-1} – 3.69×10^0	0.01–0.06	7.43×10^{-1} – 3.23×10^0	0.02–0.08
Pb	6×10^{-2} – 2.6×10^{-1}	0.15–0.65	9×10^{-2} – 2.3×10^{-1}	0.23–0.58
Zn	1.34×10^0 – 5.47×10^1	< 0.01–0.18	1.63×10^0 – 2.54×10^1	0.01–0.08
Ni	1.7×10^{-1} – 5.69×10^0	0.02–0.28	2.3×10^{-1} – 5.4×10^{-1}	0.01–0.03
Cr	4×10^{-1} – 1.13×10^1	0.10–1.94	8.86×10^{-1} – 1.29×10^0	0.18–0.26
Mn	5.71×10^{-1} – 6.28×10^1	0.02–1.37	8.86×10^{-1} – 2.49×10^0	0.02–0.05

^aRisk assessment was calculated only for those metals which have RfD values.

extremes. The highest ADI values of Mn in groundwater were attributed to solid waste dump alongside Mingora city. The ADI values of the study area were noted to be higher than those reported by Khan *et al.* (2013a) for drinking water in upper Swat. These higher ADI values for Mn, Fe, Cr in drinking water may be attributed due to mafic, ultramafic bed rocks and the solid waste dump in the vicinity.

Chronic risk assessment

The DIM values were further evaluated for the chronic risk assessment or HQ. The HQ value was found highest (1.94) for Cr, whereas lowest (<0.01) for Zn (Table 2). The chronic risk of TM depends on type, variety, toxicity, consumption rate and concentration (Kapaj *et al.* 2006). These higher HQ values in drinking water may be due to their higher concentration. These HQ values were noted to be higher than those reported by Muhammad *et al.* (2011) for drinking water of the mafic and ultramafic rocks in the Kohistan region, Pakistan but lower than drinking water of Thiva area, Greece (Kelepertzis 2014). Therefore, the exposed population may be at chronic risk of Cr and Ni contamination.

Statistical analyses

Statistical comparison using one-way ANOVA for different water sources revealed significant variations at the level of $p < 0.05$, which means that these sources contribute differently to the mean water contamination of Mg, Ni, Cr and Mn (Table 1). The Mingora-Shangla mélange zone horizon may be contributing to high contamination levels in the groundwater sources of the study area. The Pearson correlation matrices between the selected physico-chemical parameters in groundwater and surface water are shown in Tables 3 and 4, respectively. Many physico-chemical parameters showed strong significant correlations in groundwater and surface water. High correlation at a significant level were found between the metal pairs including Mg-Ni ($r=0.734$) and Mg-Cr ($r=0.840$) showing a common source of these metals. Mn showed high correlation with Na ($r=0.757$) and Co (0.526) suggesting their geochemical association. In

surface water, the metal pairs such as Na-Ca ($r=0.880$), K-Ca ($r=0.684$) showed higher correlation (Table 4).

The PCA results for metals concentration in groundwater are shown in Table 5. The PCA method resulted in a reduction of initial dimension of dataset to five components having eigenvalues higher than 1.00 (before and after rotation), and explained 73.56% of the data variation in groundwater. The PC1, PC2, PC3, PC4 and PC5 components accounted for the 21.07, 19.43, 12.06, 10.54 and 10.45% of the total variance. TMs including Ni and Cr were found to be strongly associated with Mg in the first component (PC1) suggesting the influence of the olivine and pyroxene minerals of ultramafic rock on groundwater. High association was observed by EC with TDS and K due to inorganic dissolved solids and ionic species (Jonnalagadda & Mhere 2001). PC3 includes Mn, Co, Na, and Pb with high loadings and demonstrates the contribution of carbonate bed rock minerals such as talc carbonate schist. The natural or background contribution of metals to groundwater is also represented by PC4 and PC5. The five components of PCA in surface water explained 88.48% of the data variation (Table 6). The PC1, PC2, PC3, PC4 and PC5 components accounted for the 36.75, 16.08, 14.03, 10.89 and 10.74% of the total variance in surface water. MCC including Na, Fe and Ca were found to be associated with TDS and EC in the first component (PC1) suggesting the strong influence of carbonate bedrocks such as talc carbonate schist in surface water. Iron was found to be associated with Co (PC2); Cr with Ni (PC4), and Cu, and Mg with the K (PC3) suggesting the mafic and ultramafic bed rocks contributed to the surface water contamination. This study is in good agreement with previous studies reported by Krishna *et al.* (2009), Muhammad *et al.* (2010, 2011) and (Kelepertzis 2014).

CONCLUSIONS

Results of the study showed that physico-chemical parameters were found to be within the drinking water permissible limit set by the WHO, except for Mn, Fe, Ni, Cr and Co in a small number of samples. The ADI and HQ through drinking water consumption were found in

Table 3 | Pearson correlation of physico-chemical parameters in groundwater ($n = 82$)

Parameters	pH	EC	TDS	Na	K	Ca	Mg	Fe	Mn	Pb	Zn	Ni	Cr	Co	Cu
pH	1	0.030	0.061	-0.150	0.014	-0.200	-0.010	-0.080	-0.130	0.262	0.142	0.057	0.056	0.044	0.099
EC		1	0.999	0.208	0.610	<i>0.534</i>	0.383	-0.070	0.208	-0.010	-0.220	0.484	0.367	0.230	-0.260
TDS			1	0.209	0.610	0.329	0.380	-0.080	0.208	-0.000	-0.220	0.483	0.367	0.239	-0.250
Na				1	0.219	0.056	-0.060	0.021	0.757	0.290	-0.110	-0.180	-0.174	0.207	-0.090
K					1	0.033	0.168	-0.030	0.077	-0.200	-0.140	0.467	0.272	-0.060	-0.160
Ca						1	-0.373	0.013	0.109	-0.160	-0.120	-0.402	-0.445	0.096	-0.060
Mg							1	-0.110	-0.080	0.255	-0.240	0.734	0.840	0.195	-0.240
Fe								1	-0.020	-0.040	0.175	-0.100	-0.116	0.084	-0.150
Mn									1	0.342	-0.050	-0.080	-0.063	0.526	-0.020
Pb										1	-0.010	0.121	0.214	0.336	-0.020
Zn											1	-0.130	-0.124	0.132	0.324
Ni												1	0.930	0.110	-0.180
Cr													1	0.162	-0.180
Co														1	-0.120
Cu															1

Italic correlation is significant at the 0.05 level (2-tailed).

Bold correlation is significant at the 0.01 level (2-tailed).

Table 4 | Pearson correlation of physico-chemical parameters in surface water ($n = 33$)

Parameters	pH	EC	TDS	Na	K	Ca	Mg	Fe	Mn	Pb	Zn	Ni	Cr	Co	Cu
pH	1	0.310	0.249	0.444	0.728	0.656	0.090	0.358	-0.060	-0.640	-0.180	0.057	0.354	0.405	-0.260
EC		1	0.975	0.929	0.250	0.835	-0.140	0.415	-0.590	-0.540	0.096	0.504	-0.040	0.181	0.076
TDS			1	0.945	0.220	0.824	-0.200	0.354	-0.620	-0.480	0.313	0.495	-0.040	0.127	0.017
Na				1	0.420	0.880	-0.000	0.237	-0.659	-0.480	0.262	0.415	0.032	0.207	-0.180
K					1	0.684	0.353	-0.160	-0.560	-0.280	-0.100	0.016	-0.040	-0.180	0.108
Ca						1	-0.130	0.279	-0.630	-0.610	0.124	0.382	0.064	0.011	0.054
Mg							1	-0.380	-0.320	0.331	-0.280	-0.030	-0.200	0.113	-0.030
Fe								1	0.375	-0.420	-0.170	0.284	0.464	0.525	0.056
Mn									1	0.062	-0.230	-0.400	0.387	0.426	-0.290
Pb										1	0.144	-0.110	0.072	-0.430	0.036
Zn											1	0.057	0.038	-0.190	-0.250
Ni												1	0.427	-0.180	0.159
Cr													1	0.200	-0.460
Co														1	-0.490
Cu															1

Italic correlation is significant at the 0.05 level (2-tailed).

Bold correlation is significant at the 0.01 level (2-tailed).

Table 5 | Factor loading for selected physico-chemical parameters in groundwater ($n = 82$)

Parameters	PC1	PC2	PC3	PC4	PC5
pH	0.08	0.11	0.05	0.64	0.12
EC	0.17	0.92	0.09	-0.11	-0.09
TDS	0.16	0.93	0.11	-0.02	-0.06
Na	-0.44	0.05	0.52	-0.30	-0.34
K	0.07	0.78	0.03	0.09	-0.08
Ca	-0.80	0.19	-0.11	-0.11	0.01
Mg	0.74	0.25	0.12	-0.17	-0.35
Fe	-0.11	0.04	-0.06	-0.75	0.29
Mn	-0.09	0.21	0.85	0.04	-0.02
Pb	0.35	-0.16	0.65	0.29	0.02
Zn	-0.13	-0.23	-0.04	0.04	0.88
Ni	0.85	0.38	-0.09	0.04	0.00
Cr	0.87	0.37	0.00	0.05	0.05
Co	0.18	0.22	0.56	-0.06	0.54
Cu	-0.22	-0.18	-0.02	0.60	0.37
Eigen values	3.16	2.91	1.81	1.58	1.57
% of Variance	21.07	19.43	12.05	10.54	10.45
Cumulative %	21.07	40.50	52.55	63.09	73.54

Extraction method: principal component analysis.
 Rotation method: Varimax with Kaiser Normalization.
 Values of dominant parameters in each factor is reported in bold.

the order of Mn > Zn > Fe > Cr > Ni > Cu > Pb and Cr > Fe > Mn > Pb > Ni > Cu > Zn, respectively. Statistical analyses revealed that different water sources contribute significantly ($p < 0.05$) to the mean contamination. In the Mingora site, dug wells water showed higher level of TM (Ni and Cr). Statistical analyses showed that the main contamination sources are geogenic. Enrichment of these potentially hazardous metals in the water can be attributed to the ultramafic rocks of the mélange zone in the area. High intake of these metals through drinking water could have chronic effects on human health which need to be explored by carrying out epidemiological research in the target area. These remote areas in northern parts of Pakistan need special attention as far as metal contaminations through geogenic sources are concerned. Further studies need to consider the spatial and temporal variations in potentially toxic metal contaminants in greater detail as a matter of urgency.

Table 6 | Factor loading for selected physico-chemical parameters in surface water ($n = 33$)

Parameters	PC1	PC2	PC3	PC4	PC5
pH	0.33	0.76	0.35	0.20	0.06
EC	0.97	0.11	-0.09	0.08	0.07
TDS	0.98	0.06	-0.10	0.07	-0.04
Na	0.96	0.17	0.05	0.10	-0.14
K	0.49	0.02	0.79	0.01	0.05
Ca	0.97	0.12	0.03	0.14	0.05
Mg	-0.28	0.02	0.87	-0.02	0.03
Fe	0.38	0.39	-0.45	0.38	0.35
Mn	-0.76	0.27	-0.53	0.17	-0.01
Pb	-0.48	-0.67	0.18	0.11	-0.22
Zn	0.28	-0.29	-0.16	-0.05	-0.80
Ni	0.49	-0.26	0.03	0.70	0.17
Cr	-0.06	0.24	-0.07	0.91	-0.23
Co	-0.12	0.86	-0.11	0.04	-0.14
Cu	0.18	-0.38	-0.10	-0.21	0.81
Eigen values	5.51	2.41	2.10	1.63	1.61
% of Variance	38.42	17.49	13.09	11.03	8.44
Cumulative %	36.75	52.82	66.85	77.74	88.48

Extraction method: principal component analysis.
 Rotation method: Varimax with Kaiser Normalization.
 Values of dominant parameters in each factor is reported in bold.

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