



Health risk assessment via surface water and sub-surface water consumption in the mafic and ultramafic terrain, Mohmand agency, northern Pakistan

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ABSTRACT

This study investigates drinking water (surface water and sub-surface water) quality and potential health risk assessment in the mafic and ultramafic terrain of Bucha area, Mohmand agency, northern Pakistan. Heavy metal (HM) concentrations were analyzed using graphite furnace atomic absorption spectrometer. Statistical analyses like one-way ANOVA, correlation analysis, cluster analysis (CA) and principal component analysis (PCA) were used for contamination sources. Furthermore, HM health risk assessment showed that average daily dose (ADD) and hazard quotient (HQ) were found in the order of Cr>Fe>Ni>Cu>Mn>Zn>Co>Pb>Cd and Ni>Cd>Cu>Mn>Pb>Zn>Cr, respectively. Water contamination was the main source of diseases like diarrhea, viral hepatitis, headache, hypertension, abdominal pain, liver and kidney problems and fatal cardiac arrest as complained by most of the respondents during field visit and reported in basic health unit (BHU). In order to reduce the health risk, it is necessary that government immediately stop the contaminated sites for drinking water and should supply clean potable water to the inhabitants.

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1. Introduction

Water is a vital substance in all parts of the environment (Bell, 1998). Physical, chemical and biological characteristics of water are considered as a major health controlling factor and the state of disease in the living organisms (Kazi et al., 2009). Water contamination with light metal (LM) and heavy metal (HM) are mainly determined by natural (i.e., weathering, erosion of bed rocks and ore deposits) and anthropogenic (i.e., mining, smelting, industries, agriculture and waste water irrigation) processes (Ahmet et al., 2006; Ettler et al., 2011; García-Lorenzo et al., 2011; Khan et al., 2008; Muhammad et al., 2010, 2011a; Sracek et al., 2011). These processes degrade water quality and impair their use for drinking, domestic, agricultural and industrial purposes (Krishna et al., 2009). Chemistry of surface water and sub-surface water is influenced by the local geology of an area. Reactions between rain water and bed rock are responsible for the mineral contents of sub-surface water. The extent to which reaction with the host rock proceeds is governed by water residence time, which in turn, may be influenced by type of flow moment, that is inter

granular or fissure flow, and the mineralogy of the aquifer. Carbon dioxide (CO₂) concentrations in the soil influence the degree of reaction of carbonate or silicate minerals in rock mass (Bell, 1998). By contrast, deeper groundwater can undergo notable changes in mineral composition with increasing residence time (Edmunds et al., 1987).

Certain LM and HM like sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), Manganese (Mn), copper (Cu), cobalt (Co), and zinc (Zn) are essentially required for living organism in specific concentration but may produce toxic effects in high concentrations. However, HM like lead (Pb), mercury (Hg), cadmium (Cd) nickel (Ni) and chromium (Cr) are extremely toxic owing to their toxicity, persistent and bio-accumulative nature. Their toxic effects include headache, hypertension, irritability, abdominal pain, nerve damages, liver and kidney problems, sideroblastic anemia, intellectual disabilities, fatal cardiac arrest and carcinogenesis (Jarup, 2003; Muhammad et al., 2011a,b; Pekey et al., 2004).

Mafic and ultramafic rocks are responsible for HM enrichment, like Cr and Ni, in different components of ecosystem and hence resulted in the environmental degradation (Desideri et al., 2010; Dhakate et al., 2008; Muhammad et al., 2010, 2011a; Yang et al., 2011). Further, HM may contaminate drinking and irrigation water (Krishna et al., 2009). Previously, HM health risk assessment and using statistical analyses have been reported in different parts of the world (Ako et al., 2011; Jang, 2010; Muhammad et al., 2010, 2011b). These HM contaminate drinking water and food stuff, which may have potential human health risk (Avino et al., 2011;

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Lim et al., 2008; Muhammad et al., 2010). Geological work, especially in regard to the petrochemical aspects of the mafic and ultramafic rocks and associated chromites deposits in Mohmand agency has been carried out by Badshah (1979) and Jehan (1996). However, drinking water degradation of the area has not been carried out so far. In this regard this study aimed to evaluate the effects of mafic and ultramafic rocks on water in terms of contamination and health risk and further used the statistical analyses for source apportionment of contaminations in the study area.

2. Materials and methods

2.1. Study area

The study area is mainly comprised of Bucha and surrounding areas in Mohmand agency, north of Peshawar, Pakistan which is located between longitudes 71°35' to 71°38' E and latitudes 34°20' 35" to 34°25'40" N. Main settlements in the Mohmand agency are in the valleys of the Shilman, Gandab, Pindiali and along the bank of Kabul River. These settlements generally have dry and arid water-courses. Running water is hard to find in most of these valleys, except in Gandab and Shilman valleys. Climate of Mohmand agency is hot in summer and cooler in winter. Most of the rainfall is during winter season. This area is generally mountainous; however, low lying plains are also present. These plains are irrigated by Kabul and Swat rivers and their tributaries. The study area is generally covered by the low lying hills in the north and north-western part and the adjoin piedmont fluvial plain in the southern and south-eastern part (Fig. 1). Population in the hilly areas is sporadic, while in the plain areas, it is generally found in small clusters. Majority of population in the hilly areas uses water from streams and springs and in the plain

areas from dug wells for drinking and other domestic uses (DCR, 1998).

Rocks of the study area are part of the Kot-Prang Ghar mélange complex (Hussain et al., 1984). It is mainly composed of metamorphites such as chlorite-micaschist, graphitic schist, calcareous schist, marble, quartz-mica schist, metacherts and ophiolitic complex composed of ultramafic rocks, gabbros, pillow lavas and chert. Mafic and ultramafic rocks exposed in the Bucha and surrounding areas are dominantly gabbros, greenstones/pillow lavas, peridotite, dunite and serpentinite. Chromites and asbestos and talc stringers are generally cross cutting the rocks in the area (Jehan, 1996). Chromite also occurs as pods and lensoidal masses within the ultramafic rocks of the area (Rafiq, 1984).

2.2. Sampling

Representative water samples were collected in triplicate from surface water (stream) and sub-surface water (dug wells and springs) in the cleaned polyethylene bottles from already selected sampling sites of the study area in spring season (month of March) (Fig. 1). Polyethylene bottles were washed with double deionized water (DDW) before taking the representative water samples. Temperature (T), pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured on spot using a CONSORT C931 instrument. Each water sample was filtered through whatman (0.45 µm) filter paper and added few drops of nitric acid (HNO3) in bottle on spot. All the collected water samples were transported to the Geochemistry laboratory of the National Center of Excellence in Geology, University of Peshawar and stored in a refrigerator at 4 °C for further analyses.

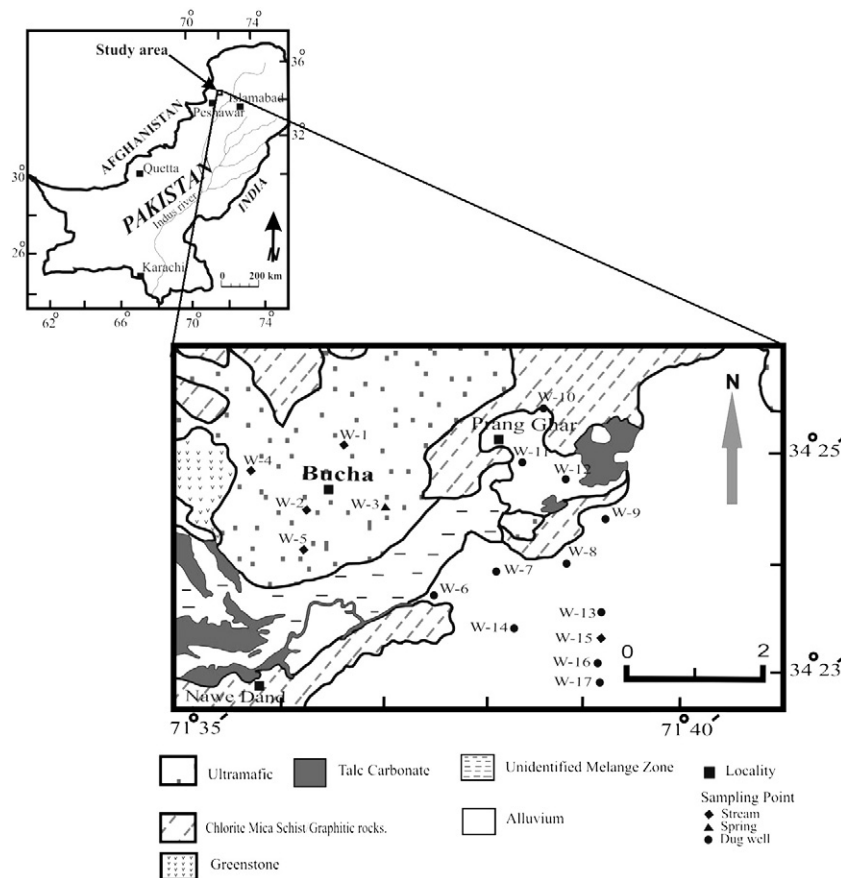


Fig. 1. Geological and sample location map of the Bucha and surrounding area. Modified after Hussain, 2005.

Table 1
Instrumental analytical condition for analyses of selected LM and HM.

Metal	Acetylene (L/min)	Air (L/min)	Wavelength (nm)	Slit width (nm)	Lamp current (Ma)	Detection limits (µg/L)
Na	2.0	17.0	589.0	0.2	8	0.3
K	2.0	17.0	766.5	0.7	12	3
Ca	2.0	17.0	422.7	0.7	10	1.5
Mg	2.0	17.0	285.2	0.7	6	0.15
Fe	2.3	17.0	288.3	0.2	30	5
Pb	2.0	17.0	283.3	0.7	30	15
Ni	2.0	17.0	232.0	0.2	25	6
Cr	2.5	17.0	357.9	0.7	25	3
Cu	2.0	17.0	324.8	0.7	15	1.5
Co	2.0	17.0	240.7	0.2	30	9
Mn	2.0	17.0	279.5	0.2	20	1.5
Cd	2.0	17.0	228.8	0.7	4	0.8
Zn	2.0	17.0	213.9	0.7	15	1.5

2.3. Chemical analyses

Acidified water samples were analyzed for LM (Na, K, Ca, Mg) and HMs (Fe, Mn, Ni, Cr, Co, Cu, Pb, Cd and Zn) using atomic absorption spectrometer (Perkin Elmer, AAS-PEA-700) under standard operating conditions having $r > 0.999$. The integration and delay time of AAS was 5 s. Instrumental parameters of each metal are listed in Table 1. In view of the data quality assurance, each sample was analyzed in triplicate and after every 10 samples a blank and two standards (i.e., 2.5 mg/L and 5 mg/L for LM and 2.5 µg/L and 5 µg/L for HM) of respective metal were analyzed on atomic absorption. The reproducibility was found to be at 95% confidence level. Therefore, average value of each water sample was used for further interpretation. Working standard solutions of all metals were prepared by the appropriate dilution of 1000 mg/L certified standard solutions Fluka Kamica (Buchs, Switzerland) of corresponding metal ions with DDW. All the acids and reagents used were of analytical grade.

2.4. Health risk assessment

2.4.1. Average daily dose (ADD) and hazard quotient (HQ)

Heavy metal enters into human body through several pathways including food chain, dermal contact and inhalation but in comparison to oral intake all others are negligible (ATSDR, 2000). ADD through water intake was calculated according to the modified equation US EPA (1998):

$$ADD = C \times IR / BW \quad (1)$$

Table 2
Physico-chemical parameters of surface water and sub-surface water samples collected from the study area ($n^a = 51$).

Statistics	T °C	pH	EC µS/cm	TDS mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	Fe µg/L	Mn µg/L	Cu µg/L	Pb µg/L	Zn µg/L	Ni µg/L	Cr µg/L	Co µg/L	Cd µg/L
Surface water																	
Mean	21.6	7.00	659.2	309	7.4	4.4	73	129	158	35	65.4	5.2	21.4	105.2	318.6	35.6	1.8
St dev ^b	1.3	0.02	97.5	140	3.9	2.1	32	69	39	10	14.9	3.1	26.8	42.5	75.6	12.5	0.9
Maximum	23.5	7.04	774	412	12	6	117	168	225	51	91	8	68	141	377	52	2
Minimum	20.1	6.99	509	63	2	1	43	7	125	23	52	1	4	32	190	17	1
Sub-surface water																	
Mean	17.5	6.97	730.2	397	15.9	4.6	153	82	50	28	59.1	4.3	41.4	40.4	203.4	24.8	1.9
St dev	2.1	0.07	283.1	152	9.8	3.4	122	45	45	23	8.8	1.66	43.5	32.1	51.6	29.3	0.5
Maximum	16.3	7.21	1319	708	30	13	400	189	164	89	83	7	141	138	361	113	3
Minimum	19.4	6.97	455	243	4	1	30	26	5	11	46	2	6	23	157	9	1
WHO standards	30–45	6.5–8.5	1000	1400	200	12	200	50	300	400	2000	10	3000	20	50	40	3

^a Number of water samples.

^b Standard deviation.

Where, C, IR and BW represent the metal concentrations in water (mg/L), water ingestion rate (2 L/day) and body weight (73 kg) respectively (Muhammad et al., 2011a).

To estimate the non-carcinogenic/chronic risk, HQ can be calculated by the following equation (Khan et al., 2008):

$$HQ = ADD / RfD \quad (2)$$

Where, according to US EPA database the oral toxicity reference dose values (RfD) are 5.0E-04, 3.6E-02, 3.0E-01, 1.5, 2.0E-02, 3.7E-02 and 1.4E-01 mg/kg-day for Cd, Pb, Zn, Cr, Ni, Cu and Mn, respectively (US EPA, 2005). The exposed population is assumed to be safe when $HQ < 1$ (Khan et al., 2008; Muhammad et al., 2010).

2.5. Statistical analyses

Mathematical calculations (means, ranges and standard deviations) were calculated using Excel 2007 (Microsoft Office). Univariate and multivariate statistical analyses like one-way ANOVA, correlation analysis, cluster analysis (CA) and principle component analysis (PCA) were performed using the SPSS software version 17.

3. Results and discussion

3.1. Physico-chemical parameters

Physico-chemical parameters in surface water and sub-surface water of the study area are summarized in Table 2. In surface water and sub-surface water, T values ranged from 20.1–23.5 and 16.3–19.4, with mean values of 21.6 and 17.5, respectively (Table 2). The highest T value (23.5) was observed in surface water sample (w-15) collected from a stream. pH values in surface water and sub-surface water ranged from 6.99–7.04 and 6.97–7.21, with mean values of 7.00 and 6.97, respectively (Table 2). The highest pH value (7.21) was observed in sub-surface water sample (w-11) collected from a dug well. EC values in surface water and sub-surface water ranged from 509–774 and 455–1319 µS/cm with mean values of 659.2 and 730.2 µS/cm, respectively (Table 2). The highest EC value (1319 µS/cm) was found in sub-surface water sample (w-12) collected from dug well. Similarly, TDS concentrations in surface water and sub-surface water ranged from 63–412 and 243–708 mg/L, with mean concentrations of 309 and 397 mg/L, respectively (Table 2). The highest TDS concentration (708 mg/L) was found in sub-surface water sample (w-12) collected from dug well. These parameters were found within the permissible limits set by WHO (2008). Their comparison in Fig. 2a revealed that surface water and sub-surface water were contributing equally to the mean contamination load of pH, EC and TDS in drinking water.

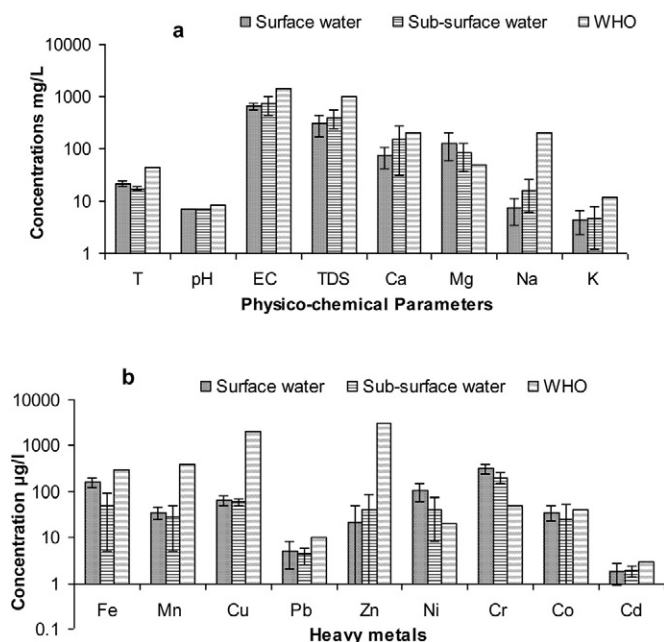


Fig. 2. Comparison physico-chemical parameter in surface water and sub-surface water with WHO drinking water permissible limits.

The concentrations of LM such as Na in surface water and sub-surface water ranged from 2–12 and 4–30 mg/L with mean concentrations of 7.4 and 15.9 mg/L, respectively (Table 2). The highest Na concentration (30 mg/L) was found in sub-surface water sample (w-11) collected from a dug well. K concentrations in surface water and sub-surface water ranged from 1–6 and 1–13 mg/L with mean concentrations of 4.4 and 4.6 mg/L, respectively (Table 2). The highest K concentration (13 mg/L) was found in sub-surface water sample (w-12) collected from a dug well. Ca concentrations in surface water and sub-surface water ranged from 43–117 and 30–400 mg/L with mean concentrations of 73 and 157 mg/L, respectively (Table 2). The highest Ca concentration (400 mg/L) was found in sub-surface water sample (w-16) collected from a dug well. Similarly, Mg concentrations in surface water and sub-surface water ranged from 7–168 mg/L and 26–189 mg/L with mean concentrations of 129 and 82 mg/L, respectively (Table 2). The highest Mg concentration (189 mg/L) was found in sub-surface water sample (w-3) collected from spring water. Na, K, Ca and Mg concentrations were generally found within the permissible limits set by WHO (2008). However, 6%, 33% and 70% water samples showed higher concentrations than their respective permissible limits of K, Ca and Mg, respectively. This comparison showed that surface water was highly contributing to the mean contamination level of Mg in drinking water (Fig. 2a). Surface water samples collected from the mafic and ultramafic horizon of the study area showed higher Mg concentration, as these rocks are generally rich in Mg. Mg enrichment in bed rocks suggests the possible leaching of Mg and its dissolution in water during percolation through the mafic and ultramafic rocks horizon. K, Ca and Mg concentrations in the studied water samples were found higher than that reported by Muhammad et al. (2010) for drinking water in the Kohistan region, northern Pakistan.

Iron concentrations ranged from 125–225 and 5–164 µg/L with mean concentrations of 158 and 50 µg/L in surface water and sub-surface water, respectively (Table 2). The highest Fe concentration (225 µg/L) was found in surface water sample (w-15) collected from a dug well. Mn concentrations ranged from 23–51 and 11–89 µg/L with mean concentrations of 35 and 28 µg/L in surface water and sub-surface water, respectively (Table 2). The highest Mn

concentration (89 µg/L) was found in sub-surface water sample (w-12) collected from a dug well. Cu concentrations ranged from 52–91 and 46–83 µg/L with mean concentrations of 65.4 and 59.1 µg/L in surface water and sub-surface water, respectively (Table 2). The highest Cu concentration (91 µg/L) was found in surface water sample (w-2) collected from a stream. Pb concentrations ranged from 1–8 and 2–7 µg/L with mean concentrations of 5.2 and 4.3 µg/L in surface water and sub-surface water, respectively (Table 2). The highest Pb concentration (8 µg/L) was noticed in surface water sample (w-5) collected from a stream. Similarly, Cd concentrations ranged from 1–2 and 1–3 µg/L with mean concentrations of 1.8 and 1.9 µg/L in surface water and sub-surface water, respectively (Table 2). The highest Cd concentration (3 µg/L) was found in sub-surface water sample (w-6) collected from a dug well. Zn concentrations ranged from 4–68 and 6–141 µg/L with mean concentrations of 21.4 and 41.4 µg/L in surface water and sub-surface water, respectively (Table 2). The highest Zn concentration (141 µg/L) was observed in sub-surface water sample (w-12) collected from a dug well. Fe, Mn, Cu, Pb, Zn and Cd concentrations were found within their respective permissible limits set by WHO (2008). Their comparison in Fig. 2b suggests that surface water was highly contributing to mean contamination level of Fe, Cu and Pb, while sub-surface water to Mn, Zn and Cd concentrations in drinking water of the study area.

The concentrations of Ni ranged from 32–141 and 23–138 µg/L with mean concentrations of 105.2 and 40.4 µg/L in surface water and sub-surface water, respectively (Table 2). The highest Ni concentration (141 µg/L) was noticed in surface water sample (w-5) collected from a stream. Cr concentrations ranged from 190–377 and 157–361 µg/L with mean concentrations of 318.6 and 203.4 µg/L in surface water and sub-surface water, respectively (Table 2). The highest Cr concentration (377 µg/L) was found in surface water sample (w-1) collected from a stream. Co concentrations ranged from 17–52 and 9–113 µg/L with mean concentrations of 35.6 and 24.8 µg/L in surface water and sub-surface water, respectively (Table 2). The highest Co concentration (113 µg/L) was observed in sub-surface water sample (w-8) collected from a dug well. It was noticed that 100%, 100%, and 18% water samples of the study area showed higher concentration for Cr, Ni and Co, respectively than their permissible limits set by WHO (2008). Ni, Cr and Co concentrations were also found higher

Table 3
Health risks assessment of HM in surface water and sub-surface water samples collected from the study area (n^a = 51).

Chronic risk assessment	Co ^b							Fe	Mn	Ni	Pb	Zn
	Statistics	Cd	Cr	Cu	Co	Fe	Mn					
ADD ^c mg/kg-day	Surface water											
	Mean	4.28E-05	8.85E-03	1.82E-03	4.39E-03	9.78E-04	2.92E-03	1.44E-04	5.94E-04			
	St dev ^d	1.77E-05	2.10E-03	4.15E-04	1.09E-03	2.82E-04	1.18E-03	8.65E-05	7.45E-04			
	Range	1.94E-05–5.56E-05	5.28E-03–1.05E-02	1.44E-03–2.53E-03	3.47E-03–6.25E-03	6.39E-04–1.42E-03	8.89E-04–3.92E-03	2.78E-05–2.22E-04	1.11E-04–1.89E-03			
	Sub-surface water											
Mean	5.32E-05	5.65E-03	1.64E-03	1.39E-03	7.66E-04	1.12E-03	1.18E-04	1.15E-03				
St dev	1.43E-05	1.43E-03	2.44E-04	1.26E-03	6.24E-04	8.92E-04	4.61E-05	1.21E-03				
Range	2.78E-05–8.33E-05	4.36E-03–3.14E-03	1.28E-03–2.31E-03	1.39E-04–4.56E-03	3.06E-04–2.47E-03	6.39E-04–3.83E-03	5.56E-05–1.94E-04	1.67E-04–3.92E-03				
HQ ^e	Surface water											
	Mean	8.56E-02	5.90E-03	4.91E-02	1.46E-01	6.98E-03	1.46E-01	4.01E-02	1.98E-03			
	St dev	3.55E-02	1.40E-03	1.12E-02	5.90E-02	2.01E-03	5.90E-02	2.40E-02	2.48E-03			
	Range	3.89E-02–1.11E-01	3.52E-03–6.98E-03	3.90E-02–6.83E-02	4.44E-02–1.96E-01	4.56E-03–1.01E-02	4.44E-02–1.96E-01	7.72E-03–6.17E-02	3.70E-04–6.30E-03			
	Sub-surface water											
Mean	2.26E-02	1.02E-03	5.50E-03	2.82E-03	1.49E-02	2.82E-03	2.60E-03	3.84E-02				
St dev	3.85E-02	9.39E-04	3.15E-03	2.15E-03	2.33E-02	2.15E-03	3.10E-03	6.57E-02				
Range	5.56E-02–1.67E-01	2.91E-03–6.69E-03	3.45E-02–6.23E-02	3.19E-02–1.92E-01	2.18E-03–1.77E-02	3.19E-02–1.92E-01	1.54E-02–5.40E-02	5.56E-04–1.31E-02				

^a Number of water samples.

^b No RID are available.

^c Average daily dose.

^d Standard deviation.

^e Hazard quotient.

than those reported by Muhammad et al. (2011a) in the water samples of Kohistan region, northern Pakistan.

3.2. Ni and Cr as the metals of concern

In the study area, Ni and Cr concentrations were found multifold higher than their respective permissible limits in both surface water and sub-surface water samples. It was noticed that surface water contained relatively high concentration of Ni and Cr as compared to sub-surface water (Fig. 2b). It was also observed that among sub-surface water, spring water contained similar amount of Ni as of surface (stream) water and was found many fold higher than those of dug wells. However, frequency of Cr concentrations is generally consistent with Ni concentrations as of having relatively higher concentration in surface water. The reason for relatively lower concentrations of Ni and Cr in dug wells water of the study area could be the fact that these dug wells are not present within the mafic and ultramafic horizon but all dug wells are in the fluvial plain having input from adjacent mafic and ultramafic terrains in the form of eroded soil (Badshah, 1979; Hussain et al., 1984; Jehan, 1996; Rafiq, 1984). Streams and spring water, however, has direct contact with the mafic and ultramafic rocks. Enrichment of Ni and Cr in water of the study area can be attributed to leaching of Cr and Ni in percolating water through these rocks under the oxidation condition. As local people of the area are generally using the water of streams, dug wells and springs for drinking and domestic purposes, therefore, this water may cause carcinogenic health effects (IARC, 1990; ICNCM, 1991), which should be extensively investigated by the team of geoscientist, epidemiologists and environmental scientists.

3.3. Health risk assessment

In the study area, inhabitants were interviewed for age, sex, health status, dietary habits and drinking water sources information. It was noted during field work that these inhabitants were generally using surface water (streams) and sub-surface water (springs and dug wells) for drinking and other domestic purposes. Diseases that were reported in the study area were diarrhea, vomiting, gastroenteritis, dysentery, viral hepatitis, headache, hypertension, irritability, abdominal pain, nerve damages, liver and kidney problems, anemia, intellectual disabilities and fatal cardiac arrest case. Therefore, health risk assessment for HM (ADD and HQ indices) in both surface water and sub-surface water samples was calculated.

3.3.1. Average daily dose (ADD) and hazard quotient (HQ)

In the study area, ADD values for consumption of drinking water were calculated and summarized in Table 3. ADD results suggest that people who consumed surface water contaminated with HM, had the average ADD values of 4.28E-05, 9.89E-04, 8.85E-03, 1.82E-03, 4.39E-03, 9.78E-04, 2.92E-03, 1.44E-04 and 5.94E-04 mg/kg-day for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, respectively (Table 3). Similarly, the people who consumed sub-surface water, had average ADD values of 5.32E-05, 6.90E-04, 5.65E-03, 1.64E-03, 1.39E-03, 7.66E-04, 1.12E-03, 1.18E-04

Table 4

One-way ANOVA table for comparison of sampling sites with regards to selected physico-chemical parameter pollution.

Source of variation	Sum of squares	Degree of freedom	Mean square	Factor	Significance
Between groups	177049.631	16	11065.602	0.254	0.999
Within groups	11055059.43	254	43523.856		
Total	11232109.06	270			

The mean difference is significant at a level of 0.05.

Table 5
Correlation matrix of selected physico-chemical parameters in surface water (n^a = 30).

Physico-chemical parameters	pH	EC	TDS	Ca	Mg	Na	K	Fe	Mn	Cu	Pb	Zn	Ni	Cr	Co	Cd
pH	1															
EC	0.009	1														
TDS	0.075	0.941^b	1													
Ca	-0.576	-0.525	-0.432	1												
Mg	0.141	0.902	<i>0.991^c</i>	-0.478	1											
Na	-0.146	0.782	0.797	0.055	0.720	1										
K	0.244	0.703	0.871	-0.146	0.870	0.825	1									
Fe	-0.342	-0.883	-0.962	0.552	-0.972	-0.713	-0.894	1								
Mn	-0.552	-0.645	-0.818	0.441	-0.857	-0.586	-0.921	0.926	1							
Cu	0.058	0.290	0.260	-0.728	0.334	-0.332	-0.127	-0.253	-0.103	1						
Pb	-0.480	0.574	0.711	0.025	0.722	0.517	0.565	-0.546	-0.406	0.342	1					
Zn	-0.426	0.495	0.204	-0.074	0.081	0.456	-0.076	-0.061	0.262	-0.105	-0.004	1				
Ni	0.056	0.757	0.921	-0.125	0.919	0.833	0.972	-0.89	-0.859	-0.004	0.740	-0.026	1			
Cr	0.260	0.748	0.910	-0.239	0.917	0.797	0.994	-0.934	-0.942	-0.015	0.601	-0.078	0.978	1		
Co	0.596	0.667	0.800	-0.447	0.822	0.638	0.914	-0.920	-0.984	0.002	0.291	-0.150	0.826	0.926	1	
Cd	0.420	0.707	0.691	-0.947	0.974	-0.279	-0.522	-0.761	-0.087	0.597	-0.494	0.382	-0.884	-0.427	0.187	1

^a Number of water samples.^b Bold correlation is significant at the 0.05 level (2-tailed).^c Italic correlation is significant at the 0.01 level (2-tailed).

and 1.15E-03 mg/kg-day for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, respectively (Table 3).

Table 3 also summarizes HQ indices of HM through consumption of drinking water in the study area. HQ indices suggest that people who have consumed surface water contaminated with HM had the mean HQ values of 8.56E-02, 5.90E-03, 4.91E-02, 6.98E-03, 1.46E-01, 4.01E-02 and 1.98E-03 for Cd, Cr, Cu, Mn, Ni, Pb and Zn, respectively (Table 3). Similarly, people who have consumed sub-surface water had the mean HQ values of 2.26E-02, 1.02E-03, 5.50E-03, 1.49E-02, 2.82E-03, 2.60E-03 and 3.84E-02 for Cd, Cr, Cu, Mn, Ni, Pb and Zn, respectively (Table 3). HQ indices of HM in all the water samples suggest low level of chronic risks. However, HQ indices of Cr, Mn and Ni were found higher than those reported by Muhammad et al. (2011a) in Kohistan region, northern Pakistan and Kavcar et al. (2009) in Turkey for drinking water. Major health problems in the study area 20–40%, 15–25% and 37–45% respondents reported the gastroenteritis, dysentery and diarrhea, respectively. 22–29%, 13–16% and 3–5% respondents reported the hepatitis-A, hepatitis-B and hepatitis-C, respectively. Similarly, 0.5–1.2%, 2–7% and 3–6% respondents reported cancer, anemia and kidney problems, respectively. Although, the ADD and HQ have low level risk but the high metal concentrations may be attributing to these diseases.

3.4. Statistical analyses

The statistical comparison of contamination from different sampling sites using one-way ANOVA revealed no statistical significant variation ($p = 0.999$), which means that these sampling sites contribute insignificant or equally to the mean contaminations in surface water and sub-surface water (Table 4). In surface water, physico-chemical correlation matrices show that various parameter pairs have positive significant correlations like TDS-EC ($r = 0.941$), EC-Mg ($r = 0.902$), TDS-Mg ($r = 0.991$), TDS-Ni ($r = 0.921$), TDS-Cr ($r = 0.910$), Mg-Ni ($r = 0.919$), Mg-Cr ($r = 0.917$), Mg-Cd ($r = 0.974$), K-Ni ($r = 0.972$), K-Cr ($r = 0.994$), K-Co ($r = 0.914$), Fe-Mn ($r = 0.926$), Cr-Co ($r = 0.926$) as shown in Table 5. Similarly, in sub-surface water, correlation matrices show that various physico-chemical parameter pairs have positive significant correlations like pH-Cu ($r = 0.770$), EC-TDS ($r = 1.000$), EC-Na ($r = 0.728$), EC-K ($r = 0.815$), EC-Mn ($r = 0.621$), Mg-Fe ($r = 0.642$), Mg-Ni ($r = 0.698$), Mg-Cr ($r = 0.790$), K-Mn ($r = 0.748$), Fe-Ni ($r = 0.704$), Fe-Cr ($r = 0.702$), Mn-Zn ($r = 0.893$), Ni-Cr ($r = 0.938$) as shown in Table 6. In both surface water and sub-surface water, correlation of physico-chemical parameters was further supported by dendrogram of CA (Figs. 3 and 4). Dendrogram of physico-chemical parameters in surface water showed one very large and one very small cluster

Table 6
Correlation matrix of selected physico-chemical parameters in sub-surface water (n^a = 21).

Physico-chemical parameters	pH	EC	TDS	Ca	Mg	Na	K	Fe	Mn	Cu	Pb	Zn	Ni	Cr	Co	Cd
pH	1															
EC	0.227	1														
TDS	0.224	<i>1.000</i>	1													
Ca	-0.221	-0.674^b	-0.674	1												
Mg	0.129	0.511	0.507	-0.427	1											
Na	0.308	0.728	0.725	-0.318	0.226	1										
K	0.099	0.815	0.817	-0.359	0.285	0.545	1									
Fe	0.241	0.043	0.039	0.044	0.642	0.003	-0.084	1								
Mn	-0.047	0.621	0.626	-0.183	0.221	0.185	0.748	0.098	1							
Cu	<i>0.770^c</i>	0.350	0.350	-0.081	0.031	0.403	0.446	0.259	0.286	1						
Pb	0.398	0.262	0.263	-0.220	-0.165	0.164	0.388	-0.428	0.357	0.254	1					
Zn	-0.080	0.431	0.434	-0.068	0.418	-0.013	0.553	0.459	0.893	0.273	0.064	1				
Ni	0.070	-0.111	-0.115	0.131	0.698	-0.130	-0.142	0.704	-0.175	-0.014	-0.311	0.160	1			
Cr	-0.054	0.052	0.049	-0.064	0.790	-0.049	-0.091	0.702	-0.101	-0.067	-0.445	0.235	0.938	1		
Co	0.081	-0.138	-0.135	-0.378	0.098	-0.400	-0.312	0.173	-0.213	-0.095	-0.136	-0.129	0.161	0.231	1	
Cd	-0.240	-0.193	-0.190	0.393	-0.121	-0.255	-0.279	0.346	0.256	-0.018	-0.506	0.420	-0.086	0.025	0.041	1

^a Number of water samples.^b Bold correlation is significant at the 0.05 level (2-tailed).^c Italic correlation is significant at the 0.01 level (2-tailed).

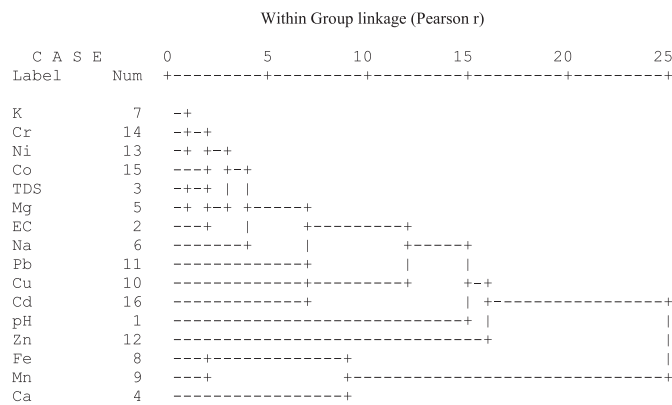


Fig. 3. A dendrogram of selected physico-chemical parameter in surface water samples.

(Fig. 3). Similarly, dendrogram of Physico-chemical parameters in sub-surface showed two broad clusters of nearly equal size (Fig. 4). As noted earlier in correlation that some parameter pairs have strong correlation and due to which they form primary cluster pairs. Therefore, primary clusters were found between K–Cr, Ni–Cr and Cr–Co in surface water and EC–TDS and Cr–Ni in sub-surface water.

For qualitative analysis of clustering behavior, the PCA was applied and the results are summarized in the Table 7. This table shows qualitative evaluation result of PCA with varimax normalization (PCA-V) in surface water. PCA results indicated physico-chemical association and grouping with three factors having a total variance of 100%. Factor-1 contributed 43.629% to the total variance with a high loading on Ca ($r=0.860$), Na ($r=0.748$), K ($r=0.840$), Ni ($r=0.973$) and Cr ($r=0.739$). Ni and Cr sources could be the erosion from mafic and ultramafic rocks and mining of chromites ore deposits. It means that factor-1 has geogenic and anthropogenic sources. Factor-2 contributed 35.171% to the total variance with a high loading on Fe ($r=0.894$), Mn ($r=0.907$) and Pb ($r=0.969$). Fe, Mn and Pb level could have also been influenced by erosion of mafic and ultramafic rocks. It means that factor-2 has geogenic sources. Factor-3 contributed 21.200% to the total variance with a high loading on EC ($r=0.947$), TDS ($r=0.957$), Zn ($r=0.978$) and Cd ($r=0.485$). EC, TDS, Zn and Cd level indicated the likely influenced by erosion of schistose rocks having sulfide seams. It means that factor-3 also has geogenic sources.

Table 8 summarizes the result of PCA with varimax normalization (PCA-V) in sub-surface water. This table exhibits the physico-chemical association and grouping with six factors having a total variance 94.145%. Factor-1 contributed 32.204% to the total variance with a high loading on EC ($r=0.917$), TDS ($r=0.916$), Na ($r=0.827$) and K ($r=0.650$). The sources of TDS, EC, Na and K could be the leaching of

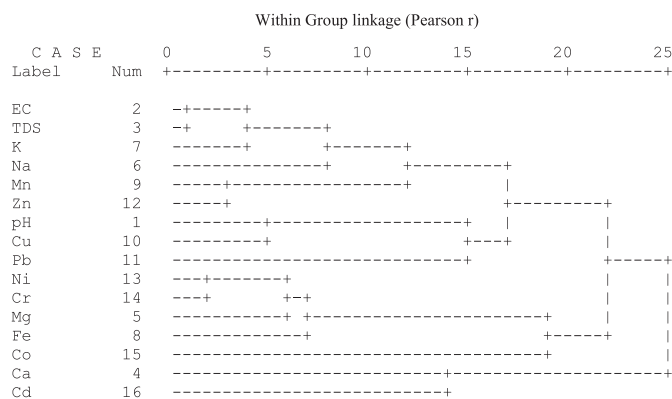


Fig. 4. A dendrogram of selected physico-chemical parameter in sub-surface water samples.

Table 7
Factor loading for selected physico-chemical parameters in surface water ($n^a=30$).

Physico-chemical parameters	Factor 1	Factor 2	Factor 3
pH	-0.197	-0.951	-0.238
EC	-0.321	0.003	0.947
TDS	-0.29	-0.005	0.957
Ca	0.860^b	0.477	-0.181
Mg	-0.872	-0.198	0.448
Na	0.748	0.049	0.662
K	0.840	-0.518	-0.162
Fe	0.323	0.894	-0.311
Mn	-0.103	0.907	0.408
Cu	-0.968	0.203	-0.15
Pb	-0.02	0.969	-0.246
Zn	0.011	0.207	0.978
Ni	0.973	0.045	-0.227
Cr	0.739	-0.635	-0.225
Co	0.191	-0.975	-0.117
Cd	-0.776	-0.402	0.485
Eigen value	6.981	5.627	3.392
Loading%	43.629	35.171	21.2
Cumulative%	43.629	78.8	100

^a Number of water samples.

^b Values of dominant heavy metals in each factor are reported in bold.

the bed rocks suggesting that factor-1 has geogenic sources. Factor-2 contributed 22.794% to the total variance with a high loading on Mg ($r=0.834$), Fe ($r=0.771$), Ni ($r=0.970$) and Cr ($r=0.961$). Mg, Fe, Ni and Cr level could have been influenced by leaching of mafic and ultramafic rocks and mining of chromites ore deposits. It means that factor-2 also has geogenic and anthropogenic sources. Factor-3 contributed 13.893% to the total variance with a high loading on Mn ($r=0.937$) and Zn ($r=0.933$). Mn and Zn levels are also influenced by leaching of mafic rocks, suggesting that factor-3 also has geogenic sources. Factor-4 contributed 10.457% to the total variance with a high loading on pH ($r=0.927$) and Cu ($r=0.900$). pH and Cu levels are probably influenced by agriculture activities. It means that factor-4 has anthropogenic sources. Factor-5 contributed 8.173% to the total variance with a high loading on Cd ($r=0.864$). Cd level is probably influenced by leaching of local mafic and ultramafic rocks. It means that factor-5 also has geogenic sources. Factor-6 contributed 6.624% to the total variance with a high loading on Ca ($r=0.617$). Ca

Table 8

Factor loading for selected physico-chemical parameters in sub-surface water ($n^a=21$).

Physico-chemical parameters	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
pH	0.126	0.062	-0.115	0.927	-0.202	-0.125
EC	0.917^b	0.053	0.345	0.118	-0.156	-0.033
TDS	0.916	0.048	0.351	0.116	-0.099	-0.036
Ca	-0.699	-0.023	-0.007	-0.001	0.238	0.617
Mg	0.430	0.834	0.177	-0.032	-0.048	-0.135
Na	0.827	-0.026	-0.144	0.277	-0.005	0.375
K	0.650	-0.043	0.566	0.108	-0.287	0.211
Fe	-0.046	0.771	0.179	0.316	0.414	-0.071
Mn	0.321	-0.083	0.937	0.032	-0.003	0.061
Cu	0.206	-0.012	0.212	0.961	0.022	0.105
Pb	0.062	-0.351	0.297	0.289	-0.776	-0.006
Zn	0.129	0.256	0.933	0.043	0.183	0.032
Ni	-0.175	0.970	-0.05	0.031	-0.064	0.033
Cr	0.027	0.961	-0.024	-0.097	0.102	-0.088
Co	-0.147	0.132	-0.115	0.029	0.069	-0.919
Cd	-0.260	-0.069	0.354	-0.019	0.864	-0.006
Eigen value	5.153	3.647	2.223	1.673	1.308	1.064
Loading%	32.204	22.794	13.893	10.457	8.173	6.624
Cumulative%	32.204	54.998	68.892	79.348	87.521	94.145

^a Number of water samples.

^b Values of dominant heavy metals in each factor are reported in bold.

level is probably influenced by leaching of talc carbonate rocks or local seams of CaCO₃ suggesting that factor-6 has geogenic sources. This study supports previous similar studies carried out by Muhammad et al. (2010, 2011a) and Krishna et al. (2009) for surface water and sub-surface water.

4. Conclusions

In the Bucha area, majority of physico-chemical parameters including pH, EC, TDS, Na, K, Cu, Mn, Pb, Zn and Cd concentrations were found within the permissible limits set by world health organization (WHO). However, the concentrations of light metals and heavy metals such as Ca, Mg, Co, Cr and Ni exceeded their permissible limits in 33%, 71%, 18%, 100% and 100% water samples, respectively. Statistical analyses like PCA concluded that enrichment of these contaminants into surface water and sub-surface water can be attributed substantially to the weathering/leaching of the mafic and ultramafic rocks and mining chromite ores in the study area. Although, health risk assessment revealed no health risk (HQ<1) when compared with US EPA. However, multifold higher concentrations of Cr and Ni in the drinking water of the Bucha area may pose a potential health risk to the local inhabitants. Although, Pakistan has Environmental Protection Act, 1997 that forced monitoring of portable water regularly. The study area is not easily accessible, therefore, monitoring inspector could not be able to monitor drinking water regularly. Therefore, it is recommended that drinking water from surface water and sub-surface water in the Bucha area should be banned and alternative sources should be provided to the inhabitants for drinking purposes.

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