Journal of Himalayan Earth Sciences Volume 48, No. 2, 2015 pp.62-73

Health risk associated with heavy metals via consumption of surface and groundwater in District Shangla, Pakistan

Javed Nawab[1, 2], Sharafat Ali[1], Adnan Rauf[3], Ubaid Ur Rehman[2], Akbar Ali Khan[2], Muhammad Sajjad[2] and Wajid Khan[2]

[1]Department of Environmental & Conservation Sciences, University of Swat, Pakistan
[2]Department of Environmental Sciences, University of Peshawar, Pakistan
[3]Institute of Chemical Sciences, University of Swat, Pakistan

Abstract

The study aimed to investigate the heavy metals (Cr, Ni, Cd, Pb, Mn and Zn) concentrations in both surface and groundwater sources and their respective health risk in District Shangla, Pakistan. The concentrations of heavy metals were analyzed through AAS (atomic absorption spectrometer) and the detectable values were compared with the standard limit of WHO (world health organization). The concentration of Cd (87%), Pb (58%), Cr (24%) and Ni (8%) samples exceeded than the acceptable limit of WHO, while Mn and Zn were found within permissible limits. The health risk like chronic daily intakes (CDIs) and health risk indices (HRIs) were carried out for both children and adults. The values of CDI were observed in the order of Pb> Zn > Ni >Mn> Cr > Cd and Zn >Pb>Mn> Cd > Cr > Ni through consumption of surface and groundwater, respectively. HRI values were observed >1 in drinking water for Cd showing possible health risk in Alpurai, Lelonai and Ranyal areas, while other heavy metals showed no health risk. In the study area, the results revealed that high contamination of heavy metals in both surface and groundwater may be due to geogenic activities (Mafic and Ultramafic rocks and Pb-Zn sulfide ore deposits).

Keywords: Geochemistry; Health risk; Heavy metals; Geogenic; Permissible limit; Consumption.

1. Introduction

Recently, the heavy metals study in water has become the main focus of environmental scientist (Khan et al., 2015). Heavy metals originate from natural sources like goegenic activities and ore deposits, and man-made sources like smelting, mining, intensive, agriculture industries and wastewater irrigation (Nawab et al., 2015, Shah et al., 2012). Furthermore, heavy metals pollute both ground and surface water resulting in declining water quality parameters in terms of drinking and irrigation (Krishna et al., 2009). Both surface and ground water contamination is globally related to health problems, which become significant issue after 1990s (Khan, et al., 2013; Khan, et al., 2012). Heavy metals are considered as environmental contaminants because of its persistence, toxicity and bio-accumulative nature in the environments (Pekey et al., 2004).The water contain several types of toxic metals which may cause different type of health problem like respiratory problem and some type of cancers in humans (Kavcar et al., 2009). Several heavy metals such as chromium (Cr), copper (Cu), zinc (Zn), cadmium (Cd), cobalt (Co), manganese (Mn), nickel (Ni) and lead (Pb) are basically necessary for regular body development and functions of living organisms, although it can create toxicity at higher concentrations. On the other hand, some heavy metals like Pb, Mn and Cd are highly toxic for both marine life and human even at low concentration (Ouyang et al., 2002). The heavy metals in mining areas are released in to the water without any treatment (Das et al., 2013).

In developing countries, the provision of safe and clean drinking water supply schemes is considered to be the key responsibilities of the government because people have limited access to safe drinking water. Transfer of pathogen into human body in drinking water mainly occurs due to human and animal feces. Inadequate chlorination, irregular water supply and improper sewage management system appear to be linked with self-reported diseases (Abu-Amr and Yassin, 2008). The majority of developing countries face two main problems in which one is persistent shortages of fresh waterand the other is heavily contamination of accessible water. The rapid urbanization

together with poor socioeconomic development, poor sanitation and limited water supply play a major role in increasing the risk of water borne diseases (Lehloesa and Muyima, 2000; Khan et al., 2013).

The aim of this study was to quantify the concentrations of heavy metal in both ground and surface water and to identify their health risk to the local community of the study area.

2. Material and methods

2.1. Study area

Shangla district is one of the most beautiful hilly areas blessed with plenty natural resources, rich in esteemed biodiversity and situated in the KPK province of Pakistan. The total area of the district is 1,586 square kilometers. There are two major subdivisions of the district; Tehsil Puran and Tehsil Alpuri, which are further, classified into four sub Tehsils comprising Besham, Makuzai, Martungand Chakesar. The district is surrounded by strategically important regions such as District Swat in the west, District Kohistan in the north, District Battagram in the east, in association with tribal areas of Kala Daka (Black Mountain of Hazara) and District Buner in the south.The northern region of Mingora ophiolitic mélange mainly contains ultramafic rocks and it lays beside the Main Mantle Thrust (MMT) between the Kohistan Island Arc and Indo- Pakistan plate. These rocks include disseminated particles and vast bodies of isolated chromites (Arif and Jan 2006). The district lies at an average elevation of 2000-3000 meters with the highest peak of the area is (3, 440 m) located in the north of the district near Kuz Ganrshal and contains many sloppy terrains, which have made this district sufficient in hydro power generation. According to GoP, 1998, a census report, the population density of the area was 274 persons per square Kilometer with an average annual growth rate of 3.3% and a total population of 435,563. The total number of households is 64,391 with an average household size of 8.1. District Shangla is full of natural resources, which can play a vital role in the sustainable development of the region and to achieve the millennium development goals if properly invested and managed.

2.2. Water Sampling

Water samples were collected from both ground and surface water from different locations (Lelonai, Alpuri, Bele Baba, Dherai, Opal, Ranyal and Chakesar) of the study area as shown in (Figure 1). The procedure used for sampling of water was adopted from Khan et al., 2013. The methodology of water sampling included sample collection from groundwater reserves (springs) and surface water such as rivers and streams. Water samples from the study area were collected in clean polyethylene plastic bottles. The bottles were washed before collection of samples with double deionized water containing HNO_3 (20%). In order to avoid contamination the sampling bottles were sterilized before sampling and the gas in the bottles was removed by filling up the bottle from water and then emptied and again refilled in the same manner from the same water source. A total of 92 samples were collected from different locations of the study area including 51 ground water samples and 41 surface water samples. The pH of water samples were measured on the spot through CONSORT pH meter (Model C931, Turn hout, Belgium). For chemical analysis all water samples was filtered through Whitmann (0.45µm) and added a few drops of 5% HNO_3 to prevent further growth microbes and then transported to the Environmental and Conservation Sciences Laboratory, University of Swat, Pakistan for further analysis.

2.2. Chemical analysis procedures

For the preparation and analysis of samples analytical grade chemicals with 99.9% (Merck Darmstadt, Germany) were utilized. For making standard solution of all of the six elements, their corresponding metal ions were diluted in 1000 mg/L certified standard solution (Fluka Kamica, Buchs, Switzerland) in double distilled water being used throughout the analytical process. Graphite furnace atomic absorption spectrophotometer (GFAAS AAS-700 Perkin Elmer, USA) under standard condition was used for the evaluation of concentrations of the selected heavy metals (Cd, Mn, Cr, Zn, Pb and Ni) in water samples.

For Cr, Ni, Cd, Mn, Zn and Pb the limit of detection were 0.0015, 0.0060, 0.0030, 0.0015, 0.0015 and 0.0150 mg/L, respectively and the AAS assimilation delay time was 5 second.

2.3. Human health risk assessment

2.3.1. Chronic daily intake (CDI) indices

In human body the heavy metals enter through different sources such as food chains, contact through skin and inhalation, but comparatively oral intake is much more involved in the heavy metals accumulation in the human body as compare to all other pathways (ATSDR, 1993). CDI for water consumption was adapted from (US EPA, 1999; Chrostowski, 1994):

$$CDI = C \times \frac{DI}{BW} \qquad (1)$$

Where, C represent concentration of heavy metals in water (µg/L), DI is the average daily intake rate of water (2 L/day) and BW represent body weight (72 kg) and 1 L/day for child's body weight (32.7 kg) (US EPA, 2011; Khan et al., 2010)

2.3.2. Health Risk indices (HRI)

The determination of non-carcinogenic risks of heavy metals was carried out through the following equation (US EPA, 1999).

$$HRI = \frac{CDI}{RfD} \qquad (2)$$

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

2.4. Statistical analyses

Statistix version (8.1) was used for conducting all calculations.The statistical package for social sciences (SPSS version 21) was used for carrying out inter-metals correlation and the Arc Geographic Information System was used for the preparation of the location map of the study area.

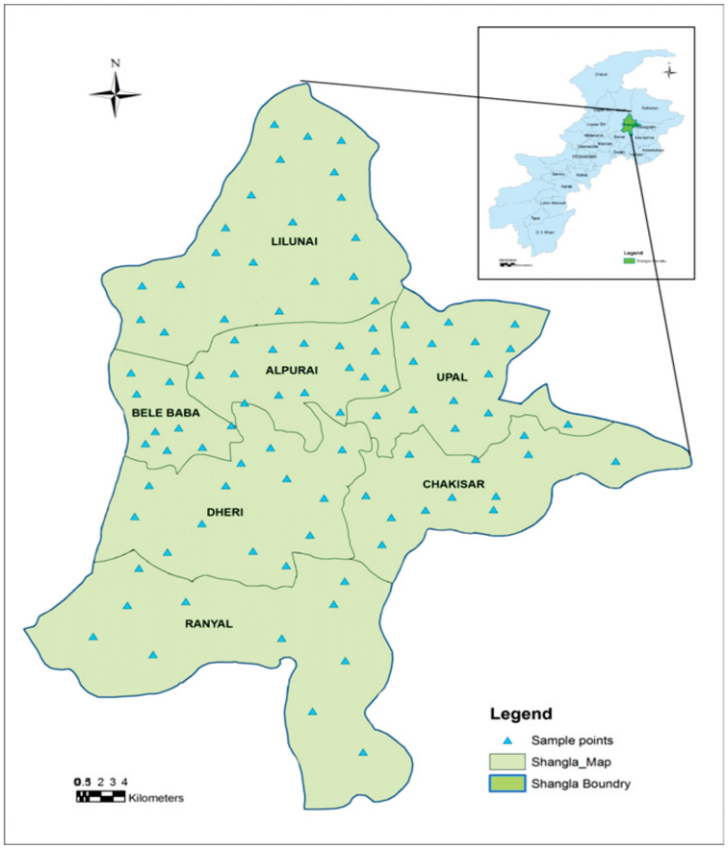

Fig. 1. Map showing location of the sampling points in the study area.

3. Result and discussion

3.1. pH:

The values of pH in ground water samples of the study area were ranged from 6.90-7.60, 7.40-8.20, 7.40-7.60, 7.50-7.60, 7.60-7.80, 7.40-7.60 and 7.00-8.00, while in surface water it ranged from 7.20-7.80, 7.60-8.00, 7.40-7.80, 7.60-7.80, 8.00-8.20, 7.60-7.80 and 7.80-8.30 in Lelonai, Alpurai, Bele Baba, Dherai, Ranyal, Opal and Chakesar area, respectively (Table 1). The mean values of pH in ground water of the study area were found in the order of Alpurai> Ranyal> Dherai> Opal> Bele Baba> Lelonai> Chakesar and that of surface water were in the order of Ranyal> Chakesar> Alpurai> Opal> Dherai> Bele Baba> Lelonai. The lowest value of pH (6.90) was recorded in ground water (spring) at Leolanai area, while the highest value of pH (8.30) was recorded in surface water (perennial river) at Chakesar area. In the study area all of the pH values were observed within the acceptable limit of WHO (2008).

3.2. Heavy metals concentration

The Cr concentration in ground water samples ranged from 0.00-90.00, 0.00-95.00, 0.00-34.00, 0.71-85.00, 2.00-90.00, 0.09-94.00, 0.02-49.00 µg/L, although in water samples collected from surface water ranged from 0.01-61.00, 0.00-33.00, 0.01 -59.00, 0.20-105.00,1.00-40.00, 0.21-62.00, 0.20-62.00 µg/L in Chakesar, Opal, Ranyal, Lelonai, Alpuri, Dherai and Bele Baba areas, respectively. The Cr (105.00 µg/L) maximum concentration was assessed in surface water sample (Main River) collected from Lelonai area as shown in Table 1. Such a high concentration may be due to result from mafic and ultramafic rocks, which are exposed in the area (Nawab et al., 2015; Mohammad et al., 2010). In the study area Cr concentration in 24% of samples are exceeded from the acceptable limit of WHO (2008).

Cd concentration in ground water ranged from 0.00-23.00, 0.00-34.00, 0.00- 31.00, 10.00-21.00, 4.00-35.00, 09.00-15.00, 10.00-19.00 µg/L, however, in surface water samples it found in the ranged of 0.00-16.00, 0.00-32.00, 0.00-39.00, 2.00-34.00, 13.00 -32.00, 0.00-28.00, 04.00-15.00 µg/L in Chakesar, Opal, Ranyal, Lelonai, Alpuri, Dherai and Bele Baba sites, respectively. The Cd (39.00 µg/L) highest concentration was assessed in water sample collected from ground water (spring) of Ranyal area are given in Table 1. Cd concentrations in 87% samples are exceeded from the permissible limits of WHO(2008). The occurrence of mafic and ultramafic rocks and Pb/Zn sulfide deposits may be responsible for such high concentration of heavy metals in the area (Mohammad et al., 2011).

Similarly, the concentration of Mn in ground water samples ranged from 0.00-26.00, 0.00-169.00, 0.00-31.00, 0.00-10.00, 0.00-22.00, 0.00-10.00, 0.00-13.00 µg/L, on the other side in surface water, it ranged from 2.00-210.00, 0.00-16.00, 0.00-24.00, 0.00-11.00, 0.00-20.00, 0.00-9.00, 4.00-50.00 µg/L in Chakesar, Opal, Ranyal, Lelonai, Alpuri, Dherai and Bele Baba sites, respectively. The Mn (210.00 µg/L) highest concentration was found in surface water (Perennial River) sample collected in Chakesar site.Zn concentration in ground water samples typically ranged from 0.00-588.00, 0.00-1107.0, 0.00-372.00, 0.00-2097.0, 0.00-962.00, 0.00-519.00, 0.00-156.00 µg/L, while in surface water samples, it ranged from 0.00-0.00, 0.00-180.00, 0.00-410.00, 0.00 -10.00, 0.00-0.00, 0.00-300.00, 0.00-13.00 µg/L in Chakesar, Opal, Ranyal, Lelonai, Alpuri, Dherai and Bele Baba sites, respectively as shown in Table 1. The Zn (2097.0 µg/L) highest concentration was found in ground water (spring) samples collected in Lelonai area. In the study area, both Mn and Zn concentration were found within the permissible limit set by WHO (2008) for drinking water.

Ni concentration in ground water samples ranged from 0.00-45.00, 0.00-72.00, 0.00-28.00, 0.00-60.00, 4.00-83.00, 0.10-64.00, 9.00-47.00 µg/L, although in surface water samples it ranged from 0.03-79.00, 0.07-310.00, 0.12-103.00, 0.06-49.00, 0.56-200.00, 0.00-43.00, 0.70-200.00 µg/L correspondingly in Chakesar, Opal, Ranyal, Lelonai, Alpuri, Dherai and Bele Baba areas. The Ni (310.00 µg/L) maximum concentration was identified in water samples collected from surface water (perennial river) in Opal area. In the study area 8% of the samples exceeded their permissible limit set by WHO (2008), such high concentration may be due to mafic and ultramafic rocks and Pb/Zn sulfide ore deposits in the study area (Mohammad et al., 2011).

Table 1. Heavy metal concentration (ug/L) in surface and ground water in the study area (a n=92).

Parameters	Statistics	Alpurai		Dherai		Lelonai		Ranyal	
		[b] S. water n=6	[c] G. water n=9	S. water n=7	G. water n=6	S. water n=9	G. water n=9	S. water n=5	G. water n=6
pH	Range	7.60-8.00	7.40-8.20	7.60-7.80	7.50-7.60	7.20-7.800	6.90-7.60	8.00-8.20	7.60-7.80
	Mean	7.80±0.14	7.90±0.33	7.70±0.10	7.56±0.05	7.50±0.40	7.3±0.17	8.13±0.11	7.70±0.14
Cd	Range	13.00-32.00	4.00-35.00	BDL-28.00	09.00-15.00	2.00-34.00	10.00-21.00	BDL-39.00	0.00-31.00
	Mean	21.66±3.84	20.77±8.02	13.71±9.17	11.83±2.09	17.50±7.03	15.66±4.71	13.2±15.63	18.33±13.50
Cr	Range	1.00-40.00	2.00-90.00	0.21-62.00	0.09-94.00	0.20-105.00	0.71-85.00	0.01-59.00	0.00-34.00
	Mean	23.33±15.61	44.66±32.87	19.54±28.14	35.07±34.84	47.57±38.96	32.56±30.06	29.08±27.59	15.18±16.72
Mn	Range	0.00-20.00	0.00-22.00	0.00-9.00	0.00-10.00	0.00-11.00	0.00-10.00	0.00-24.00	0.00-31.00
	Mean	6.33±7.28	7.33±6.74	3.14±4.01	2.83±3.92	3.88±3.55	3.55±3.94	9.00±9.27	13.66±13.48
Ni	Range	0.56-200.00	4.00-83.00	0.00-43.00	0.10-64.00	0.06-49.00	0.00-60.00	0.12-103.00	0.00-28.00
	Mean	50.26±74.74	33.77±25.27	18.71±12.84	22.85±24.15	11.38±15.36	16.23±19.55	30.67±42.44	9.50±12.02
Pb	Range	0.00-410.00	0.01-815.00	0.00-860.00	0.06-168.00	0.00-587.00	0.00-676.00	0.00-660.00	0.54-170.00
	Mean	87.83±161.35	111.91±265.88	469.71±430.86	64.02±63.98	97.77±190.35	147.89±204.98	215.20±260.07	72.04±80.01
Zn	Range	[e]BDL	0.00-962.00	0.00-300.00	0.00-519.00	0.00-10.00	0.00-2097.00	0.00-410.00	0.00-372.00
	Mean		226.67±334.95	57.14±113.39	86.50±211.88	3.77±4.11	284.46±684.76	166.00±152.74	132.17±139.93

Parameters	Statistics	Bele Baba		Chakesar		Opal		Permissible Limits
		S. water n=4	G. water n=5	S. water n=4	G. water n=8	S. water n=6	G. water n=8	[d]WHO
pH	Range	7.40-7.80	7.40-7.60	7.80-8.30	7.00-8.00	7.60-7.80	7.40-7.60	6.50-8.50
	Mean	7.57±0.17	7.52±0.09	8.07±0.22	7.40±0.42	7.70±0.14	7.53±0.11	
Cd	Range	4.00-15.00	10.00-19.00	4.00-15.00	0.00-23.00	0.00-32.00	0.00-34.00	3.00
	Mean	9.25±4.06	13.4±3.36	9.25±6.40	13±9.41	13.33±11.91	14.87±14.22	
Cr	Range	0.20-62.00	0.02-49.00	0.01-61.00	0.00-90.00	0.00-33.00	0.00-95.00	50.00
	Mean	18.24±29.51	21.01±21.92	15.36±30.42	22.89±36.60	7.78±12.94	17.77±32.36	
Mn	Range	4.00-50.00	0.00-13.00	2.00-210.00	0.00-26.00	0.00-16.00	0.00-169.00	400.00
	Mean	16.50±22.36	4.40±5.85	60.50±100.02	15.25±9.23	4.66±6.77	31.25±57.01	
Ni	Range	0.70-200.00	9.00-47.00	0.03-79.00	0.00-45.00	0.07-310.00	0.00-72.00	70.00
	Mean	62.67±92.26	23.80±15.83	20.50±39.03	7.00±15.73	72.96±117.59	32.12±32.43	
Pb	Range	0.00-87.00	0.00-124.00	0.00-3.60	0.00-88.00	0.00-164.00	0.00-113.00	10.00
	Mean	48.25±43.95	48.00±52.82	0.90±1.80	26.62±32.47	46.33±61.38	36.41±45.05	
Zn	Range	0.00-13.00	0.00-156.00	BDL	0.00-588.00	0.00-180.00	0.00-1107.00	3000.00
	Mean	5.25±6.02	36.00±67.72		171.75±204.91	37.83±69.98	332.13±487.08	

[b] Surface water, [c] ground water, [d] world health organization, [e] below detection limits, ± standard deviation

Similarly, in the study area lead (Pb) concentration in ground water samples ranged from 0.00-88.00, 0.00-113.00, 0.54-170.00, 0.00-676.00, 0.01-815.00, 0.06-168.00, 0.00-124.00 µg/L, although in surface water, it ranged from 0.00-3.60, 0.00-164.00, 0.00-660.00, 0.00-587.00, 0.00-410.00, 0.00-860.00, 0.00-87.00 µg/L (Table 1) in Chakesar, Opal, Ranyal, Lelonai, Alpuri, Dherai and Bele Baba sites, respectively. The maximum Pb (860.00 µg/L) concentration was detected in water samples collected from surface water (Perennial River) in Dherai site. The Pb concentration in 58% samples exceeded their permissible limit set by WHO (2008). Such high concentration may be due to the mafic and ultramafic rocks and Pb/Zn sulfides deposit ores in the study area.

3.3. Health risk assessment

3.3.1. Chronic daily intake

Table 2 (for adults) and 3 (for children) summarizes the CDI values of selected heavy metals in drinking water. CDIs of heavy metals in the study area were identified in the order of Pb> Zn> Ni> Mn> Cr> Cd and Zn> Pb> Mn> Cd> Cr> Ni through consumption of surface and ground water.

The CDIs values of selected heavy metals in Alpurai area for adults were found in the ranged of 0.02-1.11, 0.01-5.55, 0.36-0.88, 0.00-11.38, 0.00-0.55 and 0 (BDL) µg/kg per day for Cr, Ni, Cd, Pb, Mn and Zn, respectively through surface water consumption. Likewise, in ground water it ranged from 0.06-2.50, 0.11-2.31, 0.11-0.97, 0.00-22.64, 0.00-0.61 and 0.00-26.72 µg/Kg per day for Cr, Ni, Cd, Pb, Mn and Zn, respectively (Table 2). Similarly, in children who consumed surface water in Alpurai area, the CDIs ranged from 0.03-1.22, 0.01-6.11, 0.39-0.97, 0.00-12.53, 0.00-0.61 and 0 (BDL) µg/kg per day for Cr, Ni, Cd, Pb, Mn and Zn, respectively. While through ground water consumption, it ranged from 0.06-2.70, 0.12-2.54, 0.11-1.07, 0.00-24.92, 0.00-0.67 and 0.00-29.41 µg/Kg per day for Cr, Ni, Cd, Pb, Mn and Zn, respectively (Table 3).

Whereas, in Dherai area the CDIs values for adults were ranged from 0.00-1.72,0.00-1.19,0.00-0.77,0.00-23-88, 0.00-0.25, 0.00-8.33 and 0.00-2.61,0.00-1.78,0.25-0.41,0.00-4.67, 0.00-0.27and 0.00-14.41 µg/kg per day for Cr, Ni, Cd, Pb, Mn and Zn, respectively through surface and ground water consumption as shown in Table 2. While in children who consumed surface and ground water in Dherai area, the CDIs ranges from 0.00-1.89, 0.00-1.31, 0.00-0.85, 0.00-26.30, 0.00-0.27, 0.00-9.17 and 0.00-2.87, 0.00-1.96, 0.27-0.45, 0.00-5.14, 0.00-0.30 and 0.00-15.87µg/Kg per day for Cr, Ni, Cd, Pb, Mn and Zn, respectively (Table 3).

In Lelonai area the CDIs values for adults were ranged from 0.00-2.19, 0.00-1.36,0.05-0.94, 0.00-16.30, 0.00-0.30, 0.00-0.27 and 0.02-2.36, 0.00-1.67, 0.27-0.58, 0.00-18.78, 0.00-0.27, and 0.00-58.25 µg/kg per day for Cr, Ni, Cd, Pb, Mn and Zn, respectively (Table 2) through surface and ground water consumption contaminated with heavy metals. While in children, it ranged from 0.00-3.21, 0.00-1.49, 0.06-1.03, 0.00-17.95, 0.00-0.30, 0.00-0.30 and 0.02-2.60, 0.00-1.83, 0.30-0.61, 0.00-20.67, 0.00-0.30 and 0.00-64.12 µg/kg per day for Cr, Ni, Cd, Pb, Mn and Zn through surface and ground water consumption, respectively (Table 3).

In Ranyal area the CDIs values for adults who consumed contaminated surface and ground water ranged from 0.00-1.63, 0.00-2.86, 0.00-1.08, 0.00-18.33, 0.00-0.66, 0.00-11.83 and 0.00-0.94, 0.00-0.78, 0.00-0.86, 0.02-4.72, 0.00-2.22 and 0.13-10.33 µg/Kg per day for Cr, Ni, Cd, Pb, Mn and Zn, respectively (Table 2). While in children it ranged from 0.00-1.80, 0.00-3.14, 0.00-1.19, 0.00-20.18, 0.00-0.73, 0.00-12.53 and 0.00-1.04, 0.00-0.86, 0.00-0.94, 0.02-5.20, 0.00-2.44 and 0.15-11.37 µg/Kg per day for Cr, Ni, Cd, Pb, Mn and Zn, respectively (Table 3) through surface and ground water consumption.

In Bele Baba area, the calculated CDIs values for adults through surface water consumption were ranged from 0.00-1.72, 0.01-5.55, 0.16-0.41, 0.00-2.41, 0.11-1.38 and 0.00-0.36 µg/Kg per day for Cr, Ni, Cd, Pb, Mn and Zn, respectively, while through ground water consumption, it ranged from 0.00-1.36, 0.25-1.31, 0.27-0.52, 0.00-3.44, 0.00-0.36 and

0.00-4.33 µg/kg per day for Cr, Ni, Cd, Pb, Mn and Zn, respectively (Table 2). However, in Bele Baba area the CDI value for children were ranged from 0.00-1.89, 0.02- 6.11, 0.12-0.45, 0.00-2.66, 0.12-1.52, 0.00-0.39 and 0.00-1.50, 0.28-1.44, 0.30-0.58, 0.00-3.79, 0.00-0.39 and 0.00-4.77 µg/kg per day for Cr, Ni, Cd, Pb, Mn and Zn through surface and ground water consumption, respectively as shown in Table 3.

In Chakesar area the CDIs values of selected heavy metals for adults were ranged from 0.00-1.69, 0.00-2.19, 0.00-0.44, 0.00-0.10, 0.05-5.83, 0 (BDL) and 0.00-2.50, 0.00-1.25, 0.00-0.63, 0.00-2.44, 0.00-0.72 and 0.00-16.33 µg/kg per day for Cr, Ni, Cd, Pb, Mn and Zn respectively through surface and ground water consumption. Similarly, in Chakesar area the CDIs for children were ranged from 0.00-1.86, 0.00-2.41, 0.00-0.48, 0.00-0.11, 0.00-6.42, and 0 (BDL) µg/kg per day for Cr, Ni, Cd, Pb, Mn and Zn respectively through surface water consumption, while through ground water consumption it ranged from 0.00-2.75, 0.00-1.38, 0.00-0.70, 0.00-2.69, 0.00-3.18 and 0.00-17.98 µg/kg per day for Cr, Ni, Cd, Pb, Mn and Zn respectively (Table 3).

In Opal area, the CDIs values for adults through surface water consumption were ranged from 0.00-0.91, 0.00-8.61, 0.00-0.88, 0.00-4.55, 0.00-0.44 and 0-00-5.00 µg/kg per day for Cr, Ni, Cd, Pb, Mn and Zn respectively. While through ground water consumption it ranged from 0.00-2.64, 0.00-2.00, 0.00-0.94, 0.00-3.14, 0.00-2.69 and 0.00-30.75 µg/kg per day for Cr, Ni, Cd, Pb, Mn and Zn respectively (Table 2). However, in children the CDIs values ranged from 0.00-1.00, 0.00-9.48, 0.00-0.97, 0.00-5.01, 0.00-0.48, 0.00-5.50 and 0.00-2.91, 0.00-2.20, 0.00-1.03, 0.00-3.46, 0.00-5.16 and 0.00-33.85 µg/kg per day for Cr, Ni, Cd, Pb, Mn and Zn through surface and ground water consumption, respectively given in Table 3. In the study area, the CDI values for Cd, Pb, Zn, Mn, Cr and Ni may be attributed to the Pb-Zn sulfide mineralization and mafic and ultramafic bed rocks hosting chromite deposits (Mohammad et al., 2011).

3.3.2. Health risk indices

In the study areas, the HRIs values of Cd for adults through consumption of surface water were 1.2, 0.76, 0.98, 0.71, 0.50, 0.61 and 0.74 respectively, and through consumption of ground water the values were 1.14, 0.66, 0.86, 1.00, 0.74, 0.72 and 0.80. For children through consumption of surface water the values were 1.32, 0.82, 1.08, 0.88, 0.59, 0.68 and 0.80, respectively and through ground water consumption the values were 1.26, 0.72, 0.94, 1.12, 0.80, 0.78 and 0.90 in Alpurai, Dherai, lelonai, Ranyal, Bele Baba, Chakesar and Opal area, respectively given in Table 4. The HRIs values of Cr for adults through consumption of surface water were 4.26E-04, 3.93E-04, 8.80E-04, 5.33E-04, 3.33E-04, 2.80E-04 and 1.40E-04, respectively, and 8.26E-04, 1.15E-03, 6.66E-04, 2.80E-04, 3.86E-04, 4.20E-04 and 3.26E-04, respectively through ground water consumption. For children the HRIs values of Cr were 4.73E-04, 3.60E-04, 9.66E-04, 5.86E-04, 3.66E-043.06E-04 and 1.53E-04, respectively through consumption of surface water and ground water, the values were 9.06E-04, 7.13E-04, 6.66E-04, 2.80E-04, 3.86E-04, 4.20E-04 and 3.60E-04, respectively in all the seven locations.The HRIs values of Mn for adults were 1.21E-03, 5.71E-04, 7.85E-04, 1.78E-03, 3.21E-03, 1.20E-02 and 8.57E-04 respectively through surface water consumption and through ground water consumption, the values were 1.42E-03, 5.00E-04, 6.42E-04, 3.64E-03, 8.57E-04, 3.00E-03 and 6.14E-03 respectively. For children the values were 1.35E-03, 6.42E-04, 7.14E-04, 192E-03, 3.57E-03, 1.32E-02 and 1.00E-03 respectively through surface water consumption and 1.57E-03, 5.71E-04, 7.14E-04, 2.92E-03, 9.28E-04, 3.28E-03 and 6.78E-03,respectively through ground water consumption in the study area.The HRIs values of Ni for adults were 6.95E-02, 2.55E-02, 1.55E-02, 4.25E-02, 8.70E-02, 2.80E-02, 1.01E-01 and 4.65E02, 3.15E-02, 2.25E-02, 1.25E-02, 3.30E-02, 9.50E-03 and 4.45E-02 respectively through surface and ground water consumption. For children the HRIs values of Ni through consumption of surface and ground water were 7.65E-02, 2.85E-02, 1.70E-02, 4.65E-02, 9.55E-02, 3.10E-02, 1.11E-01 and 5.15E-02, 3.45E-02, 2.45E-02, 1.35E-02, 3.60E-02, 1.05E-02 and 4.90E-02 respectively in all areas. The HRIs of Pb for adults through surface water consumption were 6.75E-02, 3.61E-01, 6.41E-02, 1.65E-01, 3.72E-02,

5.55E-04 and 3.55E-02 respectively and through ground water consumption the HRIs of Pb were 8.16E-02, 4.91E-02, 1.13E-01, 5.55E-02, 3.69E-02, 2.01E-02 and 2.80E-02 respectively. For children the HRIs of Pb through surface and ground water consumption were 7.44E-02, 3.98E-01, 8.30E-02, 1.82E-01, 4.08E-02, 5.55E-04, 3.91E-02 and 9.50E-02, 5.41E-02, 1.25E-01, 6.11E-02, 4.05E-02, 2.25E-02 and 3.08E-02 respectively in all the seven locations as shown in Table 4. The HRIs of Zn for adults were 0, 5.26E-02, 3.33E-03, 1.53E-01, 4.66E-03, 0 and 3.46E-02 respectively through surface water consumption and the HRIs of Zn through ground water for adults were 2.09E-01, 813E-02, 2.63E-01, 1.34E-01, 3.33E-02, 1.59E-01 and 3.07E-01 respectively. For children the HRIs of Zn were 0, 5.80E-02, 3.66E-03, 1.69E-01, 5.33E-03, 0 and 3.83E-02 respectively through consumption of surface water and 2.31E-01, 8.83E-02, 2.89E-01, 1.34E-01, 3.66E-02, 1.75E-01 and 3.38E-01 respectively the HRIs of Zn through ground water consumption. In the study area no health risk was found for heavy metals when compared with US EPA (1999) except Cd in Alpurai, lelonai and Ranyal area. The health risk for heavy metals such as Cr, Ni, Mn, Pb and Zn was reported higher than reported by Muhammad et al., 2011 in surface and ground water in Kohistan region, northern Pakistan.

3.4. Inter metal correlation

The inter metal correlation in both surface and ground water is summarized in Table 5. The metal correlation gives us valuable information about the sources and pathways of heavy metals (Khan et al., 2013). In surface water the heavy metal shows significant ($P<0.01$) positive correlation Pb-Zn ($r=0.427$), while in ground water Cr-Ni ($r=0.328$) and Cd-Zn ($r=0.278$) were significant at ($P< 0.05$) as shown in Table 5. The significant correlation between the pairs of heavy metals shows that they originate from the same pollution source (i.e., mafic and ultramafic rocks) and Pb/Zn sulfide ores deposits in the study area (Mohammad et al., 2011).

4. Conclusion

Several anthropogenic and natural sources are considered as the main source of heavy metals contamination in the environment. The heavy metal concentrations were observed in order of Pb> Zn> Ni> Mn> Cr> Cd and Zn> Pb> Mn> Cd> Cr> Ni through consumption of surface and ground water in Shangla District respectively. Mn and Zn were observed within their permissible limit, while Cd, Ni, Cr and Pb exceeded their safe limit set by world health organization. The health risk indices value was observed >1 for Cd and showed possible health risk in Alpurai, Lelonai and Ranyal, while other heavy metals showed HRIs< 1 in the study area. Some of the heavy metals originate from the same polluting source and showed significant ($P<0.01$) positive correlation for Pb-Zn ($r=0.427$), while in ground water Cr-Ni ($r=0.328$) and Cd-Zn ($r=0.278$) were significant at $P< 0.05$. Such high heavy metal contamination in both surface and ground water may be due to geogenic activities (Mafic and Ultramafic rocks and Pb/Zn sulfide ore deposits) in the study area.

It is concluded that Cd in drinking water (both surface and ground) poses potential health risk for the local community of Alpurai, Lelonai and Ranyal, while the other heavy metals exceeded their respective permissible limits but showed no potential health risk in the study area. So it is suggested that contaminated water with heavy metals should not be used for drinking purposes in order to reduce health risk.

Acknowledgment

The financial support was provided by the Higher Education Commission of Pakistan (HEC) in the form of (SRGP 0.5 million) to the first author. The NCE in Geology and University of Swat is highly acknowledged for providing instrumental facility.

Table 2. Chronic daily intakes (CDIs, ug/kg per day) of heavy metals for adults in surface and ground water (na=92).

Heavy metals	Statistics	Alpurai		Dherai		Lelonai		Ranyal		Bele Baba		Chakesar		Opal	
		S. water n=6	G. water n=	S. water n=7	G. water n=6	S. water n=9	G. water n=9	S. water n=5	G. water n=	S. water n=4	G. water n=	S. water n=4	G. water n=	S. water n=6	G. water n=
Cd	Range	0.36-0.88	0.11-0.97	0.00-0.76	0.25-0.41	0.05-0.94	0.27-0.58	0.00-1.08	0.00-0.86	0.16-0.41	0.27-0.52	0.00-0.44	0.00-0.63	0.00-0.88	0.00-0.94
	Mean	0.60±0.10	0.57±0.32	0.38±0.25	0.32±0.14	0.49±0.44	0.43±0.13	0.36±0.62	0.50±0.70	0.25±0.25	0.37±0.09	0.31±0.29	0.36±0.53	0.37±0.46	0.41±0.80
Cr	Range	0.02-1.11	0.06-2.50	0.00-1.72	0.00-2.61	0.00-2.91	0.02-2.36	0.00-1.63	0.00-0.94	0.00-1.72	0.00-1.36	0.00-1.69	0.00-2.50	0.00-091	0.00-264
	Mean	0.64±0.43	1.24±0.91	0.54±0.78	0.97±0.96	1.32±1.08	0.90±0.83	0.80±0.76	0.42±0.46	0.50±0.81	0.58±0.60	0.42±0.84	0.63±1.01	0.21±0.35	0.49±0.89
Mn	Range	0.00-0.55	0.00-0.61	0.00-0.25	0.00-0.27	0.00-0.30	0.00-0.27	0.00-0.66	0.00-2.22	0.11-1.38	0.00-0.36	0.05-5.83	0.00-072	0.00-0.44	0.00-469
	Mean	0.17±0.20	0.20±0.18	0.08±0.11	0.07±0.10	0.10±0.09	0.09±0.10	0.25±0.25	1.38±0.92	0.45±0.62	0.12±0.16	1.68±2.77	0.42±0.25	0.12±0.18	0.86±1.58
Ni	Range	0.01-5.55	0.11-2.31	0.00-1.19	0.00-1.78	0.00-1.3	0.00-1.67	0.00-2.86	0.00-0.78	0.01-5.55	0.25-1.31	0.00-2.19	0.00-1.25	0.00-8.61	0.00-2.00
	Mean	1.39±2.07	0.93±0.70	0.51±0.35	0.63±0.67	0.031±0.42	0.45±0.54	0.85±1.17	0.26±0.33	1.74±2.56	0.66±0.44	0.56±1.08	0.19±0.43	2.02±3.26	0.89±0.89
Pb	Range	0.00-11.38	0.00-22.64	0.00-23.88	0.00-4.67	0.00-16.30	0.00-18.78	0.00-18.33	0.02-4.72	0.00-2.41	0.00-3.44	0.00-0.10	0.00-2.44	0.00-4.55	0.00-3.14
	Mean	2.43±4.48	3.10±7.38	13.04±11.96	1.77±1.77	2.71±5.28	4.10±5.69	5.97±7.22	2.00±2.22	1.34±1.22	1.33±1.46	0.02±0.05	0.73±0.90	1.28±1.70	1.01±1.25
Zn	Range	[b]BDL	0.00-26.72	0.00-8.33	0.00-14.41	0.00-0.27	0.00-58.25	0.00-11.38	0.13-10.33	0.00-0.36	0.00-4.33	BDL	0.00-16.33	0.00-5.00	0.00-30.75
	Mean		6.29±9.30	1.58±3.14	2.40±5.88	0.10±0.11	7.90±19.02	4.61±4.24	4.40±3.85	0.14±0.16	1.00±1.88		4.77±5.69	1.05±1.94	9.22±13.53

[a] Number of samples, [b] below detection limits, ± standard deviation

Table 3. Chronic daily intakes (CDIs, ug/(kg.day)) of heavy metals for children in surface and ground water (na=92)

Heavy metals	Statistics	Alpurai		Dherai		Lelonai		Ranyal		Bele Baba		Chakesar		Opal	
		S. water n=6	G. water n=	S. water n=7	G. water n=6	S. water n=9	G. water n=	S. water n=5	G. water n=6	S. water n=4	G. water n=5	S. water n=4	G. water n=	S. water n=6	G. water n=
Cd	Range	0.39-0.97	0.11-1.07	0.00-0.85	0.27-0.45	0.06-1.03	0.30-0.61	0.00-1.19	0.00-0.94	0.12-0.45	0.30-0.58	0.00-0.48	0.00-0.70	0.00-0.97	0.00-1.03
	Mean	0.66±0.11	0.63±0.58	0.41±0.46	0.36±0.15	0.54±0.49	0.47±0.14	0.43±0.69	0.56±0.77	0.30±0.27	0.40±0.10	0.34±0.32	0.39±0.59	0.4±0.51	0.45±0.88
Cr	Range	0.03-1.22	0.06-2.70	0.00-1.89	0.00-2.87	0.00-3.21	0.02-2.60	0.00-1.80	0.00-1.04	0.00-1.89	0.00-1.50	0.00-1.86	0.00-2.75	0.00-1.00	0.00-2.91
	Mean	0.71±0.47	1.36±1.00	0.54±0.86	1.07±1.06	1.45±1.19	0.99±0.92	0.88±0.84	0.46±0.51	0.55±0.90	0.64±0.67	0.49±0.93	0.70±1.11	0.23±0..39	0.54±0.99
Mn	Range	0.00-0.61	0.00-0.67	0.00-0.27	0.00-0.30	0.00-0.30	0.00-0.30	0.00-0.73	0.00-2.44	0.12-1.52	0.00-0.39	0.06-6.42	0.00-3.18	0.00-0.48	0.00-5.16
	Mean	0.19±0.22	0.22±0.20	0.09±0.12	0.08±0.11	0.10±0.75	0.10±0.12	0.27±0.28	1.52±1.01	0.50±0.68	0.13±0.17	1.85±0.05	1.48±1.14	0.14±0.20	0.95±1.74
Ni	Range	0.01-6.11	0.12-2.54	0.00-1.31	0.00-1.49	0.00-1.49	0.00-1.83	0.00-3.14	0.00-0.86	0.02-6.11	0.28-1.44	0.00-2.41	0.00-1.38	0.00-9.48	0.00-2.20
	Mean	1.53±2.28	1.03±0.77	0.57±0.39	0.69±0.74	0.34±0.47	0.49±0.59	0.93±1.29	0.29±0.36	1.91±2.82	0.73±0.48	0.62±1.19	0.21±0.48	2.23±3.59	0.98±0.99
Pb	Range	0.00-12.53	0.00-24.92	0.00-26.30	0.00-5.14	0.00-17.95	0.00-20.67	0.00-20.18	0.02-5.20	0.00-2.66	0.00-3.79	0.00-0.11	0.00-2.69	0.00-5.01	0.00-3.46
	Mean	2.68±4.93	3.42±8.13	14.36±13.17	1.95±1.95	2.99±5.82	4.52±6.26	6.58±7.95	2.20±2.44	1.47±1.34	1.46±1.61	0.02±0.05	0.81±0.99	1.41±1.87	1.11±1.37
Zn	Range	[b]BDL	0.00-29.41	0.00-9.17	0.00-15.87	0.00-0.30	0.00-64.12	0.00-12.53	0.15-11.37	0.00-0.39	0.00-4.77	BDL	0.00-17.98	0.00-5.50	0.00-33.85
	Mean		6.93±10.24	1.74±3.46	2.64±6.47	0.11±0.12	8.69±20.94	5.07±4.67	4.85±4.24	0.16±0.18	1.10±2.07		5.25±6.26	1.15±2.14	10.15±14.89

[a] Number of samples, [b] below detection limits, ± standard deviation

Table 4.Health risk indices (HRIs) of heavy metals in surface and ground water (na=92) consumption

Parameters	Individuals	Alpurai		Dherai		Lelonai		Ranyal		Bele Baba		Chakesar		Opal	
		S. water n=6	G. water n=9	S. water n=7	G. water n=6	S. water n=9	G. water n=9	S. water n=5	G. water n=6	S. water n=4	G. water n=5	S. water n=4	G. water n=8	S. water n=6	G. water n=8
Cd	Adults	1.20	1.14	0.76	0.66	0.98	0.86	0.71	1.00	0.50	0.74	0.61	0.72	0.74	0.80
	Children	1.32	1.26	0.82	0.72	1.08	0.94	0.88	1.12	0.59	0.80	0.68	0.78	0.80	0.90
Cr	Adults	4.26E-04	8.26E-04	3.93E-04	1.15E-03	8.80E-04	6.66E-04	5.33E-04	2.80E-04	3.33E-04	3.86E-04	2.80E-04	4.20E-04	1.40E-04	3.26E-04
	Children	4.73E-04	9.06E-04	3.60E-04	7.13E-04	9.66E-04	6.60E-04	5.86E-04	3.06E-04	3.66E-04	4.26E-04	3.06E-04	4.66E-04	1.53E-04	3.60E-04
Mn	Adults	1.21E-03	1.42E-03	5.71E-04	5.00E-04	7.85E-04	6.42E-04	1.78E-03	2.64E-03	3.21E-03	8.57E-04	1.20E-01	3.00E-03	8.57E-04	6.14E-04
	Children	1.35E-03	1.57E-03	6.42E-04	5.71E-04	7.14E-04	7.14E-04	1.92E-03	2.92E-03	3.57E-03	9.28E-04	1.32E-02	3.28E-03	1.00E-03	6.78E-03
Ni	Adults	6.95E-02	4.65E-02	2.55E-02	3.15E-02	1.55E-02	2.25E-02	4.25E-02	1.25E-02	8.70E-02	3.30E-02	2.80E-02	9.50E-03	1.01E-01	4.45E-02
	Children	7.65E-02	5.15E-02	2.85E-02	3.45E-02	1.70E-02	2.45E-02	4.65E-02	1.35E-02	9.55E-02	3.60E-02	3.10E-02	1.05E-02	1.11E-02	4.90E-02
Pb	Adults	6.75E-02	8.61E-02	3.61E-01	4.91E-02	6.41E-02	1.13E-01	1.65E-01	5.55E-02	3.72E-02	3.69E-02	5.55E-04	2.01E-02	3.55E-02	2.80E-02
	Children	7.44E-02	9.50E-02	3.98E-01	5.41E-02	8.30E-02	1.25E-01	1.82E-01	6.11E-02	4.08E-02	4.05E-02	5.55E-04	2.25E-02	3.91E-02	3.08E-02
Zn	Adults	[b]BDL	2.09E-01	5.26E-02	8.03E-02	3.33E-03	2.63E-01	1.53E-01	1.22E-01	4.66E-03	3.33E-02	BDL	1.59E-01	3.46E-02	3.07E-01
	Children	BDL	2.31E-01	5.80E-02	8.83E-02	3.66E-03	2.89E-01	1.69E-01	1.34E-01	5.33E-03	3.66E-02	BDL	1.75E-01	3.83E-02	3.38E-01

[a] Number of samples, [b] below detection limits

Table 5. Pearson correlation in surface water and ground water.

Parameters	Cr	Ni	Cd	Mn	Pb	Zn
Surface water						
Cr	1.00	.147	.038	.141	.294	-.159
Ni		1.00	-.044	-.135	.184	-.137
Cd			1.00	-.166	.109	.048
Mn				1.00	-.120	.-.059
Pb					1.00	.427**
Zn						1.00
Ground water						
Cr	1.00	.328*	.250	.198	.049	.224
Ni		1.00	-.033	.108	.123	-.137
Cd			1.00	.142	.156	.278*
Mn				1.00	-.120	.-.065
Pb					1.00	.010
Zn						1.00

**Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

References

Abu-Amr, S.S., Yassin, M.M., 2008.Microbial contamination of the drinking water distribution system and its impact on human health in Khan Yunis Governarate, Gaza strip. Journal Royal Institute of Public Health, 10, 10-16.

Agency for Toxic Substances and Disease Registry (ATSDR), 1993.Toxicological profile for arsenic.TP-92/02. Atlanta, GA, U.S. Department of Health and Human Services.

Arif, M., Jan, M.Q., 2006. The Petro tectonic significance of the chemistry of chromites in the ultramafic–mafic complexes of Pakistan. Journal of Asian Earth Sciences 27, 628–646.

Chrostowski, P.C., 1994. Exposure assessment principles, in: Patrick, D.R., (Ed), Toxic Air Pollution Handbook. Van Nostrand Reinhold. New York. 133- 163.

Das, S., Patnaik, C.S., Sahu, K.H., Chakraborty, A., Sudarshan, M., Thatoi, N.H., 2013. Heavy metal contamination, physico-chemical and microbial evaluation of water samples collected from chromite mine environment of Sukinda, India. Transaction of Non ferrous Metals Society of China, 23, 484-493

GOP, 1998. Population Census Ministry of Population Welfare and National Planning Commission Pakistan Secretariat Islamabad.

Kavcar, P., Sofuoglu, A., Sofuoglu, S.C., 2009. A health risk assessment for exposure to trace metals via drinking water ingestion pathway. International Journal of Hygiene and Environmental Health, 212(2), 216–227.

Khan, K., Lu, Y., Khan, H., Zakir, S., Ullah, I., Khan, S., Khan, A.A., Wei, L., Wang, T., 2013. Health risks associated with heavy metals in the drinking water of Swat, northern Pakistan. Journal of Environmental Sciences, 25(10), 2003-2013.

Khan, S., Haq, F., Saeed, K., 2012. Pollution load in industrial effluent and ground water due to marble industries in district buner, Khyber Pakhtunkhwa, Pakistan. International Journal of Recent Scientific Research, 3(5), 366-368.

Khan, S., Rehman, S., Khan, A.Z., Khan, M.A., Shah, M.T., 2010.Soil and vegetables enrichment with heavy metals from geological sources in Gilgit, northern Pakistan. Ecotoxicology and Environmental Safety, 73(7), 1820–1827.

Khan, S., Shah, I.A., Muhammad, S., Malik,

R.N., Shah, M.T., 2015. Arsenic and Heavy Metal Concentrations in Drinking Water in Pakistan and RiskAssessment: A Case Study, Human and Ecological Risk Assessment: An International Journal, 21(4), 1020-1031.

Krishna, A.K., Satyanarayanan, M., Govil, P.K., 2009. Assessment of heavy metal pollution in water using multivariate statistical techniques in an industrial area: A case study from Patancheru, Medak District, Andhra Pradesh India. Journal of Hazardous Material, 167, 366-373.

Lehloesa, L.J., Muyima, N.Y.O., 2000. Evaluation of the impact of household treatment procedures on the quality of groundwater supplies in the rural community of Victoria district, Eastern Cape: technical note. WATER SA-PRETORIA-, 26(2), 285-290.

Muhammad, S., Shah, M.T., Khan, S. 2011. Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. Microchemical Journal, 98, 334-343.

Nawab, J., Shah, M.T., Khan, S., Qing, H., Khan, K., Ali, R., 2015.Quantification of heavy metals in mining affected soil and their bioaccumulation in native plant species. International Journal of Phytoremediation, 17, 801-813.

Ouyang, Y., Higman, J., Thompson, J., Toole, O.T., Campbell, D., 2002.Characterization and spatial distribution of heavy metals in sediment from Cedar and Ortega Rivers sub-basin. Journal of Contaminant Hydrology, 54, 19-35.

Pekey, H., Karaka, D., Bakoglu, M., 2004. Source apportionment of heavy metals in surface waters of a polluted stream using multivariate statistical analyses. Marine Pollution Bulletin, 49, 809-818.

Shah, M.T., Ara, J., Muhammad, S., Khan, K., Tariq, S., 2012.Health risk assessment via surface water and sub-surface water consumption in the mafic and ultramafic terrain, Mohmand agency, northern Pakistan. Journal of Geochemical Exploration, 118, 60-67.

US Environmental Protection Agency (US EPA), 1999.Guidance for Performing Aggregate Exposure and Risk Assessments, Office of Pesticide Programs, Washington DC.

US EPA, 2005. Guidelines for carcinogen risk assessment. Risk Assessment Forum, United States Environmental Protection Agency, Washington, DC. EPA/630/P-03/001F.

US EPA, 2011. Exposure Factors Handbook.United States Environmental Protection Agency, Washington, DC.EPA/600/R-09/052F.

WHO, 2008.Guidelines for Drinking-Water Quality 3rd edition, Vol.1, Recommendations. World Health Organization, Geneva.