

Potentially toxic elements in drinking water and associated health risk assessment in Abbottabad city, northern Pakistan

Sarib Jadoon^{a,†}, Zakir Hilal^{a,†}, Muhammad Ali^{a,†}, Said Muhammad^{a,b,*}

^aDepartment of Earth Sciences, COMSATS University Islamabad, Abbottabad 22060, Pakistan, Tel. +92 91 9221254–6; Fax: +92 919221228; emails: saidmuhammad1@gmail.com (S. Muhammad), sarib_jadoon@outlook.com (S. Jadoon), zakirhilal101@gmail.com (Z. Hilal), aligeophysix@gamil.com (M. Ali) ^bNational Center of Excellence in Geology, University of Peshawar, Peshawar 25130, Pakistan

Received 25 October 2018; Accepted 3 February 2019

ABSTRACT

Potentially toxic elements (PTE) are contaminants with perilous impacts on environment due to their perseverance, persistence and toxicity. This study aspires to investigate the PTE in drinking water and associated health risk assessment. For this purpose, samples were gathered from various drinking water sources of Abbottabad city, Khyber Pakhtunkhwa, Pakistan. The PTE concentrations were assayed using atomic absorption spectrometer and observed to be in order of iron (Fe) > manganese (Mn) > cobalt (Co) > cadmium (Cd) > zinc (Zn) > nickel (Ni) > copper (Cu) > lead (Pb). Among observed PTE concentrations, the admissible limits established by world health organization were only crossed by Ni, Fe, Pb, Co and Cd. The PTE were evaluated for the potential health risk assessment and source apportionment. The average daily dose (ADD) and hazard quotient (HQ) values were calculated based on PTE concentrations in drinking water, the values of HQ were < 1 for all PTE except Cd. Higher HQ values of PTE could cause hazardous health problems in the study area. Statistical analysis revealed that PTE and other water quality contaminants of the study area were attributed by both geogenic and anthropogenic sources.

Keywords: Drinking water sources; Average daily dose; Hazard quotient; Statistical analysis

1. Introduction

Potentially toxic elements (PTE) contamination in drinking water has become one of the major global environmental issues. The PTE contamination resulted in quality deterioration of both groundwater and surface water [1]. These PTE are derived from natural (erosion and weathering of ore bodies and bedrocks) and anthropogenic (agriculture, mining and industrial activities) sources [2,3]. The discharge of PTE into water bodies have grave repercussions for aquatic life [4]. The PTE contaminated water and food are the prime pathways to human exposure. The bioaccumulation, perniciousness and perseverance of these PTE entitles them to be considered as hazardous contaminants [5,6]. The PTE including zinc (Zn), cobalt (Co), manganese (Mn), copper (Cu) and iron (Fe) are essential for normal functioning and growth of living organisms. Low concentration of these elements could cause deficiency effects and high are harmful. However, PTE like arsenic (As), lead (Pb), nickel (Ni), chromium (Cr) and cadmium (Cd) are considered lethal in minute quantities for human and aquatic life [3,7]. The deleterious effects of PTE include mutagenic, carcinogenic, teratogenic and neurotoxic effects [8,9].

Cobalt is required for normal growth of human body as a fragment of vitamin B_{12} and high concentration cause polycythemia, excessive red blood cell production and atypical thyroid artery [10,11]. The Zn is important for

* Corresponding author.

[†]Authors have contributed equally to this research work.

^{1944-3994/1944-3986} ${\ensuremath{\mathbb C}}$ 2019 Desalination Publications. All rights reserved.

normal functioning of human body, its deprivation can lead to lower efficiency of respiratory muscles, decreased healing of wounds, neurosensory disorders, dermatitis, depression and diarrhea. Excessive intake of Zn can lead to anemia, nausea, lethargy and metal fume fever [11,12]. Mental diseases like Manganism and Alzheimer can occur due to intake of highly contaminated water with Cu and Mn [13]. The Cd intoxication can lead to both acute and chronic health problems [14,15]. Toxic accumulation of Fe can lead to a condition called hemochromatosis which increases risk of liver problems, arthritis, diabetes, heart failure and cancer, if left untreated [16,17]. The Pb is considered to be highly pernicious and carcinogenic and can engender nerve damage, kidney damage, abdominal pain, headaches, gliomas along with lung and blood cancer. Children are more prone to Pb toxicity and it can lead to behavioral complexities, memory degeneration and less comprehension aptitude [18-20]. Similarly, the harmful effect of NO₂ and Cl are including blue baby syndromes and hypertension [21].

Globally, the drinking water contamination has been focused by a number of environmental studies in both developed and developing countries [2,3]. The contamination due to various PTE is more prominent in developing countries due to poor economic conditions, high population growth and low per capita investment on drinking water supply [22]. Drinking water contamination studies are limited and rare in northern Pakistan. Previously, PTE concentration has been determined in wastewater and food crops of Abbottabad that exceeded the permissible limit established by world health organization/food and agriculture organization (WHO/FAO) [23]. However, no attention has been paid to the PTE concentration in drinking water and its associated potential risk assessment of Abbottabad city and surrounding areas. Therefore, this was first and baseline research to determine the quality of drinking water and its associated health risks to the exposed local population. Further, quantitative sources apportionment of PTE in water samples were conducted by various statistical techniques such as one-way ANOVA, inter-element correlation, and principal component analysis (PCA).

2. Material and methods

2.1. Study area

The study area (Abbottabad city) is a part of south-east Hazara with an area of 54 km² in the Khyber Pakhtunkhwa (KPK) province of Pakistan. Abbottabad is located in Orash Valley, geographically stretching from $34.12^{\circ}N-34.23^{\circ}N$ latitude and $73.15^{\circ}E-73.28^{\circ}E$ longitude with elevation of 4,120 feet (Fig. 1) [24]. The agriculture land sporadically lies in valleys surrounded by mountain and hills. The region has a humid sub-tropical climate, with moderate temperature (maximum $38^{\circ}C$) in summer and low temperature (minimum $-5^{\circ}C$) in winters. The region receives scanty snowfall during winter months but hefty rainfall during monsoon season, which causes minor flooding in low lying areas of city. The city averages 1,269 mm (49.95 inch) of precipitation per year [25].

Geologically, the study area is located to the north of Main Boundary Thrust (MBT), south of Panjal Thrust, was Hazara



Fig. 1. Location map of study area, indicating the sampling points in the study area.

Unit trails the Hazara Slates and was ultimately overlain by Abbottabad formation in North and Jurrasic formations in the south [26]. The region is structurally very intricate and has undergone several phases of deformation resulting in various folds and faults. Geological formations range in age from Pre-Cambrian to Paleocene with Hazara Slate, Samana Suk limestone, Kawagarh limestone, Lockart limestone and Abbottabad formation as prominent in study area [27]. The nodules, bands and lenses of phosphate rock deposits are present in Abbottabad formation which cover an area of 30 km² and mined in various locations across Abbottabad [28]. The phosphate rock samples collected in the vicinity of Abbottabad city showed high concentration of Pb, Zn and Cu as compared with other PTE [28,29]. There is indication of small scale Pb mineralization in Abbottabad which represents injection of hydrothermal fluid and material along fractures in host rocks but ore concentration is not adequate enough to support local mining industry [30]. Various phases of Mn and Fe have been identified in the ferromanganese ores, present in the vicinity of Abbottabad city within Hazira formation [31]. There is lot of mining activity in the vicinity that could have possibly resulted in water contamination of Abbottabad city [32].

2.2. Water sampling

Water sources such as bore wells, springs, hand pumps and tube wells were selected for sampling during February 2018. Water from hand pump, tube well and bore well was left to run for 3–5 min before collection of samples. Two low-density polyethylene (LDPE) bottles, pre-washed with 10% nitric acid (HNO₃) and deionized water were filled after 3 times washing with sampling water. One of two bottles for all water samples was filtered through filter paper and adds few drops of nitric acid (HNO₃) on spot. Consort (CONSORT 6030) instrument was used to assay non-acidified samples for physical parameters like Temperature (T), pH, electrical conductivity (EC) and total dissolved solids (TDS) on spot and for anions

393

concentration. All water samples were stored at 4°C and acidified samples were further assayed for PTE intoxication in laboratory as well.

2.3. Analytical techniques

For sample preparation and analysis, analytical grade chemicals with spectroscopic purity of 99.8% were used and 1,000 ppm certified stock solutions of selected PTE and ions were diluted to prepare standard solutions. The concentrations of ions like sulfate (SO₄), nitrate (NO₃) and chloride (Cl) were determined using Ion-selective electrodes (CONSORT 6030). The concentrations of Pb, Ni, Co, Cu, Cd, Fe, Zn and Mn were determined by atomic absorption spectrometer (Perkin Elmer, AAnalyst 700) maintaining standard analytical conditions. The delay and integration time of (AAnalyst 700) was 5 s. The quality control and quality assurance methodology was adopted using blank control, duplicate samples and standard solutions of selected PTE. All water samples were assayed in triplicates with standard deviation ranging within 4% and after every 10 samples; one blank and three standard solutions of respective element was assayed throughout the whole procedure.

2.4. Health risk assessment

Several pathways such as intake through mouth, inhalation and dermal contact were used by the PTE to gain entrance into human body but all pathways are considered negligible beside oral intake [33]. Average daily dose (ADD) of contaminated water consumption was determined by modified equation [34].

$$ADD = C \times IR/W \tag{1}$$

where W, C and IR represent the average body weight (72 kg), PTE concentration in water (μ g L⁻¹) and ingestion rate (2 L d⁻¹), respectively [3].

Chronic risk or hazard quotient (HQ) can be determined by following equation [35]:

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

where oral toxicity reference dose (RfD) values are 3.6E + 01, 2.0E + 01, 3.0E + 01, 1.5E + 03, 5.0E - 01, 7.0E + 02, 3.0E + 02 and 3.7E + 01 for Pb, Ni, Co, Cu, Cd, Fe, Zn and Mn, respectively [36–38]. The exposure is considered safe for HQ values less than one [35].

2.5. Statistical analysis

Descriptive statistics (mean, standard deviation and ranges) were calculated using Microsoft Excel (2015) software. Descriptive statistics revealed that data of physicochemical parameters and PTE passed the Kolmogorov–Smirnov (p > 0.05) test of normality except for Co and Cu. After log-normal distribution, the Cu data passed the Kolmogorov–Smirnov (p > 0.05) test of normality. However, Co data passed the Kolmogorov–Smirnov (p > 0.05) test of normality after a two-step approach was used for its normalization as it failed to pass the Kolmogorov–Smirnov (p > 0.05)

test even after log-normal transformation [39]. Distinct statistical analyzes like one-way ANOVA, inter-metal correlation and PCA were performed in SPSS ver. 25 (SPSS Inc., Chicago, IL, USA). The spatial maps exhibiting PTE concentrations were prepared with IDW interpolation technique using Arc GIS software.

3. Results and discussion

3.1. Physicochemical parameters

The pH and T values ranged 7.20-7.80, 6.90-7.50, 6.60-7.50, 6.80-7.90 and 11.6°C-22.2°C, 17.0°C-19.2°C, 14.0°C-20.6°C 11.3°C-23.0°C in drinking water of bore well, hand pump, springs and tube wells, respectively (Figs. 2 and 3). The highest pH and T values (7.9°C and 23.0°C) were recorded in water collected from the tube well sources of Jharian Road and Hassan Town, TM. The high values of pH can be attributed to leaching of carbonates from surrounding geological formations [40]. However, pH and T values of samples were recorded within the safe limits set by WHO [41]. The values of TDS and EC ranged 189-476, 298-518, 172-377, 198-372 mg L⁻¹, and 385-966, 603-836, 342-809, 403-732 µS cm⁻¹ in drinking water of bore well, hand pump, spring and tube well sources, respectively (Figs. 2 and 3). The highest TDS and EC values (518 mg L⁻¹ and 966 µS cm⁻¹) were recorded in water sample collected from a hand pump and bore well sources of agriculture institute and Stadium Road mosque, respectively. The high TDS and EC values can be attributed to leaching/weathering/erosion of ions from surrounding geological formations and inclusion of leaching material from mining activities [42].

The NO₃ SO₄ and Cl concentrations ranged 5.63–9.46, 8.32–13.9, 6.27–10.2, 5.34–10.5 mg L⁻¹ and 182–381, 201–450, 177–521, 192–486 mg L⁻¹ and 41.9–78.0, 52.9–69.4, 43.6–92.1, 22.8–89.5 mg L⁻¹ in bore well, hand pump, spring and tube well sources, respectively (Figs. 2 and 3). The highest concentrations 13.9, 521 and 92.1 mg L⁻¹ of NO₃, SO₄ and Cl were recorded in water collected from a hand pump and spring water sources of Lambi Dehri and Salhad Chasma, respectively. The source of high values of NO₃, SO₄ and Cl were attributed to ions leaching from geologic formation mining sites by clastic movement through water and wind [42]. The NO₃ and SO₄ concentrations exceeded the drinking water guidelines set by WHO [41] in 40% and 8% of samples in the study area.

The Cd, Pb and Zn concentrations ranged 69–178, BD-16, BD-103, BD-184 μ g L⁻¹, BD-30, BD-38, 35–45, BD-43 μ g L⁻¹ and 19–47, 9–53, 42–95, BD-63 μ g L⁻¹ in bore well, hand pump, spring and tube well sources, respectively (Figs. 2 and 4). The highest Cd, Pb and Zn concentrations 178, 45 and 95 μ g L⁻¹ were recorded in water collected from a tube well and spring sources of Nawanshehr Nare and Mera Mirpur, respectively. The high values of Cd, Pb and Zn can be attributed to enrichment of PTE in bedrocks and surrounding geological formations [43,44]. Result showed that Cd and Pb concentrations surpassed the drinking water guidelines set by WHO [41] in 76% and 76% of water samples of the study area, while that of Zn was under permissible limit.



Fig. 2. Concentrations (°C, μ S cm⁻¹ and mg L⁻¹ for Temperature, EC and anions) of various physicochemical parameters in various drinking water sources of the study area.



Fig. 3. Comparisons (°C, μ S cm⁻¹ and mg L⁻¹ for Temperature, EC and anions) of physicochemical parameters in various drinking water sources and WHO guidelines.



Fig. 4. Concentrations (µg L-1) of various PTE in various drinking water sources of the study area.

The Ni, Co and Cu concentrations values ranged 17-58, BD-10, 15-46, 12-43 µg L⁻¹, 108-223, 45-91, BD-192, 13–253 µg L⁻¹ and 23–77, 13–36, 20–34, 15–34 µg L⁻¹ in bore well, hand pump, spring and tube well sources, respectively (Figs. 2 and 4). The highest Ni, Co and Cu concentrations of 58, 253 and 77 μ g L⁻¹ were recorded in water samples collected from a bore well and tube well sources of Police Colony and Jharian Road, respectively. The high concentrations of these PTE can be attributed to upstream mining and leaching from geogenic sources [3,42]. Results revealed that Ni and Co concentration had surpassed the drinking water standards set by WHO [41] in 60% and 86% of studied water samples, while Cu concentration values did not crossed admissible limits [41] in all of recorded water samples. The concentrations of Cd, Co, Zn and Pb were found higher when compared with findings of Muhammad et al. [33] and Shah et al. [45] in Kohistan and Mohmand agency, northern areas of Pakistan, respectively.

The Fe and Mn concentrations ranged 47–339, 23–245, 218–357, 207–508 µg L⁻¹ and 82–207, BD-179,

100–256, 42–389 μ g L⁻¹ in hand pump, bore well, tube well sources, spring and respectively (Figs. 2 and 4). The Fe and Mn highest concentrations 508 and 389 μ g L⁻¹ were recorded in water samples collected from a tube well source of Salhad Chasma, respectively. The high values of these PTE could have been resulted from weathering/erosions/leaching of surrounding geological formations and run offs including mines drainage and corrosion associated with plumbing systems [46,47]. Results revealed that Mn concentrations were within the safe drinking water standards set by WHO [41], however, that of Fe exceeded in 64% of studied water samples.

3.2. Cadmium and lead as element of concern

In study area, the concentrations of Cd and Pb were observed to be multifold higher than the safe drinking water standards set by WHO [41]. In study area, water samples collected from bore well sources contained higher Cd concentrations as compared with other sources. Similarly, spring water source showed higher concentration values of Pb upon comparison with other water sources (Fig 2(b)). These higher concentrations of Cd and Pb in drinking water samples could be attributed to erosion and weathering of Cd and Pb from bedrocks and mining activities in the vicinity of Abbottabad city [32]. In study area, local inhabitants are utilizing water from bore wells, hand pumps, springs and tube wells for drinking purposes and other household purposes. Therefore, the PTE consumption in drinking could be sources of health problem in local population of the study area.

3.3. Health risk assessment

Local inhabitants were questioned for data related to food intake, drinking water, gender, age, health problems and dietary habits. As a result of interviews, it was concluded that residents were using all type of water sources for drinking and household purposes. The dominant source of drinking water is bore well (over 60%), followed by tube well. Therefore, drinking water samples from all water sources were selected for PTE health risk assessment using (ADD and HQ) indices.

The ADD values showed significant variation among different locations and water sources. Shallow water sources like hand pumps and bore wells showed higher ADD values upon comparison with deep water sources such as tube wells. The higher ADD values can be attributed to their high extent of contamination in those sources. Results showed that inhabitants who consumed water from bore well sources, had calculated ADD values BD-0.83, 0.47–1.61, 3.0–6.19, 0.64–2.14, 1.92–4.94, 0.64–6.81, 0.53–1.31 and BD-4.97 µg kg-d⁻¹, with mean values of 0.48, 0.98, 4.11, 1.02, 3.22,

4.47, 0.86 and 2.44, and µg kg-d⁻¹ for Pb, Ni, Co, Cu, Cd, Fe, Zn and Mn, respectively (Table 1). Likewise, the inhabitants who ingested water from hand pump sources, had ADD values ranged from BD-1.06, BD-0.28, 1.25-2.53, 0.36-1.0, BD-0.44, 1.31-9.42, 0.25-1.47 and 2.28-5.75 µg kg-d⁻¹, with mean values of 0.53, 0.19, 1.72, 0.64, 0.30, 6.63, 0.82 and 3.63, µg kg-d⁻¹ for Pb, Ni, Co, Cu, Cd, Fe, Zn and Mn, respectively (Table 1). The residents who consumed water from spring sources, had ADD values ranged from 0.97-1.25, 0.42-1.28, BD-5.33, 0.56-0.94, BD-2.86, 5.75-14.1, and $1.17-2.64 \ \mu g \ kg \cdot d^{-1}$ with mean values of 1.09, 0.82, 2.82, 0.70,0.75, 10.3, 1.89 and 5.27 µg kg-d⁻¹ for Pb, Ni, Co, Cu, Cd, Fe, Zn and Mn, respectively (Table 1). Similarly, the inhabitants who consumed water from tube well sources had ADD values ranged BD-1.19, 0.33-1.19, 0.36-7.03, 0.42-0.94, BD-5.10, 6.10-9.92, 0-1.75 and 2.78-7.11 μg kg-d⁻¹) with mean values of 0.53, 0.81, 3.42, 0.63, 1.24, 8.54, 1.01 and 5.08 µg kg-d⁻¹ for Pb, Ni, Co, Cu, Cd, Fe, Zn and Mn, respectively (Table 1). Among PTE the highest ADD values were recorded for Fe followed by Mn, owing to their high contamination level in water, while lowest for Ni which can be attributed to its low contamination level.

In study area, HQ indices of PTE through consumption of drinking water were calculated and summarized (Table 2). The HQ indices not only depend on concentration, but also on the toxicity and Rfd value of corresponding PTE. The HQ indices indicate that inhabitants who consumed contaminated water from bore well sources, had the mean HQ values of 1.34E-05, 4.89E-05, 1.37E-04, 2.76E-05, 6.43E-03, 6.39E-06, 2.85E-06 and 1.74E-05 for Pb, Ni, Co, Cu, Cd, Fe, Zn and Mn, respectively (Table 2). Among the water samples taken from bore well sources, the highest

Table 1

Average daily dose (μ g kg-d⁻¹) of PTE through various drinking water sources consumption ($n^a = 62$)

0 , 10 0		Ũ	0		•			
Statistics ADD ^b	Pb	Ni	Co	Cu	Cd	Fe	Zn	Mn
Bore well								
Mean	0.48	0.98	4.11	1.02	3.22	4.47	0.86	2.44
Std D ^c	0.3	0.44	1.3	0.64	1.14	2.52	0.35	1.84
Range	BDd-0.83	0.47 - 1.61	3-6.19	0.64–2.14	1.92-4.94	0.64–6.81	0.53-1.31	BD-4.97
Hand pump								
Mean	0.53	0.19	1.72	0.64	0.3	6.63	0.82	3.63
Std D	0.44	0.13	0.57	0.28	0.2	3.82	0.5	1.61
Range	BD-1.06	BD-0.28	1.25-2.53	0.36-1.00	BDd-0.44	1.31–9.42	0.25-1.47	2.28-5.75
Spring								
Mean	1.09	0.82	2.82	0.7	0.75	10.27	1.89	5.27
Std D	0.11	0.37	1.9	0.16	1.19	4.04	0.57	3.48
Range	0.97-1.25	0.42-1.28	BD-5.33	0.56-0.94	BD-2.86	5.75–14.1	1.17–2.64	1.17-10.8
Tube Well								
Mean	0.53	0.81	3.42	0.63	1.24	8.54	1.01	5.08
Std D	0.42	0.31	1.92	0.16	1.74	1.22	0.72	1.35
Range	BD-1.19	0.33–1.19	0.36–7.03	0.42-0.94	BD-5.1	6.10–9.92	BD-1.75	2.78–7.11

^aNumber of water samples.

^bAverage daily dose.

Standard deviation.

^dBelow detection.

Statistics HQ ^b	Pb	Ni	Co	Cu	Cd	Fe	Zn	Mn
Bore well								
Mean	1.34E-05	4.89E-05	1.37E-04	2.76E-05	6.43E-03	6.39E-06	2.85E-06	1.74E-05
Std D ^c	8.41E-06	2.22E-05	4.33E-05	1.72E-05	2.28E-03	3.59E-06	1.18E-06	1.32E-05
Range	BD ^d -2.31E-05	2.36E-05-8.06E-05	1.00E-04-2.06E-04	1.73E-05-5.78E-05	3.83E-03-9.89E-03	9.13E-07-9.72E-06	1.76E-06-4.35E-06	BD-3.55E-05
Hand pump								
Mean	1.01E-01	1.08E-01	4.59E-01	1.11E-01	4.78E-01	7.33E-02	2.15E-02	1.49E-01
Std D	1.92E-01	2.19E-01	8.99E-01	2.10E-01	4.44E-01	1.43E-01	4.20E-02	2.76E-01
Range	BD-4.44E-01	BD-5.00E-01	4.17E-02-2.07E+00	9.76E-03-4.86E-01	BD-8.89E-01	1.87E-03-3.29E-01	8.33E-04-9.67E-02	1-63E-02-6.43E-01
Spring								
Mean	3.02E-02	4.11E-02	9.41E-02	1.89E-02	1.50E+00	1.47E-02	6.30E-03	3.77E-02
Std D	3.11E-03	1.84E-02	6.33E-02	4.36E-03	2.38E+00	5.78E-03	1.90E-03	2.48E-02
Range	2.70E-02-3.47E-02	2.08E-02-6.39E-02	BD-1.78E-01	1.50E-02-2.55E-02	BD-5.72E+00	8.821E-03-2.02E-02	3.89E-03-8.80E-03	8.33E-03-7.72E-02
Tube well								
Mean	1.48E-02	4.04E-02	1.14E-01	1.69E-02	2.47E+00	1.22E-02	3.36E-03	3.63E-02
Std D	1.16E-02	1.54E-02	6.41E-02	4.36E-03	3.47E+00	1.74E-03	2.40E-03	9.63E-03
Range	BD-3.32E-02	1.67E-02-5.97E-02	1.20E-02-2.34E-01	1.13E-02-2.55E-02	BD-1.02E+01	8.65E-03-1.42E-02	BD-5.83E-03	1.98E-02-5.08E-02
^a Number of wat ^b Hazard quotier ^c Standard devia	ter samples. nt. tion.							

Parameters		Sum of squares	Df ^a	Mean square	F ^b	Significance
pН	Between groups	1.17	3	0.39	4.24	0.017 °
-	Within groups	1.93	59	0.09		
	Total	3.10	62			
Т	Between groups	2.27	3	0.76	0.09	0.965
	Within groups	178	59	8.46		
	Total	180	62			
EC	Between groups	1,72,227	3	57,409	2.30	0.107
	Within groups	5,23,990	59	24,952		
	Total	6,96,217	62			
TDS	Between groups	52,125	3	17,375	2.50	0.087
	Within groups	1,45,843	59	6,945		
	Total	1,97,969	62			
NO	Between groups	44.2	3	14.8	4.76	0.011
3	Within groups	65.1	59	3.10		
	Total	109	62			
SO	Between groups	12,497	3	4.166	0.37	0.778
4	Within groups	2.38.445	59	11.355		
	Total	2,50,942	62			
Cl	Between groups	386	3	129	0.37	0 777
Ci	Within groups	7.354	.59	350	0.07	0.777
	Total	7.740	62	000		
Pb	Between groups	1.685	3	562	3.34	0.039
	Within groups	3,536	59	169		
	Total	5,221	62			
Ni	Between groups	2,058	3	686	4.78	0.011
	Within groups	3,016	59	144		
	Total	5,073	62			
Co	Between groups	24,668	3	8,223	2.02	0.143
	Within groups	85,691	59	4081		
	Total	1,10,359	62			
Cu	Between Groups	0.12	3	0.04	1.82	0.174
	Within Groups	0.46	59	0.02		
	Total	0.57	62			
Cd	Between Groups	30.782	3	10.261	4.04	0.02
	Within Groups	53,330	59	2540		
	Total	84,113	62			
Fe	Between groups	1.26.357	3	42.119	4.57	0.013
10	Within groups	1.93.637	59	9221	1.07	01010
	Total	3.19.994	62	/==1		
Zn	Between groups	4 932	3	1 644	3 43	0.036
2.11	Within Groups	10.066	59	479	0.10	0.000
	Total	14,998	62	±.,		
Mn	Between Groups	39.515	3	13.172	2.43	0.094
	Within groups	1,13,840	59	5,421		
	Total	1,53,355	62	-,		

One-way ANOVA comparison of selected physicochemical parameters for selected water sources in the study area

Mean difference is significant at level of 0.05.

^aDegree of Freedom. ^bFactor.

Table 3

Bold values are significant.

HQ value was recorded for Cd in water sample taken from bore well source of Jinnahabad. The inhabitants who consumed contaminated water from hand pump sources, had the mean HQ values of 1.01E-01, 1.08E-01, 4.59E-01, 1.11E-01, 4.78E-01, 7.33E-02, 2.15E-02 and 1.49E-01 for Pb, Ni, Co, Cu, Cd, Fe, Zn and Mn, respectively (Table 2). In water samples taken from hand pump sources, the highest HQ value was observed for Co collected from Khola Khyal. Similarly, the mean HQ values for residents who consumed contaminated water from spring sources are 3.02E-02, 4.11E-02, 9.41E-02, 1.89E-02, 1.50E+00, 1.47E-02, 6.30E-03 and 3.77E-02 for Pb, Ni, Co, Cu, Cd, Fe, Zn and Mn, respectively (Table 2). The highest HQ value in water samples taken from spring sources was record for Cd in water sample taken from Imam Bargah. The residents who consumed contaminated water from tube well sources, had the mean HQ values of 1.48E-02, 4.04E-02, 1.14E-01, 1.69E-02, 2.47E+00, 1.22E-02, 3.63E-02 and 3.36E-03 for Pb, Ni, Co, Cu, Cd, Fe, Zn and Mn, respectively (Table 2). From tube well sources, the highest HQ value was record for Cd in water sample taken from Nawansheher nare. Upon comparison of HQ values in all water samples, it was observed that Cd showed high mean HQ values, followed by Co, while Zn showed the lowest ones. The high HQ value of Cd and Co can be attributed to their toxicity, concentration and corresponding PTE Rfd values. The HQ indices of all PTE indicate no chronic risk to local population when compared with USEPA [48], except for HQ indices of Cd for tube well and spring sources whose value was > 1. However, the HQ indices of Cd and Pb were found higher than those reported by Muhammad et al. [33] and Shah et al. [45] in Kohistan and Mohmand agency regions of Pakistan, respectively.

3.4. Statistical analysis

Upon comparison of PTE contamination levels from selected water sources using one-way ANOVA, significant statistical variation (p < 0.05) was found, which indicates that different sources participate differently or significantly in mean element contamination of drinking water (Table 3).

Table 4 summarizes the correlation of various physicochemical parameters and PTE. Upon correlation analysis, positive significant correlation were shown by various PTE and parameter pairs like EC-TDS (r = 0.882), Fe-Cd (r = 0.418), Co-Ni (r = 0.510), Cu-Ni (r = 0.504), Zn-Pb (r = 0.488), Cu-Co (r = 0.950), Zn-Fe (r = 0.402) and Pb-Zn (r = 0.488), while some pairs have shown negative significant correlation like Cd-Pb (r = -0.479), Fe-Cd (r = -0.418) and Zn-pH (r = -0.487).

Quantitatively evaluated results using PCA with varimax normalized rotation (PCA-V) are summarized in Table 5. The PCA analysis of various physicochemical parameters and PTE indicate their grouping and association with three factors in drinking water from all water sources. The three factors have shown total cumulative variance of 54.617%. Factor-1 contributed 20.118% to the total variance with a high loading on NO₂ (r = 0.182), Fe (r = 0.851), Mn (r = 0.851), Pb (r = 0.700) and Zn (r = 0.649) as shown in Table 5. The sources of NO₃, Fe, Mn, Pb and Zn could be the weathering/leaching/ erosions of minerals from bedrocks/ore deposits and mining activities in the vicinity of Abbottabad city, suggesting that factor-1 can be attributed to geogenic and anthropogenic sources. Factor-2 contributed 17.924% to the total variance with a high loading on TDS (r = 0.874), EC (r = 0.891), SO₄ (r = 0.362) and Cd (r = 0.224) as shown in Table 5. The values of TDS, EC, SO₄ and Cd are probably influenced by agriculture and plumbing in the vicinity of Abbottabad city, suggesting

Table 4 Correlation matrix of selected physicochemical parameters in drinking water ($n^a = 62$)

Parameters	Т	PH	EC	TDS	NO ₃	SO_4	Cl	Pb	Ni	Со	Cu	Cd	Fe	Zn	Mn
Т	1														
PH	0.047	1													
EC	0.394	0.261	1												
TDS	0.312	0.166	0.882 ^c	1											
NO ₃	-0.229	-0.160	-0.111	0.074	1										
SO_4	0.126	0.036	0.081	0.034	-0.012	1									
Cl	0.073	0.076	-0.091	-0.062	0.097	0.037	1								
Pb	-0.210	0.045	-0.043	-0.056	0.158	0.055	0.100	1							
Ni	-0.076	0.315	-0.162	-0.348	-0.384	0.077	0.174	-0.002	1						
Со	0.195	0.207	0.173	0.159	-0.208	-0.107	0.039	-0.021	0.510	1					
Cu	0.123	0.210	0.124	0.117	-0.150	-0.207	0.042	-0.156	0.504	0.950	1				
Cd	0.185	0.024	0.127	0.095	-0.073	0.128	-0.022	-0.479	-0.067	-0.092	-0.020	1			
Fe	-0.029	-0.151	0.021	0.120	0.212	0.230	0.051	0.377	0.088	0.017	-0.057	-0.418	1		
Zn	-0.312	-0.487^{b}	-0.156	-0.149	0.097	0.068	-0.094	0.488	0.055	0.211	0.141	-0.318	0.402		
Mn	0.181	0.097	0.263	0.283	-0.168	0.364	0.071	0.280	0.132	0.077	-0.060	-0.450	0.759	0.109	1

^aNumber of water samples.

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

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

Table 5

Factor loading for selected physicochemical parameters in drinking water $(n^a = 62)$

Parameters	Factor 1	Factor 2	Factor 3
pН	-0.214	0.286	0.334 ^b
EC	-0.073	0.891	0.002
TDS	-0.017	0.874	-0.111
NO ₃	0.182	-0.105	-0.424
SO ₄	0.328	0.362	-0.037
Cl	0.076	-0.039	0.121
Pb	0.700	-0.172	-0.147
Ni	0.098	-0.211	0.789
Со	0.070	0.127	0.897
Cu	-0.063	0.049	0.887
Cd	-0.729	0.224	-0.009
Fe	0.851	0.193	-0.012
Zn	0.649	-0.310	0.100
Mn	0.723	0.484	0.093
Eigen values	3.028	2.689	2.476
% of variance	20.188	17.924	16.506
Cumulative %	20.188	38.111	54.617

^aNumber of water samples.

^bBold values represent dominant physicochemical parameters in factor.

that factor-2 can be attributed to anthropogenic sources. Factor-3 contributed 16.506% to the total variance with a high loading on pH (r = 0.334) and Cl (r = 0.121), Co (r = 0.897), Cu (r = 0.887) and Ni (r = 0.789) as shown in Table 5. The values of pH, Cl, Co, Cu and Ni are probably influenced by weathering/leaching/erosions of minerals from bedrocks/ore deposits in the vicinity of Abbottabad city. It means that factor-3 can be attributed to geogenic sources only.

4. Conclusion

In study area, PTE concentration levels were observed to be in order of Fe>Mn>Co>Cd>Zn>Ni>Cu>Pb in drinking water. Majority of physicochemical parameters like T, pH, EC, TDS, SO₄, NO₂ and PTE such as Cu, Mn and Zn were within the admissible safety standards set by WHO. Although, PTE like Cd, Co, Fe, Ni, and Pb exceeded safety standards set by WHO in 76%, 86%, 64%, 60% and 76% of drinking water samples, respectively. The health risk assessment revealed no possible chronic health risk upon comparison with US EPA (HQ < 1) for all physicochemical parameters except for Cd (HQ > 1). The one-way ANOVA analysis concluded that different sources of drinking water were contributing differently or significantly to the mean metal concentration (p < 0.05), spring sources are significantly highly contaminated as compared to other sources of drinking water. The PCA analysis attributed element contamination to both geogenic (weathering/leaching/erosion) and anthropogenic (agriculture/mining activities) sources. This study strongly recommended that water from contaminated sources should not be used for drinking purposes and alternative sources need to be provided by government in affected areas.

Acknowledgments

This research work was financially supported by COMSATS University Abbottabad. The Department of Environmental Sciences, COMSATS University Abbottabad is thankfully acknowledged for providing the instrumental support. We also thank the anonymous reviewers for their comments which improved the quality of manuscript.

Conflict of interest

Authors declare that there are no conflicts of interest.

References

- A.K. Krishna, M. Satyanarayanan, P.K. Govil, 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, J. Hazard. Mater., 167 (2009) 366–373.
- [2] A. Demirak, F. Yilmaz, A.L. Tuna, N. Ozdemir, Heavy metals in water, sediment and tissues of Leuciscus cephalus from a stream in southwestern Turkey, Chemosphere, 63 (2006) 1451–1458.
- [3] K. Khan, Y. Lu, H. Khan, S. Zakir, S. Khan, A.A. Khan, L. Wei, T. Wang, Health risks associated with heavy metals in the drinking water of Swat, northern Pakistan, J. Environ. Sci., 25 (2013) 2003–2013.
- [4] F.A. Alkarkhi, N. Ismail, A.M. Easa, Assessment of arsenic and heavy metal contents in cockles (*Anadara granosa*) using multivariate statistical techniques, J. Hazard. Mater., 150 (2008) 783–789.
- [5] H. Pekey, D. Karakaş, M. Bakoglu, Source apportionment of trace metals in surface waters of a polluted stream using multivariate statistical analyses, Mar. Pollut. Bull., 49 (2004) 809–818.
- [6] M. Ishtiaq, N. Jehan, S.A. Khan, S. Muhammad, U. Saddique, B. Iftikhar, Potential harmful elements in coal dust and human health risk assessment near the mining areas in Cherat, Pakistan, Environ. Sci. Pollut. Res. Int., 25 (2018) 14666–14673.
- [7] Y. Ouyang, J. Higman, J. Thompson, T. O'Toole, D. Campbell, Characterization and spatial distribution of heavy metals in sediment from Cedar and Ortega rivers subbasin, J. Contam. Hydrol., 54 (2002) 19–35.
- [8] R.K. Sharma, M. Agrawal, F.M. Marshall, Heavy metal (Cu, Zn, Cd and Pb) contamination of vegetables in urban India: a case study in Varanasi, Environ. Pollut., 154 (2008) 254–263.
- [9] A.K. Patra, S. Wagh, A. Jain, A. Hegde, Assessment of daily intake of trace elements by Kakrapar adult population through ingestion pathway, Environ. Monit. Assess., 169 (2010) 267–272.
- [10] G. Robert, G. Mari, Human health effects of metals, in: US Environmental Protection Agency Risk Assessment Forum, Washington, DC, 2003.
- [11] S. Strachan, Trace elements, Curr. Anaesth. Crit. Care., 21 (2010) 44–48.
- [12] L.M. Plum, L. Rink, H. Haase, The essential toxin: impact of zinc on human health, Int. J. Environ. Res. Public. Health., 7 (2010) 1342–1365.
- [13] H.H. Dieter, T.A. Bayer, G. Multhaup, Environmental copper and manganese in the pathophysiology of neurologic diseases (Alzheimer's disease and Manganism), Acta. Hydrochim. Hydrobiol., 33 (2005) 72–78.
- [14] C. Compounds, Beryllium, cadmium, mercury, and exposures in the glass manufacturing industry, IARC Monogr. Eval. Carcinog. Risks. Hum., 58 (1993) 119–237.
- [15] J.J. Barbee, T. Prince, Acute respiratory distress syndrome in a welder exposed to metal fumes, South. Med. J., 92 (1999) 510–512.
- [16] A. Pietrangelo, Hereditary hemochromatosis: pathogenesis, diagnosis, and treatment, Gastroenterology, 139 (2010) 393–408. e392.

- [17] R.E. Fleming, P. Ponka, Iron overload in human disease, N. Engl. J. Med., 366 (2012) 348-359.
- [18] K. Steenland, P. Boffetta, Lead and cancer in humans: where are we now?, Am. J. Ind. Med., 38 (2000) 295-299.
- [19] W. Mortada, M. Sobh, M. El-Defrawy, S. Farahat, Study of lead exposure from automobile exhaust as a risk for nephrotoxicity among traffic policemen, Am. J. Nephrol., 21 (2001) 274-279.
- [20] L. Järup, Hazards of heavy metal contamination, Br. Med. Bull., 68 (2003) 167-182.
- [21] S. Khan, M. Shahnaz, N. Jehan, S. Rehman, M.T. Shah, I. Din, Drinking water quality and human health risk in Charsadda district, Pakistan, J. Clean. Prod., 60 (2013) 93-101.
- [22] L. Fewtrell, R.B. Kaufmann, D. Kay, W. Enanoria, L. Haller, J.M. Colford Jr, Water, sanitation, and hygiene interventions to reduce diarrhoea in less developed countries: a systematic review and meta-analysis, Lancet. Infect. Dis., 5 (2005) 42–52.
- [23] N.U. Hassan, Q. Mahmood, A. Waseem, M. Irshad, A. Pervez, Assessment of Heavy Metals in Wheat Plants Irrigated with Contaminated Wastewater, Polish. J. Environ. Stud., 22 (2013) 115-123.
- [24] R. Authority, Abbottabad: District profile, in, Earthquake Reconstruction and Rehabilitation Authority (ERRA), 2007.
- [25] Weatherbase., Weather records and averages, (2010).[26] M. Coward, R. Butler, Thrust tectonics and the deep structure of the Pakistan Himalaya, Geology, 13 (1985) 417-420.
- [27] R. Bilgees, T. Tahirkheli, N. Pirzada, S.M. Abbas, Industrial applications of Abbottabad limestone; utilizing its chemical and engineering properties, J. Himalaya. Earth. Sci., 45 (2012) 91–96.
- [28] F. Faridullah, M. Umar, A. Alam, M.A. Sabir, D. Khan, Assessment of heavy metals concentration in phosphate rock deposits, Hazara basin, Lesser Himalaya Pakistan, Geosci. J., 21 (2017) 743-752.
- [29] T. Mehmood, M. Chaudhry, M. Tufail, N. Irfan, Heavy metal pollution from phosphate rock used for the production of fertilizer in Pakistan, Microchem. J., 91 (2009) 94-99.
- [30] F. Shams, Lead mineralization in the Abbottabad area, Hazara District, West Pakistan, Econ. Geol., 58 (1963) 605-608.
- [31] M.T. Shah, C.J. Moon, Mineralogy, geochemistry and genesis of the ferromanganese ores from Hazara area, NW Himalayas, northern Pakistan, J. Asian. Earth. Sci., 23 (2004) 1-15.
- [32] A. Raza, I.A. Raja, S. Raza, Land-use change analysis of district Abbottabad, Pakistan: taking advantage of GIS and remote sensing analysis, Sci. Vis., 18 (2012) 43-49.
- [33] S. Muhammad, M.T. Shah, S. Khan, Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan, Microchem. J., 98 (2011) 334-343.
- [34] I. DDT, D. DDE, USA: US Environmental Protection Agency; 1998, US EPA Integrated Risk Information System. Silverplatter, 3.
- [35] S. Khan, Q. Cao, Y. Zheng, Y. Huang, Y. Zhu, Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China, Environ. Pollut., 152 (2008) 686-692.

- [36] U.S. Environmental Protection Agency, R.A. Forum, Guidelines for carcinogen risk assessment, in, Risk Assessment Forum, US Environmental Protection Agency, 2005.
- [37] U.S. Environmental Protection Agency, Marc and M Klotzbach, Julie and Ingerman, L and Thayer, William and Diamond, G L, Provisional Peer Reviewed Toxicity Values for Iron and Compounds (CASRN 7439-89-6) Derivation of Subchronic and Chronic Oral RfDs., Office of Research and Development, National Center for Environmental Assessment, Superfund Health Risk Technical Support Center, (2006).
- [38] B.L. Finley, A.D. Monnot, D.J. Paustenbach, S.H. Gaffney, Derivation of a chronic oral reference dose for cobalt, Regul Toxicol Pharmacol., 64 (2012) 491-503.
- [39] G.F. Templeton, A two-step approach for transforming continuous variables to normal: implications and recommendations for IS research, CAIS, 28 (2011) 41-58.
- [40] H.A. Aziz, M.N. Adlan, K.S. Ariffin, Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr (III)) removal from water in Malaysia: post treatment by high quality limestone, Bioresour. Technol., 99 (2008) 1578-1583.
- [41] World Health Organization (WHO), Guidelines for drinkingwater quality: second addendum. Vol. 1, Recommendations, 2008
- [42] M.C. Jung, Heavy metal contamination of soils and waters in and around the Imcheon Au-Ag mine, Korea, Applied. Geochem., 16 (2001) 1369-1375.
- [43] U. Rehman, S. Khan, S. Muhammad, Associations of potentially toxic elements (PTEs) in drinking water and human biomarkers: a case study from five districts of Pakistan, Environ. Sci. Pollut. Res. Int., 25 (2018) 27912-27923.
- [44] M. Nafees, M. Jan, H. Khan, N. Rashid, F. Khan, Soil contamination in Swat valley caused by cadmium and copper, Sarhad. J. Agr., 25 (2009) 37-43.
- [45] M. Shah, J. Ara, S. Muhammad, S. Khan, S. Tariq, Health risk assessment via surface water and sub-surface water consumption in the mafic and ultramafic terrain, Mohmand agency, northern Pakistan, J. Geochem. Explor., 118 (2012) 60 - 67
- [46] H.-S. Lim, J.-S. Lee, H.-T. Chon, M. Sager, Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au-Ag mine in Korea, J. Geochem. Explor., 96 (2008) 223-230.
- [47] S. Khan, S. Rehman, A.Z. Khan, M.A. Khan, M.T. Shah, Soil and vegetables enrichment with heavy metals from geological sources in Gilgit, northern Pakistan, Ecotoxicol. Environ. Safe., 73 (2010) 1820-1827.
- [48] USEPA, Guidance for performing aggregate exposure and risk assessments, in, Office of Pesticide Programs Washington, DC, USA, 1999.