Contamination Level, Source Identification And Health Risk Assessment of Potentially Toxic Elements In Drinking Water Sources of Mining And Non-Mining Areas of Khyber Pakhtunkhwa, Pakistan

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Contamination level, source identification and health risk assessment of potentially toxic elements in drinking water sources of mining and non-mining areas of Khyber Pakhtunkhwa, Pakistan

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Abstract

Accelerated mining activities have increased water contamination with potentially toxic elements (PTEs) and their associated human health risk in developing countries. The current study investigated the distribution of PTEs, their potential sources and health risk assessment in both ground and surface water sources in mining and non–mining areas of Khyber Pakhtunkhwa, Pakistan. Water samples (n=150) were taken from selected sites and were analyzed for six PTEs (Ni, Cr, Zn, Cu, Pb and Mn). Among PTEs, Cr showed high mean concentration (497) µg L^{-1}, followed by Zn (414) µg L^{-1} in mining area, while Zn showed lowest mean value (4.44) µg L^{-1} in non-mining areas. Elevated concentrations of Ni, Cr and moderate level of Pb in ground and surface water of Mohmand District exceeded the permissible limits set by WHO (2017). Multivariate statistical analyses showed that pollution sources of PTEs were mainly from mafic-ultramafic rocks, acid mine drainage, open dumping of mine-wastes and mine tailings. The hazard quotient (HQ) was highest for children relatively to adults, but not higher than the US-EPA limits. The hazard index (HI) for ingestions of all selected PTEs were lower than the threshold value (HI_{ing} <1), except Mohmand District which showed (HI >1) in mining areas through ingestion. Moreover, the carcinogenic risk (CR) values exceeded the threshold limits for Ni and Cr set by the US-EPA (1.0E−04 to 1.0E−06). In order to protect the drinking water sources of the study areas from more contamination, the management techniques and policy for mining operations need to be implemented.

Keywords*:* PTEs, Source apportionment, Health risks, Drinking water resources, Mining and Non-Mining areas

Introduction

Water is one of the essential natural resources for human life and development, and an important part of the biological system. Less than 3% of the total water resources are freshwater resources, and only less than 1% is usable for human use (Saleh et al. 2019). In sustaining aquatic and terrestrial life, freshwater resources play an unavoidable role and are directly linked to drinking, agriculture, and aquaculture (Pilotto et al. 2019). Water resources could be vulnerable to potentially toxic elements (PTEs) contamination in the environment (Ciazela et al. 2018). In fresh water ecosystems, PTEs have become one of the most toxic chemicals due to their persistence in nature (Strungaru et al. 2018). PTEs are released to environment by anthropogenic activities including mining, smelting, metallurgical and industrial beneficiation processes, excavation, and transportation lead to further contaminate the surrounding environment (Santana et al. 2020; Nawab et al. 2017, 2019; Vinod et al. 2019; Oyebamiji et al. 2018; Zhang et al. 2017; Li et al. 2014). Natural processes also result in occurrence of PTEs due to complex physiochemical reactions by weathering of parent rocks, oxidation, minerals dissolution, and migration of acid mine drainage containing high contents of PTEs that could extremely affect and deteriorate the geochemical surrounding environment, and reach to the groundwater by erosion or leaching process (Nawab et al. 2018a; Kefeni et al. 2017; Moye et al. 2017), as well as natural geochemical impacts created by mining operations, could alters and affect the surface and groundwater quality for decades on regional basis, even after closing the mining activities (Baeten et al. 2018). Freshwater resources are mostly susceptible to the direct impacts of mining in the environment (Santana et al. 2020).

Mining operations are considered as the most influential anthropogenic activities which could damages the natural habitats, and degrade the land resources, result in soil and water contamination with PTEs (Shifaw 2018). For instance, the mine tailings are exposed to the agriculture lands of non-mining areas, resulting to serious pollution by dispersion and mobilization of PTEs (Zhu et al. 2018). As a result, the PTEs including Pb, Cd, As, Cu and Zn could discharge to rivers due to surface runoff by wastewater or excess of rainwater, leading to contaminate the waterbodies and aquatic ecosystem (Mohammadnejad et al. 2018). In spite of these natural processes, improper treatment of abandoned old mines as well as mine tailings may pose more PTEs pollution in adjacent (non-mining) regions of agricultural soils, surface water and groundwater (Wang et al. 2019; Sun et al. 2018; Queiroz et al. 2018). Numerous studies have been conducted on PTEs contamination in mining and adjacent non-mining surrounding areas (Santana et al. 2020; Wang et al. 2019; Wang et al. 2019). Previous studies of abandoned mines, and tailing ponds showed the high contents of PTEs in mining areas and lead to contaminate the local soil, and rivers water due to mobilization of mining wastes (Shen et al. 2019). Due to these factors, mining is perceived to be one of human activities with the biggest detrimental effects on the environment (Paraguassú et al. 2019). Therefore, a comparative study is needed to conduct the assessment of PTEs distribution in mining and non-mining areas, by identifying their potential sources contributed to contaminate the surface and groundwater sources.

Groundwater pollution has been recognized as an actual route to transfer pollutants to surface water sources (Xiao et al. 2019; Adyasari et al. 2018). The pollutants such as PTEs can migrate more readily through water sources and drastically decrease the consistency of water in rivers, reservoirs and groundwater (Northey et al. 2016). Elevated concentrations of PTEs could deteriorate water quality and pose significant public health risks due to their toxicity, persistence and bio–accumulative nature (Yang et al. 2018; Alves et al. 2018; Muhammad et al. 2011), and adversely impact human health (Rehman et al. 2018). For instance, high concentration of toxic PTEs in surface and groundwater may have unforeseeable adverse effects on people of all age classes, particularly in children (Yang et al. 2013). Further, it has been well known that long–term exposure to toxic PTEs can result in adverse effects on the nervous, immune, and endocrine systems (Li et al. 2014), and lead to cancer or disability in both children and adults (Wu et al. 2018; Patlolla et al. 2012). And other health problems such as stomach and heart diseases, hypertension, and anorexia (Qian et al. 2020). Chronic PTEs toxicity has adverse effects on human health, such as lung disease, renal failure, bone fracture, and may lead to hypertension, fertility and hormonal, immune, liver function, and endocrine system deficiency (Yuanan et al. 2020). To understand this kind of threat, it is important to evaluate the surface and groundwater quality by means of PTEs distribution in disaster prone mining and non-mining areas and their associated health risk.

In Pakistan, most of the mining sites are located in high mountainous and rural regions where people are illiterate, poor, and mostly unaware of the health impacts of mining. The open dumping practices of mine-wastes are common in Pakistan, leading to impact the agricultural soils by surface runoff, erosion and landslides (Nawab et al. 2018b). Major developments were made in recent times in the evaluation of the threat and effect of mine-impacted water and even in the remediation technological tools to minimize the burden of point source pollution of mining water on groundwater and surface water (Liu and Li 2019). Significant environmental evaluation of water resources is still required as water contamination of PTEs contributes to over–exploitation of groundwater and surface water. The local inhabitants have been using drinking water from both the (surface and groundwater) sources in Khyber Pakhtunkhwa (KPK) newly merged districts of Pakistan. In the previous administrative system, the newly merged districts were termed as agencies and had separate laws and regulations. For this reason, the quality and exposure assessment of contaminated surface water and groundwater are important before its utilization in mining and non-mining regions of three newly merged districts including (Mohmand, Bajaur and Khyber) in KPK province. Therefore, the primary objectives of the present study were (i) to investigate the PTEs distribution in surface, and groundwater of mining and non-mining areas (ii) to identify the potential sources of PTEs by multivariate statistical methods, and (iii) to evaluate the health risks assessment of PTEs for inhabitants of the study area. Our findings would provide a solid framework for further decision–making to take the appropriate steps to manage contamination in order to protect the quality of drinking water and to prevent public health hazards from the source of drinking water.

Materials and Methods

Study Area Description

The study area of Mohmand, Khyber and Bajaur Districts is located in Khyber Pakhtunkhwa province of Pakistan. Mohmand District is located in Peshawar division at latitude of 34° 22' 20" N and longitude 71° 27' 26" E, and the region is geographically made up of mountainous ranges with rocky hills and scattered along the sides of the Kabul River. The Lower Mohmand region is very fertile, while the Upper area is generally less productive. Much farmlands are rain–fed with adequate rainfall. Mohmand chromite reserves are primarily located within harzbergite and dunite system containing metagabbro minerals, which extend through Dargai across Skhakot to Mohmand DistrictDistrict as linear chain of approximately 60 km in width and 2–6 km in length. Almost all of the dunite sandstones are barren, but chromites mostly occur in lowest layer in areas and bands are well known in the region. The entire ultramafic complex is sporadically crossed by a thin pyroxenite dyke. In locations tremolite veins and talc–carbonate and quartz are common (Rafiq et al. 1984; Uppal 1972).

The Bajaur District is situated in Malakand division at 34° 41′ 0′ N, 71° 30′ 0′ E in the northern region of Khyber Pakhtunkhwa province (Fig. 1). Regionally, it is a situated region in east of the Kunar Valley in Afghanistan and sharing borders with the Malakand District in the south–east, the Dir district in the north–east and the Mohmand District in the south (FATA 2014). It has a surface area of 1,290 km^2. About 40% of the District's territory is protected by desolate mountains and 60% by broad valleys (Government of KPK 1994). Crop farming, small–scale enterprise and skilled employment are the primary forms of jobs. The region has simple to medium igneous minerals, which are pyroxenite, goethite, pegmatite, norite, hypersthene, granite and diorite. The middle section of Bajaur consists of Kamila amphibolites, diorites and a few tiny flecks of granodiorites, whereas the southern part is inhabited by the Main Mantle Thrust (MMT) region. The MMT region consists of volcanic, ultramafic, granite, marble, gneiss, salt, calcareous shale, quartzite, respectively (Ullah et al. 2017).

The Khyber District is located at 34.02° N latitude and 71.28° E longitude with total elevation of 1070 m, and area of 2.567 km^2. The temperature ranges from 25°C (77°F) to over 40°C (104°F) in summer and from 4°C to 18.35°C in winter. Its boundaries Peshawar to the east, Afghanistan to the west, Orakzai to the south and Kurram to the southwest. It has an area of 2,576 sq km with a population of 8, 45,309 people. Sedimentary rocks at the Khyber District contain granite tiles, granite, dolomite, sand, barite, malachite, graphite and quartz. Mullagori marble is among the largest deposits in the study field, and soapstone is the second largest element in the area (Khan 2001). The region has a very small manufacturing base, oil mills, tobacco factories, steel plants and marble factories in Barra, Shakas Jamrud and Mullagori are the main industries in the district.

Samples Collection

A total (n=150) of drinking water samples were collected from Mohmand, Bajaur and Khyber (50 each from these Districts) in January 2018, from the surface water and groundwater sources. All the water samples were collected from different sources including water pumps, bore wells, dug wells, tap water, hand pumps, and spring water. Sampling sites were chosen on the basis of mining operations in the surrounding areas and non–mining areas. All the water samples were collected in pre-washed high density 500 mL polyethylene bottles, containing 10% nitric acid (HNO_3) solutions. Before water sampling, water from water pumps, bore wells, and tap water were allowed to continuously run for few minutes, according to procedure adopted by (Khan et al. 2013). The geographical location of the samples was recorded using the GPS coordinates. Water samples were acidified with HNO3 to pH <2 to minimize microbial growth, precipitation and solubility of PTEs in container walls. While sampling, every bottle was labelled and then were immediately transported to the laboratory and stored at 4 °C for further analyses (Ullah et al. 2019).

Analytical Procedure

The water samples were analyzed for selected PTEs such as Ni, Cr, Zn, Cu, Pb and Mn by graphite furnace atomic absorption spectrophotometer (PerkinElmer, USA, ASS-PEA-700) through the standard conditions. The acids and reagents used in the study were 99.9 % analytical grade with spectroscopic purity (Merck Darmstadt, Germany). For the study of PTEs, the samples were transformed to a pH standard of <2 with conc. HNO_3 as a preservative for further analysis. The standard solutions of PTEs were prepared by diluting 1000 mg/L standard certified solution (Fluka Kamica, Buchs, Switzerland).

Data Precision and Accuracy

The atomic absorption spectrometry (AAS) was calibrated to a validated level from Fluka Kamica (Buchs, Switzerland) with a dilution of 1000 mg/L of DI water after each 10 samples. Each sample was determined in triplicate under normal optimum AAS conditions with error >0.999. The findings of the AAS were verified by examining standard blanks and replicating them as unknown samples at intervals of every 10 samples. Reproducibility and recovery of these findings was detected at confidence levels of 93±6 and 91±5, overall. Mean results were used for the analysis of the data. Analytical grade reagents (Merck, Germany) were used to ensure quality data, and glassware and new plastic items were washed with 10% HNO_3 solution with water and dried in the oven.

Health Risk Assessment

Oral absorption and dermal contact are known to be the main pathway (over 90%) of human exposure to PTEs (Ullah et al. 2019). The chronic and cancer risks associated with the ingestion of PTEs in drinking water sources were analyzed. The persistent vulnerability was measured by exposure risk assessment. The average daily intake (ADI) shows the PTEs consumption and is calculated by ingestion and dermal contact using the given equations. Exposure can be measured by multiplying the PTEs concentration by the duration of the contact. The average daily dose (ADD) (mg/kg/day), reflecting the average dose dosage over the duration of treatment, occurred.

Average Daily Intake

The calculation of ADI through ingestion for selected PTEs was calculated by the following Eq. (1) (Long et al. 2020).

$$ADI_{ing} = \frac{\mathrm{C}_S \times \mathrm{IR}_{water} \times \mathrm{ED} \times \mathrm{EF} \times \mathrm{ABS}}{\mathrm{BW} \times \mathrm{AT}} \qquad (1)$$

Where, Cs is the concentration of selected PTEs in the sample, IR is the ingestion rate, ED is the exposure duration, EF is the exposure frequency and BW is the body weight of children and adults given (Table S1). AT is the average time for both adults and children.

The ADI dermal values calculations were performed using the Eq. (2), adopted by (Ngo et al. 2020).

$$ADI_{derm} = \frac{\mathrm{C}_S \times \mathrm{SA} \times \mathrm{Kp} \times \mathrm{ET} \times \mathrm{ED} \times \mathrm{EF} \times \mathrm{CF} \times \mathrm{ABS}}{\mathrm{BW} \times \mathrm{AT}} \qquad (2)$$

Where Cs is the concentration of selected PTEs in the sample, SA is the surface area of the skin exposed to PTEs, Kp is the permeability coefficient, ET is the exposure time, CF is the conversion factor, and ABS is dermal absorption factor (USDOE 2011)

Hazard Quotient

Hazard quotient (HQ) indicates non–carcinogenic risk of PTEs via ingestion and dermal contact and were calculated Eq. (3), as the ratio of ADI by the reference dose (RfD) (mg/kg/ day):

$$HQing = \frac{\mathrm{ADI}}{\mathrm{R}f\mathrm{Ding}} \qquad (3)$$

Where, RfD is the oral reference doses of PTEs as shown in (Table S2). HQ < 1 means that the metal has a potential non-carcinogenic health risk in the assessment system (Qiao et al. 2020).

$\mathrm{HQ}_{\mathrm{derm}}$ is non carcinogenic risk, calculated by the following Eq. (4).

$$HQderm = \frac{\mathrm{ADI}}{\mathrm{R}f\mathrm{Dderm}} \tag{4}$$

Where ADI is the average daily intake via dermal contact, and RfD is the dermal reference dose provided in (Table S2). Reference doses for dermal absorption have been calculated by multiplying the water ingestion reference doses with gastrointestinal absorption (GIABS) variables as indicated by USDOE–RAIS (Eq. 12) (USDOE 2011).

Hazard Index

Health index (HI) was calculated using the given Eq. (5), adopted from (Nyambura et al. 2020).

$$HI = \sum HQ\ ing/derm \tag{5}$$

Where HQ ing/dermal of the selected PTEs were calculated to find HI values. HI < 1 shows the non–carcinogenic risk due to a particular route of exposure or chemical is assumed to be insignificant.

Cancer Risk

Cancer risk through consumption of selected PTEs in drinking water was calculated for oral ingestion and dermal contact (USEPA 2005).

$$CR = \mathrm{ADIing} \times CSF \tag{6}$$

Where $\mathrm{CSF}_{\mathrm{ing}}$ is a slope factors of Ni, Cr and Pb as shown in (Table S2).

$$CR = \mathrm{ADIderm} \times CSF \tag{7}$$

Where $\mathrm{CSF}_{\mathrm{derm}}$ in s dermal factors given in (Table S2). However, the CSF for dermal absorption are calculated by multiplying the ADI values with CSF ingestion and divided by GIABS factors suggested by (USDOE 2011).

Statistical Analysis

Analytical tools such as MS–Excel 2019 has been used for statistical analysis of mean, range and standard deviation of PTEs. The principal component analysis (PCA) was used for PTEs source identification and Pearson's correlation analysis for metals correlations, using OriginPro (2018 version) and SPSS (17) version. The geo statistical analysis and spatial distribution maps was identified by ArcGIS 10.1.

Results and Discussion

PTEs Distribution in Mining and Non–mining Areas

The descriptive results of PTEs concentrations in ground and surface water of mining and non-mining areas are summarized in Table 1. The concentrations of PTEs in groundwater sources were moderate to high, ranged from 43-177, 56-612, 16-95, 15-81, 14-78, and 217-326, with mean values of 92.3, 414, 47, 40, 37 and 242 μg L^{-1} for Ni, Cr, Zn, Cu, Pb and Mn, respectively. The high concentrations were observed for Cr, with mean values of 414, and 497 μg L^{-1} for both the ground and surface water, respectively. While the lowest mean values were detected for Pb (37.0, and 46.4) μg L^{-1}, in groundwater and surface water, respectively in Mohmand District. For surface water samples, the concentrations of Ni, Cr, Zn, Cu, Pb and Mn were highly observed as compared to groundwater, with mean values of 110, 497, 58, 50.2, 46.44 and 179 μg L^{-1} respectively in Mohmand District. Among PTEs, elevated concentrations of Ni, Cr and Pb in the ground and surface water of Mohmand District exceeded the standard permissible limits of WHO (2017). These elevated PTEs concentration in both water resources could be attributed to mine tailings, and acid mine drainage wastes, released from mining sites and deposited to the underlying bedrocks (Taylor 2007), which can contaminate both the groundwater and surface water resources. Due to the fact, that mining operations are well-known for the main sources of environmental contaminants (Razo et al. 2004). For instance, Nawab et al. (2019) also reported that the concentration of PTEs like Cr, Cd, Cu, Pb, and Zn has increased due to mining activities in the past century. Moreover, these PTEs could be originated from the waste tailings, left over in the environment for a long period of time by mining activities due to improper treatment and management (Rashed 2010). For Bajaur District, the concentrations of PTEs were relatively lower than Mohmand District, with mean values of 12.8, 112, 59.3, 19.9, 10.1 and 19.2 μg L^{-1} in groundwater sources, while surface water sources had moderate mean concentrations (16.9, 19.4, 19, 20.2, 90, and 15.9) μg L^{-1} for Ni, Cr, Zn, Cu, Pb and Mn respectively. Moreover, the mean concentrations of PTEs in Khyber District were (11.2, 19.6, 56.7, 19.4, 10.5, and 18.9) μg L^{-1}, and (12.0, 21.3, 77.2, 21.3, 12.6, and 21.5) μg L^{-1} for Ni, Cr, Zn, Cu, Pb and Mn in groundwater and surface water respectively, and were comparatively lower than the Mohmand District, and Bajaur District of mining regions.

The overall results showed that Cr had high concentrations in ground and surface water sources of mining areas, followed by Zn, and Mn. The high Cr concentration could be associated to chromite ore deposits and ultramafic rocks in the region, that could be transfer from old mine tailings to the groundwater system through leaching from the surface waterbodies (Dhakate and Singh, 2008). Mafic and ultramafic rocks deposits and mining wastes are primary source of high levels of PTEs release to the environment (Nawab et al. 2015). Furthermore, the concentrations of Pb in all three agencies were exceeded, as well as Ni, and Cr concentrations in Mohmand District were above the permissible limits of WHO (2017) in both water resources of mining areas. The high enrichment of Pb in the water sources of the mining areas could be resulted from possible geogenic mafic and ultramafic rocks that have already been reported by several researchers (Liu et al. 2020; Khan et al. 2018; Rashid et al. 2018). While, elevated Ni concentrations and high occurrence of other PTEs in the water resources could be related to mining and regional industrial activities, smelting, mafic and ultra-mafic rocks and drainage discharges as reported elsewhere (Zhang et al. 2018, 2020; Xia et al. 2018). Moreover, Ni could mainly originate from the leaching of ultramafic rocks in drinking water sources (Aleksandra and Urszula 2008). Overall, the mean concentrations of PTEs in mining areas of Mohmand District, Bajaur District, and Khyber District were found in decreasing order of; Cr>Mn>Ni>Zn>Cu>Pb, Cr>Pb>Zn>Cu>Mn>Ni, and Zn>Cr>Cu>Mn>Ni>Pb in all the groundwater and surface water sources, respectively. The results of present study were found in agreement with the previous studies conducted in mining areas of Hunan province, China (Gong et al. 2014), in Dabaoshan of Guangdong province, China (Wang et al. 2019), in Palma, Spain (Rodellas et al. 2014), in Brajrajnagar of Jharsuguda district, India (Sahoo and Khaosh 2020), in Taojian, China (Chen et al. 2019), in Maracas at Port of Spain (Santana et al. 2020), and in Mantaro, Peru (Custodio et al. 2020), respectively as shown in (Table S3).

In non–mining areas, there is moderate variation observed in mean concentrations of PTEs as presented in Table 1. The results showed that mean concentrations of Mn had high mean concentration (227 μg L^{-1}), followed by Zn (203 μg L^{-1}) in groundwater. Whereas, Mn also showed high mean concentration (254 μg L^{-1}), followed by Zn (225 μg L^{-1}) in surface water sources of Mohmand District. For Bajaur and Khyber Districts, the concentrations of PTEs were comparatively lower than the Mohmand District, with high mean values of Cu (23.1 μg L^{-1}), and Mn (18 μg L^{-1}) in surface water, and low mean value of (5.11 μg L^{-1}) for Zn in groundwater, and (4.44 μg L^{-1}) for Zn in surface water, respectively. The high enrichment levels of Cr, Ni, and Pb (except Zn) in the present study were found lower than the previous study of non-mining site of agriculture soils near the mining-impacted northern areas of Pakistan (Nawab et al. 2016). Mean concentrations of all PTEs were low in non-mining areas, as compared to the mining areas, and were found within acceptable limits except Pb had exceeded in both water sources in Mohmand District than the standard limit of WHO (2017). Furthermore, the studied mean concentrations of PTEs in non–mining areas of Mohmand District, Bajaur District, and Khyber District were observed in decreasing order of Zn>Mn>Cr>Cu>Ni>Pb, Zn>Cu>Cr>Mn>Pb>Ni, and Cu>Zn>Mn>Cr>Ni>Pb in both water sources, respectively. PTEs concentrations in present study were relatively lower than the previous studies reported by (Qin et al. 2014) and (Huang et al. 2013). In addition, the Cr, Zn, Cu, Mn had comparatively high concentrations among PTEs in all three districts of non-mining areas. However, the elevated values of PTEs in both water sources of non-mining areas could be associated to mafic and ultramafic rocks and open dumping of chromite mining wastes that could be dispersed through runoff by rainfall and wind erosion, and thereby accumulated in surrounding areas (Nawab et al. 2015). In addition, numerous studies showed high PTEs concentrations in the surrounding mining areas and ore deposits as well as in terrestrial ecosystems (Rashed 2010).

Correlation Matrix of PTEs in Surface Water and Groundwater

Pearson's correlation coefficient values of PTEs in surface water and groundwater parameters for mining and non-mining sites are shown in Table 2. The correlation coefficient values support the PCA results in present study. A significant positive correlation has been observed in the groundwater and surface water samples of PTEs to obtain the relevant information of common sources. The significant correlation positive values were observed for Cr and Ni (r = 0.98), Cu and Ni (r = 0.99), Cu and Cr (r = 0.97), Pb and Zn (r = -0.86), Mn and Ni (r = 0.94), Mn and Cr (r = 0.93), and Mn and Cu (r = 0.90) in the study area of mining site, indicating a common origin of PTEs. High metals concentrations and their strong correlations (r > 0.50) in the groundwater and surface water of mining areas indicate the high anthropogenic and geochemical natural sources.

In contrast, the significant positive correlation pairs were dominantly observed in non-mining areas for all the PTEs to be; Cr and Ni (r = 0.97), Zn and Ni (r = 0.96), Zn and Cr (r = 0.97), Cu and Ni (r = 0.78), Cu and Cr (r = 0.82), Cr and Zn (r = 0.78), Pb and Ni (r = 0.84), Pb and Cr (r = 0.85), Pb and Zn (r = 0.93), Pb and Cu (r = 0.62), Mn and Ni (r = 0.96), Mn and Cr (r = 0.97), Mn and Zn (r = 0.99), Mn and Cu (r = 0.78), and Mn and Pb (r = 0.92), suggesting the common origin in non-mining areas. The results of these strong positive correlations demonstrate that surface water and groundwater variables were influenced by the common geogenic or anthropogenic sources in the study area, that could be resulted from mafic and ultramafic rocks deposits and mining wastes, releasing high levels of PTEs to the environment (Nawab et al. 2015), as well as open dumping and mobilization of mining wastes in abandoned mines, and tailing ponds could be another reason, lead to contaminate the surrounding local soils, surface rivers water and groundwater with PTEs (Shen et al. 2019). The results of these correlation analysis of major ions in present study showed similarity with the previous studies, conducted by Wang et al. (2019) and Santana et al. (2020).

Source Identification of PTEs

Principal component analysis (PCA) is an important technique used to describe and identify the pollution sources via dimension reduction method (Kannel et al., 2007). The PCA results of six target PTEs observations of mining and non-mining agencies are listed in Table 3. Overall, three loading factors (F1 and F2) were obtained with eigenvalues of (> 1) for the surface water and groundwater of mining and non-mining agencies. The two principal components F1, and F2 described 95.9 % and 97.1 % variance with the eigenvalues of 5.76 and 6.18 for mining and non-mining areas, respectively as shown in (Fig. 2). First two significant factors were observed for mining and non-mining areas are presented in Fig. 3.

The first factor F1 described the 65.2 %, and 90.4 % of total variance with eigenvalues of 3.91, and 5.43, respectively for mining and non-mining sites. F1 showed the high positive loadings of significant correlation coefficient (r) values of Ni (r = 0.99), Cr (r = 0.98), Cu (r = 0.98) and Mn (r = 0.95) for mining sites. While F1 had the strong positive loadings of significant correlation coefficient (r) values of all PTEs like Ni (r = 0.97), Cr (r = 0.98), Zn (r = 0.99), Cu (r = 0.83), Pb (r = 0.91), and Mn (r = 0.99) for non-mining areas. Hence, F1 contributed the strong loadings of PTEs for the surface water and ground water of mining and non-mining sites in PCA results, suggesting the origin of natural and anthropogenic sources. Moreover, the strong loadings of aforementioned PTEs are associated to their high concentration in the study area. The elevated PTEs concentration in both water resources could be attributed to mine tailings, and acid mine drainage wastes, released from mining sites and deposited to the underlying bedrocks (Taylor 2007). Thus F1 showed the mixed sources of anthropogenic and natural sources in the study area.

Factor 2 (F2) accounted for 30.7 %, and 6.74 % of total variability with the eigenvalues of 1.85, and 0.75. The significant correlation coefficient (r) values of surface water and groundwater variables were Zn (r = 0.96), and negative loading of Pb (r = -0.93) for mining site. Whereas, the significant positive correlation coefficient (r) value of F2 was Cu (r = 0.82), and also a negative loading of Pb (r = -0.52) for the surface water and groundwater of non-mining areas. The high loadings of PTEs demonstrate the origin of open dumping of mine-wastes, resulting to contaminate the environment by surface runoff, erosion and landslides (Nawab et al. 2018b). Hence, F2 is assumed to show the mixed sources of both natural geo-genic and anthropogenic sources in mining and non-mining sites.

Average Daily Intake Dose

The ADI ingestion and dermal contact values of selected PTEs for both the adults and children are summarized in Table 4. The respective ADI values of PTEs via consumption of ground and surface water in mining and non–mining areas were calculated, according to USEPA (2011), adopted values. The results showed that ADI values of all the groundwater and surface water were lower for adults and children in Khyber District than the Mohmand and Bajaur Districts. The Cr had the highest ADI ingestion value (4.97E–05) for children, via groundwater consumption. Whereas, Pb had lowest ADI values (4.44E–06, and 1.15E-06) for both the children and adults, via ground water consumption in Mohmand District, respectively. Similar trend of high ADI of Cr value (1.35E-05) was observed for children, while low ADI value of Pb (3.16E-07) was observed for adults in groundwater of Bajaur District, respectively. All the other calculated PTEs had intermediate ADI ingestion values for both the adults and children in Mohmand and Bajaur Districts. For Khyber District, Zn had high ADI values (6.81E-06, and 1.76E-06) for children and adults in groundwater, respectively. The high ADI levels of Cr, and Zn could be associated to their high concentration levels in ground and surface water of mining areas. Higher ADI's of Cr and Zn values may contribute to a number of problems in the exposed human population. Based on the drinking water quality in mining areas, the ADI ingestion values for Mohmand District, Bajaur District and Khyber District were observed in decreasing order of; Cr>Mn>Ni>Zn>Pb>Cu, Cr>Pb>Zn>Cu>Mn>Ni, and Zn>Cr>Cu>Mn>Ni>Pb in mining areas via both the surface water and groundwater consumption for adults and children, respectively.

The results of ADI ingestion values of non–mining water sources were varied and lower, as compared to mining water sources as shown in Table 5. The lowest ADI ingestion values of Pb (4.22E-07 and 5.27E-07) were calculated for adults, while Mn exhibit highest ADI values (3.06E-05 and 2.73E-05) for children via surface and groundwater consumption, respectively. For Bajaur

District, the high ADI ingestion values of Cu (2.77E-06) were recorded for children in ground water, while Zn had lowest ADI value (1.58E-07) for adults in groundwater respectively. Similar results were observed for Khyber District via groundwater and surface water consumption. Comparatively, the ADI ingestion values of PTEs were found in order of; Mn>Zn>Cr>Cu>Ni>Pb, Cu>Cr>Mn>Pb>Zn>Ni, and Zn>Cu>Mn>Cr>Ni>Pb in non–mining areas of three agencies, respectively. As a result, mining areas via water sources consumption showed relatively higher ADI ingestion values as compared to non–mining areas for children and adults. Children showed high ADI ingestion values in both mining and non–mining areas due to their high consumption rate and low body weight. However, the ADI ingestion values of all PTEs were observed within the safe limits (<1). In addition, several ADI intake levels of PTEs are significantly similar to their respective reference dosage limits, suggesting whether the use of these polluted drinking water supplies tends to have an effect over the lifespan of both adults and children.

Among the source classification of water in mining areas, the Bajaur District showed the lowest ADI dermal value 4.81E-08 of Pb in groundwater for adults. High ADI dermal value of Cr (2.35E-05) was observed for children in surface water of mining areas in Mohmand District, as listed in Table 4. Likewise, Zn was observed with ADI dermal values (1.61E-05, and 2.19E-05) for adults in the groundwater and surface water of Khyber District, respectively. Based on the ADI dermal values calculation, it was observed that the children were more exposed to PTEs as compared to adults. Similarly, Custodio et al. (2020) also reported high ADI values for children in drinking water sources due to elevated PTEs concentration level resulted in mining activities. For non–mining areas of Mohmand District, Pb was observed for low ADI dermal value (8.02E-08) for adults, via surface water consumption, whereas the highest ADI dermal value (1.80E-04) was observed for Zn through surface water consumption for children (Table 5). Furthermore, the highest Zn ADI dermal value (1.56E-05), followed by Cu (1.08E-05) were recorded for children in Bajaur District through groundwater and surface water consumption, respectively. Whereas, the lowest Pb ADI values of 3.09E-08, and (2.62E-08) were observed for adults through ground water, in in Bajaur District and Khyber District, respectively. Overall, the ADI dermal values were frequently low among all agencies for the adults and children in non–mining areas. Although, high ADI dermal contact values for children were highly recorded followed by adults. And consumption of PTEs-contaminated drinking water and by dermal contact could thus be high enough to require action to reduce adverse health threats to the exposed public (Rajeshkumar et al. 2018).

Non Carcinogenic Health Risk

HQs of ingestion and dermal contact were calculated for individual PTEs in three agencies of mining and non-mining areas, presented in Table 6 and 7. The results showed that all the calculated HQs of individual PTEs were less than 1, suggesting that intake of PTEs via ingestion of water do not pose a potential health hazard. The intake of PTEs in children were higher than that of adults, resulting in comparatively higher HQ values. The lowest HQ ingestion (1.88E-05) was recorded for Zn via ground water consumption, while the highest value 6.33E-04 was observed for Mn through surface water consumption for children in Mohmand District of mining areas. Low HQ value was observed for Zn (7.60E-06) through surface water consumption for children, and high value was recorded for Ni (7.70E-05) via groundwater intake of Bajaur District, and similar results were observed for Khyber District. The HQ values are dependent on toxicity, RfD values and metal concentrations. The HQ ingestion values of PTEs for Mohmand District, Bajaur District and Khyber District were observed in order of; Mn>Ni>Cu>Cr>Pb>Zn, Ni>Mn>Cu>Cr>Pb>Zn, and Mn>Ni>Cu>Cr>Pb>Zn in mining areas via the surface water and groundwater consumption for adults and children, respectively. In Mohmand District of non-mining areas, the high HQ value was calculated for Mn (6.65E-04), while lowest was recorded for Cr (6.73E-07) via groundwater and surface water consumption for children and adults, respectively. Similar results of HQ's were found for both the Bajaur and Khyber Districts as shown in Table 7. The HQ indices for all PTEs were (<1) and do not indicate any risk to the local population, according to US-EPA, (2005). However, the HQ indices of Cu, Mn, Ni, Pb and Zn metals tend to be higher than that reported in drinking water study reported by Kavcar et al. (2009), and in groundwater and surface water by Lim et al. (2008).

The lowest HQ dermal value 1.77E–05 was observed for Pb by children from surface water in Mohmand District in mining areas. While, the Mn showed the high HQ dermal values through surface water for Bajaur and Khyber Districts. The HQ dermal values in non–mining areas of Mohmand, Bajaur and Khyber Districts are presented in Table 6. In Mohmand District, Pb had low HQ value (6.46E–06) in non–mining areas for children, while maximum value of 1.17E–03 was recorded for Cr in children in ground water. Similarly, Cr and Mn had highest HQ dermal values for children in both the Bajaur and the Khyber District of non–mining areas. Results revealed that children showed higher HQ values than adults due to their body weight and vulnerability. The HQ values were found lower than 1, as compared to US-EPA (2005) threshold values. All the HQ's of dermal contact of PTEs were found in the same order of HQ's ingestion values via surface water and groundwater consumption in three agencies of mining and non-mining areas. In addition, HI values for both the adults and children exposed to all PTEs via ingestion and dermal contact, indicating low non–carcinogenic risks (Table 6 and 7). However, the total HI values in both mining and non–mining areas of Mohmand District were found higher for children indicating that there may be potential non–carcinogenic risk via ingestion continually. Finally, more analysis related to the analyzed HQ, HI and CR supports this study by showing that intake or contact with water polluted with toxic PTEs presents a risk to human health.

Carcinogenic Risk

The carcinogenic risk (CR) associated with selected PTEs (Ni, Cr and Pb) were calculated via ingestion and dermal contact for both the adults and children in mining and non–mining areas. Based on the ingestion exposure, the CR ingestion values for Ni was found lower 8.92E-07 in Bajaur District via surface water consumption, as listed in (Table 8). The highest CR ingestion value of Cr (2.98E-05) in groundwater, and lowest CR value of Pb (9.75E-09) in surface water was recorded for children and adults in Mohmand District of mining areas, respectively. The highest CR ingestion value 3.02E-07 in Bajaur District was found for Cr through surface water and lowest 2.68E-09 for Pb through ground water for adults, respectively. Similarly, the CR ingestion values were found higher for Cr and lower for Pb respectively through ground and surface water consumption in mining areas of Khyber District. Moreover, the non–mining data show relatively low carcinogenic risk as compared to mining areas water sources. The CR ingestion highest value 4.48E-07 for Ni was observed in Bajaur District through surface water for children, whereas the lowest value 8.73E–09 was also found for Pb through surface water, respectively. Furthermore, the Cr had high CR ingestion value 2.65E-06 via surface water for children, while Pb had lowest values for children and adults in all agencies of non–mining areas. However, the CR values of PTEs were found in order of Ni>Cr>Pb through surface and ground water consumption in all three agencies of mining areas. The CR value of 1.0E−6 (one person per million) is considered to be carcinogenic risk for the both the adults and children, according to US-EPA (2011) while, the values lower than 1.0E−6 are negligible, indicating no carcinogenic risks. CR values of Cr and Ni were found to be higher than the standard limit of (1.0E−6) in mining areas for children. The high CR of Ni and Cr and its exposure to high toxicity could be potentially harmful in their early stages of growth and may affect the immune, digestive, reproductive and nervous systems of children (Peek et al. 2018).

Thus, high approximate CR of Cr, and Ni via surface and groundwater consumption in mining regions could pose carcinogenic risk to children, and require high enough treatment of water sources to minimize the adverse health threats to the exposed public in study area. According to (WHO), children are more prone to health hazards because of high drinking water consumption, ingest more calories and breathe more air in comparison with adults. The results of present study were found consistent with related previous studies of drinking water sources, conducted in mining areas (Ewusi et al. 2017; Dorleku et al. 2018; Bhattacharya et al. 2012).

All the calculated CR dermal values of selected PTEs were low for all districts of mining areas as listed in (Table 8). Cr had high CR dermal value 1.16E-04 among other PTEs for children in Mohmand District, while Pb showed the lowest CR value 5.08E-10 for adults in surface water of Khyber District. Similarly, the Ni showed high CR dermal value 1.03E-05 in Mohmand District, whereas Pb had low CR dermal value 9.67E-10 in surface water of Bajaur District for children in non–mining areas. Overall, Cr and Ni showed relatively high CR dermal values for children in surface water of Mohmand District, as compared to Bajaur and Khyber Districts (Table 9). In children, increased ingestion and dermal contact of these PTEs had shown the negative effects in development of intestinal system, kidney disorders and lung function in early stages of growth (Plum et al. 2010). As a result, the CR values of PTEs were found in order of Ni>Cr>Pb through surface and ground water in all three agencies of non-mining areas. The CR dermal contact results were also below the permissible standard (1×10^{-4}), suggested by the (USEPA 2011), indicating that carcinogenic risk could be appropriate for both adults and children in the study area by dermal contact, except that Ni in the study area exceeded the threshold limits (1.0E−04) set by the (USEPA 2011). The present study proposed that effective purification enhancement systems should be introduced to protect the health of people in the study area, particularly in the Mohmand District.

Conclusions

The distribution levels of PTEs were investigated in surface and groundwater sources of mining and non-mining areas of the newly merged districts (Mohmand, Bajaur and Khyber). In this study, the PTEs concentrations were varied in mining and non–mining water sources. Among PTEs, Cr showed highest concentrations, followed by Zn and Mn in surface water and groundwater sources, while Pb showed the lowest concentration in surface water sources of non-mining areas. The concentrations of Ni, Cr and Pb in the ground and surface water of Mohmand District were exceeded the permissible limits of WHO. The Pearson's correlation matrix and PCA results showed that pollution sources of PTEs were mainly originated from common geogenic sources of mafic-ultramafic rocks, acid mine drainage released to the regions by erosion, leaching and surface runoff. The anthropogenic sources such as open dumping of mine-wastes and mine tailings in the study area were highly contributed towards water contamination. Drinking water consumption was the primary route of metal exposure for the Mohmand District, followed by a dermal contact route. For both target classes, the daily intake of PTEs from water consumption was at least four to ten times higher than dermal interaction. In the case of dermal exposure, the non–carcinogenic and carcinogenic risk threshold for PTEs indicates no health risk hazard for both adults and children. However, the risk assessment revealed that there is a non–carcinogenic risk to children at the Mohmand District by ingestion exposure. Risk assessment of exposure to PTEs has shown that the carcinogenic risk from drinking water use ingestion in mining areas is relatively high, in comparison with protection standard of US-EPA risk; thus, people in this study area may be at greater risk and serious attention needs to be paid to this area. Exposure assessments performed by children, resulted in more carcinogenic and non–carcinogenic risks through ingestion, and residents of the Mohmand District were more exposed to Ni and Cr. More research work is required to reduce the levels of PTEs in drinking water sources of these regions. In addition, appropriate management measures for mine waste must be set in place to protect the local population and reduce public health threats. Further research on the dynamics of other PTEs in mining and non–mining regions should also be undertaken to determine long–term health risks.

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Competing Interests:

The authors declare no competing financial interest.

References

Alves RN, Maulvault AL, Barbosa VL, Fernandez-Tejedor M, Tediosi A, Kotterman M, van den Heuvel FH, Robbens J, Fernandes JO, Rasmussen RR, Sloth JJ (2018) Oral bioaccessibility of toxic and essential elements in raw and cooked commercial seafood species available in European markets. Food Chem 30(267):15–27. https://doi.org/10.1016/j.foodchem.2017.11.045

Adyasari D, Oehler T, Afiati N, Moosdorf N (2018) Groundwater nutrient inputs into an urbanized tropical estuary system in Indonesia. Sci Total Environ 15(627):1066–79. https://doi.org/10.1016/j.scitotenv.2018.01.281

Ahmad B, Rehman AU, Malik S (2016) Consanguinity and inbreeding coefficient in tribal Pashtuns inhabiting the turbulent and war-affected territory of Bajaur Agency, North-West Pakistan. J Biosoc Sci 48(1):113–28. https://doi.org/10.1017/S0021932014000558

Aleksandra D, Urszula B (2008) The impact of Nickel on human health. J Elementol 13 (4):685–96.

Bhattacharya P, Sracek O, Eldvall B, Asklund R, Barmen G, Jacks G, Koku J, Gustafsson JE, Singh, N Balfors BB (2012) Hydrogeochemical study on the contamination of water resources in a part of Tarkwa mining area, Western Ghana. J Afr Earth Sci 66:72–84. https://doi.org/10.1016/j.jafrearsci.2012.03.005

Baeten J, Langston N, Lafreniere D (2018) A spatial evaluation of historic iron mining impacts on current impaired waters in Lake Superior's Mesabi Range. Ambio. 47, 231–244. https://doi.org/10.1007/s13280-017-0948-0

Ciazela J, Siepak M, Wojtowicz P (2018) Tracking heavy metal contamination in a complex river-oxbow lake system: Middle Odra Valley, Germany/Poland. Sci Total Environ 616:996–1006. https://doi.org/10.1016/j.scitotenv.2017.10.219

Chen M, Li F, Tao M, Hu L, Shi Y, Liu Y (2019) Distribution and ecological risks of PTEs in river sediments and overlying water in typical mining areas of China. Mar Pollut Bull 146:893–899. https://doi.org/10.1016/j.marpolbul.2019.07.029

Connor R (2015) The United Nations world water development report 2015: water for a sustainable world (Vol. 1). UNESCO publishing.

Custodio M, Álvarez D, Cuadrado W, Montalvo R, Ochoa S (2020) Potentially toxic metals and metalloids in surface water intended for human consumption and other uses in the Mantaro River watershed, Peru. Soil Water Res 15(4):237–45. https://doi.org/10.17221/152/2019-SWR

Custodio M, Cuadrado W, Peñaloza R, Montalvo R, Ochoa S, Quispe J (2020) Human Risk from Exposure to PTEs and Arsenic in Water from Rivers with Mining Influence in the Central Andes of Peru. Water 12(7):1946.

Dhakate R, Singh VS (2008) Heavy metal contamination in groundwater due to mining activities in Sukinda valley, Orissa-A case study. J Geogr Reg Plann 1(4):058–067. https://doi.org/10.5897/JGRP.9000068

Dorleku MK, Nukpezah D, Carboo D (2018) Effects of small-scale gold mining on heavy metal levels in groundwater in the Lower Pra Basin of Ghana. Appl Water Sci 8(5):1–11. https://doi:10.1007/s13201-018-0773-z

EPA A (2004) Risk Assessment Guidance for Superfund. Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment) (Vol. 5). EPA/540/R/99.

Ewusi A, Apeani BY, Ahenkorah I, Nartey RS (2017) Mining and metal pollution: assessment of water quality in the Tarkwa mining area. Ghana Min J 17(2):17–31. https://doi:10.4314/gm.v17i2.4

Gong X, Chen Z, Luo Z (2014) Spatial distribution, temporal variation, and sources of heavy metal pollution in groundwater of a century-old nonferrous metal mining and smelting area in China. Environ Monit Assess 186(12):9101–9116. https://doi:10.1007/s10661-014-4069-y

Government of KPK (1994) Population of FATA. Pakistan Bureau for Statistics, Development Statistics, Peshawar.

Huang X, Zhu Y, Ji H (2013) Distribution, speciation, and risk assessment of selected metals in the gold and iron mine soils of the catchment area of Miyun Reservoir, Beijing, China. Environ Monit Assess 185(10):8525–8545. https://doi:10.1007/s10661-013-3193-4

Kavcar, P., Sofuoglu, A. and Sofuoglu, S.C., 2009. A health risk assessment for exposure to trace metals via drinking water ingestion pathway. Int. J. Hyg. Environ. Health. 212 (2), 216–227.

Kavcar P, Sofuoglu A, Sofuoglu SC (2009) A health risk assessment for exposure to trace metals via drinking water ingestion pathway. Int J Hyg Environ Health 212(2):216-27. https://doi.org/10.1016/j.ijheh.2008.05.002

Khan, K., Lu, Y., Saeed, M.A., Bilal, H., Sher, H., Khan, H., Ali, J., Wang, P., Uwizeyimana, H., Baninla, Y. and Li, Q., 2018. Prevalent fecal contamination in drinking water resources and potential health risks in Swat, Pakistan. J. Environ. Sci. 72, 1–12.

Khan K, Lu Y, Saeed MA, Bilal H, Sher H, Khan H, Ali J, Wang P, Uwizeyimana H, Baninla Y, Li Q (2018) Prevalent fecal contamination in drinking water resources and potential health risks in Swat, Pakistan. J Environ Sci 72:1–2. https://doi.org/10.1016/j.jes.2017.12.008

Khan, S., Shahnaz, M., Jehan, N., Rehman, S., Shah, M.T. and Din, I., 2013. Drinking water quality and human health risk in Charsadda district, Pakistan. J. Clean. Prod. 60, 93–101.

Khan S, Shahnaz M, Jehan N, Rehman S, Shah MT, Din I (2013) Drinking water quality and human health risk in Charsadda district, Pakistan. J Clean Prod 60:93–101. https://doi.org/10.1016/j.jclepro.2012.02.016

Khan K, Lu Y, Khan H, Zakir S, Ullah I, Khan S, Khan AA, Luo W, Tieyu W (2013) Health risks associated with PTEs in the drinking water of Swat, northern Pakistan. J Environ Sci 25:2003–2013. https://doi.org/10.1016/S1001-0742(12)60275-7

Kefeni KK, Msagati TAM, Mamba BB (2017) Acid mine drainage: prevention, treatment options, and resource recovery: a review. J Clean Prod 151:475–493. https://doi.org/10.1016/j.jclepro.2017.03.082

Li Z, Ma Z, van der Kuijp TJ, Yuan Z, Huang L (2014) A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. Sci Total Environ 468–469:843–853. https://doi.org/10.1016/j.scitotenv.2013.08.090

Lim HS, Lee JS, Chon HT, Sager M (2008) Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au–Ag mine in Korea. J Geochem Explor 96(2–3):223–230. https://doi.org/10.1016/j.gexplo.2007.04.008

Liu M, Xu Y, Nawab J, Rahman Z, Khan S, Idress M, Ali A, Ahmad R, Khan SA, Khan A, Khan MQ (2020) Contamination features, geo-accumulation, enrichments and human health risks of toxic heavy metal (loids) from fish consumption collected along Swat river, Pakistan. Environ Technol Innov 17:100554. https://doi.org/10.1016/j.eti.2019.100554

Liu S, Li W (2019) Zoning and management of phreatic water resource conservation impacted by underground coal mining: A case study in arid and semiarid areas. J Clean Prod 224:677–685. https://doi.org/10.1016/j.jclepro.2019.03.282

Long X, Liu F, Zhou X, Pi J, Yin W, Li F, Huang S, Ma F (2021) Estimation of spatial distribution and health risk by arsenic and heavy metals in shallow groundwater around Dongting Lake plain using GIS mapping. Chemosphere 269:128698. https://doi.org/10.1016/j.chemosphere.2020.128698

López-Pacheco IY, Silva-Núñez A, Salinas-Salazar C, Arévalo-Gallegos A, Lizarazo-Holguin LA, Barceló D, Iqbal HM, Parra-Saldívar R (2019) Anthropogenic contaminants of high concern: existence in water resources and their adverse effects. Sci Total Environ 690:1068–88.

Meng, Y, Li G, Lin W, Gilmore JH, Shen D (2014) Spatial distribution and longitudinal development of deep cortical sulcal landmarks in infants. Neuroimage 100:206–218. https://doi.org/10.1016/j.neuroimage.2014.06.004

Moyé J, Picard-Lesteven T, Zouhri L, El Amari K, Hibti M, Benkaddour A (2017) Groundwater assessment and environmental impact in the abandoned mine of Kettara (Morocco). Environ Pollut 231:899–907. https://doi.org/10.1016/j.envpol.2017.07.044

Muhammad S, Shah MT, Khan S (2011) Health risk assessment of PTEs and their source apportionment in drinking water of Kohistan region, northern Pakistan. Microchem J 98(2): 334–343. https://doi.org/10.1016/j.microc.2011.03.003

Mohammadnejad S, Noaparast M, Hosseini S, Aghazadeh S, Mousavinezhad S, Hosseini F (2018) Physical methods and flotation practice in the beneficiation of a low grade tungsten-bearing scheelite ore. Russ J Non-Ferr Met 59(1):6-15.

Nawab J, Khan S, Khan MA, Sher H, Rehamn UU, Ali S, Shah SM (2017) Potentially toxic metals and biological contamination in drinking water sources in chromite mining-impacted areas of Pakistan: a comparative study. Expos Health 9:275–287. https://doi:10.1007/s12403-016-0240-8

Nawab J, Ghani J, Khan S, Xiaoping W (2018b). Minimizing the risk to human health due to the ingestion of arsenic and toxic metals in vegetables by the application of biochar, farmyard manure and peat moss. J Environ Manage 214:172–183. https://doi.org/10.1016/j.jenvman.2018.02.093

Nawab J, Khan S, Xiaoping W, Rahman A, Ali H, Qamar Z, Khan ZA, Rehman ZU, Rahman H, Muhammad J, Khan A (2018a) Spatial distribution of toxic metals in drinking water sources and their associated health risk in district buner, Northern Pakistan. Hum Ecol Risk Assess 24(3):615–626. https://doi.org/10.1080/10807039.2017.1395684

Nawab J, Khan N, Ahmed R, Khan S, Ghani J, Rahman Z, Khan F, Wang X, Muhammad J, Sher H (2019) Influence of different organic geo-sorbents on Spinacia oleracea grown in chromite mine-degraded soil: a greenhouse study. J Soil Sediment 19:2417–2432. https://doi:10.1007/s11368-019-02260-3

Nawab J, Khan S, Shah MT, Qamar Z, Din I, Mahmood Q, Gul N, Huang Q (2015) Contamination of soil, medicinal, and fodder plants with lead and cadmium present in mine-affected areas, Northern Pakistan. Environ Monit Assess 187:605. https://doi:10.1007/s10661-015-4807-9

Nawab J, Khan S, Aamir M, Shamshad I, Qamar Z, Din I, Huang Q (2016) Organic amendments impact the availability of heavy metal (loid) s in mine-impacted soil and their phytoremediation by Penisitum americanum and Sorghum bicolor. Environ Sci Pollut Res 23(3):2381–2390. https://doi:10.1007/s11356-015-5458-7

Ngo HT, Watchalayann P, Nguyen DB, Doan HN, Liang L (2020) Environmental health risk assessment of heavy metal exposure among children living in an informal e-waste processing village in Viet Nam. Sci Total Environ 142982. https://doi:10.1016/j.scitotenv.2020.142982

Qiao D, Wang G, Li X, Wang S, Zhao Y (2020) Pollution, sources and environmental risk assessment of PTEs in the surface AMD water, sediments and surface soils around unexploited Rona Cu deposit, Tibet, China. Chemosphere. 248:125988 https://10.1016/j.chemosphere.2020.125988.

Northey SA, Mudd GM, Saarivuori E, Wessman-Jääskeläinen H, Haque N (2016) Water footprinting and mining: where are the limitations and opportunities? J Clean Prod. 135:1098–1116. https://doi.org/10.1016/j.jclepro.2016.07.024

Nyambura C, Hashim NO, Chege MW, Tokonami S, Omonya FW (2020) Cancer and non-cancer health risks from carcinogenic heavy metal exposures in underground water from Kilimambogo, Kenya. Groundw Sustain Dev 10:100315. https://doi.org/10.1016/j.gsd.2019.100315

Oyebamiji A, Odebunmi A, Ruizhong H, Rasool A (2018) Assessment of trace metals contamination in stream sediments and soils in Abuja leather mining, southwestern Nigeria. Acta Geochim 37:592–613. https://10.1007/s11631-017-0256-1

Paraguassú L, Leite MG, Moreira FW, Mendonça FP, Eskinazi-Sant'Anna EM (2019) Impacts of mining in artificial lake of Iron Quadrangle-MG: past marks and changes of the present. Environ Earth Sci 78(5):1–10.

Patlolla AK, Berry A, May L, Tchounwou PB (2012) Genotoxicity of silver nanoparticles in Vicia faba: a pilot study on the environmental monitoring of nanoparticles. Int J Environ Res Public Health 9(5):1649–1662. https://10.3390/ijerph9051649

Peek L, Abramson DM, Cox RS, Fothergill A, Tobin J (2018) Children and disasters. In Handbook of disaster research (pp. 243-262). Springer, Cham.

Pilotto F, Tonkin JD, Januschke K, Lorenz AW, Jourdan J, Sundermann A, Hering D, Stoll S, Haase P (2019) Diverging response patterns of terrestrial and aquatic species to hydromorphological restoration. Conserv Biol 33(1):132–141. https://doi.org/10.1111/cobi.13176

Plum LM, Rink L, Haase H 2010. The essential toxin: impact of zinc on human health. Int. J. Environ. Res. Public Health 7(4):1342–1365. https://doi.org/10.3390/ijerph7041342

Qin F, Ji H, Li Q, Guo X, Tang L, Feng J (2014) Evaluation of trace elements and identification of pollution sources in particle size fractions of soil from iron ore areas along the Chao River. J Geochem Explor 138:33–49. https://doi.org/10.1016/j.gexplo.2013.12.005

Qian Y, Cheng C, Feng H, Hong Z, Zhu Q, Kolenčík M, Chang X (2020) Assessment of metal mobility in sediment, commercial fish accumulation and impact on human health risk in a large shallow plateau lake in southwest of China. Ecotoxicol Environ Saf 194:110346 https://doi.org/10.1016/j.ecoenv.2020.110346

Queiroz HM, Nóbrega GN, Ferreira TO, Almeida LS, Romero TB, Santaella ST, Bernardino AF, Otero XL (2018) The Samarco mine tailing disaster: a possible time-bomb for PTEs contamination? Sci Total Environ 637–638:498–506. https://doi.org/10.1016/j.scitotenv.2018.04.370

Rashed MN 2010 Monitoring of contaminated toxic and PTEs, from mine tailings through age accumulation, in soil and some wild plants at Southeast Egypt. J Hazard Mater 178:739–746. https://doi.org/10.1016/j.jhazmat.2010.01.147

Rafiq M, Shah MT, Ahmad I (1984) Note on tremolite zone from the extension of Skhakot-Qila ultramafic complex in Utman Kheil, Momand District. Geol Bull Univ Peshawar 17:178–179.

Rajeshkumar S, Liu Y, Zhang X, Ravikumar B, Bai G, Li X (2018). Studies on seasonal pollution of PTEs in water, sediment, fish and oyster from the Meiliang Bay of Taihu Lake in China. Chemosphere. 191, 626–638. https://10.1016/j.chemosphere.2017.10.078

Rashid A, Guan DX, Farooqi A, Khan S, Zahir S, Jehan S, Khattak SA, Khan MS, Khan R (2018) Fluoride prevalence in groundwater around a fluorite mining area in the flood plain of the River Swat, Pakistan. Sci Total Environ 635, 203–215. https://doi.org/10.1016/j.scitotenv.2018.04.064

Razo I, Carrizales L, Castro J, Díaz-Barriga F, Monroy M (2004) Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. Water Air and Soil Pollution 152(1):129–152. https://doi10.1023/B:WATE.0000015350.14520.c1

Rehman K, Fatima F, Waheed I, Akash MSH (2018) Prevalence of exposure of PTEs and their impact on health consequences. J Cell Biochem 119(1):157–184. https://doi10.1002/jcb.26234

Rodellas V, Garcia-Orellana J, Tovar-Sánchez A, Basterretxea G, López-Garcia JM, Sánchez-Quiles D, Garcia-Solsona E, Masqué P (2014) Submarine groundwater discharge as a source of nutrients and trace metals in a Mediterranean bay (Palma Beach, Balearic Islands). Mar. Chem. 160, 56–66. https://doi.org/10.1016/j.marchem.2014.01.007

Sahoo S, Khaoash S (2020) Impact assessment of coal mining on groundwater chemistry and its quality from Brajrajnagar coal mining area using indexing models. J Geochem Explor 215:106559. https://doi.org/10.1016/j.gexplo.2020.106559

Santana CS, Olivares DM, Silva VH, Luzardo FH, Velasco FG, de Jesus RM (2020). Assessment of water resources pollution associated with mining activity in a semi-arid region. J Environ Manage 273:111148. https://doi.org/10.1016/j.jenvman.2020.111148

Saleh TA, Parthasarathy P, Irfan M (2019) Advanced functional polymer nanocomposites and their use in water ultra-purification. Trends Environ Anal Chem 24:00067. https://doi.org/10.1016/j.teac.2019.e00067

Shifaw E (2018) Review of PTEs pollution in China in agricultural and urban soils. J Health Pollut 8(18):1–14. https://doi.org/10.5696/2156-9614-8.18.180607.

Shen Z, Xu D, Li L, Wang J, Shi X (2019) Ecological and health risks of heavy metal on farmland soils of mining areas around Tongling City, Anhui, China. Environ Sci Pollut Res Int 26:15698–15709. https://doi.org/10.1007/s11356-019-04463-0

Strungaru SA, Nicoara M, Teodosiu C, Baltag E, Ciobanu C, Plavan G (2018) Patterns of toxic metals bioaccumulation in a cross-border freshwater reservoir. Chemosphere 207:192–202. https://doi.org/10.1016/j.chemosphere.2018.05.079

Sun DT, Peng L, Reeder WS, Moosavi SM, Tiana D, Britt DK, Oveisi E, Queen WL (2018) Rapid, selective heavy metal removal from water by a metal–organic framework/polydopamine composite. ACS central science 4(3):349–356. https://doi.org/10.1021/acscentsci.7b00605

Taylor MP (2007) Distribution and storage of sediment-associated PTEs downstream of the remediated Rum Jungle Mine on the East Branch of the Finniss River, Northern Territory, Australia. J Geochem Explor 92(1):55–72. https://doi.org/10.1016/j.gexplo.2006.07.005

Ullah R, Muhammad S, Jadoon IA (2019) Potentially harmful elements contamination in water and sediment: Evaluation for risk assessment and provenance in the northern Sulaiman fold belt, Baluchistan, Pakistan. Microchem J 147:1155–1162. https://doi.org/10.1016/j.microc.2019.04.053

Ullah Z, Naz A, Saddique U, Khan A, Shah W, Muhammad S (2017) PTEs concentrations and human health risk assessment of food crops in Bajaur District, Pakistan. Environ Earth Sci 76 (14):1–8. https://doi.org/10.1155/2018/2198176

Uppal IH (1972) Geology Department, Punjab University, Lahore. The Geological Bulletin of the Punjab University, (9):53.

USDOE (2011) The Risk Assessment Information System (RAIS), U.S. Department of Energy's Oak Ridge Operations Office (ORO), Washington, DC, USA.

USEPA (2011) Screening Levels (RSL) for Chemical Contaminants at Superfund Sites. U.S. Environmental Protection District.

Kumar V, Parihar RD, Sharma A, Bakshi P, Sidhu GP, Bali AS, Karaouzas I, Bhardwaj R, Thukral AK, Gyasi-Agyei Y, Rodrigo-Comino J (2019) Global evaluation of trace metal content in surface water bodies: a meta-analysis using trace metal pollution indices and multivariate statistical analyses. Chemosphere 236:124364–124364. https://10.1016/j.chemosphere.2019.124364

Wang B, Bai Z, Jiang H, Prinsen P, Luque R, Zhao S, Xuan J (2019) Selective heavy metal removal and water purification by microfluidically-generated chitosan microspheres: Characteristics, modeling and application. J Hazard Mater 364:192–205. https://doi.org/10.1016/j.jhazmat.2018.10.024

Wang Y, Dong R, Zhou Y, Luo X (2019) Characteristics of groundwater discharge to river and related heavy metal transportation in a mountain mining area of Dabaoshan, Southern China. Sci Total Environ 679:346–358. https://doi.org/10.1016/j.scitotenv.2019.04.273

Wang, P., Sun, Z.H., Hu, Y.N., Cheng, H.F., 2019. Leaching of PTEs from abandoned mine tailings brought by precipitation and the associated environmental impact. Sci. Total Environ. 695, 133893.

Wang L, Yang D, Li Z, Fu Y, Liu X, Brookes PC, Xu JA (2019). A comprehensive mitigation strategy for heavy metal contamination of farmland around mining areas–Screening of low accumulated cultivars, soil remediation and risk assessment. Environ Pollut 245:820–828. https://doi.org/10.1016/j.envpol.2018.11.062

Wang J, Su J, Li Z, Liu B, Cheng G, Jiang Y, Li Y, Zhou S, Yuan W (2019) Source apportionment of heavy metal and their health risks in soil-dustfall-plant system nearby a typical non-ferrous metal mining area of Tongling, Eastern China. Environ Pollut 254:113089. https://doi.org/10.1016/j.envpol.2019.113089

WHO (2017) Guidelines for drinking-water quality. World Health Organization 216, 303–304.

Wu W, Wu P, Yang F, Sun DL, Zhang DX, Zhou YK (2018) Assessment of heavy metal pollution and human health risks in urban soils around an electronics manufacturing facility. Sci Total Environ 630:53–61. https://doi.org/10.1016/j.scitotenv.2018.02.183

Xia K, Chen C, Deng Y, Xiao G, Zheng Y, Liu X, Fu H, Song X, Chen L (2018) In situ monitoring and analysis of the mining-induced deep ground movement in a metal mine. Int J Rock Mech Min Sci 109:32–51.

Xiao K, Li H, Shananan M, Zhang X, Wang X, Zhang Y, Zhang X, Liu H 2019. Coastal water quality assessment and groundwater transport in a subtropical mangrove swamp in Daya Bay, China. Sci Total Environ 646:1419–1432. https://doi.org/10.1016/j.scitotenv.2018.07.394

Yang K, Yu Z, Luo Y, Yang Y, Zhao L, Zhou X 2018. Spatial and temporal variations in the relationship between lake water surface temperatures and water quality-A case study of Dianchi Lake. Sci Total Environ 624:859–871. https://doi.org/10.1016/j.scitotenv.2017.12.119

Yang Y, He Z, Wang Y, Fan J, Liang Z, Stoffella PJ (2013) Dissolved organic matter in relation to nutrients (N and P) and PTEs in surface runoff water as affected by temporal variation and land uses–A case study from Indian River Area, south Florida, USA. Agric Water Manag 118:38–49.

Yuanan H, He K, Sun Z, Chen G, Cheng H (2020) Quantitative source apportionment of heavy metal (loid) s in the agricultural soils of an industrializing region and associated model uncertainty. J Hazard Mater 391:122244. https://doi.org/10.1016/j.jhazmat.2020.122244

Zhu G, Xiao H, Guo Q, Song B, Zheng G, Zhang Z, Zhao J, Okoli CP (2018) Heavy metal contents and enrichment characteristics of dominant plants in wasteland of the downstream of a lead-zinc mining area in Guangxi, Southwest China. Ecotoxicol Environ Saf 151:266–271. https://doi.org/10.1016/j.ecoenv.2018.01.011.

Zhang S, Chen S, Liu F, Li J, Liang X, Chu S, Xiang Q, Huang C, Yin H (2018) Effects of Mn average oxidation state on the oxidation behaviors of As (III) and Cr (III) by vernadite. J Appl Geochem 94:35–45. https://doi.org/10.1016/j.apgeochem.2018.05.002

Zhang Y, Chu C, Li T, Xu S, Liu L, Ju M (2017) A water quality management strategy for regionally protected water through health risk assessment and spatial distribution of heavy metal pollution in 3 marine reserves. Sci Total Environ 599:721–731. https://doi.org/10.1016/j.scitotenv.2017.04.232

Zhang JQ, Tian Q, Xu DM, Zhan CL, Liu T, Yao RZ, Liu XL, Xiao WS (2017) Pollution characteristics and risk assessment of PTEs in water and sediment from Daye Lake. J Environ Sci 38:2355–2363 (in Chinese). https://10.13227/j.hjkx.201610160

Table 1

PTEs concentration (µg L^{-1}) in the drinking water sources of the study regions (mining and non-mining) and WHO guideline values.

Mining													
	Statistics	Ni		Cr		Zn		Cu		Pb		Mn	
Location		Ground	Surface	Ground	Surface	Ground	Surface	Ground	Surface	Ground	Surface	Ground	Surface
Mohmand Agency	Range	43-177	51-188	56-612	305-678	16-95	21-98	15-81	21-87	14-78	16-85	217-326	123-234
	Mean	92.3	110	414	497	47.0	58.0	40.0	50.2	37.0	46.4	242	179
	Std	48.4	49.5	160	118	26.3	25.7	22.3	22.1	22.7	23.1	39.6	39.14
Bajaur Agency	Range	12-13	12-43	18-225	10-27	50-70	15-23	16-24	12-27	5-15	85-98	14-27	13-18
	Mean	12.8	16.9	112	19.4	59.3	19.0	19.9	20.2	10.1	90.4	19.2	15.9
	Std	0.5	9.89	90.2	5.54	7.15	2.78	2.61	5.33	3.64	4.5	4.1	1.94
Khyber Agency	Range	5-19	9-17	15-24	14-2	52-61	71-86	15-24	13-29	10-11	9-17	14-23	17-27
	Mean	11.2	12.0	19.6	21.3	56.7	77.2	19.4	21.3	10.5	12.6	18.9	21.5
	Std	4.65	2.4	2.8	3.67	3.37	5.01	2.84	5.48	0.37	2.62	2.94	3.15
Non-Mining													
Mohmand Agency	Range	16-38	23-48	19-56	32-63	119-327	117-339	14-33	16-48	13-24	9-23	140-318	139-371
	Mean	25.7	31.5	32.5	44.2	203	225	23.0	32.2	17.0	13.6	227	254
	Std	7.39	8.63	12.3	11.0	97.4	70.7	6.38	9.24	3.77	4.78	47.5	77.3
Bajaur Agency	Range	3--8	2-9	5-17	10-18	2-9	10-27	17-31	9-19	4-10	2-16	3-19	2-24
	Mean	5.33	5.78	11.1	14.3	5.11	19.5	23.11	14.1	6.56	8.56	9.78	13.4
	Std	1.58	2.63	4.24	2.95	2.57	6.83	4.67	4.19	2.06	4.63	5.95	8.94
Khyber Agency	Range	2-21	7-21	9-14	10-21	2-8	12-24	2-21	15-22	2-9	2-10	7-21	7-18
	Mean	7.87	12.8	11.8	15.3	4.44	18.0	12.3	17.7	5.56	5.90	13.5	13.5
	Std	2-21	7-21	9-14	10-21	2-8	12-24	2-21	15-22	2-9	2-10	7-21	7-18
WHO, (2017)		70		50		3000		2000		10		300	

Std: Standard Deviation

Table 2
Pearson's correlation matrix of selected PTEs concentrations in mining and non-mining areas.

Mining	HMs	Ni	Cr	Zn	Cu	Pb	Mn
	Ni	1.00					
	Cr	**0.98**	1.00				
	Zn	-0.03	0.03	1.00			
	Cu	**0.99**	**0.97**	0.04	1.00		
	Pb	0.22	0.12	**-0.86**	0.19	1.00	
	Mn	**0.94**	**0.93**	-0.03	**0.90**	0.14	1.00
Non-Mining							
	Ni	1.00					
	Cr	**0.97**	1.00				
	Zn	**0.96**	**0.97**	1.00			
	Cu	**0.78**	**0.82**	**0.78**	1.00		
	Pb	**0.84**	**0.85**	**0.93**	**0.62**	1.00	
	Mn	**0.96**	**0.97**	**0.99**	**0.78**	**0.92**	1.00

Table 3
Principal component analysis results of mining and non-mining water sources of KPK Pakistan

	Mining		Non-mining	
HMs	F1	F2	F1	F2
Ni	**0.99**	0.03	**0.97**	0.00
Cr	**0.98**	0.12	**0.98**	0.04
Zn	-0.07	**0.96**	**0.99**	-0.10
Cu	**0.98**	0.09	**0.83**	**0.82**
Pb	0.25	**-0.93**	**0.91**	**-0.52**
Mn	**0.95**	0.07	**0.99**	-0.08
Eigenvalue	3.91	1.85	5.43	0.75
Variability (%)	65.22	30.77	90.44	6.74
Cumulative %	65.22	95.99	90.44	97.17

Table 4
Average daily intake dose (μg kg^{-1} day^{-1}) of PTEs via ingestion and dermal contact for adults and children in mining areas.

Mining													
ADI ingestion Adults							ADI dermal Adults						
	Mohmand		Bajaur		Khyber			Mohmand		Bajaur		Khyber	
	Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water		Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water
Ni	2.86E-06	3.42E-06	3.98E-07	5.25E-07	3.49E-07	3.73E-07	Ni	4.36E-06	5.20E-06	6.06E-07	8.00E-07	5.31E-07	5.68E-07
Cr	1.28E-05	1.54E-05	3.49E-06	6.04E-07	6.08E-07	6.61E-07	Cr	1.96E-05	2.35E-05	5.32E-06	9.20E-07	9.27E-07	1.01E-06
Zn	1.46E-06	1.80E-06	1.84E-06	5.89E-07	1.76E-06	2.39E-06	Zn	1.33E-05	1.64E-05	1.68E-05	5.38E-06	1.61E-05	2.19E-05
Cu	1.24E-06	1.56E-06	6.18E-07	6.27E-07	6.03E-07	6.60E-07	Cu	1.89E-06	2.37E-06	9.42E-07	9.55E-07	9.19E-07	1.01E-06
Pb	1.15E-06	1.44E-06	3.16E-07	2.80E-06	3.27E-07	3.92E-07	Pb	1.75E-07	2.19E-07	4.81E-08	4.27E-07	4.98E-08	5.97E-08
Mn	7.52E-06	5.56E-06	5.96E-07	4.93E-07	5.87E-07	6.68E-07	Mn	1.15E-05	8.47E-06	9.07E-07	7.51E-07	8.94E-07	1.02E-06
ADI ingestion Children							ADI dermal Children						
	Mohmand		Bajaur		Khyber			Mohmand		Bajaur		Khyber	
	Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water		Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water
Ni	1.11E-05	1.32E-05	1.54E-06	2.03E-06	1.35E-06	1.44E-06	Ni	4.31E-05	5.14E-05	5.99E-06	7.90E-06	5.25E-06	5.62E-06
Cr	4.97E-05	5.97E-05	1.35E-05	2.34E-06	2.36E-06	2.56E-06	Cr	1.93E-04	2.32E-04	5.26E-05	9.09E-06	9.16E-06	9.96E-06
Zn	5.64E-06	6.96E-06	7.12E-06	2.28E-06	6.81E-06	9.27E-06	Zn	3.76E-06	4.64E-06	4.75E-06	1.52E-06	4.54E-06	6.18E-06
Cu	4.80E-06	6.03E-06	2.39E-06	2.43E-06	2.33E-06	2.56E-06	Cu	1.89E-05	2.37E-05	9.42E-06	9.55E-06	9.19E-06	1.01E-05
Pb	4.44E-06	1.54E-05	1.22E-06	1.09E-05	1.26E-06	1.52E-06	Pb	4.93E-07	6.19E-07	1.36E-07	1.21E-06	1.40E-07	1.69E-07
Mn	2.91E-05	2.15E-05	2.31E-06	1.91E-06	2.27E-06	2.58E-06	Mn	1.13E-05	8.37E-06	8.97E-07	7.43E-07	8.83E-07	1.00E-06

Table 5

Average daily intake dose (μg kg^{-1} day^{-1}) of PTEs via ingestion and dermal contact for adults and children in non-mining areas.

Non-Mining													
ADI ingestion Adults							ADI dermal Adults						
	Mohmand		Bajaur		Khyber			Mohmand		Bajaur		Khyber	
	Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water		Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water
Ni	7.99E-07	9.77E-07	1.65E-07	1.79E-07	2.44E-07	4.00E-07	Ni	1.22E-06	1.49E-06	2.52E-07	2.73E-07	3.71E-07	6.08E-07
Cr	1.01E-06	1.37E-06	3.44E-07	4.44E-07	3.66E-07	4.76E-07	Cr	1.54E-06	2.09E-06	5.24E-07	6.77E-07	5.57E-07	7.25E-07
Zn	6.31E-06	6.98E-06	1.58E-07	6.06E-07	1.38E-07	5.58E-07	Zn	5.76E-05	6.37E-05	1.45E-06	5.53E-06	1.26E-06	5.09E-06
Cu	7.13E-07	9.99E-07	7.16E-07	4.37E-07	3.82E-07	5.49E-07	Cu	1.09E-06	1.52E-06	1.09E-06	6.66E-07	5.82E-07	8.35E-07
Pb	5.27E-07	4.22E-07	2.03E-07	2.65E-07	1.72E-07	1.83E-07	Pb	8.02E-08	6.42E-08	3.09E-08	4.04E-08	2.62E-08	2.78E-08
Mn	7.04E-06	7.90E-06	3.03E-07	4.17E-07	4.17E-07	4.21E-07	Mn	1.07E-05	1.20E-05	4.62E-07	6.35E-07	6.35E-07	6.41E-07
ADI ingestion Children							ADI dermal Children						
	Mohmand		Bajaur		Khyber			Mohmand		Bajaur		Khyber	
	Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water		Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water
Ni	3.09E-06	3.78E-06	6.40E-07	6.93E-07	9.44E-07	1.55E-06	Ni	1.20E-05	1.47E-05	2.49E-06	2.70E-06	3.67E-06	6.02E-06
Cr	3.91E-06	5.31E-06	1.33E-06	1.72E-06	1.42E-06	1.84E-06	Cr	1.52E-05	2.07E-05	5.18E-06	6.69E-06	5.51E-06	7.18E-06
Zn	2.44E-05	2.70E-05	6.13E-07	2.35E-06	5.33E-07	2.16E-06	Zn	1.63E-04	1.80E-04	4.09E-06	1.56E-05	3.56E-06	1.44E-05
Cu	2.76E-06	3.87E-06	2.77E-06	1.69E-06	1.48E-06	2.12E-06	Cu	1.07E-05	1.50E-05	1.08E-05	6.59E-06	5.76E-06	8.27E-06
Pb	2.04E-06	1.63E-06	7.87E-07	1.03E-06	6.67E-07	7.08E-07	Pb	2.26E-07	1.81E-07	8.72E-08	1.14E-07	7.39E-08	7.85E-08
Mn	2.73E-05	3.06E-05	1.17E-06	1.61E-06	1.61E-06	1.63E-06	Mn	1.06E-04	1.19E-04	4.57E-06	6.28E-06	6.28E-06	6.35E-06

Table 6
Hazard quotient (HQ) and hazard index (HI) indices of PTEs for adults and children in mining areas.

Mining													
HQ ingestion Adults							HQ dermal Adults						
	Mohmand		Bajaur		Khyber			Mohmand		Bajaur		Khyber	
	Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water		Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water
Ni	1.43E-04	1.71E-04	1.99E-05	2.62E-05	1.74E-05	1.87E-05	Ni	1.09E-04	1.30E-04	1.51E-05	2.00E-05	1.33E-05	1.42E-05
Cr	8.56E-06	1.03E-05	2.33E-06	4.03E-07	4.06E-07	4.41E-07	Cr	1.51E-03	1.81E-03	4.09E-04	7.08E-05	7.13E-05	7.75E-05
Zn	4.86E-06	5.99E-06	6.13E-06	1.96E-06	5.86E-06	7.98E-06	Zn	4.44E-05	5.48E-05	5.60E-05	1.79E-05	5.36E-05	7.29E-05
Cu	3.10E-05	3.89E-05	1.55E-05	1.57E-05	1.51E-05	1.65E-05	Cu	4.72E-05	5.93E-05	2.35E-05	2.39E-05	2.30E-05	2.51E-05
Pb	3.28E-05	4.11E-05	9.02E-06	8.01E-05	9.33E-06	1.12E-05	Pb	4.99E-06	6.27E-06	1.37E-06	1.22E-05	1.42E-06	1.71E-06
Mn	1.63E-04	1.21E-04	1.29E-05	1.07E-05	1.28E-05	1.45E-05	Mn	6.22E-03	4.60E-03	4.93E-04	4.08E-04	4.86E-04	5.53E-04
HI	3.84E-04	3.88E-04	6.58E-05	1.35E-04	6.09E-05	6.93E-05	HI	7.94E-03	6.66E-03	9.99E-04	5.53E-04	6.48E-04	7.44E-04
HQ ingestion Children							HQ dermal Children						
	Mohmand		Bajaur		Khyber			Mohmand		Bajaur		Khyber	
	Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water		Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water
Ni	5.54E-04	6.61E-04	7.70E-05	1.02E-04	6.75E-05	7.22E-05	Ni	1.08E-03	1.29E-03	1.50E-04	1.98E-04	1.31E-04	1.40E-04
Cr	3.32E-05	3.98E-05	9.01E-06	1.56E-06	1.57E-06	1.71E-06	Cr	1.49E-02	1.79E-02	4.04E-03	7.00E-04	7.04E-04	7.66E-04
Zn	1.88E-05	2.32E-05	2.37E-05	7.60E-06	2.27E-05	3.09E-05	Zn	1.25E-05	1.55E-05	1.58E-05	5.07E-06	1.51E-05	2.06E-05
Cu	1.20E-04	1.51E-04	5.98E-05	6.07E-05	5.84E-05	6.39E-05	Cu	4.72E-04	5.93E-04	2.35E-04	2.39E-04	2.30E-04	2.51E-04
Pb	1.27E-04	1.59E-04	3.49E-05	3.10E-04	3.61E-05	4.34E-05	Pb	1.41E-05	1.77E-05	3.88E-06	3.45E-05	4.01E-06	4.82E-06
Mn	6.33E-04	4.68E-04	5.01E-05	4.15E-05	4.94E-05	5.62E-05	Mn	6.15E-03	4.55E-03	4.87E-04	4.04E-04	4.80E-04	5.46E-04
HI	1.49E-03	1.50E-03	2.55E-04	5.23E-04	2.36E-04	2.68E-04	HI	2.26E-02	2.43E-02	4.94E-03	1.58E-03	1.56E-03	1.73E-03

Table 7

Hazard quotient (HQ) and hazard index (HI) indices of PTEs for adults and children in non-mining areas.

Non-Mining													
	HQ ingestion Adults							HQ dermal Adults					
	Mohmand		Bajaur		Khyber			Mohmand		Bajaur		Khyber	
	Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water		Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water
Ni	4.00E-05	4.88E-05	8.27E-06	8.96E-06	1.22E-05	2.00E-05	Ni	3.04E-05	3.72E-05	6.29E-06	6.82E-06	9.28E-06	1.52E-05
Cr	6.73E-07	9.14E-07	2.29E-07	2.96E-07	2.44E-07	3.18E-07	Cr	1.18E-04	1.61E-04	4.03E-05	5.20E-05	4.28E-05	5.58E-05
Zn	2.10E-05	2.33E-05	5.28E-07	2.02E-06	4.59E-07	1.86E-06	Zn	1.92E-04	2.12E-04	4.82E-06	1.84E-05	4.19E-06	1.70E-05
Cu	1.78E-05	2.50E-05	1.79E-05	1.09E-05	9.56E-06	1.37E-05	Cu	2.71E-05	3.80E-05	2.73E-05	1.67E-05	1.46E-05	2.09E-05
Pb	1.51E-05	1.20E-05	5.81E-06	7.58E-06	4.92E-06	5.23E-06	Pb	2.29E-06	1.83E-06	8.84E-07	1.15E-06	7.49E-07	7.96E-07
Mn	1.53E-04	1.72E-04	6.59E-06	9.06E-06	9.06E-06	9.16E-06	Mn	5.80E-03	6.50E-03	2.49E-04	3.43E-04	3.43E-04	3.47E-04
HI	2.48E-04	2.82E-04	3.93E-05	3.88E-05	3.64E-05	5.03E-05	HI	6.17E-03	6.95E-03	3.29E-04	4.38E-04	4.15E-04	4.56E-04
	HQ ingestion Children							HQ dermal Children					
	Mohmand		Bajaur		Khyber			Mohmand		Bajaur		Khyber	
	Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water		Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water
Ni	1.55E-04	1.89E-04	3.20E-05	3.47E-05	4.72E-05	7.73E-05	Ni	3.01E-04	3.68E-04	6.23E-05	6.75E-05	9.18E-05	1.50E-04
Cr	2.60E-06	3.54E-06	8.88E-07	1.15E-06	9.44E-07	1.23E-06	Cr	1.17E-03	1.59E-03	3.99E-04	5.15E-04	4.24E-04	5.52E-04
Zn	8.14E-05	9.00E-05	2.04E-06	7.82E-06	1.78E-06	7.20E-06	Zn	5.43E-04	6.00E-04	1.36E-05	5.21E-05	1.19E-05	4.80E-05
Cu	6.90E-05	9.67E-05	6.93E-05	4.23E-05	3.70E-05	5.31E-05	Cu	2.69E-04	3.76E-04	2.70E-04	1.65E-04	1.44E-04	2.07E-04
Pb	5.83E-05	4.66E-05	2.25E-05	2.93E-05	1.90E-05	2.02E-05	Pb	6.46E-06	5.17E-06	2.49E-06	3.25E-06	2.11E-06	2.24E-06
Mn	5.93E-04	6.65E-04	2.55E-05	3.51E-05	3.51E-05	3.54E-05	Mn	5.74E-02	6.43E-02	2.47E-03	3.39E-03	3.39E-03	3.43E-03
HI	9.59E-04	1.09E-03	1.52E-04	1.50E-04	1.41E-04	1.95E-04	HI	5.96E-02	6.73E-02	3.22E-03	4.20E-03	4.07E-03	4.39E-03

Table 8

Carcinogenic risk (CR) by ingestion and dermal contact in mining areas for adults and children.

Mining													
	CR ingestion Adults							CR dermal Adults					
	Mohmand		Bajaur		Khyber			Mohmand		Bajaur		Khyber	
	Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water		Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water
Ni	4.86E-06	5.81E-06	6.76E-07	8.92E-07	5.93E-07	6.34E-07	Ni	7.41E-06	8.85E-06	1.03E-06	1.36E-06	9.03E-07	9.66E-07
Cr	6.42E-06	7.71E-06	1.75E-06	3.02E-07	3.04E-07	3.31E-07	Cr	9.79E-06	1.17E-05	2.66E-06	4.6E-07	4.63E-07	5.04E-07
Pb	9.75E-09	1.22E-08	2.68E-09	2.38E-08	2.78E-09	3.33E-09	Pb	1.49E-09	1.86E-09	4.09E-10	3.63E-09	4.23E-10	5.08E-10
	CR ingestion Children							CR dermal Children					
	Mohmand		Bajaur		Khyber			Mohmand		Bajaur		Khyber	
	Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water		Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water
Ni	1.88E-05	2.25E-05	2.62E-06	3.45E-06	2.30E-06	2.45E-06	Ni	7.32E-05	8.74E-05	1.02E-05	1.34E-05	8.93E-06	9.55E-06
Cr	2.49E-05	2.98E-05	6.76E-06	1.17E-06	1.18E-06	1.28E-06	Cr	9.67E-05	1.16E-04	2.63E-05	4.55E-06	4.58E-06	4.98E-06
Pb	3.77E-08	4.74E-08	1.04E-08	9.23E-08	1.07E-08	1.29E-08	Pb	4.19E-09	5.26E-09	1.15E-09	1.03E-08	1.19E-09	1.43E-09

Table 9

Carcinogenic risk (CR) by ingestion and dermal contact in non-mining areas for adults and children.

Non-Mining													
	CR ingestion Adults							CR dermal Adults					
	Mohmand		Bajaur		Khyber			Mohmand		Bajaur		Khyber	
	Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water		Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water
Ni	5.59E-07	6.84E-07	1.16E-07	1.25E-07	1.71E-07	2.80E-07	Ni	8.52E-07	1.04E-06	1.76E-07	1.91E-07	2.6E-07	4.26E-07
Cr	5.05E-07	6.85E-07	1.72E-07	2.22E-07	1.83E-07	2.38E-07	Cr	7.68E-07	1.05E-06	2.62E-07	3.38E-07	2.78E-07	3.63E-07
Pb	4.48E-09	3.58E-09	1.73E-09	2.25E-09	1.46E-09	1.55E-09	Pb	6.82E-10	5.46E-10	2.63E-10	3.43E-10	2.23E-10	2.37E-10

	CR ingestion Children							CR dermal Children					
	Mohmand		Bajaur		Khyber			Mohmand		Bajaur		Khyber	
	Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water		Ground Water	Surface Water	Ground Water	Surface Water	Ground Water	Surface Water
Ni	2.17E-06	2.65E-06	4.48E-07	4.85E-07	6.61E-07	1.08E-06	Ni	8.43E-06	1.03E-05	1.74E-06	1.89E-06	2.57E-06	4.21E-06
Cr	1.95E-06	2.65E-06	6.66E-07	8.60E-07	7.08E-07	9.22E-07	Cr	7.6E-06	1.04E-05	2.59E-06	3.35E-06	2.76E-06	3.59E-06
Pb	1.73E-08	1.39E-08	6.69E-09	8.73E-09	5.67E-09	6.02E-09	Pb	1.92E-09	1.54E-09	7.41E-10	9.67E-10	6.28E-10	6.67E-10

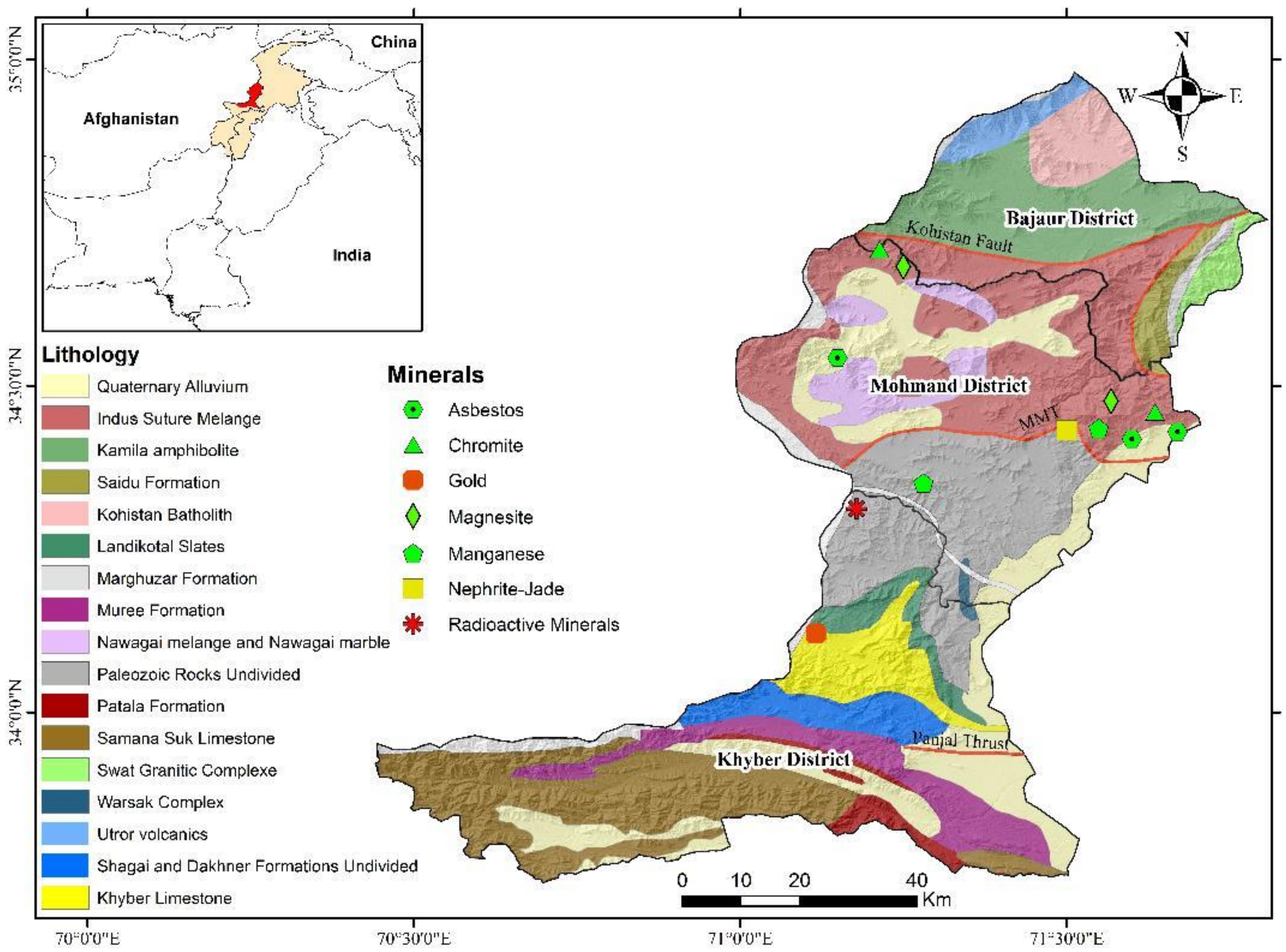

Fig 1. Location map of the study area showing the sampling Districts

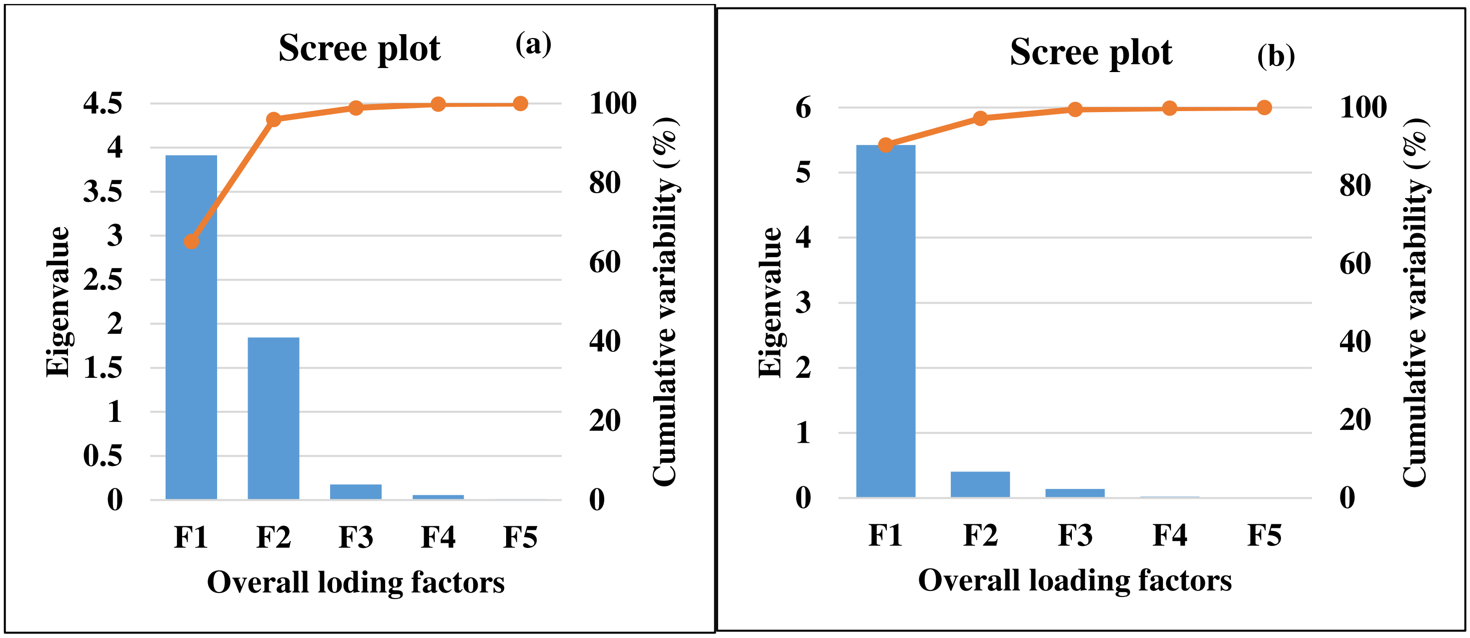

Fig. 2. Overall loading factors of (a) Mining, and (b) Non-mining areas of water sources in KPK

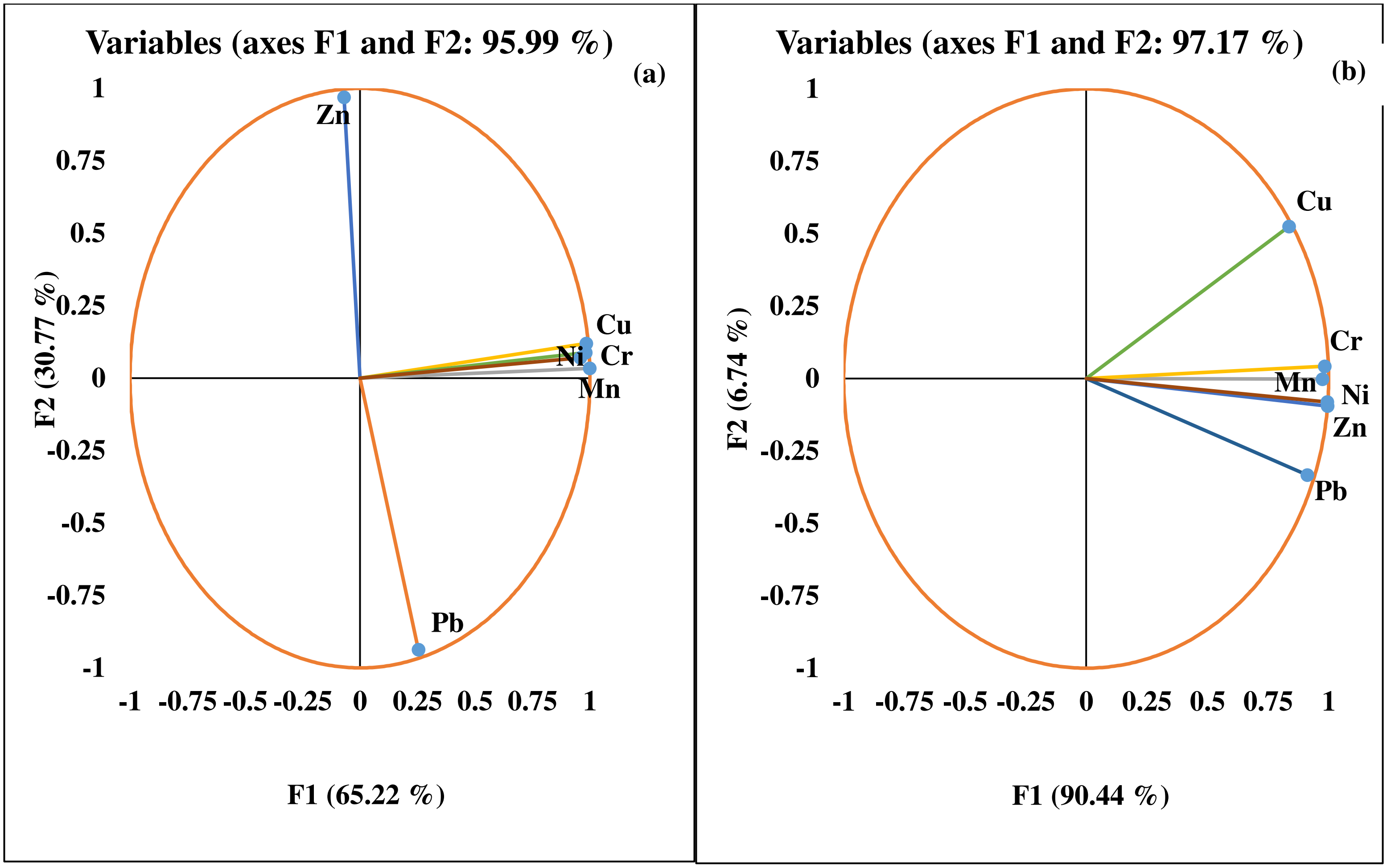

Fig. 3 First two significant factors (a) Mining, and (b) Non-mining areas of water sources in KPK.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- MiningandNonMiningSupportingdataTables.docx