



## Shallow water proved higher levels of potentially harmful elements and human health risk along the Sadkal oil exploration and production

Said Akbar Khan<sup>a</sup>, Hizbullah Khan<sup>b</sup>, Muhammad Ishtiaq<sup>b</sup>, Umar Saddique<sup>c</sup>, Said Muhammad<sup>d,\*</sup>, Muhammad Farooq<sup>d</sup>

<sup>a</sup>Department of Earth and Environmental Sciences, Bahria University, Islamabad 44000, Pakistan, email: saidakbar2008@yahoo.com

<sup>b</sup>Department of Environmental Sciences, University of Peshawar, Peshawar 25120, Pakistan, emails: hizbullah@uop.edu.pk (H. Khan), drishtiaq250@yahoo.com (M. Ishtiaq)

<sup>c</sup>Department of Chemistry, Abdul Wali Khan University, Mardan 23200, Pakistan, email: umar32146@yahoo.com

<sup>d</sup>Department of Earth Sciences, COMSATS University, Abbottabad 22060, Pakistan, Tel. +92 992 383591-6; Fax: +92 992 383441; emails: saidmuhammad1@gmail.com (S. Muhammad), farooq@ciit.net.pk (M. Farooq)

Received 29 December 2017; Accepted 13 April 2018

### ABSTRACT

This study investigates the concentrations of potentially harmful elements (PHEs) in various drinking waters along the Sadkal oil exploration and production in Fateh Jang, Pakistan. For this purpose, representative water samples were collected from various drinking water sources (bore wells, dug wells and hand pumps). Water samples were analyzed for physicochemical parameters, such as anions using electrochemical analyzer (C6030) and titration methods, and PHEs by graphite furnace atomic absorption spectrophotometer (Perkin-Elmer model 700, USA). Results revealed that especially in shallow waters (hand pumps), the pH, chloride (Cl), nitrate (NO<sub>3</sub>) and PHEs including chromium (Cr), nickel (Ni), manganese (Mn), iron (Fe), cadmium (Cd), lead (Pb) and copper (Cu) concentrations surpassed their respective safe drinking water guidelines set by World Health Organization (WHO). Determined PHEs concentrations in drinking water were evaluated for the potential risk assessment through the daily intake (DI) of metals and health risk index (HRI). Higher DI values for Zn (1.90E-01 mg kg<sup>-1</sup>-d), and the HRI values >1 for Cd and Ni through hand pumps water consumptions were observed. Higher HRI values could cause various chronic and acute health problems to the exposed human population.

*Keywords:* Wastewater; Drinking water; Physicochemical parameters; Fateh Jang

### 1. Introduction

Oil and gas are the main sectors of energy, economic development and social prosperity. However, the by-product of oil and gas exploration and exploitation resulted in environmental contaminations such as the potentially harmful elements (PHEs) and hydrocarbons [1–3]. Among these contaminants, the PHEs are considered as more hazardous due to their toxic, non-degradable and bioaccumulative nature [4–9]. The PHEs enriched effluents find their ways to environmental compartment such as water

and soil, and cause contamination of such resources [10,11]. The effluents flow to surface water much more easily and adversely affects and deteriorates its quality and inhabits living organisms, making the surface water systems more vulnerable to contamination [12–14]. Therefore, groundwater is considered safe [15,16] and preferably used for drinking and other domestic purposes [12,13]. However, recently the PHEs contaminations in groundwater have been documented in various environmental studies [17,18].

The PHEs' contaminations in water lead to direct exposure via the most common routes, including oral intake and dermal contact with the consumers. Oral intake of PHEs is considered as the major pathway for human exposure and causes various health problems [19,20]. Among PHEs, the

\* Corresponding author.

Fe, Mn, Cr, Ni, Zn and Cu are required in a specific amount for normal function of body and classified as essential elements. Deficiencies of essential elements lead to various health effects, while higher concentrations cause toxicity. Non-essential elements including Cd, Pb, Hg and As are extremely toxic to human even in minute quantities [21–23]. Toxic effects of non-essential elements include hypertension, headache, asthma, anemia, liver and kidney problems, immune dysfunction and cardiovascular diseases, cancer and memory deterioration in children [17,24].

Globally, the PHEs contamination in drinking water has been well studied. However, the problem of PHEs contamination is often more severe in the developing countries due to higher population growth, low economy and lack of treatment facility [25,26]. Like other developing countries, Pakistan is also facing higher population growth, low-income and drinking water exploitation and contaminations' problems [19]. The PHEs contamination in sediments [27], and ecological communities such as mussels [2] resulting from the oil exploration and production have been studied. Similarly, the PHEs contaminations of soil near to Sadkal oil exploration and production were reported by Khan et al. [28]. The PHEs could leach down, lead to groundwater contaminations, and pose potential health risk via consumption of contaminated drinking water. So far, the drinking water quality and its potential health risk along the Sadkal oil exploration and production have not been explored. Therefore, this study was aimed to investigate whether the high levels of PHEs previously observed in soil are getting into groundwater. Further, drinking water sources at various depths were evaluated for potential health risk assessment through consumption of PHEs that could be used as a benchmark against future sampling efforts, to track trends over time.

## 2. Materials and methods

### 2.1. Study area

Sadkal oil exploration and production unit is located in the Sadkal village, Fateh Jang town, Pakistan, lies between latitude 33°34'N and longitude 72°45'E having 866 km<sup>2</sup> area (Fig. 1). The study area mainly consists of rain fed agriculture lands. Natural vegetation such as forest, shrubs, grasses and the wastelands exist on non-cultivated areas. Two major seasons prevails, but the rainfall is more in summer monsoon than winter. Seasonal mean rainfall ranges in summer (300–500 mm) and winter (250–300 mm) seasons with temperature (5°C–30°C) [29,30].

This study area was selected to investigate the levels of PHEs and other contaminations in drinking water near the Oil and Gas Development Company (OGDC) activities. The oil exploration in Sadkal village has been started by OGDC since 1980s. Wastewater is produced as a by-product of oil during the exploration and exploitation activities. Unfortunately, wastewater is released without any treatment and accumulated in open ponds closely <1 km located to human settlements. High levels of PHEs contamination in soil near the Sadkal village were reported by Khan et al. [28]. Water could dissolve PHEs in the percolation or leaching due to lithogenic process (weathering and erosion) and result in drinking water contamination of area.

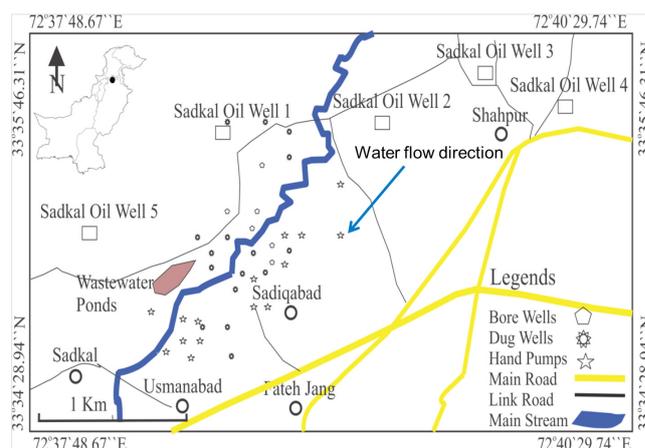


Fig. 1. Map of the study area showing oil and gas exploration wells and sampling sites.

### 2.2. Samples collection and analysis

Water samples were collected in 500 mL clean polythene bottles from the available drinking water sources, including shallow (hand pumps 8–12 m), medium (dug well 16–22 m) and deep (bore wells 25–35 m) along the Sadkal village in June 2014. Basic parameter such as pH was measured on site using the electrochemical analyzer C6030 and two bottles were pre-washed three times with respective samples and filled from each sampling source. One of the two-bottle water was filtered through Whatman (0.45 µm) filter paper and acidified with few drops of nitric acid (HNO<sub>3</sub>). Water samples were properly marked, transported to Centralized Resource Laboratory (CRL), University of Peshawar and stored in dark at 4°C till further analyses [31].

### 2.3. Analytical procedure

Each non-acidified water sample was analyzed for anions, including chloride (Cl), fluoride (F), sulfate (SO<sub>4</sub>), nitrate (NO<sub>3</sub>) and nitrite (NO<sub>2</sub>) using the titration method and electrochemical analyzer C6030. Acidified samples were analyzed for sodium (Na), potassium (K), calcium (Ca), magnesium (Mg) by Ion Chromatography (Metrohm, 800 series) and PHEs concentrations using the Graphite furnace atomic absorption spectroscopy (G-FAAS Perkin-Elmer model 700, USA) at the CRL, University of Peshawar. Each sample was analyzed in triplicates having reproducibility at 90% ± 5% confidence level and mean values were used for results' interpretation. For the G-FAAS calibration and data confirmation, three standards (2.5, 5.0 and 10.0 µg L<sup>-1</sup>) and a blank (0.0 µg L<sup>-1</sup>) with regular interval of 10 samples were used within this study. Standards for each corresponding element were prepared from the stock Fluka Kamica (Buchs, Switzerland) solution of 1,000 mg L<sup>-1</sup> with deionized water.

### 2.4. Risk assessment

In the study area, residents were interviewed/surveyed for drinking water habits, sources, collection and storage vessels, common health diseases, age, body weight and income level. Questionnaire was developed for collection of basic

health information from previous study by Muhammad et al. [17]. After approval from the department board, this study randomly surveyed the local respondents ( $n = 380$ ) included both genders, i.e., male ( $n = 190$ ) and female ( $n = 190$ ), children (1–16 years,  $n = 140$ ) and adults (17–65 years,  $n = 240$ ).

Oral intake via contaminated drinking water [17,32] and food [33,34] is the major pathway for human exposure to PHEs. Potential risk assessment of PHEs through drinking consumption was calculated by average daily intake (DI) of element and health risk index (HRI) using equations adopted from US EPA [35].

$$DI = (CW \times IR \times EF \times ED)/(BW \times AT) \quad (1)$$

where CW is the concentration of PHEs in water ( $\text{mg L}^{-1}$ ), IR ingestion rate of water ( $2 \text{ L d}^{-1}$ ), EF exposure frequency ( $365 \text{ d y}^{-1}$ ), ED exposure duration (30 y), BW body weight (children 30 kg and adults 70 kg) and AT averaging time, that is,  $365 \text{ d y}^{-1} \times ED$  for non-carcinogens [36].

The intake of PHEs was used for the HRI calculation.

$$HRI = DI/RfD \quad (2)$$

where the oral toxicity reference dose (RfD,  $\text{mg kg}^{-1}\text{-d}$ ) values of PHEs are Cd ( $5.0\text{E-}04$ ), Cr (1.5), Cu ( $3.7\text{E-}02$ ), Mn ( $1.4\text{E-}01$ ), Ni ( $2.0\text{E-}02$ ), Pb ( $3.6\text{E-}02$ ) and Zn ( $3.0\text{E-}01$ )  $\text{mg kg}^{-1}\text{-d}$ . Exposed population is assumed to be safe if  $HRI < 1$  [17].

### 2.5. Statistical analyses

Data were analyzed using computer software's such as MS Excel (Office 2010), Sigma plot 12.5 for the arithmetic mean, standard deviation and range, and SPSS 21 (SPSS Inc., Chicago, IL, USA) for one-way analysis of variance (ANOVA), correlation and principal components' analyses (PCA).

## 3. Results and discussion

### 3.1. Physicochemical parameters

Table 1 summarizes the concentrations of physicochemical parameters in the study area. The pH has indirect effects to human health by affecting the ions' solubility and aquatic life survival. The pH values ranged from 6.80 to 8.50, 7.90 to 8.23 and 8.30 to 9.10 in bore wells, dug wells and hand pumps water, respectively (Table 1). Hand pump showed the highest mean pH values as compared with bore wells and dug wells water sources. The pH values for bore wells and dug wells were found within the safe permissible limits of drinking water guidelines set by the World Health Organization (WHO) [37]. However, 50% of hand pumps water samples surpassed this limit. Higher pH in shallow (hand pumps) drinking water sources within the study area was found consistent with those reported by Gul et al. [38] for shallow drinking water in Mardan district of the surroundings.

Anions such as Cl, F and  $\text{SO}_4$  are required in a limited amount for normal body functions. However, higher concentrations than the fixed amount could cause toxicity in living beings [36,39,40]. In the study area, Cl concentrations ranged ( $75.02\text{--}624.13$ ,  $147.45\text{--}380.43$  and  $522.17\text{--}2,441.09 \text{ mg L}^{-1}$ ), F

( $0.16\text{--}5.75$ ,  $0.53\text{--}0.60$  and  $0.90\text{--}1.62 \text{ mg L}^{-1}$ ),  $\text{SO}_4$  ( $4.12\text{--}143.32$ ,  $86.60\text{--}200.39$  and  $54.28\text{--}280.18 \text{ mg L}^{-1}$ ),  $\text{NO}_3$  ( $4.60\text{--}266.01$ ,  $22.40\text{--}200.11$  and  $18.60\text{--}576.37 \text{ mg L}^{-1}$ ) and  $\text{NO}_2$  ( $0.12\text{--}2.02$ ,  $0.34\text{--}0.70$  and  $1.04\text{--}4.02 \text{ mg L}^{-1}$ ) in bore wells, dug wells and hand pumps water, respectively (Table 1). Results revealed that majority of anions showed the highest concentrations in hand pumps' water as compared with deep water (bore wells) and surpassed their respective drinking water guidelines set by the WHO. High levels of anions' contaminations in soil were due to wastewater discharge of the Sadkal oil exploration and production [28]. Hand pumps' water sources stay close to the surface; therefore, the contaminants could easily seep or leach down from wastewaters and soils to the water. High concentrations of  $\text{NO}_3$  and  $\text{NO}_2$  could cause various health problems, especially in babies. Anion's results of this study were found higher than those reported for drinking water by Khan et al. [19] in the Peshawar district and Iqbal et al. [41] Rawalpindi/Islamabad districts.

Specific amounts of Na, K, Ca and Mg are essentially required for normal functions of human being. Deficiency effects of Na, K, Ca and Mg include dehydration, fatigue, muscle and bladder weakness, hypertension, depression, asthma, heart problems and kidney diseases. However, higher concentrations may cause toxicity or health problems, including rapid heartbeat, hypertension, headaches, edema, stroke, kidney damages, stomach problems, nausea, cystitis, ovarian cysts, reduced renal function and abnormal metabolism of protein [36,42,43]. The concentrations of Na ranged ( $68.23\text{--}233.34$ ,  $100.29\text{--}139.21$  and  $96.41\text{--}708.29 \text{ mg L}^{-1}$ ), K ( $0.21\text{--}1.34$ ,  $0.40\text{--}0.51$  and  $0.43\text{--}15.50 \text{ mg L}^{-1}$ ), Ca ( $10.20\text{--}167.37$ ,  $22.50\text{--}60.44$  and  $170.34\text{--}490.16 \text{ mg L}^{-1}$ ) and Mg ( $24.8\text{--}116.50$ ,  $19.60\text{--}50.10$  and  $30.20\text{--}40.18 \text{ mg L}^{-1}$ ) in bore wells, dug wells and hand pumps water, respectively (Table 1). The safe drinking water guidelines set by WHO were surpassed by Na (40%, 100% and 75%), K (25%, 0% and 0%), Ca (50%, 0% and 0%) and Mg (40%, 50% and 10%) samples of bore wells, dug wells and hand pumps water. Although, water dissolves these elements due to natural lithogenic processes (weathering and erosion) along the flow, however, the various anthropogenic (industrial, mining and agriculture) activities could affect their concentrations in water as well [18,38].

The PHEs are extremely hazardous, owing to their toxicity, persistence and bioaccumulative nature [44]. Instrumental detection limits of PHEs Cd, Cr, Cu, Mn, Ni, Pb, Zn and Fe were 0.002, 0.004, 0.005, 0.005, 0.07, 0.05, 0.02 and 0.06  $\mu\text{g L}^{-1}$ , respectively. Chromium concentrations ranged from 0.01 to 0.06, 0.01 to 0.97 and 0.006 to 0.97  $\text{mg L}^{-1}$  in bore wells, dug wells and hand pumps water, respectively (Table 1). The concentrations of Cr were found below than the safe drinking water guidelines set by WHO, except for 10%, 20% and 50% samples of bore wells, dug wells and hand pumps water, respectively. Chromium is one of the required elements for lipid and glucose metabolism, and amino acid utilization [45]. However, higher concentrations of Cr may cause toxicity and affect the kidneys, liver and respiratory organs and human cancer [46]. Nickel concentrations ranged from 0.01 to 0.30, 0.01 to 0.10 and 0.13 to 1.48  $\text{mg L}^{-1}$  in bore wells, dug wells and hand pumps water, respectively (Table 1). Nickel concentrations have surpassed the drinking water guidelines set by the WHO for 30%, 40% and 100% samples of bore wells, dug wells and hand pumps water, respectively.

Table 1  
Physicochemical parameter concentrations (mg L<sup>-1</sup>) in various drinking water sources of the study area

	Bore wells ( <i>n</i> <sup>a</sup> = 30)		Dug wells ( <i>n</i> = 09)		Hand pumps ( <i>n</i> = 12)		WHO
	Range	Mean ± Std <sup>b</sup>	Range	Mean ± Std	Range	Mean ± Std	
pH <sup>c</sup>	6.80–8.50	7.70 ± 0.17	7.90–8.23	8.05 ± 0.15	8.30–9.10	8.58 ± 0.18	6.50–8.50
Chloride	75.02–624.13	249.36 ± 45.98	147.45–380.43	263.50 ± 116.50	522.17–2,441.09	1,491.50 ± 515.17	250.00
Fluoride	0.16–5.75	1.50 ± 0.57	0.53–0.60	0.57 ± 0.04	0.90–1.62	1.35 ± 0.17	1.50
Sulfate	4.12–143.32	64.02 ± 12.56	86.60–200.39	143.30 ± 56.70	54.28–280.18	165.00 ± 48.31	250.00
Nitrate	4.60–266.01	104.11 ± 24.33	22.40–200.11	111.20 ± 88.80	18.60–576.37	235.05 ± 122.43	10.00
Nitrite	0.12–2.02	0.94 ± 0.35	0.34–0.70	0.52 ± 0.18	1.04–4.02	2.50 ± 0.74	1.00
Na	68.23–233.34	142.2 ± 715.53	100.29–139.21	119.50 ± 19.50	96.41–708.29	395.50 ± 128.58	200.00
K	0.21–1.34	0.69 ± 0.12	0.40–0.51	0.46 ± 0.06	0.43–15.50	6.29 ± 3.25	12.00
Ca	10.20–167.37	59.47 ± 16.11	22.50–60.44	41.25 ± 18.75	170.34–490.16	278.50 ± 72.74	200.00
Mg	24.8–116.50	51.69 ± 8.64	19.60–50.10	34.85 ± 15.25	30.20–40.18	34.73 ± 2.1	50.00
Cr	0.01–0.06	0.02 ± 0.00	0.01–0.60	0.30 ± 0.30	0.01–0.97	0.65 ± 0.22	0.05
Ni	0.01–0.30	0.05 ± 0.03	0.01–0.10	0.05 ± 0.05	0.13–1.48	0.73 ± 0.29	0.02
Mn	0.05–1.03	0.40 ± 0.10	0.01–0.90	0.46 ± 0.45	0.43–1.70	1.03 ± 0.26	0.40
Fe	0.04–1.50	0.52 ± 0.15	0.21–0.40	0.31 ± 0.10	0.82–1.30	1.03 ± 0.1	0.30
Cd	BDL <sup>c</sup> –0.07	0.01 ± 0.01	0.02–0.07	0.05 ± 0.03	0.01–0.30	0.12 ± 0.06	0.003
Pb	0.01–0.20	0.05 ± 0.02	0.01–0.10	0.01 ± 0.01	0.01–0.60	0.25 ± 0.13	0.01
Zn	0.01–3.28	1.96 ± 0.35	0.32–2.60	1.46 ± 1.14	1.92–4.00	2.91 ± 0.55	3.00
Cu	0.08–2.10	0.75 ± 0.23	0.39–2.50	1.45 ± 1.06	2.30–3.10	2.83 ± 0.19	2.00

<sup>a</sup>Number of samples.

<sup>b</sup>Standard deviation.

<sup>c</sup>Unitless.

Exposure to high levels of Ni may cause different diseases including allergic dermatitis, lung fibrosis and cancer in respiratory tract, vomiting, nausea, abdominal discomfort, headaches, cough and shortness of breath [47]. Manganese concentrations ranged from 0.05 to 1.03, 0.01 to 0.90 and 0.43 to 1.70 mg L<sup>-1</sup> in bore wells, dug wells and hand pumps water, respectively (Table 1). Bore wells (40%), dug wells (50%) and hand pumps (75%) of water samples have surpassed the safe drinking water guidelines set by WHO. Manganese is one of the essential elements for all living beings [17,48]. However, exposure to be higher level of Mn could cause severe health issues such as dizziness, muscle tremors, liver disease, and effect nervous system and other function of human beings [49]. Iron concentrations ranged from 0.04 to 1.50, 0.21 to 0.40 and 0.82 to 1.30 mg L<sup>-1</sup> in bore wells, dug well and hand pumps water, respectively (Table 1). A majority (66%) of sampling showed higher concentrations of Fe in all water sources and surpassed the safe drinking water guidelines set by WHO. Like Mn, Fe is also essentially required for normal human function in a specific amount. However, higher concentrations of Fe could produce human toxicity, including vomiting, diarrhea, blood, kidney and liver, cardiovascular and central nervous systems problems [18].

Cadmium concentration ranged from <0.01 to 0.07, 0.02 to 0.07 and 0.01 to 0.30 mg L<sup>-1</sup> in bore wells, dug wells and hand pumps water, respectively (Table 1). Bore wells (40%), dug wells (100%) and hand pumps (100%) of water samples showed higher Cd concentrations than the safe drinking water guidelines set by WHO. Exposure to higher levels of Cd contaminations could cause acute and chronic toxicity.

Acute toxic effects include gastrointestinal problems, such as vomiting and diarrhea [50], while chronic exposure may cause kidney and skeleton damage [51,52]. Lead concentrations ranged from below detection limit (BDL) to 0.20, 0.01 to 0.10, 0.01 to 0.60 mg L<sup>-1</sup> in bore wells, dug wells and hand pumps water, respectively (Table 1). Bore wells (30%), dug wells (10%) and hand pumps (50%) of water samples have surpassed the drinking water guideline set by the WHO. Lead toxic effects include nervous, damage to digestive system and kidneys [52]. Children are more sensitive to Pb toxicity, which deteriorate their mental sharpness, memory and cause anemia [17,53]. Zinc and Cu concentrations ranged from BDL to 3.28, 0.32 to 2.60 and 1.92 to 4.00 mg L<sup>-1</sup> and 0.08 to 2.10, 0.39 to 2.50 and 2.30 to 3.10 mg L<sup>-1</sup>, respectively (Table 1). In the study area, bore wells (30%, 20%), dug wells (10%, 10%) and hand pumps (75%, 100%) of water samples showed higher concentrations that the safe drinking water guidelines set by the WHO. Zinc and Cu are essential metals and required for normal body function. However, their higher concentration could cause toxicity such as sideroblastic anemia and Alzheimer's disease [17,54].

### 3.2. Shallow and deep groundwater comparison

Groundwater's that stay close to surface is considered shallow water such as the hand pump source. Shallow water showed significantly ( $p < 0.05$ ) higher level of contaminations as compared with deep water sources. Higher level of contaminations could be attributed to aboveground soil contamination, oil and gas exploration activities [28]. Water

in the percolation or leaching due to lithogenic process could dissolve most of the contaminant and bring in shallow-water sources as these sources along with surface water are more susceptible to contaminations. These results were found consistent with those reported by Begum et al. [18] for drinking water along mafic and ultramafic rocks, where the shallow water revealed higher contamination levels as compared with deep water sources. Anions and PHEs concentrations of this study were found higher than those reported by Khan et al. [19] in the Peshawar district and Iqbal et al. [41] Rawalpindi/Islamabad districts.

### 3.3. Risk assessment

In the field survey, we observed that many of the local inhabitants had a low literacy rate, income level and are unaware of the importance of clean and safe water. Residents cannot afford bottled water and are dependent on the local groundwater for their drinking water. A majority (over 60%, 10% and 15%) of the population were using bore wells, dug wells and hand pumps drinking water within the study area. Female's especially young ladies use manual or electric power to collect water from mentioned sources and were stored in close polythene or cemented brick tanks. Waters are used for drinking and other domestic purposes without filtration, filtered through nylon cloth for dirt, or allowed to settle for suspended particles. Basic information together with the PHEs concentrations in drinking water were used for the risk assessment via average DI and HRI.

Potential risk depends on the concentrations and variety of PHEs, consumption rate, type and toxicity [19,44]. The highest DI of Zn occurred through hand pumps water consumption as compared with other PHEs and water sources (Fig. 2). Higher Zn intakes as compared with other PHEs were attributed to its high contamination level in the drinking water. The DI values of PHEs through water consumption were different for various age groups such as adults and children. Children showed the highest DI values for Zn ( $190 \mu\text{g kg}^{-1}\text{-d}$ ) and the lowest for Cd ( $0.91 \mu\text{g kg}^{-1}\text{-d}$ ). Similarly, the adults' highest DI values for Zn was ( $80.7 \mu\text{g kg}^{-1}\text{-d}$ ) and the lowest for Cd ( $0.39 \mu\text{g kg}^{-1}\text{-day}$ , Fig. 2).

The highest HRI values (16.01) were observed for Cd occurred through hand pumps water consumption as compared with other PHEs and water sources (Fig. 3). These higher HRI values for the Cd as compared with other PHEs were attributed to its higher toxicity and low reference dose. Hand pumps' water posed higher HRI values to the exposed human population as compared with bore wells. Higher HRI values were attributed to the high levels of PHEs contaminations in hand pumps' water that led to their higher intake and resulted in higher HRI. Higher doses of Cd could cause acute and chronic toxicity in the exposed population. The HRI values were  $<1$  for Cr, Mn, Pb, Zn and Cu, therefore, pose no potential risk when compared with the US EPA limits. Children showed the highest HRI values for all PHEs as compared with adults. Higher HRI values for children were attributed to low body weight. In the study area, HRI values were found higher than those reported in drinking water of Peshawar district by the Khan et al. [19] and Mardan district by Gul et al. [38].

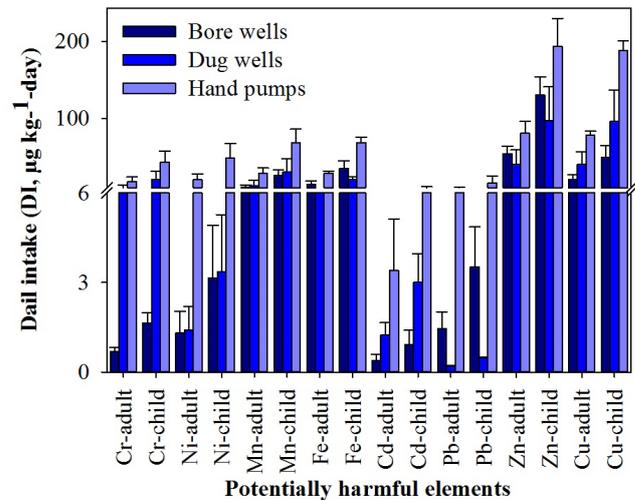


Fig. 2. Daily intake through PHEs consumptions in drinking water sources.

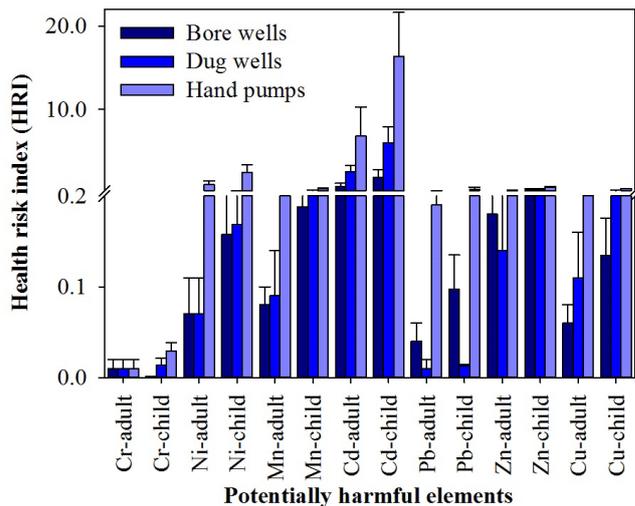


Fig. 3. Health risk assessment through PHEs consumptions in drinking water sources.

### 3.4. Statistical analyses

One-way ANOVA analysis for statistical comparison of water sources revealed the significant variations in the level of  $p < 0.05$ , which means that the sources contribute differently to the mean water contamination. Table 2 summarizes the Pearson correlation matrices of selected physicochemical parameters in drinking water of the study area. Physicochemical parameters showed significant correlations in drinking water. Highly significant correlations were found between the parameter pairs, including Na–K ( $r = 0.951$ ), Na–Cr ( $r = 0.771$ ) and Na–Pb ( $r = 0.814$ ) showing a common source of these elements. Other pairs like Cr–Ni ( $r = 0.812$ ), Cr–Mn ( $r = 0.753$ ), Cr–Cd ( $r = 0.814$ ) and Cr–Cu ( $r = 0.671$ ) showed significant correlation suggesting their geochemical association (Table 2). Results of the PCA for selected physicochemical parameters in drinking water were summarized

Table 2  
Correlation matrix of physicochemical parameters in drinking water ( $n^a = 51$ ) of the study area

	pH	Chloride	Fluoride	Sulfate	Nitrate	Nitrite	Na	K	Ca	Mg	Cr	Ni	Mn	Fe	Cd	Pb	Zn	Cu
pH	1.000	0.358	0.113	<b>0.699</b>	0.317	0.327	0.481	0.517	0.501	-0.031	0.478	0.443	0.088	0.460	0.333	0.540	0.176	<b>0.618</b>
Chloride		1.000	-0.139	0.112	-0.016	0.449	0.570	0.396	<b>0.804</b>	-0.056	<b>0.756</b>	<b>0.904</b>	0.597	0.460	<b>0.740</b>	0.342	0.343	0.523
Fluoride			1.000	-0.035	-0.078	-0.143	-0.122	-0.014	-0.130	-0.245	-0.088	-0.115	-0.062	0.162	-0.180	0.034	-0.238	-0.023
Sulfate				1.000	0.449	0.253	0.432	0.547	0.385	-0.174	0.342	0.256	0.152	0.162	0.249	0.572	0.266	0.485
Nitrate					1.000	0.290	0.105	0.127	0.192	0.331	-0.152	-0.114	-0.302	0.019	-0.201	0.043	0.265	0.341
Nitrite						1.000	<b>0.713</b>	0.588	0.429	0.192	0.472	0.305	0.177	0.138	0.180	0.555	0.484	0.227
Na							1.000	<b>0.951</b>	<b>0.620</b>	-0.022	<b>0.771</b>	0.554	0.478	0.266	0.459	<b>0.814</b>	0.539	0.545
K								1.000	0.517	-0.171	<b>0.703</b>	0.465	0.438	0.305	0.406	<b>0.869</b>	0.496	0.516
CA									1.000	0.113	<b>0.735</b>	<b>0.874</b>	0.592	0.341	<b>0.823</b>	<b>0.630</b>	0.307	<b>0.624</b>
Mg										1.000	-0.333	-0.222	-0.448	-0.270	-0.272	-0.095	0.176	-0.130
Cr											1.000	<b>0.812</b>	<b>0.753</b>	0.397	<b>0.814</b>	<b>0.660</b>	0.243	<b>0.671</b>
Ni												1.000	<b>0.677</b>	0.535	<b>0.921</b>	0.536	0.297	0.497
Mn													1.000	0.282	<b>0.689</b>	0.482	-0.115	0.530
Fe														1.000	0.386	0.374	0.352	0.269
Cd															1.000	0.525	0.154	0.472
Pb																1.000	0.396	0.366
Zn																	1.000	-0.006
Cu																		1.000

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

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

<sup>a</sup>Number of samples.

Table 3  
Factor loading of selected physicochemical parameters in drinking water ( $n^a = 51$ )

Parameters	PC1	PC2	PC3	PC4	PC5
pH	0.25	0.26	<b>0.76</b>	-0.11	0.28
Chloride	<b>0.86</b>	0.19	0.05	0.17	0.28
Fluoride	-0.23	-0.11	0.14	-0.61	0.31
Sulfate	0.07	0.39	<b>0.76</b>	-0.13	-0.03
Nitrate	-0.21	0.04	<b>0.72</b>	0.46	0.11
Nitrite	0.16	<b>0.73</b>	0.11	0.33	0.10
Na	0.40	<b>0.86</b>	0.20	0.04	0.01
K	0.27	<b>0.87</b>	0.29	-0.15	0.02
Ca	<b>0.81</b>	0.28	0.33	0.22	0.12
Mg	-0.21	-0.03	0.06	<b>0.81</b>	0.03
Cr	<b>0.79</b>	0.49	0.14	-0.19	-0.01
Ni	<b>0.91</b>	0.21	0.09	-0.03	0.27
Mn	<b>0.79</b>	0.23	-0.05	-0.34	-0.26
Fe	0.37	0.11	0.15	-0.27	<b>0.77</b>
Cd	<b>0.91</b>	0.16	0.04	-0.09	0.07
Pb	0.33	<b>0.79</b>	0.26	-0.18	0.08
Zn	0.03	<b>0.61</b>	-0.03	0.38	0.54
Cu	0.57	0.13	<b>0.67</b>	-0.06	-0.16
Eigen value	5.32	3.78	2.52	1.91	1.34
% of variance	29.54	20.98	14.01	10.59	7.44
Cumulative %	29.54	50.53	64.54	75.13	82.57

Extraction method: principal component analysis.

Rotation method: Varimax with Kaiser normalization.

Bold values reported the dominant parameters in each factor.

<sup>a</sup>Number of samples.

(Table 3). This method resulted in reduction of large dataset to five components having eigenvalues >1 (before and after rotation) that explained 82.57% of the data variation in drinking water. Each factors components PC1 (29.54%), PC2 (20.98%), PC3 (14.01%), PC4 (10.59%) and PC5 (7.44%) accounted for the total variance. The Cr, Ni, Mn and Cd were strongly associated with Ca (PC1) suggesting higher contaminations from anthropogenic (wastewater ponds on the surface) and lesser to lithogenic (influence of carbonate bedrock minerals such as talc carbonate schist) sources. Higher PHEs contaminations in surface soil were attributed from the wastewater ponds in the vicinity [28] which could be the cause of drinking water contaminations. Pb and Zn with Na and K (PC2) observed high associations due to drinking water percolation through bedrock. PC3 includes pH, sulfate and nitrates high loadings and demonstrates the seepage of surrounding wastewater of Sadkal oil exploration, surface soil contamination, agriculture and other human activities to groundwater. Lithogenic or background contribution of metals to groundwater is also represented by PC4 and PC5 (Table 3).

#### 4. Conclusions

This study concluded that majority of physicochemical parameters have surpassed their respective safe drinking water guidelines set by the WHO in hand pumps (50%–100%)

and in bore wells and dug wells (10%–40%) water samples. Shallow water showed significantly ( $p < 0.05$ ) higher levels of contaminations as compared with deep wells water sources. Higher contaminations of the hand pump as compared with bore wells drinking water led to higher intake of PHEs that resulted in higher HRI values. The highest DI values were observed for Zn and HRI values for Cd and Ni in children through hand pump water consumption of local population (15% of total population). Statistical analyses such as correlation analysis and PCA revealed that anthropogenic (exploration industrial wastewater) activities and contaminated soil contributed to drinking water contaminations. This study recommends stopping the use of hand pumps' water for drinking and other domestic purposes and emphasis on deep boring tube wells installation and regular monitoring and treatment of drinking water. This study strongly suggests the wastewater treatment for efficient removal of PHEs before releasing to the surrounding ecosystem.

#### Acknowledgments

We acknowledge the financial support of Higher Education Commission (HEC) Islamabad, Pakistan and technical support of the Director of Centralized Resources Laboratory, University of Peshawar for technical support.

#### Disclosure statement

No potential conflict of interest was reported by the authors.

#### References

- [1] R. Efe, M. Ozturk, I. Atalay, M.A. Askarova, A.N. Mussagaliyeva, 3rd International Geography Symposium, GEOMED2013, 10–13 June 2013, Antalya, Turkey, The Ecological Situation in Contaminated Areas of Oil and Gas Exploration in Atyrau Region, *Procedia Soc. Behav. Sci.*, 120 (2014) 455–459.
- [2] I.U. Santiago, M.M. Molisani, A.H. Nudi, A.L. Scofield, A.d.L.R. Wagener, A.M. Limaverde Filho, Hydrocarbons and trace metals in mussels in the Macaé coast: preliminary assessment for a coastal zone under influence of offshore oil field exploration in southeastern Brazil, *Marine Pollut. Bull.*, 103 (2016) 349–353.
- [3] S.C. Izah, N. Chakrabarty, A.L. Srivastav, A review on heavy metal concentration in potable water sources in Nigeria: human health effects and mitigating measures, *Exposure Health*, 8 (2016) 285–304.
- [4] Z. Ullah, A. Naz, U. Saddique, A. Khan, W. Shah, S. Muhammad, Potentially toxic element concentrations and human health risk assessment of food crops in Bajaur Agency, Pakistan, *Environ. Earth Sci.*, 76 (2017) 482.
- [5] N.A. Mousavian, N. Mansouri, F. Nezhadkurki, Estimation of heavy metal exposure in workplace and health risk exposure assessment in steel industries in Iran, *Measurement*, 102 (2017) 286–290.
- [6] M. Noreen, M. Shahid, M. Iqbal, J. Nisar, Measurement of cytotoxicity and heavy metal load in drains water receiving textile effluents and drinking water in vicinity of drains, *Measurement*, 109 (2017) 88–99.
- [7] M. Zahoor, F. Ali Khan, M. Azam, Bacteriological, inorganic and heavy metal evaluation of drinking water of the specified flood affected areas of Dir (Lower) Pakistan, *Desal. Wat. Treat.*, 57 (2016) 13938–13957.
- [8] H.W. Ji, S.-I. Lee, Use of pollutant release and transfer register (PRTR) to assess potential risk associated with chemicals in a drinking water supply facility, *Desal. Wat. Treat.*, 57 (2016) 29228–29239.

- [9] M. Ishtiaq, N. Jehan, S.A. Khan, S. Muhammad, U. Saddique, B. Iftikhar, Zahidullah, Potential harmful elements in coal dust and human health risk assessment near the mining areas in Cherat, Pakistan, *Environ. Sci. Pollut. Res.*, (2018). doi: 10.1007/s11356-018-1655-5.
- [10] V.A. Makokha, Y. Qi, Y. Shen, J. Wang, Concentrations, distribution, and ecological risk assessment of heavy metals in the East Dongting and Honghu Lake, China, *Exposure Health*, 8 (2016) 31–41.
- [11] E. Hiller, R. Tóth, G. Kučerová, L. Jurkovič, P. Šottník, B. Lalinská-Voleková, J. Vozár, Geochemistry of mine tailings from processing of siderite–Cu ores and mobility of selected metals and metalloids evaluated by a pot leaching experiment at the Slovinky Impoundment, Eastern Slovakia, *Mine Water Environ.*, 35 (2016) 447–461.
- [12] M.T. 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.
- [13] Z. Ismail, K. Salim, S.Z. Othman, A.H. Ramli, S.M. Shirazi, R. Karim, S.Y. Khoo, Determining and comparing the levels of heavy metal concentrations in two selected urban river water, *Measurement*, 46 (2013) 4135–4144.
- [14] R.P. Van Hille, G.A. Boshoff, P.D. Rose, J.R. Duncan, A continuous process for the biological treatment of heavy metal contaminated acid mine water, *Resour. Conserv. Recycl.*, 27 (1999) 157–167.
- [15] G.W. Page, Comparison of groundwater and surface water for patterns and levels of contamination by toxic substances, *Environ. Sci. Technol.*, 15 (1981) 1475–1481.
- [16] T. Asano, J.A. Cotruvo, Groundwater recharge with reclaimed municipal wastewater: health and regulatory considerations, *Water Res.*, 38 (2004) 1941–1951.
- [17] 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.
- [18] S. Begum, M.T. Shah, S. Muhammad, S. Khan, Role of mafic and ultramafic rocks in drinking water quality and its potential health risk assessment, Northern Pakistan, *J. Water Health*, 13 (2015) 1130–1142.
- [19] S. Khan, R. Rauf, S. Muhammad, M. Qasim, I. Din, Arsenic and heavy metals health risk assessment through drinking water consumption in the Peshawar District, Pakistan, *Human Ecol. Risk Assess.*, 22 (2016) 581–596.
- [20] J.M. Trujillo-González, M.A. Torres-Mora, S. Keesstra, E.C. Brevik, R. Jiménez-Ballesta, Heavy metal accumulation related to population density in road dust samples taken from urban sites under different land uses, *Sci. Total Environ.*, 553 (2016) 636–642.
- [21] F. Cubadda, B.P. Jackson, K.L. Cottingham, Y.O. Van Horne, M. Kurzius-Spencer, Human exposure to dietary inorganic arsenic and other arsenic species: state of knowledge, gaps and uncertainties, *Sci. Total Environ.*, 579 (2017) 1228–1239.
- [22] A.H. Panhwar, T.G. Kazi, H.I. Afridi, S.A. Arain, M.S. Arain, K.D. Brahaman, Naeemullah, S.S. Arain, Correlation of cadmium and aluminum in blood samples of kidney disorder patients with drinking water and tobacco smoking: related health risk, *Environ. Geochem. Health*, 38 (2016) 265–274.
- [23] A. Riaz, S. Khan, S. Muhammad, C. Liu, M.T. Shah, M. Tariq, Mercury contamination in selected foodstuffs and potential health risk assessment along the artisanal gold mining, Gilgit-Baltistan, Pakistan, *Environ. Geochem. Health*, 40 (2018) 625–635.
- [24] K. Pinar, S. Aysun, C.S. Sait, A health risk assessment for exposure to trace metals via drinking water ingestion pathway, *Int. J. Hyg. Environ. Health*, 212 (2009) 216–227.
- [25] H. Ding, H. Ji, L. Tang, A. Zhang, X. Guo, C. Li, Y. Gao, M. Briki, Heavy metals in the gold mine soil of the upstream area of a metropolitan drinking water source, *Environ. Sci. Pollut. Res.*, 23 (2016) 2831–2847.
- [26] P.F. Ávila, E. Ferreira da Silva, C. Candeias, Health risk assessment through consumption of vegetables rich in heavy metals: the case study of the surrounding villages from Panasqueira mine, Central Portugal, *Environ. Geochem. Health*, 39 (2017) 565–589.
- [27] J.H. Trefry, R.D. Rember, R.P. Trocine, J.S. Brown, Trace metals in sediments near offshore oil exploration and production sites in the Alaskan Arctic, *Environ. Geol.*, 45 (2003) 149–160.
- [28] S.A.K. Khan, H. Khan, I. Ahmad, M. Ishtiaq, A. Khan, Geochemical impact assessment of produced water of Sadkal oil and gas field on the soil surrounding the storage ponds in Fateh Jang area, Punjab, Pakistan, *J. Himalayan Earth Sci.*, 48 (2015) 75–84.
- [29] A. Shaheen, M. Shafiq, M.A. Naeem, G. Jilani, Soil characteristics and plant nutrient status in the eroded lands of Fatehjang in the Pothwar plateau of Pakistan, *J. Soil Environ.*, 27 (2008) 208–214.
- [30] R. Roohi, A. Ashraf, S. Ahmad, Identification of land-use and vegetation types in Fateh Jang Area, using Landsat-Tm data, *Water Resour. Res. Inst.*, 9 (2004) 81–88.
- [31] APHA, American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 21st ed., Washington, D.C., USA, 2005.
- [32] N. Ali, S. Khan, I. Rahman, S. Muhammad, Human health risk assessment through consumption of organophosphate pesticide-contaminated water of Peshawar Basin, Pakistan, *Exposure Health*, (2018), doi: 10.1007/s12403-017-0259-5.
- [33] M.U. Khan, S. Muhammad, R.N. Malik, S.A. Khan, M. Tariq, Heavy metals potential health risk assessment through consumption of wastewater irrigated wild plants: a case study, *Human Ecol. Risk Assess.*, 22 (2016) 141–152.
- [34] L. Chen, S. Zhou, Y. Shi, C. Wang, B. Li, Y. Li, S. Wu, Heavy metals in food crops, soil, and water in the Lihe River Watershed of the Taihu Region and their potential health risks when ingested, *Sci. Total Environ.*, 615 (2018) 141–149.
- [35] US EPA, United States Environmental Protection Agency, Integrated Risk Information System (IRIS), 1998.
- [36] S. Muhammad, M.T. Shah, S. Khan, Arsenic health risk assessment in drinking water and source apportionment using multivariate statistical techniques in Kohistan region, northern Pakistan, *Food Chem. Toxicol.*, 48 (2010) 2855–2864.
- [37] WHO (World Health Organization), World Health Organization Guidelines for Drinking Water Quality, 4th ed., Recommendations, Vol. 1, Geneva, Switzerland, 2011.
- [38] N. Gul, M. Shah, S. Khan, N. Khattak, S. Muhammad, Arsenic and heavy metals contamination, risk assessment and their source in drinking water of the Mardan district, Khyber Pakhtunkhwa, Pakistan, *J. Water Health*, 13 (2015) 1073–1084.
- [39] A. Schafer, H. Rossiter, P. Owusu, B. Richard, E. Awuah, Developing country water supplies: physico-chemical water quality in Ghana, *Desalination*, 251 (2010) 193–203.
- [40] L. Fewtrell, Drinking-water nitrate, methemoglobinemia, and global burden of disease: a discussion, *Environ. Health Perspect.*, 112 (2004) 1371–1374.
- [41] J. Iqbal, M.H. Shah, G. Akhter, Characterization, source apportionment and health risk assessment of trace metals in freshwater Rawal Lake, Pakistan, *J. Geochem. Explor.*, 125 (2013) 94–101.
- [42] J. Marijic, L. Toro, Voltage and calcium-activated K<sup>+</sup> channels of coronary smooth muscle, *Heart Physiol. Pathol.*, (2001) 309–325.
- [43] G. Robert, G. Mari, Human Health Effects of Metals, US Environmental Protection Agency Risk Assessment Forum, Washington, D.C., USA, 2003.
- [44] S. Kapaj, H. Peterson, K. Liber, P. Bhattacharya, Human health effects from chronic arsenic poisoning – a review, *J. Environ. Sci. Health A*, 41 (2006) 2399–2428.
- [45] A. Eaton, L.S. Clesceri, E.W. Rice, A.E. Greenberg, M. Franson, APHA: Standard Methods for the Examination of Water and Wastewater, Centennial Edition, APHA, AWWA, WEF, Washington, D.C., USA, 2005.
- [46] J. DeZuane, Handbook of Drinking Water Quality, John Wiley & Sons, New York, 1997.
- [47] C. Ifegwu, C. Anyakora, Screen for eight heavy metals from groundwater samples from a highly industrialized area in Lagos, Nigeria, *Afr. J. Pharm. Sci. Pharma.*, 3 (2012) 1–16.

- [48] M.T. Shah, J. Ara, S. Muhammad, S. Khan, S.A. Asad, L. Ali, Potential heavy metals accumulation of indigenous plant species along the mafic and ultramafic terrain in the Mohmand Agency, Pakistan, *Clean-Soil Air Water*, 42 (2014) 339–346.
- [49] D. Mergler, Neurotoxic effects of low level exposure to manganese in human populations, *Environ Res.*, 80 (1999) 99–102.
- [50] G.F. Nordberg, Cadmium and health in the 21st century-historical remarks and trends for the future, *Biometals*, (2004) 485–490.
- [51] O. Barbier, G. Jacquillet, M. Tauc, M. Cougnon, P. Poujeol, Effect of heavy metals on, and handling by, the kidney, *Nephron Physiol.*, 99 (2005) 105–110.
- [52] R. Qadeer, Pollutants in drinking water; their sources, harmful effect and removal procedure, *J. Chem. Soc. Pak.*, 26 (2004) 293–301.
- [53] L. Järup, Hazards of heavy metal contamination, *Br. Med. Bull.*, 68 (2003) 167–182.
- [54] H.H. Dieter, T.A. Bayer, G. Multhaup, Environmental copper and manganese in the pathophysiology of neurologic diseases (Alzheimer's disease and Manganism), *Acta Hydroch. Hydrob.*, 33 (2005) 72–78.