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Quantification of essential elements, their daily intake and health risk via drinking water collected from Southern Khyber Pakhtunkhwa, Pakistan

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Abstract

Water is a key component for all living beings on the earth and comprises about 70% of the earth. Being an essential component and universal solvent, water contains several light and trace metals. The present study was conducted to evaluate drinking water, collected from different sources, for essential elements including iron (Fe), magnesium (Mg), manganese (Mn), potassium (K), phosphorous (P) and zinc (Zn). The results indicated that light metal concentrations showed substantial variation among different sampling sources. Similarly other essential elements were also greatly changed among the different sources. However, the highest light metal concentration was reported for the samples collected from hand pumps. The average daily dose (ADD) and hazard quotient (HQ) assessment showed that the ADD and HQ values were higher for children than adults; however, all the values of HQ were less than one which could not be caused any health problem in the residents of the study area.

Keywords: Drinking water, Light metals, Average daily dose, Health risks.

1. Introduction

Water is the fundamental component for plants, animals and human beings. Access to clean water is the basic right of every human being and clean water is the key for good health (Tahir, 2004; Ilyas et al., 2017). Water sources are broadly categorized in surface and ground water, both of which have been used by human beings for various purposes including drinking, agriculture, recreation, cleaning, food production, personal hygiene and other house hold activities (Shirley et al., 2000: Cahill, 2000), however, the use of water from mentioned sources is strictly depend upon the quality of water (Eldon and Bradley, 2004). For safe and healthy use drinking water bust have a balance in biological, chemical and physical properties (Rezaee et al., 2001). Any change in these parameters may unfit water for healthy use. Both surface and ground water are exposed to various natural and anthropogenic contaminations (Khan et al., 2013; Jabeen et al., 2014).

Water is considered as a universal solvent which has the capability to dissolve various chemical and also contain impurities in suspended form, therefore natural water from both, surface and ground water sources may not be considered as pure water and may not be fit for drinking (WHO, 1998). Due to its characteristic of being universal solvent water have both essential and non essential elements. The presence and amount of essential and toxic elements in the water depend upon the land use, topography, geology of the concerned area and human activates. Water that are exposed to industrial effluents have high concentration of non essential toxic metals like Pb, Cd, Cr, Cu, Ni and other trace metals. High concentration of these metals in drinking water may severely affect the quality of water and cause adverse health effects (Storelli et al., 2005; Zhang et al., 2014).

Drinking water has been exposed to natural and anthropogenic source of contamination. Among the natural sources bed rocks contribute substantially to water characteristic, while anthropogenic sources may include industrial effluent discharge, sewage water and agriculture runoff (Nawab et al., 2016). These sources release considerable amount of essential and non essential toxic elements to water bodies (Santos et al., 2005; Kumar and Ramanathan, 2015).

Traditionally, the physiochemical and biological characteristics are used the key factors used to determine the water quality of an area (Radtke et al., 2005). Several, physiochemical and biological parameters have been used to evaluate water quality according to international standards and norms, these parameters include pH, electrical conductivity (EC), temperature (T), total suspend solids (TSS), total dissolved solids (TDS), dissolved oxygen (DO), chemical oxygen demand (COD), biological oxygen demand (BOD5), chloride, total nitrate, nitrite, ammonia, phosphate and trace metals concentrations (WHO, 2008). Among these parameters pH, temperature (T), TSS, COD and BOD5 and COD are the most important for the determination of components and quality of water (Radtke et al., 2005; Neal et al., 2006).

Wastewater from house hold and industries have been used for agriculture purposes, which resulted in deteriorating of ground water quality and the water are unfit for drinking purpose (Nasir et al., 2012). Trace elements have been added regularly to our water bodies through both natural and anthropogenic activities, some of these metals are essential in water while others are non essentials. The common essential and non essential elements found in water include As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn. Mo, Na, Ni, Pb, Se and Zn, among these elements Ca, Co, Fe, K, Mg, Mn, Na and Zn are essential for living organism in varying amounts (Hussein et al., 2005).

The present study was aimed to assess the concentrations of essential elements in surface and ground water samples of five districts of southern Khyber Pakhtunkhwa Pakistan.

2. Experimental

2.1 . Study area description

The study area is comprised of five districts including Bannu, Dera Ismail Khan, Lakki Marwat, Karak and Tank (Fig. 1) of the Southern Khyber Pakhtunkhwa Province, Pakistan, It has a total population of about 4.949 million. The people of the study area use springs, streams, tube wells, dug wells, bore holes and hand pumps as the main source of water for drinking, domestic and agriculture purposes. The main sources of irrigation in the study area include tube wells and rivers such as Indus, Gambila and Kuram. The primary profession of the people of the study area is agriculture. Main agriculture crops include maize, sugarcane, rice, wheat, grams, barley and vegetables. The climate of the study area is suitable for these crops. In summer the temperature is very high while winter is cold.

2.2. Drinking water sampling

Drinking water samples (n=190) were collected from different sources including ponds, springs, streams, dug wells, tube wells, bore holes and hand pumps, of five selected districts. Basic physical parameters including pH and electrical conductivity (EC) were measured on the spot. The samples were collected in polythene bottles washed with deionized. Few drops of HNO_3 were added in to avoid microbial activity, metals and metalloid adsorption on plastic. All the samples were collected in triplicates. Different sampling strategies were adopted for different sources of waters. Global

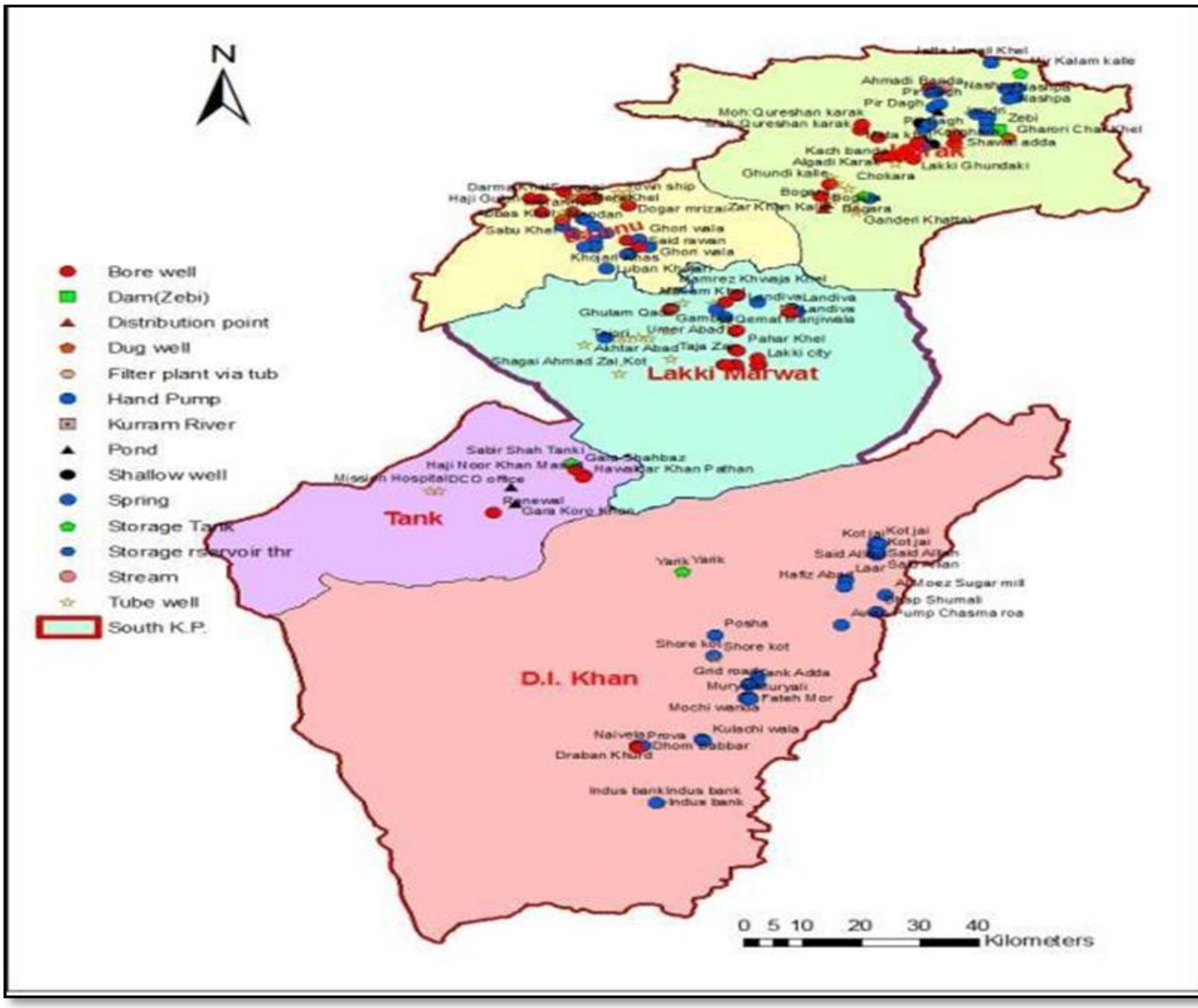

Fig.1. Location map of the study area showing the sampling sites and sources.

positioning system (GPS) was used for recording coordinates of the sampling points and later on developing maps using geographic information system (GIS) software's. All samples were labeled and transfer to laboratory for further investigations.

2.3. Preparation and analysis of water samples

Acidified water samples were separated in new plastic bottles and analyzed for selected nutrients using inductive couple plasma spectrophotometer (ICP-MS). All the samples were analyzed in triplicate.

For precision and accuracy of the measurements mix standards of selected elements were run before running the actual water sample and after each 10 samples another separate standard was run to check the accuracy of machine and method.

2.4. Average daily dose

The average daily dose (ADD) for selected elements were calculated following USEPA (1998) equation

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

In the equation C concentration of selected elements in drinking water (mg l^{-1}), IR is water ingestion rate (2 l day^{-1}), while, EF, ED, BW and AT are exposure frequency (365 days/year), exposure duration (30 years), body weight of children (30.6 kg) and adults (70 kg) and averaging time (365 days $year^{-1}$ × ED), respectively, (Muhammad et al. 2010).

Average daily dose values of Fe, Mn and Zn were used for the hazard quotient (HQ) values. The equation used for HQ was adopted from USEPA (1998).

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

Where, RfD the reference dose (mg kg^{-1}-day) of selected elements, having value of 0.7, 0.14 and 0.3 mg kg^{-1}-day for Fe, Mn and Zn, respectively (US EPA 1998). Exposed population is assumed to be safe if HQ < 1(Muhammad et al., 2011).

2.5. Mapping

Global positioning system (GPS) was used to collect the coordinates of each sampling point. Those coordinates were put in ArcGIS software to produce digital maps for every element. These maps include the general location map, the sampling sites and sources map of the study area showing high, medium and low concentrations zones of each metals. Figure 1 and 2 show the location and elemental distribution maps, respectively.

2.6. Statistical analysis

Data collected in the field were evaluated for mean, ranges and standard deviation. Data were presented graphically using Sigma plot 12.5. Statistical analyses like one-way ANOVA and correlations were determined using SPSS 21 (SPSS Inc., Chicago, IL, USA).

3. Results and discussion

3.1. Light metal concentrations in water

Selected light metal concentrations in water samples of five districts including Bannu, Laki Marwat, Tank, Karak and DI Khan are shown in Table 1, while their distribution throughout the study area is shown in Fig. 3. The results showed that elemental concentrations in the selected samples were varied significantly among different sampling points and districts.

The Na concentration showed significant variation among different districts. For instance the highest mean Na concentration was reported in water of Bannu, while the lowest was recorded in Tank. However, the concentration of Na was below detection limit in the samples collected from district Karak. The Na concentrations in the selected districts were ranged from 0.9-73.65, 6.17-15.75, 11.27-15.41 and 5.15-5.15 mg/l for Bannu, Lakki Marwat, DI Khan and Tank, respectively. For P and K, the highest concentration was reported in Bannu, while the lowest concentration was reported in Karak and Lakki Marwat water samples, respectively. P concentrations in water samples were ranged from 0.07-2.53, 0.03-0.26, 0.03-0.40, 0.07-0.28 and 0.09-0.25 in the samples of Bannu, Lakki Marwat, DI Khan, Tank and Karak, respectively. K concentrations were observed in the range of 0.24-49.22, 0.49-37.23, 5.34-57.34, 2.21-19.69 and 1.49-37.88 mg/l in water samples collected from Bannu, Lakki Marwat, DI Khan, Tank and Karak, respectively (Table 1 and Fig. 3).

Other elements like Mg, Mn, Fe and Zn also showed substantial variation in both range and the mean concentrations among different sampling points and districts (Table 1 and Fig. 3). The minimum and maximum values of these elements in water samples are given in Table 1. The mean concentrations for these elements were in the range of N.A-29.34 mg/l (Na), 20.45-6.28 mg/l (K) 15.67-34.33 mg/l (Mg), 0.03-0.52 mg/l (P) 0.03-1.02 mg/l (Fe), 0.01-0.30 mg/l (Mn) and 0.03-0.21 mg/l (Zn). Among different elements, the highest concentration was noted for Mg, while the lowest was observed for Mn (Table 1 and Fig. 3).

Table 1. Mean and range values of light metals in selected districts of Khyber Pakhtunkhwa.

	Na	K	Mg	P	Fe	Mn	Zn
				Bannu			
Min	0.09	0.24	0.09	0.07	0.01	0.00	-.02
Max	73.65	49.22	62.93	2.53	0.05	0.20	0.61
Mean	29.34	7.93	34.33	0.52	-0.01	0.01	0.14
SD	24.84	10.12	23.87	0.86	0.01	0.04	0.14
				Lakki Marwat			
Min	6.17	0.49	1.90	0.03	0.01	0.00	0.00
Max	15.75	37.23	60.67	0.26	5.79	0.13	1.62
Mean	12.72	6.28	15.89	0.11	0.24	0.03	0.17
SD	4.27	8.06	15.88	0.08	1.16	0.03	0.36
				DI Khan			
Min	11.27	5.34	8.15	0.03	0.01	0.00	0.00
Max	15.41	57.34	63.40	0.40	4.80	0.80	0.96
Mean	13.34	20.45	29.55	0.17	0.71	0.30	0.13
SD	2.07	14.62	16.73	0.09	1.18	0.23	0.23
				Tank			
Min	5.15	2.21	1.66	0.07	0.01	0.00	0.01
Max	5.15	19.69	58.51	0.28	0.62	0.72	1.69
Mean	5.15	8.70	27.31	0.14	0.21	0.19	0.21
SD	0.00	6.72	21.40	0.08	0.23	0.28	0.64
				Karak			
Min	N.D	1.49	6.34	0.09	0.01	0.00	0.02
Max	N.D	37.88	57.96	0.25	0.30	0.12	0.51
Mean	N.D	9.95	23.90	0.03	0.03	0.01	0.03
SD	N.D	8.03	13.13	0.08	0.08	0.02	0.11

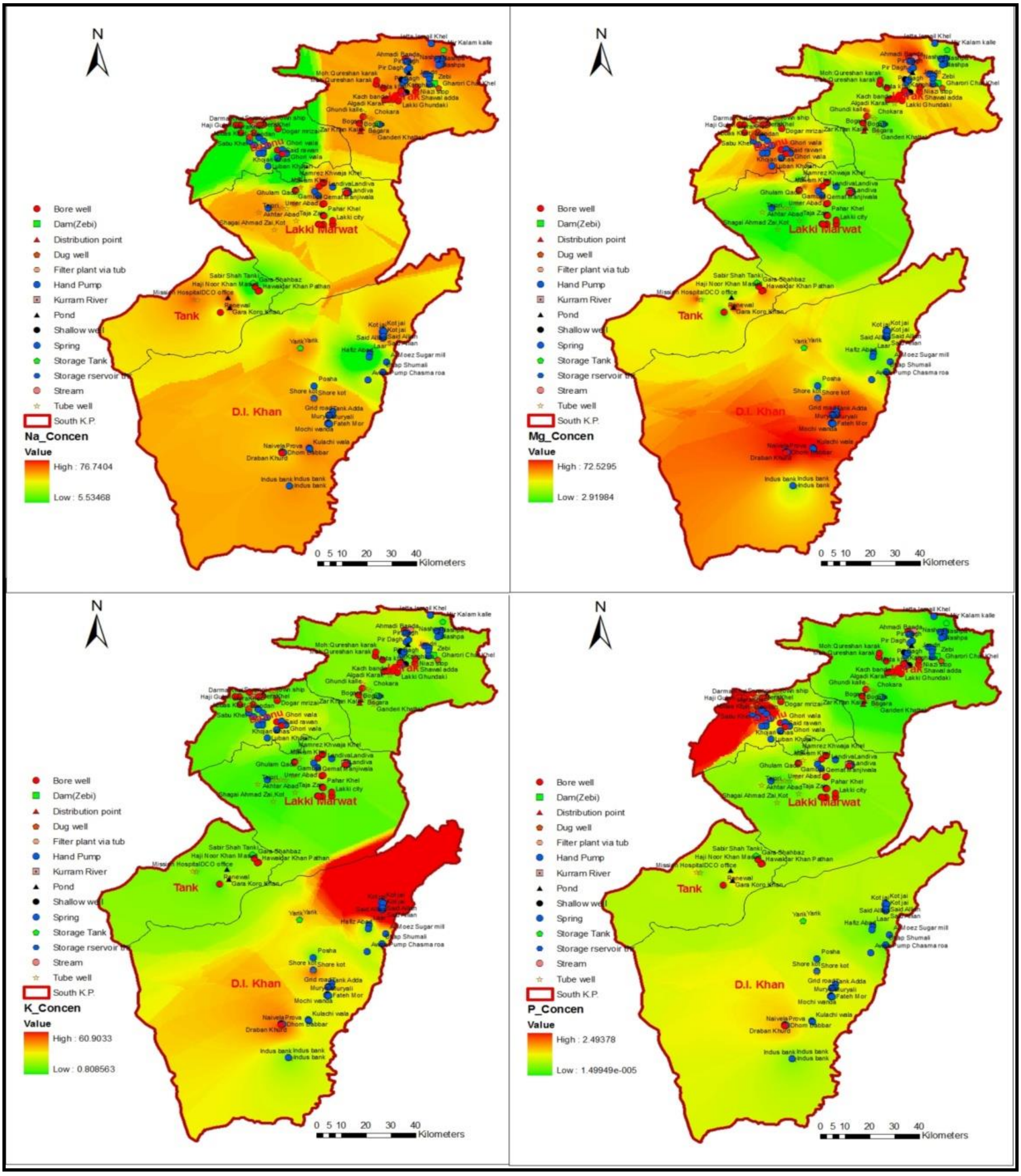

Fig. 2. Elements (Na, K, Mg and P) distribution maps of the study area.

Table 2. Source apportionment of light metals in drinking water.

Source type		Na	K	Mg	P	Fe	Mn	Zn
Tube Well (49)	Mean	16.62	6.64	23.12	0.23	0.11	0.03	0.06
	SD	15.37	7.28	19.62	0.57	0.26	0.08	0.06
	Min	5.02	0.78	2.27	0.07	0.01	0.01	0.02
	Max	56.29	42.84	61.36	2.46	1.54	0.40	0.28
Bore well (42)	Mean	16.09	7.38	23.74	0.24	0.04	0.02	0.09
	SD	17.11	7.33	17.14	0.54	0.09	0.12	0.13
	Min	0.09	0.24	0.09	0.07	0.01	0.01	0.02
	Max	55.87	44.22	61.09	2.29	0.35	0.80	0.61
Dug Well (02)	Mean	N.D	5.40	30.99	0.06	0.01	0.002	0.03
	SD	N.D	1.62	10.53	0.08	0.03	0.001	0.05
	Min	N.D	4.25	23.55	0.01	0.01	0.002	0.01
	Max	N.D	6.54	38.44	0.11	0.03	0.003	0.06
Hand Pump (72)	Mean	45.28	15.43	30.40	0.21	0.41	0.14	0.18
	SD	22.18	11.59	19.14	0.40	1.03	0.19	0.29
	Min	7.58	1.49	3.02	0.08	0.01	0.01	0.02
	Max	73.65	57.34	63.40	2.53	5.79	0.78	1.62
Filtration Plants (02)	Mean	8.90	1.86	7.95	0.03	0.01	0.02	0.15
	SD	2.75	0.28	1.86	0.02	0.00	0.02	0.06
	Min	6.96	1.66	6.64	0.02	0.01	0.01	0.11
	max	10.84	2.06	9.27	0.04	0.01	0.02	0.19
Pressure Pump (06)	Mean	13.81	3.55	24.79	0.10	0.07	0.03	0.12
	SD	N.D	1.66	21.71	0.08	0.05	0.02	0.07
	Min	13.81	0.49	2.82	0.01	0.00	0.01	0.01
	Max	13.81	5.15	60.67	0.22	0.15	0.06	0.20
Storage Tanks (06)	Mean	N.D	10.83	21.82	0.06	0.14	0.01	0.03
	SD	N.D	12.07	8.05	0.13	0.22	0.01	0.04
	Min	N.D	3.19	10.04	0.09	0.01	0.00	0.01
	Max	N.D	34.87	29.43	0.26	0.57	0.04	0.11
Rivers/Springs (07)	Mean	N.D	8.06	18.44	0.03	0.03	0.01	0.01
	SD	N.D	2.92	9.57	0.06	0.08	0.01	0.01
	Min	N.D	5.16	9.97	0.06	0.01	0.00	0.02
	Max	N.D	13.20	33.84	0.11	0.21	0.03	0.02

The difference in concentrations of different elements in water samples of different locations and sources may be due to difference in geographical and geological features of the area, level of pollution, sources from where these samples were collected, climatic conditions and anthropogenic inputs. The common sources from where the samples were collected include well, Tube well, Bore well, hand pumps, pressure pump, filtration plants, dug well, storage tanks, stream, ponds, dams, springs and rivers etc. The source distribution showed that the changes in nutrients concentration from different sources and sampling point is obvious. Similarly, the water chemistry also affects nutrient concentrations. Atmospheric deposition, gaseous exchange, photosynthesis and photosynthetic process are key factors responsible for change in characteristics of water. The presence of micro flora and fauna have important role in biogeochemical cycling of elements and the micro flora and fauna abundance in drinking water is affected by natural and anthropogenic inputs.

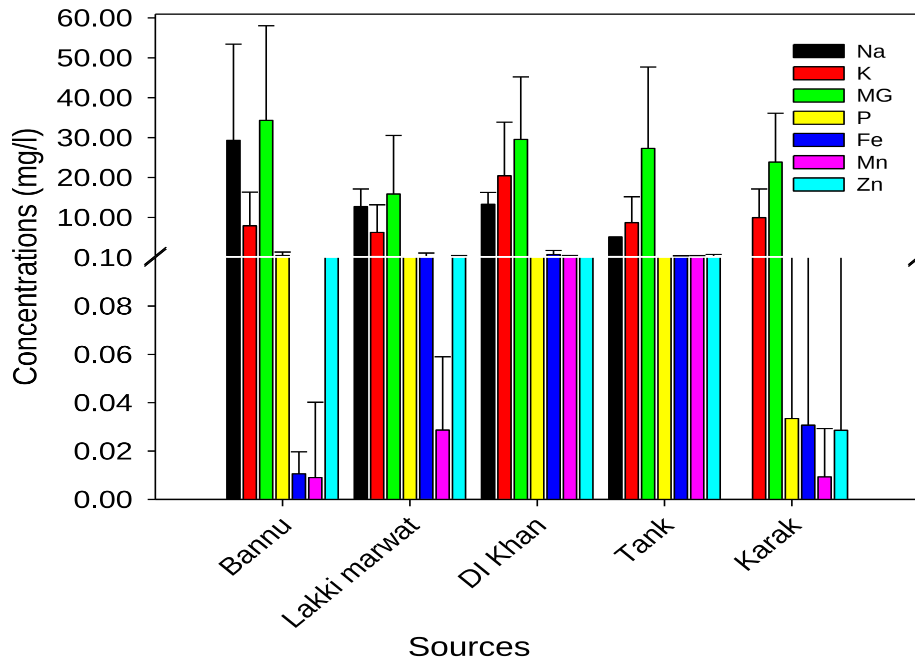

Fig. 3. Mean and standard deviation selected elements in water collected from selected districts of Khyber Pakhtunkhwa.

3.2. Source apportionment

Water samples were collected from different sources of drinking water in the study area. Those sources include tube well, bore well, dug well, hand pumps, pressure pumps, storage tanks, rivers, streams and springs. The most common sources of drinking water in the study area were hand pumps (72), tube wells (49) and bore wells (42), while pressure pumps and filtration plants were the least common source of drinking water. The results showed that the among different sources the highest Na concentration as noted for hand pumps (73.65 mg/l), while the lowest was noted for bore well (0.09) mg/l). However, no Na concentration was detected in dug well, storage tank and river/spring samples (Table 2 and Fig. 4). K is considered as one of the essential element for plants and animals and its presence in the water is of pivotal importance. However, excess of K in water may result in eutrophication. The K concentration in different water sources showed significant variation ($p<0.05$). The highest K concentration was reported in water samples of hand pump (57.34 mg/l), while the lowest was reported in bore well water samples (0.24 mg/l). Zn is an essential element for living organisms and is found in all foods and drinking waters (Khan et al., 2013), but if its concentration increases in water then it become a toxic metal and may cause serious health hazards. In the present study source distribution of Zn showed great variation. For instance groundwater i.e. tube well, bore well, hand pump etc. have a concentration range of 0.01-1.62 mg/l, while surface water like river spring and stream have a concentration of 0.02 mg/l (Table 2 and Fig. 4). The high concentration in groundwater may be of geogenic nature as bed rocks have substantial contribution to elemental concentrations of groundwater. Previously, high Zn concentration was reported in groundwater samples than surface water samples in Kohistan region of Khyber Pakhtunkhwa (Muhammad et al., 2010). Similarly, Khan et al. (2013) also reported similar concentrations of Zn in ground and surface water of Swat areas of Khyber Pakhtunkhwa. They concluded that high concentrations of trace metals in groundwater may be due to mafic and ultramafic rocks in the study area presenting Zn sulfide mineralization (Khan et al., 2013; Muhammad et al., 2011). Other light metals including Mg, Mn, Fe and P also showed great variation in source distribution as presented in Table 2 and Fig. 4 that could be linked with the geological set up including mineral composition of the study area and anthropogenic activities.

3.3. Risk assessment

Water is one of the essential and vital components of human lives. Fresh water comprises of a variety of essential elements required by human lives. The deficiency or over abundance of these elements may prove to be fatal. The daily burden of light and trace metals through consumption of drinking water is a good way to estimate the human exposure. The risk assessment via human exposure to light metals through consumption of drinking water from different sources was presented in the Table 3-4. The results revealed the highest ADD value was reported for consumers via consumption of water collected from hand pump (1.38 and 1.26 for children and adults, respectively), followed by dug well (0.95 and 0.86 for children and adults, respectively), while the lowest ADD value was reported for consumers of the water obtained filtration plants (5.60E-05 and 5.08E-05 for children and adults, respectively). Similarly, among different elements the highest ADD value was recorded for Na for both adults and children followed by Mg, while the lowest value was reported for Mn through consumption of drinking water from different sources (Table 3).

In the present study, the HQ value was only calculated for Fe, Mn and Zn because the USEPA did not recommend any oral reference dose for Na, Mg, P and K. The calculated HQ values for selected elements are shown in table 4. It is revealed from the results that the HQ values showed substantial variation among different sources of drinking water and elements. The result indicated that the highest HQ value was reported for water consumers from hand pump followed by filtration plants, while the lowest HQ value was calculated for dug well water consumers (Table 4). The high ADD and HQ value through consumption of filtration plants revealed technical faults in the filtration plants. It is assumed that these plants were not installed as per WHO guidelines, which had led to high concentrations of metals. When compared the three elements the highest HQ value was reported for Mn followed by Zn and Fe. The ADD and HQ values of Mn in surface and ground waters were consistent with the findings of Jabeen et al. (2014). They reported similar values in both ground and surface water samples of Haripur District, Khyber Pakhtunkhwa (Jabeen et al., 2014). Although Mn showed the highest HQ values all the values reported were below the critical limit of 1 which showed that the water of these sources is safe for drinking and other house hold activities. However, public awareness is necessary because the high illiteracy rate, ignorance and poverty in the study area make them vulnerable to health risks through consumption of contaminated water and food stuff. In the study area, women are responsible to bring water from remote distances for their daily uses. Unfortunately they have no or very little knowledge of water and sanitation and hygiene promotion.

Table 3. Average daily dose of light metals from different water sources.

Source type		Na	K	Mg	P	Fe	Mn	Zn
Tube Well	Children	5.08E-01	2.03E-01	7.07E-01	7.08E-03	3.33E-03	9.88E-04	1.81E-03
	Adult	4.62E-01	1.84E-01	6.42E-01	6.43E-03	3.03E-03	8.97E-04	1.64E-03
Bore well	Children	4.92E-01	2.26E-01	7.26E-01	7.33E-03	1.29E-03	7.28E-04	2.80E-03
	Adult	4.47E-01	2.05E-01	6.60E-01	6.65E-03	1.17E-03	6.61E-04	2.54E-03
Dug Well	Children	ND	1.65E-01	9.48E-01	1.74E-03	2.78E-04	7.50E-05	9.60E-04
	Adult	ND	1.50E-01	8.61E-01	1.58E-03	2.52E-04	6.81E-05	8.72E-04
Hand Pump	Children	1.38E+00	4.72E-01	9.30E-01	6.53E-03	1.26E-02	4.38E-03	5.46E-03
	Adult	1.26E+00	4.29E-01	8.45E-01	5.93E-03	1.15E-02	3.97E-03	4.96E-03
Filtration Plants	Children	2.72E-01	5.69E-02	2.43E-01	8.97E-04	-3.32E-04	5.60E-05	4.56E-03
	Adult	2.47E-01	5.17E-02	2.21E-01	8.15E-04	-3.01E-04	5.08E-05	4.14E-03
Pressure Pump	Children	4.22E-01	1.09E-01	7.58E-01	3.14E-03	2.05E-03	9.93E-04	3.60E-03
	Adult	3.84E-01	9.86E-02	6.89E-01	2.85E-03	1.86E-03	9.02E-04	3.27E-03
Storage Tanks	Children	ND	3.31E-01	6.67E-01	1.83E-03	4.28E-03	4.26E-04	1.06E-03
	Adult	ND	3.01E-01	6.06E-01	1.66E-03	3.89E-03	3.87E-04	9.64E-04
Rivers/Springs	Children	ND	2.47E-01	5.64E-01	1.04E-03	9.67E-04	1.90E-04	1.19E-04
	Adult	ND	2.24E-01	5.12E-01	9.47E-04	8.78E-04	1.73E-04	1.08E-04

Table 4. Health risk assessment through consumption of drinking water from different sources.

Source type	Age group	Fe	Mn	Zn
Tube Well	Children	4.76E-03	7.06E-03	6.03E-03
	Adult	4.32E-03	6.41E-03	5.48E-03
Bore well	Children	1.84E-03	5.20E-03	9.33E-03
	Adult	1.67E-03	4.72E-03	8.47E-03
Dug Well	Children	3.97E-04	5.36E-04	3.20E-03
	Adult	3.61E-04	4.87E-04	2.91E-03
Hand Pump	Children	1.80E-02	3.13E-02	1.82E-02
	Adult	1.64E-02	2.84E-02	1.65E-02
Filtration Plants	Children	4.74E-04	4.00E-04	1.52E-02
	Adult	4.30E-04	3.63E-04	1.38E-02
Pressure Pump	Children	2.92E-03	7.10E-03	1.20E-02
	Adult	2.65E-03	6.44E-03	1.09E-02
Storage Tanks	Children	6.11E-03	3.04E-03	3.54E-03
	Adult	5.55E-03	2.76E-03	3.21E-03
Rivers/Springs	Children	1.38E-03	1.36E-03	3.96E-04
	Adult	1.25E-03	1.24E-03	3.60E-04

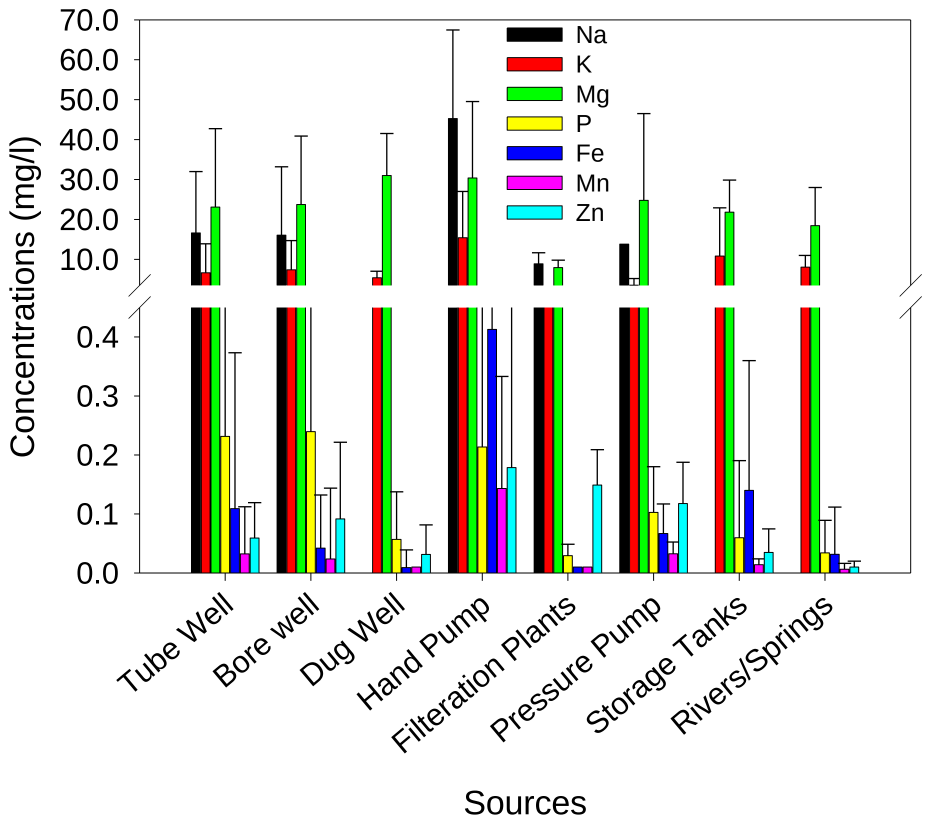

Fig. 4. Source apportionment of essential elements in drinking water samples collected from selected districts of Khyber Pakhtunkhwa.

4. Conclusion

Essential element concentrations in drinking water varied greatly from source to source and also from location to location in the study area. The geographical distribution also showed great variation in light metal concentrations. Among different elements the highest light metal concentration was reported for Na followed by Mg and K, while the lowest was reported for Mn. The geographical distribution showed that water samples from Bannu showed the highest light metal concentration than other districts. Source apportionment assessment showed that hand pumps contributed the highest level of light metal concentrations than other sources. The ADD and HQ of different water sources showed that hand pumps have the highest ADD and HQ values however all the values of HQ were <1, showing no health risk to the consuming populations.

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