Assessment of metals and other trace elements in the drinking water along River Indus, Allai and Nagar

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Abstract

Trace element contamination in water is a global issue due to its widespread occurrence and health effects. Regular intake of elevated metal levels in drinking water can unequivocally cause several types of cancers. This study was primarily focused to assess the quality of drinking water in Allai, Nagar and along River Indus. So for this study a total of 64 spring, 14 waterfall and 7 glacier water samples were collected. Additionally, 13 sediment samples were also collected from Allai and Nagar which were located in the vicinity of mountainous River Indus, Pakistan. The samples were tested for arsenic, calcium, chromium, copper, iron, lead, magnesium, potassium, sodium and zinc using inductively coupled plasma optical emission spectroscopy so as to get the elemental concentrations in parts per billion. The range of metals and other trace elements were compared with the guidelines of World Health Organization (WHO) and the standards laid down by Environmental Protection Agency of Pakistan. The results revealed the (minimum-maximum) concentrations (µg/L) of drinking water quality parameters as follows: arsenic 0-0.06, calcium 1.74-176.87, chromium 0-0, copper 0-0, iron 0-0.25, sodium 1.27-292, potassium 0-24.01, magnesium 0.05-120.22, lead 0-0 and zinc 0-0. Moreover, the (minimum-maximum) concentrations (µg/L) of sediment samples were recorded as arsenic 0-0. 88, calcium 42.98-2068, chromium 0.16-0.65, copper 0.12-1.76, iron 166-544, sodium 8.99-15.36, potassium 35.57-247, magnesium 47.14-453, lead 0-0.23 and zinc 0.67-1.66. The study concluded that all the samples collected from the vicinity of River Indus had elemental concentrations within the recommended guidelines set by the National Drinking Water Quality Standards of Pakistan and WHO. Furthermore, a detailed study encompassing samples from the springs, glaciers, waterfalls and lakes is recommended to evaluate the possible trace element contamination either due to deposition or mixing of metal bearing rocks with water both in the low lying and highland areas of Upper Indus Basin. The outcomes of this research can be useful for the concerned authorities of Gilgit Baltistan and Khyber Pakhtunkhwa Province in the provision of safe drinking water to the people living in the vicinity of River Indus, Pakistan.

Keywords: Trace elements, Spring water, River Indus, glacier, waterfall, water quality

Introduction:

Water is a crucial natural resource that sustains ecological systems, environment and human existence. It is essential for all living things for a variety of reasons. Water covers 71% of the Earth's surface. Out of which 96.5% share is of surface water, 1.7% of groundwater and 1.7% of glaciers and ice caps. Water is mainly classified as freshwater or saltwater. Seas and oceans contain 96.5% saltwater, whereas lakes, groundwater, glaciers and rivers contain the remaining 3.5% fresh water. The supply of safe drinking water is a basic necessity of life and plays a significant role in the sustainability of living things all over the globe. Drinking unhealthy water predisposes remarkable risks to the environment and human health. Fresh water is usually considered a healthy and safe drinking water resource but unfortunately, fresh water available for human consumption is not adequate [1]. Surface or glaciated water, a natural source of drinking water, is of paramount importance in the Upper Indus Basin, Pakistan. Several chemical reactions of water occur in the geological settings of mountains. Consuming heavy metal-contaminated water can have negative effects on both humans and environment [2]. Sediments and streams include several elements and compounds that can be potentially injurious to human health, such as lead (Pb), cadmium (Cd), arsenic (As), and copper (Cu) [3]. According to World Health Organization (WHO), about one-quarter of human ailments are attributed to the polluted environment [4]. The issue of water pollution is more serious and terrifying in poverty- stricken nations due to lack of facilities, resources and inadequate management. Water quality analysis is crucial for identifying health hazards and for creating management frameworks for safe drinking water supplies.

Several studies have been conducted across Pakistan [5-8] to investigate the water quality from various sources and assess the potential health risks associated with certain toxic heavy metals such as As, Cr, Pb, Cd, Co, Mn, Cu and Ni. The human bodies contain biochemical essential elements like Mg, Na, Mn, Zn, Cu, and Fe which are vital for a variety of important functions and serve as a catalyst for enzymatic activities. However, when the concentrations of these elements are escalated, it becomes difficult for humans to metabolize them, increasing the likelihood of health risks and susceptibility. Some elements present in nature such as Cadmium, Arsenic, lead, etc. are poisonous to humans even in low quantities and their bioaccumulation in the body causes drastic illness [9].

The contamination of potentially toxic chemicals in water may cause multiple health consequences in human beings such as stomach pain, peripheral neuropathy, immune dysfunction, bone fractures, cardiovascular and musco-skeletal disorders, pulmonary adenocarcinomas, intellectual abnormalities, different types of cancer and dyspnea, damage of central nervous system and death.

Mercury, cadmium, lead and chromium have the potential to cause a wide range of toxic effects such as carcinogenicity, mutagenicity and teratogenicity [10]. The increased quantities of toxic metals pollute aquifers, substantially enhance the cancer risk and are responsible for disruption in the normal functioning of biota [11].

The Geographic Information System (GIS) is used to highlight water related problems worldwide [12]. GIS supports the mapping of chemical, physical and microbiological parameters of water [13]. It is an efficient technique to depict spatiotemporal water quality analysis and comprehensive modeling of major contaminated sites [14-15]. Groundwater vulnerability assessment maps represent an

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understanding of the environment and its sensitivity to contamination [16]. Therefore, the mapping of water quality parameters is need of the hour to take preventive measures so as to save people from possible cancer risk.

The Indus plains are widely contaminated with heavy metal pollution [17]. Recently, many studies have determined the exceptionally elevated levels of intrinsic trace elements from natural or anthropogenic sources both in the surface water [18] and groundwater [19] of Pakistani metropolitans, notably, along the sedimentary rocks of the Indus River and its tributaries [20-22].

To our knowledge, very few studies have been conducted so far to detect the heavy metals and other trace elements in the Upper Indus Basin, Pakistan. Consequently, it is critical to determine the trace element levels in the drinking water along the River Indus, Allai, and Nagar.

Materials and methods

Study area

The geographical coordinates of the study area vary from 33.7° to 37.2°N and 70.5° to 77.5°E. The Indus River Basin (IRB), with an extent of 139,202 km^2, is Pakistan's main river basin [23]. This region is recognized as a major supply of fresh water for Pakistan and it contributes considerably to the country's long-term economic growth. The snow and glacier melt from Hindukush-Karakoram Himalayan ranges provide 50% of Pakistan's surface water discharge to Upper Indus Basin (UIB) system [24-25]. The elevation of UIB varies between 200 m to 8500 meters above mean sea level [25]. The UIB boundary derived from Digital Elevation Model (DEM) is shown in Figure 1. The geographical locations of sampling sites are represented in Figures 2-4.

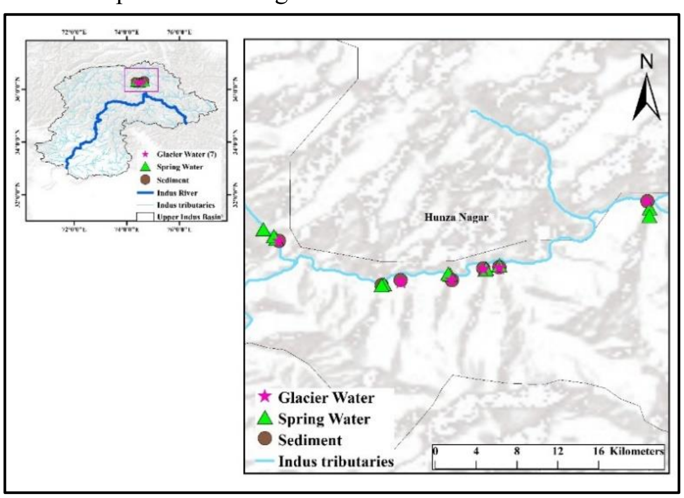

Figure 1: Study area map showing digital elevation model of the Upper Indus Basin, Pakistan.

Field survey and samples collection

A field survey was conducted for water sampling along the mountainous River Indus (from Thakot to Sakrdu) and from two different areas (Allai and Nagar) located in the vicinity of the mighty River Indus, Pakistan. The samples were collected in 240 milliliters plastic bottles with sealed caps. So, for this study a total of 64 spring, 14 waterfall and 15 glacier water samples were collected. Additionally, 13 sediment samples were also collected from the vicinity of Indus River, Pakistan (Table 1). The geographical coordinates of the sampling points were recorded using a global positioning system (GPS).

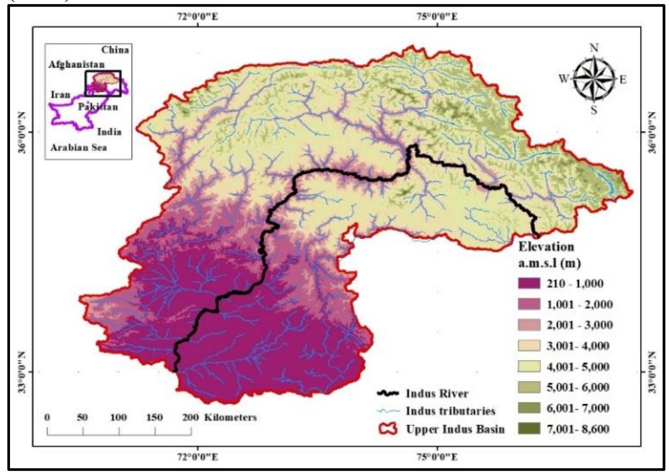

Figure 2: Geographical locations of collected samples along the River Indus.

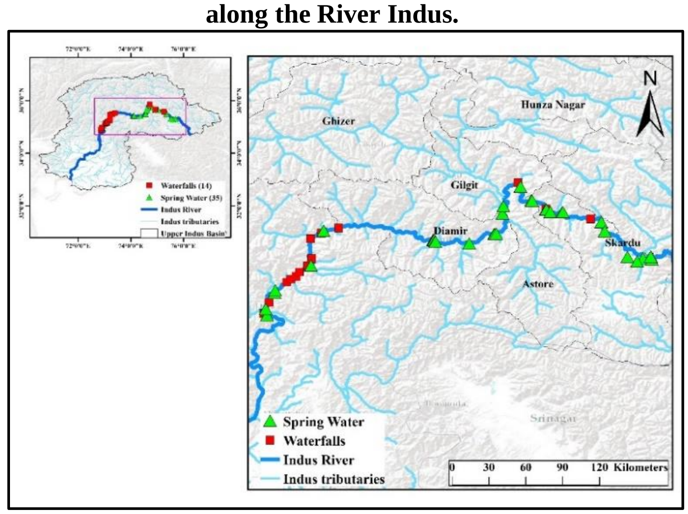

Figure 3: Geographical locations of samples collected from Nagar District.

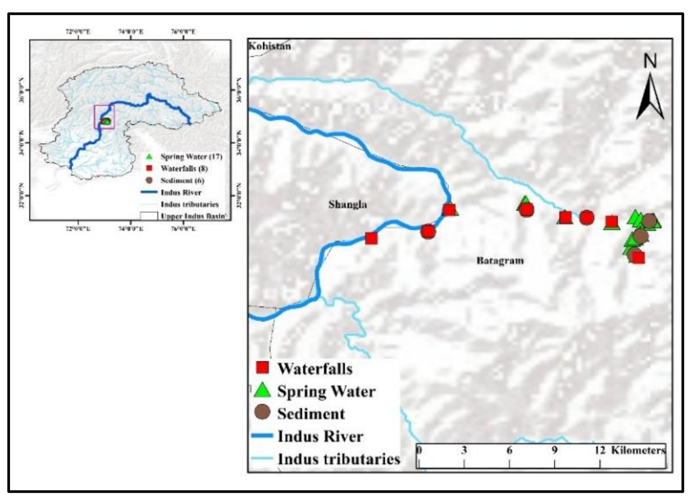

Figure 4: Geographical locations of samples collected from Allai District.

Table 1
List of samples collected from Allai, Nagar and along the River Indus.

Area	Name of Source	Total Samples
Along Indus River	**Waterfalls**	14
	Spring Water	35
Total	49	
Nagar	**Glacier Water**	7
	Sediment	7
	Spring Water	12
Total	26	
Allai	**Sediment**	6
	Glacier Water	8
	Spring Water	17
Total	31	

Laboratory Analysis and Data Generation

The samples were tested using Inductively Coupled Plasma Optical Emission spectroscopy so as to get the elemental concentrations in parts per billion. The concentration data of metals and other trace elements related to glacier water, spring water, waterfalls, and sediment samples was statistically analyzed in Microsoft Excel. The drainage streams and UIB boundary were generated using the Shuttle Radar Topographic Mission's (SRTM) Digital Elevation Model having 90m resolution. The SRTM DEM was used to delineate the UIB river basin using terrain processing in the Arc Hydro extension of ArcGIS software. The GPS coordinates of the sampling sites were imported into ArcGIS and the data related to water quality parameters was entered in the shapefile against these coordinates. The water quality standards and guidelines of different elements are provided in Table 2.

Table II
The permissible concentration (standard/ guideline) of water quality parameters in drinking water.

Serial N0.	Parameter	Symbol	Water quality Standard/ guideline (µg/L)
1	Arsenic	As	50 in NSDWQ and 10 by WHO
2	Calcium	Ca	200000 by WHO [37]
3	Chromium	Cr	50 by PEPA
4	Copper	Cu	2000 by WHO
5	Iron	Fe	300 [40]
6	Potassium	K	10000-12000 [37]
7	Magnesium	Mg	150000 by WHO [44]
8	Sodium	Na	200000 by WHO [4]
9	Lead	Pb	10 by PEPA
10	Zinc	Zn	5000 [29]

**NSDWQ* National standards for drinking water quality of Pakistan

**PEPA* Pakistan Environmental Protection Act

**WHO* World Health Organization

Results and Discussions

The descriptive statistics of tested parameters (arsenic, calcium, chromium, copper, iron, potassium, magnesium, sodium, lead and zinc) from the collected drinking water and sediment samples are provided in Table 3 and Table 4, respectively.

Table III
Descriptive statistics for tested water quality parameters from glacier, waterfalls and springs (n = 93) in (µg/L) collected along River Indus, Allai and Nagar, Pakistan.

Parameters	Min	Max	Mean	Std dev.	Kurtosis	Skewness	Range
Arsenic	0	0.06	0	0.01	28.65	5.45	0.06
Calcium	1.74	176.87	47.92	37.29	2.29	1.43	175.13
Chromium	0	0	0	0	0	0	0
Copper	0	0	0	0	0	0	0
Iron	0	0.25	0.01	0.03	49.19	6.87	0.25
Potassium	0	24.01	4.68	4.85	4.53	1.98	24.01
Magnesium	0.05	120.22	19.75	28.09	5.38	2.46	120.17
Sodium	1.27	292	22.71	54.78	13.83	3.80	290.73
Lead	0	0	0	0	0	0	0
Zinc	0	0	0	0	0	0	0

Table IV
Descriptive statistics for tested sediment samples (n = 13) in (µg/L), collected from Nagar and Allai, Pakistan.

Parameters	Min	Max	Mean	Std dev.	Range
Arsenic	0	0.88	0.22	0.22	0.88
Calcium	42.98	2068	790.05	775.26	2025.02

Chromium	0.16	0.65	0.44	0.12	0.49
Copper	0.12	1.76	0.75	0.52	1.64
Iron	166	544	370	93.29	378
Potassium	35.57	247	85.30	56.82	211.43
Magnesium	47.14	453	196.46	79.71	405.86
Sodium	8.99	15.36	11.25	1.35	6.37
Lead	0	0.23	0.11	0.06	0.23
Zinc	0.67	1.66	1.04	0.31	0.99

Arsenic (As)

Arsenic (As) is a naturally occurring element that can be found in both dissolved and undissolved forms of organic and inorganic substances. Arsenic levels in drinking water samples collected along the Indus River ranged from 0 to 0.06 µg/L and in sediment samples it varied from 0 to 0.88 µg/L. The mean As concentrations (µg/L) were recorded as (0 ± 0.01) in drinking water and (0.22 ± 0.22) in sediment samples, summarized in Table 3 and Table 4, respectively. The arsenic levels found there were very low as compared to other parts of the world [19]. The WHO recommends a guideline of 10 µg/L for As in drinking water, but the National Standards for Drinking Water Quality (NSDWQ) have prescribed a limit of 50 µg/L. As all the samples had arsenic concentrations less than 10 µg/L, so, they do not pose any serious threat to population drinking water from these sources. The concentration of arsenic found in the vicinity of Indus River is comparable to those previously found in several settlements of the Nagar valley [26] and from Besham and Alpuri areas of the Kohistan region [27]. Their conclusions were consistent with those of our investigation, which determined that the element under inspection had concentrations below the acceptable threshold established by the EPA and the WHO. The arsenic concentrations in the study area are considerably lesser than those reported in Mailsi (18 to 828 µg/L) [28] and in Mancher Lake (35.00-157.00 µg/L) [29]. This study reports an arsenic concentration of less than 1 part per billion at the sample locations, confirming that the nearby areas of River Indus, Allai and Nagar are in the safe zone. It means that the water from these sites is almost free from arsenic pollution and is fit for consumption. Whereas, the As concentrations in Lahore, Vehari, Multan, and Jhang were 51, 50.4, 24, and 22 µg/L, respectively [5]. These values exceeded the WHO guideline, implying that the Lower Indus Basin is contaminated with groundwater arsenic. The countries with high As concentrations in drinking water than this study include China [30], Bangladesh [31], India [32], Mongolia [33], Canada [34], Argentina [35] and Vietnam [36].

Calcium (Ca)

Calcium may be found naturally in water. Marble, limestone, calcite, dolomite, gypsum, apatite, and fluorite may all dissolve it. According to WHO, appropriate Ca concentrations in drinking water should be 75 mg/L, however, its concentration in water may increase owing to human activities. The hardness of water indicates the presence of calcium and magnesium ions. Calcium concentrations ranged from 1.74 to 176.87 µg/L in drinking (glacier, waterfall and spring) water samples, whereas, its concentration varied from 42.98 to 2068 µg/L in the sediments collected from Allai and Nagar. The mean Ca values (47.92 ± 37.29) µg/L determined in drinking water are shown in Table 3 and the mean Ca values (790.05 ± 775.26) µg/L in sediment samples are presented in Table 4. It has been reported in 2018 that the calcium levels (20680 ± 8860 µg/L) in the Indus River Basin were within the permissible range [23]. Another study that evaluated drinking water samples from three distinct areas of the Nagar Valley (Gulmet, Thole, and Nilt) reported the calcium hardness variation from 4660 to 16660 µg/L [26]. This study also reported that the calcium concentrations in the study area were well within the guideline (200 mg/L) defined by WHO.

Chromium (Cr)

The most frequent type of chromium found in water is hexavalent Cr, while trivalent Cr is less frequent. Regular exposure to hexavalent chromium compounds increase the chances of developing lung cancer. The consumption of chromium (VI) has the potential to cause ulcers or pain in the stomach and intestines. Chromium (VI) concentrations of more than 0.05 mg/L in drinking water can cause liver and kidney damage, seizures, diarrhea, stomach discomfort, vomiting and indigestion [37]. The WHO and Pak-EPA suggest an allowed level of 0.05 (mg/L) or 50µg/L for Cr in drinking water. The analysis showed that no chromium concentration has been detected in any drinking water sample. However, the chromium concentrations ranged from 0.16 to 0.65 µg/L in sediment samples. The mean Cr values in sediment samples were 0.44 ± 0.12 µg/L.

Similarly, it has been reported that the Cr concentration was below detection limit in all drinking water samples from District Vehari [38]. However, the concentration of Cr found in this study was lower than that of reported Cr concentrations in the drinking water of Malakand Agency, Pakistan [6].

Copper (Cu)

Copper occurs naturally in water and is crucial in terms of water quality. The appropriate levels of copper in human body have several positive health effects. Copper is recognized as the first potent antibacterial element by the USEPA [39]. Prolonged copper exposure can harm the liver and kidneys and potentially result in death. It can also irritate the nose, mouth, eyes and induce headaches, stomachaches, dizziness, vomiting and diarrhea [40]. None of the drinking water samples contained copper. Copper concentrations in sediment samples varied between 0.12 to 1.76 µg/L. Table 4 shows the calculated average Cu values (0.75 ± 0.52) µg/L in sediment samples. The guideline set by WHO and PEPA for Cu in drinking water is 2.00 mg/L or 2000 µg/L [41]. A study conducted in 2021 to evaluate the surface water quality of springs in Skardu reported the mean concentrations of trace elements Cr and Cu in the spring waters as 16 µg/L and 3.6 µg/L, respectively [42]. These values were below the WHO's recommended guideline of 50 µg/L for Cr and 2000 µg/L for Cu [43].

Iron (Fe)

Iron is an essential mineral and is vital for healthy body operation. Hemochromatosis, which is accompanied by exhaustion, joint pain, and stomach discomfort is associated with elevated levels of iron. The amount of iron in glacier, waterfall and spring water samples varied from 0 to 0.25 µg/L. The average values for Fe (0.01 ± 0.03) µg/L are shown in Table 3. The WHO and PEPA have recommended the guideline for Fe in drinking water as 0.3 mg/L [40]. In contrast to this study, a wider range (0.03 to 13.43 mg/L) of Fe concentrations with a mean of 1.67 mg/L was found in the water samples of Tehsil Vehari [38]. Iron concentrations in sediment samples ranged from 166 to 544 µg/L. The results indicate the mean Fe concentrations in sediment samples as (370 ± 93.29) µg/L.

Sodium (Na)

The WHO recommends a sodium (Na) salt concentration of 200 mg/L in drinking water [44]. Chlorides, such as NaCl, CaCl, and MgCl are present in water because of both natural and human activities. Elevated dosage of salt results in high blood pressure. Following sodium, the second most important cation for the development of phytoplankton along with other aquatic creatures is potassium. The drinking water exhibiting elevated K^+ concentrations could result in hypertension, high blood pressure, and hyperkalemia. The World Health Organization prescribes potassium concentration of 10 mg/L and 12 mg/L in drinking water. This study reveals that the sodium and potassium concentrations ranged from 1.27 to 292 µg/L and 0 to 24.01 µg/L, respectively. The average Na and K values in drinking water were computed as 22.71 ± 54.78 µg/L and 4.68 ± 4.85 µg/L, respectively (Table 3). Another study also reported that the concentrations of K and Na in the surface water quality of the Indus River Basin were within the WHO's permitted guideline [23]. Sodium and Potassium concentrations in the sediment samples ranged from 8.99 to 15.36 µg/L and 35.57 to 247 µg/L, respectively. The mean concentrations of Na and K in the sediment samples are provided in Table 4.

Magnesium (Mg)

Magnesium is found in several minerals including dolomite and magnesite. It is naturally found in water. Mg may also become a component of the water because of anthropogenic activity. The World Health Organization prescribes a Mg concentration of 50 mg/L in drinking water [44]. Excessive Mg concentration in drinking water might result in serious health consequences with symptoms like vomiting and nausea. Low magnesium status is linked to endothelial dysfunction, increased vascular reactions, elevated C-reactive protein, decreased insulin sensitivity and metabolic syndrome which are risk factors for coronary heart disease. Calcium and magnesium are essential for bone formation, teeth solidification, reducing neuromuscular excitability, myocardial contractility and cell metabolism. Inadequate or excess intake can lead to health issues [37]. Magnesium concentrations in drinking samples ranged from 0.05 to 120.22 µg/L. Table 3 shows the mean magnesium concentration of 19.75 ± 28.09 µg/L in drinking water. Magnesium concentrations in sediment samples ranged from 47.14 to 453 µg/L. The average Mg values in sediments were recorded as 196.46 ± 79.71 µg/L (Table 4). These findings are in line with the findings of another study conducted in 2022 that reported mean trace element values of 10 µg/L for As, 280 µg/L for Fe, 33200 µg/L for Ca and 4.85 mg/L for Mg in the drinking water samples of Basho Valley, Skardu [45]. These levels were lower than the WHO guidelines, whereas in contrast to our study, the mean trace element concentrations of Cu (400 ± 160 µg/L) and Zn (6770 ± 27100 µg/L) were peculiarly high and had surpassed the WHO guidelines for drinking water. Similarly, the average Ca, Mg, and Na concentrations in the ground and surface water of the Haripur, Khyber Pakhtunkhwa were found to be within the WHO's guidelines [46].

Lead (Pb)

According to Pakistan's Environment Protection Act, the lead concentrations in drinking water should not be above 10 ppb. Increased lead concentrations in drinking water lead to neurological disorders, psychological delays, nerve damage, and neurological issues [37]. None of the drinking water samples in the study area contained Pb. However, the lead concentrations ranged from 0 to 0.23 µg/L in sediment samples and the mean lead concentration were 0.11 ± 0.06 µg/L as shown in Table 4. In contrast to our study, the lead concentrations across different districts including Lahore, Jhang, and Vehari have surpassed the safe levels as defined by WHO (0.01 mg/L) [5]. Furthermore, the elevated lead concentration of 0.391 mg/L was found in the drinking water samples from Rabwah, Pakistan [47]. This value is considerably higher than the WHO guideline.

Zinc (Zn)

According to WHO, the permissible limit for zinc in drinking water is 3 mg/L [48]. Zinc deficiency can cause various health issues, including vomiting, dehydration, fatigue, abdominal discomfort, poor coordination, renal failure, malabsorption, liver damage, kidney damage, and chronic illnesses [40]. The study revealed that Zn concentration was not detected in any drinking (glacier, waterfall and spring) water sample (Table 3). Zinc concentrations ranged from 0.67 to 1.66 µg/L in the sediment samples and the mean Zn values were recorded as 1.04 ± 0.31 µg/L (Table 4). These results are also consistent with those of a study conducted in 2021`that evaluated numerous samples from the glacier water sources of Gilgit Baltistan [49]. The study exhibited trace element values ranging from 35 to 135 mg/L for Ca, 2 to 12.2 mg/L for K, 0 to 17.9 mg/L for Mg, 2 to 2.76 mg/L for Na, 0 to 3.5 mg/L for Zn, and 270 to 3510 µg/L for Cu. Overall, the drinking (glacier, waterfall and spring) water quality along River Indus, Allai, and Nagar is excellent as the concentrations of metals and other trace elements in any sample did not exceed either the guidelines provided by WHO or the standards defined by PEPA.

Conclusion

This research focused on determining metal and other trace element (arsenic, calcium, chromium, iron, lead, magnesium, copper, potassium, sodium and zinc) contamination in the drinking (glacier, waterfall and spring) water along the River Indus, Allai and Nagar. The results pertaining to drinking water quality from different locations in the vicinity of River Indus revealed that the concentrations of metals and other trace elements from all the samples were well within the guidelines provided by WHO or the standards set by PEPA. This study concluded that the drinking water along the River Indus is generally safe from toxic heavy metals and it does not pose any serious threat to human health, so it can be used for drinking, irrigation, and other domestic purposes. However, as there was lack of proper sewerage network in most of the areas along the River Indus so a detailed study is recommended to investigate the bacteriological contamination of water in the villages and towns located in the vicinity of River Indus so as to save the population from waterborne diseases. In order to mitigate future risks, it's crucial to periodically monitor the water sources for contamination. Furthermore, a detailed study encompassing samples from the springs, glaciers, waterfalls and lakes is recommended to evaluate the possible trace element contamination, either due to deposition or mixing of metal bearing rocks with water, both in the low lying and highland areas of Upper Indus Basin, Pakistan. The insights of this study can be helpful to the concerned government officials in Gilgit Baltistan and KPK province in delivering clean drinking water to those residing near the mighty River Indus, Pakistan.

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