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Assessment of heavy metals and physico-chemical characteristics of water and sediments, Kurram River (Pakistan)

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Abstract

This study was conducted to analyze water and sediment samples of Kurram River from upstream to downstream to observe the trend of changes in physico-chemical properties like pH, E.C, TSS, TDS, Ca, K, Mg and Na and heavy metal concentrations (Cr, Zn, Cu, Ni, Pb, Cd, Mn and Fe). The results of the study revealed that Kurram River quality is continuously degrading day by day by entry of toxic metals from different sources like discharge from industries, municipalities, waste dumping in the vicinity of the river, urban and agriculture runoff and atmospheric deposition. A decrease in water and sediments contamination level was observed down the stream. The physico-chemical parameters of water samples were observed within the permissible limits of World Health Organization (WHO), except for dumping sites near Ghori wala and Sikna Sikander Khel. TDS concentrations (553 mg L^{-1}) and TSS concentrations (6.60 mg L^{-1}) were above the permissible limits of United States Environmental Protection Agency (USEPA). The concentrations of Cr (2.50-8.0 mg L^{-1}, Zn (3.5-6.0 mg L^{-1}), Cu (2.5-7 mg L^{-1}), Ni (2.0-10.5 mg L^{-1}), Pb (2.5-9.5 mg L^{-1}), Cd (0.042-0.14), Mn (4-10 mg L^{-1}) and Fe (3.5-13.25 mg L^{-1}) were observed to be higher in water samples of dumping site near Bannu city as compared to WHO, USEPA and Pakistan Environmental Protection Agency (PakEPA). In sediment samples great variations in the concentrations of Cr (10.2-18.5 mg kg^{-1}), Zn (3.0-8.5) mg kg^{-1}, Cu (3.50-13.2 mg kg^{-1}), Ni (3.5-12 mg kg^{-1}), Pb (1.0-12.5 mg kg^{-1}), Cd (0.101-0.151 mg kg^{-1}), Mn (8.7-14 mg kg^{-1}) and Fe (12-46.5 mg kg^{-1}) were observed. Heavy metal concentrations in sediment samples were higher than water samples. While individual heavy metal concentrations in sediment samples followed the order of Fe>Cr>Mn>Pb>Cu>Ni>Zn>Cd whereas in water the order was Fe>Mn>Ni>Pb>Cu>Zn>Cr>Cd.

Keywords: Water quality; Sediments; River pollution; Light metals; Heavy metals.

1. Introduction

The presence of heavy metals and other chemical compounds in a concentration greater than their natural or normal conditions cause pollution which in turn effect human health and other ecological resources and processes and of the ecosystem (Duruibe et al., 2007). The entry of different toxic materials into water bodies cause water pollution which can effect aquatic life and human beings (Tsai et al., 2003). Occurance of various pollutants including heavy metals deteriorate the quality of water (Gül et al., 2009). Organic chemicals, nutrients, crude oil, microbes, toxic metals and other chemical compounds are the major water and sediments pollutants. These pollutants from water accumulate in the sediments because the sediments act not only as a sink but a source as well for the contaminants (Jalil et al., 2017; Riaz et al., 2017). A number of environmental problems including the deterioration of water quality and aquatic ecosystem are faced by Pakistan. Third world countries including Pakistan are limited with resources and unable to manage and properly dispose of their wastes generating daily during different anthropogenic activities due to lack of technology (Arian et al., 2008). The presence of heavy metals in environment can cause various problems because of their toxicity (Gale et al., 2004). Simple remediation techniques cannot remove these heavy metals from. These toxic metals enter into human bodies though different pathways i.e. inhalation, ingestion and dermal contact. The settling of solid materials as sediments cause the entry of heavy metals into water bodies with time. Similarly the discharge of waste water (industrial or municipal), urban effluents, agriculture runoff also enter into water bodies and pollute water and sediments (Olajire et al., 2003; Siddique et al., 2017). The water and sediments of the rivers are increasingly contaminated with heavy metals with the passage of time due to the entry of solid and liquid wastes. These heavy metals accumulate in the food crops when this contaminated river water is used for irrigation purposes (Ubaidullah et al., 2004). Heavy metals reach to the environment through different chemical, biological and physical processes and finally enter the water bodies and deposit in sediments (Antonious and Snyder, 2007; Sekomo et al., 2011; Ali and Malik, 2011; Wen et al., 2011). Metals are characterized as non-essential and essential groups based on their roles and needs for development and growth of human, animals and plants. Metals like Cadmium (Cd), Nickle (Ni), Lead (Pb) and Chromium (Cr) are considered to be non-essential metals while Iron (Fe), Manganese (Mn), Zinc (Zn) and Copper (Cu) are essential metals, but these must be with in their respective permissible limits. Cd is highly toxic environmental pollutant and it cause various disease like failure of kidney, heart problems, blood pressure cancer and bone damage (Mijal and Holzman, 2010). Similarly high concentrations of Cr effect red blood cells (RBCs) production, cause thyroid glands disorder, polycythemia and coronary artery. Ni in aces amount can cause heart and respiratory problems, cause asthma and lung cancer (Zhao et al., 2012). Pb in high concentrations can effect nerve system, cause headache, high blood pressure, lungs and stomach problems (Jan et al., 2011; Muhammad et al., 2011). Moreover other disorders like memory loss or weakness and behavioral disorders are also reported to be caused by high concentrations of heavy metals (Er et al., 2012). High concentrations of Cu cause neurological disorder and cancer whereas its deficiency cause neutropenia, leucopenia, hypo chronic anemia and normocytic (Pasha et al., 2010). Similarly Mn is essential for brain and liver function, yet its high amount can cause nerve system damage (Bocca et al., 2011).similarly Zn is required for cell membrane, protein metabolism, carbohydrates and lipids whereas excess amount of Zn cause anemia, while its deficiency effects sexual maturation, mental growth, causes anorexia and immune dysfunction (Muhammad et al., 2011). Heavy metals are released in to aquatic environment from industrial waste discharge, mining activities, sewage sludge and discharge of municipal wastes (Gautam et al., 2013), similarly atmospheric deposition of pollutants and agriculture application of fertilizers and pesticides also cause heavy metals enter into aquatic ecosystem (Adaikpoh et al., 2005; Amin et al., 2014; Chen et al., 2004; Singh et al., 2017; Lepane and Heonsalu, 2007). Moreover land use or land cover changes also effect the flow of river which in turn contribute in accumulation of heavy metals in aquatic ecosystem (Bharose et al., 2013; Kumar et al., 2017; Narsimlu et al., 2015; Singh et al., 2014).

This study was conducted to investigate the physicochemical properties of water and analyze water and sediment samples of the selected river for heavy metal concentrations like Cr, Zn, Ni, Pb, Fe, Cu, Cd and Mn. In this paper, the changes in pollution loads from upstream (Suranai Bridge Bannu) to downstream (Indus River, Mianwali, Punjab) relative to the leaching from dumping sites of cities in the vicinity of the river and the effects of mixing of the tributaries i.e Tochi and Gambella on the concentrations of heavy metals were also assessed.

2. Materials and methods

2.1. Study area description

The studied Kurram River runs in the provinces of Paktia and khost of Afghanistan then flows into Kurram Agency, Pakistan (See Fig. 1), draining the mountainous range of Spin Ghar. In the province of Paktia, Afghanistan, River Kurram rises about 20 Km in the south east of Gardez. It runs in the north eastern mountains and then enters into Pakistan at almost 80 km in the south west of Jalalabad. After draining Koh-e- Sufed Mountains (southern sides) reaches River Indus plains in north of Bannu. After traveling more than 320 km distance it joins Indus River near Essa Khel (Mirza et al., 1993).

2.2. Samples collection and preparation

The samples of water (30) and sediments (30) from Kurram River were collected from upstream to downstream as mentioned in figure 1. Pre labeled plastic bottles (half liter) were used for the collection of water samples. The bottles were first washed with detergents and then rinsed with deionized water to avoid any contamination. The water samples were collected at a distance of 1-2 m from the bank and at least 1m depth from surface. While zipper bags were used for sediment samples collection. The sediment samples were collected (0-25 cm depth) with the help of stainless steel scoop and core. The samples after transporting to the laboratory were air dried and then powdered and stored for further analysis.

2.3. Chemical analyses

The pH of water and electrical conductivity were determined with pH and EC electrodes. Total dissolved solids (TDS) and total suspended solids (TSS) were measured using standard procedures (APHA, 1992). To extract of heavy metals, 2.0 g of sediment sample was digested in beaker and acids mixture (HCl, HNO_3 and $HCLO_4$) was added using the method adopted by Khan et al. (2010). Auto control furnace was used to heat the samples till the solution became clear and whitish then diluted HNO_3 was added. After cooling the solution was filtered and to rise the volume to 50 ml deionized water was added dropwise (Khan et al., 2008). Heavy metal concentrations in the prepared solution were determined using graphite furnace atomic absorption spectrometer (AAS, Perkin-Elmer Analyst 700). While flame atomic absorption spectrometer (FAAS) was used for the quantification of light metals like Magnesium (Mg), Sodium (Na), Potassium (K) and Calcium (Ca). The physicochemical characteristics of water samples were determined using standard procedures and then compare with the limits of different agencies like WHO (WHO, 2004)., USEPA and Pak-EPA whereas the results of sediment samples were compare with the limits of USEPA.

2.4. Quality control

The soil (GBW07406-GSS-6) certified reference materials and blank reagents were used to check the accuracy of the measurement. The percent recovery for Cr, Zn,Cu, Ni, Pb, Fe, Cd and Mn were 88, 91, 96, 89, 98, 85, 92 and 93 % respectively.

2.5. Statistical analysis

The obtained data were statistically analyzed using different statistical packages like SPSS version 1.7 and Microsoft excel 2010. The graphs were prepared using sigma plot.

3. Results

3.1. Water physico-chemical parameters

The water characteristics at different locations exhibited huge variations (Fig. 2). The mean pH was 8 while ranging between 8.31 to 8.75. Majority of the observed samples were beyond the permissible limit (6.5-8.5) set by WHO (2004). The EC varied between 420 to 860 µs/cm, while mean EC value was 633 µs/cm (see Fig. 2). High values of EC were investigated in Nali Chak, Tochi River, Topa Wala, Kurram River, Dara Tang and Pyinda Khan Banda. However, WHO and other organizations have not shown any fresh water permissible limits for EC, but water is not recommended as good water with an EC value above 500 µs/cm. The TDS concentrations ranged between 350 - 551 mg L^{-1} with a mean of 553 mg L^{-1}. Few samples of Kurram River indicated TDS concentrations above the permissible limit (500 mg L^{-1}) of WHO. The mean TTS (Fig. 2) concentrations was 6.6 mg L^{-1} , with lowest value of 4.2 and highest 7.8 mg L^{-1} . In water samples mean Na concentration was 163.7 mg L^{-1} with a range of 134.4 - 184.4 mg L^{-1}. Sample at Bannu City near dumping point displayed a maximum (184 mg L^{-1}) concentration. However, all Na concentrations of water samples observed below the permissible limit (200 mg L^{-1} for Na in fresh water, WHO, 2004).

Light metals demonstrated great variation in concentrations at different sampling sites. The mean K concentration (Table. 1) observed was 8.78 mg L^{-1} and with range of 6.2 - 10.8 mg L^{-1}. Mean concentration of Ca was 64.87 mg L^{-1} and ranged from 41.7 to 76.6 mg L^{-1}. In all samples, the concentrations of Ca were below the limit (75 mg L^{-1}) recommended by WHO, except in the sample at dumping point which revealed high value (76.6 mg L^{-1}). The mean concentration of Mg was 24.0 mg L^{-1} with range of 13.2 - 40.5 mg L^{-1}, and remained within the WHO permissible limit (150 mg L^{-1}).

3.2. Heavy metal concentrations in water

The values of the detected heavy metals in water of Kurram River are summarized in Table 2. The mean Cd concentration observed was 0.093 mg L^{-1} with a range of 0.042 - 0.138 mg L^{-1} (Table 2). The concentration of Cd was increased downward from dumping point till Nar Ghazni Khel (Kurram Bridge), again increases were observed to Indus River. Cr concentrations showed a range of 2.5 -8.0 mg L^{-1}. The concentrations of Cr at River Kurram and the point where Tochi rivershad and Kurram are intermingling were 6.75 and 3.5 mg L^{-1}, respectively. Cu showed a ranged of 2.5- 7 mg L^{-1}, and dumping site had the highest and Ihsan Pur Banda I, BadShah Khan and Atasshi Banda had the lowest Cu concentrations. The concentrations of Cu decreased from upstream to downstream then increased at Kurram Bridge and followed a decrease to Pinjama. The concentration of Mn observed near Kurram Bridge was 8.75, Tochi River was 6.75 and near the intermixing site of Tochi and Kurram was 5.75 mg L^{-1}. Decreases in Mn concentration were noticed downwards in the Kurram River. Mean Ni contents were 5.9 mg L^{-1} and ranging between 2 and 10.5 mg L^{-1}. Pb concentrations were observed between 2.5 - 9.5 mg L^{-1} (Fig. 3), with a highest value recorded at dumping point. Zn concentration showed a range between 3.5 - 6 mg L^{-1}. Highest Zn concentrations was observed in water samples of dumping point and lowest in the samples of Surrani Bridge and Pyanda Khan Banda. Similar results were found in water samples of Kurram Bridge and intersecting point of Kurram River and Tochi.

3.3. Heavy metal concentration in sediments

The concentration of heavy metals investigated in samples of sediments are shown in figure 4. Mean Cd concentration was 0.124 mg kg^{-1} and range was 0.101-0.151 mg kg^{-1} (Table 2). Cd was highest near dumping site and lowest value was in sample of Surrani Bridge. The concentration of Cr ranged (10.2 - 18.5 mg kg^{-1}) with the highest concentration observed near dumping site and lowest at Dara Tang. The concentration of Cu was maximum at dumping point (13.25 mg kg^{-1}) and lowest at Surrani Bridge (3.5 mg kg^{-1}). Fe mean concentration of 31.1 mg kg^{-1} was observed with a range of 12 - 46.5 mg kg^{-1}. Highest concentrations of Fe were found at dumping point and lowest at Atasshi Banda. The concentration of Ni ranged between 3.5 and 12 mg kg^{-1} and pb showed a range of 1.0 - 12.5 mg kg^{-1}. The highest concentrations were reported at near Bannu in dumping site samples and the lowest Surrani Bridge. Zn concentrations ranged between 3.0 - 8.5 mg kg-1 with 5.5 mg kg^{-1} mean value. Highest Zn concentration was observed at dumping point whereas the minimum Zn concentration was observed at Pir Wala 2. Zn concentrations in the samples of Tochi, Kurram and the junction of these two rivers were 6.25, 6.5 and 5.25 mg kg^{-1}, respectively.

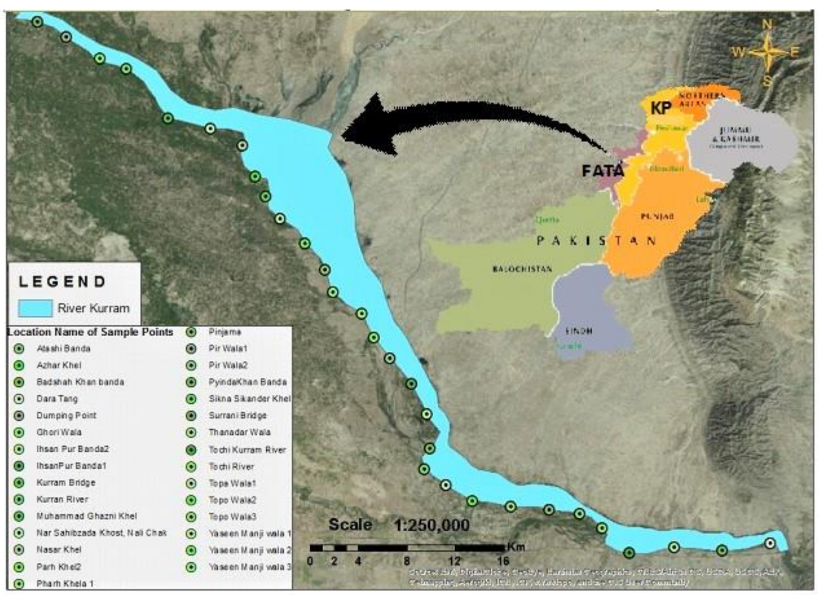

Fig.1. Location map and sampling sites along Kurram River.

4. Discussion

4.1. Physico-chemical properties of water

Water physico-chemical parameters play a very crucial role regarding quality of water and change in their concentrations can directly or indirectly effect human health. The variations in physicochemical properties of water may adversely affect aquatic biota (Azmat et al., 2016). pH is the most influencing factor determining the quality of water in aquatic ecosystem (Jonnalagadda and Mhere, 2001), fresh water ecosystem having neutral pH favors fast and better growth of ecological biota and vice versa. It is clear from figure 2 that the concentrations of K and N were within the permissible limit, however continues anthropogenic activities like direct dumping of wastes in to the river have greatly affected their concentrations and these continues anthropogenic activities may pose risk in the future. In the dumping areas the concentrations of Ca were observed above the permissible limits, suggesting that these wastes contain high concentrations of Ca. The concentration of Mg was observed below the safe limit of WHO. There may be several possible reasons for the increases in the values K, Ca, Na, and Mg. One of the possible reasons is the leachate from dumping sites in to the river. In the study area the leachate with hospital and municipal wastes of Bannu City, is one of the major causes of the observed metals in water of the studied river. The second reason may be the small clusters of population which reside on the river banks which throw directly their wastes without any treatment into the river and also flush out directly municipal waste water, which may increase toxic metal concentrations in the studied river. In the study area, inverse relation between the values of physicochemical parameters in the collected samples and the distance from the source point was observed.

4.2. Heavy metal concentrations in water

All the studied toxic metals were detected in all the water samples of the selected river. The results of the study revealed that the concentrations of Zn were higher dumping site compared to the other selected sites of the river. Move over the concentrations of other selected heavy metals including Cu, Pb, Cr, Fe, Ni, Cd and Mn were also observed above their respective WHO permissible limits. The high concentrations of these heavy metals could be linked with many possible reasons including the direct discharge of untreated domestic waste water and agriculture runoff. Generally, leachates have higher concentrations of heavy metals and their release from dumping sites into the river water may also contribute substantially to Kurram river water contamination. Open dumping of hospital and municipal solid wastes alongside Kurram river are the major source of heavy metals contamination of river Kurram water. Similarly, people resides in small clusters near river Kurram also release their solid waste and waste water directly in the river Kurram which may also contribute to increase in heavy metals concentration and contamination of river water. Furthermore, another reason that can result in an increase in heavy metals concentrations is the use of fertilizers in the vicinity of river Kurram. The sampling survey reveals that with increasing distance from the source point a decrease in heavy metals concentration were observed, which may be attributed to dilution along the run of flow. Fresh water contamination with toxic metals is fetal for aquatic biota. The bioaccumulation and biomagnifications of heavy metals in aquatic food chain may also be fetal for the local residents because of their dependency on River Kurram for water and food Continues disposal of wastewater and solid wastes in the fresh water bodies may severely affect the photosynthetic activities of phytoplankton thus affecting the oxygen availability which will affect the fish and other aquatic biota. The uses of fertilizers and pesticides to enhance plant growth and control diseases, are important tools in modern days agriculture, which contribute to the constant degradation of the fresh water bodies (Hassan et al., 2012).

4.3. Heavy metal concentrations in sediments

River sediments contamination with heavy metals is one of the main environmental concerns because of the fact that sediments act like a sink and source of contaminants for aquatic ecosystem. The analysis of sediments plays a pivotal role in the assessment of pollution loads whether organic or inorganic or both contaminants (Mucha et al., 2003). Toxic metal concentrations in sediments more specifically in the fine grained sediments which behaves as a carrier agent in water system, are observed to be three times higher than the concentrations of the same toxic metal in the surrounding water. The analysis of sediment samples for the quantification of heavy metals helps in determining the water quality (Heiny and Tate, 1997). The concentrations of toxic metals can indirectly be determined from the analysis of sediments even if they cannot be detected in water samples (Soares et al., 1999). In environmental research, the quantification and speciation of toxic metals in sediment samples is one of the main concerns (Warren and Zimmerman, 1994; Nowack et al., 2001). The data concerning toxic metals concentrations in sediment samples give evidence about water quality and water pollution loads and pollution load points (Fabbri et al., 2001; Bordes and Bourg, 2001). Toxic metals can easily be deposited and accumulated on sediments surface which ultimately act as a source and sink of contaminants in aquatic ecosystem (Vard and Sen, 2012). The results of the present study reve aled that all the studied heavy metals concentration in the samples collected from Sikna Sikander Khel, dumping point and Ghori Wala were above the safe limits of WHO. There might be many reasons and sources of high concentrations of heavy metals in sediments but among these sources and reasons direct dumping of municipal and hospital wastes near Bannu city without any treatment played a pivotal role. The dumping of these contaminated wastes are responsible for releasing toxic metals contaminated leachate into the river. The toxic metals contained in the leachate are released and transported by the river water and ultimately settled down in the sediments (Fig. 4). The other possible reason for sediment contamination with heavy metals may the direct discharge of contaminated sewage water in to the selected river without any treatment form the villages on the river banks and nearby. The runoff from agriculture containing agrochemicals particularly toxic metals was observed to be the third possible reason for the high concentrations of heavy metals in the sediments. Transportation and shifting of heavy metals with water and ultimate settling in the river sediments is also one of the main reasons for the high concentrations of toxic metals in the sediments. The observed decreases in the heavy metal concentrations can be linked with the dilution phenomenon and also with the increased distance from the source points like human settlements and dumping sites.

5. Conclusion

Contamination of water and sediments of the studied Kurram River with heavy metals from point sources including municipal/industrial discharge and dumping of untreated waste along the bank of the river and non-point sources i.e agriculture/urban runoff and atmospheric deposition were observed. A decreasing trend of contamination level of water and sediments was observed from up to downstream due increasing distance from source point and dilution phenomenon. Sediments of the river were more contaminated as compared to the water. In sediment samples heavy metal concentration followed the order of Fe>Cr>Mn>Pb>Cu>Ni>Zn. To protect the river from contamination and preserve aquatic ecosystem and its ecological resources, it is necessary to strictly implement, monitor and follow national environmental quality standards (NEQs) and create awareness in local community about the hazards associated with the dumping of untreated wastes along the river bank and direct discharge of municipal waste into the river.

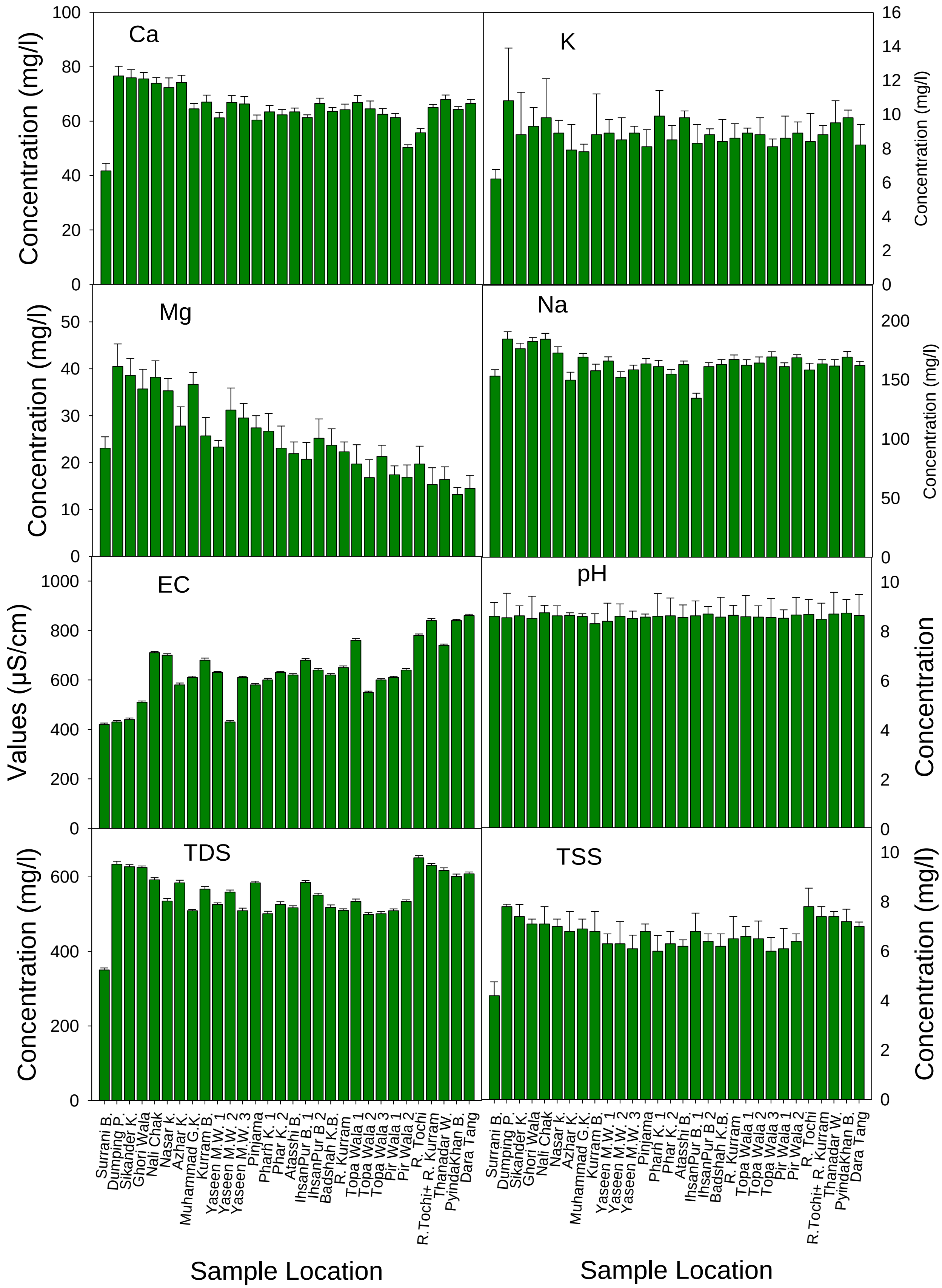

Fig. 2. The values of physico-chemical properties of water samples collected from Kurram River.

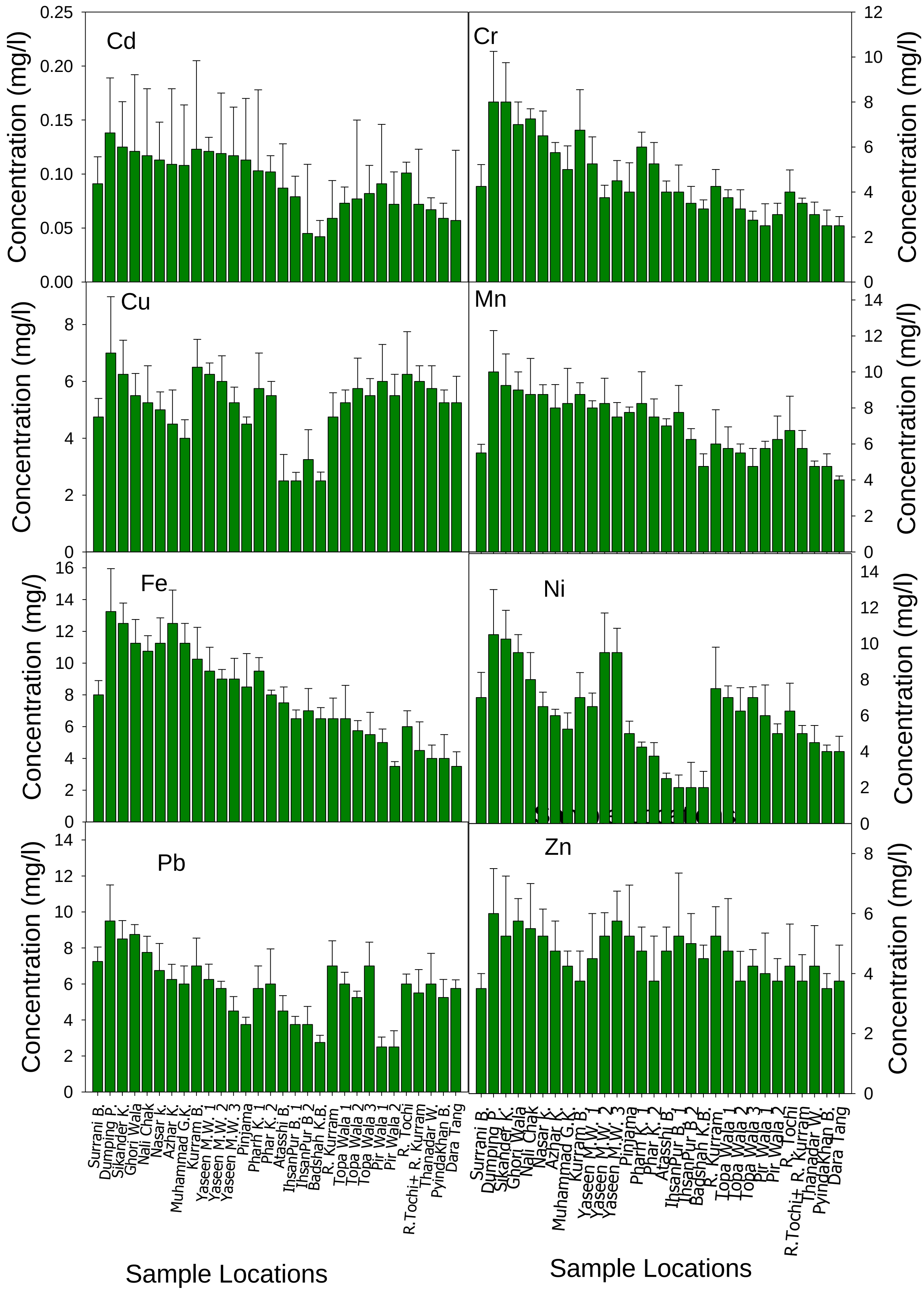

Fig. 3. The concentrations (mg/L) of heavy metals in water samples collected from Kurram River.

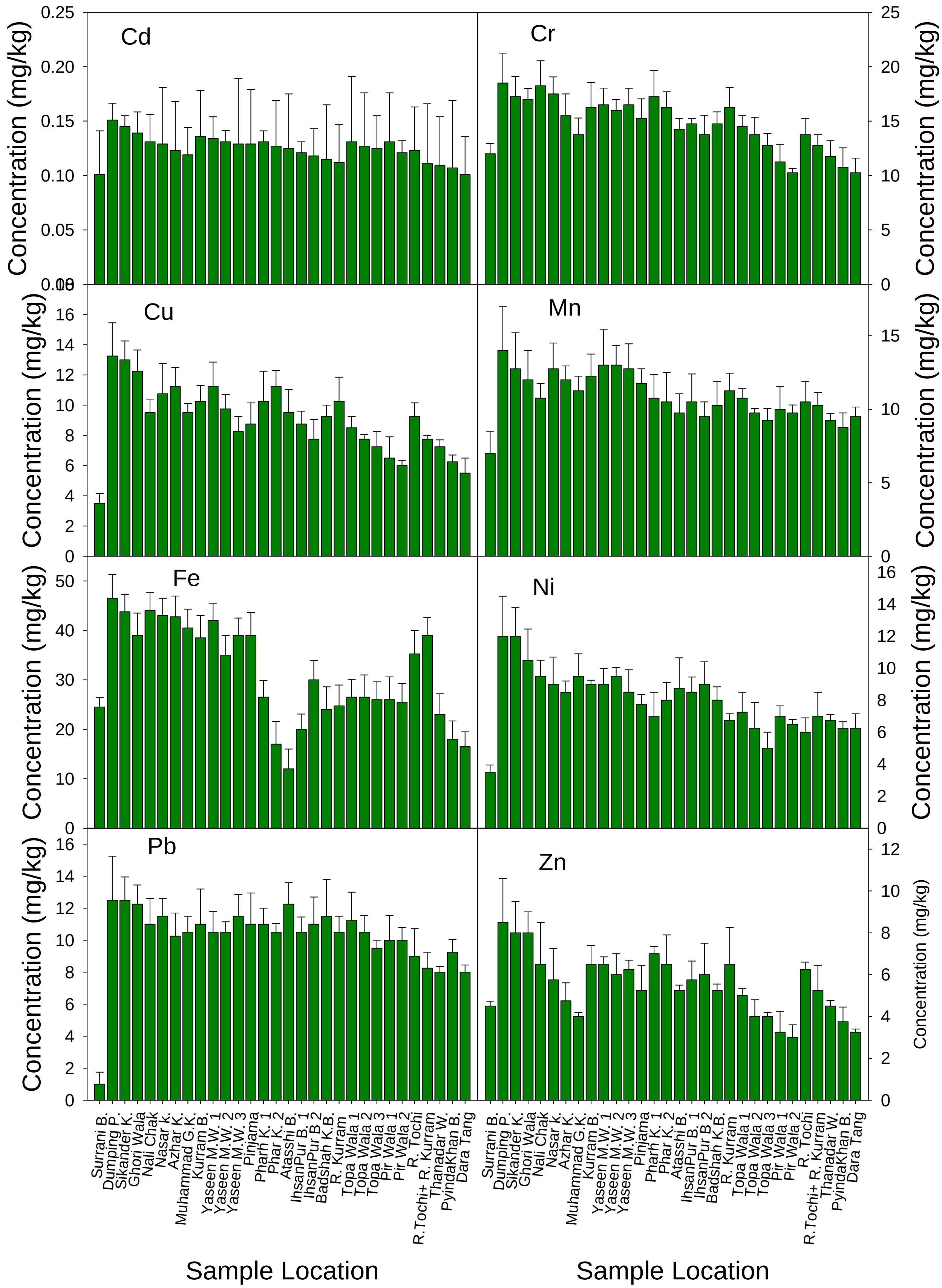

Fig. 4. Heavy metal concentrations (mg/kg) in the sediments collected from Kurram River.

Table 1. The values of selected physico-chemical parameters and light metals determined in the water of Kurram River

Values	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	pH	EC (uS/cm)	TSS (mg/L)	TDS (mg/L)
Maximum	184	10.8	76.6	40.5	8.75	860	7.80	651
Minimum	134	6.20	41.7	13.2	8.31	420	4.20	350
Mean	164	8.77	64.9	24.9	8.60	633	6.65	553
Standard deviation	10.3	0.82	7.28	7.79	0.09	117	0.69	61.4

Table 2. The concentrations of heavy metals determined in the water and sediments of Kurram River

	Zn	Cr	Cu	Pb	Ni	Fe	Mn	Cd
Water of Kurram River (mg/L)								
Maximum	6.00	8.00	7.00	9.50	10.50	13.25	10.00	0.14
Minimum	3.50	2.50	2.50	2.50	2.00	3.50	4.00	0.04
Mean	4.60	4.57	5.13	5.78	5.98	7.89	6.98	0.09
Standard deviation	0.74	1.65	1.17	1.75	2.41	2.87	1.62	0.03
Sediment of Kurram River (mg/kg)								
Maximum	8.50	18.5	13.2	12.5	12.0	46.5	14.0	0.15
Minimum	3.00	10.25	3.50	1.00	3.50	12.00	7.00	0.10
Mean	5.50	14.6	9.01	10.2	7.95	31.1	10.8	0.12
Standard deviation	1.44	2.38	2.24	2.12	1.87	9.83	1.54	0.01

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Authors' Contribution

Jawad Ali did the field and analytical work. Muhammad Amjad Khan did analysis and helped in preparation of graphs. Shahla Nazneen helped in laboratory work and preparation of samples. Juma Muhammad did drafting and helped in sampling and laboratory work. Muhammad Jamal Nasir did review of paper and finishing of graphs. Muhammad Tahir Shah did supervision of research work and reviewed the paper. Zahidullah also did review and proof reading of the paper. Sardar Khan also did supervision of overall work and reviewed comments responses and prepared the paper.

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