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Macrophytes as potential indicator of heavy metals in river water

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ABSTRACT

The aim of the present study was to investigate macrophytes as indicator in comparison with sediments and surface water for heavy metal pollution in the aquatic ecosystem of river Jhelum, Pakistan. Samples of different macrophytes, water, and sediments were collected and preserved from the three nominated sampling locations, viz., Mangla Dam, Rasul Barrage, and Trimmu Barrage. Macrophytes and sediment samples underwent the wet acid digestion procedures as a pretreatment for heavy metal analysis. Physicochemical parameters of surface water were compared with National Environmental Quality Standards (NEQS) while inorganic parameters (Ca, Mg, Na, K, CO_3, HCO_3, Cl^-, SO_4, NO^{3-}, sodium absorption ratio, and residual sodium carbonate) were compared with WHO limits for drinking water and Pakistan Standards and Quality Control Authority (PSQCA) Water Quality Standards for irrigation. Results showed a progressive decline in the river water quality moving toward the downstream areas. Heavy metal analysis of water showed descending order of element concentrations Mn > Zn > Pb > Cr and in sediments was Zn > Mn > Pb > Cr. The macrophytes of Trimmu Barrage showed Cr and Zn toxicity only, and all others were within permissible limit. Heavy metal pollution index in water samples were 13 fold high, representing unsafe water for drinking. Degree of contamination was also higher in water samples. Study demonstrated that macrophytes have high potential to accumulate heavy metals and they can serve as excellent biomonitoring tools in rivers at early stages.

Keywords: Aquatic system; Jhelum water quality; Metal analysis; Phytoremediation at river

1. Introduction

Water is a vital element for life. Exponential increase in world's population, agriculture, industrialization, and unsustainable water consumption in different sectors of life are the major contributors of putting this small percentage of fresh water under massive scarcity [1]. There has been always limited awareness regarding strength and weaknesses of many institutional frameworks to deal with environment, ecosystems, and their effects on biota [2]. Constituent matrix in water quality explains the limiting value of each parameter, and the value beyond the limit is referred to as unsuitable water sample [3]. Pakistan is one of the developing countries of the world which is facing acute shortage of water resources, as the annual rainfall in Pakistan is less than the annual evaporation. This is the reason behind the decline of water availability in the rivers, lakes, and canals [4].

Many metals are circulating in the ecosystems through different biogeochemical cycles. However, industrial and municipal activities are contributing anthropogenically for

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increasing metal concentrations, which interfere with the natural balances in the ecosystem through leachate, surface water runoff, domestic effluents, and other atmospheric origins [5]. Concentrations of metals vary considerably due to the variations in sewage and industrial effluents discharged into water bodies through different tributaries [6]. Water quality of the rivers is degrading continuously due to lack of proper water use management systems including high rates of deforestation and soil erosion [7]. It is documented that sediments serve as significant sinks for heavy metals discharged from anthropogenic sources. Sediments also proved to be non-point contamination source that can directly distress overlying waters and aquatic life [8]. Heavy metals have the tendency to adhere with sediment particles and dissolve in the pore of sediments [9]. Pollutant's tendency to accumulate in sediments and continuous increases in the pollution levels of sediments are posing threats to the nearby living biota, especially to those which are directly linked to the sediments [10]. Quantification and spatial variability of these metals between the solid and aqueous phases (i.e., sediments and river water) of aquatic environment are necessary for the determination of potential hazards, dangers, and toxic effects [11]. Therefore, the analysis of river sediments along with surface water is an advantageous approach for investigating the heavy metal pollution in an area [12]. Usage of biological materials as indicators for detecting environmental pollution is a simple, economical, and reliable substitute to the conventional methods of sampling. Many organisms have been used as bioindicators, and the results were significantly positive. These organisms include fish, plants such as mosses and vascular plants, and periphyton [13]. Macrophytes are known to be the significantly vital constituents of the aquatic environments. They play an important role in the food chain and serve as main source of food and energy for the invertebrates [14]. The aquatic macrophytes are capable of accumulating substantial higher aggregates of heavy metals in their organs and tissues; they are suggested to be efficient pollution monitoring organisms [15]. However, the selection criterion for the macrophyte species is highly dependent on their availability and indigenous climatic conditions [16]. Many higher aquatic plants can store significant quantities of metals dissolved in water and retain them in tissues for a long time [17]. To estimate the water pollution level, water pollutant categories can be better explained by index methods than modelling and mathematical analysis. It better provides mechanism for water quality health in a numerical expression [18].

The present study was the evaluation of the quality status of aquatic ecosystem analysis of water, sediments and aquatic plants to determine the cause of pollution, heavy metal pollution index (HPI), and contamination index (Cd) and to find the ways for the reduction and eradication of the pollution sources.

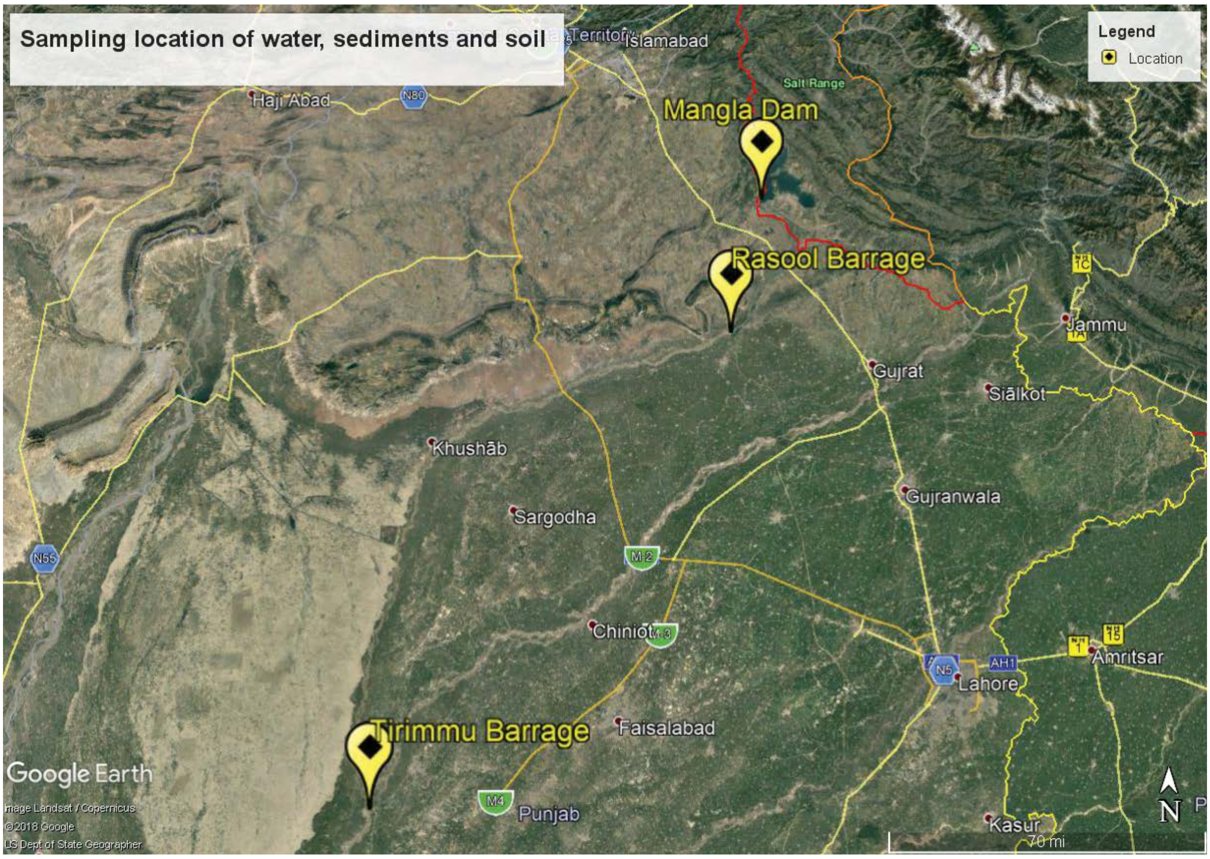

Fig. 1. Map showing sampling location.

2. Methodology

River Jhelum, a major tributary out of five major tributaries, viz., Satluj, Beas, Ravi, Chenab, and Jhelum which are ultimately merging with river Indus in Pakistan, is the west flowing river. The river features several barrages and dams such as the Rasul Barrage, the Mangla Dam, and the Trimmu Barrage (Fig. 1).

2.1. Sampling points

Grab samples were collected from three sampling points of river Jhelum to cover the entire length of study area (Table 1).

These sampling points are

- Mangla Dam,
- Rasul Barrage,
- Trimmu Barrage.

2.2. Sample collection

Random samples of surface water were taken by immersing the bottles and lifting it up from three different places in each sampling point. Pipette drops of concentrated HNO_3 were poured in each bottle containing surface water samples to maintain the sample pH < 2 for metal analysis. DO and pH were measured at each sampling point. Other parameters including total dissolved solids (TDS), total suspended solids (TSS), electrical conductance (EC), etc. were measured in the laboratory. Three sediment samples were collected by using the method of random sampling in pre-cleaned polythene zipper bags from each sampling point. Sediments were collected with the help of augar and shifted to the laboratory where they are stored at 4°C before further processing. Samples of dominated different species of aquatic plants were collected in polythene bags from each sampling point. These were taken to the laboratory, identified, and stored at 4°C before any other treatment process.

2.3. Sample analysis

2.3.1. Water analysis

Surface water samples were analyzed for different parameters such as pH (by pH meter HANNA HI-98129), TDS, TSS, EC, (by EC meter YSI EC 300), and dissolved oxygen (DO) (by DO meter YSI DO 200). Obtained results were compared with the permissible limits of Punjab Environmental Quality Standards (PEQS), 2016. For inorganic parameters, calcium (Ca) and magnesium (Mg) were determined by complexometric titration, sodium (Na) and potassium (K) by flame photometer (Jenway PFP7, Corning 410, Sherwood 410), chloride (Cl) by argentometric titration, carbonates (CO_3) and bicarbonates (HCO_3) by acid-base titration, sulphates (SO_4) by absorption spectroscopy double beam UV/VIS spectrophotometer (Spectra UVD 1000), and nitrates (NO^{3-}) by colorimetric method while sodium absorption ratio (SAR) and residual sodium carbonate (RSC) by using Eqs. (1) and (2), respectively.

$$\text{SAR} = \frac{\text{Na}}{\sqrt{\frac{(\text{Ca}+\text{Mg})}{2}}} \tag{1}$$

$$\text{RSC} = (\text{HCO}_3 + \text{CO}_3) - (\text{Ca}+\text{Mg}) \tag{2}$$

For heavy metal (Cr, Mn, Pb, and Zn) analysis of water samples, atomic absorption spectrophotometer (AAS Thermo Scientific M series Zeeman Furnace, Waltham, Massachusetts, USA) was used.

2.3.2. Sediment analysis

For heavy metal analysis, samples were prepared by following the procedure described by Ye et al. [19] and analyzed by atomic absorption spectrophotometer (AAS Thermo Scientific M series Zeeman Furnace) to determine the concentrations of Cr, Mn, Pb, and Zn in sediment samples.

2.3.3. Macrophyte analysis

After collection of macrophytes, samples were washed with tap water and rinsed with distilled water twice. These samples were dried at room temperature for 24 h and then oven dried for 8 h at 40°C, and samples were grounded. These grounded samples then underwent an overnight wet acid digestion procedure by utilizing concentrated HNO_3. For this purpose, 2 g of the dried homogenized sample was taken into a beaker of 50 ml. A 20 ml of concentrated

Table 1
Species of macrophytes at three selected sampling points of river Jhelum

	Sampling points at river Jhelum		
	Mangla Dam	Rasul Barrage	Trimmu Barrage
Plant species	*Ageratum conyzoides*	*Ampelopteris prolifera*	*Cynodon dectylon*
	Euphorbia hirta	*Ecchiornia crassipes*	*Typha australis*
	Polygonum roylianum	*Phragmites karka*	*Eicchornia crassipes*
	Cencharus biflorus	*Desmotachya bipinnata*	*Eclypta alba*
	Malvastrum coromandilian	*Polygonum roylianum*	
	Ecchiornia crassipes		
	Croton sparciflorus		

HNO_3 was added into it. Sample was left overnight and then heated on a hot plate for approximately 5 h at 110°C, until the production of red fumes of NO_2 ceased. These samples were then allowed to cool and subsequently let them evaporate to a small volume. After this, they were filtered in a 100-ml volumetric flask and diluted with deionized water to a volume of 100 ml. The samples were then analyzed for Cr, Mn, Pb, and Zn by means of atomic absorption spectrometry (AAS Thermo Scientific M series Zeeman Furnace).

2.4. Statistical analysis

2.4.1. Heavy metal pollution index

HPI was calculated by using the following formulas step by step:

$$\text{HPI} = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \tag{3}$$

where W_i is the unit weightage and Q_i is the sub index of ith parameter. Q_i was calculated by the following equation:

$$Q_i = \sum_{n}^{i=1} \frac{M_i - I_i}{S_i - I_i} \tag{4}$$

where M_i is the mean concentration of parameter, I_i is the highest desirable limit of ith parameter, and S_i is the standard value of ith parameter in µg/L [18].

2.4.2. Contamination index (Cd)

Cd was used to describe the concentration of parameters and upper permissible limit of pollutants:

$$\text{Cd} = \sum_{i=1}^{n} \text{Cf}_i \tag{5}$$

where Cd is the degree of contamination, Cf_i is the contamination factor of each parameters, which was calculated by the following equation:

$$\text{Cf}_i = \frac{C_i}{C_i\text{mpl}} - 1 \tag{6}$$

where C_i is the analytical values of ith parameter and C_i mpl is the maximum permissible limit of ith parameters. Ratio >1 represents the safe side, >1 Cd < 3 represents moderate contamination, and value <3 represents the highest contamination [18].

3. Results and discussion

Physicochemical analysis of the surface water collected from all the three sites, viz., Mangla Dam, Rasul Barrage, and Trimmu Barrage was conducted. Parameters measured include pH, TDS, TSS, EC, and DO. Results showed the comparison between values of the parameters measured and their variation among the three sampling points. Average values were calculated for each parameter and compared with PEQS. Results obtained from the analysis showed the variations of different parameters in all the sampling sites. Average values were calculated for each parameter-(Table 2). Comparison of average values with WHO and Pakistan Standards and Quality Control Authority (PSQCA) Water Quality Standards showed that the water of river Jhelum is feasible for irrigation as values of selected parameters were within the permissible limit of irrigation water quality standards.

Surface water and sediments of the river Jhelum were analyzed for Pb, Zn, Mn, and Cr. Concentrations of Pb, Zn, Mn, and Cr were recorded maximum in both surface water and sediment samples collected from Trimmu Barrage and minimum in Mangla Dam (Figs. 2 and 3, respectively). These results showed that the downstream sampling site of river Jhelum has higher concentrations of the heavy metals as compared with upstream sampling sites. This result agreed with another study conducted by Harguinteguy et al. [20]. This might be due to the reason that many drainage canals of municipal waste in addition to the irrigation canals were

Table 2
Comparison of mean values of physicochemical parameter of surface water samples with NEQS

Parameters	Sampling points			PEQS*
	Mangla Dam	Rasul Barrage	Trimmu Barrage	
pH	7.63	8.0	6.86	6–9
TDS (mg/L)	143.67	109.83	381.67	1,000
TSS (mg/L)	20.67	23	46.3	150
EC (µS/cm)	223.3	171.67	600	–
DO (mg/L)	7.167	7.56	6.07	–
Ca^{+2} (mg/L)	31.3	14.67	44.67	–
Mg^{+2} (mg/L)	6.4	4	9.2	–
Na^{+} (mg/L)	3.07	15.3	66.3	–
K^{+} (mg/L)	0.39	0.91	3.25	–
Chloride (mg/L)	5.3	3.57	79.27	–
CO_3^{-2} (mg/L)	NIL	NIL	NIL	–
HCO_3 (mg/L)	124	42.7	156.57	–

*Punjab Environmental Quality Standards 2016.

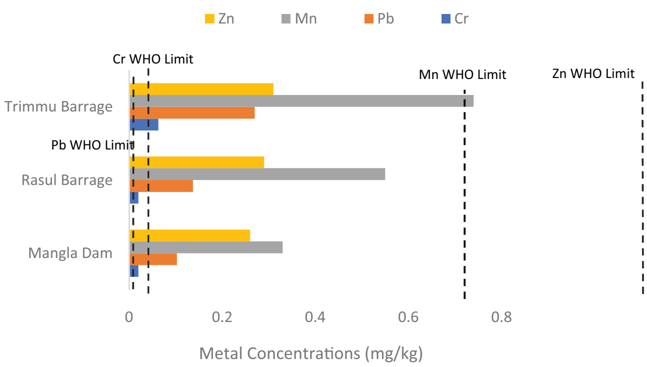

Fig. 2. Metal concentration in different surface water samples.

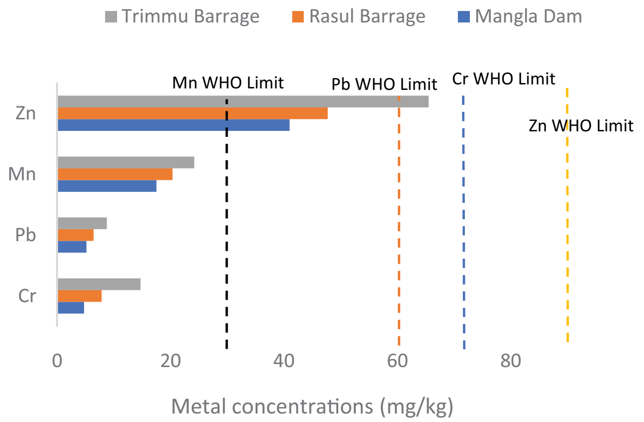

Fig. 3. Metal concentration in sediment samples.

discharged into the river along its pathway. This pollution load is being transferred from the upstream areas to the downstream areas.

The comparison showed that the water of all the selected sampling points of river Jhelum is suitable for irrigation purposes. All the three selected sampling points, i.e., Mangla Dam, Rasul Barrage, and Trimmu Barrage, of river Jhelum showed higher concentrations of lead 0.103, 0.137, and 0.27 mg/L, respectively, which is beyond the permissible limits of WHO standard for drinking water, i.e., 0.01 mg/L. However, the water of all the sampling points is suitable for irrigation. Same results have been observed by Khan et al. [21] in a study conducted on river Jhelum.

Average concentrations of heavy metals in sediments were compared with sediment quality guidelines proposed by United States Environmental Protection Agency (USEPA). Comparison suggested that concentrations of Cr, Pb, Mn, and Zn of all the sampling sites belong to unpolluted sediments.

Concentration of heavy metals in the sediments was many folds higher than the concentration in surface water. This result agreed with two other studies: one was conducted by Tabinda et al. [22] and the other was conducted in India by Kuntal and Reddy [23]. Once heavy metal was being accumulated in bottom sediments, they begin to move up the food chain, often biomagnifying at higher trophic levels and ultimately causing various chronic and acute ailments in humans and animals. The relation of heavy metal concentration in water and sediments is as follows:

Concentration of heavy metals in sediments > concentration of heavy metals in water.

3.1. Heavy metal pollution index and contamination index (Cd)

Table 3 represents the results for HPI for surface water of all locations. The value of index is 13 folds higher, presenting the unsuitable water in terms of metal pollution. Same study was conducted by Kumar et al. [18]; HPI was calculated and found that water quality was at threshold level of index. The results for contamination index (Cd) (Fig. 4) for all samples showed that water has more degree of contamination in comparison with sediments and macrophyte samples because values per sample of water is higher than its upper permissible limit.

3.2. Heavy metal analysis of macrophytes

In the present study, 13 species of macrophytes were analyzed from all the sampling sites of river Jhelum for their potential heavy metal accumulation which in turn indicates the potential of these macrophyte species to be used as bioindicators of heavy metal pollution.

Species concentration of the macrophytes at all the sampling points showed that Mangla Dam has rich biodiversity of macrophyte species among all the sampling points (Table 4). It was observed that *Eichhornia crassipes* was present in all the sampling points of river Jhelum and *Polygonum roylianum* was present at two sampling points of the Jhelum river, viz., Mangla Dam and Rasul Barrage. The accumulation capacity

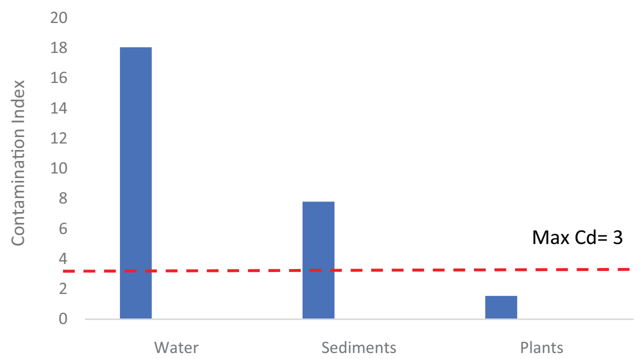

Fig. 4. Contamination index of water, sediment, and plant samples.

Table 3
Heavy metal pollution index (HPI) for surface water samples

	Mean value (M_i)	Standard value (S_i)	Unit weightage (W_i)	Highest desirable value (I_i)	Sub Index (Q_i)	W_iQ_i
Cr	0.034	0.05	0.020	-	64	1.28
Mn	0.54	0.3	0.003	0.1	220	0.66
Pb	0.17	0.01	0.100	-	1,700	170
Zn	0.28	5	0.0002	3	136	0.027
			Σ0.1231			Σ171.9

HPI = $\Sigma W_iQ_i/\Sigma W_i$ = 1,395.

of each macrophyte for all heavy metals representing Rasul Barrage is shown in Table 5. Chromium and zinc in all macrophytes resided in the permissible range recommended by WHO except *Eicchornia crassipes* and *Polygonum roylianum*. Both of these macrophytes accumulated slightly higher concentrations Zn and Cr that exceeded the permissible ranges. However, *Eicchornia crassipes* accumulated higher amount of zinc 105.5 mg/kg and chromium 1.7 mg/kg compared with *Polygonum roylianum* which accumulated 102 mg/kg and 1.35 mg/kg of zinc and chromium, respectively. This result showed that different macrophyte species present at the same site have different accumulation capacities for the same heavy metals. However, average metal concentration in macrophytes did not exceed the permissible limits (Fig. 5).

Results showed that the metal accumulation of lead and manganese in all macrophytes of Trimmu Barrage did not exceed the recommended permissible limits (Table 6). In the case of zinc, all macrophytes accumulated higher concentrations of zinc than the permissible range recommended

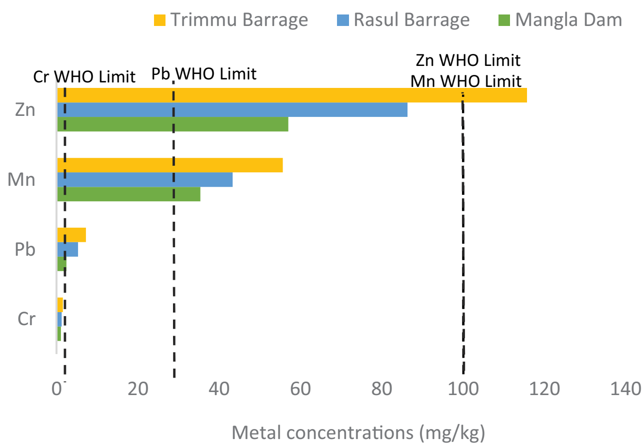

Fig. 5. Metal concentration in plant samples.

Table 4
Concentrations of Cr, Pb, Mn, and Zn in all macrophytes representing Mangla Dam

Sample location	Sample name	Conc. Cr	Conc. Pb	Conc. Mn	Conc. Zn
		mg/kg			
Mangla Dam	*Ageratum conyzoides*	0.55	1.05	27.5	61.5
	Euphorbia hirta	1.05	2.5	35.5	13.5
	Polygonum roylianum	1.3	3	30.5	45.5
	Cencharus biflorus	1.1	3.6	38.5	67
	Malvastrum coromandilian	0.85	3.2	37.5	56
	Eicchornia crassipes	1.6	4.05	44	76
	Croton sparciflorus	0.7	2.65	34	79.5

Table 5
Concentrations of Cr, Pb, Mn, and Zn in each macrophyte species collected from Rasul Barrage

Sample location	Sample name	Conc. Cr	Conc. Pb	Conc. Mn	Conc. Zn
		mg/kg			
Rasul Barrage	*Ampelopteris prolifera*	1.09	5.55	40.5	51.5
Rasul Barrage	*Ecchiornia crassipes*	1.7	6	47.5	105.5
Rasul Barrage	*Phragmites karka*	0.95	5.1	38	80.5
Rasul Barrage	*Desmotachya bipinnata*	1.05	4.5	44.5	93.5
Rasul Barrage	*Polygonum roylianum*	1.35	5.25	46	102

Table 6
Concentrations of Cr, Pb, Mn, and Zn in each macrophyte species collected from Trimmu Barrage

Sample location	Sample name	Conc. Cr	Conc. Pb	Conc. Mn	Conc. Zn
		mg/kg			
Trimmu Barrage	*Cynodon dectylon*	1.55	6.1	67	106.5
Trimmu Barrage	*Typha australis*	1.45	7.25	45.5	116.5
Trimmu Barrage	*Eicchornia crassipes*	1.95	8.5	60.5	129
Trimmu Barrage	*Eclypta alba*	1.1	7	49.5	111

by WHO. All macrophytes at Trimmu Barrage accumulated higher chromium concentrations which exceed the permissible limits except *Eclypta alba*. This macrophyte species exhibits lower accumulation tendency toward chromium, and the absorbed concentration of chromium (1.1 mg/kg) is less than the permissible limit for Cr in plants recommended by WHO (1.3 mg/kg). Heavy metal concentrations in macrophytes showed the accumulation capacity of each species of macrophytes. This capacity varies from species to species. Results showed that *Eichhornia crassipes* accumulated large amounts of heavy metals in its tissues. *Eichhornia crassipes* exhibits higher affinity to heavy metals and can absorb higher heavy metal concentration from the surrounding aquatic habitat. Results showed the same descending order of mean heavy metal concentrations in macrophytes of all the three sampling sites of river Jhelum. This descending order is Zn > Mn > Pb > Cr. Least concentration of chromium in macrophytes according to our results agrees with another study conducted by Bonanno and Giudice [15]. The study showed the least accumulation of chromium as compared with other metals by the selected macrophyte species *Phragmites australis*.

4. Conclusion

It is concluded from the results of the surface water quality analysis of river Jhelum that the values of physicochemical and inorganic analysis are within the permissible limits of PEQS and WHO standards for drinking water. Heavy metal analysis of surface water for Cr, Pb, Mn, and Zn possesses more concentrations of these heavy metals than the upstream areas. The comparison of these results with WHO permissible limits for heavy metals in plants showed that the macrophytes present at Trimmu Barrage exhibit a slight toxicity of chromium and zinc. Descending order of concentration of heavy metals in macrophytes, sediments, and water is as follows: Macrophytes > sediments > surface water. *Eichhornia crassipes* exhibits greater accumulation potential for heavy metals as compared with other macrophytes present at the site. The results from the HPI showed that metal pollution is higher than pollution index in surface water samples and contamination index is also higher in water samples because the upper permissible limit per sample is higher in mean values of surface water samples. So, the order for degree of contamination (Cd) is as follow: surface water > sediments > macrophytes. Based on this study, it can be concluded that macrophytes can be potential indicators for metal concentration.

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