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Seasonal characterization and potential human health risk of heavy metals contamination in sediments of the River Jindi, Pakistan

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Abstract

In this study, the sediments of River Jindi (Pakistan) were sampled in summer and winter to explore heavy metals contamination (i.e. Fe, Cr, Ni, Zn, Co, Cu, Pb and Cd) using Atomic Absorption Spectrophotometer. The results show that the Fe and Ni concentration was beyond the allowable limits of USEPA (2005). Water physicochemical parameters of both season showed that the concentrations of NO3, total dissolved solids (TDS) and total suspended solids (TSS) surpass the allowable levels set by the National Environmental Quality Standard and/or World Health Organization. Potential ecological risk, geo-accumulation index (Igeo), enrichment factor and contamination factor demonstrated high metals contamination in sediments and were moderately polluted with Cd and Ni. Principle component analysis indicated that in both seasons heavy metals contamination occurred through similar sources. Strong correlations ($p<0.05$) among heavy metals and water physicochemical parameters showed that in both seasons, physicochemical parameters played a key role in metal retention and accumulation.

Keywords: River Jindi, Heavy metals, Sediment, Water quality, Pollution.

1. Introduction

Water and sediments are socially and economically important natural resources for human beings (Hanemann, 2006). Sediments are the basic component of the aquatic environment, which substantially effect aquatic organisms (Yang et al., 2017). Contamination of sediments with heavy metals is an issue worldwide, because of their toxic nature, tenacity in the environment and bio-accumulation (i.e. in aquatic microbes, animals and plants), and finally become the component of the food chain (Zhang et al., 2014).

Various natural and anthropogenic sources could pollute rivers with heavy metals such as ore deposits, wastewater irrigation, weathering and erosion of bedrocks, agriculture and mining activities. Studies showed that almost 85% to 90% of the entirety heavy metals may trap in sediments after entering the aquatic ecosystem (Zhang et al., 2016; Zahra et al., 2014). The concentrations of heavy metals in sediments depend upon the source of contamination, capacity of sediments to trap heavy metals and water and sediment properties (Zhang et al., 2016). While, the potential mobilization, immobilization and bioavailability of sedimentary heavy metals to aquatic biota could occur due to changes in conditions of an aquatic environment (Liu et al., 2019; Gao et al., 2008). Therefore, researchers have elucidated that sedimentary heavy metals contamination may cause substantial harmful effects on the health of aquatic communities (Vega et al., 1998), and consequently human health hazards (Rumisha et al., 2012). Sedimentary heavy metals in high levels near to urban area might be due to anthropogenic inputs to aquatic ecosystem (Zhang et al., 2014). Studies revealed that physicochemical parameters of overlying water have significant effects on the heavy metals concentration of the sediment (Kang et al., 2019). In view of the importance of water and sediments quality of the aquatic environment, various researchers have demonstrated the enrichment, contamination profile, potential risk and index of geo-accumulation of heavy metals (Bing et al., 2019; Saher and Siddiqui, 2019; Ma et al., 2016). However, seasonal variations in heavy metals contamination in rivers remain poorly understood.

The study aimed to determine (1) physicochemical speciation of pollutants in River Jindi, and (2) seasonal concentration (i.e. summer and winter) of heavy metals in sediments. The study also highlights potential health risks of heavy metals.

2. Materials and methods

2.1. Site description

The river Jindi originates from the mountains of district Malakand and passes from the major urban areas of district Charsadda, and thereafter it meets with the Kabul river in Khyber-Pakhtunkhwa Province, Pakistan. During winter, the river water quantity slightly decrease, however, it has much water in summer due to rainy season. Local people use this river water for irrigation purposes, as both Jindi and Kabul river irrigate largest cultivated areas in Khyber-Pakhtunkhwa. Due to rapid pace of urbanization in the area, the runoff pattern and water quality of River Jindi is affected in a number of ways in recent decades. Such as municipal waste discharge, agriculture activities, industrial effluents, hardened surfaces like roads, pavements shopping centers and parking lots accelerate the rate of pollution. This had not only accelerated water pollution but clean water access difficulty to its close population.

2.2. Sediment and water sampling and analysis

Sediments and water were sampled at the end of summer and winter seasons in major towns including Kandyre, Kanewar, Sherpao, Alishah-Qila, Umarzai, Utmanzai, Rajjar, Qazikhel, Chotipul, Harbila, Prang and Motorway-Pul (Fig. S1). Sediment and water samples were collected in uncontaminated polythene bottles and polythene bags, respectively (Trivedi and Raj, 1992). Some drops of Nitric acid (HNO3) were added in water samples in order to avoid microbial activity, metals, and metalloid adsorption. The GPS was utilized to know sampling coordinates for constructing map using geographic information system software. Samples were carried out to Pakistan Council of Scientific and Industrial Research Laboratories Complex, Peshawar and stored in refrigerator for future analyses.

Temperature and pH were recorded on-spot using water quality checker (U-10 Horiba, Japan) and pH meter (Mettler Delta 320, UK). Nitrate (NO3), sulfate (SO4), phosphate (PO4) and ammonia (NH3) were analyzed by using UV spectrophotometer HACH 2800 (APHA, 1992). Openrefleux method was used for the determination chemical oxygen demand and biological oxygen demand. Standard procedures were used to measure total suspended solids (TSS) (Peavey et al., 1985; Trivedi and Raj, 1992) and TDS (Greenberg et al., 1992). Samples of sediment were oven-dried and then passed through a 2-mm mesh to get a homogenize size. One gram sediment sample of each site was extracted with aqua-regia. The extracts were filtered and the volume was adjusted to 50 ml with deionized water and kept for further analysis. The heavy metals concentration was observed on Atomic Absorption Spectrophotometer (Z-2000, Hitachi). The precision was ensured by parallel running of blanks with extracted solutions.

2.3. Statistical analysis

Bar graphs were constructed using Origin Lab (Northampton, MA). To visualize seasonal distribution patterns of sedimentary heavy metals and water physicochemical parameters, principle component analysis (PCA) was applied using CANOCO5 (Microcomputer Power, Ithaca, NY). Pearson's correlations were accomplished amongst water physicochemical factors and sedimentary heavy metals using SPSS 21 (SPSS Inc., Chicago, IL, USA).

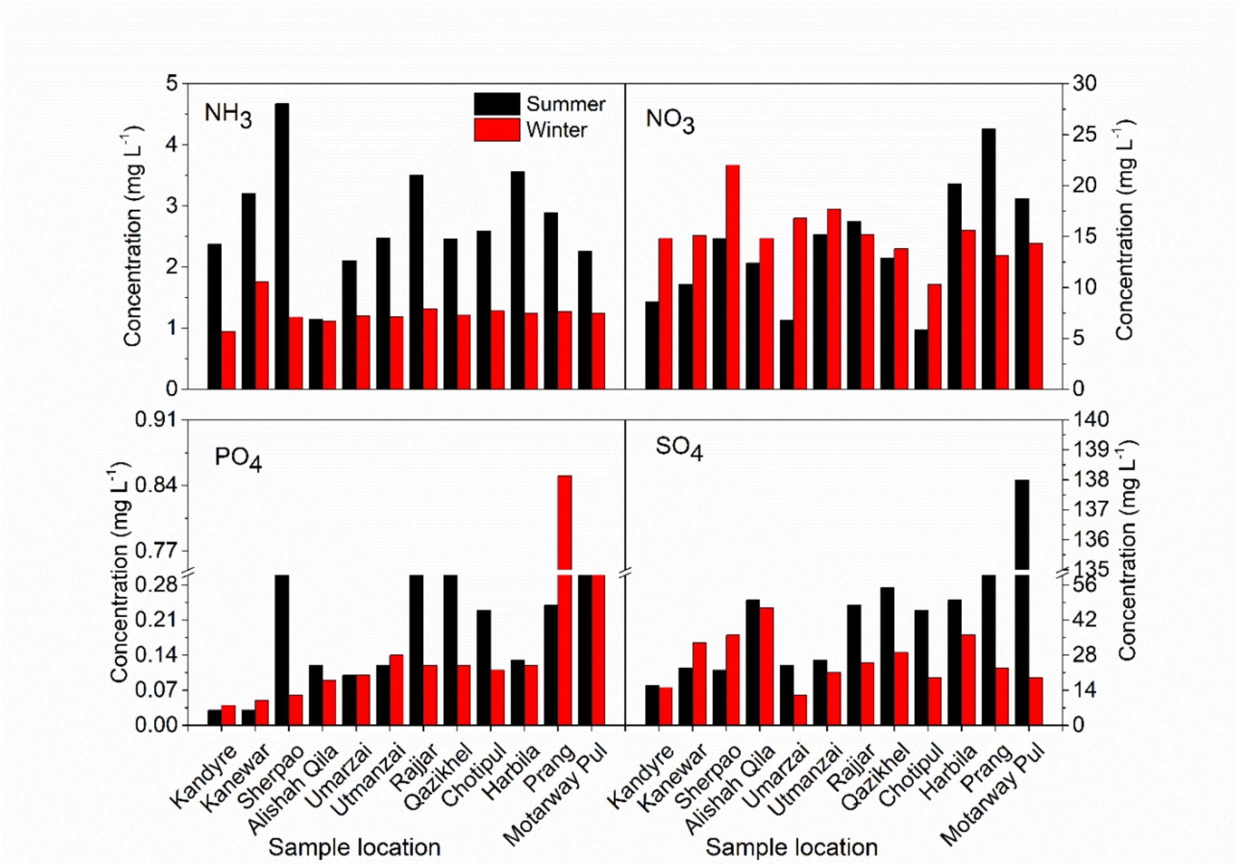

Fig. 1. Seasonal concentration of different anions in surface water of the River Jindi.

2.4. Contamination factor

Contamination factor (CF) is the proportion of a metal content in soil to its background value (Hakanson, 1980). Thus, CF> 6, 3< CF< 6, 1< CF< 3 and CF< 1 indicates very high contamination, high contamination, moderate contamination and low contamination, respectively (Hakanson, 1980). The background values taken for Zn, Pb, Ni, Fe, Cu, Cr, Co and Cd were 175, 70, 68, 35900, 50, 90, 29 and mg/kg, respectively (Ma et al., 2016; Hakanson, 1980).

$$CF = \frac{C\ (\text{Heavy metal})}{\text{Background}} \quad (1)$$

2.5. Geo-accumulation Index

The geo-accumulation index (Igeo) is the index of geo-accumulation (Muller, 1969), and can be assessed using the following formula.

$$Igeo = \log 2\left[\frac{Cn}{1.5 \times Bn}\right] \quad (2)$$

Where Bn and Cn indicate the geochemical background and measured concentration, respectively of an element. Various conservative elements for example silicon (Si), aluminum (Al) and Fe have been used (Nazeer et al., 2014). Though in the current study, Fe has been used for normalization of heavy metals. According to Muller (1969), Igeo index is categorized into seven classes such as Igeo> 5, 4<Igeo≤5, 3<Igeo≤4, 2<Igeo≤3, 1<Igeo≤2, 0 <Igeo≤1 and Igeo≤0 indicates extremely polluted, severe to extremely polluted, severely polluted, moderately to severely polluted, moderately polluted, unpolluted to moderately polluted and unpolluted (Chen et al., 2015; Hussain et al., 2015; Wei and Yang, 2010).

2.6. Enrichment factor

The enrichment factor (EF) is applied to identify heavy metal contamination by anthropogenic sources (Atgin et al., 2000; HuuHieu et al., 2002). Thus, it can be computed by Eq. 3.

$$EF = \frac{\left(\frac{\text{Metal}}{\text{Fe}}\right)\text{sample}}{\left(\frac{\text{Metal}}{\text{Fe}}\right)\text{Background}} \quad (3)$$

In this study, Fe has been used as a reference metal for geochemical normalization concentration for other elements because; (1) it is observed frequently in combination with very fine surfaces of solids; (2) it has similar geochemistry to majority of the trace-elements and (3) it has identical tendency of natural occurrence (Varol, 2011). The EF values categorized as, EF> 50, 25< EF< 50, 10< EF< 25, 5< EF< 10, 3< EF< 5, 1< EF< 3 and EF< 1 indicates extremely robust, robust, substantial, moderately severe, moderate, slight and no enrichment, respectively (Sakan et al., 2009).

2.7. Potential ecological risk index

To assess the inclusive contamination risk of heavy metals at a particular site (sediments/soils), the potential ecological risk index (PERI) has been computed by the by Eq 4:

$$PERI = \sum_{i=1}^{n} Eri \quad (4)$$

$$Eri = Tr \times CF$$

Where PERI is the sum of all risk values of heavy metals in sediments/soils, Tr is characterized as the toxic/lethal response factor, CF is the contamination factor and Eri indicates the monomial ecological risk value. The Tr values for Pb, Zn, Ni, Cu, Cr, Co and Cd as 5, 1, 5, 5, 2, 5, 30, respectively (Rehman et al., 2018; Hakanson, 1980). Eri was graded as; Eri> 320, 160<Eri< 320, 80<Eri< 160, 40<Eri< 80 and Eri< 40 indicates very severe, high, substantial, moderate and low ecological risk, respectively (Hakanson, 1980). Likewise, values suggested for PERI were, PERI> 380, 190< PERI< 380, 95< PERI< 190 and PERI< 95 shows very high, substantial, moderate and low ecological risk, respectively (Soliman et al., 2015; Hakanson, 1980).

3. Results and discussion

3.1. Surface water quality

Different physicochemical parameters including pH, temperature, TSS, TDS, BOD and COD were analyzed in the water samples of the River Jindi (Table 1). These parameters were compared with river water quality guidelines provided by WHO and National Environmental Quality Standard (NEQS). Furthermore, to assess the impact of seasons on water quality a comparative analysis was done for summer and winter. The pH values of all samples in both seasons were under the allowable level set by WHO (6.5-8.5). Water temperatures remained stable to 21°C in winter and to 26°C in summer in all sampling points of the river, and are under the permissible limits set by WHO (25-31°C). The majority of water samples indicated TSS values above the NEQS permissible limits (150 mg L-1) in both seasons. Only the summer water samples of few sites showed high TDS values than WHO standards (500 mg L-1). BOD was below the NEQS limiting values (80 mg L-1) in both season samples. Similarly, other parameters showed variable concentrations depend upon sampling sites and seasonal variations (see supporting information).

3.2. Heavy metals in sediments

In sediments heavy metal concentration in both seasons at selected sites are given in Fig 2, and were found in the order of Fe>Ni>Cr>Zn>Cu>Co>Pb>Cd. The metals contamination in sediments were compared with the sediment quality guideline proposed by the United States Environmental Protection Agency (USEPA). The concentration of Fe was slightly higher in summer ranged from 161.4 to 263 mg Kg-1 than in winter ranged from 152.9 to 210 mg Kg-1, as in summer dissolved oxygen (DO) decreases with increasing water temperature, therefore, the oxidation of soluble Fe+2 to insoluble Fe+3 compounds remain slow (Dojlido and Best, 1993). The highest Fe concentration was observed in the sediments of Chotipul followed by Kandyre. Excessive Fe can cause hemochromatosis in humans with symptoms like impotence and sterility, diabetes, thyroid disease, cirrhosis, arthritis, heart disease and chronic fatigue (Huang, 2003). Moreover, facilitates persistent hepatitis B or C contagion, malignant tumors, kidney cancers, stomach, lung, liver and colorectal (Huang, 2003).

The concentration of Ni was ranged from 6.9 to 49.2 mg Kg-1 in winter and from 0.05 to 41 mg Kg-1 in summer. The highest Ni concentration was observed in winter at Kandyre site and in summer at Alishah-Qila. Elevated Ni levels (≥20 mg Kg-1) were detected in summer at Kandyre and Umarzai sites, and in winter at Kanewar, Sherpao and Alishah-Qila. According to the USEPA (1997) guidelines for Ni pollution (20-50 mg Kg-1), River Jindi is moderately polluted at some sites. In this study, a downstream decrease in Ni level could be due to dilution factor. The amount of Ni intake of 0.7 mg Kg-1 is potentially lethal for fish (Lemly, 1993) because high Ni concentration has been found to create reproductive impairment in fish (Akoto et al., 2014). Plants have normal Ni concentrations from 0.5 to 5 mg Kg-1 while exceeding levels could cause plant toxicity (Allen et al., 1989).

In summer, Cr concentration was ranged from 1.25 to 10.2 mg Kg-1 and in winter from 2.20 to 6.10 mg Kg-1. The highest Cr concentration was observed in summer in the sediment samples of Utmanzai followed by Alishah-Qila. The concentrations of Cr may be associated with furniture paint and varnish and domestic activities prevailed along the River Jindi. According to the USEPA (1999) permissible limit for Cr (43.4 mg Kg-1), the River Jindi is free from Cr pollution. Cr is not considered as a micronutrient for plants, though its accumulation in several aquatic plants has been observed, ranging from 1-21 mg Kg-1 in polluted waters (Martin and Knaeur, 1973). However, Cr with a concentration of 0.5 mg Kg-1 in plants is toxic (Allen et al., 1989).

The concentration of Zn ranged from 0.4 to 9.65 mg Kg-1 in summer and from 1.15 to 6.9 mg Kg-1 in winter. The maximum level was observed in sediments sample of Umarzai. The USEPA (1999) limiting levels for Zn is 121 mg kg-1, indicated that all the current sites are unpolluted in both seasons. The high Zn concentrations in some locations could be due to sewage discharge, while low Zn levels could be related to dilution effect. Zn is an important nutrient for growth of plants that absorb through roots (Aubert and Pinta, 1977). However, if Zn levels in plants increase from 5–20 mg kg-1, it causes toxicity (Allen et al., 1989; Demırezen and Aksoy, 2004).

In fish, high Zn affects the growth and causes reproductive impairments and even death (Sorensen, 1991).

The concentration of Cu ranged from 0.05 to 4.5 mg kg-1 in summer and from 0.85 to 4.25 mg kg-1 in winter. The highest Cu was determined in summer sediment samples of Motorway-Pul followed by Prang in winter. According to USEPA (1999), maximum permissible limit for Cu in the river sediments is 31.6 mg Kg-1, indicating that all the site samples were safe from Cu pollution. Cu is highly dangerous to aquatic plants, invertebrates and a majority of the fish than some other trace metals except mercury. Aquatic plants uptake three times Cu as compared to the terrestrial plants. The higher value of Cu substance can restrain root development, formation of many short auxiliary roots and harm plant roots by destroying the cell membrane structure (Singh et al., 2017).

Table 1. Physicochemical and biological characteristics of water of the River Jindi.

	pH		Temp (^{0}C)		TSS (mg L^{-1})		TDS (mg L^{-1})		BOD (mg L^{-1})		COD (mg L^{-1})	
Location	S	W	S	W	S	W	S	W	S	W	S	W
Kandyre	7.90	8.12	25.0	21.0	240	170	710	454	8.00	9.00	25.0	25.0
Kanewar	7.90	8.40	26.0	21.0	138	142	500	380	5.00	3.00	40.0	22.0
Sherpao	7.03	8.33	26.0	21.0	942	214	560	360	10.0	11.0	45.0	23.0
AlishahQila	7.60	8.35	26.0	21.0	1246	192	520	362	12.0	8.00	30.0	25.0
Umarzai	7.90	8.50	26.0	21.0	360	178	510	366	7.00	7.00	38.0	28.0
Utmanzai	7.75	8.55	26.0	21.0	156	120	290	360	8.00	8.00	48.0	30.0
Rajjar	7.60	8.42	26.0	21.0	294	230	320	355	24.0	6.00	80.0	33.0
Qazikhel	7.65	8.15	26.0	21.0	234	210	330	350	8.00	9.00	60.0	27.0
Chotipul	7.45	8.00	26.0	21.0	390	225	330	342	18.0	10.0	40.0	29.0
Harbila	7.05	7.90	25.0	21.0	356	240	350	342	12.0	12.0	40.0	26.0
Prang	7.08	7.95	26.0	21.0	308	274	330	345	15.0	14.0	40.0	35.0
MotarwayPul	7.06	7.95	26.0	21.0	880	260	330	348	16.0	18.0	40.0	40.0

TDS; total dissolved solids, BOD; biological oxygen demand, COD; chemical oxygen demand, S; summer, W; winter

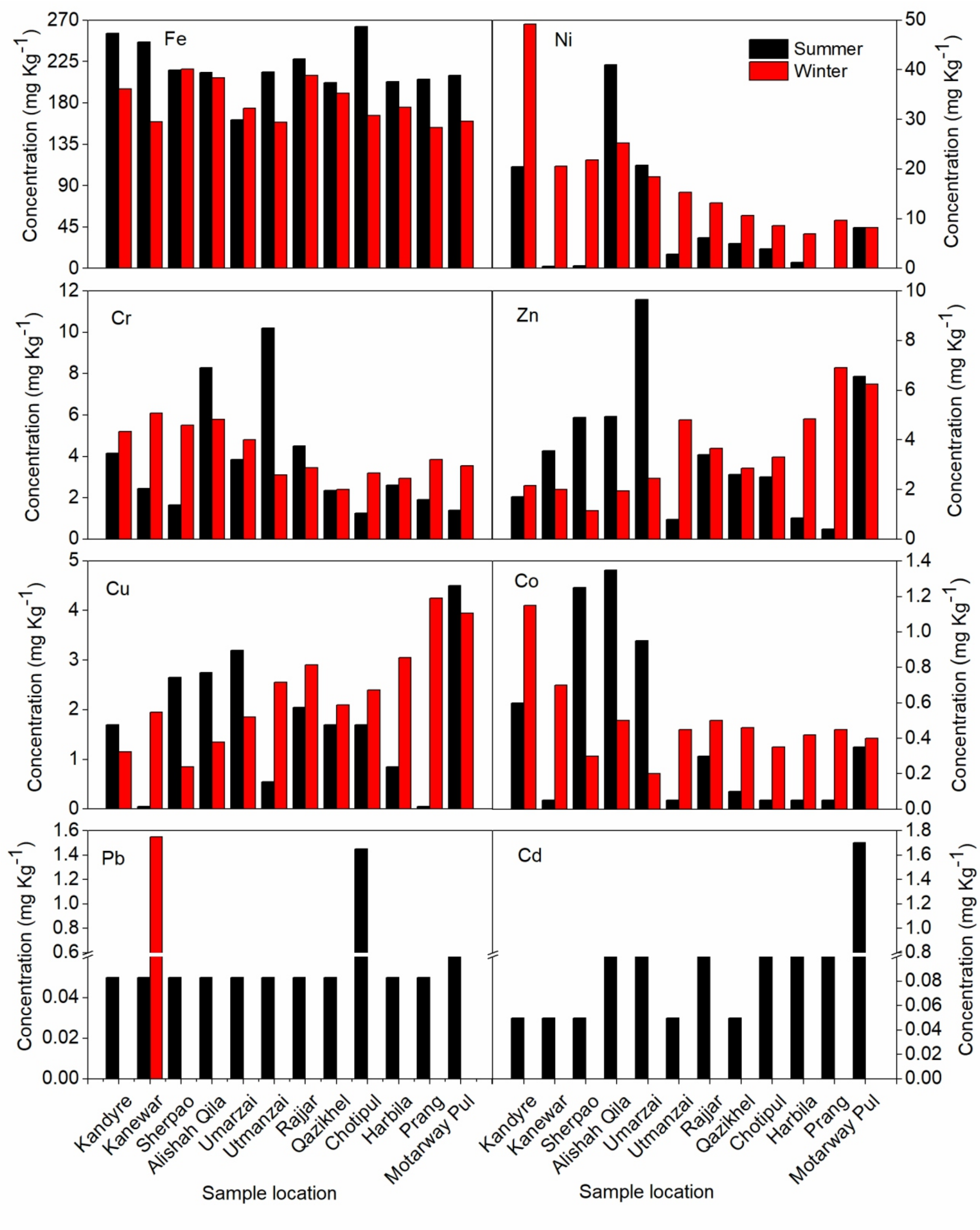

Fig. 2. Seasonal concentrations of heavy metals in the sediments samples of River Jindi.

The Co concentrations ranged from 0.05 to 1.35 mg Kg-1in summer and from 0.20 to 1.15 mg Kg-1 in winter. The highest Co concentration was found in summer samples of Alishah-Qila followed by Sherpao, while in winter, Kandyre revealed maximum Co concentration. The concentration of Co was lower in sediments than the benchmark established by USEPA (1999) (50 mg Kg-1). The Pb contamination in sediments was low in all sites, ranging from 0.05 to 1.45 mg Kg-1 in summer, while Pb concentration of 1.55 mg Kg-1 was only detected in winter at Chotipul. According to USEPA (1997) guidelines for Pb (<40 mg kg-1), all sites were safe from Pb pollution. Sources that cause Pb contamination in rivers could be discharge from municipal waste incinerators, vehicular emissions, lead-acid battery industry, coal burning and Pb compounds disposal (Smith et al., 2011). High Pb levels ranging from 30 to 300 mg Kg-1 can be toxic to plants (Ross, 1994), indeed at low level, it is extremely poisonous to fish (Rompala et al., 1984; El-Naggar et al., 2009). Other biological impacts of Pb incorporate kidney dysfunction, enzyme inhalation, neurological problems, inhibition of growth and restrained reproduction and late embryonic growth (Rompala et al., 1984).

Cd concentration was only detected in summer ranging from 0.05 to 1.7 mg kg-1, with the maximum level observed in sediments of Motorway-Pul. Only Motorway-Pul was observed beyond the permissible index for Cd in sediments set by USEPA (1999) (0.99 mg Kg-1). Allen et al (1989) observed that plants in unpolluted environment contain Cd levels from 0.01 to 0.3 mg kg-1. Prolonged exposure to Cd may damage kidney (Bandara et al., 2008). Cd can retain in the human body for up to 38 years, which indicates the environmental alarms of its exposure to humans (Chen et al., 2006). Aquatic organisms have different liabilities to Cd, for instance, freshwater organisms are highly vulnerable comparatively those in saltwater (Chowdhury et al., 2004).

Many point and nonpoint sources could be the cause of water and sediment contamination in River Jindi. The domestic sewage emissions, automobiles washing stations, and marble industries in the river catchment area are the major causes of physicochemical, biological and heavy metals pollution in this river. In addition, infrastructures, motorways, grazing lands, agricultural runoff is considered the main nonpoint source of above pollutants existed in the catchment of this river. These pollutants with the passage of time get settled at the bottom of the river.

3.3. Sediment contamination level assessment

In order to assess the pollution load in the River Jindi, various pollution indices have been calculated including CF, EF, Igeo and PERI. The results revealed that continuous flow of waste materials from various municipal, agriculture and industrial sources has substantially contributed to river's sediment contamination (Table S1-4, Fig. 3).

The CF values have been categorized from low contamination (CF<1) to very high contamination (CF>6). Results indicated that the CF values for the entire metals in all sampling points collected in summer and winter were less than 1, except for one sample collected near motorway-pull in summer, where the CF value for Cd was greater than 1 (Table S1). Thus, the sediments of the River Jindi fall under the category of low contamination except for motorway-pull that exhibits a slightly high CF value and placed under the category of moderately contaminated. Motorway-Pull receives heavy pollution load from two major cities namely Majoky and Shabara and has extensive agriculture activities along with heavy traffic load, the CF value might be affected by vehicular emission, agriculture runoff, industrial (marble industries) and domestic effluents. Similar, results have been reported previously elsewhere in the world. For instance, Alahabadi and Malvandi (2018) reported low to moderate contamination of river sediments with high contamination in areas probably affected by anthropogenic inputs. The comparative analysis of the two seasons revealed that the contamination was high in winter compared to summer (Fig. 3), which might be due to a decrease in the river water flow. As agriculture practices and municipal activities remain the same almost throughout the year but in winter the runoff is comparatively less than summer.

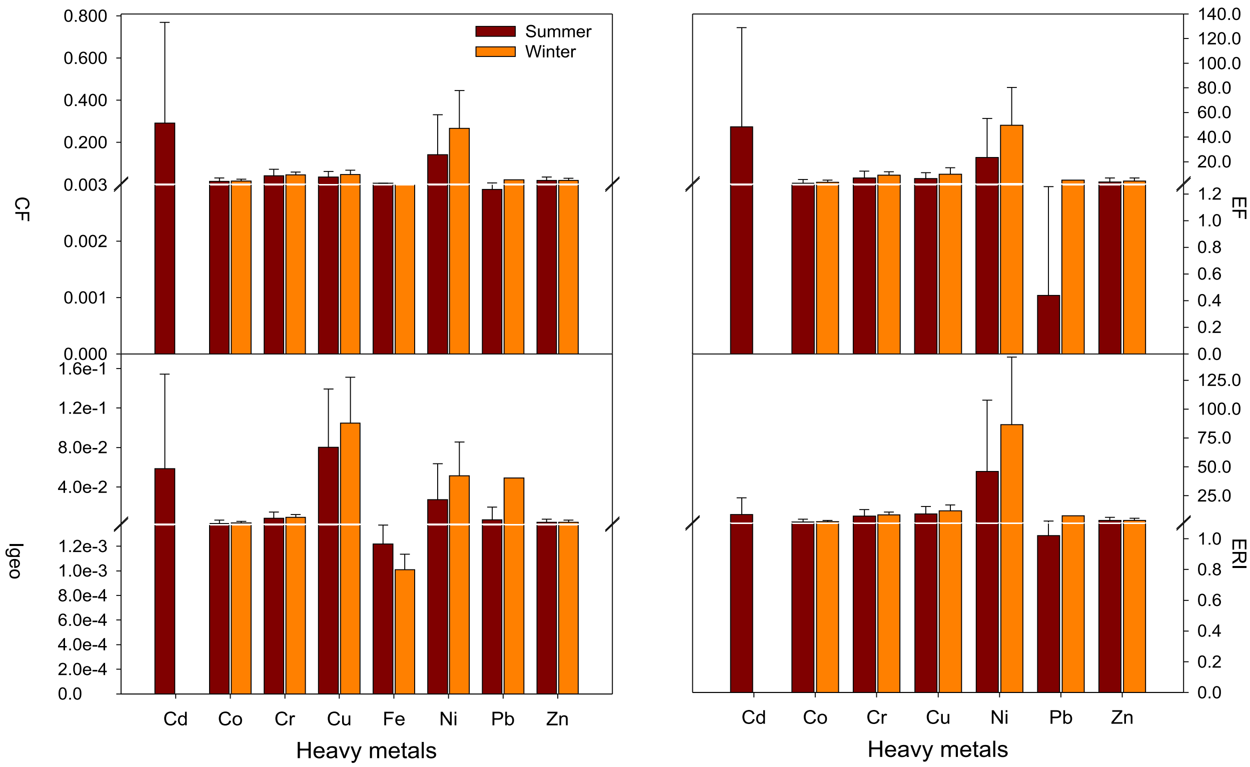

Fig. 3. Pollution indices indicated the level of contamination in sediments of River Jindi, CF: Contamination factor, EF: Enrichment factor, Igeo: Index of Geo-accumulation: ERI: Ecological risk Assessment.

The level of sediment contamination with heavy metals is categorized on the bases of degree of Igeo as class 1 (unpolluted) to class 7 (extremely polluted). In the current examinations, the values of Igeo for different heavy metals were ranged from 0.0001 to 0.3412 indicated that the river sediment lies in the category of "unpolluted to moderately polluted". The Igeo value for Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn were ranged from 0.0100-0.3412, 0.0003-0.0093, 0.0028-0.0227, 0.0022-0.1993, 0.0009- 0.0015, 0.0001-0.1210, 0.0016-0.0459 and 0.0005-0.0111, respectively (Table S2). Similarly, mean Igeo values are given in Fig. 3. According to Muller (1969) classification, all the values were less than 1, and fall in the category of "unpolluted to moderately polluted". The Igeo maximum value was reported for Cd in the samples collected near Motorway-Pull indicated anthropogenic inputs. Similarly, comparative analysis of summer and winter showed significant variation for Cu, Ni and Pb, where high Igeo values were reported for winter compare to summer, thus, higher Igeo value near Motorway-Pull may be due to asphalt plants as the study area has several asphalt plants which may pollute water and sediment either through direct input or atmospheric deposition. Furthermore, the study area is famous for intensive agriculture, where use of pesticides and fertilizers is obvious. The outcomes are in concurrence with the results of Ma et al. (2016) that sediments of inner magnolia were categorized as "unpolluted to moderately polluted".

The mean estimations of EF are given in Fig. 3, while the detail of all sampling points is available in Table S3. According to Sakan et al (2009) classification, sediment enrichment with heavy metals has been classified in 7 classes from no enrichment to extremely severe enrichment. In the current investigations, like CF and Igeo the enrichment was maximum in winter compared to summer except for Cd, where no enrichment was calculated in winter. The detail of different heavy metals enrichment showed that the highest enrichment was observed for Cd (extremely severe enrichment) at sampling site of Motorway-Pull (Table S3). The mean values for all samples collected in summer showed that Cd is the richest metal in the sediments of River Jindi under the category of very severe enrichment followed by Ni (severe enrichment). While, Cr and Cu exhibit "moderately severe enrichment", rest of the metals were under the categories of minor to moderate enrichment. Similarly, in winter the highest enrichment was reported for Ni (very sever enrichment), rest of the heavy metals pursued the order Cu>Cr>Pb>Zn>Co (Fig. 3). Previous studies revealed that EF <1.5 exhibits natural origin while, greater than 1.5 indicates anthropogenic inputs (Malvandi, 2017; Chen et al., 2015). The aim of EF value is to distinguish natural contamination from anthropogenic contamination. In the current examination, the entire values were >1.5 revealed significant anthropogenic contamination in the area.

In order to get a broader picture of sediment contamination and associated ecological risk Hakanson's approach was used (Table S4 and Fig. 3). For this purpose indicators such as ERI and PERI were assessed. In summer, ERI for most of the elements at all sampling sites were observed under the category of "low ecological risk", except for Cd moderate ecological risk at Motorway-Pull (ERI> 50), and for Ni high ecological risk at Alishah-Qilla (ERI: 205) and considerable ecological risk at Kandyre and Umarzai (ERI> 100). In winter, considerable to high ecological risk was observed for Ni in most of the sampling points, while rest of the elements were under the category of low ecological risk. Similarly, the values of PERI indicated that only sampling sites of Alishah-Qilla (in summer) and Kandyre (in winter) were under the classification of considerable ecological risk (>190 PERI <380), and almost 50% of the remaining were under the classification of moderate ecological risk, while rest of the sampling points were under the category of low ecological risk. In view of the findings of ERI and PERI, it can be assumed that potential hazards exist, and if control measures are not taken against potential contamination sources (i.e. agriculture runoff, municipal wastewater and industrial effluents along with atmospheric deposition from vehicular emission), the situation may worsen in future. That will pose great threats to river biota and ultimately human health through food chain contamination.

3.4. Multivariate statistical analysis

The distributional structure of sediment contamination with heavy metals in both seasons was displayed using PCA (Fig. 4). In summer, PCA1 explained 95.36% variance with high loading values for Fe, TDS, TSS, Pb, Cd, Co and PO4, and PCA2 explained 2.29% with high loading value for Ni (Fig. 4a). In winter, PCA1 explained 97.97% with high loading values for Fe, TDS, TSS, Pb, PO4 and NH3, while PCA2 explained 1.20% (Fig. 4b). Heavy metals and physicochemical parameters in both seasons followed almostsame pattern and clustered into three groups. In summer PCA, first group consisted of Pb, Co, Cd, Cu, Zn, Cr, Ni, PO4 and NH3, second group consisted of BOD, COD, NO3 and NO4, and third group consisted of Fe, TDS and TSS. In winter PCA, first group was related to Pb, Cu, Zn, Cr, NH3 and PO4, second group related to Ni, BOD, COD, NO3, pH and SO4, and third group related to Fe, TDS and TSS. These findings suggested that similar sources are involved continuously polluting River Jindi throughout the year. Many studies have used PCA to recognize anthropogenic or natural sources of elements contamination in different environments (Alahabadi and Malvandib, 2018; Ma et al., 2016; Wang et al., 2015).

Pearson's correlation was used to determine the relationship between physicochemical parameters and heavy metals in both seasons (Table 2). In summer samples, TSS was positively correlated with Co ($p<0.01$) and Cu ($p<0.05$), and TDS and SO4 were positively correlated with Co ($p<0.05$) and Cd ($p<0.001$), respectively, while NH3 had a negative correlation with Ni ($p<0.01$). In winter, TDS was positively correlated with Co and Ni ($p<0.001$), BOD with Zn ($p<0.05$) and COD and PO4 with Zn and Cu ($p<0.001$) and NH3 with Pb ($p<0.001$). Correlation among different heavy metals revealed that in summer samples Co waspositively correlated with Zn, Cu and Ni ($p<0.05$), and Zn was positively correlated with Cu ($P<0.01$). In winter samples, Co was positively correlated with Ni ($p<0.01$) and Ni was positively correlated with Cr ($p<0.05$), while Fe was negatively correlated with Cu and Zn ($p<0.05$). These findings revealed that chemical and biological parameters greatly affect the accumulation of certain elements in sediments. Besides this, heavy metals also affect the accumulation of other heavy metals in the sediments. Among the these metals Fe showed negative correlation with most of the other heavy metals. Fe has considered an essential element for aquatic biota and its negative correlation with heavy metals specify that toxic metals may significantly affect the concentration of essential elements in the sediments.

Table 2. Pearson's correlation analysis of water quality parameters and heavy metals in sediments of River Jindi.

Summer																
	pH	**TSS**	**TDS**	**BOD**	**COD**	**NH_3**	**PO_4**	**NO_3**	**SO_4**	**Co**	**Pb**	**Fe**	**Zn**	**Cu**	**Cd**	**Ni**
pH																
TSS	-0.433															
TDS	0.36	0.219														
BOD	-0.43	0.168	-0.494													
COD	-0.0186	-0.279	-0.57	0.501												
NH_3	-0.44	-0.175	-0.035	0.123	0.386											
PO_4	-0.534	0.262	-0.528	0.737**	0.674*	0.28										
NO_3	-0.708**	0.0808	-0.478	0.332	0.224	0.293	0.412									
SO_4	0.594*	0.336	0.521	0.48	0.063	-0.214	0.633*	0.559								
Co	0.0301	0.752**	0.651*	-0.159	-0.304	-0.129	-0.0709	-0.271	-0.225							
Pb	-0.164	0.0539	-0.287	0.415	-0.109	-0.12	0.199	-0.355	0.243	-0.253						
Fe	0.142	-0.156	0.178	0.204	-0.0864	0.131	-0.0922	-0.285	-0.174	-0.274	0.472					
Zn	0.155	0.445	0.28	-0.102	-0.0846	-0.222	0.139	-0.397	0.0997	0.615*	-0.00048	-0.482				
Cu	-0.155	0.663*	0.158	0.215	-0.0436	-0.253	0.465	-0.204	0.414	0.591*	0.174	-0.301	0.782**			
Cd	0.501	0.322	-0.357	0.405	-0.129	-0.179	0.512	0.239	0.875***	-0.186	0.522	0.0257	0.238	0.538		
Ni	0.385	0.53	0.504	-0.108	-0.419	-0.738**	-0.298	-0.379	-0.0889	0.693*	-0.14	-0.149	0.431	0.457	-0.11	
Cr	0.46	0.0635	0.02	-0.176	-0.0164	-0.456	-0.337	-0.0838	-0.323	0.214	-0.351	-0.112	-0.103	-0.111	-0.39	0.481

Winter															
	pH	**TSS**	**TDS**	**BOD**	**COD**	**NH_3**	**PO_4**	**NO_3**	**SO_4**	**Co**	**Pb**	**Fe**	**Zn**	**Cu**	**Ni**
pH															
TSS	-0.747**														
TDS	0.165	-0.489													
BOD	-0.742**	0.728**	-0.305												
COD	-0.348	0.571	-0.386	0.649*											
NH_3	0.149	-0.111	-0.315	-0.371	-0.0832										
PO_4	-0.507	0.638*	0.343	0.682*	0.749**	0.0283									
NO_3	0.533	-0.317	0.108	-0.114	-0.346	-0.123	-0.301								
SO_4	0.0478	0.0334	-0.261	-0.146	-0.464	0.189	-0.213	0.236							
Co	-0.0806	-0.326	0.869***	-0.235	-0.265	-0.142	-0.18	-0.173	-0.0847						
Pb	0.245	-0.427	0.168	-0.532	-0.395	0.856***	-0.186	-0.0219	0.208	0.275					
Fe	0.283	0.00769	0.23	-0.245	-0.405	-0.403	-0.521	0.427	0.428	0.112	-0.293				
Zn	-0.522	0.53	-0.437	0.664*	0.832***	0.0212	0.83***	-0.361	-0.295	-0.198	-0.265	-0.652*			
Cu	-0.508	0.6*	-0.532	0.566	0.84	0.228	0.812**	-0.449	-0.264	-0.261	-0.124	-0.642*	0.958***		
Ni	0.266	-0.497	0.953***	-0.332	-0.489	-0.405	-0.401	0.23	-0.0714	0.775**	0.088	0.414	-0.575	-0.685*	
Cr	0.392	-0.374	0.512	-0.378	-0.529	0.149	-0.252	0.364	0.295	0.315	0.487	0.285	-0.607	-0.594*	0.65*

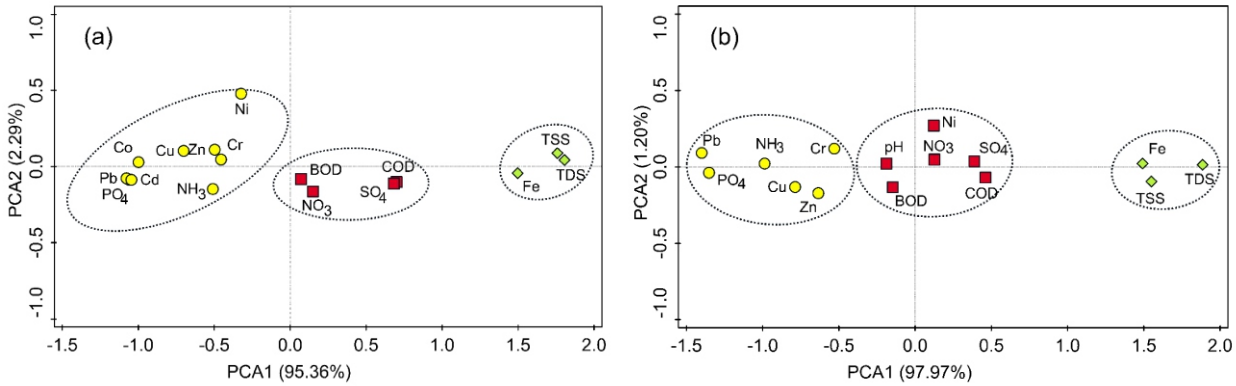

Fig. 4. Principal component analysis (PCA) plot of heavy metals concentrations in sediments collected from the River Jindi (a) summer season (b) winter season.

4. Conclusions

Pollution assessment indices (i.e. PERI, EF, Igeo and CF) shown that the heavy metals moderately polluted the sediments of the River Jindi and high sediment pollution in winter than summer. In sediments the Ni and Fe were found in higher concentration, and high concentrations of NO3, TDS and TSS were found in river. PCA along with high CF and EF values showed that similar anthropogenic sources contaminating sediment with heavy metals throughout the year. Correlation of sedimentary heavy metals concentration with water physicochemical parameters revealed that TSS (Co, Cu), TDS (Co), SO4 (Cd) and NH3 (Ni) were the most influencing parameters in heavy metals distribution in summer. While, TDS (Co, Ni), BOD (Zn), COD (Zn), PO4 (Cu) and NH3 (Pb) were the most influencing parameters in heavy metals distribution in winter. Further research work is needed to investigate the heavy metals bioaccumulation in high trophic levels (i.e. fish and aquatic plants) in the study area.

Author's contribution

Saeeda Yousaf, proposed the main concept and provided guidelines. Muhammad Shakil, did work in data collection and sample analysis. Ajmal Khan did write up of the manuscript. Muhammad Ilyas helped in drafting and reviewing the manuscript. Qamaruddin Jogi, Seema Anjum and Shahla Nazneen conducted all calculations using Excel 2010. Anwarzeb Khan reviewed manuscript and checked the statistics. Junaid Iqbal critically reviewed the manuscript.

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