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ORIGINAL PAPER

Assessment of heavy metal pollution using contamination factor, pollution load index, and geoaccumulation index in Kalpani River sediments, Pakistan

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Abstract

Kalpani River, Pakistan is an important stream that collects more than two third of the untreated domestic, commercial, industrial, and sewerage water, agricultural overflow, and other unwanted effluents of the surrounding area. These effluents have degraded the overall quality of this river water. The current study aims to examine the concentration of selected heavy metal (HM) contamination in Kalpani River sediments. The HMs studied were Pb, Cd, Zn, Ni, Fe, and Cu. Sediment samples were taken from nine selected locations (labeled as P1, P2, P3, … P9) and tested for HM contamination. The HMs contamination level in the sediment was computed using the contamination factor (CF), pollution load index (PLI), and geo-accumulation index (I_{geo}). All three indicators revealed that the Kalpani River in Mardan city is polluted with hazardous HMs such as Cd, Pb, and Zn. Pb, Ni, Fe, and Cu CF levels in sediment samples ranged from low (< 1) to moderate (1–3). However, the CF values for Cd and Zn indicated being highly polluted (> 6). The PLI values along the Kalpani River varied considerably and were observed lower upstream (P1 and P2, i.e., 0.821), highest (1.229) at the middle course, and lower (0.897) downstream. The I_{geo} for the studied HMs ranged from moderately to strongly polluted. The primary anthropogenic sources responsible for HM pollution in the Kalpani River were improper waste dumping, untreated sewage urban and industrial wastewater into the river, and excessive pesticide usage.

Keywords Heavy metals · River sediments · Water quality · Contamination factor · Geo-accumulation index · Pollution load index

Introduction

Heavy metals (HMs) are metallic elements having a density of more than 5 to 6 gcm^3. They may be harmful to the ecosystem's flora and fauna if present at higher concentrations (Sthanadar et al. 2013; Mishra et al. 2019). Industrial effluents, agricultural runoff, and municipal sewage all contribute to the accumulation of HM contaminants in river systems (Fang et al. 2019). The accumulation of HMs is attributed to natural and anthropogenic causes (Mohammed et al. 2011; Muhammad et al. 2011). The primary natural sources of HM buildup in fluvial environments are leachates and chemical discharge of rocks and geological formations (Upadhyay et al. 2006; Zare Khosheghbal et al. 2020). Mining activities, industrial wastages, sewage effluent, fossil fuel combustion, and the use of pesticides are examples of anthropogenic sources (Javed 2004; Goudie and Viles 2013; Sodrzeieski et al. 2019). The toxicity, persistence, and non-degradability of HMs make them a significant contaminant in aquatic and

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terrestrial ecosystems (Suja et al. 2009; Yang et al. 2009). HMs infiltrate into soil and groundwater aquifers and enter into the food chain (Balkhair and Ashraf 2016). If these metals accumulate to dangerous amounts, they can have serious ecological consequences for both aquatic and terrestrial organisms (Sharley et al. 2016; Green and Planchart 2018; Gupta et al. 2019)

River sediment, which is a mixture of organic and inorganic mineral components, serves as the last resting place/reservoir for HM release into the environment (Fawzy et al. 2012; Varol and Şen 2012; Pigneret et al. 2016). Several investigations have confirmed HM contamination in river sediment on a worldwide scale (Khan et al. 2010; Huang et al. 2014; Harguinteguy et al. 2014). Many HMs released into the fluvial environment may not only damage the water quality and render it unfit for its intended purposes but it may also pose a severe health risk to the local population owing to HM settling along riverbanks and inside the stream channel. Riverbanks are common leisure places for individuals who live near rivers and streams, and a significant number of riverside eateries operate locally. Similarly, being a picnic and recreational point, river is a source of frequent HM expoxure for visitors. Such HMs enter human bodies through ingestion, inhalation or dermal contact, and bioaccumulate in the human bodies, leading to serious biological and physiological consequences (Briffa et al. 2020). There has been no systematic research work on HM concentrations and their spatial distribution in Kalpani River sediment, which is a significant stream of Mardan city and carries the wastewaters of the entire city (commercial and residential). Having in view, the aim of this study is to assess HM pollution in the Kalpani River sediment using the three most widely used pollutants assessment indices, i.e., geo-accumulation index (Igeo), pollution load index (PLI), and contamination factor (CF).

Study area

Mardan city is the administrative center of District Mardan in Khyber Pakhtunkhwa, Pakistan, and is the province's second most populous city after Peshawar. Mardan's exact coordinates are 34° 05′ 0″ N to 34° 32′ 0″ N latitude and 72° 3′ 11″ to 72° 5′ 0″ E longitude. Mardan district is limited to the north by Malakand district, to the northeast by Bunir hills. Towards the east lies district Swabi and Bunir, to the south, it is surrounded by district Nowshera, and to the east, it is bordered by district Charsadda. The total geographical area of district Mardan is 632 km^2 whereas the Mardan city covered an area of 32 km^2. The Mardan area is traversed by three major streams, as well as several minor tributaries and nullahs. Among these, Kalpani is the primary stream that originates in the Malakand mountains in the district's south-eastern corner. After flowing through Lund Khwar, Katti Ghari and Mardan join the Kabul River at Pirsabak, in district Nowshera. Another stream goes from Sangao to Babozai, Katlang, and Jamal Ghari before its confluence with the Kalpani River. Similarly, the third stream originates in the Bunir area flows through Rustam, Shahbaz Garhi, and finally joins the Kalpani River. The flow of the Kalpani River and the location of the research area in Mardan city are depicted in Fig. 1.

The Kalpani River investigation area is located between 34°11′15″ N and 34°14′15″ N latitudes and 72° 01′40″ E and 72° 04′10″ E longitudes. It extends from Bangla Koroona near Gujar Garhi to Baghdad, Kasai Bazar bridge, Seraii Baba, Sikandary, Parhoti Bridge, Sherabad, and Sanger Baba at the southern by-pass of the ring road, district Mardan. The Kalpani River's headwaters are in the Malakand district, which is mostly composed of the auger and flaser granite and granodiorite gneiss intruded by tourmaline granite, meta gabbro, amphibolite, and pegmatite (Ahmad et al. 2003; Ashraf and Dawood 2010). The major elements of the igneous, metamorphic complex are quartz, feldspar, biotite, and muscovite, with garnet, amphibole, and chlorite as accessories. The region has also got minerals such as mica, chlorite, quartz, and amphibolite (Rashid et al. 2020). The primary minerals include feldspar, mica, garnet, and quartz, while the secondary minerals are graphite, magnetite, amphibole, apatite, magnetite, muscovite, etc. (Khaliq et al. 2003; Ahmad et al. 2003).

The majority of district Mardan is made up of quaternary alluvium, an unconsolidated deposits of gravels, sand, silt, and clay. In the district's northwestern corner, isolated outcrops of garnet schist, schistose marble, calcareous phyllite, dolomite marble, graphitic phyllite, and schist are exposed. The Shewa-Shahbaz Garhi complex is a remote outcrop (34.10′ to 34.30′ N and 72.10′ to 72.12 E) dominated by alkali granites with a little amount of basic injections (Sajid et al. 2018). This area also has an outcrop of the Nowshera formation, which consists mostly of sandy dolomite, limestone, and marble with calcareous quartzite and calcareous argillite. Analysis of heavy metals in rock samples collected from the catchment area of Kalpani River (Malakand District) confirmed the existence of copper (Cu), iron (Fe), nickel (Ni), zinc (Zn), manganese (Mn), lead (Pb), and chromium (Cr). According to Zahoor et al. (2014), the Mn concentration in the rock samples of Malakand district ranges between 235 and 889 ppm, Cr 38.7 to 89.6 ppm, and Zn 51.3 to 94.7 ppm, Cu ranged from 27.6 to 34.7 ppm, whereas Ni ranged from 23.2 to 59.1 ppm, whereas Pb levels ranged from 0 to 24.0 ppm.

Material and methods

A total of nine sites (P1, P2, P3,… P9) along the Kalpani River were selected for the assessment of HMs such as copper (Cu), iron (Fe), nickel (Ni), zinc (Zn), cadmium (Cd),

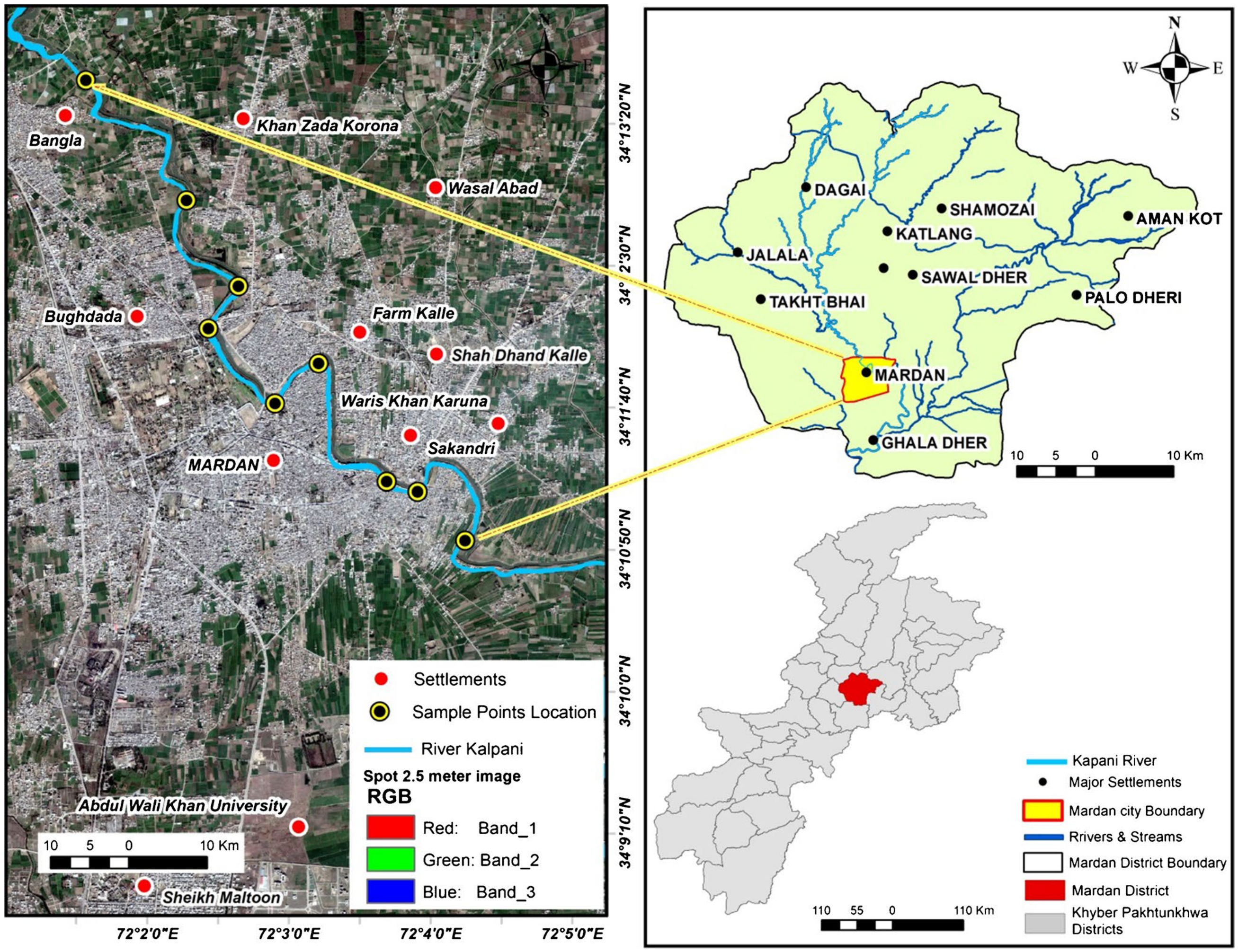

Fig. 1 Kalapani River passes through Mardan city originated from Malakand and its courses are present (start to end) passing through Mardan and Nowshera

and lead (Pb) contamination, and concentration in fluvial sediment (Fig. 2). P1 is the starting point of the study area located upstream toward the north of Mardan city at Bangla Korona and P9 is the ending point located in the South at Khan Kotay. The P1 and P2 are surrounded by agricultural land and get the runoff land along with sewerage from the surrounding villages. Sample points P3 to P8 are the mid-stream points surrounded by densely built areas and mostly get the untreated municipal waste and runoff from some small-scale industries like furniture, automobile repairing, welding, aluminum goods, soaps, etc. The P9 located in the south of Mardan city mostly gets agricultural runoff (Fig. 2). The GPS coordinates of selected sample points along the stream were recorded and saved using Magellan Triton 1500 GPS as waypoints are shown in the table given in SI (Table S1), and the spatial distribution is shown in Fig. 2. Sample of sediments was collected using an auger tube (12-inch-long and 2-inch diameter tube with 12-inch extension rod handle) from Kalpani stream in mid-April 2019. Such auger is usually used for shallow fluvial sediment sampling having a thickness of 0 to 10 inches and water depth of 0 to 24 inches. The collected sediment samples were kept in polythene bags and transferred to the laboratory. The samples were dried at 104 °C in the oven for 48 h. The materials were then grounded to a fine powder, sieved (106 m copper mesh wire), and kept at 4 °C for subsequent examination.

The samples were acid processed using the protocol described by Mingbiao et al. (2008) and Ipeaiyeda and Ayoade (2017), and then analyzed using a process known as flame atomic absorption spectrometry (FAAS) using an Atomic Absorption Spectrophotometer (Perkin Elmer AS 3100) at Centralized Resource Laboratory, University of Peshawar. The FAAS technique is based on the concept that certain wavelengths of light are absorbed by metals. Metal ions in the solution are converted to their atomic state by a

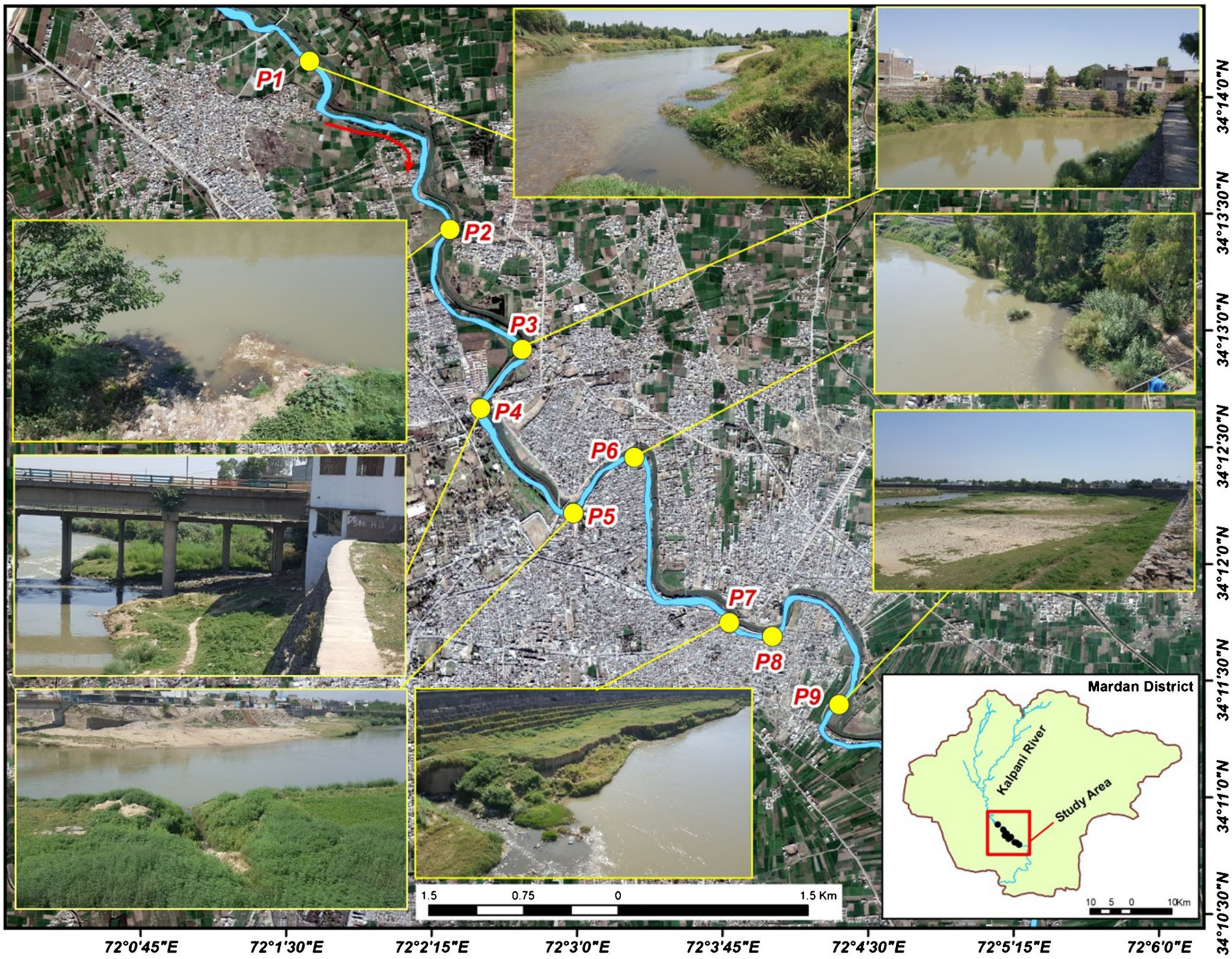

Fig. 2 Sample locations along river Kalpani through Mardan city. Background image acquired from SUPARCO, SPOT 5 m resolution

flame. When the correct wavelength of light is utilized, the amount of light absorbed is measured, and the concentration is calculated (Rezende et al. 2011; Acar 2012; Tareen et al. 2014; Sthanadar et al. 2015; Zhong et al. 2016; Nazir et al. 2022). The global mean concentration of Pb was 20 μg/g, Cd was 0.3 μg/g, Zn was 127 μg/g, Ni was 68 μg/g, Fe was 35,900 μg/g, and Cu was 45 μg/g and is considered the background values reported by Turekian and Wedepohl (1961) and Martin and Meybeck (1979).

ArcGIS 10.5 was used to create the geographical distribution and visualization of HMs. It is a handy and frequently used tool for quickly analyzing the distribution of HM and the amount of contamination (Kumar et al. 2007; Singh et al. 2015; Forsythe et al. 2016; Rawat et al. 2018). To measure the HM contamination in the sample sediments, three indices were used: CF, PLI, and Igeo.

Contamination factor (CF)

The CF indicates the extent to which the sediment is polluted. It is expressed by the following formula (Sabo et al. 2013).

$$CF = Cm\ Sample \ / \ Cm\ Background \quad (1)$$

where Cm sample is the total metal concentration and Cm background value represents the average background value of the element in sediment.

Background value of HMs is a measure that is used to differentiate between the concentration of the naturally occurring HMs and the concentration with an anthropogenic influence in a given sample (Matschullat et al. 2000; Garcia et al. 2010). The CF value of <1 means low, >1 to <3 indicates moderate, >3 to <6 considerable, and >6 is considered very high concentration (Harikumar and Jisha 2010; Soliman et al. 2015).

Table 1 HM concentration (mg/kg) (mean value ± SD) in sediments samples collected from 9 sampling points along the Kalpani River

Sample points	Pb	Cd	Zn	Ni	Fe	Cu
P1	1.60 ± 0.100	0.04 ± 0.014	5.57 ± 0.100	2.19 ± 0.082	35.34 ± 0.235	1.58 ± 0.008
P2	1.02 ± 0.150	0.04 ± 0.005	3.80 ± 0.013	5.39 ± 0.051	36.83 ± 1.783	1.47 ± 0.000
P3	1.49 ± 0.160	0.04 ± 0.004	25.18 ± 1.097	3.84 ± 0.050	36.70 ± 2.447	2.20 ± 0.000
P4	2.69 ± 0.140	0.04 ± 0.017	37.39 ± 4.435	4.23 ± 0.058	36.46 ± 2.295	2.55 ± 0.002
P5	0.88 ± 0.070	0.02 ± 0.009	1.40 ± 0.027	0.97 ± 0.033	31.66 ± 0.287	0.52 ± 0.002
P6	1.65 ± 0.130	0.04 ± 0.009	11.28 ± 0.300	2.64 ± 0.045	33.89 ± 0.182	1.43 ± 0.010
P7	1.34 ± 0.080	0.07 ± 0.002	4.50 ± 0.094	5.00 ± 0.017	34.75 ± 0.147	2.29 ± 0.003
P8	1.58 ± 0.060	0.05 ± 0.003	6.35 ± 0.082	2.20 ± 0.515	34.79 ± 0.677	1.57 ± 0.008
P9	1.838 ± 0.019	0.06 ± 0.009	10.35 ± 0.317	4.58 ± 0.057	34.53 ± 0.468	2.46 ± 0.010

Pollution load index (PLI)

The PLI for a specific site may be calculated using the technique given by Tomlinson et al. (1980). It is a helpful indicator for comparing the pollution levels of various sample sites (Adebowale et al. 2009). PLI is useful for determining the amount of an HM in a given environment. The PLI is expressed as:

$$PLI = (CF1 \times CF2 \times CF3 \times CF4 \times \ldots\ldots\ldots CFn)^{1/n} \quad (2)$$

where, n is the number of metals and CF1 and CF2 are the contamination factor of sample 1 and 2, respectively (Raju et al. 2012).*The PLI value > 1 is considered polluted,while < 1 not polluted* (Harikumar et al. 2009).

Geoaccumulation index (I_{geo})

Muller (1969) developed this measure to quantify the amount of HM contamination in sediment. The geo-accumulation index is denoted by I_{geo} and expressed as:

$$Igeo = log2\left(\frac{Cn}{1.5Bn}\right) \quad (3)$$

where Cn is the concentration of metal pollutant; Bn is the geochemical background concentration of the pollutant in sediment and 1.5 is the lithogenic effect: the background matrix correction factor. Igeo is useful to evaluate anthropogenic contamination of HMs in sample by comparing it with background concentration of that particular HM (Ackah 2019).

The I_{geo} is divided into seven classes, from unpolluted to severely contaminated (Chakravarty and Patgiri 2009; Fagbote and Olanipekun 2010; Sabo et al. 2013; Legorburu et al. 2013). Muller's categorization for the I_{geo} is shown in the table given in SI (Table S2).

Results and discussion

The HMs' mean value and standard deviation in sediment samples of various sample points are shown in Table 1. The calculated mean concentration for Pb, Cd, Zn, Ni, Fe, and Cu were 0.88–2.69, 0.02–0.07, 4.50–37.39, 0.97–5.39, 31.66–36.83, and 0.52–2.55, respectively. The highest concentrations for Pb, Zn, and Cu were found at P4 while for Ni and Fe were at P2, and for Cd was found at P7, whereas the lowest concentrations for Pb, Cd, Ni, Fe, and Cu were found at P5 while for Zn was found at P7. In the study area, the main anthropogenic factors responsible for HMs contamination in Kalpani River are garbage disposed directly into the river, discharge of untreated urban and industrial effluents, and indiscriminate use of pesticides and fertilizers having HMs in agricultural fields. The primary source of Pb in Kalpani River sediments is concrete structures, as Pb is found in cement, petrol stations and vehicle services,

Table 2 Some common sources of studied HMs

HMs	Sources	References
Cd	Welding plants, electroplating, pesticides, fertilizer, batteries repairs, metal plating and tire elastic are viewed as the probable wellsprings of Cd in urban soil and road dust	Taylor et al. 2010
Cu	Pesticides, mining, electroplating, landfills and waste disposals	Dragović et al. 2008
Pb	Paint, pesticides, batteries, automobile emission, burning of coal, toys paint, electronic equipment, recycled scrap metal, printing, photographic materials	Luo et al. 2015
Ni	Battery industry, electroplating, Zn base casting, domestic utensils and coins	Zhang et al. 2009
Zn	Refineries, brass manufacture, metal plating	Luo et al. 2015
Fe	Rusting of cars, household item, buildings and bridges steel, recycling	Salehi et al. 2014

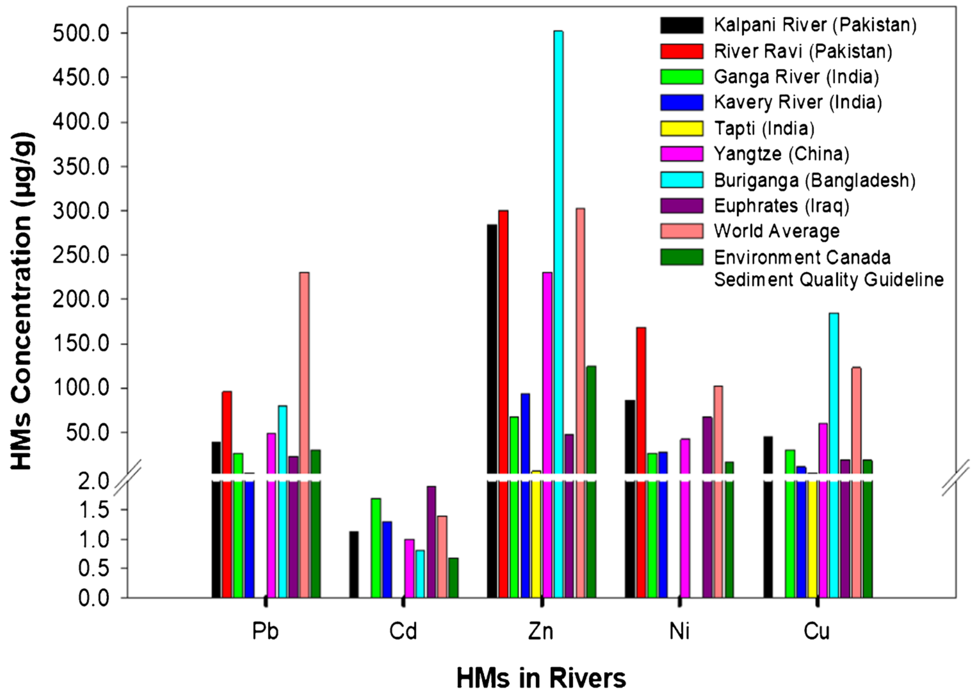

Fig. 3 Comparison of heavy metals (average concentration (µg/g)) in Kalpani River sediments with other rivers in the world

oil change services, and the furniture sector (Sulaiman et al. 2017; Taher et al. 2021). The samples obtained from sites P3 and P4, which are located in the middle course of the river, have the highest concentration of HMs. The primary causes of high concentrations of HMs in these areas include big oil service stations, vehicle repair shops, densely built-up areas, and municipal effluent discharge. Furthermore, when HMs are released into the fluvial system, they are often transported downstream by water for a few kilometers before settling in the fluvial silt. Table 2 lists some of the most prevalent sources of HMs. The study of Tian et al. (2021) also found various ions, i.e., Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-, and SO_4^{2-}, and HCO_3^- in the water and soil samples of the Shahu lake, China, and the concentrations were found higher at the upstream samples than the low stream samples. Chatterjee et al. (2022) found that ion-exchange and silicate weathering processes are the two important mechanisms controlling the concentrations of the dissolved solutes in the thermal waters of the Northeast Hamalayan, India.

Figure 3 shows the comparative analysis of concentrations of HMs in the sediment of River Kalpani with world's rivers. Data is given in SI (Table S3). The available literature on heavy metal concentration in global rivers suggests that the concentration of HMs not only varies from river to river but also varies at various locations along the same river course. Certain HMs, such as Pb, are higher in sediment samples from the Kalpani River than the average concentration of Pb in the Ganga, Kaveri, and Buriganga rivers (Bangladesh).

Table 3 Contamination factor (CF) for heavy metals Kalpani River

HMs		Pb	Cd	Zn	Ni	Fe	Cu
Concentrations in sediment (µg/g)		**39.12**	**1.13**	**284.38**	**86.25**	**874.85**	**45.25**
Sample sites	P1	2.006 ^{M}	5.500^C	1.078 ^{M}	0.806^L	0.0153^L	1.447 ^{M}
	P2	1.270 ^{M}	5.00^C	0.737^L	1.981 ^{M}	0.0160^L	1.147 ^{M}
	P3	1.858 ^{M}	5.625^C	0.50^C	1.411 ^{M}	0.0159^L	1.716 ^{M}
	P4	3.361^C	5.375^C	7.246^H	1.555 ^{M}	0.0158^L	1.990 ^{M}
	P5	1.097 ^{M}	2.125 ^{M}	0.271^L	0.356^L	0.0137^L	0.403^L
	P6	2.058 ^{M}	5.500^C	2.180^L	0.970^L	0.0147^L	1.117 ^{M}
	P7	1.677 ^{M}	8.375^H	0.089^L	1.840 ^{M}	0.0151^L	1.789 ^{M}
	P8	1.977 ^{M}	1.227 ^{M}	1.271 ^{M}	0.808^L	0.0151^L	1.227 ^{M}
	P9	2.297 ^{M}	1.921 ^{M}	2.004 ^{M}	2.053 ^{M}	0.0150^L	1.921 ^{M}

^{L}Low < 1. ^{M}Moderate 1–3. ^{C}Considerable 3–6. ^{H}High > 6

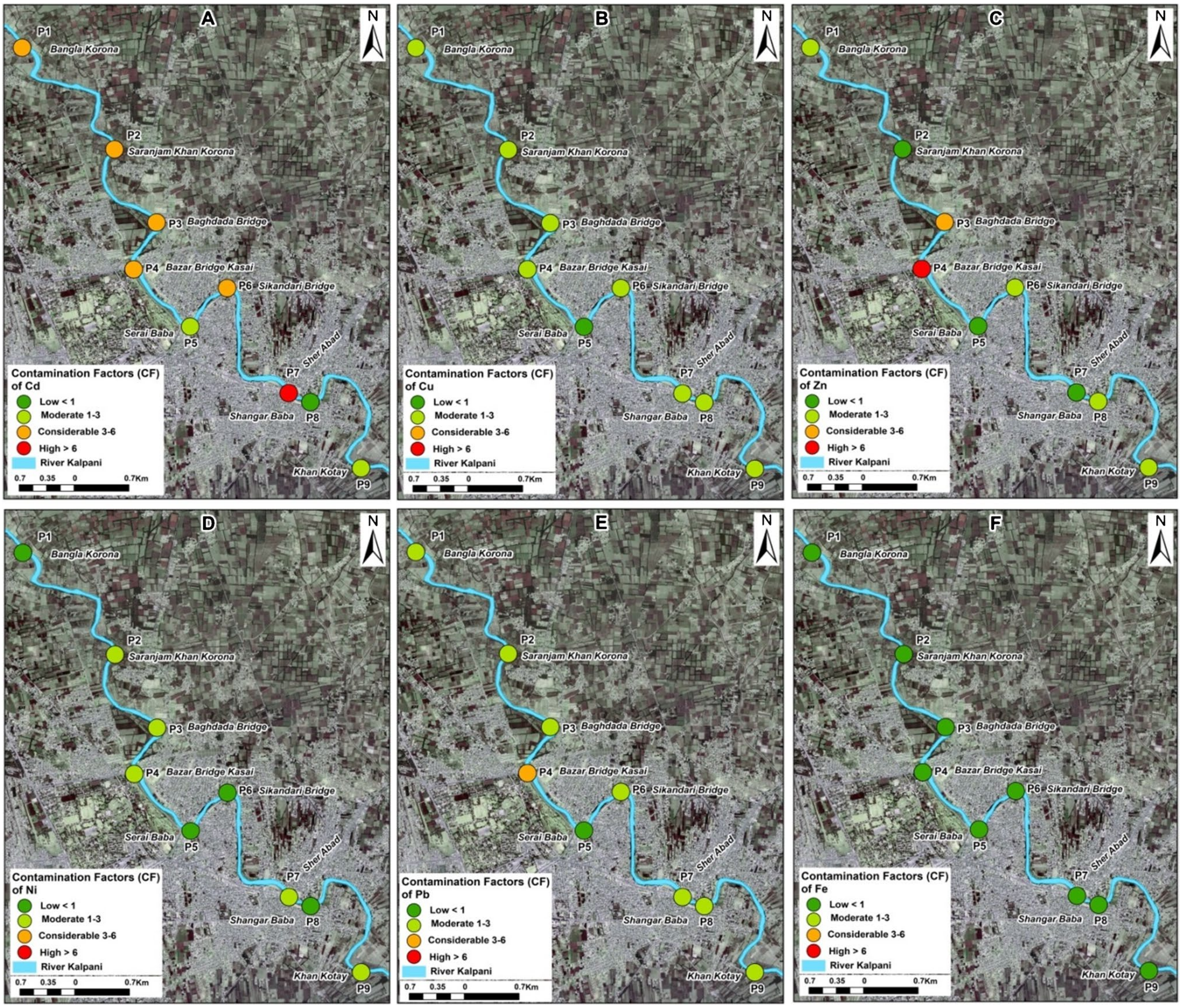

Fig. 4 Spatial distribution of contamination factor (CF) calculated for HMs {**A** Cd, **B** Cu, **C** Zn, **D** Ni, **E** Pb, and **F** Fe}

Similarly, Ni concentrations in Kalpani sediment samples are substantially higher than in other global rivers. The average Ni concentration in Kalpani was 86.25 g/g, compared to 26.7 g/g in the Ganga River, 27.7 g/g in the Kaveri River, India, and 41.9 g/g in the Yangtze River China; however, it is lower than the world average. The analysis of Zn concentration revealed the same results. When compared to the River Ravi in Pakistan, the HM content in the Kalpani River was much lower; nevertheless, the HM concentration in the Kalpani River was greater when compared to the Environment Canada sediment quality requirements. A study conducted by Zahoor et al. (2014) in Malakand district from where the Kalpani River takes its origion determine the presence of copper (Cu), iron (Fe), nickel (Ni), zinc (Zn), manganese (Mn), lead (Pb), and chromium (Cr) in rock samples with variying concentrations.

Contamination factor (CF)

Table 3 shows the CF of the investigated HMs in the sediments of the Kalpani River, whereas Fig. 4 shows their geographical distribution. The quantity of Pb showed a significant concentration only at one site P4 (mid-course of the stream), while a moderate amount was recorded at the downstream five sites P5… P9, and sites P1, P2, and P3 upstream. Anthropogenic activities were identified at site P4 in the catchment region of the nallah draining into the Kalpani River. The sample site was surrounded by densely populated urban areas and get the urban effluents and discharge from oil change shops, denting painting shops, and car mechanic shops. The CFs of Cd at sample sites P5, P8, and P9 were found for moderate level, P1… P4 and P6 for considerable level and P7 for high level. The CF values of

Table 4 Pollution load index (PLI) of selected HMs in Kalpani River (Harikumar et al. 2009)

Samples **HMs**	P1	P2	P3	P4	P5	P6	P7	P8	P9
Pb	2.006	1.270	1.858	3.361	1.097	2.058	1.677	1.977	2.297
Cd	5.500	5.00	5.625	5.375	2.125	5.500	8.375	1.227	1.921
Zn	1.078	0.737	5.00	7.246	0.271	2.180	0.089	1.271	2.004
Ni	0.806	1.981	1.411	1.555	0.356	0.970	1.840	0.808	2.053
Fe	0.0153	0.0160	0.0159	0.0158	0.0137	0.0147	0.0151	0.0151	0.0150
Cu	1.447	1.147	1.716	1.990	0.403	1.117	1.789	1.227	1.921
PLI	0.821	0.744	1.080	1.229	0.475	0.901	0.734	0.740	0.897
	Unpolluted	Unpolluted	Polluted	Polluted	Unpolluted	Unpolluted	Unpolluted	Unpolluted	Unpolluted

Zn at three sites P2, P5, and P7 indicate low level; four sites P1, P6, P8, and P9 indicate moderate level; only P3 for considerable and P4 suggests a high CF value. Ni has moderate CF at sites P2, P3, P4, P7, and P9 while at sample sites P1, P5, P6, and P8 have low CF. All of the sample locations had a low Fe CF. Similarly, except for P5, all of the selected sites had a moderate Cu CF (low). The CF for Pb was found moderate to considerable at all the sample sites and for Cd and Zn, it was found moderate to high. Ni, Zn, and Cu, on the other hand, were found in considerably lower quantities. As a result, frequent monitoring for Cd, Zn, and Pb concentrations is recommended, as their CF at all sample locations except P1 exceeded the acceptable level and may provide a future pollution concern.

The observation indicated that these HMs were transported via urban wastewater discharge, industrial outflow, and agricultural overflows. The highest levels of HMs at site P9 suggested that these sources had an effect. The relatively high concentrations of HMs, particularly for Zn and Cu at sites P4 and P7, appeared to be caused by wastewater, as well as household and agricultural runoff. Furthermore, Cu is a component of pesticides that reach the river through agricultural runoff. The CF values computed by Rabee et al. (2011) for Tigris River sediment suggested that CF values of Cu and Ni were low compared to Pb and Cd which were higher (> 1). They attributed the higher CF values to agricultural and industrial activities in the region. Similarly, another study found that most sampling sites along the Euphrates River (Iraq) were moderately contaminated with Pb, having a CF value of 1–3. All the sampling sites were highly contaminated with Cd with a CF value of more than 6 (Salah et al. 2012). The high concentrations of HMs in the water of Kalpani River Mardan districts might be the consequence of both geogenic and human inputs. Mafic rocks and fertilizers all add a significant impact on heavy metal concentration. The available literature suggests that HMs such as Cu, Pb, Ni, and Cd came from the geogenic sources, whereas Fe and Zn came from anthropogenic sources.

Pollution load index (PLI)

The variation in the sediment samples and degree of severity of pollution were determined through PLI that represents the ratio by which the HMs in sediment exceed the background concentration and provides the overall level of HMs toxicity in a sample. Table 4 summarizes the computed PLI for various sample points and the special distribution of PLI of selected HMs in Kalpani River sediment is shown in Fig. 5.

The study indicated that the PLI values for the two sample sites P3 and P4 were 1.080 and 1.229, respectively, i.e., greater than 1. If the PLI value is greater than one, the point is deemed contaminated (Harikumar et al. 2009). The calculated PLI value for the remaining locations was less than one, indicating no pollution. The upper stream region of the Kalpani River, where it reaches Mardan, was an agricultural area, and the pollutants were primarily sourced from overflow from fertilized fields. The intermediate course involved collecting effluents and municipal waste from heavily inhabited regions such as Sakandary, Mardan city, Baghdada, Dagar Shah, and Farm kilay. These regions are densely populated with auto shops, automobile service stations, and other minor enterprises such as the furniture industry and companies. As a result, the sediment sample exhibited significant HM concentrations and the highest PLI, 1.082 and 1.229 in sampling sites P3 and P4, respectively. Another major impact was may be the loop/meander in the middle course of the Kalpani River. As water flows through a meander, it swings toward the outer bank, where erosion is greatest, and then spirals back toward the inside banks. The frictional drag generated by the channel bed slows the waterflow as it spirals toward the inner of the meander and causes the deposition of HM contaminated silt. The PLI values obtained by Barakat et al. (2012) for Day River, Morocco vary from 1.57 to 2.20, suggesting that Cd, Cu, Pb, and Zn concentrations surpassed the background value. The significant prevalence of these HMs was linked to human activities in the catchment region. Xu et al. (2017) also reported the similar findings for the Jiaozhou Bay catchment region, as

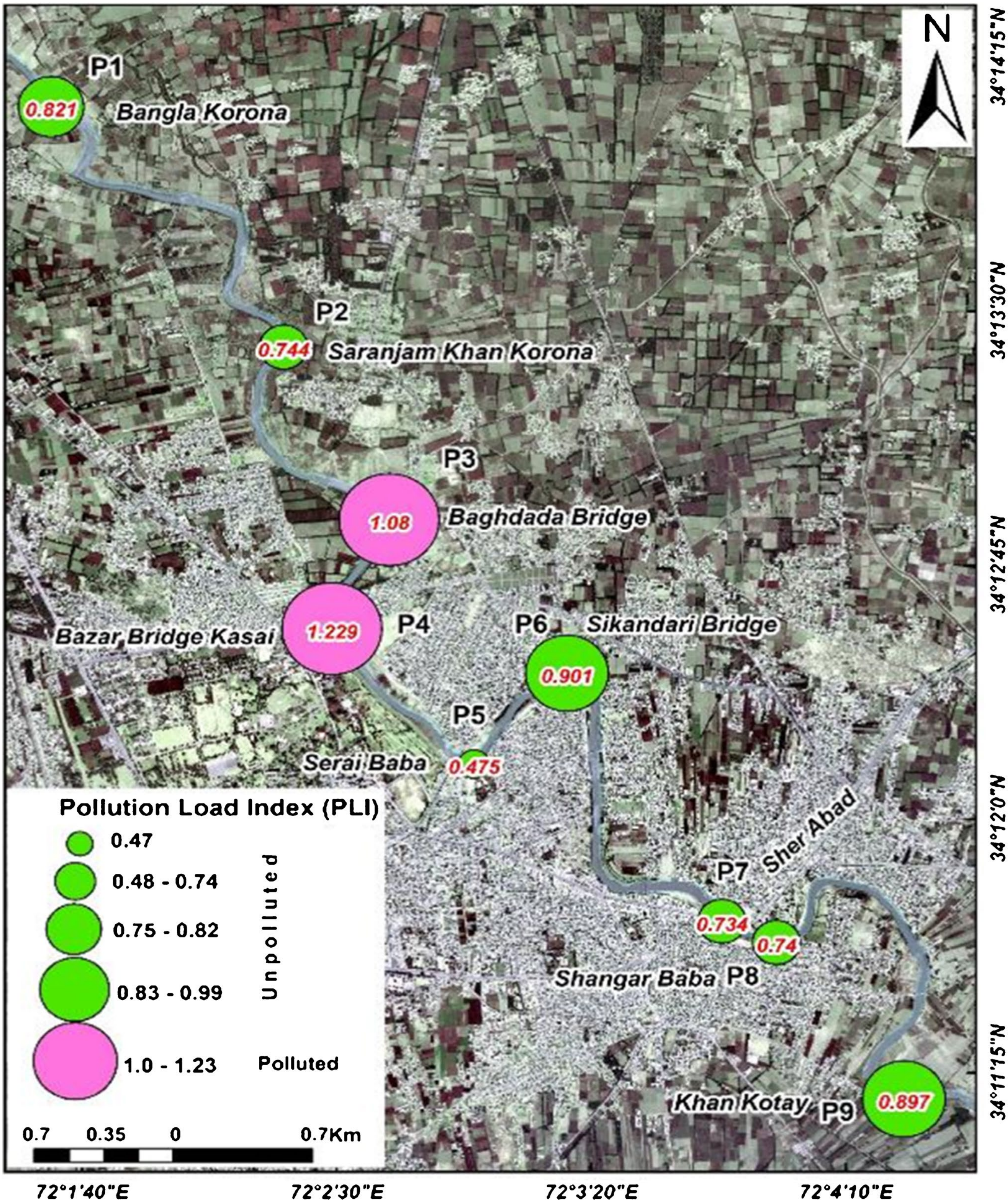

Fig. 5 Spatial distribution of pollution load index of sediment samples. The size of the circles represents the value of pollution load index

the PLI values of the urban river silt ranged from 0.2 to 4.1, suggesting that 34% of the sample locations were polluted. Banu et al. (2013) calculated PLI values for Turag River, Bangladesh, and found that all 5 locations investigated were contaminated, with PLI values ranging from 1.35 to 3.3 on the Wilson (1987) scale.

Table 5 Geo-accumulation index (I_{geo}) of HMs in Kalpani River

Sample	Pb	Cd	Zn	Ni	Fe	Cu
P1	−2.862[a]	1.874[c]	−1.0244[a]	−6.983[a]	−22.424[a]	−5.05[a]
P2	−0.240[a]	1.736[c]	−1.0244[a]	−5.686[a]	−22.359[a]	−0.386[a]
P3	0.307[b]	1.906[c]	0.157[b]	−6.175[a]	−22.368[a]	−4.448[a]
P4	1.140[c]	1.772[c]	2.272[d]	−6.035[a]	−22.377[a]	0.408[b]
P5	−0.450[a]	0.502[b]	−2.466[a]	−8.162[a]	−22.583[a]	−1.895[a]
P6	0.456[b]	1.874[c]	−2.776[a]	−6.716[a]	−22.481[a]	−0.424[a]
P7	0.161[b]	2.481[d]	−0.290[a]	−5.792[a]	−22.443[a]	0.254[b]
P8	0.308[b]	2.058[d]	0.037[b]	−0.632[a]	−22.443[a]	−0.289[a]
P9	0.615[b]	2.22[d]	0.037[b]	−5.632[a]	−22.452[a]	0.357[b]

[a]Shows uncontaminated; [b]shows uncontaminated to moderately contaminated; [c]shows moderately contaminated; [d]shows moderate to strongly contaminated; [e]shows strongly contaminated; [f]shows strongly to extremely contaminated; [g]shows extremely contaminated

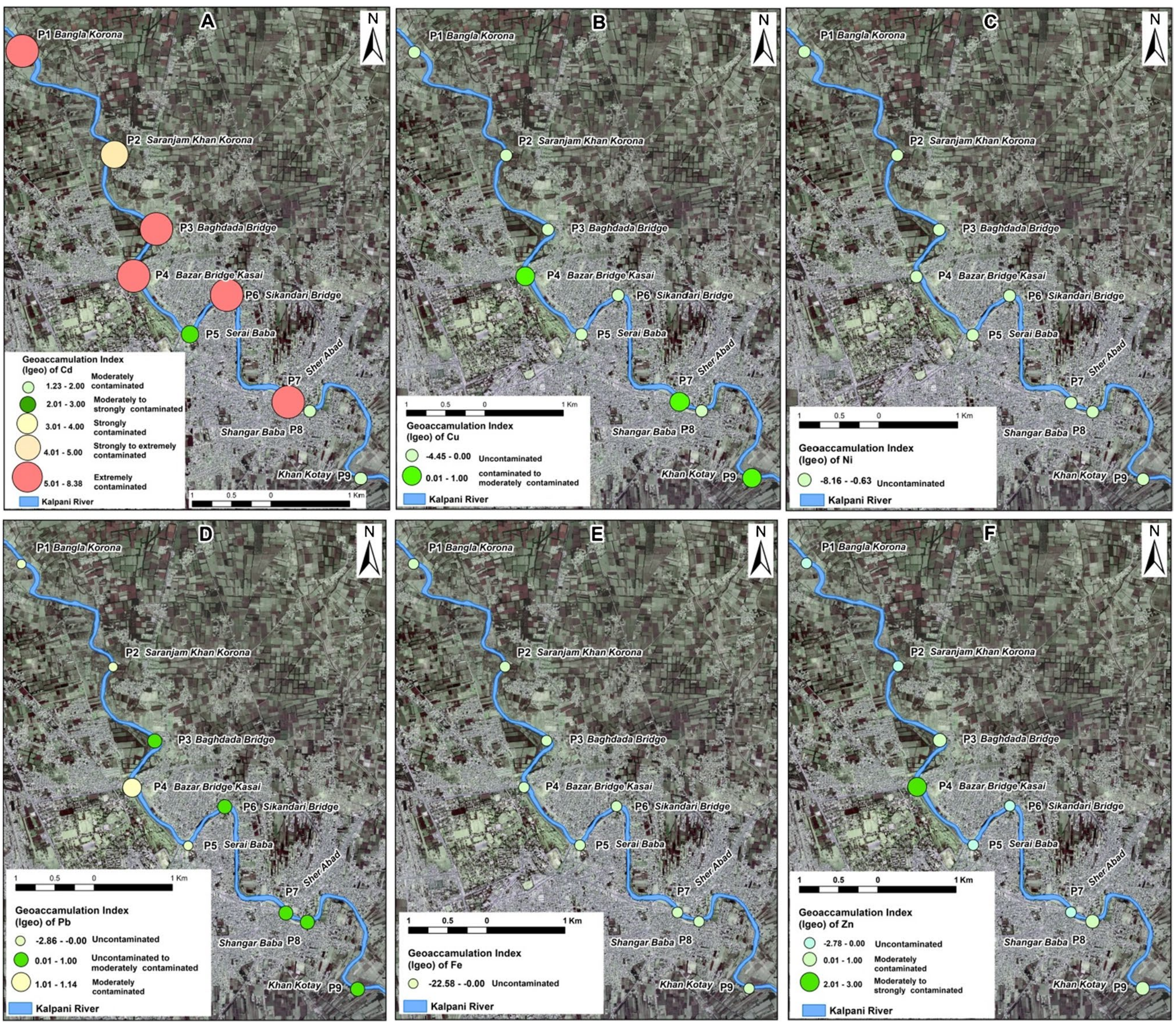

Fig. 6 Spatial distribution of geo-accumulation index (Igeo) calculated for HMs {**A** Cd, **B** Cu, **C** Ni, **D** Pb, **E** Fe, and **F** Zn}

Geo-accumulation index (I_{geo})

The I_{geo} was computed for the selected HMs in sediment samples taken from the Kalpani River in Mardan. Table 5 displays the I_{geo} of various HMs in the research region, and Fig. 6 depicts the spatial distribution of I_{geo} computed for selected HMs in sediment samples taken from the Kalpani River. The I_{geo} of the sediment samples obtained from the Kalpani River ranged from uncontaminated to moderately to highly polluted, according to the study. The research revealed that Pb I_{geo} for sites P1, P2, and P5 was uncontaminated, while P3, P6, P7, P8, and P9 ranged from unpolluted to moderately polluted, and P4 was moderately polluted. Site P5 had an I_{geo} of Cd ranging from unpolluted to moderately polluted; P1, P2, P3, P4, and P6 had an I_{geo} of Cd ranging from moderately polluted to highly polluted; and P7, P8, and P9 had an I_{geo} of Cd ranging from moderately polluted to strongly contaminated. The I_{geo} of Zn was moderate to strong for P4; however, the I_{geo} of all other selected HMs was either uncontaminated or unpolluted to moderately polluted in the remaining study locations.

Figure 7 shows the comparison of the average I_{geo} of HMs in the Kalpani River with other world rivers. The data is given in SI (Table S4). The analysis revealed that the studied watercourses were contaminated and do not meet the criteria for drinking or even for irrigation water. It can be seen that the concentrations of some HMs, i.e., Cd and Pb were quite high (Table S4). Within the listed river the Khoshk River, Iran seems to be the most contaminated river. Similarly, the Tigris River, Turkey, and Khoshk River, Iran were relatively polluted for all the studied HMs, while Benin River Nigeria was the least polluted watercourse. As far as the Kalpani River is concerned, it has a high concentration of Cd and Cu compared to other HMs.

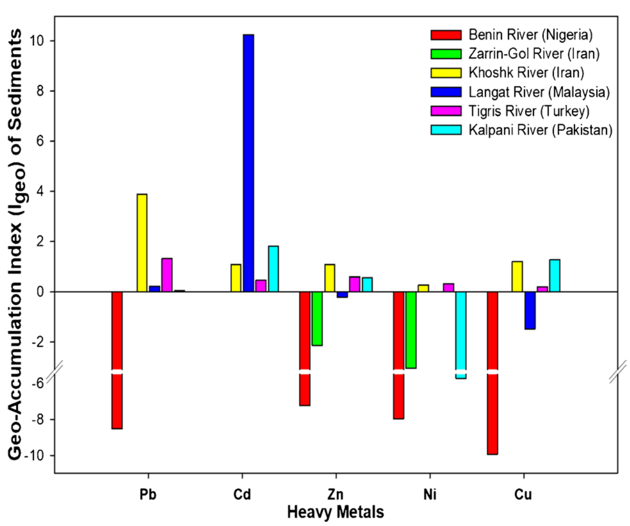

Fig. 7 Comparison of average geoaccumulation index (I_{geo}) of heavy metals in Kalpani River with other world rivers

Conclusion

The study attempted to assess the status of Cd, Cu, Ni, Zn, Pb, and Fe in the sediment of Kalpani River in Mardan, Khyber Pakhtunkhwa, Pakistan, using the contamination factor, pollution load index, and geo-accumulation index. The study concluded that the CF values for Pb, Ni, Fe, and Cu in sediment samples were ranged from low to moderate. However, recorded high (8.37 and 7.25) for Cd and Zn, respectively. These high concentrations indicated the wastewater flow from industrial and agricultural operations. The PLI values along Kalpani River varied considerably lowered at upstream (0.82), highest at middle (1.23), and lowest at the lower reaches (0.89). Igeo computed for the studied HMs revealed that Igeo of the sediment sample ranged from uncontaminated to moderate and strongly contaminated. The results of all three indices concluded that the Kalpani River in Mardan city is severely polluted with HMs such as Cd, Pb, and Zn, which clearly indicates the heavy input of Cd, Cu, Ni, Zn, Pb, and Fe in Kalpani River from Mardan city. This variation in CF, PLI, and Igeo values in sediment samples was because of meandering course of the river and source of contamination. The high concentration of Cd at P1 was mainly because of excessive use of pesticides, fertilizer on the crops, and overflow of agricultural wastewater. Similarly, the high concentrations at the middle course from P3 to P7 were because of road dust, iron works/welding, batteries repair, untreated industrial and urban wastewater discharge, disposal of solid waste and open defecation, use of leaded petrol, etc. For the rest of the HMs, the Igeo values were ranging from uncontaminated to moderately contaminated. The comparative analysis of studied watercourse with the world important rivers revealed that the Kalpani River is highly contaminated and does not meet the criteria for drinking or even for irrigation water. This study suggested that the urban wastewater and agricultural and industrial effluents must be monitored periodically for maintaining the national and international HM standards.

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Data availability Data availability statement is not applicable.

Declarations

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Consent to participate Not applicable.

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