Heliyon 8 (2022) e12499

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

Sediment-associated heavy metal contamination and potential ecological risk along an urban river in South Africa

Chaka Mohajane [a], Munyaradzi Manjoro [a,b,*]

[a] Department of Geography and Environmental Sciences, North-West University, Mafikeng Campus, Private Bag X2046, Mmabatho 2745, South Africa
[b] Department of Physical and Earth Sciences, Sol Plaatje University, Private Bag X5008, Kimberley 8300, South Africa

ARTICLE INFO

Keywords:
Heavy metals
Potential ecological risk
Pollution indices
Sediment contamination

ABSTRACT

Sediment contamination by heavy metals poses one of the worst environmental risks to aquatic ecosystems worldwide. The study explored sediment-associated heavy metal contamination and potential ecological risk along the Molopo River in Mahikeng, South Africa. Total concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) were analysed using inductively coupled plasma mass spectrometry. Various indices were applied to assess the level of contamination and ecological risk. Most heavy metal concentrations at selected upstream and downstream sites were below average shale, except Cr, Cu, Hg, Pb, and Zn. The contamination factor (CF) indicates that the level of contamination was low ($CF < 1$) at most sampling sites, except Cr, Cu, Pb and Zn, which varied from moderate ($1 CF < 3$) to considerable ($3 \leq CF < 6$) contamination. The enrichment factor (EF) shows that Cd, Cr, Cu, and Zn were moderate ($2 EF < 5$) to significantly enriched ($5 EF < 20$) at the affected sites. The results suggest anthropogenic enrichment ($EF > 2$) of Cd, Cr, Cu, and Zn. The threshold effect concentration and probable effect concentration sediment quality guidelines predicted that Cr, Cu, and Ni concentrations were more likely to have harmful effects on bottom-dwelling organisms. Pearson correlation and principal component analysis reveal that Cd, Cr, Cu, Ni, Pb, and Zn had a common anthropogenic source. We attribute the source to industrial and wastewater effluent, vehicle traffic, and runoff from various urban surfaces in the city. The study provides baseline data for heavy metal monitoring in the study area. Future research and monitoring should focus on heavy metals that cause concern because of their concentrations (Cr, Cu, Pb, and Zn) and potential ecological risk (Cr, Cu, and Ni).

1. Introduction

Heavy metal contamination is a threat to the environment and society (Ali et al., 2022; Sekabira et al., 2010). Sediment contamination is of particular concern due to the persistence and environmental toxicity of heavy metals in this matrix (Coulthard and Macklin, 2003). Heavy metals have low solubility – only 10% exist in dissolved form in the water column (Zahra et al., 2014) and the rest is adsorbed to fine sediment particulate, most of which accumulate as bottom sediments (Coulthard and Macklin, 2003; Zheng et al., 2008). The bottom sediment has a high capacity to accumulate and integrate low concentrations of heavy metals over time (Islam et al., 2018; Suresh et al., 2012). Heavy metals associated with bottom sediments can easily be released into the water column through mechanical disturbances and bioturbation (Shafie et al., 2014) or changes in temperature, pH, and dissolved oxygen conditions (Huang et al., 2017). Therefore, sediment can be a source of heavy metals that will be released into the water column in the future.

Fine sediment particulate is an essential component of the aquatic environment (Dahms et al., 2017; Saroop and Tamchos, 2021), and many aquatic organisms depend on sediment quality for their well-being (Vivien et al., 2020). However, if it is contaminated with heavy metals, sediment may pose risks to aquatic organisms. This can occur through bio-accumulation or biomagnification of heavy metals (Suresh et al., 2012), which may lead to changes in organism reproduction cycles, diversity, and density of benthic micro-invertebrates (Dalu et al., 2017; Li et al., 2020), organ histopathology in aquatic fauna (Khan et al., 2018), and eventual death. It has, however, been observed that aquatic organisms respond in different ways to heavy metal contamination (Brito et al., 2015). For example, microorganisms are more sensitive than other aquatic flora and fauna (Li et al., 2020). Research is essential to understand the severity of sediment heavy metal contamination and its potential ecological risks.

In South Africa, sediment contamination by heavy metals is increasingly being investigated in the context of water quality and ecological studies (Abia et al., 2015; Addo-Bediako et al., 2021; Dahms et al., 2017;

* Corresponding author.
E-mail address: munyaradzi.manjoro@spu.ac.za (M. Manjoro).

https://doi.org/10.1016/j.heliyon.2022.e12499
Received 20 August 2022; Received in revised form 3 November 2022; Accepted 13 December 2022

Dalu et al., 2017; Edokpayi et al., 2017, 2022). The focus of studies in South Africa has been on urban areas, ecologically sensitive waterways and wetlands, and regions with a strong anthropogenic influence from mining and agriculture. To extract heavy metals, total digestion techniques are mostly used. The most reported sediment contaminants are Cd Cr, Cu, Ni, Pb, and Zn. Various indices and sediment quality guidelines (SQGs) for freshwater and marine ecosystems are used to assess the severity of heavy metal contamination and predict the potential ecological risk. Despite the many studies conducted in the country, there are some regions without data. For example, there is very little information on sediment-associated heavy metal contamination for rivers along urban areas in the North West province. Baseline information on heavy metals will help with future monitoring of heavy metals. It will also enable environmental managers and policymakers to identify the heavy metals of concern, and assess the severity of the contamination and its potential impact on aquatic ecosystems and human health.

The current study was carried out in the city of Mahikeng in the North West province of South Africa, which faces serious water challenges in terms of both scarcity and quality. Previous studies evaluating water pollution in the Molopo River focused on the total metal concentration and distribution in the water column (Mathuthu and Olobatoke, 2016; Nyirenda et al., 2013). The purpose of the current study was to explore the severity of sediment-associated heavy metal contamination along selected reaches of the Molopo River and to assess the ecological risk it can pose to aquatic organisms. The total concentration of As, Cd Cr, Cu, Hg, Ni, Pb, and Zn in riverbed sediments was analysed as they are commonly reported in pollution studies in the city (Munyati 2016; Nyirenda et al., 2013). Various indices and SQGs were used to express heavy metal levels and predict potential ecological impacts. The study may provide baseline information that can be used for future monitoring of heavy metal contamination in the study area.

2. Materials and methods

2.1. Study area

Mahikeng (25°51′56″S 25°38′37″E) is the capital of the North West province of South Africa. The Molopo River is an ephemeral river that passes through the city (Figure 1). The river originates from a spring called the Molopo Eye, east of the city. From there, the river flows mostly through extensively grazed rangeland. According to the North West Parks Board (interview, 2020), the flow of water from the source has not reached Mahikeng in more than a decade. Therefore, the flow observed in Mahikeng is mainly from broken water pipes and return flows from wastewater treatment plants (Van Vuuren, 2013). Four reservoirs (Cooke's Lake, Lotlamoreng Dam 1, Lotlamoreng Dam 2, and Modimola Dam, also known as Setumo Dam) were built across the river within the city limits. The Modimola Dam is located downstream of the city and feeds the Mmabatho Water Treatment Plant. It is also used for recreational fishing. Two wastewater treatment plants discharge treated effluent into the Molopo River. Furthermore, a cement factory is located at Slurry, 20 km to the north-east of the city. The geology around Mahikeng is dominated by dolomitic limestone with abundant calcite ($CaCO_3$) and aragonite (Ca, Sr, Pb, Zn) CO_3 (Munyati, 2016). The soil type is classified as Hutton form (Materechera, 2014). The climate is tropical semi-arid, with a mean annual precipitation of 539 mm and a temperature that ranges from 12 °C to 27 °C (Thomas et al., 2007).

2.2. Sample collection, preparation, and analysis

Riverbed sediment (up to 5 cm depth) was sampled during the dry season month of October in 2018, from selected sites along the Molopo River (Figure 1). A plastic scoop (Shafie et al., 2014) was used to collect three to five sediment samples of the same size at each location. The material was composited on site (Ali et al., 2022) before it was placed in sealed polyethylene sampling bags and transported to the laboratory for processing within 2 h. Sampling was not possible upstream of Cooke's Lake (Figure 1), because the river was dry.

All glassware and crucibles used were acid-washed (10% HNO_3 for 24 h) prior to use. The sediment was oven-dried at 40 °C for 48 h. The dried material was manually disaggregated with mortar and pestle and screened through a 63 μm aperture sieve to capture the fine-grained fraction. This sediment fraction has a strong association with heavy metals and other contaminants (De Groot et al., 1982). Each sample was digested according to EPA Method 3051A (US Environmental Protection Agency, 1994). Exactly 200 mg of the sample was placed in a Teflon tube and 9 ml 65% nitric acid (HNO_3) and 3 ml 32% hydrochloric acid (HCL) was added, the tube was closed, and placed in a microwave digestion system (Milestone, Ethos UP, Maxi 44). A period of 20 min allowed the system to reach 1 800 MW at a temperature of 200 °C, which was maintained for 15 min. The sample was brought to a final volume of 50 ml after cooling, before it was analysed for As, Cd Cr, Cu, Hg, Ni, Pb and Zn using inductively coupled

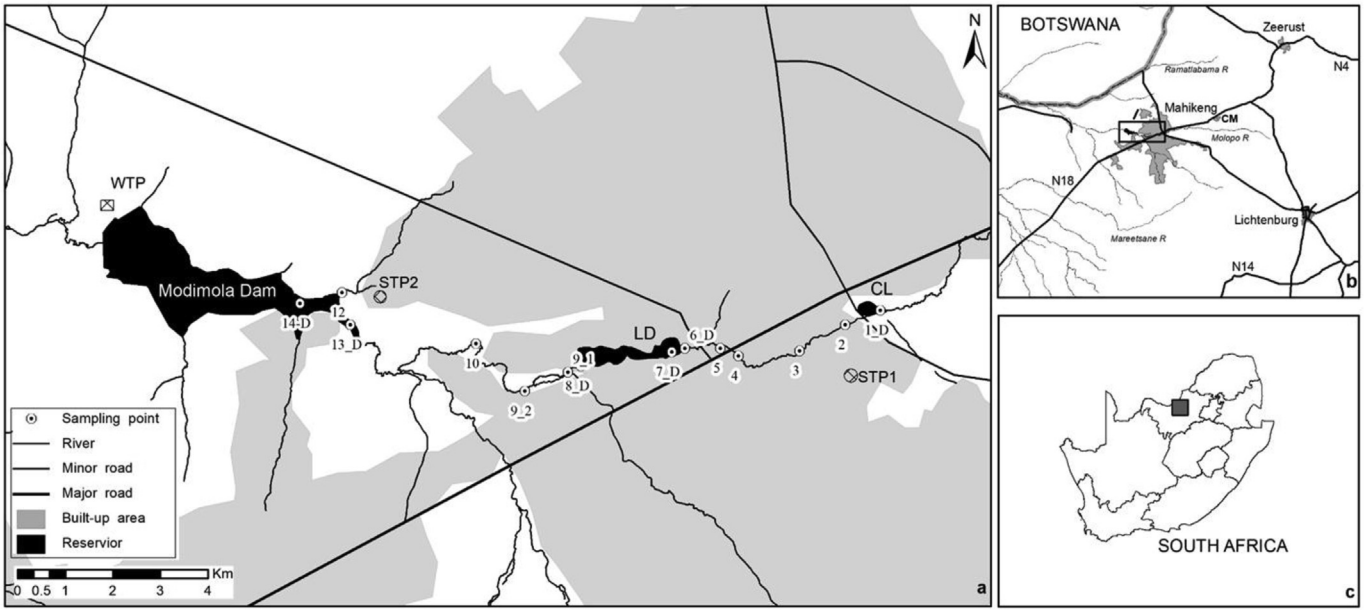

Figure 1. Map of the study area. LD indicates Lotlamoreng Dam 1 and 2, CL, Cooke's Lake, CM, cement factory, and STP, sewage treatment plant.

plasma mass spectrometry (ICP-MS) (NexION 300Q, PerkinElmer, US). Instrument optimisation was achieved using a solution containing Li, Y, Ce and Tl (1 ppb) for standard low-oxide/low interference levels (≤1.5%) while maintaining high sensitivity across the mass range. Instrument conditions are displayed in Table 1.

A certified mixed multi-element stock standard solution (De Bruyn Spectroscopic Solutions, South Africa) was used to calibrate the ICP-MS. For quality control, an ultrapure water blanks and certified reference material (Spex Certi Prep®, USA) were used. For all the investigated heavy metals, relative standard deviations were less than 5 %.

The total organic carbon (TOC) content of each sediment sample was measured using the low-temperature loss-on-ignition (LOI) (550 °C) procedure described by Martínez et al. (2018). The organic carbon content was expressed as percentage weight loss.

2.3. Assessing the contamination status of the sediment

Various indices have been successfully used to assess heavy metal contamination of soil and sediments, predict the potential ecological risk, and infer the anthropogenic or natural origin of heavy metals. To assess the level of contamination from an individual heavy metal, Contamination Factor (CF) (Eq. (1)) was used. The CF assesses the level of contamination by a given metal compared to pre-industrial reference levels (Hakanson, 1980). However, various studies used measured heavy metal baseline values from an area with geologically similar material (control) (Siddiquee et al., 2012) or average crustal composition (Addo-Bediako et al., 2021). This index is defined by Hakanson (1980) as follows:

$$CF = \frac{C_{(metal)}}{C_{(background)}} \quad (1)$$

where $C_{(metal)}$ is the concentration of the heavy metal of interest measured at a particular site. $C_{(background)}$ is the concentration of heavy metal measured at a reference or control site. Average shale values (Ali et al., 2022; Turekian and Wedepohl, 1961) were used, because of the absence of local or regional reference values for the heavy metals of interest. Similar studies in South Africa (Addo-Bediako, 2020; Edokpayi et al., 2017) and elsewhere globally (Cui et al., 2019; Sekabira et al., 2010) used this approach when local or regional reference values were not available. There are four levels of contamination according to the CF: CF < 1 – low contamination, 1 ≤ CF < 3 – moderate contamination, 3 ≤ CF < 6 – considerable contamination, and CF ≤ 6 – very high contamination (Kowalska et al., 2018).

The enrichment factor (EF) (Li et al., 2013; Sutherland, 2000) is a pollution index that is used to assess whether heavy metal contamination in each sediment sample is of natural (EF < 2) or anthropogenic origin (EF > 2). The EF compares the concentration of each heavy metal with the abundance of that metal at an uncontaminated baseline (Eq. (2)) (Li et al., 2013).

$$EF = \left(\frac{\frac{M_{sample}}{Fe_{sample}}}{\frac{M_{baseline}}{Fe_{baseline}}} \right) \quad (2)$$

Table 1. ICP-MS instrument conditions.

Parameter	Value
Forward power	1 550 W
Plasma gas flow	15 L/min
Nebuliser gas flow	1.2 L/min
Sampling depth	8 mm
Spray camber temp	2 °C

where M_{sample} is the level of the selected heavy metal measured in the sample and Fe_{sample} is the iron concentration in each sample. Typically, iron or aluminium are used as normalising factors (Kumar et al., 2018), due to their low occurrence variability in the environment (Kowalska et al., 2018). The $M_{baseline}$ is the measured reference for each heavy metal, which, in this study, was estimated from average shale values, as explained earlier. The EF also assesses the level of enrichment of each heavy metal. The following EF classes were used for interpretation: EF < 2 – no enrichment, 2 ≤ EF < 5 – moderate enrichment, 5 ≤ EF < 20 – significant enrichment, 20 ≤ EF < 40 – very high enrichment and ≥40 – extremely high enrichment (Li et al., 2013).

The pollution load index (PLI) (Abdullah et al., 2015; Tomlinson et al., 1980) indicates the number of times the heavy metal concentration in the sediment exceeds the average uncontaminated baseline concentration. The PLI was used to assess whether each sample was polluted or unpolluted, considering all heavy metals together. The PLI value provides an overall indication of heavy metal toxicity in a particular sample (Chan et al., 2001). The PLI was calculated using Eq. (3).

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n} \quad (3)$$

where CF is the contamination factor for each heavy metal under consideration, calculated according to Eq. (1), and n is the number of heavy metals under consideration. The following classes of PLI were used for interpretation: 1 > PLI – no contamination, PLI = 1 – only baseline levels of contamination, and 1 < PLI – deterioration of site quality (Kowalska et al., 2018).

2.4. Assessing the potential ecological risk of sediment

South Africa does not have national SQGs for freshwater ecosystems. Therefore, the threshold effect concentration (TEC) and probable effect concentration (PEC) SQGs (MacDonald et al., 2000; Vivien et al., 2020) were used. These SQGs are consensus-based and were developed from ecotoxicological and ecological data from different regions of the world and are, thus, applicable to any area where local SQGs are not available. The TEC reflects the heavy metal concentration below which adverse ecological impacts are not expected to occur (MacDonald et al., 2000). Concentrations equal to or above the TEC but less than the PEC signify the limits within which ecological impacts rarely occur. Concentrations above the PEC represent a range in which negative ecological impacts are likely to occur frequently (Vivien et al., 2020).

Furthermore, the potential ecological risk index (PERI) (Decena et al., 2018; Hakanson, 1980) was used to predict the likely impact of heavy metals on aquatic organisms. The index represents the potential ecological risk caused by the contamination of all heavy metals together considering the synergy, toxic level, and ecological sensitivity of each heavy metal (Kowalska et al., 2018). It is calculated using Eq.4 and Eq.5.

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

$$E_r^i = T_r^i \times C_r^i \quad (5)$$

where n is the number of heavy metals, i is the heavy metal of interest in the sediment, E_r^i is the potential ecological risk coefficient of a single heavy metal and T_r^i is the toxic response factor for the heavy metal of interest. The following toxic response factors were used: Cu = Pb = Ni = 5; Hg = 40; As = 10, Cd = 30, Cr = 2 and Zn = 1 (Hakanson, 1980). C_f^i represents the CF for each heavy metal i (see Eq. (1)). The E_r^i was interpreted as follows: $E_r^i < 40$ – low risk, $40 \leq E_r^i \leq 80$ – moderate risk, $80 \leq E_r^i < 160$ – considerable risk, $160 \leq E_r^i < 320$ – high risk and $E_r^i \geq 320$ – very high risk (Decena et al., 2018). The following PERI classes were recognised: PERI <90 – low risk, 90 ≤ PERI <180 – moderate risk, 180 ≤ PERI <360 – strong risk, 360 ≤ PERI <720 – very strong risk, and ≥PERI

720 – very high risk (Hakanson, 1980). The conjunctive use of SQGs and potential ecological risk indices offered an opportunity to assess the consistency of the prediction of potential ecological risk.

2.5. Statistical analyses

The arithmetic mean and standard error of the total heavy metal concentrations were calculated. An independent sample t-test was performed to assess whether each heavy metal concentration was significantly different from the corresponding average shale values. Statistical significance was tested at 0.05 for all cases. Multivariate statistics, which are commonly used to evaluate associations between sediment heavy metal compositions, were also used (Kumar and Fulekar, 2019). Pearson correlation was used to determine the associations between the heavy metals and to identify their sources. Principal component analysis (PCA) with Varimax rotation was used to extract key components of the data responsible for explaining variation in heavy metal concentrations and to infer whether they had a common source (Zhou et al., 2008). Hierarchical cluster analysis (HCA) using Ward's method, with Euclidian distance as a measure of similarity (Kumar et al., 2018), was used to assess the degree of similarity between heavy metals, to infer their potential source. Site knowledge was then used to infer the most likely origin of the heavy metals. All analyses were performed in the Statistical Package for Social Sciences (SPSS) v. 26.0.

3. Results and discussion

3.1. Total concentration of heavy metals

The total concentration of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn is shown in Table 2. Heavy metal concentrations in the sediment decreased in the following order: Zn > Cr > Cu > Ni > Pb > As > Hg > Cd. The mean concentrations of Cu and Zn significantly exceeded the corresponding average shale values ($p < 0.05$) in the study. The Cr, Cu, Pb and Zn concentrations were significantly higher than average shale values ($p < 0.05$) at selected upstream and downstream sites. The Cr concentrations at the upstream sites (M1_D, M2 and M3) were between 1.1 and 1.7 times higher than the average shale values, between 2.7 and 3.2 for Cu, 1.82 and 1.9 times for Pb and 1.38 and 3.9 times for Zn. M1_D represents CL, the most upstream dam sampling site, while M2 and M3 represent a site 100 m below a busy traffic route (R503) and a site downstream of a wastewater effluent outlet (STP 1), respectively. At M6_D (LD), Cu, Pb and Zn concentrations were 1.36, 1.39, and 1.78 times higher than the corresponding average shale values, respectively, while at M13_D (Modimola Dam), Cr, Cu and Hg concentrations were 1.3, 1.39 and 1.48 times higher, respectively. At M12 and M14_D Cr concentrations were between 1.16 and 1.19 times higher than average shale. These two sites were located downstream of STP 2. The number of times that heavy metal concentrations in a sediment sample exceeds the corresponding average reference background concentration provides an overall indication of the degree of contamination in that sample (Chan et al., 2001).

Analysis of the TOC content of each sample showed that it ranged from 2.33% to 4.78%. There was no significant correlation between the TOC content of the sediment and the concentration of any of the heavy metals.

3.2. Severity of sediment contamination by heavy metals

The CF, EF and PLI were used to assess the severity of heavy metal contamination of the sediment. The contamination level decreased in the following order: Cu > Zn > Cr > Pb > Ni > Hg > As > Cd. Furthermore, the level of contamination for the majority of the heavy metals was low ($CF < 1$) at most sampling sites (Figure 2). However, at the problem sites identified above, the CF suggested moderate ($1 CF < 3$) to considerable levels of contamination ($3 \leq CF < 6$) by Cr, Cu, Pb and Zn.

According to EF, the level of heavy metal enrichment was ranked as follows: Cu > Cr > Hg > Zn > Cd > Ni > Pb > As. It was also evident that there was generally no anthropogenic enrichment ($EF < 2$) of heavy metals at most sites (Figure 3). Cu had the highest EF values in the study area, between 3.81 and 9.19 at M1_D, M2 and M3, and 4.02 at the downstream site (M13_D). It should also be noted that all sampling sites from M7_D (LD) to 14_D (Modimola Dam) showed Cr enrichment. This strongly implies that the source of Cr was most likely related to diffuse or point sources around or upstream of the LD. The EF also suggests that the observed enrichment in Cd, Cr, Cu and Zn at the most contaminated

Table 2. Heavy metal concentration and TOC of the sediment.

Sample ID	Concentration (mg/kg)									TOC (%)
	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn	
M1_D	2.18	0.36	99.30*	97.87*	24 410	0.25	48.64	36.63	279.10*	3.15
M2	2.06	0.41	100.10*	141.20*	17 660	0.33	41.42	36.79	341.50*	3.08
M3	2.03	0.43	151.90*	170.90*	25 010	0.41	64.58	36.52	349.80*	4.78
M4	2.23	0.20	71.77	33.70	14 030	0.09	36.72	37.56	130.90*	4.74
M5	0.95	0.05	47.73	27.60	17 430	0.29	29.45	8.33	25.57	4.75
M6_D	1.64	0.23	91.21	61.36*	8 908	0.19	36.95	27.74*	169.10*	3.28
M7_D	0.88	0.05	67.97	18.13	9 619	0.06	20.88	9.01	27.54	2.33
M8_D	0.84	0.04	70.71	16.39	11 110	0.11	26.24	5.69	16.52	2.97
M9_1	0.79	0.04	80.30	15.07	11 110	0.15	27.11	7.66	23.81	2.88
M9_2	0.88	0.06	87.83	19.75	14 570	0.07	25.56	7.04	22.96	4.48
M11	1.04	0.07	91.33	24.00	17 870	0.05	31.06	9.17	28.89	2.35
M12	1.31	0.06	107.00*	32.05	14 750	0.04	38.26	8.16	26.57	2.84
M13_D	1.24	0.12	117.20*	62.37*	19 510	0.59*	33.61	8.55	82.50	2.86
M14_D	4.53	0.05	113.80*	25.37	24 410	0.04	35.09	9.77	27.77	2.66
Mean ± SE	1.61 ± 0.27	0.16 ± 0.04	92.73 ± 6.87	53.27 ± 13.26	16456.93 ± 1457.56	0.19 ± 0.04	35.40 ± 2.96	17.76 ± 3.63	110.90 ± 33.34	
Average shale[a]	13.00	19.00	90.00	45.00	47 200.00	0.40	68.00	20.00	95.00	

A sample ID with a D suffix was collected from a reservoir.
* values significantly higher than average shale value.
[a] Turekian and Wedepohl (1961).

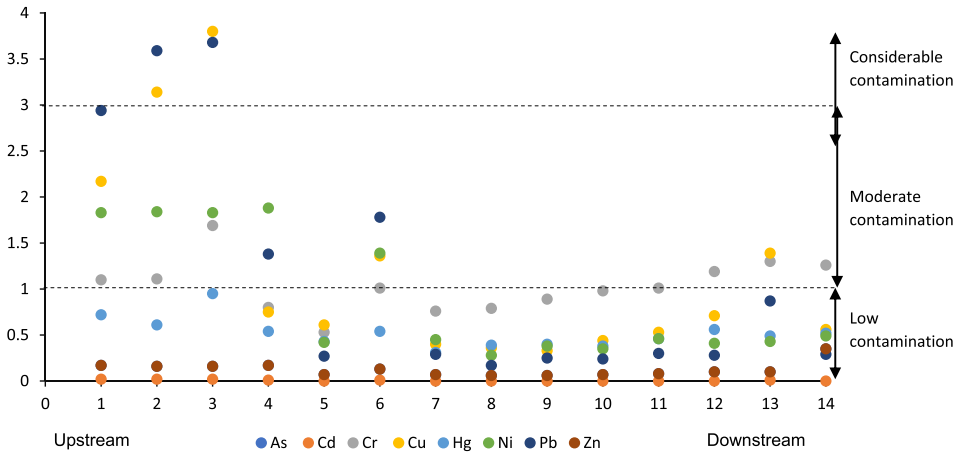

Figure 2. Sediment contamination factor plot. Sampling sites are labelled from 1 to 14, representing M1_D, M2, M3, M4, M5, M6_D, M7_D, M8_D, M9_1, M9_2, M11, M12, M13_D and M14_D, respectively.

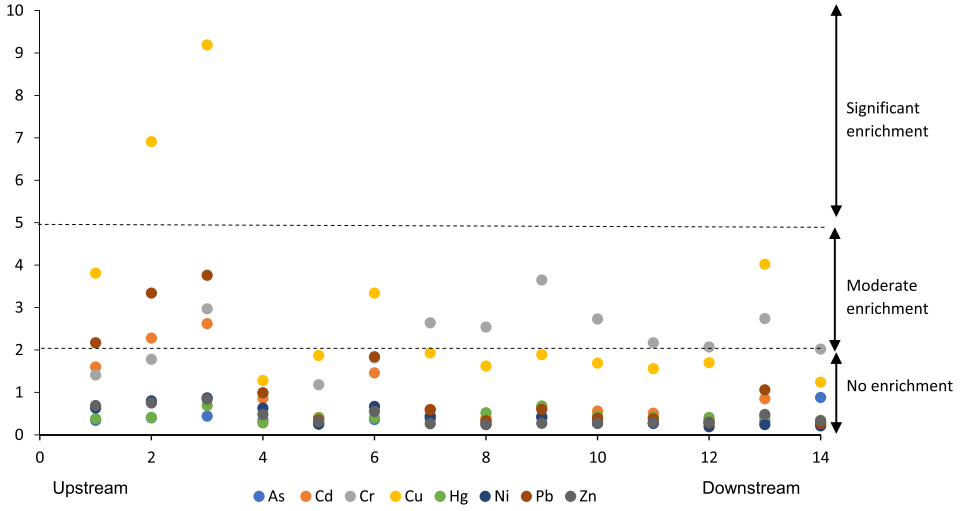

Figure 3. Sediment enrichment factor plot. Sampling sites are labelled from 1 to 14 representing M1_D, M2, M3, M4, M5, M6_D, M7_D, M8_D, M9_1, M9_2, M11, M12, M13_D and M14_D, respectively.

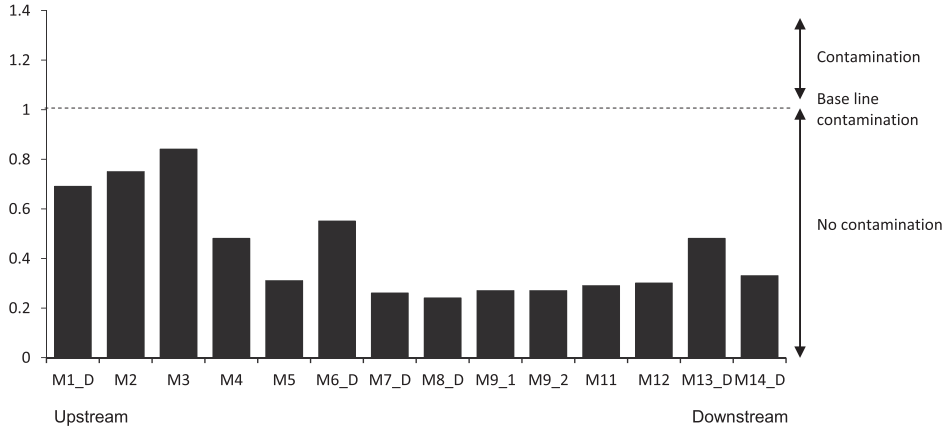

Figure 4. The PLI values for each sampling station.

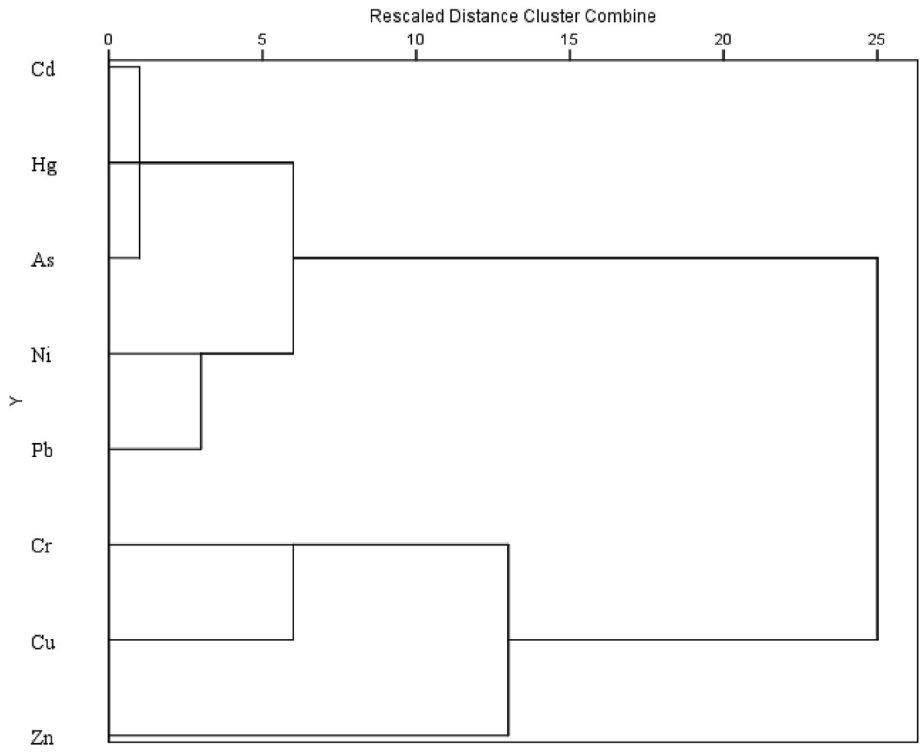

Figure 5. The dendrogram of heavy metal concentrations.

upstream and downstream sites was due to anthropogenic activities (EF < 2), while, at the rest of the sites, natural enrichment (EF < 2) is implied. Therefore, some heavy metals had either natural or anthropogenic enrichment, depending on location. The natural enrichment of Pb and Zn at most sampling sites can be explained by the dominant geology of the study area. According to Munyati (2016), the main bedrock around Mahikeng contains aragonite ((Ca, Sr, Pb, Zn) CO_3), which is rich in Pb and Zn, among other metals.

Table 3. Comparison of heavy metal concentrations (mg/kg) and SQGs.

	Sample ID	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Heavy metal concentration in sediment	M1_D	2.18	0.36	99.3	97.87	0.25	48.64	36.63	279.1
	M2	2.06	0.41	100.1	141.2	0.33	41.42	36.79	341.5
	M3	2.03	0.43	151.9	170.9	0.41	64.58	36.52	349.8
	M4	2.23	0.2	71.77	33.7	0.09	36.72	37.56	130.9
	M5	0.95	0.05	47.73	27.6	0.29	29.45	8.33	25.57
	M6_D	1.64	0.23	91.21	61.36	0.19	36.95	27.74	169.1
	M7_D	0.88	0.05	67.97	18.13	0.06	20.88	9.01	27.54
	M8_D	0.84	0.04	70.71	16.39	0.11	26.24	5.69	16.52
	M9_1	0.79	0.04	80.3	15.07	0.15	27.11	7.66	23.81
	M9_2	0.88	0.06	87.83	19.75	0.07	25.56	7.04	22.96
	M11	1.04	0.07	91.33	24	0.05	31.06	9.17	28.89
	M12	1.31	0.06	107.00	32.05	0.04	38.26	8.16	26.57
	M13_D	1.24	0.12	117.20	62.3	0.59	33.61	8.55	82.5
	M14_D	4.53	0.05	113.80	25.37	0.04	35.09	9.77	27.77
Minimum		0.79	0.04	47.73	15.07	0.04	20.88	5.69	16.52
Maximum		4.53	0.43	151.9	170.9	0.59	64.58	37.56	349.8
Mean ± SE		1.61 ± 0.27	0.16 ± 0.04	92.73 ± 6.87	53.27 ± 13.26	0.19 ± 0.04	35.40 ± 2.96	17.76 ± 3.63	110.90 ± 33.34
SQGs[a]	TEC	9.79	0.99	43.4	31.6	0.18	22.7	35.8	121
	PEC	33.0	4.99	111	149	1.06	48.6	128	459
% of samples < TEC		100	100.0	0.0	50.0	57.1	7.1	71.4	64.3
% of samples between TEC and PEC		0	0	78.57	42.86	42.86	78.57	28.57	35.71
% of samples > PEC		0	0.0	21.4	7.1	0.0	14.3	0.0	0.0

TEC: threshold effect concentration.
PEC: probable effect concentration.
[a] MacDonald et al. (2000).

Table 4. Potential ecological risk assessment of sediment.

Ecological risk for single metal (E_r^i)										
Samples ID	Cr	Ni	Cu	Zn	As	Cd	Hg	Pb	PERI	Grade of PERI
M1_D	2.21	3.58	10.87	2.94	1.68	0.57	24.66	9.16	3.58	low risk
M2	2.22	3.05	15.69	3.59	1.59	0.64	33.29	9.20	3.05	low risk
M3	3.38	4.75	18.99	3.68	1.56	0.67	41.04	9.13	4.75	low risk
M4	1.59	2.70	3.74	1.38	1.72	0.31	9.17	9.39	2.70	low risk
M5	1.06	2.17	3.07	0.27	0.73	0.08	28.61	2.08	2.17	low risk
M6_D	2.03	2.72	6.82	1.78	1.26	0.37	19.13	6.94	2.72	low risk
M7_D	1.51	1.54	2.01	0.29	0.67	0.08	5.89	2.25	1.54	low risk
M8_D	1.57	1.93	1.82	0.17	0.64	0.06	11.25	1.42	1.93	low risk
M9_1	1.78	1.99	1.67	0.25	0.61	0.07	14.94	1.92	1.99	low risk
M9_2	1.95	1.88	2.19	0.24	0.68	0.09	6.86	1.76	1.88	low risk
M11	2.03	2.28	2.67	0.30	0.80	0.11	4.97	2.29	2.28	low risk
M12	2.38	2.81	3.56	0.28	1.01	0.09	3.94	2.04	2.81	low risk
M13_D	2.60	2.47	6.93	0.87	0.95	0.18	58.67	2.14	2.47	low risk
M14_D	2.53	2.58	2.82	0.29	3.48	0.07	3.89	2.44	2.58	low risk

Figure 4 shows the variation of the PLI at the sampling sites. The PLI values were highest at the first three upstream sites (M1_D, M2 and M3), followed by M6_D, M4, and M13_D. However, the PLI values were less than unity, suggesting that there was no pollution at the study sites (Abdullah et al., 2015). This finding is explained by the fact that the PLI assesses the overall status of pollution per each sampling site, considering all heavy metals (Kowalska et al., 2018), not only those that have high concentrations.

In summary, Cu, Cr, and Zn were identified as the heavy metals of concern in the study area. This is also reflected in the results of the cluster analysis (Figure 5), where the three heavy metals formed a statistically different cluster.

3.3. Potential ecological risk assessment of sediments

Comparison of heavy metal concentrations with the TEC and PEC SQGs (Table 3) shows that none of the samples had Cr concentrations above the TEC, while 21.4% of the samples were above the PEC. About 42.86% of the samples had a Cu concentration between the TEC and the PEC, and 7.1% of the samples had Cu concentrations above the PEC. Approximately 98.57% of the samples had Ni concentrations between the TEC and the PEC, and 14.3% above the PEC. Concentrations above the PEC pose a potential ecological risk. Thus, Cr, Cu, and Ni were identified as likely to have harmful effects on aquatic organisms in the study area. The results also showed that, although the contamination indices did not indicate that Ni was of concern in the study area, it was singled out by the SQGs. This finding can be explained by the ecotoxicological properties of Ni, which manifest even at low concentrations (Naz et al., 2022).

The potentially negative impact posed by heavy metal contamination was also assessed using indices (Table 4). The E_r^i was below 40 at all sampling sites. In turn, the PERI for all sampling sites was below 90. Both the E_r^i and PERI suggest low potential ecological risk. These results mirror those of Decena et al. (2018), in whose study the TEC and PEC SQGs were able to predict heavy metal concentrations that posed a risk to aquatic organisms in an urban river, though PERI indicated a low potential ecological risk.

3.4. Source of heavy metals

Using multivariate statistics, we inferred the potential sources of heavy metals. The Pearson correlation coefficients (Table 5) showed that there were significant positive correlations ($p < 0.05$) between Cd, Cr, Cu, Ni, Pb and Zn, except for As and Hg. On the other hand, the PCA extracted two components (Figure 6) that explained 82.16% of the total variance in the data. The first component retained 68.54% of the data variation and was associated with Cd, Cr, Cu, Ni, Pb, and Zn. The second component explained 13.62% of the variation and was associated with As and Hg.

The correlation analysis and PCA results were consistent. The results suggest similarity in the anthropogenic source of Cd, Cr, Cu, Hg, Ni, Pb, and Zn. The high concentrations of Cr, Cu, Pb, and Zn in M1_D (CL) may be related to sediment mobilised from areas affected by cement dust fallout upstream of this site, where a cement factory is located. However, because it was not possible to collect samples upstream of CL, we can only identify it as a possibility. On the other hand, the high concentrations of Cr, Cu, Pb and Zn also found in M2 and M3 can be attributed to vehicle traffic (vehicle exhaust, wear and tear of brake pads and tyres) and wastewater. M2 is located 100 m below a busy traffic route (R503) that connects Johannesburg and Botswana. Munyati (2016) provides evidence of contamination by Fe, Mn, Zn, Pb, Ni, Cu, Cr, and Cd along the main routes in Mahikeng and, particularly, the R503, near where the M2 sampling site is located. However, the levels of contamination observed

Table 5. Pearson correlation coefficients of all heavy metals.

	Cr	Ni	Cu	Zn	As	Cd	Hg	Pb
Cr	1.000							
Ni	**0.766**	1.000						
Cu	**0.682**	**0.879**	1.000					
Zn	**0.551**	**0.844**	**0.959**	1.000				
As	0.457	0.447	0.287	0.321	1.000			
Cd	**0.534**	**0.846**	**0.944**	**0.997**	0.314	1.000		
Hg	0.437	0.495	**0.661**	**0.554**	-0.008	**0.534**	1.000	
Pb	0.353	**0.759**	**0.777**	**0.908**	0.395	**0.928**	0.342	1.000

Bold: correlation is significant at the 0.05 level (2-tailed).

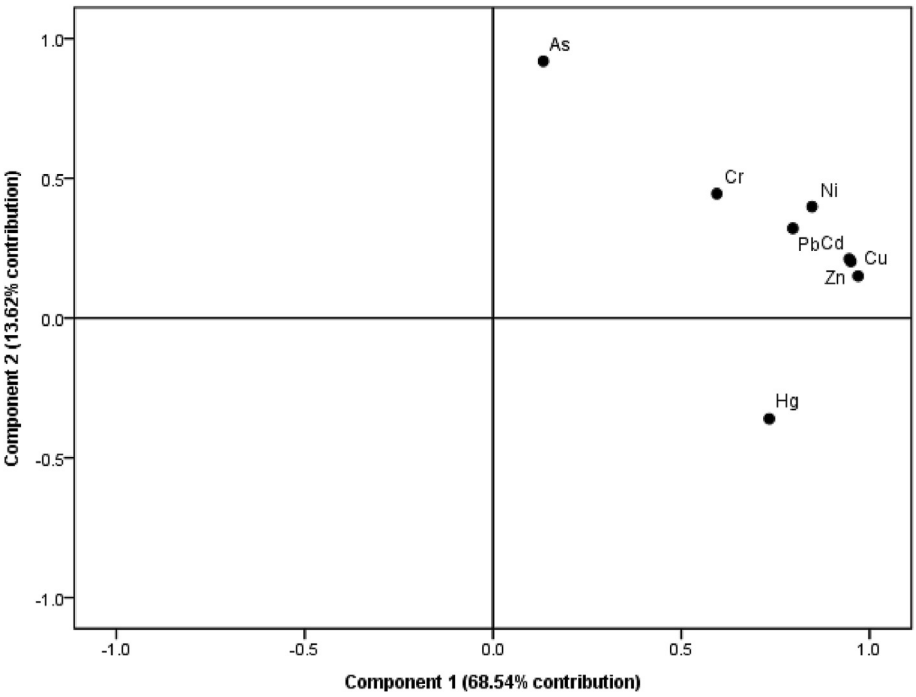

Figure 6. PCA plot of heavy metals in Varimax rotated space.

by Munyati (2016) were lower than those of the current study. This could be explained by the high capacity of sediment to integrate low concentrations of heavy metals over time. M3 is located downstream of both the R503 and STP 1. Thus, this site is likely to be affected by heavy metals related to both traffic and wastewater effluent. This conclusion also applies to the observations at M12, M13_D, and M14_D, which were most likely affected by STP 2. M6_D, which is the only site in the middle of the study area with a high concentration of Cu, Cr, Pb and Zn could be related to runoff from various urban surfaces in the city. Contamination by these heavy metals has generally been associated with various activities that include deterioration of paint work, electroplating, vehicle traffic and sewage and industrial effluent (Ali et al., 2022; Decena et al., 2018).

4. Limitations

Sediment sampling upstream of the city could have provided more precise data on the impact of the cement factory. However, this was not possible, because the river has been dried for several years. To mitigate this limitation, sediment sampling was carried out from the most upstream available water body, Cooke's Lake. Furthermore, the current study was based on total metal concentrations rather than specific chemical species of each heavy metal. Although total concentrations of heavy metals are widely used for this kind of research, the analysis of specific heavy metal species could have provided information on mobility, bioavailability, and related ecotoxicity. However, that approach was not suitable for an exploratory investigation such as this study. Future studies may consider sequential extraction to identify specific chemical species of heavy metals of interest.

5. Conclusions

The results showed that Cr, Cu, Pb, and Zn were the heavy metals of concern in the study area. Furthermore, according to the consensus-based SQGs, Cr, Cu, and Ni were likely to cause harm to bottom-dwelling organisms in the Molopo River and the associated dams. Multivariate statistics suggested that Cd, Cr, Cu, Pb and Zn in the study area were mostly associated with anthropogenic sources such as industrial and wastewater effluent, vehicle traffic, and general urban runoff. However, there was not enough information to link heavy metal contamination to the cement factory, upstream of the study area. Future research and monitoring in the study area should focus on the heavy metals that cause concern because of their concentrations (Cr, Cu, Pb, and Zn) and those that are likely to cause ecological harm (Cr, Cu, and Ni). A large effort by authorities is needed to improve industrial and waste-water effluent, which are the main anthropogenic sources of heavy metals in the study area. Although the current study was exploratory, the results provide a better understanding of the heavy metal contamination of sediments in the study area. Case studies of this type, even at the local scale, are necessary to inform decision makers about the heavy metals that affect the area, the level of contamination, and the degree of risk to aquatic ecosystems. This baseline information is necessary to design monitoring programs, inform remedial measures, and stimulate further research. At larger spatial scales, many such studies provide suitable information for policy making to protect waterways and aquatic ecosystems.

Declarations

Author contribution statement

Chaka Mohajane, MSc: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Munyaradzi Manjoro, PhD: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interest's statement

The authors declare no competing interests.

Additional information

No additional information is available for this paper.

Acknowledgements.

The authors would like to thank the reviewers for useful comments that improved the manuscript.

References

Abdullah, M.Z., Louis, V.C., Abas, M.T., 2015. Metal pollution and ecological risk assessment of Balok River sediment, Pahang Malaysia. Am. J. Environ. Eng. 5 (3A), 1–7.

Abia, A.L.K., Ubomba-Jaswa, E., Momba, M.N.B., 2015. Impact of seasonal variation on Escherichia coli concentrations in the riverbed sediments in the Apies River, South Africa. Sci. Total Environ. 537, 462–469.

Addo-Bediako, A., 2020. Assessment of heavy metal pollution in the Blyde and Steelpoort rivers of the Olifants river system, South Africa. Pol. J. Environ. Stud. 29 (5), 3023–3029.

Addo-Bediako, A., Nukeri, S., Kekana, M., 2021. Heavy metal and metalloid contamination in the sediments of the Spekboom River, South Africa. Appl. Water Sci. 11, 133.

Ali, M.M., Rahman, S., Islam, M.S., Rakib, M.R.J., Hossen, S., Rahman, M.Z., Kormoker, T., Idris, A.M., Phoungthong, K., 2022. Distribution of heavy metals in water and sediment of an urban river in a developing country: a probabilistic risk assessment. Int. J. Sediment Res. 37, 173–187.

Brito, E.M.S., De la Cruz Barrón, M., Caretta, C.A., Goñi-Urriza, M., Andrade, L.H., Cuevas-Rodríguez, G., Malm, O., Torres, J.P.M., Simon, M., Guyoneaud, R., 2015. Impact of hydrocarbons, PCBs and heavy metals on bacterial communities in Lerma River, Salamanca, Mexico: investigation of hydrocarbon degradation potential. Sci. Total Environ. 521–522, 1–10.

Chan, L.S., Ng, S.L., Davis, A.M., Yim, W.W.S., Yeung, C.H., 2001. Magnetic properties and heavy-metal contents of contaminated seabed sediments of Penny's Bay, Hong Kong. Mar. Pollut. Bull. 42, 569–583.

Coulthard, T.J., Macklin, M.G., 2003. Modeling long-term contamination in river systems from historical metal mining. Geology 31 (5), 451–454.

Cui, S., Zhang, F., Hu, P., Hough, R., Fu, Q., Zhang, Z., An, L., Li, Y.-F., Li, K., Liu, D., Chen, P., 2019. Heavy metals in sediment from the urban and rural rivers in Harbin City, northeast China. Int. J. Environ. Res. Publ. Health 16, 4313.

Dahms, S., Baker, N.J., Greenfield, R., 2017. Ecological risk assessment of trace elements in sediment: a case study from Limpopo, South Africa. Ecotoxicol. Environ. Saf. 135, 106–114.

Dalu, T., Wasserman, R.J., Tonkin, J.D., Mwedzi, T., Magoro, M.L., Weyl, O.L.F., 2017. Water or sediment? Partitioning the role of water column and sediment chemistry as drivers of macroinvertebrate communities in an austral South African stream. Sci. Total Environ. 607–608, 317–325.

Decena, S.C.P., Arguilles, M.S., Robel, L.L., 2018. Assessing heavy metal contamination in surface sediments in an urban river in the Philippines. Pol. J. Environ. Stud. 27, 1983–1995.

De Groot, A.J., Zschuppel, K.H., Salomons, W., 1982. Standardization of methods of analysis for heavy metals in sediments. Hydrobiologia 91, 689–695.

Edokpayi, J.N., Nkhumeleni, M., Enitan-Folami, A.M., Olaniyi, F.C., 2022. Water quality assessment and potential ecological risk of trace metals in sediments of some selected rivers in Vhembe district, South Africa. Phys. Chem. Earth, Parts A/B/C 126, 103111.

Edokpayi, J.N., Odiyo, J.O., Popoola, E.O., Msagati, T.A.M., 2017. Evaluation of temporary seasonal variation of heavy metals and their potential ecological risk in Nzhelele River, South Africa. Open Chem 15, 272–282.

Hakanson, L., 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res. 14, 975–1001.

Huang, Y., Zhang, D., Xu, Z., Yuan, S., Li, Y., Wang, L., 2017. Effect of overlying water pH, dissolved oxygen and temperature on heavy metal release from river sediments under laboratory conditions. Arch. Environ. Protect. 43 (2), 28–36.

Islam, Md.S., Hossain, M.B., Matin, A., Islam Sarker, Md.S., 2018. Assessment of heavy metal pollution, distribution and source apportionment in the sediment from Feni River estuary, Bangladesh. Chemosphere 202, 25–32.

Khan, M.I., Khisroon, M., Khan, A., Gulfam, N., Siraj, M., Zaidi, F., Ahmadullah, Abidullah, Fatima, S.H., Noreen, S., Hamidullah, Shah, Z.A., Qadir, F., 2018. Bioaccumulation of heavy metals in water, sediments, and tissues and their histopathological effects on Anodonta cygnea (Linea, 1876) in Kabul River, Khyber Pakhtunkhwa, Pakistan. BioMed Res. Int. 2018, e1910274.

Kowalska, J.B., Mazurek, R., Gąsiorek, M., Zaleski, T., 2018. Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination – a review. Environ. Geochem. Health 40, 2395–2420.

Kumar, V., Sharma, A., Minakshi, Bhardwaj, R., Thukral, A.K., 2018. Temporal distribution, source apportionment, and pollution assessment of metals in the sediments of Beas river, India. Hum. Ecol. Risk Assess. 24, 2162–2181.

Kumar, P., Fulekar, M.H., 2019. Multivariate and statistical approaches for the evaluation of heavy metals pollution at e-waste dumping sites. SN Appl. Sci. 1 (11), 1–13.

Li, C., Quan, Q., Gan, Y., Dong, J., Fang, J., Wang, L., Liu, J., 2020. Effects of heavy metals on microbial communities in sediments and establishment of bioindicators based on microbial taxa and function for environmental monitoring and management. Sci. Total Environ. 749, 141555.

Li, G., Hu, B., Bi, J., Leng, Q., Xiao, C., Yang, Z., 2013. Heavy metals distribution and contamination in surface sediments of the coastal Shandong Peninsula (Yellow Sea). Mar. Pollut. Bull. 76, 420–426.

MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 39, 20–31.

Martínez, J.M., Galantini, J.A., Duval, M.E., López, F.M., Iglesias, J.O., 2018. Estimating soil organic carbon in Mollisols and its particle-size fractions by loss-on-ignition in the semiarid and semihumid Argentinean Pampas. Geoderma Reg 12, 49–55.

Materechera, S.A., 2014. Influence of agricultural land use and management practices on selected soil properties of a semi-arid savanna environment in South Africa. J. Arid Environ. 102, 98–103.

Mathuthu, M., Olobatoke, R., 2016. Assessment of heavy metals and radionuclide concentrations in Mafikeng wastewater treatment plant. J. Water Resour. Protect. 8 (1), 93–99.

Munyati, C., 2016. Geospatial analyses in support of heavy metal contamination assessments of soil and grass along highways at Mafikeng, South Africa. South Afr J Geomat 5, 393–408.

Naz, M., Ghani, M.I., Sarraf, M., Liu, M., Fan, X., 2022. Ecotoxicity of nickel and its possible remediation. In: Bhat, R.A., Tonelli, F.M.P., Dar, G.H., Hakeem, K. (Eds.), Phytoremediation. Academic Press, pp. 297–322.

Nyirenda, M., Ramoabi, T.E., Dzoma, B.M., Motsei, L.E., 2013. A comparative study of the levels of heavy metals in dam water, borehole water and cattle serum around the Modimola dam of the Mafikeng, North West province, South Africa. Life Sci. 10 (1), 3096–3100.

Saroop, S., Tamchos, S., 2021. Monitoring and impact assessment approaches for heavy metals. In: Kumar, S., Sharma, A., Cerdá, S. (Eds.), Heavy Metals in the Environment: Impact, Assessment, and Remediation. Elsevier, pp. 57–86.

Sekabira, K., Origa, H.O., Basamba, T.A., Mutumba, G., Kakudidi, E., 2010. Assessment of heavy metal pollution in the urban stream sediments and its tributaries. Int. J. Environ. Sci. Technol. 7, 435–446.

Shafie, N.A., Aris, A.Z., Haris, H., 2014. Geoaccumulation and distribution of heavy metals in the urban river sediment. Int. J. Sediment Res. 29, 368–377.

Siddiquee, N.A., Parween, S., Quddus, M.M.A., Barua, P., 2012. Heavy metal pollution in sediments at ship breaking area of Bangladesh. In: Subramanian, V. (Ed.), Coastal Environments: Focus on Asian Regions. Springer, Dordrecht, pp. 78–87.

Suresh, G., Sutharsan, P., Ramasamy, V., Venkatachalapathy, R., 2012. Assessment of spatial distribution and potential ecological risk of the heavy metals in relation to granulometric contents of Veeranam lake sediments, India. Ecotoxicol. Environ. Saf. 84, 117–124.

Sutherland, R.A., 2000. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ. Geol. 39, 611–627.

Thomas, D.S., Twyman, C., Osbahr, H., Hewitson, B., 2007. Adaptation to climate change and variability: farmer responses to intra-seasonal precipitation trends in South Africa. Clim. Change 83 (3), 301–322.

Tomlinson, D.L., Wilson, J.G., Harris, C.R., Jeffrey, D.W., 1980. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgol. Meeresunters. 33, 566–575.

Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the elements in some major units of the Earth's crust. GSA Bull 72 (2), 175–192.

US Environmental Protection Agency, 1994. *Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils, and oils.* SW-846: test methods for evaluation solid waste, physical and chemical methods. Office of Solid Waste 1–20.

Van Vuuren, L., 2013. Institutional conundrum sinking groundwater supply in North West town. Water Wheel 12, 17–19.

Vivien, R., Casado-Martínez, C., Lafont, M., Ferrari, B.J.D., 2020. Effect thresholds of metals in stream sediments based on in situ oligochaete communities. Environments 7, 31.

Zahra, A., Hashmi, M.Z., Malik, R.N., Ahmed, Z., 2014. Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah—feeding tributary of the Rawal Lake Reservoir, Pakistan. Sci. Total Environ. 470, 925–933.

Zheng, N.A., Wang, Q., Liang, Z., Zheng, D., 2008. Characterization of heavy metal concentrations in the sediments of three freshwater rivers in Huludao City, Northeast China. Environ. Pollut. 154 (1), 135–142.

Zhou, J., Ma, D., Pan, J., Nie, W., Wu, K., 2008. Application of multivariate statistical approach to identify heavy metal sources in sediment and waters: a case study in Yangzhong, China. Environ. Geol. 54, 373–380.