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DOI: 10.1007/s11270-023-06184-0

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Speciation of Selected Heavy Metals in Bottom Sediments of River Rwizi, Mbarara City, Uganda

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Received: 14 March 2022 / Accepted: 19 February 2023
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Abstract This research focused on chemical speciation of six heavy metals in the bottom sediments of River Rwizi in Mbarara City, Uganda. Heavy metals cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), and iron (Fe) and physicochemical parameters, namely pH, oxidation–reduction potential (ORP), and organic matter (OM), were assessed during wet and dry seasons. Sequential extraction procedure was applied to fractionate metals into six fractions: water-soluble, exchangeable, carbonate bound, Fe–Mn oxides bound, bound to organics, and residual fraction. Quantitative determination of heavy metals was carried out using flame atomic absorption spectrophotometer. Speciation results revealed that the potential mobility of heavy metals decreased from wet to dry season, and it was in the increasing order of $Zn > Cu > Cd > Pb > Ni > Fe$, in both seasons. Higher concentrations of heavy metals were present in their immobile chemical forms than in their potentially mobile chemical forms. The total mean contents in $mg\ kg^{-1}$ (except Fe in %) of the metals were Cd: 1.63 ± 0.21 ; Cu: 106.10 ± 23.22 ; Ni: 38.17 ± 6.07 ; Pb: 33.45 ± 3.33 ; Zn: 108.34 ± 30.51 ; Fe: 3.04 ± 0.75 , and Cd: 1.64 ± 0.23 ; Cu: 111.10 ± 27.36 ; Ni: 39.81 ± 7.90 ; Pb: 33.98 ± 3.63 ; Zn: 115.72 ± 31.64 ;

Fe: 3.08 ± 0.75 during wet and dry seasons, respectively. The geochemical accumulation indices of Cd, Cu, Pb, and Zn showed that the bottom sediments of River Rwizi ranged from unpolluted to severe polluted sediments, which implied anthropogenic input. Other parameters measured from wet to dry season were, pH: $6.8 \pm 0.35 - 6.21 \pm 0.08$; ORP: $308.4 \pm 44.7\ mV - 342.1 \pm 39.6\ mV$; OM: $2.0 \pm 0.35\% - 1.4 \pm 0.31\%$. Conclusively, it was found that heavy metals (Zn, Cu, and Cd) were significantly present in their potential mobile fractions alarming that they may pose serious human and environmental problems.

Keywords Mobility factor · River Rwizi · Sequential extraction · Enrichment factor · Müller geoaccumulation index

1 Introduction

Water bodies have been the most vulnerable environment to pollutants, especially heavy metals. Unlike other metals, some heavy metals can be detrimental at sufficiently lower concentrations to humans, animals, and the environment, when they exceed their permissible limits. For example, drinking water containing cadmium at concentrations above $0.003\ mg\ L^{-1}$ is considered unsafe to humans, and it may result to cancer of the kidneys (WHO, 2008). Natural phenomena and anthropogenic activities are the major sources of heavy metals in environmental matrices (Cox et al.,

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2017; Duan et al., 2019). Naturally, weathering processes coupled with soil erosion are responsible for the displacement of metals from their original crustal distribution to new environments such as lakes, rivers, and oceans. Moreover, the increasing use of metal-based products in agriculture, homes, construction, medicine, and electronics has led to the generation of large volumes of waste containing heavy metals that finally end up in water resources (Bradl, 2005; Duan et al., 2019). The United Nations World Water Development Report through the World Water Assessment Programme (WWAP, 2021) estimated that 80% of all industrial and municipal wastewater majorly rich in nutrients associated with pathogens are released into the environment without any prior treatment, with detrimental effects on human health and ecosystems. Unfortunately, metals are not biodegradable unlike other pollutants, but they accumulate in the environment. As a result, the heavy metals enter in living organisms through food chain, and eventually cause adverse effects to the victims (Ekwutosi et al., 2020; Sibomana et al., 2019).

Heavy metals in water bodies are in various chemical forms, namely dissolved metal compounds, as suspended colloidal or particulate matter, and metals associated with bottom sediment components (Achi et al., 2011; Eggleton & Thomas, 2004; Tessier et al., 1979). In fact, the level of metals in a water body is mainly shown by their concentrations in bottom sediments due to their ability to retain metals (Laing et al., 2007; Olutona et al., 2012). Bottom sediments are complex mixture of different components, mainly organic matter, clay minerals, sand, and inorganic components. It was found that heavy metals are associated with sediment components through processes, namely adsorption, complexation, precipitation, or co-precipitation (Duan et al., 2019; Jenne, 1968; Pentreath, 1985; Olutona et al., 2012). The physical and chemical changes associated with different forms of a chemical element in sediment are the key processes in the cycling of heavy metals in natural water over a range of time scale (Duan et al., 2019; Sibomana et al., 2019).

The presence of heavy metals in bottom sediments does not necessarily imply their availability to biota, because it is the chemical species or compounds of the metal that determine its bioavailability. Besides, the use of total concentration as a criterion to assess the potential effect of sediments contamination

implies that all chemical forms of a given metal have an equal impact on the environment. Such an assumption is not justifiable (Sibomana et al., 2019). Therefore, speciation is required to understand the fate of heavy metals in different environments (Olutona et al., 2012; Tessier et al., 1979). Chemical speciation is any analytical technique that extracts an element into its different chemical forms in separate fractions using appropriate reagents.

To date, various speciation techniques are used, and each of them is quite different from the other in terms of numbers of chemical fractions it extracts. In the 1970s, a successful first sequential extraction scheme was developed by Tessier et al. (1979), which is able to extract five distinct fractions as exchangeable, carbonate bound, bound to iron and manganese oxides (Fe–Mn oxides bound), bound to organics, and residual fraction. Later on, different authors (Aigberua et al., 2018; Kraus & Wiegand, 2006; Martley & Gulson, 2003) came up with modifications based on the scheme proposed by the former authors. In their extraction schemes, a water-soluble fraction was added as the most mobile fraction. Pueyo et al. (2001) developed extraction scheme that combines carbonates bound metals, exchangeable, and water-soluble metal fractions as an acid-soluble fraction. The advantage of this extraction scheme is that it is economically reasonable, because the scheme uses less reagents. However, it is time consuming and does not detail fractionation information. Despite the disadvantages, all extraction schemes furnish information on mobility and availability of the metals extracted. Indeed, speciation reveals metal fractions that are potential threat to the environment, and which become available when the environmental conditions change (Adhikari et al., 2018; Laing et al., 2007). Several factors such as pH, oxy-reduction/redox potential (ORP), organic matter (OM), temperature, dissolved oxygen, particle size, salinity, and other metal species are critical factors that dictate metal speciation in bottom sediments (Nakiguli et al., 2020; Peng et al., 2009; Saleem et al., 2015).

Bottom sediments of water bodies are important in aquatic ecosystems. They accommodate various biological species such as fish, plants, and benthic invertebrates (Eggleton & Thomas, 2004; Sekabira et al., 2011; Sekomo et al., 2011). However, due to pollution pressure exerted on water bodies by increasing anthropogenic activities in line with rapid

development of areas nearby, bottom sediments are getting polluted and thus, become a threat to aquatic and terrestrial life. This is because aquatic sediments act as sinks of environmental pollutants such as heavy metals (Duan et al., 2019; Muhammed, 1991; Olutona et al., 2012). Therefore, it is important to assess and monitor sediments' quality with time in order to take decisive measures to protect humans and environment from hazardous chemicals, especially heavy metals.

According to Uganda Bureau of Statistics (UBOS, 2016), Mbarara Municipality in southwestern Uganda was among the 20 largest urban centers of Uganda, with rapidly increasing population which is almost five folds since 1991–2014 population censuses. Until 2019, the municipality was reformed into Mbarara City. The city is currently composed of two city divisions: Mbarara South and Mbarara North Division. Mbarara South Division is composed of three divisions, and these are Nyamitanga, Kakoba, and Nyakayojo, whereas Mbarara North is composed of Kamukuzi, Kakiika, and Biharwe divisions. Mbarara City is crossed by River Rwizi, and local people depend on its water as the only viable source, mainly for drinking, industry, irrigation, and other domestic purposes (Atwongyeire et al., 2018; Songa et al., 2015). Moreover, studies (Egor et al., 2014; Ojok et al., 2017; Walter et al., 2019) pointed out that River Rwizi water quality is deteriorating with time. However, their works were restricted on water samples, and no chemical data is available on the quality of bottom sediments for future monitoring of this valuable natural resource. This present work studied for the first time the chemical speciation of the six heavy metals (Cd, Cu, Ni, Pb, Zn, and Fe) in bottom sediments of River Rwizi, within the limits of the three divisions (Kamukuzi, Kakoba, and Nyamitanga) of Mbarara City, where this part of the river is vulnerable to intensive human activities. In addition, some other parameters, namely pH, redox potential, and total organic matter were assessed.

2 Materials and Methods

2.1 Study Area

River Rwizi is a natural surface water that originates from hilly areas of Buhweju in western Uganda. The river has got many tributaries from various hilly regions of Nkore area, and eventually pours its water

into Lake Victoria. It is approximately 55 km long with catchment area of total coverage of 2521 km² and flows eastwards from the hilly south-western area of Uganda (Songa et al., 2015). Of all the districts it transects, Mbarara District was studied within the limits of Mbarara City Divisions as shown in Fig. 1.

2.2 Sampling

Along the river, three main sampling locations were selected (upstream, within Mbarara City, and downstream). Upstream and downstream sites were used as control sites and denoted as C1 in the upstream (0°37'01.0"S, 30°36'39.7"E) and C2 in the downstream (0°37'21.4"S, 30°43'33.2"E). These two control sampling sites were selected based on the assumption that demography versus anthropogenic activities along River Rwizi outside the boundary of Mbarara City are less than those within the boundary of Mbarara City selected divisions.

The sites are not considered as uncontaminated sites; they were used to compare and monitor contamination level. Within Mbarara City, 7 catchment sites were randomly selected, roughly 2 km apart with coordinates 0°37'21.0"S, 30°37'56.3"E for site M1; 0°37'05.6"S, 30°38'31.4"E for site M2; 0°37'05.7"S, 30°39'14.1"E for site M3; 0°37'14.0"S, 30°39'33.9"E for site M4; 0°37'00.4"S, 30°40'06.2"E for site M5; 0°36'36.4"S, 30°41'19.6"E for site M6 and 0°36'30.7"S, 30°41'51.3"E for site M7. Bottom sediment samples at 10 cm depth were picked from the River Rwizi using a pipe core sampler (1.30 m long, 6 cm diameter) in the period of April to May (wet season, 5 campaigns) and June to July (dry season, 5 campaigns) in 2021. Three sediment samples were collected from each of the sampling sites making a total of 27 samples, and were made into composite nine (9) representative samples thereafter, which were subjected to analysis.

2.3 Sample Treatment and Storage

Sediment samples were collected in strong, clean, and labeled 1000 mL polyethylene terephthalate plastic bottles with wide opening and a cover. Before collection, the bottles were prewashed several times using 20% v/v nitric acid and rinsed with distilled water to get rid of any metal contamination. Samples were air dried in a shade for 3 days

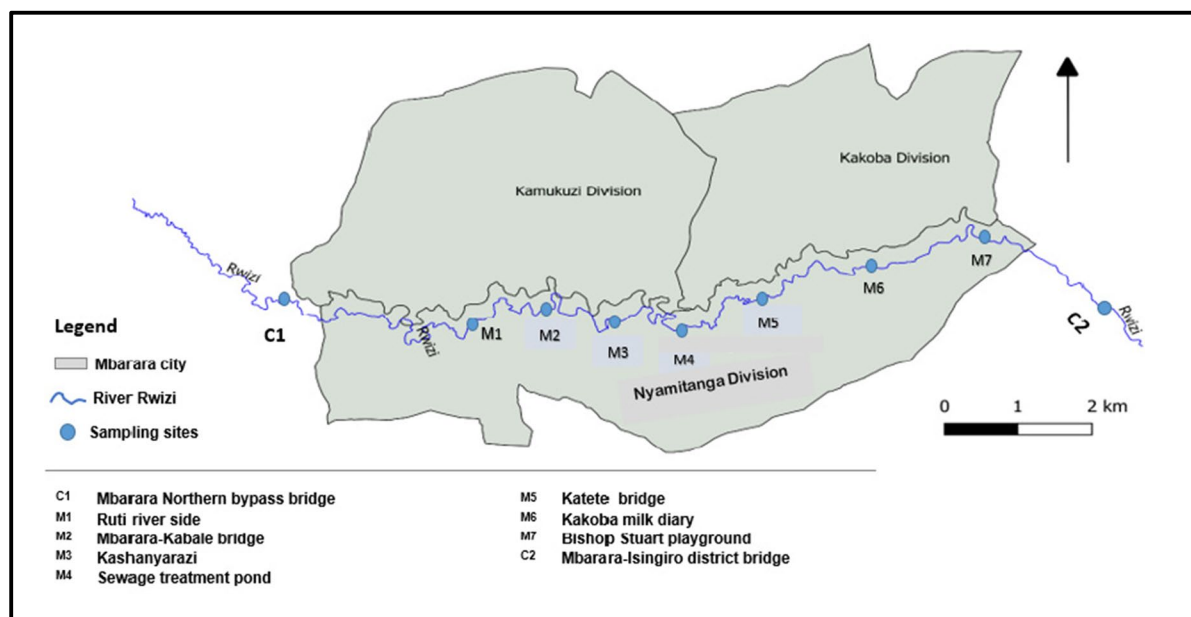


Fig. 1 The study section of River Rwizi in Mbarara City, Uganda

and then ground in an agate mortar and screened through a nylon sieve of $< 75 \mu\text{m}$ to obtain a nearly shale particle size.

2.4 Analysis

Physicochemical analyses of pH, organic matter (OM), and oxidation–reduction potential (ORP) of the samples were performed following standard methods. The pH and ORP were analyzed on 1:1 water–sediment (20 mL of deionized water to 20 g of dry sediment ration) according to USEPA Method (EPA, 2004). Measurements were done using a combined glass electrode (glass membrane pH/ORP electrode sensor, the Ag/AgCl/KCl reference electrode, and temperature recovery device maintained at a temperature of 25°C) connected to CyberScan500^{pH/T/mV} multimeter. For ORP, the measured potential (E_m) was adjusted to normal hydrogen reference electrode (E_h) by adding 199mV, and results were reported as ORP (mV). Organic matter was determined up on estimation calculation from total organic carbon (TOC) multiplied by conversion factor of 1.724 (Khan et al., 2012). Total organic carbon was determined by wet oxidation using modified Walkley–Black titration procedure (Gaudette et al., 1974).

2.4.1 Metal Digestion

Determination of total concentrations of heavy metals was done after *acid digestion* of sediment samples, which was carried out for two purposes: to leach heavy metals in the unextracted 1.0 g dry sediment so as to determine the total content and to leach heavy metals in 1.0 g of the residues obtained from extraction procedures to determine the concentration of heavy metals in that residual fraction (F6). The digestion of scaled up to 1.0 g sediment sample was carried out using a mixture of acids in ratio of 3:1 (9 mL of concentrated nitric acid and usually 3 mL hydrofluoric acid) in a microwave system (EPA, 1996). A reagent blank was also prepared with the same amount of acids without the sediment sample. The digests were then centrifuged at 4000 rpm for 30 min and the supernatant was pipetted, and diluted to 100 mL in a volumetric flask. The analysis of heavy metals was done using flame atomic absorption spectrophotometer (Agilent 280FS AA model, detection limits of 0.1 mg kg^{-1} for heavy metals, except for iron whose detection limit was 0.3 mg kg^{-1}) at wavelengths (nm): Cd: 228.8, Cu: 324.8, Ni: 231.1, Pb: 217.0, Zn: 213.9, and Fe: 248.3. The standard metal solutions and working conditions were prepared according to the instructions of the flame atomic absorption spectrophotometer (FAAS) analytical guide (Agilent, 2017).

2.4.2 Sequential Extraction of Metals

Speciation analysis was done using modified sequential extraction procedure developed by Tessier et al. (1979), and the water-soluble metal fraction was done following the procedure as described by Aigberua et al. (2018) as shown in Table 1. Heavy metals were extracted into six distinct fractions (designated as F), namely water-soluble metals (F1), exchangeable metals (F2), carbonate bound metals (F3), metals bound to Fe–Mn oxides (F4), metals bound to organics (F5), and residual metals (F6). During sequential selective extraction course, 1 g of dry and sieved sediment was carefully weighed on analytical balance and extraction was done in 50-mL centrifuge tubes. In every step, extraction was carried out in three phases: leaching, separation, and washing. Leaching of heavy metals from sediments into aqueous phase was done using appropriate reagents (Table 1). The leachates and sediment residue in the mixture were separated by centrifugation at 4000 rpm for 30 min, and the supernatant was pipetted and diluted to 100 mL in a volumetric flask for heavy metal analysis and this was done using FAAS. The residues were treated/washed with 8 mL of deionized water and centrifugation was carried out at 4000 rpm for 15 min to avoid readsorption of leached metals and the washings (second supernatant) were discarded.

2.5 Quality Control and Data Management

To ensure better quality results, the analyses were done carefully throughout the experiment. All reagents used in this study were of a good analytical grade obtained from certified stock (Sigma-Aldrich, Germany). Glass wares used during analysis and storage were first thoroughly cleaned with 20% nitric acid followed by washing them with distilled water to avoid any trace metal contamination. Analyses were done in triplicates and analytical blanks were also used in this experiment. The validity of the extraction procedure, precision and accuracy of the atomic absorption spectrophotometer were checked by spiking the experiment. The percentage metal recovery ranged from 90 to 104% for all six heavy metals. A metal recovery (MR) of more than 100 is an indication of higher efficiency of extraction procedure than total digestion of that metal as shown in Eq. (1).

$$MR = \frac{C_X}{C_M} \times 100 \quad (1)$$

where C_X is the total concentration of the extracted heavy metal in all six fractions; C_M is the concentration of the heavy metal in the digested sample.

Statistical analyses were done using statistical package for social scientists (SPSS) software version 20

Table 1 Leaching procedure and reagents for extracting selected heavy metals from sediment samples

Fraction	Leaching procedure and reagents
Water-soluble (F1)	1 g of sieved sediments was leached in 50 mL centrifuge tube at room temperature for 2 h with 8 mL of distilled water with continuous agitation (120 rpm)
Exchangeable (F2)	The residue from (F1) was treated at room temperature for 1 h with 8 mL of magnesium chloride solution (1 M $MgCl_2$, pH 7.0) with continuous agitation (120 rpm)
Carbonate bound (F3)	The residue from (F2) was leached at room temperature with 8 mL of sodium acetate (1 M NaOAc) adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation (120 rpm) was maintained for 5 h
Fe–Mn oxide bound (F4)	The residue from (F3) was extracted with 20 mL of hydroxylamine hydrochloride (0.04 M $NH_2OH \cdot HCl$) in 25% (v/v) HOAc at 96 ± 3 °C with occasional agitation and the time needed for complete dissolution of the free iron oxides was 6 h
Organically bound (F5)	To the residue from (F4) was added 3 mL of nitric acid (0.02 M HNO_3) and 5 mL of hydrogen peroxide (30% H_2O_2) adjusted to pH 2 with HNO_3 , and the mixture was heated to 85 ± 2 °C for 2 h with occasional agitation. A second 3 mL aliquot of 30% H_2O_2 (pH 2 with HNO_3) was then added and the sample was heated again to 65 ± 2 °C for 3 h with intermittent agitation. After cooling, 5 mL of ammonium acetate (3.2 M NH_4OAc) in 20% (v/v) HNO_3 was added and the sample was diluted to 20 mL and agitated continuously for 30 min. The addition of NH_4OAc is designed to prevent adsorption of extracted metals onto the oxidized sediment
Residual (F6)	The residue from (F5) was digested with a mixture of acids (HNO_3 –HF) in the ratio 3:1 following the method as described in Sect. 2.4.1. The heavy metal concentrations in all the fractions were determined using FAAS

and Microsoft excel 2016. The performed analyses were descriptive statistics (mean, standard deviation, and normality), correlation analysis (non-parametric), Kruskal–Wallis test (non-parametric) to test whether there was a significant difference in mean levels of measured parameters across all sampling sites, and paired sample *t*-test was performed to test whether there was a significant difference in mean concentrations between wet and dry seasons. Microsoft excel was used to calculate mobility factor (MF), Müller geo-accumulation indices (I_{geo}), enrichment factor (EF), and pollution load index (PLI). As illustrated in Eq. (2), the mobility factor was calculated as a percentage ration sum of potentially mobile fractions (F1, F2, and F3) to the sum to total fractions (F1, F2, F3, F4, F5, and F6) according to Aigberua et al. (2018). The higher the mobility factor, the higher the risk of availability of the metal to the environment (Ekwutosi et al., 2020; Olutona et al., 2012).

$$MF = \frac{F_1 + F_2 + F_3}{F_1 + F_2 + F_3 + F_4 + F_5 + F_6} \times 100 \quad (2)$$

Geochemical accumulation index, enrichment factor, and pollution load index were determined according to Amin et al. (2009) and Saleem et al. (2015). For I_{geo} , both authors based on the technique developed by Müller (1979) using the expression formula shown in Eq. (3). Geochemical accumulation index (I_{geo}) shows the geological accumulation of an element relative to its background value in terms of indices interpreted in reference of pollution levels as shown in Table 2. The EF shows the extent of anthropogenic input of the metal as explained in Table 3. The EF was determined using iron (Fe) as a reference tracer element based on three assumptions according to Schiff and Weisberg (1999) as explained in Sect. 3.2. The formula used to calculate EF is shown in Eq. (5). Enrichment factor is used to differentiate metals of anthropogenic from natural origin (Amin et al., 2009). Lastly, pollution load index (PLI) which is a measure of the load of metal pollutants in terms indices was calculated according to Eq. (4). The higher the index number, the higher the metal pollution loads. Note that all baseline values (shale) used in this study were adapted from the compiled list made by Turekian and Wedepohl (1961).

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \quad (3)$$

Table 2 Geoaccumulation index in relation to pollution extent

Calculated I_{geo}	I_{geo} class	Interpretation
> 5	6	Very strongly polluted
4–5	5	Strongly to very strongly polluted
3–4	4	Strongly polluted
2–3	3	Moderately to strongly polluted
1–2	2	Moderately polluted
0–1	1	Unpolluted to moderately polluted
< 0	0	Unpolluted

*Adapted from Amin et al. (2009)

where C_n is the measured concentration of the examined n metal in the sediment, and B_n is the geochemical baseline concentration of the n metal in the shale.

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times \dots \times CF_n} \quad (4)$$

Then, $CF = \frac{C_{metal}}{C_{baseline}}$, where CF=contamination factor, n =number of metals, C_{metal} =metal concentration in sediment sample, $C_{baseline}$ =base-line shale value of that metal.

$$EF = \frac{(C_x/C_{Fe})_{sample}}{(C_x/C_{Fe})_{shale}} \quad (5)$$

where $(C_x/C_{Fe})_{sample}$ and $(C_x/C_{Fe})_{shale}$ are sample and background average shale values, respectively, with metal concentration in ($\mu\text{g/g}$) dry weight and Fe levels in (%) dry weight in sediment sample.

3 Results

3.1 Physicochemical Parameters

On average, the analysis of bottom sediments of River Rwizi in Mbarara City catchment sites (M_T) showed a decrease in pH (6.80 ± 0.35 to 6.21 ± 0.08), an increase of ORP (308.4 ± 44.7 to 342.0 ± 39.6), and a decrease of OM (1.93 ± 0.34 to 1.42 ± 0.31) from wet to dry seasons (Table 4). Using Kruskal–Wallis test, organic matter (OM) was significantly different across the 9 sampling sites ($P < 0.05$), but pH and ORP were insignificant ($P > 0.05$). Seasonally, using paired sample *t*-test, this study did not show any significant difference between wet and dry season

Table 3 Interpretation of enrichment factor and pollution load index values*

EF	Severity	PLI	Action
> 50	Extremely severe	≥ 100	Immediate action to ameliorate pollution
25 – 50	Very severe	≥ 50	More details needed to monitor the site
10 – 25	Severe	< 50	Drastic rectification measures are not needed
5 – 10	Moderately severe	-	-
3 – 5	Moderate	-	-
1 – 3	Minor	-	-
< 1	No enrichment	-	-

*Adapted from Saleem et al. (2015)

($P > 0.05$) in the mean values for pH and OM except for ORP ($P < 0.05$) for all sites other than M1, M7, and C2.

3.2 Total Heavy Metal Content

The results of total concentration of heavy metals considered in this study for all the 9 sampling sites for the two seasons are given in Tables 5 and 6. They show that the total average mean concentration of Fe measured in 1 kg of dry bottom sediment of River Rwizi was always by far the highest compared to heavy metals with total average concentration ranging from $3.04 \pm 0.75\%$ ($30,381 \pm 7487 \text{ mg kg}^{-1}$) to $3.08 \pm 0.75\%$ ($30,815 \pm 7465 \text{ mg kg}^{-1}$) during wet and dry seasons, respectively. They followed an increasing order of $\text{Fe} \gg \text{Zn} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Cd}$ in both seasons. The spatial distribution of heavy metals (Cu, Ni, Pb, and Zn) was significantly different

across the 9 sampling sites ($P < 0.05$), except Cd and Fe ($P > 0.05$) performed using Kruskal–Wallis test. Moreover, all heavy metals did not show any seasonal significant difference ($P > 0.05$) when the paired sample t -test was used. Heavy metals concentrations were definitely higher than standard values set by WHO (2008) for drinking water, with Cd, Cu, Pb, and Zn being present in higher concentrations than those reported by Turekian and Wedepohl (1961) shale values.

Table 7 shows the Spearman rank correlation analysis of the variables. The results showed significant correlation between: pH and ORP ($r = -0.662$), pH and OM ($r = 0.669$), ORP and OM ($r = -0.704$). However, only OM was significantly correlated with Cd ($r = 0.695$), Ni ($r = 0.654$) and with Zn ($r = 0.654$). Moreover, Fe was significantly correlated with all the other heavy metals ($0.426 \leq r \leq 0.644$). This could be due to the interaction between iron

Table 4 Seasonal variations of pH, organic matter, and oxy-reduction potential for the sites considered in the study

Sites	Wet ($n=5$)			Dry ($n=5$)		
	pH	ORP (mV)	OM (%)	pH	ORP (mV)	OM (%)
C1 (Upstream)	6.81 ± 0.48	310.0 ± 54.6	1.12 ± 0.12	6.04 ± 0.08	349.8 ± 53.4	0.88 ± 0.11
M1	6.81 ± 0.31	317.4 ± 44.6	2.10 ± 0.04	6.19 ± 0.08	327.8 ± 45.8	1.63 ± 0.14
M2	6.80 ± 0.37	310.0 ± 48.3	1.74 ± 0.05	6.22 ± 0.10	342.8 ± 41.1	1.48 ± 0.12
M3	6.81 ± 0.41	303.0 ± 53.0	1.62 ± 0.24	6.20 ± 0.06	360.8 ± 36.5	1.04 ± 0.06
M4	6.99 ± 0.35	305.0 ± 44.1	2.44 ± 0.47	6.27 ± 0.08	339.0 ± 43.6	1.79 ± 0.25
M5	6.68 ± 0.41	307.8 ± 57.2	2.01 ± 0.20	6.14 ± 0.08	339.6 ± 44.6	1.54 ± 0.26
M6	6.80 ± 0.33	305.4 ± 46.3	1.64 ± 0.08	6.27 ± 0.09	355.2 ± 33.8	1.03 ± 0.03
M7	6.73 ± 0.39	310.2 ± 48.2	1.98 ± 0.22	6.19 ± 0.06	329.2 ± 45.2	1.45 ± 0.11
C2 (Downstream)	6.78 ± 0.40	303.6 ± 46.4	2.87 ± 1.04	6.10 ± 0.09	315.6 ± 58.4	2.27 ± 0.96
M_T^a	6.80 ± 0.35	308.4 ± 44.7	1.93 ± 0.34	6.21 ± 0.08	342.1 ± 39.6	1.42 ± 0.31

^aMean was done on 7 mean values in Mbarara City sites (M_T)

Table 5 Total concentrations (mg kg⁻¹, except Fe) of selected heavy metals in wet season

Sites	Wet season (<i>n</i> = 5)					
	Cd	Cu	Ni	Pb	Zn	Fe (%)
C1	1.75 ± 0.40	62.56 ± 5.95	33.62 ± 3.89	33.4 ± 3.25	27.03 ± 1.77	2.10 ± 0.17
M1	1.72 ± 0.12	98.43 ± 8.85	21.20 ± 2.57	23.57 ± 2.96	96.76 ± 9.99	2.58 ± 0.36
M2	1.48 ± 0.19	94.37 ± 5.77	48.88 ± 9.41	23.80 ± 2.74	75.58 ± 6.23	3.17 ± 0.75
M3	1.51 ± 0.04	82.07 ± 7.65	33.03 ± 2.43	22.93 ± 1.63	107.31 ± 12.41	2.40 ± 0.21
M4	1.92 ± 0.15	126.36 ± 13.14	41.98 ± 1.98	48.83 ± 4.43	156.96 ± 24.62	3.98 ± 0.22
M5	1.80 ± 0.14	84.73 ± 5.98	18.63 ± 1.71	30.67 ± 3.08	127.22 ± 25.51	2.74 ± 0.34
M6	1.55 ± 0.10	128.02 ± 22.70	37.30 ± 5.45	55.58 ± 1.63	80.10 ± 11.74	3.14 ± 0.12
M7	1.45 ± 0.16	128.68 ± 20.06	66.17 ± 6.89	28.78 ± 2.34	114.46 ± 16.57	2.24 ± 0.18
C2	1.72 ± 0.18	68.20 ± 17.22	50.28 ± 9.54	39.04 ± 3.48	65.78 ± 4.02	3.06 ± 0.51
M _T ^a	1.63 ± 0.21	106.10 ± 23.22	38.17 ± 6.07	33.45 ± 3.33	108.34 ± 30.51	3.04 ± 0.75
B.Values ^b	0.3	45	68	20	95	4.7

^aMean was done on 7 mean values in Mbarara City (M_T).^bBackground values provided by Turekian and Wedepohl (1961)**Table 6** Total concentrations (mg kg⁻¹, except Fe) of selected heavy metals in dry season

Sites	Dry season (<i>n</i> = 5)					
	Cd	Cu	Ni	Pb	Zn	Fe (%)
C1	1.58 ± 0.06	63.24 ± 6.47	35.07 ± 3.69	32.79 ± 3.63	25.78 ± 5.15	2.37 ± 0.13
M1	1.73 ± 0.16	108.7 ± 11.25	21.97 ± 2.45	22.88 ± 3.79	101.73 ± 9.07	2.71 ± 0.12
M2	1.64 ± 0.14	89.16 ± 13.31	53.20 ± 9.97	23.94 ± 2.36	77.59 ± 9.48	3.31 ± 0.33
M3	1.53 ± 0.08	83.01 ± 6.91	32.94 ± 3.82	24.11 ± 1.89	112.45 ± 12.03	2.42 ± 0.31
M4	1.92 ± 0.14	132.08 ± 11.49	42.45 ± 3.93	49.00 ± 3.85	165.24 ± 13.66	3.05 ± 0.84
M5	1.89 ± 0.09	86.25 ± 2.82	19.86 ± 1.74	31.07 ± 1.14	146.16 ± 15.72	2.85 ± 0.13
M6	1.54 ± 0.16	134.50 ± 23.84	37.72 ± 5.28	58.09 ± 9.02	87.00 ± 17.83	3.04 ± 0.74
M7	1.37 ± 0.10	143.88 ± 18.96	70.52 ± 13.58	28.77 ± 2.07	119.90 ± 9.57	2.20 ± 0.12
C2	1.65 ± 0.10	65.65 ± 15.37	56.72 ± 8.64	40.42 ± 3.00	63.97 ± 4.40	3.17 ± 0.33
M _T ^a	1.64 ± 0.23	111.10 ± 27.36	39.81 ± 7.90	33.98 ± 3.63	115.72 ± 31.64	3.08 ± 0.75
B.Values ^b	0.3	45	68	20	95	4.6

^aMean was done on 7 mean values in Mbarara City (M_T).^bBackground values provided by Turekian and Wedepohl (1961)**Table 7** Spearman's rank correlation of variables (*N* = 90)

Var	pH	ORP	OM	Cd	Cu	Ni	Pb	Zn	Fe
pH	1								
ORP	-0.662**	1							
OM	0.669**	-0.704**	1						
Cd	0.273	0.031	0.695*	1					
Cu	0.137	0.146	0.354	-0.076	1				
Ni	0.391	-0.029	0.654*	0.180	0.339	1			
Pb	0.007	0.170	0.258	0.274	0.201	0.244	1		
Zn	0.483	0.126	0.565*	0.262	0.573**	-0.123	0.018	1	
Fe	0.171	0.144	0.165	0.578*	0.644**	0.526**	0.620**	0.426*	1

Var. = variables

*Correlation is significant at the 0.05 level (2-tailed)

**Correlation is significant at the 0.01 level (2-tailed)

oxides or hydroxides and the heavy metals by adsorption, complexation, and coprecipitation, which makes Fe a trace metal scavenger (Gasparatos, 2012).

Iron was used as a geochemical normalizing element due to three reasons. First, iron was insensitive to anthropogenic input due its low geo-accumulation index (Table 8). Second, Fe has shown covariation (linear correlation) with the trace elements (Table 7). Last, Fe was essentially stable and was not subjected to variation in measured environmental conditions (pH, ORP, and OM), which could alter its concentrations in the sediments as shown by lowest mobility (Fig. 5), and lack of correlation between the parameters as shown in Table 7.

Among the heavy metals, only copper and zinc were significantly correlated between themselves ($r = 0.573, P < 0.01$). This strong correlation could be explained by intermetallic bonding between Zn and Cu with other elements in clays or minerals ores resulting in a synergic effect. Statistically, a significant correlation conveys information that the two variables have a strong linear relationship, where a positive correlation means a direct relationship and a negative correlation means that the variables are indirectly related. Literally, regardless of whether the correlation is significant, a non-zero positive correlation implies that correlated metals have come from the same source (both natural and anthropogenic), while a non-zero negative correlation indicates that the correlated metals come from different sources (Achi et al., 2011; Amin et al., 2009; Olutona et al., 2012). For example, cadmium is naturally found in soils and sediments as sulfide ore in association with zinc as in sphalerite ($\text{Zn}[\text{Cd}]\text{S}$) (Bradl, 2005). This implies that an increase of Zn in sediment ore will automatically lead to the increase of Cd. A negative influence between two heavy metals would occur if the metals chemically interacted each other by displacement reactions due to differences in affinity towards a ligand or by oxidation reaction. This would result into the mobility of the labile or reductant metal causing it to decrease in concentration at a given site (Laing et al., 2007).

In this study, the observed non-zero negative correlation between Zn and Ni as well as Cu and Cd were not significant which could be due to high number of samples analyzed.

3.3 Assessment of Anthropogenic Influence

The effect of anthropogenic activities was assessed using both geochemical accumulation index (I_{geo}),

enrichment factor (EF), and pollution load index (PLI), and the results obtained are presented in Table 8. The I_{geo} results obtained for the studied metals revealed that the bottom sediments of River Rwizi in Mbarara City catchment sites were in a range of unpolluted to moderately–strongly polluted (geo-class of 0 to 3) as described in Table 2. On average, the order of geochemical accumulation of the metals was $\text{Cd} > \text{Cu} > \text{Pb} > \text{Zn} > \text{Ni} > \text{Fe}$. On the other hand, using the Table 3, the extent of enrichment of heavy metals based on iron ranged from no enrichment to severe enrichment (EF ranged between 1 and 10.5) and the order obtained was $\text{Cd} > \text{Cu} > \text{Zn} > \text{Pb} > \text{Ni}$. As a result, the PLI in Mbarara City catchment and control sites followed the order of $\text{M4} > \text{M6} > \text{M7} > \text{C2} > \text{M2} > \text{M5} > \text{M3} > \text{M1} > \text{C1}$ (Fig. 2). Moreover, the trends in geochemical accumulation and extent of enrichment of the heavy metals in Mbarara City catchments sites as compared to control sites are presented in this section (Figs. 3 and 4).

3.4 Speciation Results of Heavy Metals

Speciation analysis was done on River Rwizi bottom sediment samples to determine the heavy metals' relative percentage concentrations in different chemical fractions (as a ration concentration in mg kg^{-1} of a metal in a given fraction to total sum concentrations in mg kg^{-1} of the metal in all six fractions multiplied by 100), and the results obtained are summarized in Tables 9, 10, and 11 for the wet and dry seasons. Note that the speciation results obtained for the selected heavy metals in Mbarara City catchment sites (M_T) was on seven sampling sites, and the mean percentage concentrations values were calculated. The notations, MR: metal recovery (%); F1: water-soluble metal fraction, F2: exchangeable metal fraction, F3: carbonate bound metal fraction, F4: bound to Fe–Mn oxides, F5: bound to organics, F6: residual metal fraction are used in Tables 9, 10, and 11.

4 Discussion

4.1 Physicochemical Characterization

The results of this study showed a visible decrease in pH with season from wet to dry. Such a decrease in pH is possibly due to ongoing diagenesis process in

sediments. Acid volatile sulfides (AVS) and organic matter decomposition are the primary sources of acidic environment in bottom sediments (Gale et al., 1992; Olutona et al., 2012; Virtanen et al., 2015). Bottom sediments of River Rwizi showed a fairly oxidizing environment with lowest oxy-reduction potential of 250.0 mV recorded in wet season and highest value of 397.3 mV recorded in dry season. Both values were obtained at site M3. This revealed an increasing episode of electron deficiency in the sediments from wet to dry season. In fact, electron deficiency is caused by increasing of oxidizing species in the bottom sediments. For example, some oxidizing species such as dissolved oxygen (O_2), nitrates (NO_3^-), and manganese(IV) in this range of redox potential may not be stable, and thus, they accept electrons to become reduced to water, nitrogen, and manganese(II) respectively (DeLaune & Reddy, 2005; Virtanen et al., 2015). Therefore, high oxidizing environment has a negative effect on lifetime of electron donating species such as organic matter and acid sulfide species due to their oxidation (Eggleton & Thomas, 2004). As shown by this study, the organic matter content in bottom sediments was below 3% in 1 g dry sediments with higher OM content in wet than in dry season. This gradual decrease could be linked to variation in ORP as shown by correlation results in Table 7. Organic matter serves as the primary electron donor to electron acceptors (Gale et al., 1992; Virtanen et al., 2015).

Consequently, the oxidation of organic matter may result into an acidic environment, which may lead to release of metals bound to them (Laing et al., 2007; Peng et al., 2009). Therefore, changes in pH and organic matter were generally redox potential induced as a result of oxy-reduction reaction processes as shown by the linear relationship of correlation matrix in Table 7.

4.2 Concentration of Selected Heavy Metals in Sediments of River Rwizi

The total concentration of selected toxic heavy metals in bottom sediment of River Rwizi were generally higher than the background shale values provided by Turekian and Wedepohl (1961). This indicates that the geochemical accumulation of the heavy metals exceeds the harmless natural background concentrations that can be supported by the environment. On the other hand, iron did not exceed the average shale value (4.6%) and was by far the highest in concentration compared to the other heavy metals. Higher content of iron is an indicator of crustal soil rich in iron minerals in Uganda (Mahaney et al., 1997; Minai, 2015; Sekabira et al., 2011).

The distribution of metals depends on physicochemical parameters such as pH, oxy-reduction potential, organic matter, and other factors such as cations and electric conductivity (Duan et al., 2019;

Table 8 Geochemical accumulation index, enrichment factor, and pollution load index of selected heavy metals obtained at different sampling sites

Sites	Cd		Cu		Ni		Pb		Zn		Fe		PLI
	I_{geo}	EF	I_{geo}	EF	I_{geo}	EF	I_{geo}	EF	I_{geo}	EF	I_{geo}	EF	
C1	1.9	9.7	-0.1	3.0	-1.6	1.1	0.1	2.5	-2.4	1.0	-1.7	1	0.2
M1	1.9	10.2	0.6	4.1	-2.2	1.0	-0.4	2.1	-0.5	1.9	-1.4	1	0.6
M2	1.7	8.1	1.4	5.0	-1.0	1.4	-0.3	1.2	-1.0	1.2	-1.1	1	1.0
M3	1.8	9.9	0.3	3.6	-1.6	1.0	-0.4	2.3	1.5	4.3	-1.6	1	0.7
M4	2.8	10.5	1.3	4.9	-1.3	1.0	1.0	3.9	2.2	5.0	-0.8	1	8.4
M5	2.5	10.4	0.3	3.2	-2.4	1.0	0.0	3.6	1.9	4.4	-1.3	1	0.9
M6	1.8	9.0	1.4	4.4	-1.4	1.0	1.0	3.3	-1.0	1.0	-0.8	1	3.8
M7	1.7	9.9	2.0	6.4	-0.6	2.1	-0.1	4.0	2.0	4.6	-1.7	1	2.5
C2	1.9	8.5	-0.0	2.2	-1.0	1.2	0.4	3.0	-1.1	1.0	-1.2	1	1.2
M _T ^a	2.1	10	1.0	4.7	-1.5	1.2	0.6	3.0	0.4	3.3	-1.2	1	2.6

Geochemical accumulation and enrichment factor determined using metal baseline values compiled by Turekian and Wedepohl (1961)

^aMean of geochemical accumulation and enrichment factor of metals for 7 mean values in Mbarara City sites

Laing et al., 2007; Peng et al., 2009). Therefore, a significant positive correlation between these factors and metals could imply a strong effect on the metal concentrations in different environments, since the mobility and bioavailability of metals depend on physicochemical parameters (Achi et al., 2011; Adhikari et al., 2018). The results have shown that most of the sites in the Mbarara catchment area were vulnerable to higher concentrations of heavy metals. In most cases, higher concentrations of heavy metals in sediments could be due to industrial and municipal activities, dumping and roadside runoffs, and automobile exhaust (Saleem et al., 2015).

Comparing the results of this study to those reported in other studies, the concentration of copper obtained is considered higher than for other studies as shown in Table 12. Broadly, the accumulation of heavy metals in aquatic sediments depends on socio-economic factors in the catchment areas as well as the physicochemical conditions of the sediments (Sekomo et al., 2011). This justifies the differences in the concentrations of heavy metals in the sediments of water bodies across the world. Therefore, the reported heavy metal concentrations were under specific local conditions.

Although developed countries are expected to generate higher amounts of heavy metal pollutants that can enter into water bodies, in most cases, both developing and undeveloped countries are the most vulnerable to water pollution. This is because in the former countries, pollution control measures are more prioritized than the latter. Poor waste management from various industries and traditional

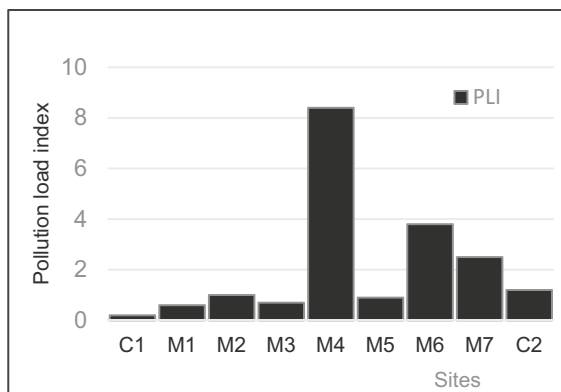


Fig. 2 Pollution load indices at different sampling sites

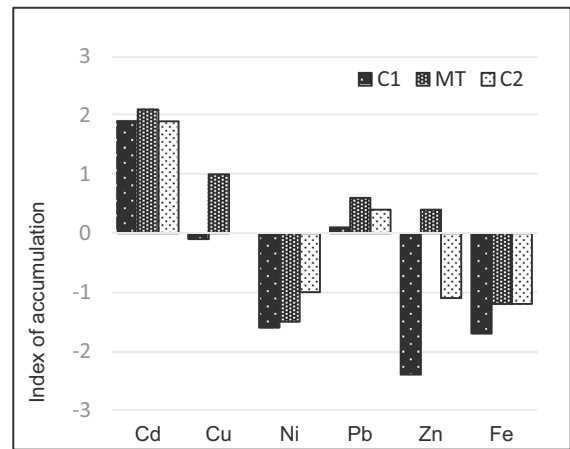


Fig. 3 Geochemical accumulation of selected heavy metals

agricultural practices in the catchment areas result in catastrophic water quality deterioration by toxic pollutants, especially heavy metals that accumulate in the bottom sediments (Bradl, 2005; Duan et al., 2019). These heavy metals can reenter into overlying water, when there is a change in the equilibrium of physicochemical parameters across the water–sediment interphase (Adhikari et al., 2018; Duan et al., 2019; Sekabira et al., 2011). The mobile species of heavy metals are the most dangerous chemical forms, because they are easily transported in water and assimilated into aquatic living organisms causing bioaccumulation (Eggleton & Thomas, 2004; Nakiguli et al., 2020).

4.3 Speciation of Selected Heavy Metals in Sediments of River Rwizi

In this section, discussion is limited to heavy metals, Cd, Cu, Ni, Pb, Zn, and Fe in bottom sediments of River Rwizi, mainly within Mbarara City catchment sites (M_T) and a comparison is made on their mobility across three main sites (C1, M_T , and C2). Generally, speciation results showed that the highest concentrations of the selected heavy metals were found in their residual fractions, while the lowest concentrations were in water-soluble fractions for both wet and dry seasons. Except Fe, the potential mobility of heavy metals decreased from wet to dry season, and the order of their increasing mobility of $Zn > Cu > Cd > Pb > Ni > Fe$, in both seasons (Fig. 5).

Table 9 Speciation of selected heavy metals obtained in wet season at 3 main sites

Fraction (%)	Upstream control site (C1), $n=5$					Mbarara City sites (M_T^a), $n=35$					Downstream control site (C2), $n=5$				
	Cd	Cu	Ni	Pb	Zn	Cd	Cu	Ni	Pb	Zn	Cd	Cu	Ni	Pb	Zn
F1	0 ^b	0 ^c	0 ^c	0 ^c	0 ^c	0 ^b	2	0 ^c	0 ^c	3	0 ^b	2	0 ^c	0 ^c	5
F2	7	12	2	6	12	9	15	5	3	16	7	11	4	6	17
F3	14	18	3	7	21	19	19	10	14	21	21	18	13	11	15
F4	11	8	21	31	7	8	7	4	34	7	12	11	20	29	7
F5	24	11	33	19	3	20	11	26	7	12	20	13	24	16	18
F6	40	50	42	37	56	40	47	55	41	41	35	45	39	39	37
MR	101	94	98	94	99	95	96	92	92	94	94	99	92	92	95

^aMean was done on 7 mean values in Mbarara City (M_T).^bUndetected %^cBetween 0 and 1%**Table 10** Speciation of selected heavy metals obtained in dry season at 3 main sites

Fraction (%)	Upstream control site (C1), $n=5$					Mbarara City sites (M_T^a), $n=35$					Downstream control site (C2), $n=5$				
	Cd	Cu	Ni	Pb	Zn	Cd	Cu	Ni	Pb	Zn	Cd	Cu	Ni	Pb	Zn
F1	0 ^b	0 ^c	0 ^c	0 ^c	0 ^c	0 ^b	2	0 ^c	0 ^c	2	0 ^b	2	0 ^c	0 ^c	5
F2	8	7	2	5	11	7	10	2	3	9	6	13	3	5	11
F3	13	18	8	6	9	13	17	8	8	20	19	12	7	7	13
F4	7	8	17	31	19	11	11	8	32	8	13	12	13	32	8
F5	29	19	29	18	4	30	8	23	18	20	21	17	26	18	16
F6	38	47	44	38	56	34	52	59	39	40	37	46	51	37	46
MR	99	92	99	99	104	91	92	96	97	96	96	102	96	98	95

^aMean was done on total 7 sites in Mbarara City (M_T).^bUndetected %^cBetween 0 and 1%**Table 11** Speciation of iron in wet and dry season ($n=5$ for C1 and C2)

Fraction (%)	Wet season			Dry season		
	C1	M_T^a	C2	C1	M_T^a	C2
F1	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b
F2	2	1	1	1	1	1
F3	2	1	1	2	1	1
F4	18	32	15	19	31	30
F5	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b
F6	78	67	83	77	67	67
MR	98	102	95	94	100	98

^aMean ($n=35$) was done on total 7 mean values in Mbarara City (M_T).^bBetween 0 and 1%

4.3.1 Cadmium (Cd)

The distribution of cadmium in bottom sediments of River Rwizi in Mbarara City sites showed that the most abundant chemical form of cadmium appears as a residual fraction (F6) and organic bound fraction (F5) with the least undetected being in the water-soluble fraction (F1) (concentration $<0.1 \text{ mg kg}^{-1}$) in both seasons. The results in this study are in agreement with the findings obtained by Sibomana et al. (2019), where cadmium was much higher in the residual forms in bottom sediments of the Mpenge River of Rwanda. Similarly, Achi et al. (2011) reported highest cadmium concentration in residual fraction among other fractions and recorded the smallest concentration in water-soluble fraction in soil samples obtained from the vicinity around automobile mechanic workshops. However, Tessier et al. (1979) reported a higher concentration of cadmium as being associated with Fe–Mn oxides with undetected cadmium (concentration $<0.1 \text{ mg kg}^{-1}$) for other fractions. The appearance of cadmium mostly in immobile chemical forms makes it less available to the environment. The potential mobility of cadmium observed within Mbarara City catchment sites during wet seasons had a mobility factor of 28%, while for upstream and downstream control sites it was 21% and 28%, respectively. During the dry season, the mobility factor of cadmium decreased to 20% within Mbarara City catchment sites and to 25% at downstream control site, but at upstream control site it remained unchanged. This decrease in mobility factor of Cd explains its seasonal chemical transformation, where some of its mobile fractions are immobilized as a result of diagenesis through physicochemical and biological processes, and hence possess no serious threat to the environment (Duan et al., 2019).

4.3.2 Copper (Cu)

The results of speciation of copper obtained in bottom sediments of River Rwizi at sampling sites within Mbarara City catchment area showed high concentration of Cu in carbonates fractions (19%) followed by residual fraction (47%) in wet season. In the dry season, the carbonate fraction had 17% and residual fraction had 52%. Some authors (Ekwutosi et al., 2020; Sibomana et al., 2019; Tessier et al., 1979) found that the distribution of copper in bottom sediments was in the most immobile, environmentally stable chemical forms of copper as residual, organically bound and bound to Fe–Mn oxides.

However, the presence of copper in potential mobile fractions (carbonate bound, exchangeable fraction) should not be underestimated. As a result, the potential mobility of copper as shown in Fig. 5 was found to be higher within Mbarara City catchment sites with an average mobility factor of 35% than upstream and downstream control sites with 30% and 31% respectively in wet season. During dry season, the potential mobility of Cu decreased for all sites. The results therefore, indicate that the presence of copper in some of its mobile fractions puts Mbarara catchment sites at a risk of contamination, especially when the sediments becomes more acidic to dissolve carbonate bound metals in pore and overlying waters, and thus, it becomes bioavailable (Peng et al., 2009; Tessier et al., 1979).

4.3.3 Nickel (Ni)

The distribution of nickel in bottom sediments of River Rwizi in Mbarara City catchment sites showed lower concentration of Ni in the potentially mobile fractions (water-soluble, F1; exchangeable, F2; and carbonate bound, F3). This caused nickel to have low mobility of 15% within Mbarara catchment sites, 11% and 17% for the upstream and downstream control sites respectively in wet season, which decreased to 10% for all sites in dry season. Higher Ni concentrations was found in organic bound fraction (F5) than in the Fe–Mn oxides bound fraction (F4), and the highest Ni concentrations was found in residual fraction (F6) in both wet and dry seasons. Large amounts of nickel bound to organics has been reported by Osakwe, (2011) and Ekwutosi et al. (2020). This was attributed to the formation of stable compounds by Ni with organic ligands. The same reason caused nickel to have a lower potential mobility than Cd, Cu, Pb, and Zn in this study. In most cases, nickel is found in large concentration in the residual fraction (Eggleton & Thomas, 2004). Higher Ni concentrations were noted in immobile fractions (F4, F5, and F6) and these increased from wet to dry seasons resulting into its low availability. The lower potential mobility of Ni indicates that it is environmentally stable and possesses no or less threat (Tessier et al., 1979).

4.3.4 Lead (Pb)

The residual fraction (F6) of the bottom sediment of River Rwizi within Mbarara City catchment sites and Fe–Mn oxides bound fractions (F4) showed a

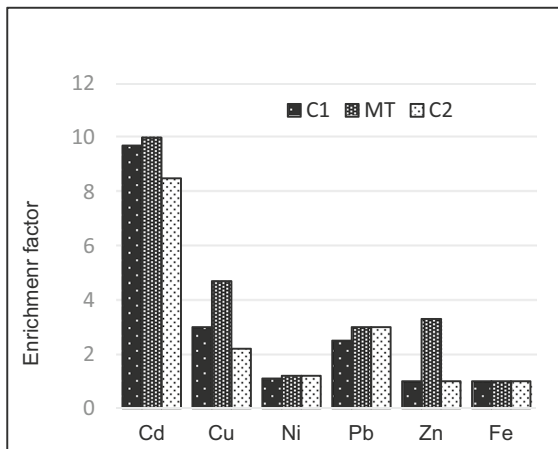


Fig. 4 Extent of enrichment of selected heavy metals with reference to iron

higher Pb concentration than other fractions in both wet and dry seasons. The high lead concentrations bound to Fe–Mn oxides was also reported by Tessier et al. (1979) in sediments of river Saint-marcel and by Olutona et al. (2012) in bottom sediments of Aiba water reservoir. In general, the relative concentration of lead in different fractions was in the order: F6 > F4 > F5 > F3 > F2 > F1 for the two seasons. Residual fraction contains most stable metals, which are resistant to changes in environmental conditions (Achi et al., 2011; Ekwutosi et al., 2020; Saleem et al., 2015). This explains why lead is less available to the biota species in bottom sediments and in water of River Rwizi, since most of it was in the immobile fractions (F4, F5, and F6). The presence of lead in Fe–Mn oxides bound fraction can only be available at extreme reducing and acid conditions which are less likely to occur in river bottom sediments (Chuan

et al., 1996; DeLaune et al., 1981; Duan et al., 2019). Therefore, the potential mobility of lead was as low as that of nickel with 18% within Mbarara City catchment sites, 13% and 16% for upstream and downstream control sites in wet season, which decreased to 11%, 12%, and 12%, respectively, in the dry season (Fig. 5).

4.3.5 Zinc (Zn)

During the wet and dry seasons, the relative concentrations of zinc in the six fractions obtained from bottom sediment samples of River Rwizi in Mbarara City catchment sites was in the order F6 > F3 > F2 > F5 > F4 > F1 and F6 > F3 > F5 > F2 > F4 > F1 respectively. The presence of high concentrations of Zn in carbonate bound and exchangeable fractions designate that all zinc would be leached from their bound substrates, and thus become available to aquatic life if environmental conditions became more acidic. In most cases, zinc was detected in the most mobile, water-soluble fraction (F1), ranging from less than 1% to 5%, that is, 0.14 ± 0.02 to 3.22 ± 0.02 mg kg⁻¹ for the two seasons considered in this study. Unfortunately, water-soluble metal fraction (F1) contains bioavailable metals and they can easily be transported to overlying water from sediment pore water. Egor et al. (2014) detected a closer concentration value of zinc in water samples of River Rwizi within Mbarara catchment sites which was above WHO permissible limit in drinking water (3 mg kg⁻¹). Above this limit, zinc would be toxic to some plants (phytotoxic) causing chlorosis and stunting (Manahan, 2000; WHO, 2008). Zinc had the highest potential mobility of 40%, and this was observed within Mbarara City catchment sites (Fig. 5). The control sites had 33% and 37% for

Table 12 Reported total mean concentrations (mg kg⁻¹, except iron) of heavy metals in sediments of different countries

Rivers/streams/lakes	Cd	Cu	Ni	Pb	Zn	Fe (%)	Reference
Mpenge stream (Rwanda)	5.0	44.2	33.3	33	136.7	n.s	Sibomana et al. (2019)
Nyabugogo river (Rwanda)	2.9	39.7	n.s	54.0	106.0	n.s	Sekomo et al. (2011)
Saint-Pierreville river (France)	<0.1	48.6	60.2	42.5	127.0	5.0	Tessier et al. (1979)
Saint Marcel river (France)	<0.1	25.0	28.8	18.2	88.0	3.6	Tessier et al. (1979)
Nakivubo stream (Uganda)	1.1	35.8	n.s	154.6	331.7	4.1	Sekabira et al. (2011)
Mangla lake (Pakistan)	4.4	22.6	70.8	30.7	127.3	0.5	Saleem et al. (2015)
River Rwizi (Uganda)	1.6	108.6	39.0	33.7	112.0	3.1	This study

n.s not specified

the upstream and downstream in wet season, which decreased to 32%, 21%, and 29%, respectively, in the dry season. As a result, bottom sediments of River Rwizi in Mbarara City catchment sites could pose a threat to the environment.

4.3.6 Iron (Fe)

Unlike the other heavy metals considered in this study, iron showed a remarkable speciation. It showed the smallest potential mobility among other heavy metals considered in this study. The prevailing species of iron were found in residual form (F6) followed by Fe–Mn oxides (F4) across the three sampling sites. The results are in agreement with the findings obtained by Tessier et al. (1979), who found that iron was much higher in the residual fraction than in other fractions. This was followed by Fe–Mn oxide and carbonate fractions in sediments of river Saint-Marcel and Pierreville (France). However, different distribution of iron was observed by Olutona et al. (2012) in bottom sediments of Aiba water reservoir and Osakwe (2011) in soils around automobile workshop both in Nigeria. In their findings, they reported high concentration of iron in the carbonate bound fraction.

Naturally, total content of iron is by far the highest and it is beyond trace level in the environment (Tessier et al., 1979). In the last centuries, it has been believed that the enormous deposits of iron oxides in crust were responsible to liberate oxygen in primitive atmosphere (Manahan, 2000). Three important and naturally occurring iron oxides/hydroxides compounds are ferric oxide, Fe_2O_3 ; ferric hydroxide, $\text{Fe}(\text{OH})_3$; and ferric oxyhydroxide, FeOOH (Cox et al., 2017; Gasparatos, 2012). These oxides are good scavengers of other trace metals in the environmental

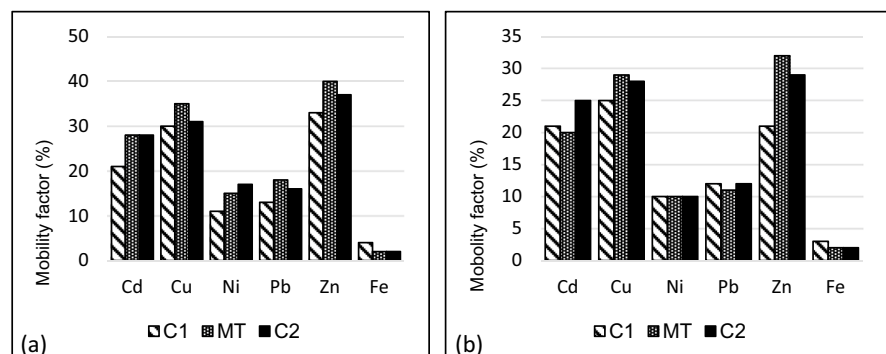
matrices, and would release them in extreme environmental conditions such as those that are reducing and low pH (Duan et al., 2019; Jenne, 1968; Tessier et al., 1979). Therefore, the high concentrations of iron in the residual fraction and in the oxides explains its stability in the environment (Gasparatos, 2012).

4.4 Influence of Anthropogenic Activities on Heavy Metal Concentrations

With respect background shale values provided by Turekian and Wedepohl (1961), it was clearly shown by this study that the geological accumulation indices (I_{geo}) of Cd, Cu, Pb, and Zn were higher in Mbarara City catchment sites (M_T) than in the upstream (C1) and downstream (C2) control sites. The I_{geo} is the quantitative measure of the pollution index in the sediments, and any increase in the current levels is envisaged to be anthropogenic in nature (Saleem et al., 2015).

Cadmium was ranked as a strong polluter due its high average I_{geo} value falling in the class of 3 (moderately to strongly polluted at sites M4 and M5). Copper was a moderate polluter, because the I_{geo} value obtained was in the class of 2. While the overall average I_{geo} of zinc fell in the class of 1 (unpolluted to moderately polluted), some sites M3, M4, M5, and M7 showed a class of moderately polluted as copper. Using iron as reference element, the extent of enrichment as indicated by enrichment factor (EF) showed that Cd, Cu, Pb, and Zn were more enriched in Mbarara City sites than in control sites. The EF values obtained ranged between 1.0 and 10.5 falling in the range of minor to severely enriched sediments (EF range of 3 – 25), while EF of Ni fell in the range of minor enrichment (1 – 3). An enrichment factor value

Fig. 5 Potential mobility trend of selected heavy metals in wet season (a) and dry season (b)



greater than 1.5 ($EF > 1.5$) is an indication of anthropogenic source, while ($EF < 1.5$) the metals originate from natural weathering (Amin et al., 2009; Müller, 1979). Consequently, Mbarara City catchment sites showed a higher pollution than the two control sites, with the highest pollution load index being obtained at site M4 near sewage treatment pond (Fig. 2). The higher PLI at site M4 may be due to the fact that this site receives all kinds of wastes from residential, industrial, institutional, and agricultural places (Walter et al., 2019).

5 Conclusion

The speciation results obtained revealed that high concentrations of selected heavy metals were present in their immobile chemical forms than mobile forms. However, the percentage fractions of the metals which were associated with the potential mobile fractions were found to be significant. In both wet and dry seasons, the order of their increasing potential mobility of the metals was $Zn > Cu > Cd > Pb > Ni > Fe$. In addition, the mobility of the heavy metals was found to decrease from wet to dry season and this was as a result of changes in environmental conditions. Meanwhile, the geological accumulation of selected heavy metals ranged from unpolluted to moderately polluted and the order followed was $Cd > Cu > Pb > Zn > Ni > Fe$, and the extent of enrichment with reference to iron ranged from minor to severe enrichment and this gave $Cd > Cu > Zn > Pb > Ni > Fe$. Generally, concentrations of heavy metals studied were essentially higher in Mbarara City catchment sites than in upstream and downstream control sites. This was due to the various anthropogenic input sources in Mbarara City and these greatly could have influenced the results obtained at the site near the treatment pond (M4). This site was more vulnerable to pollution than other studied sites. The potential mobility of the heavy metals in question shows a risk of water pollution, and there is a concern for human health through direct consumption and uptake of metals via drinking water, eating fish, and using the polluted water for irrigation of crops around the studied area. Therefore, it is important that pollution awareness be initiated for the public to know why it is necessary to protect the environment. Thus, the responsible government agencies in

Uganda, including the National Environmental Management Authority (NEMA) and Ministry of Water and Environment (MWE), as well as local authority and other relevant stakeholders should take up this noble cause seriously and then take pollution control measures as a priority so as to scale down the contamination of bottom sediments of River Rwizi with pollutants like heavy metals.

Acknowledgements The authors are grateful and acknowledge the financial support from KFW (Germany “Credit Institute for Reconstruction”) through Inter-University Council for East Africa (IUCEA) via East African Community Scholarship program, and the project management team (Adroit Consult International).

Data Availability All raw datasets generated during this study are available from the corresponding author on request.

Declarations

Conflict of Interest The authors declare no competing interests.

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