

Full Length Research Paper

A chemical speciation study of selected heavy metals in aquatic bottom sediment samples from *Mpenge* stream, *Musanze* District, Rwanda

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Mpenge stream is regarded as one of the most important domestic water resource in Musanze District; Rwanda. The chemical speciation study of selected heavy metals (Zn, Cu, Co, Cr, Ni, Pb, and Cd) in sediment samples collected from that stream was carried out by means of an analytical procedure involving sequential chemical extraction method and to determine the heavy metals content in different fractions of sediment. The heavy metals were found in five fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residual fraction. Their levels were determined by flame atomic absorption spectrophotometer and the total mean values were in the order Cr > Zn > Cu > Ni = Pb > Co > Cd. In fact the total metal content in mg/kg dry matter (mean values) were for Cr = 169.17 ± 8.77; Zn = 136.67 ± 2.88; Cu = 44.17 ± 1.44; Ni = 33.33 ± 5.22; Pb = 33.33 ± 14.33; Co = 25.00 ± 0.00; and Cd = 5.00 ± 0.00. As per United States Environmental Protection Agency's (US EPA) guidelines for sediments quality, sediments were moderately polluted for all analyzed elements apart from chromium that showed that the sediments were heavily polluted. Furthermore, the speciation results showed that high levels of these assessed metals (Zn, Cu, Co, Cr, Ni, Pb, and Cd) were associated with exchangeable and carbonate bound fractions for all heavy metals apart from copper, pointing out that they are in potentially available forms and may pose serious problems to water consumption.

Key words: Speciation, sequential chemical extraction, heavy metal, bottom sediment, stream.

INTRODUCTION

Water bodies are widely complex dynamic, chemical systems consisting of different components, namely various solutes, organic matter, and colloidal or particulate matter. Hence, a number of chemical processes between dissolved metal pollutants and components are expected

to take place in these water systems and it is the distribution of the heavy metal pollutants between the different chemical species and forms which determines their geochemical and biological reactivity (Luoma, 2017; Saleem et al., 2015a). The chemical and physical

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changes associated with different forms of a chemical element in sediment are a key process in the cycling of heavy metals in natural water on wide range of time scales. In fact, it was found that heavy metals occurring in water bodies are predominantly carried by suspended particles and only a small fraction is transported in the soluble form (Ali et al., 2016; Jiang et al., 2014). The distribution of an element among different inorganic compounds and organic complexes impacts its transport and bioavailability. In order to understand the environmental chemistry of an element, it is necessary to obtain completely the concentrations and chemistry of its various species under the different conditions possible in natural environments. (Tessier et al., 1979) pioneered the area of chemical speciation as characterizing an element's forms for understanding the transformations between different forms and their availability to living organisms' bodies (Skorbiłowicz, 2014).

Sediments in water bodies are complex mixtures of various phases, namely residues of weathering and erosion of underground mate (Islam et al., 2015b). The geochemical fractions most commonly analyzed are the following: exchangeable (Fraction I), bound to carbonate (Fraction II), reducible (Fraction III), oxidizable (Fraction IV) and residual metals, such as rocks. Fractionation of water sediment by selective chemical extraction removes or dissociates a specific phase with the associated metal bound to it (Tessier and Campbell, 1987). Among the sequential extraction schemes proposed to investigate the distribution of heavy metals in soil and sediment, the five-step extraction scheme developed by Tessier et al. (1979), was the most widely used. Different researchers have used different methods for analysis of chemical speciation, such as voltametric, inductively coupled plasma-mass spectrometry (ICP-MS) and other methods (Islam et al., 2015a, b; Rahman et al., 2008, 2014). Use of total concentration as a criterion to assess the potential effects of the sediment contamination implies that all forms (phases) of a given metal have an equal impact on the environment. Such an assumption is untenable (Huang et al., 2015; Yang et al., 2015). It is evident that just the speciation of metal pollutants with the various sediment phases determines their specific impact on the environment. Also the type of phase specific bounding of metals in contaminated natural sediments specifies suitable methods of their potential cleaning and utilization (Martín et al., 2015: 70). A common but time consuming analytical method if evaluating particular metal-sediment phase is the method of sequential extraction (SE) adapted from the methods of soil and sediment chemical analysis (Nazeer et al., 2014; Saleem et al., 2015b). The concept of the SE procedure is the portioning of a solid material into specific phases or fractions that are selectively extracted that is, liberated and released into solution (leached) along with the associated trace metals, by using appropriate reagents arranged in increasing strength. Speciation, using sequential extraction schemes,

has been developed for assessing geochemical forms in soil and sediment (Saleem et al., 2015a).

Water bodies show important parts in the ecological system. These water bodies have been contaminated by different forms of heavy metals due to rapid industrialization growth, excessive mining activities, weathering and erosion (Huang et al., 2015; Wafula et al., 2018). This contamination poses severe ecotoxicological threats to aquatic wildlife and humans. The bio-geochemical behavior, nutritional bioavailability and toxicity of metals are widely dependent on the chemical speciation (Helliweli et al., 1983). In this study, bottom sediments collected from Mpenge stream, whose untreated water is largely used by local people as domestic water, were screened for selected heavy metals using five-step extraction method developed by Tessier and Campbell (1987). The work focused on selected heavy metals namely zinc (Zn), copper (Cu), cobalt (Co), chromium (Cr), nickel (Ni), lead (Pb), and cadmium (Cd) by partitioning them into specific phases and be analyzed using flame atomic absorption spectrometer Perkin Elmer 2380, and the findings were to be compared with the guidelines values (Tessier et al., 1979).

MATERIALS AND METHODS

Mpenge stream is a natural source of water located in Musanze District, Northern Province of Rwanda. It is generally used by local people as drinking and cooking water and it is flowing through volcanic rocks. Six sampling sites in Mpenge stream were selected for sediment samples collection. Three sediment samples were collected from each of the sampling selected sites. Sediment samples from each location were made into one composite representative sample and the latter was stored in a clean, sealable, washed with distilled water and rinsed with nitric acid. The bottom sediment samples were dried in an oven at 150°C, for five hours. The samples were then ground in an agate mortar and screened through a nylon sieve. A portion (1 g) of the sample with a size <0.2 mm was assigned for further studies. The partition into fractions of sediment samples was done according to a five-step chemical speciation method proposed by Tessier and Campbell (1987) followed by the analysis of heavy metal using flame atomic absorption spectrophotometer (FAAS).

Exchangeable heavy metals

One gram of dry sediment was dissolved in 10 ml of 1 M $\text{CH}_3\text{COONH}_4$ to pH 7 and shaken at room temperature for one hour followed by the centrifugation. The supernatant was acidified with one drop of concentrated nitric acid (65% w/w) and diluted into a 25 ml beaker to the mark with distilled de-ionized water. The final solution was used to determine the exchangeable heavy metals by FAAS.

Heavy metals bound to carbonates

The residue in (i) was treated with 20 ml of 1 M ammonium acetate acidified with acetic acid to pH 5. The shaking time was Five hours at room temperature. After centrifugation, the supernatant was

acidified with one drop of concentrated nitric acid (65% w/w) and diluted into a 25 ml volumetric flask to the mark with distilled de-ionized water and used to determine the heavy metals bound to carbonates by FAAS.

Heavy metals bound to hydrated oxides of Fe and Mn

The residue in (ii) was dissolved in 20 ml of 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ (hydroxylamine hydrochloride acid) in acetic acid (25% v/v). The shaking time was two hours at 95°C. The supernatant, after centrifugation, was acidified with one drop of concentrated nitric acid (65%) and diluted into a 25 ml volumetric flask to the mark with distilled de-ionized water. Then the heavy metals bound to hydrated oxides of iron and manganese were determined by using FAAS.

Heavy metals bound to organic matter

The residue in (iii) was respectively treated with 5 ml 0.07M HNO_3 , and 5 ml of 30% H_2O_2 to pH = 2 and the mixture was shaken for two hours). Then 5 ml of 30% H_2O_2 to pH = 2 was added to the resulting solution and was shaken for three hours. Finally 10mL of 3.2 M ammonium acetate in 20% (v/v) nitric acid was added to that latter solution and the shaking time was 0.5 hour. The supernatant was acidified with one drop of concentrated nitric acid (65%) into a 25 ml volumetric flask and completed with distilled de-ionized water to the mark and used to determine the heavy metals bound to organic matter by FAAS.

Heavy metals in other forms

The heavy metal content in the last residue in (iv) was calculated by subtracting the sum of heavy metal content in Fractions I, II, III, IV, and from the total concentration of heavy metals determined by using a separate sample. To determine total heavy metals in, dried sediment sample (1 g) was transferred to a volumetric flask containing 50 ml H_2O and boiling chips. Then 50 ml HCl/HNO_3 , 3:1 was added, mixed and heated respectively to 100°C for one hour, 125°C for 15 min, 150°C for 15 min, 175°C for 15 min, and to 200°C to near dryness. The residue was concentrated to about 5 ml in concentrated nitric acid. After cooling, 1 ml 30% H_2O_2 was added to the concentrated residue and the digestion was for 10 min. The digestion in 1 ml 30% H_2O_2 was repeated twice. After cooling again, 3 ml 30% H_2O_2 was added and the digestion has been for 10 min. 50 ml water and 25 ml HCl were added, mixed, and heated till boiling. The whole solution was cooled, transferred to 250 ml volumetric flask, filled up to the mark, mixed, and left at least 15 h to settle. The clear solution was used to perform the measurements for total heavy metals by FAAS.

RESULTS AND DISCUSSION

In Mpenge sediment samples, the levels of heavy metals analyzed were shown in Table 1. It was generally observed that all elements in residual fraction were at the highest concentration. The concentration was ranged between 4.25 and 155.17 mg/kg dry matter. In that fraction heavy metals were not potentially bioavailable and might not be a threat to the environment, including living organisms. This is due to the association of heavy metals to the crystalline structure of the minerals implying that they are difficult to separate from the sediments. The

mean values of the distribution of heavy metals in residual fraction were in the order $\text{Cr} > \text{Zn} > \text{Ni} > \text{Cu} > \text{Pb} > \text{Co} > \text{Ni} > \text{Cd}$. The high concentration of total Cr and low concentration of total Cd was reported by Skorbilowicz (2014) in bottom sediments of Bug River in Poland.

Zinc

The high concentration in Fraction I and II indicated that Zn would be released into the environment once the environmental conditions could become more acidic. The two fractions contain the most labile Zn which might be available under pH change and therefore the most dangerous. Zinc was also found bound to iron and manganese oxides in Fraction III and would be released if the sediments were subjected to more reductive conditions. Metals in reducible fraction may easily undergo removal from the sediments, be bioavailable and harmful to aquatic organisms including human beings. The presence of zinc in Fraction IV revealed that it occurred as stable organic complex and this could be due to the high organic content in sediment samples. Our findings are in agreement with earlier studies (Jiang et al., 2014). In Fraction I, zinc showed significant quantity (4.25 mg/L) compared to World Health Organization (WHO) drinking water guidelines (3 mg/L). The total content of Zn showed that the stream is moderately polluted.

Copper

The results obtained for this heavy metal indicated that the main partition is between the third (reducible) and the fourth (oxidisable) fractions. Copper content in those fractions were 5.17 and 5.25 mg/kg dry matter respectively and might be released and bioavailable if its matrix underwent reducing, oxidizing conditions and microbial activity (Zhang and Gao, 2015). Therefore it should constitute a real threat to the environment. The labile copper in Fraction I and II was in lower concentration (0.33-0.91 mg/kg) compared to its occurrence in other fractions and was below WHO's drinking water standards (1993).

Cobalt

Cobalt was mainly concentrated in the residual and organic matter fractions. Their concentrations were 3.33 and 19.17 mg/kg in Fractions IV and V respectively. Organic matter bound metals would be released in more oxidizing conditions and could be a threat to living organisms. Residual fraction bound metals are blocked in crystal lattice of mineral and cannot pose any harm to environment. Exchangeable and carbonate bound cobalt

Table 1. Distribution of Zn, Cu, Co, Cr, Ni, Pb, and Cd in different fractions in sediment samples, from Mpenge.

Element	Fraction I	Fraction II	Fraction III	Fraction IV	Fraction V	Total content
	n =7	n =7	n =7	n =7	n =7	n =7
mg/kg dry matter (Mean values)						
Zinc	4.25 ±1.98	35.67±17.89	23.91±12.20	18.25±3.36	54.67±27.39	136.67 ± 2.88
Copper	0.33±0.14	0.91±0.28	5.17±0.76	5.25±0.75	32.41±1.25	44.17±1.44
Cobalt	0.83±1.44	1.67±1.44	n.d	3.33±3.81	19.17±1.44	25.00±0.00
Chromium	0.25±0.25	0.50±0.25	5.91±0.38	7.33±2.26	155.17±11.02	169.17±8.77
Nickel	0.08±0.14	0.41±0.72	n.d	0.58 ±0.62	32.60±5.96	33.33±5.20
Lead	5.00±2.50	4.17±5.20	0.83±0.14	1.67±2.88	21.67±7.21	33.33±14.43
Cadmium	0.08±0.14	0.33±0.14	n.d	0.17±0.14	4.25±0.43	5.00±0.00

n = Number of samples, n.d: not detected Fraction I: Exchangeable metals, Fraction II: Metals bound to carbonates, Fraction III: Metals bound to hydrated oxides of iron and manganese, Fraction IV: Metals bound to organic matter, Fraction V: metals in other forms (mainly metals built in crystal lattice of mineral) , Total content: I + II + III + IV + V.

was observed, and their levels were 0.83 and 1.67 mg/kg respectively. Skorbilowicz (2014) reported the same results from the chemical speciation of Bug River (2014). Such levels in the acid-soluble fractions were significant compared to the limits set by WHO (1993) which meant that Cobalt was potentially bioavailable and might be a serious threat as it is transferred into the chain food from bottom sediment. Hydrated oxides of iron and manganese bound cobalt was not detected. Compared with other analyzed heavy metals, cobalt was the less concentrated in all fractions.

Chromium

Chromium was mainly found in the residual fraction (155.1 mg/kg) in sediment samples. Its decreasing order was as follows: residual fraction bound chromium, organic matter fraction bound chromium, iron and manganese oxides fraction bound chromium, carbonate fraction bound chromium, and exchangeable metals fraction bound chromium. Metals in the above fractions are subject to the equilibrium shift with the conditions change such as pH, oxidizing, reducing factors and microbial activity (Haller et al., 2011). They could be readily bioavailable for biological uptake in the environment.

Nickel

In sediment samples, nickel was mainly detected in the residual fraction (32.67 mg/kg). This fraction is relatively stable and does not easily allow the metals to separate from the sediments. Therefore they are not bioavailable and cannot be toxic to aquatic organisms. The contribution of nickel to the fraction bound to organic matter, carbonate and exchangeable fraction decreased and was 0.58; 0.41 and 0.08 mg/kg respectively. Oxides

of iron and manganese fraction bound nickel were not detected. The concentration of nickel was not in Fraction I and II and was above the acceptable limits proposed by WHO (Organization, 1973; Roth and Hornung, 1977; Saifuddin and Raziah, 2007) and could pose health problem to living organism.

Lead

Lead was mainly present in the residual fraction (21.67 mg/kg). Less lead was identified in exchangeable (5 mg/kg) and carbonate (4.17 mg/kg) fractions. Those fractions showed the amount of elements that would be released into the aquatic system (environment) if the environmental conditions became more and more acidic. They are the fractions with the most labile metals to the environment and therefore the most likely dangerous. The minor amounts of lead were found in the forms bound to organic matter (1.67 mg/kg) and hydrated oxides of iron and manganese (0.83 mg/kg). These results are in accordance with the work done by Zerbe et al. (1999) on speciation of heavy metals in bottom sediments of lakes in Poland. The mobility of the heavy metals bound to those fractions could increase under oxidizing and reducing factors leading to the bioavailability of the toxic heavy metals to the aqua system.

Cadmium

The relative main concentration of cadmium was in residual fraction (4.25 mg/kg) and in much smaller amount in the forms of carbonates 90.33 mg/kg; organic matter (0.17 mg/kg) and exchangeable (0.08 mg/kg). Cadmium in oxides of iron and manganese was not detected. In general Cd was relatively found in a very small amount and do not constitute a potential threat to

the environment.

Conclusion

From the results, heavy metals levels were few and sporadically found in all fractions apart in residual fraction where heavy metals content was relatively high. Most heavy metals were relatively in organic bound fraction and may constitute a danger to the environment due to their release to water under aerobic and anaerobic conditions. Furthermore the findings showed that the heavy metals forms of Zn are bioavailable.

Taking into consideration the fact that the local surroundings of Mpenge stream did not show the presence of point sources of metal contamination and that legal protection of the area considerably limits anthropogenic pollution, it can be assumed that the heavy metals found in the stream sediment are to a predominant extent of natural origin and occur at concentrations typical of the geochemical background. Indeed in Musanze district (Rwanda), all sources of water used by people are groundwater and pass through volcanic rocks that may undergo the weathering processes, possibly releasing some toxic metals into those sources. The rock types are essentially volcanic. Work done by Barifaijo (2000) and Erasmus Barifaijo (2000) in the neighboring Bufumbira volcanic area (Uganda) indicates that the rocks contain some heavy metals in relatively high concentrations. Therefore, the metals content in the stream may be the result of weathering and leaching processes which take place in the studied stream. The findings of this chemical speciation analysis can be used as reference for investigating heavy metals content and chemical speciation in other local stream sediments and water. Moreover, the outcomes of this study provide a reference for monitoring the quality of local streams water and the effect of anthropopression on the natural water and for assessment of the actual hazard coming from heavy metals penetrating the environment as results of natural process and human activities.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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