Chemical speciation of selected heavy metals in surface water samples from Mpenge stream in Musanze district, Rwanda.

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Abstract: Surface water samples were collected from Mpenge spring in Musanze District, Rwanda. Many people in the District drink untreated natural water from underground water aquifer that flows through volcanic rocks suspected to contain heavy metals. In order to contribute to a better understanding of the quality of water that the population consume, a speciation study on the levels of Zinc, Copper, Cobalt, Chromium, Nickel, Lead, and Cadmium was carried out. The heavy metals bound to suspended solids were concentrated using membrane filtration technique. A packed column with Amberlite XAD-16 resin was then used to separate the free heavy metals from those bound to organic matter in the filtrate. The levels of heavy metals were determined with a Flame Atomic Absorption Spectrophotometer. The heavy metals were found in free form, form bound to suspended particles, form bound to soluble organic matter, and were ranged from 0.01 to 0.28mg/L for the total levels. The detection limit for analyzed metals was 0.01m/L. Mean recoveries were high (90-100%) for Zn, Cu, Cd, Cr, and Co, while those for lead and nickel were low (32%- 46%). Generally all the water samples had levels of free heavy metals below the set WHO values implying that the water was safe for human consumption.
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1. Introduction

A wide range of both inorganic and organic species occur in natural aquatic systems. Trace heavy metals are part of the inorganic and organic species and occur in low concentrations (Sawyer et al, 1994). In recent times, however, the occurrence of metal contaminants, especially heavy metals in excess of natural discharges has become a problem of increasing concern because of pollution (Adrian, 2000). This situation has arisen as a result of the rapid growth of the population; increased agricultural and industrial activities, exploitation of natural resources, natural processes and lack of environmental regulations and policies (Twinomuhwezi, 1998).

The term speciation of heavy metals in natural water refers to quantitative and qualitative differentiation of the forms of their occurrence (Mingbiao et al, 2008). Metal speciation in a given particular sample is of increasing interest and importance because of toxicity, bioavailability, and environmental mobility. Biogeochemical behavior and potential risk in general are strongly dependent on the chemical species of metals (Hundal, 2006). The speciation technique should facilitate the quantification of free and bound metal. In fact, there is a direct association between the physicochemical speciation of an element and its toxicity, biological activity, bioavailability, and solubility (Alonso et al, 2004) Exposure to some. Heavy metals may cause severe effects on living organisms such as reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death (Juan, 1997). The most toxic heavy metals are under free form in water (cations) (Zerbe et al, 1999) and exchangeable cations in sediment (Tessier et al.1979). The bioavailability and toxicity of an element depends on its species (Zhen and Jonhua, 1999) and the oxidation state of its cations (Yulia et al, 2008). Despite the toxicity of heavy metals some of them have beneficial effects when they are in living organisms at low concentration. Zinc is for example known to have beneficial effects on the immune function (Lattif, 2000).

Musanze District is found in northern part of Rwanda. All sources of water used by local people are groundwater and pass through volcanic rocks that may undergo the weathering process, possibly releasing some toxic metals into those sources. The rock types are essentially volcanic. Work done by Barifaijo (2000) in the neighboring Bufumbira volcanics (Western Uganda) indicates that the rocks contain some heavy metals in relatively high concentrations. In addition, excessive use of

fertilizers and pesticides in potatoes plantations combined with untreated wastes from farms/houses and burning of different substances may result into harmful substances flowing directly into potable water or infiltrate through the regolith and finally reaching the groundwater sources. For people who get water from these local aquifer springs, their drinking water is not filtered by the local government and water quality mainly depends on the local geology and ecosystem, as well as human activities. In this regard, contaminants that may be in untreated water include microorganisms such as virus and bacteria, inorganic contaminants such as salts and free metals; pesticides and herbicides as well as organic contaminants from different sources. This study is focused on the speciation of heavy metals in water samples from selected sites in the area dominated by the volcanic rocks. The heavy metals speciation of the water will help to establish its status because the present study aims at determining the distribution of chemical species of dissolved heavy metals in water and sediment samples from Musanze District.

Many people in Musanze District drink untreated natural water from underground water aquifer and flowing through volcanic rocks that contain heavy metals (Barifaijo, 2000). However no research has been reported on heavy metal speciation in the above area. The identification and quantification of physico-chemical forms of these heavy metals are still unknown and yet they may constitute a potential hazard to both human beings and marine organisms. Therefore, it is a necessity to conduct a speciation study heavy metals in water and sediments samples from Musanze in order to obtain a better understanding of the exposure of the human beings and organisms to selected heavy metals (Cu, Co, Cd, Cr, Pb, Ni, and Zn).

2. Materials And Methods

The study was carried out for the springs of Mpenge, located in Musanze District in northern region of Rwanda. The geological landscape of this region is dominated by volcanic rocks through which that steam flows. Twenty samples from Mpenge were collected in polyethylene bottles carefully rinsed before use and the pH, temperature, and conductivity values were measured at the sampling sites. The water samples were filtered and preserved by acidifying it with HNO_3 to pH less than 2 and kept at 4^oC. The membrane filters used for water sample filtration are kept for analysis of heavy metals suspended to particulate matter. Amberlite XAD-16 resin was used as the adsorbent suitable for the preconcantration of heavy metals because of its

purity and good adsorption properties (Serif et al, 2000)

Water Samples analysis

(i) Heavy metals bound to organic matter

Water sample (100mL) was filtered through a 0.45μm membrane filter and then 100mL of the filtrate was passed through an adsorbent column parked with amberlite XAD-16 resin that was meant to retain the metals bound to organic matter. The effluent (100mL) was reserved in order to determine the free metals ions. The metals bound to soluble organic substances retained to the resin were eluted with HC1 (1M) in acetone into a 25mL beaker. The eluate was evaporated to near dryness and the residue was digested in 3mL of 2M nitric acid into 25 mL beaker and diluted to the mark with distilled de-ionized water. The measurements of metals bound to organic matter were performed by FAAS in the final solution.

(ii) Free heavy metals

To determine the free metals ions in the reserved effluent (100mL), 0.475g sodium tetraborate reagent was added to the effluent. This solution was passed through the column filled with amberlite XAD-16 resin. The heavy metals adsorbed on resin were eluted again with HC1 (1M) in acetone into a 25 mL beaker. To prepare this solution, an 8.3mL of concentrated HCI (37.5%, w/w) were taken into 100mL volumetric flask and made to the mark with acetone. After the evaporation of the eluate to near dryness, the residue was dissolved in 3mL of 2mol L^{-1} nitric acid and completed to the mark with distilled de-ionized water. Then free metals were analyzed by FAAS in the final solution.

iii) Heavy metals bound to suspended particles

The membrane filters used in (i) were used to investigate the heavy metals bound to the suspended particles. The filter, loaded with the suspended particles, was digested in 5mL of concentrated HNO_3, (65%w/w) centrifuged and evaporated to near dryness. The residue was then dissolved in HNO_3 (3mL, 2M) into a 25 mL beaker and diluted to the mark with de-ionized distilled water. The determination of heavy metals bound to suspended particles was performed by FAAS.

iv) Heavy metals recovery in water

To determine the recovery values for water samples, an aliquot of 100mL of water sample containing a known-concentration (0.5mg/L) of each metal ion (Zn, Cu, Co, Cr, Ni, Pb, and Cd) was filtered using 0.45 μm membrane filter. Therefore the filtrate was passed through the column packed with amberlite XAD-16 resin and the metals content was performed by FAAS.

3. Results And Discussion

This chapter reports on the results of the measurements for heavy metals in surface water samples from Mpenge sampling site, in Rwanda. It includes identification and quantification as well as the interpretation of the obtained data. The discussion was done on basis of recovery values, heavy metal total content, and its distribution in different fractions.

In order to decide on the efficiency of the analytical procedure, the recovery work was carried out on the samples to be analyzed. For that purpose the recovery values given in Table 1 below were calculated from the concentration of the bound and free-metal cations in spiked and non-spiked water sample The relatively high ratios of the bound zinc (0.09 and 0.08mg/L) in the spiked and non-spiked water sample may be due to the high metal-loading relative to humic acid levels and the high complexation rate between metals ions and humic substances. The same behavior was observed for the bound lead in the spiked (0.09mg/L) and non-spiked water sample (0.1mg/L).

Table 1: Recovery values (%) for Zn, Cu, Co, Cr, Ni, Pb, and Cd in Mpenge water samples

Element	Concentration in mg / L in the spiked water samples.			Concentration in mg/ L in water samples.		
	Added (mg/L)	Bound n =20	Free n =20	Bound n =20	Free n =20	Recovery Values (%)
Zn	0.5	0.09 ±0.02	0.53±0.02	0.08±0.04	0.09±0.01	90
Cu	0.5	0.04±0.01	0.52±0.04	0.04±0.01	0.02±0.01	100
Co	0.5	0.02±0.01	0.55±0.05	0.09±0.05	n.d	96
Cr	0.5	0.04±0.01	0.47±0.05	n.d	0.01	100
Ni	0.5	n.d	0.16±0.03	n.d	n.d	32
Pb	0.5	0.09±0.01	0.25±0.01	0.1±0.1	0.01±0.02	46
Cd	0.5	0.02±0.01	0.48±0.04	n.d	n.d	100

n= 20, pH=7; conductivity = 0.1S/m; T = 22^0 C; volume = 100mL.
Added: A known concentration of heavy metals added in water samples, Fraction I: Metals bound to suspended particles in water sample (on filter), Fraction II: Metals bound to soluble organic matter in water sample (bound). Fraction III: Free heavy metals (free), n = Number of samples, n.d = Not detected, Total content: sum of fraction I, fraction II, and fraction III.

As can be seen in Table 1, the recovery values (%) for Zn (90%), Cu (100%), Co (96%), Cr (100%), and Cd (100%) were relatively high for all analyzed elements in a water sample but not for Ni (32%) and Pb (46%). The recovery values for Zn, Cu, Co, Cr, and Cd, showed that the methods used were efficient (>90%). Those results were similar to those found by *Serif et al*, (2000) for a speciation of Cu, Co, Cr and cadmium in water samples collected from Sultansazligi stream. The poor recovery of Pb and Ni showed that the interaction between sodium tetraborate reagent and free metals Pb and Ni was weak or moderate and may be also explained by a negative effect of chemical interferences due to some elements on their signals during flame atomic absorption spectrophotometer measurements. Lead signal could increase when the concentration of iron (10mg/L) in the water sample was higher. Likewise, the presence of higher concentration of iron or chromium may interfere with the nickel signal (Lajunen, 1992).

Even if the recovery of most of analyzed elements was relatively higher, an excess of some transition and heavy metal depresses some elements signals such as the cobalt response (Lajunen, 1992). Chromium absorption is suppressed in the air-acetylene flame by the presence of iron and nickel, and an excess of phosphate will depress the chromium response. For cadmium, the high concentration of silicate interferes in its determinination. The detection limits (in mg/L) were 0.01for zinc; 0.01 for copper; 0.01 for cobalt; 0.01 for chromium; 0.01 for nickel; 0.01 for lead and 0.01 for cadmium.

Results of the speciation of the water samples collected from Mpenge site are summarized in Table 2 below.. As can be seen from this table, the bound forms of Co (0.05 mg.L^{-1}) and Pb(0.1 mg.L^{-1})were higher than the free forms of these elements in free form. Indeed Co content was not detected and Pb was 0.01mg.L^{-1}. These results were also found by *Serif et al* (2000) for the speciation of Cu, Cd, Mn, Pb, Co, Ni, and Cr in water samples from Sultansazligi River in Poland, *Yulia et al* (2008) for Cd, Cu, Ni, Pb, and Zn in natural water samples, and by Yu and Malofeeva (1987) for Cd, Cu, Ni in natural water samples.

Table 2: Distribution of Zn, Cu, Co, Cr, Ni, Pb, and Cd in different fractions in water samples from Mpenge

Element	Mean concentrations of metals in different chemicals forms/mg.L-1			
	On filter n =20	Bound n =20	Free n =20	Total Content n=20
Zn	0.11±0.01	0.08±0.04	0.09±0.01	0.28±0.01
Cu	0.03±0.02	0.01±0.00	0.02±0.01	0.06±0.01
Co	n.d	0.05±0.00	n.d	0.05±0.02
Cr	0.11±0.02	0.02±0.00	0.01±0.00	0.12±0.06
Ni	n.d	n.d	n.d	n.d
Pb	0.05±0.00	0.1±0.02	0.01±0.05	0.16±0.04
Cd	n.d	n.d	n.d	n.d

pH= 6.9; conductivity = 0.1S/m ; T= 22^0 C
Fraction I: Metals bound to suspended particles in the water sample (on filter), Fraction II: Metals bound to soluble organic matter in the water sample(bound), Fraction III: Free heavy metals(free), = Number of samples, n.d = Not detected, Total content: sum of fraction I, fraction II, and fraction III.

Specifically, the free forms for zinc (0.09mg/L), chromium (0.01 mg.L^{-1}), and copper (0.02mg/L) were relatively higher compared to the bound forms of the same elements.. These values mean that those elements may not interact strongly with the organic matter, particularly with the humic acids in water: $4O=CH-CH=CH-COOH +M^{2+} \rightarrow [(O=CH-CH=CH-COOH)_4M]^{2+}$ and also may due to the absence of the latter. From the same table, the ratios for all elements show that nickel, cobalt, and cadmium were less abundant of all analyzed elements in both bound and free forms. In Mpenge water samples, their three forms were generally not detected. The results also showed that the concentrations of the analyzed elements in the particulate form (on filter) were relatively highly predominant to the bound and free forms. Those findings were confirmed *by Serif et al* (2000) for speciation of heavy metals in water samples from Sultansazligi. The same results showed that the total concentrations of Cr, Zn, and Pb in the study area were relatively higher. Indeed the concentrations were 0.28 mg/L, 0.12mg /L and 0.16mg /L respectively in Mpenge water samples.

In Mpenge sampling site the pH was measured and found to be around 7. This value matches WHO's guidelines for drinking water, and the recommended pH is in the range 6.5 and 8.5.The same pH was reported by EWSA for different springs from the study area, the service of water sanitation in Rwanda. That pH indicates that water from the study area was almost neutral and does not favor the high formation of the free metals as shown by the obtained results. Indeed the higher the pH the lower the free metals content.In addition the found pH showed that the analyzed water was from the same origin since the area through which it flows has the same chemical composition (volcanic soil). The conductivity in both sampling sites was 0.1S/m and was below the guidelines set by WHO (2.5S/m) and

that shows that there was not presence of huge amount of inorganic dissolved solids. The lower the conductivity, the lower the dissolved salts. Then the free heavy metals content obtained was function of the conductivity. The temperature of 22 ^{0}C was the same for the sampling site and similar to that reported by EWSA in the study area. This temperature is function of the local climate which is normally cold due to the high altitude of volcanoes chain.

The concentration of free heavy metals which are relatively most toxic among the three forms were found in Mpenge water samples but was lower than that of WHO's guidelines for drinking water. Consequently the danger of heavy metals to residents of the study area is not to be considered.

4. Conclusion

The main objective of this work was to carry out a speciation study of selected heavy metals (Zn, Cu, Co, Cr, Co, Pb, and Ni) in water samples from Mpenge spring in Musanze District, Rwanda.

In water samples from the above sites, the specific objectives were to determine the heavy metal content bound to suspended particles (I), bound to organic matter (II), and free heavy metal (III). For this purpose, membrane filters and a packed column with amberlite XAD-16 resin were used as preconcentration of the heavy metals prior to their determination by FAAS. The results showed that the three fractions of analyzed heavy metals were present in water samples but the metals levels found, particularly those of the most toxic heavy metals (free heavy metals) were well below those legally allowed by World Health Organization (WHO). The method seemed to be successful because the recovery values were greater than 90% for all studied heavy metal except Ni (32%), and Pb (46%).

Taking into account the fact that local surrounding area of Musanze did not show the

presence of point sources of metal contamination since there are neither mining sites nor industrial areas, it can be assumed that the heavy metals found in water samples from Mpenge spring are to a predominant extent of natural origin and occur at concentrations typical of geochemical background. Therefore, the results of this speciation analysis can be used as a reference for investigating heavy metal content and speciation in sediment and water samples from other springs of the same area.. The monitoring of the population activities in the catchment area must be done to prevent the eventual water pollution due to the random or disordered dumping of household wastes. Through some government institutions such as Rwanda Environment Management Authority (REMA) Energy and Water Sanitation Authority (EWSA), it should be required to constantly monitor the levels of heavy metals pollution in the water and sediments flowing through volcanic rocks in Musanze District by monitoring and controlling of the quantitative amount in domestic wastes before they are discharged in surrounding area.

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