

The Speciation of Selected Trace Metals in Nairobi River Water, Kenya

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ABSTRACT

Metal ions form complexes with naturally occurring ligands released from industrial effluent. The complexes are transported and enter the environment and biological system leading to environmental degradation and health problems. This contribution investigates the speciation of trace metals in water samples collected from Nairobi River. Heavy metals (Pb, Mn, Cu, Fe, Cr and Zn) were determined using spectroscopic techniques whereas sulfamer 4 method, diazotization, and titration methods were used to determine the concentration of SO_4^{2+} , NO_2^- , F^- and Cl^- respectively. It was found that ~ 69.8% of total iron was in oxidation state III; the dominant species being Fe^{2+} , $\text{Fe}(\text{OH})\text{SO}_4$, $[\text{FeF}_4]^-$, FeSO_4 , Fe^{2+} and $[\text{Fe}(\text{OH})_2]^+$ during both the dry and wet seasons. Manganese was found exclusively in oxidation state II (100%) in which some of its major chemical forms were Mn^{2+} and $[\text{MnF}_6]^{4-}$. Copper was present mostly in oxidation state II (Cu^{2+}) while lead and zinc existed chiefly as $([\text{Zn}(\text{SO}_4)_4]^{6-})$ and $([\text{Pb}(\text{SO}_4)_3]^{4-})$ complexes. Chromium was trivalent with its main complexes being $[\text{Cr}_4(\text{OH})_6]^{6+}$ and $\text{Cr}(\text{OH})(\text{SO}_4)$. Traces of free metal ions (Cu, Fe and Mn) were found in Lenana section of Nairobi River. Traces of free metal ions are the most aggressive water toxicants due to their high solubility in biological systems.

Keywords: trace metals, free ions, speciation

INTRODUCTION

Metal speciation analysis in aquatic ecosystems is emerging as a powerful basis for development of predictions of bioavailability and reliable risk assessment strategies [1]. Conventionally, chemical speciation is the identification and quantitation of different chemical forms of elements in any environmental matrix considered harmful to natural ecosystems. This contributes heavily to water pollution which is presently an escalating global problem because of the serious health impacts associated with it [2, 3]. Toxic trace metals in addition to other pollutants pose a serious health risk to both aquatic and human life. The major metal species in fresh water includes but not limited to, inorganic complexes with various oxidation states, organometallic complexes, and particulate metal adsorbed on soil sediments.

Trace metals bioaccumulate in the body system causing cell injury, oxidative stress, renal problems and mental illnesses. The speciation of trace metals and heavy metals in various forms including the free ionic forms are a serious health concern to clean drinking water. The events leading to the speciation of trace metals and heavy metals is central to this investigation from both an experimental and a computational perspective. Literature data obtained from the World Health Organization (WHO) indicate that about 1.1 billion people representing approximately one sixth of the global population lack safe drinking water [4]. Majority of these people live in China, India, Africa, Middle East and Latin America [5]. For instance, in developing countries water pollution problems are attributed to industrialization and agricultural practices. Surface waters are most prone to pollution mainly because of the ease of accessibility for disposal by wastewaters [6]. The anthropogenic effects like industrial, urban and agricultural activities, increasing exploitation of water resources [7] and also natural processes like erosion,

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precipitation inputs and weathering of crustal constituents degrade surface waters and therefore compromise their use for industrial, drinking, and agricultural practices [6]. Of the possible pollutants in water, trace metals have attracted a lot of attention owing to their high toxicities even at low concentrations. Most trace metals exhibit a wide range of oxidation states which determine their physical chemical forms [8]. Metal speciation is fundamental to the understanding and forecasting of metal behaviour and its impact on any environmental ecosystem [9-11]. This is because it gives information about toxicity, environmental mobility, biogeochemical behaviour, bioavailability, and potential risk at large that are strongly dependent on the chemical species of trace metals [12, 13]. For instance, the free Cu^+ is the most toxic form of copper with toxicity of copper forms decreasing in the order $\text{Cu}^+ > \text{Cu}^{2+} > \text{inorganic copper} > \text{organic copper}$ [14]. Moreover, Cr(VI) is 10 to 100 times more toxic than Cr(III) [15]. Therefore, the problem of element speciation in waters is of growing interest and speciation analysis is presently performed regularly by most researchers to monitor the quality of the environment [11, 16].

The main factors influencing the speciation of metals in water are mainly; the solubility of the metal compounds, the oxidation state of the metals, availability of complexing agents, ion-pair formation, complex formation, adsorption or desorption to particulate material, redox and pH condition of the environment and biochemical processes [17]. Studies on toxicity of trace metals show that the free hydrated ion is the most toxic form [18]. This is because the free metal ion is significantly easier and rapidly adsorbed on suspended particles [19]. If the ions are bound to natural organic matter (NOM) or adsorbed to solids, they are no longer free and therefore less bioavailable [20]. Previous studies on Nairobi River targeted only the total concentrations of trace metals [21, 22] – this gives little information about toxicity, and potential risks in general which are strongly dependent on chemical species of trace metals. Interests in metals such as copper, zinc, manganese and iron considered essential for metabolic functions in organisms rely on their nutritional value as well as their toxicity. Lead and chromium may exhibit extreme toxicity even at low concentrations under certain conditions [23].

The principals focus of this study was to determine the speciation of trace metals (Cu, Cr, Fe, Mn, Pb and Zn) using JESS computer program in the water of Nairobi River. JESS model is a large body of computational programs concerned primarily with modeling of chemical phenomena in aqueous solutions especially water systems. The model takes into account variations in the relative amounts of components, ionic strength, solution pH and temperature. The program (JESS) speciates trace metal species into their various forms and predicts the most stable state of a given metal. Moreover, it gives information on the most toxic form of the metal. Therefore, this investigation is critical in understanding polluted water systems and specifically in providing information regarding the quality of water for both domestic and commercial purposes.

Description of the Study Area

Nairobi River flows through the Kenyan capital city (Nairobi) and is the main river of the Nairobi River Basin. It is a complex of several streams that join together, and flow towards the larger Athi River which drains its water into the Indian Ocean. The source of Nairobi River is Ondiri swamp in Kikuyu Township at the foot of Mount Kenya. Downstream from its source, there is change from subsistence farming into residential estates. In some instances, raw sewage from residential estates is discharged into the river. As the river cuts across the central part of Nairobi city, it passes through areas of commercial and industrial activities.

The river also passes through the areas reserved for industrial establishments where effluent discharge waste into existing municipal sewerage system which occasionally burst and drains its contents into the river.

Six sampling points along Nairobi River were selected for this study as indicated the map, **Figure 1**. These sampling points were Chiromo, Kirichwa, Kileleshwa, Lenana School, Lenana dam and Riara. The sampling points lie approximately between longitudes 036.3658° to 036.4694°E, latitude 01.1744° to 01.16965°S. Nairobi River is situated at an altitude of 1601-1787 metres above sea level.

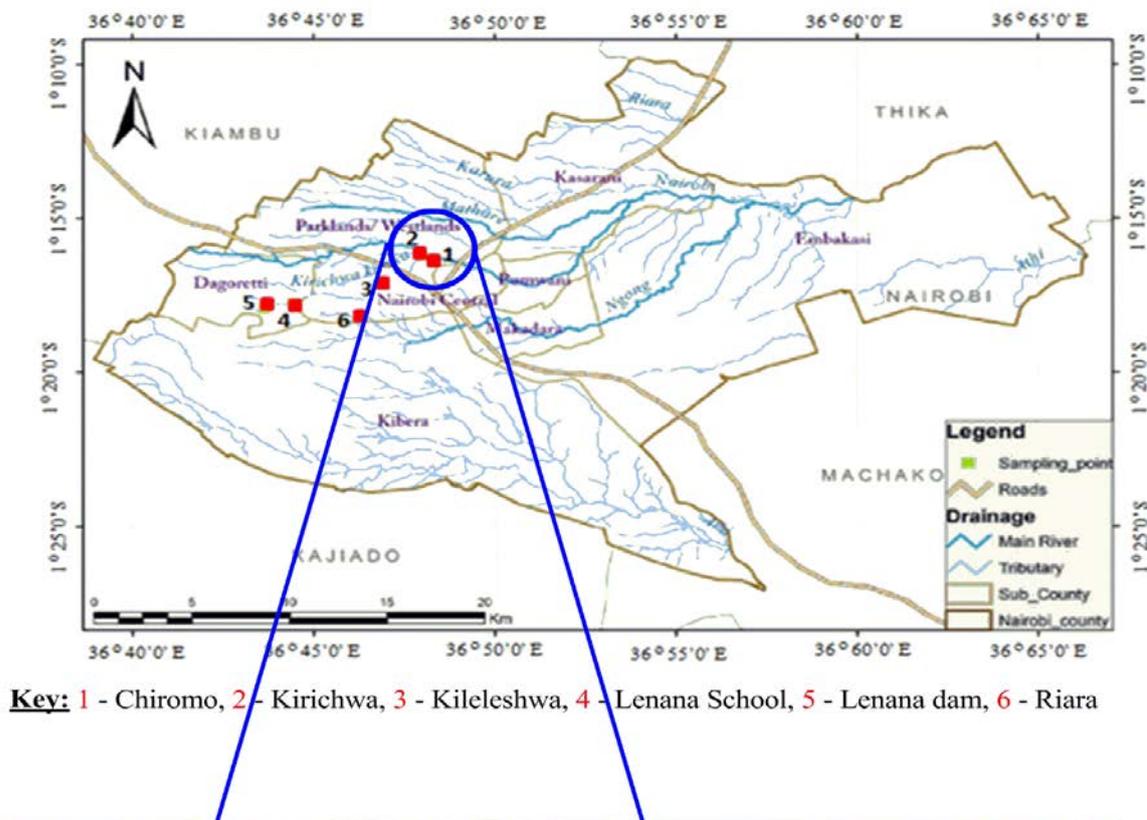


Figure 1. A map of Nairobi County including sections of Nairobi River basin (the sampling points are indicated in red)

MATERIALS AND METHODS

The reagents used in this study were of analytical grade; potassium chromate, silver nitrate, sodium chloride, nitric acid Sulfaver 4 sulphate reagent, SPADNS reagent, Nitrivier 3 nitrite reagent, molybdate and amino acid reagents, nitrite, fluoride, phosphate and sulphate standard solutions, copper, lead, manganese, chromium, iron and zinc standard solutions (purity $\geq 99\%$) were purchased from Sigma Aldrich, Inc., St. Louis, Missouri, USA.

Sample Collection

Sampling was carried out during the wet (November 2013) and dry (June 2013) seasons. At the points of sampling, sampling containers were rinsed with deionized water before being filled with water samples. The

samples were collected in duplicate at each sampling point and concentrated nitric acid was added to containers containing water samples for metal analysis in order to preserve the samples and prevent oxidation. The pH, conductivity, total dissolved solids (TDS) and temperature measurements were measured *in situ* as soon as the samples were collected using a portable EC/TDS/NaCl/Temp/pH meter model MI 306. Dissolved oxygen (DO) was also determined *in situ* using a dissolved oxygen meter model HI 9146. The water samples were then transported to the laboratory for analysis.

Laboratory Analysis

Standard methods used for chemical analysis in this study were sulphate (sulphate 4 method), nitrite (diazotization method), fluoride (SPADNS method), and chloride (titration method) [24]. The determination of trace metals (Cu, Fe, Pb, Mn, Cr and Zn) was carried out using flame atomic absorption spectrometry (AAS) model SHIMADZU 6300. A spectrophotometer model DR 3900 was used to determine the levels of sulphate, nitrite and fluoride [24].

Speciation Analysis Using JESS Computational Code

The temperature, pH and concentration of Pb, Mn, Cu, Fe, Zn, Cr, NO₂⁻, Cl⁻, F⁻ and SO₄²⁻ were fed into the JESS computer program (version 7.3) [25] in order to carry out speciation analysis. JESS operates with input files in which the calculation instructions are arranged according to keywords which are largely self-instructive. The chemical elements (Pb, Mn, Cu, Fe, Zn, Cr, NO₂⁻, Cl⁻, F⁻ and SO₄²⁻) for each sampling site were fed into the JESS computer program (version 7.3), after which the system extracts the relevant information from the main JESS database and created a sub-database. The pH, temperature and concentration of Pb, Mn, Cu, Fe, Zn, Cr, NO₂⁻, Cl⁻, F⁻ and SO₄²⁻ for each sampling site were fed into the program and all possible species relative to a particular set of species present are identified. The speciation distribution was determined in terms of concentration and percentage abundance of each species based on the total concentration of the ions [25].

The models for chemical speciation rely on thermodynamics and mass balance to determine the concentration of every species that comprises a given component. Mass balances are set to be equal to the concentration of every element into the system (commonly measured analytically), and mass action equations are well-defined based on the mass balance equation 1 below [26]:

$$M_i = \sum_{j=1}^{N_c} \Sigma A_{ij} \frac{\chi_i}{\gamma_i} \quad (1)$$

where M_i is the total mass of component j ; A_{ij} is the stoichiometric coefficient giving the number of moles of component j in species i ; χ_i is the activity of the aqueous species i ; γ_i is the activity coefficient of species i ; and N_c is the number of components. The mass action equation expressed as shown in equation 2:

$$\chi_i = \beta_i \prod_{j=1}^{N_c} C_j^{A_{ij}} \quad (2)$$

β_i is the overall equilibrium formation constant for species i [26].

This point illustrates the essential concept that the total amount of an element in an environmental setting is not necessarily a good measure of its potential health threat [27].

RESULTS AND DISCUSSION

Chemical Speciation of Iron

Iron speciation indicated that 69.8% existed in oxidation state +3, and about 30% were in +2 oxidation state. The common species of iron II observed during the dry season (Figure 2b) were iron (II) sulphate, hydroxyl-sulphate, fluoride, and hydroxide complexes. The other important species were the free Fe²⁺ ion, Fe(OH)₃, and [Fe(OH)₄]⁺. These observations are consistent with the high levels of the anions responsible for the formation of the iron complexes during the dry period as presented in Table 1. Water is a very complex matrix and therefore variation in physico-chemical parameters such as pH is not unusual taking into consideration pollutant components from industrial, farm practices, and geologic sources which may alter the acidic or the alkalinity nature of the water. Additionally, dissolved minerals can cause the pH of water to fluctuate. Generally from this study, the pH during the wet season is low possibly because of surface run offs containing dissolved minerals such as carbonates and massive industrial effluents which are usually released during the rainy season. Evaporation effects during the dry season may result in the water becoming slightly alkaline.

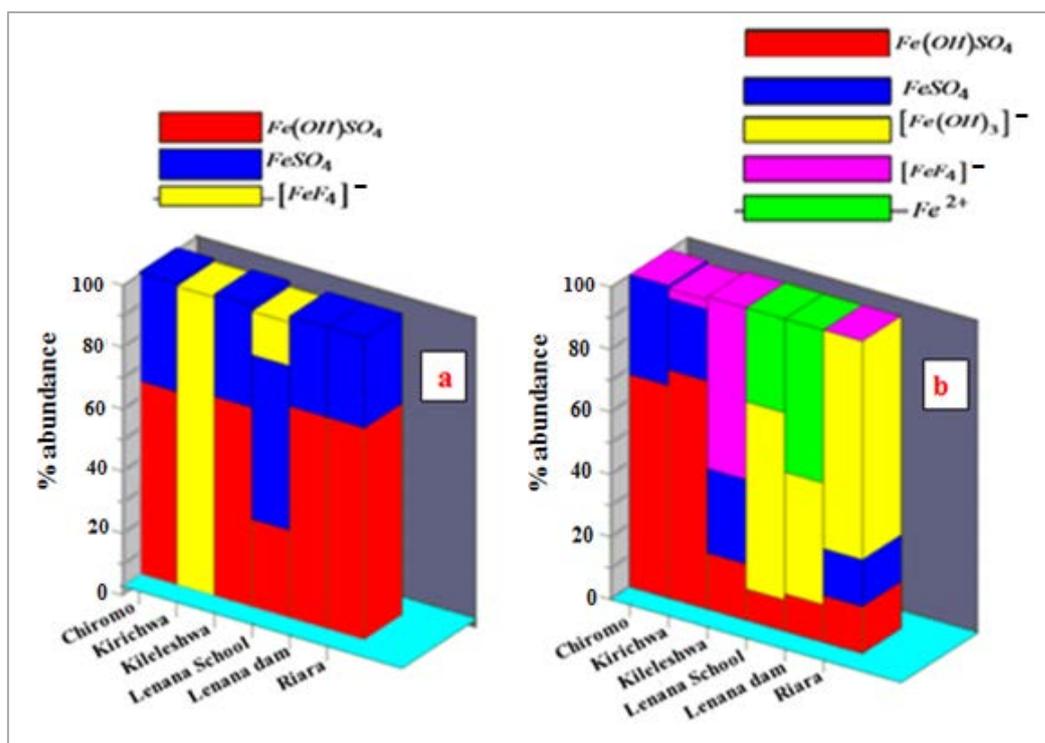


Figure 2. Percentage abundance of major Fe species during the wet season (a) and the dry season (b)

Table 1. The level of physico-chemical parameters analyzed during the wet and dry seasons

Parameter	pH		Temp. °C		DO (mg/L)		sulphate (mg/L)		nitrite (mg/L)		chloride (mg/L)		fluoride (mg/L)	
	Wet	dry	Wet	dry	Wet	Dry	wet	Dry	wet	dry	wet	dry	wet	dry
Chiromo	7.54	7.6	19.9	18.4	17.23	14.80	37.0	14.0	0.556	0.125	0.886	0.071	1.47	0.66
Kirichwa	7.59	7.15	19.2	20.0	19.83	11.30	36.0	14.0	0.553	0.373	0.525	0.043	0.95	0.39
Riara	7.67	7.68	21.9	20.4	22.72	13.06	68.0	3.0	0.585	0.279	0.256	0.029	2.21	1.18
Lenana School	7.05	7.32	21.7	20.3	22.67	8.10	35.0	1.0	0.048	0.002	0.185	0.01	2.87	1.81
Lenana dam	6.89	7.04	22.3	20.1	21.85	10.61	6.0	nd	0.308	0.002	0.085	0.029	2.54	1.54
Kileleshwa	7.50	7.77	25.0	18.3	24.29	13.31	39.0	16.0	0.004	0.057	0.54	0.014	1.86	0.81

nd: not detected

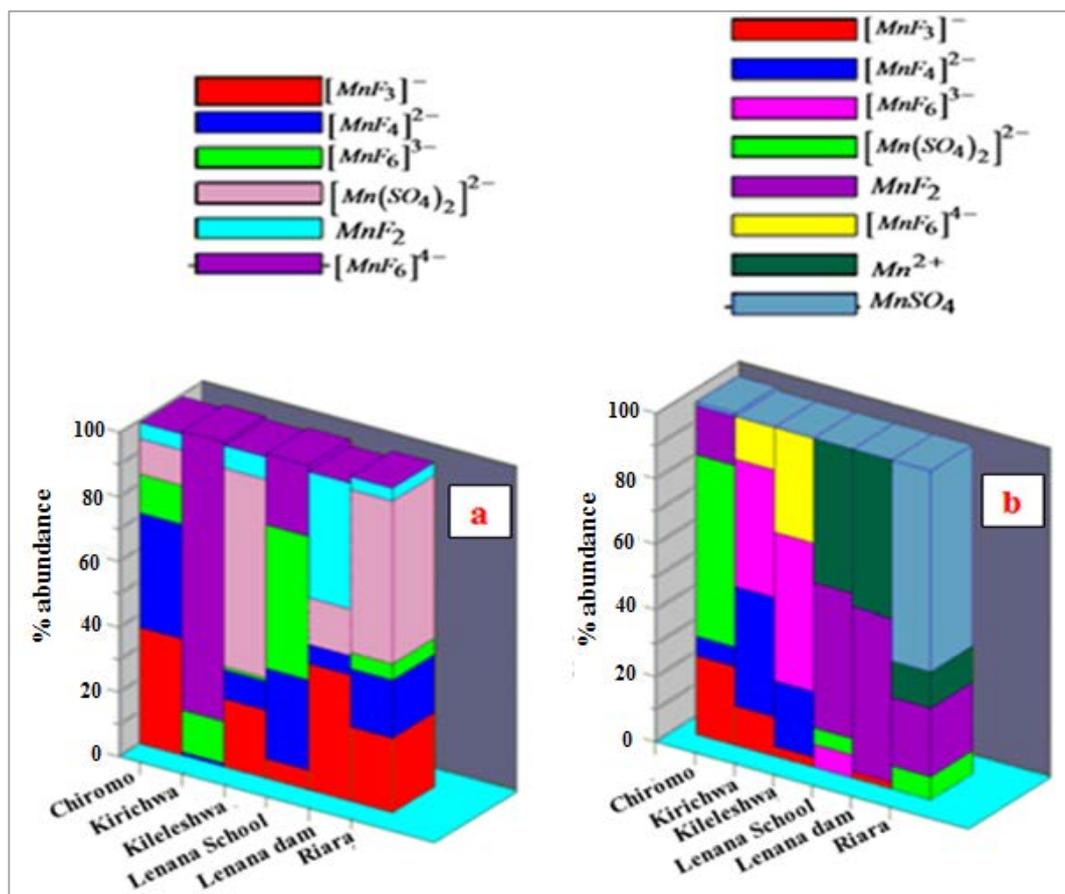
Moreover, during the dry season, the free Fe^{2+} ions were present in substantial quantities around Lenana School (0.4582 mg/L) and Lenana dam (0.4699 mg/L), **Figure 2b**. These values are above the WHO limits for total iron in drinking water [5]. This is because the anion concentrations (fluorides, sulphates, nitrites and chlorides) were generally low around Lenana School and Lenana dam and also contains the lowest amount of dissolved oxygen (**Table 1**). The graph work presented in this investigation were done using Grapher software (*ver.* 10) and Igor *ver.* 5.0.

The metal speciation in Kirichwa during the wet season was remarkably different from the other sampling points because of the dominance of the fluoride complex, $[FeF_4]^-$, **Figure 2a**. This is most probably due to the high fluoride concentration at this sampling point. The reactive F^- ion reacts with all the available iron and thus the complex dominates ($[FeF_4]^-$). This observation fundamentally changes during the dry season where the concentration of iron supposedly increases and fluoride concentration decreases significantly. As a result, the hydroxyl-sulphate species which was the highest at Riara during the dry season (**Figure 2b**) dominate. Furthermore, during the dry season, the speciation results indicate that the free ion form was found in Lenana area in significant concentration as opposed to the chemically complexed forms. The free iron in Lenana area might have been facilitated by both low dissolved oxygen and low pH values. The free ion form is more mobilized and transported in environmental and biological systems. The high solubility of free ions is capable of causing serious cell damage and therefore can act as precursors for more grave biological concerns such as mental retardation, cancer, and tremours [28].

Table 2. Total concentration of trace metals recorded in various sections of Nairobi River water

Sampling Site	Trace metal (mg/L)											
	Mn		Fe		Pb		Zn		Cu		Cr	
	wet	dry	Wet	Dry	Wet	dry	wet	dry	wet	dry	wet	dry
Chiromo	0.446	0.556	0.327	0.497	0.018	nd	0.197	0.019	0.180	0.040	nd	0.085
Kirichwa	0.041	0.158	0.154	0.316	nd	nd	nd	nd	0.153	0.010	nd	nd
Riara	0.778	0.009	0.563	0.097	0.063	0.442	0.018	nd	0.146	0.005	nd	nd
Lenana School	0.451	2.064	1.039	3.144	nd	0.036	0.004	nd	0.141	0.015	nd	0.033
Lenana dam	1.165	1.539	2.866	0.967	nd	0.047	0.006	nd	0.135	nd	nd	0.075
Kileleshwa	1.258	3.684	0.298	1.263	nd	nd	nd	nd	0.141	nd	nd	nd

nd: not detected

**Figure 3.** Percentage abundance of major Mn species during the wet season (a) and the dry season (b)

The trace metals which are central to this investigation are presented in Table 2. The heavy metals; Mn, Fe, and Pb were common along Nairobi River waters whereas trace metals including Zn, Cu, and Cr were either absent or were detected in low concentrations. Remarkably, Cr was completely absent during the wet season in all the sampling areas of the river.

Chemical Speciation of Manganese

Manganese was chiefly found in oxidation state II, which is the most soluble form, and hence the most bioavailable form of manganese compared to other forms [29]. 72% of manganese formed complexes with fluoride and the rest were sulphates and free Mn^{2+} (Figure 3b). It is evident that manganese II complexes dominate at pH 7.59 - 7.15 (mainly manganese sulphate and manganese fluoride complexes). The $[MnF_6]^{4-}$ complex dominated in Kirichwa during the wet season (Figure 3a) due to relatively high fluoride concentration at Kirichwa (Table 1). Manganese sulphate was in excess of 60% of the total manganese speciated forms in Riara area during the dry period.

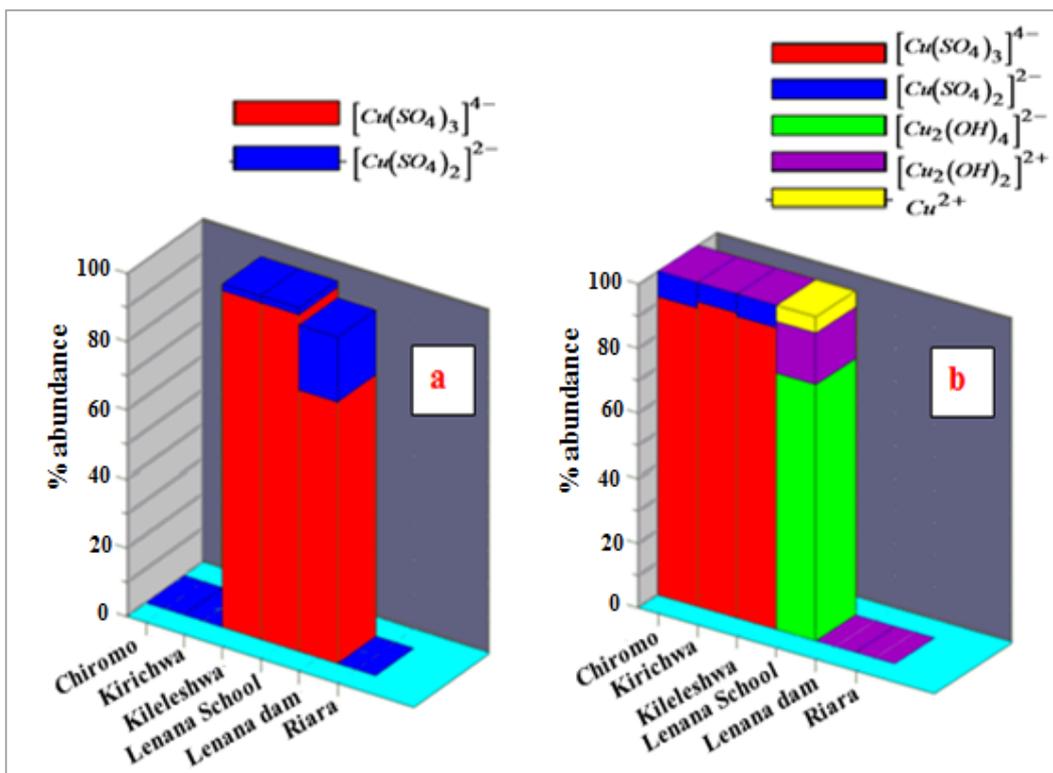


Figure 4. Percentage abundance of major Cu species during the wet season (a) and the dry season (b)

Manganese sulphate species dominates in Kileleshwa and Riara during the wet season probably because of the high sulphate ion concentration. During the dry season (**Figure 3b**), the free Mn^{2+} was observed at Riara (0.4018 mg/L), Lenana School (1.166 mg/L) and Lenana dam (0.7793 mg/L) which is similar to the results observed with iron speciation when the lower anion concentration triggered the presence of Fe^{2+} . The presence of free ions of Mn^{2+} and Fe^{2+} around Lenana School and Lenana dam may be attributed to effluent discharge or leachate from the School laboratory and other anthropogenic sources including quarry mining around Lenana area or natural geological sources.

Chemical Speciation of Copper

Copper was found mainly (> 98%) in oxidation state II, while about 2% was in oxidation state I. The chemical forms of copper in oxidation state II were mainly Cu^{2+} , sulphate, and hydroxide complexes. It is clear that at a pH range of 6.89-7.77 copper predominates at oxidation state II and is mostly bound to sulphates during both the wet and dry seasons. This is because this study has shown that 99% of copper was in form of copper sulphate complexes (**Figure 4**) while other species (nitrites, and chlorides) were present in very small quantities. Nonetheless, the complex $[Cu_2(OH)_4]^{2-}$ dominated at Lenana School possible because of laboratory effluent from the school since copper sulphate is a very important laboratory chemical and coincided with the time when schools do their end of year practical tests (November). Cu^{2+} which is the second most toxic form of copper [14] was present at Lenana School during the wet season (**Figure 4b**).

The difference in speciation at Lenana dam during the wet season was mainly due to the lower sulphate concentration (**Table 1**) and therefore $[Cu(SO_4)_2]^{2-}$ was observed whereas in the other sampling points the dominant chemical form of copper was $[Cu(SO_4)_3]^{4-}$. During the dry season, (**Figure 3b**) the speciation of copper at Lenana School was remarkably different from speciation in other sampling points. This may be attributed to low concentration of ligands (sulphates, fluorides, nitrites and chlorides) at this sampling point. Consequently, the main speciated forms of copper were entirely the $[Cu_2(OH)_4]^{2-}$ complex and free Cu^{2+} .

The concentration of copper was significantly higher during the wet season as compared to the dry season (**Table 2**). This could be a consequence of persistent copper complexes in the sediments which occurred when the volume of water increased during the rainy season. Nonetheless, the concentration of copper was relatively low in most of the points sampled. The source of copper species in the water may point to mineralization reactions and weathering. Similar observations have been documented in literature [30].

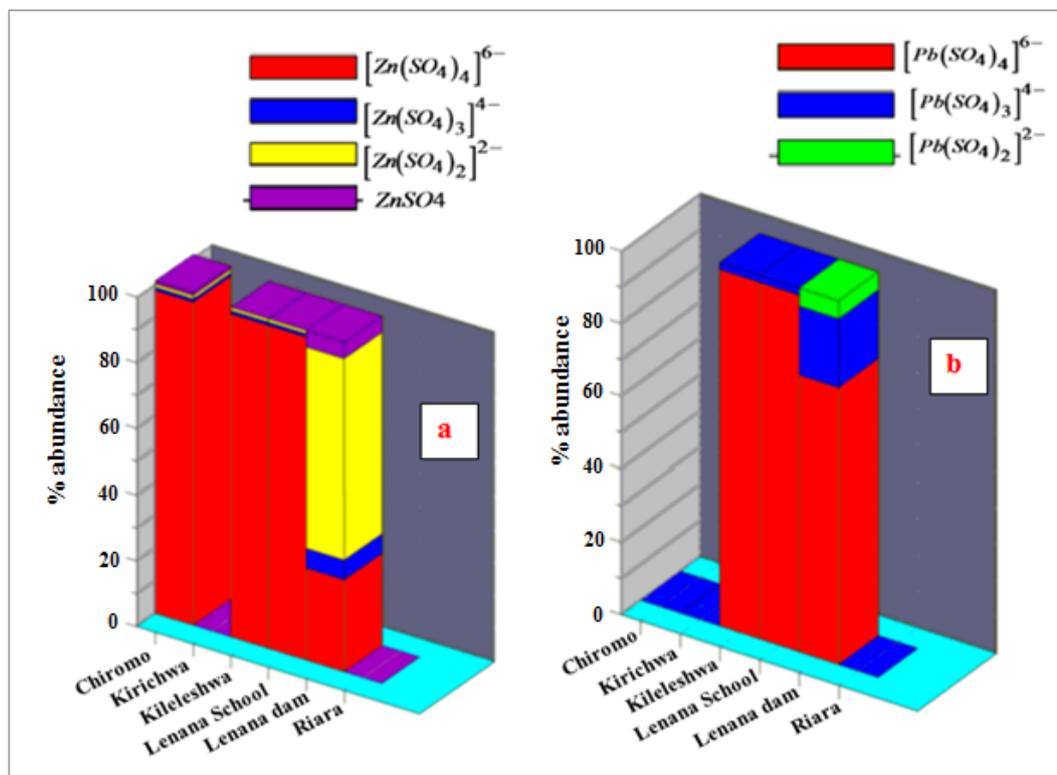


Figure 5. Percentage abundance of Zn (a) and Pb (b) species during the wet season

Chemical Speciation of Zinc and Lead

Zinc was chiefly divalent and its major chemical forms were sulphate complexes (Figure 5a). This is possibly because of the high concentrations of sulphate compared to all the other ligands. The dominance of $[Zn(SO_4)_4]^{6-}$ was as a result of relatively higher concentrations of sulphate (Table 1) and lower concentration of zinc. At Lenana dam during the wet season, $[Zn(SO_4)_2]^{2-}$ dominated probably due to low concentration of sulphate at this sampling point which was also coupled to other metals (copper, lead and iron) possibly present in this section of the River. The percentage abundance of zinc species during the dry season were $[Zn(SO_4)_4]^{6-}$ (90%), $[Zn(SO_4)_2]^{2-}$ (6%) and $[Zn(SO_4)_3]^{4-}$ (3%).

Interestingly, the complexes $[Zn(SO_4)_4]^{6-}$ and $[Pb(SO_4)_4]^{6-}$ were the most dominant in various sampling sites as presented in Figure 5. These complexes accounted for nearly 90% of the species speciated in the water. The high concentration of lead (Table 2) obtained during the wet season might be attributed to the surface runoff from a point source. For instance, lead present at Lenana School and Lenana dam during the wet season might be attributed runoff of lead from paint since the school buildings had been renovated during the sampling period.

On the one hand, lead sulphate complexes were the dominant species probably attributed to high concentration of sulphate in comparison to other anions (fluorides, chlorides and nitrites). The dominant chemical form of lead was found to be $[Pb(SO_4)_4]^{6-}$ (Figure 5b). This is possibly due to relatively higher concentration of sulphate (Table 1). Unlike other sampling points, $[Pb(SO_4)_3]^{4-}$ was present in Lenana dam during the wet season in significant quantities. This observation may be attributed to low concentration of sulphate at Lenana dam compared to the other sampling sections of the river. This investigation has shown that, the total concentration of zinc was higher during the wet season as compared to the dry season (Table 2). This might be due to contributions from surface runoff, soils that may contain natural traces of zinc or dissolution of zinc from the soil sediments. Moreover, leachate from fertilizers and insecticides, urban runoff and municipal effluents are the chief sources of zinc in water bodies [31]. Since the concentration of zinc in this study was very low, its source was attributed to mineralogy and weathering.

Chemical Speciation of Chromium

It is remarkably clear that chromium was not detected during the wet season (Table 2), an observation which was attributed to the dilution of effects during the rainy period. During the dry season, however; chromium was

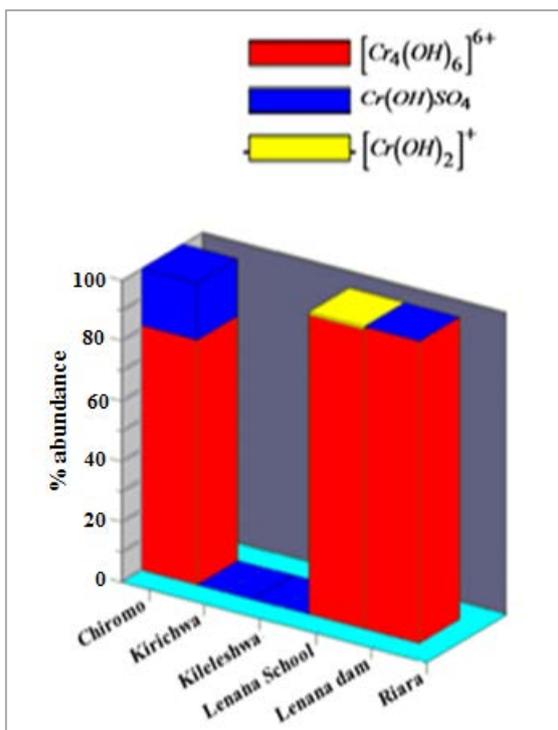


Figure 6. Percentage abundance of Cr species during the dry season

present almost entirely in oxidation state III, which accordingly is the dominant chromium form in surface waters [32]; this form is stable in nature and in biological systems.

The chemical complexes were mainly hydroxides and hydroxide-sulphate complexes (**Figure 6, *vide infra***). $[Cr_4(OH)_6]^{6+}$ was the major chemical form of chromium. $Cr(OH)(SO_4)$ was present only in Chiromo and may be attributed to high concentration of sulphates at this sampling point (14 mg/L) as compared to Lenana School (1.0 mg/L) and Lenana dam (~ 0.0 mg/L). The contribution of chlorides, nitrites, and fluorides to chromium at pH 6.89 - 7.77 was insignificant.

It is, however; well established in literature that chromium in the oxidation state +6, is the most toxic form and is the most aggressive toxicant believed to be a precursor for serious health consequences to both aquatic life and terrestrial organisms [31]. However, this study did not detect any speciated forms of Cr^{+6} . Clearly, **Figure 6** suggests that the concentration of chromium was significant only during the dry season and completely absent during the wet season. We therefore believe that the source of chromium at Lenana School and Lenana dam might be from domestic and industrial effluents which may contain detergents or possibly from natural sources such as rock leachates and soil sediments.

It is evident from this investigation that almost all metal forms were present during the dry period possibly because of evaporation effects which enhanced their concentrations. During the wet season, dilution effects arise and some metal forms may not be detected in significant amounts. For instance, chromium species were detected in low amounts during the wet season.

CONCLUSION

This study has demonstrated that chemical speciation gives information regarding toxicity, mobility and potential health risks which are dependent on chemical species of elements. Speciation of trace metals using JESS program was applied in this investigation and found that Cu, Pb, Fe, and Zn formed complexes mostly with sulphate and hydroxyl ions. The complexes of Mn and Cr were mainly fluoride and hydroxide respectively. Free Fe^{2+} , Mn^{2+} and Cu^{2+} ions were found in Lenana School, Lenana dam and Riara during the dry season. This is a remarkable concern because free metal ions are highly soluble and their inherent toxicity is related to their bioavailability and biotransformation, and is by far the most aggressive toxicants in the biological system. They are readily responsible for a variety of health problems such as oxidative stress, mental illness, and nervous breakdown. Waters from these sampling points are toxic and therefore unfit for domestic, industrial and agricultural purposes. Generally, Nairobi River waters are polluted with a matrix of toxic metals either in their free ionic forms or in their complex forms.

COMPETING INTERESTS

The authors declare that there are no competing interests regarding the publication of this article.

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