Levels of Heavy Metal Contaminants in River Chemosit, Due to Urbanization of Chemosit Town, Kericho County, Kenya

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Abstract

Access to clean water is a key aspect in modern day life. Heavy metal contamination is a detrimental aspect in drinking water. River Chemosit serves as a crucial water source for domestic, agricultural, and industrial purposes, thus sustaining the local livelihoods. The escalating concern regarding river pollutants poses a significant threat to public health. This study aimed to evaluate the water quality of River Chemosit to assess its pollution current status. Both upstream and downstream areas of Chemosit Centre were surveyed in this study while monitoring the vary levels of Heavy metals. Water samples were systematically collected during Wet and Dry seasons along this river from Kipkerieny, Chemosit Centre, and Kabitungu sampling points. These samples underwent comprehensive analysis for Heavy metals analysis where ICP-MS was used. The collected data was statistically analyzed using SPSS version 22. Spatially, the mean values for the parameters were as follows: copper (Cu) and zinc (Zn) met WHO guidelines for domestic water use both spatially and seasonally. However, mean values for aluminum (Al) and iron (Fe) exceeded WHO limits during the dry season. Pollutants originating from anthropogenic activities and discharge from domestic and industrial sources underscores the imperative for continuous water quality monitoring to ensure compliance with NEMA and WHO standards.

Keywords: Toxicity, Ligand, Oxidation, Anthropogenic Activities and Spectrometry

Introduction

Water plays a vital role in sustaining human health and well-being, serving essential functions such as drinking, cooking, and sanitation, as well as supporting industrial processes. Access to clean water remains a challenge in third world countries, leading to millions of deaths annually from waterborne diseases. Consequently, ensuring water quality has emerged as a paramount concern globally [1&2].

The issue of water pollution, particularly by metals, has escalated since the agricultural and industrial revolutions. Presently, a significant portion of water sources worldwide are tainted with heavy metals stemming from various human activities, including domestic and industrial processes [3, 4, 5 & 6].

The environmental impact of trace metals surpasses that of other pollutants because of their non-biodegradable nature, tendency to accumulate, and extended biological half-lives. Consequently, their levels in water frequently surpass permissible thresholds. Hence, they find their way up the food pyramid, can profoundly disrupt biological processes and could potentially lead to severe disruptions in the ecological equilibrium of natural water systems, resulting in the depletion of aquatic biodiversity [7 & 8].

Chemical speciation indicates the diverse chemical forms of elements and their distribution in a specific sample [9 & 10]. It is also valuable for knowing the oxidation state in which heavy metals exist in water, the type of binding ligand, and the development of definite forms of heavy metals in the location; this is because oxidation states of heavy metals can affect their toxicity and bioavailability, absorption and elimination of heavy metals, for instance, toxicity of Mn (III) species are higher than +2, +4, +6, and +7 in their oxidation states [11].

River Chemosit provides several benefits to local community that include source of water for domestic, industrial and agricultural uses. It is also a source of livelihood as majority of the population along the river relies on Commercial activities (car wash business, and water vending) as their main source of income.

River Chemosit is a river that serves Bomet County and the larger Kericho County, and it is mainly used for agricultural, industrial and domestic purposes. A previous study by [12] reported that rivers feeding Lake Victoria contain high heavy metals. A separate study by [13] on environmental conservation indicated that embracing modern technological methods in agriculture ultimately increase productivity and reduce the cost of production resulting in higher profits to farmers [8].

However, farm inputs like fertilizers, and agrochemicals used by farmers destroy the soil and also pollutes water bodies negatively impacting the fauna and flora. This study identified anthropogenic sources as the primary contributors to heavy metals, and other emerging pollutants like pesticides pollution in the river. Anthropogenic activities in the vicinity of water bodies, such as agricultural practices, domestic and automotive washing, industrial discharges, bathing, and water extraction for construction and household use, are implicated.

Various analytical techniques have been established for metal examination in environmental samples. These include sequential leaching methods [14], hyphenated techniques like GC-ICP-MS [7], and X-ray spectroscopic techniques. These methods offer valuable insights into the chemical species present in the environment [15 & 5].

Regarding analysis, it's feasible to detect and measure species in environmental samples [17]. Other methods include coupled plasma atomic emission spectrometry (ICP-AES), also known as inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS). For instance, [18] utilized inductively coupled plasma optical emission spectrometry (ICP-OES) to ascertain the concentration of copper and its chemical forms in soil extracts. Additionally, electro-analytical techniques like anodic stripping voltammetry (ASV) and amperometry potentiometry have been employed to quantify various oxidation states of elements [15 & 19].

While heavy metals are often viewed as pollutants, it's important to recognize that they naturally exist in the environment. These metals enter surface waters through various pathways, including atmospheric deposition during heavy precipitation, leaching from bedrock or soil, and human activities. However, industrial releases often surpass permitted concentrations set by environmental regulations [20 & 21]. Environmental protection agencies have established permissible levels of heavy metals in natural water bodies, as outlined in Table 1,

Table 1: WHO Permissible levels of heavy metals in natural water bodies

Metal	**Maximum allowed concentration mg/L**
Aluminum	0.2
Lead	0.015
Copper	1.3
Zinc	24
Chromium	0.1
Iron	0.3

Human activities contribute to the transportation of various substances, like aluminum, cadmium, manganese, chromium, copper, iron, lead, and zinc. Heavy metals, being non-biodegradable, persist in the environment without breaking down into less harmful forms [8 & 22].

Metals and Their Toxicity

Toxicity denotes the harmful effects exerted by a substance on living organisms, influenced by several factors including the amount absorbed, the way of exposure, and the period of exposure. Metal toxicity, in particular, is contingent upon the chemical types formed by the metal, primarily correlating with the concentration of free metal ions, which serves as a reactivity index. Furthermore, the physiological impacts of a metal can be attributed to its interaction with various cellular ligands [23].

Assessment of toxicity typically involves quantifying alterations in specific biological characteristics following contact to known concentrations of a particular element. Notably, heavy metals in water manifest in diverse chemical forms and oxidative states, leading to variations in their toxicity based on their chemical configuration [24].

Metal toxicity is influenced by the complex interplay of water chemistry, ligand interactions, and the presence of competing ions, which regulate their bioavailability. The partitioning of metals into different chemical forms dictates their mobility and bioavailability in the environment, with the oxidation state playing a crucial role in determining toxicity. Metal speciation, therefore, significantly impacts their bioavailability and associated risks [25]. The buildup of metals in various body organs may lead to adverse effects because of their non-biodegradable nature and prolonged biological half-lives. For instance, aluminum accumulation in the brain is linked to the onset of Alzheimer's and Parkinson's diseases [9], as well as slow growth in children, muscle weakness, and skeletal deformities. Aluminum interference with phosphorus metabolism further exacerbates symptoms such as weakness, anorexia, and bone pain [9]. Similarly, excessive exposure or ingestion of manganese can result in conditions like Manganese, characterized by neurodegenerative effects [24].

Lead toxicity poses significant risks to the nervous system, impacting human beings. Prolonged exposure can impair nervous system function, leading to diminished physical development and cognitive growth [24]. Furthermore, chronic exposure to soluble lead salts or potent oxidants can induce nephropathy and abdominal colic-like pains [27]. Elevated lead levels interfere with the activity of crucial enzymes essential for the synthesis of bone marrow haem, a pivotal component of hemoglobin formation [28].

Similarly, loosely bound copper can induce toxicity by generating responsive oxygen species like superoxide, hydrogen peroxide, and the hydroxyl radical, thereby causing harm to proteins, lipids, and DNA [29 & 30].

Excessive consumption of copper can aggravate irritation in the nose, mouth, and eyes, accompanied by symptoms such as headaches, diarrhea, dizziness, and vomiting. Prolonged exposure may lead to complications for individuals with Wilson's disease, characterized by the excessive absorption and accumulation of copper [31]. Furthermore, elevated copper intake is associated with conditions like coronary heart disease, high blood pressure, and the risk of liver and kidney failure [32].

Similarly, an overabundance of zinc can manifest in symptoms like impaired muscle coordination, dehydration, gastric ulcers, fatigue, and potential renal failure. In drinking water, iron exists as either Fe^{2+} or Fe^{3+} in suspended form, leading to staining of clothes and imparting a bitter taste. Excessive iron intake may elevate pulse rate, promote blood vessel coagulation, contribute to hypertension, and induce drowsiness.

Materials and Methods

Study Area

The features of Chemosit River as a potential source of fresh water to Chemosit Residents, lies in Southwest of Mau complex forest in Kericho County and covers an area of $1023km^2$ at 0.14^0-0.78^0 south. Chemosit River flows through Kimulot, Itare and Nyakach before entering Lake Victoria.

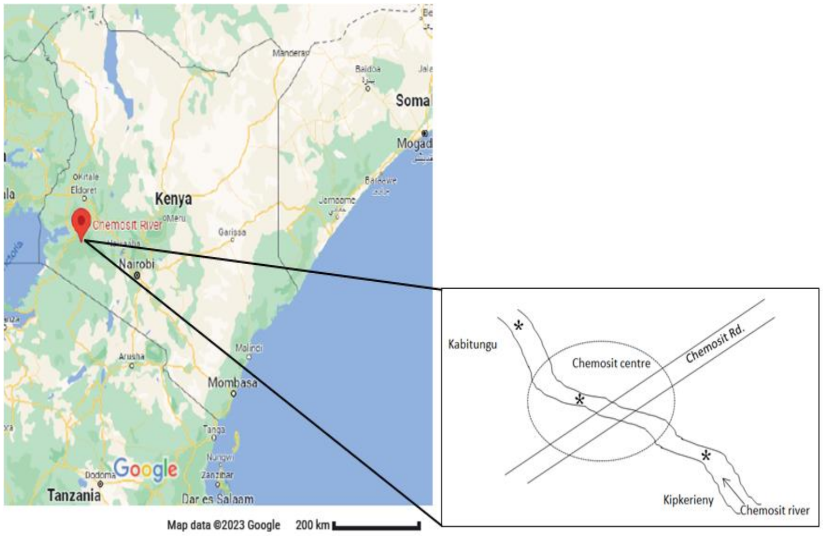

Figure 1: Study area map and sampling stations along River Chemosit which are marked with asterix (*)

Research Design

Stratified sampling was used to obtain water samples. An experimental research design was used. Metals were examined using inductively coupled plasma mass spectrometry (ICP-MS) to determine their meditation.

Data Collection Instruments

All glassware underwent thorough cleaning with detergent followed by rinsing with deionized water. Subsequently, they were immersed in a solution containing equal parts of nitric (V) acid for duration of 24 hours. Afterward, the apparatus was meticulously washed, rinsed with deionized water, and dried using an oven [33].

Prior to usage, calibration of the instruments (ICP-MS and UV-VIS) was conducted. The reagents utilized, including hydrochloric acid, nitric (V) acid, and hydrogen peroxide, were of analytical grade. Careful handling of samples was ensured to prevent contamination, and deionized water was consistently employed during the study. Reagent blank determinations were employed for correcting instrument readings [34].

Sampling Procedures

Water samples were collected from three distinct locations: that’s Chemosit Shopping Centre, Kipkerieny, and Kabitungu. These sampling spots were confined to a 200-meter stretch upriver on either side of the riverbank, aimed at optimizing accessibility. Sampling was executed from the central region as well as the two peripheries of the riverbank, maintaining a distance of 5 meters away from the boundaries of the river. This practice was replicated thrice at intervals of 20 meters to ensure comprehensive coverage.

At every sampling point, 500 ml of water samples were collected in triplicate. Prior to collection, containers underwent cleaning by immersion in a 10% HNO_3 solution and then by rinsing with distilled water. The collected samples were then placed in sterile containers, clearly labeled with the collection location, and stored at ambient temperatures until analysis.

Determination of Metal Ions

Water samples were placed in a PTFE beaker, acidified with 2ml of concentrated nitric (v) acid, and HNO_3 acid, and heated to boiling for two hours in a fume extraction hood. After reaching room temperature, the samples were prudently shifted to 50 ml volumetric bottles and mixed with ultrapure water. To optimize signal intensity, each sample underwent filtration and dilution with 2% ultrapure perchloric acid ($HClO_3$) until reaching a concentration level that ensured a signal intensity below approximately 10^6 counts.

Subsequently, the diluted liquid trials were presented into an argon-based, high-temperature radio frequency plasma. Within this controlled environment, metal ions moved near the detector to be accurately measured and reported by ICP-MS in terms of both counts per second and concentration.

Data Analysis and Presentation

A total of 54 water samples from River Chemosit underwent thorough examination. The data were then laid open to descriptive statistical summaries at a 95% confidence interval. Statistical analyses, including ANOVA, and t-tests, using SPSS version 22. Spatial and temporal variations in physico-chemical parameters were evaluated through ANOVA, with a predetermined significance level ($\alpha = 0.05$). In cases where significant differences in means stood observed, post hoc examination using Tukey pairwise comparisons in SPSS helped identify specific variations between sampling stations and months. To examine seasonal differences, independent sample *t*-tests were employed to assess variations in mean values of physicochemical parameters, inorganic ligands, and heavy metals between wet and dry seasons. Furthermore, Pearson correlation was utilized to calculate the coefficient of correlation between metals, physicochemical parameters, and inorganic ligands, with statistical significance set at P values of 0.05.

Results

Spatial Variations of Heavy Metals

Figure 2 shows the summary of the mean and standard error (±S. E) and ANOVA comparisons of the measured heavy metals concentrations from the different sampling stations along river Chemosit during the study period.

The mean concentration of zinc in the sampling stations fluctuated from 0.01 $mgL^{-1}$to 0.35 mgL^{-1}. Kabitungu station had the highest zinc mean concentration with 0.09 mgL^{-1}± 0.03. The mean concentration of zinc was not important among the sampling stations ($p = 0.41$) (figure 2).

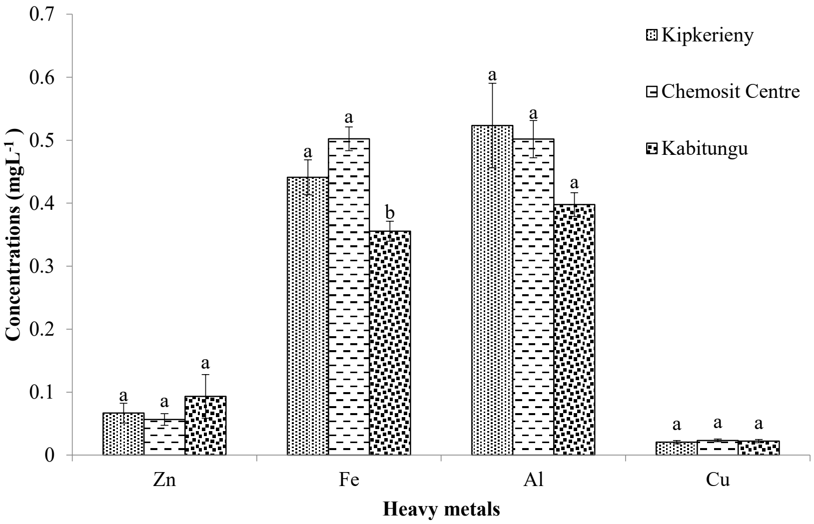

Figure 2: Mean ± SE spatial variations for heavy metals (mgL-1) concentrations from the different sampling stations. Means followed by different letters (a, and b) are significantly different ($p < 0.05$) with respect to heavy metal and stations

The average concentration of iron in the sampling stations fluctuated from 0.27 mgL^{-1}to 0.71 mgL^{-1}. The Chemosit Centre sampling station had the highest iron concentration with 0.5022 mgL^{-1}± 0.02 (figure 2). It was significant among the sampling stations given p-value of 0.05 while p*ost hoc* showed that the iron mean in Kabitungu station was significantly lower compared with Chemosit Centre which recorded the highest iron concentrations.

The mean absorption of Aluminium in the sampling stations fluctuated from 0.2 mgL^{-1} to 1.04 mgL^{-1}. The Kipkerieny sampling station had the highest concentration of Aluminium with 0.5233 mgL^{-1}± 0.07 (figure 2). Its mean concentration was not substantial among the sampling stations at 5% S.I.

The concentration of copper in the sampling stations also averaged from 0.01 mgL^{-1}to 0.05 mgL^{-1}. Kipkerieny sampling station had the lowest concentration of copper (figure 2). ANOVA test indicated that the mean concentration of copper was insignificant among the sampling stations ($p = 0.728$).

Temporal Variations of Heavy Metals

Figure 3 shows the temporal variations of the mean, standard error (±S. E) and ANOVA comparisons of the measured heavy metals concentrations along River Chemosit during the study period.

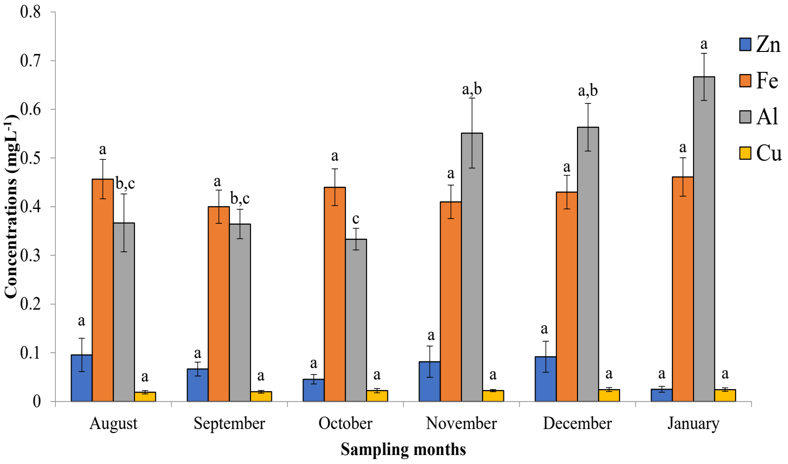

Figure 3: Mean (± SE) temporal variations for heavy metals (mgL-1) concentrations from the different sampling months along river Chemosit. Means followed by different letters (a, b, and c) are significantly different (p < 0.05) with respect to heavy metal and months

The average concentration of zinc in the sampling stations fluctuated from 0.01 mgL^{-1}to 0.35 mgL^{-1}.

The month of January recorded the lowest mean concentration with 0.03 mgL^{-1}± 0.006. Results show zinc was insignificantly dissimilar among the sampling stations ($p > 0.05$) (figure 3). The results are the same with Iron having values between 0.27 mgL^{-1}and 0.71 mgL^{-1}. September had the lowest concentration of iron followed by November. Hypothesis tests showed that the mean of iron concentration was not meaningfully different among the months ($p > 0.05$) (Figure 3).

The mean concentration of Aluminium in the sampling stations was between 0.2 mgL^{-1}to 1.04 mgL^{-1}. These results were significant at 5% S.I. The *Post hoc* showed that the three groups of months in which their mean concentrations of Aluminium did not differ significantly from each other (Figure 3). The mean concentration of copper at the sampling stations ranged from 0.01 mgL^{-1}to 0.05 mgL^{-1}.

The month of August had the least concentration of copper. The mean concentration of copper was insignificant amongst the sampling months ($p > 0.05$) (Figure 3). For heavy metals, the independent sample *t*-test showed that the means of zinc, iron and copper concentration were insignificantly different between the two seasons except for Aluminium ($t_{(52)} = -5.91$; $p = 0.0$) (Table 2).

Table 2: Seasonal variations of the physico-chemical parameters, inorganic ligands, and heavy metals

Parameter	**Season**	**Mean ± SE**	***t*- value**
Zn (mgL^{-1})	Wet	0.07 ± 0.01	$t_{(43)} = 0.15$; $p = 0.88$
	Dry	0.07 ± 0.02	
Fe (mgL^{-1})	Wet	0.43 ± 0.02	$t_{(52)} = -0.05$; $p = 0.96$
	Dry	0.43 ± 0.02	
Al (mgL^{-1})	Wet	0.35 ± 0.02	$t_{(52)} = -5.91$; $p = 0.0$
	Dry	0.59 ± 0.03	
Cu (mgL^{-1})	Wet	0.02 ± 0.002	$t_{(52)} = -1.19$; $p = 0.24$
	Dry	0.02± 0.002	

In the selected heavy metals, a momentous strong negative relationship between temperature and Aluminium($r_{(54)}=-.583$, $p<0$), and Iron with nitrates($r_{(54)}=-.342, p=0.011$). A substantial strong positive association between iron and electrical conductivity ($r_{(54)}=0.473$, $p<0$), and Aluminium with total dissolved solids ($r_{(54)}$)=.679,$p<0$). In contrast, a significant negative relationship between aluminium and nitrates ($r_{(54)}=-.317, p=0.02$, and a substantial strong positive association with iron($r_{(54)}=.579, p<0$).

Compliance with National and International Standards

As shown in Table 3, the measured water quality standards of river Chemosit in Kericho County during the study period, aluminum, and iron exceeded the NEMA and WHO standards during wet and dry seasons while all the other limits were within the satisfactory limits.

Table 3: Heavy Metals compliance to NEMA and WHO standards

Parameter	Season	Mean ± SE	NEMA standards for domestic water sources	NEMA standards for irrigation	WHO Standards for Domestic water
Zn (mgL^{-1})	Wet	0.07 ± 0.01	1.5	2	5
	Dry	0.07 ± 0.02			
Fe (mgL^{-1})	Wet	0.43 ± 0.02	0.3	1	0.3
	Dry	0.43 ± 0.02			
Al (mgL^{-1})	Wet	0.35 ± 0.02	0.1	5	0.2
	Dry	0.59 ± 0.03			
Cu (mgL^{-1})	Wet	0.02 ± 0.002	0.05	0.05	0.1
	Dry	0.02 0.002			

Presence and Concentration of Metals

The study found that Al, Fe, Cu, and Zn were present and their concentrations were: Al 0.474 mgL^{-1}±0.03, Fe 0.433 mgL^{-1}±0.01, Cu 0.022 mgL^{-1}± 0.001and Zn 0.068mg/l±0.01 in river Chemosit waters. According to WHO recommended limits, Al 0.2 mgL^{-1}, Fe 0.3 mgL^{-1}, Cu 0.1 $mgL^{-1}$and Zn 5 mgL^{-1}. From the study aluminium and iron were above the recommended limits while zinc and copper were within acceptable limits. The findings showed that Aluminium and iron concentrations were high and falls within the same other study in Ewaso Nyiro river [35].

Human Health: These metals can carry a significant threat to human well-being if they are present in high concentrations in drinking water [36]. For example, copper can cause gastrointestinal distress and liver damage at high levels. Aquatic Ecosystems can be affected by elevated concentrations of metals [37]. For example, Fe also is restricted to reduce the instances of staining cloths and plumbing materials, Aluminium beyond 0.2 mgL^{-1}results in human memory loss, dementia, and severe trembling can interfere with aquatic plant growth [38]. Water quality has a link to the presence of metals in river Chemosit waters and can indicate poor water quality and may be indicative of anthropogenic activities such as industrial activities and agricultural runoff.

Presence and concentration of Al, Fe, Cu, and Zn in river Chemosit was confirmed. Iron showed a varying result from the different stations while Aluminium, zinc and copper were not significantly different.

Aluminium showed statistically significant while the rest of the metals did not differ significantly to months and seasons. Aluminium and iron were above the NEMA and WHO limits for domestic water.

Abbreviations

NEMA	National Environmental Management Authority
WHO	World Health Organization
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
UV-VIS	Ultraviolet Visible Spectrometry
GC-ICP-MS	Gas Chromatogram Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission spectroscopy
ASV	Anodic Stripping Voltammetry
ICP-AES	Inductively coupled plasma atomic emission spectrometry
GC-ICP-MS	Gas Chromatography - Inductively Coupled Plasma - Mass Spectrometry

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