



Determination of Heavy Metals in Waters of Lower River Kuywa

Stephen Wekesa Muchanga¹ and Ali Mohammed Salim^{1*}

¹Department of Chemistry, Jomo Kenyatta University of Agriculture and Technology (J.K.U.A.T),
P.O.Box 62,000-00200, Nairobi, Kenya.

Authors' contributions

This work was carried out in collaboration between both authors. Author SWM designed the study, managed the literature searches, wrote the protocol, wrote the first draft of the manuscript and performed the statistical analysis. Author AMS supervised and managed all the analyses of the study. Both authors read and approved the final manuscript.

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ABSTRACT

Heavy metals are required by the biological organisms as nutrients but their availability above certain limits leads to adverse conditions such as bone, nerve and internal body organs damage like liver, high blood pressure, acute poisoning and death in animals and human beings and reduction of photosynthesis production, inhibition of seed germination and decreased crop yield in plants. River Kuywa being in a rich inorganic farming of sugarcane and maize area as well as industrial and urban environment, it is exposed to pollution. The objective was to determine the levels of heavy metal concentration using an Atomic absorption spectrometer and the effects of physicochemical parameters to the metal ions concentration which could arise from pollution. Temperature, pH, electrical conductivity and total dissolved solids were found to be (22.9, 23.3 °C), (7.19, 4.34), (312.43, 318.45 µS) and (201, 204 mg/L) for upstream and downstream side of pollutants entry point respectively. Chromium, Copper and Zinc ions had relatively high concentrations compared to Cadmium ions. Lead ions were below the detection limit. Chromium, Copper and Zinc had (0.2660

*Corresponding author: E-mail: alisa22002@yahoo.co.uk;

ppm, 0.4276 ppm), (0.1306 ppm, 0.085 ppm) and (0.1369 ppm, 0.1395 ppm) while Cadmium had (0.0684 ppm, 0.0513 ppm) for upstream and downstream respectively. All physicochemical parameters were within WHO limits except pH. Chromium and Cadmium concentrations were above WHO limits while Copper and Zinc were below. Chromium had elevated concentration compared to other metals. There should be continuous and close monitoring of Chromium levels by reducing the factors leading to high rate of rock weathering and leaching. The water having Chromium and Cadmium concentrations above recommended limits, it should be treated first for Quality Assurance before it is consumed. Agencies like NEMA and WARMA should increase water quality surveillance operations for surface water.

Keywords: Heavy metals; quality assurance; WHO; effluents; physicochemical parameters.

1. INTRODUCTION

The atmosphere is essential to any kind of life. One of the life necessities in the atmosphere is water. Water quality data is put in place for water quality assurance that means it is clean, slightly polluted or polluted category. Departments of Environment worldwide are mandated to monitoring the quality of surface waters since the late seventies to establish the status of water quality, detect changes and identify pollution sources to ensure its suitability for general use. As a result of pollution, contaminated surface water greatly influences the surrounding groundwater and flora and fauna of the riparian area. Water quality data is monitored at numerous stations throughout [1,2]. In the last few years there has been an inadequate supply of water in the big cities, unexpected floods threatening human lives and property [1,2].

In sub-Saharan Africa, water quality aspects do prevail. Water bodies are largely affected by all adverse pollutants leading to human appraisal in order to maintain its purity [3]. In Kenya especially in the Lake Victoria basin, there has been a rising concern about water quality status. This water is mostly consumed domestically and may cause adverse health effects to plants, aquatic and human [4]. This led to several studies on the water quality in the region. Bungoma County is a rich agricultural area of maize and sugar and also in the industrial and municipal zone [5]. The area has loam soils which weather from exposed rocks in the area thus supporting the agricultural activities. These give rise to the use of agrochemicals, and the evolution of industrial and municipal effluents in the area [5]. The effluents and pollutants released into the river prompted this study on heavy metals. Heavy metals are required by the biological organisms as nutrients but their availability above certain limits leads to adverse conditions such as bone, nerve and internal body

organs damage like liver, high blood pressure, acute poisoning and death in animals and human beings and reduction of photosynthesis production, inhibition of seed germination and decreased crop yield in plants [6]. Human and natural activities are majorly depended on water sources like Rivers. There are a number of rivers in the region like Nzoia, Kuywa, Sio and Malakisi River. These rivers navigate through this region hence transporting a wide variety of organic and inorganic components both useful and harmful to living organisms. The sources of these components are domestic rubbish, effluents from industries like iron and steel, saw-milling, sugar factories, and battery production, deforestation and overflows from broken manholes and septic tanks [3]. Inefficient drainage systems and seepage of leachate from landfills and petroleum spills also contribute to the problem. Most common causes of chronic water poisoning are these heavy metals at a significantly high concentration level. Sources of heavy metals in river water could be due to the discharge of effluents from industries [1] or geological origin [2]. Use of weed killers, fungicides, insecticides and rat poison [6] is mentioned as one of the sources of zinc and Manganese. Iron, which is used as a construction material and as a vessel for piping drinking water ends up dissolving in water. The existence of these metals to some extent are affected by physical parameters like temperature, pH, total dissolved solids and electrical conductivity [5] among others.

This study entailed the determination of the specified heavy metals in sampled area and some of the physicochemical parameters and their effects on cation concentration in sampled water. Then, all tested aspects of water quality were compared to WHO standards. Temperature, pH, total dissolved solids and electrical conductivity were determined using a multi-parameter probe (equipment from ISOLAB laborgerate GmbH manufactures). Heavy metal

concentration was determined by a Shimadzu AA-6200 Atomic Absorption Spectrophotometer.

2. MATERIALS AND METHODOLOGY

2.1 Sampling Area

Sampling was done in Bungoma County in the Western part of Kenya. The actual sampling site was done along River Kuywa that is in Kanduyi constituency, South of Bungoma County. Samples were done systematically along the river both upstream and downstream of sugarcane plantation and Nzoia sugar and municipality effluents entrance vicinity. Distance from the vicinity to sampling sites was 1 kilometer while sampling spots along the river were half a kilometer apart. Samples were collected at a depth of 0.03 meters beneath water surface using plastic sampling bottles treated with 10% nitric acid analytical grade [3].

2.2 Analytical Methods

Sampling was done in consideration of NEMA and the general environmental preservation and protection guidelines. Physicochemical were

determined onsite. Analytically cleaned, using dilute nitric acid, plastic vessels were dipped in water from respective spots of the river's course and a multi-parameter probe calibrated on site for every sample was dipped in each sample one after the other and readings recorded [3,5]. The temperature, pH, conductivity and Total Dissolved Solids (TDS) changes with a change in the environment. Waters from different regions have a varied temperature and this and temperatures affects the dissolution of particles which may consequently affect the pH and ion conductivity of the water. The heavy metal analysis was done according to established standard procedures [3]. Sample preparation including transportation of samples from the field to the laboratory at controlled temperatures of between 22 to 26 degrees Celsius and digestion of the samples using 67% nitric acid for 10 minutes, 10:50 v/v acid to sample ratio while heating on a sand bath was performed and ready samples stored in flat glass bottom flasks ready for analysis. Metal salts standards for respective test metals were prepared by dissolving analytical standard metal salts using distilled water by serial dilution to come up with required metal standards [7].



Fig. 1. River Kuywa sampling sites

Experimental standards like frequency, light, cathode lamps, type of flame, detector and read out modes to be used were also set. Then actual cations analysis was carried out in the laboratory using a Shimadzu AA-6200 model Atomic Absorption Spectrophotometer [3]. First, the blank solution made of distilled water treated by nitric acid was aspirated in to the AAS system to correct any background interferences followed by running of the standard solution of a specific test metal to be tested in order to obtain the calibration curve for that particular metal ion. Finally, the intended samples were introduced into the AAS system in triplicates obtaining the signal of metal absorbance vs the standard concentration curve. Using the regression equation, sample concentration was obtained from the curves by interpolating the calibration curves [1]. In order to achieve the accuracy and precision of the analyses; physicochemical measurements were taken on site due to their variation in their surroundings, sample containers were pretreated by dilute analytical nitric acid and preserved under controlled conditions to preserve the sample integrity, operating standards were set and followed for the whole experiment for signal uniformity, the blank solutions used were treated by the same quantity and conditions as the samples in order maintain the signal consistence and uniformity, all analyses and testing were done in triplicate in order to obtain the mean representative signal of the experiment.

2.3 Statistical Analysis

Descriptive Statistics Analysis Tool pack for data analysis of Excel was employed. Confidence levels used were 95%. Data was subjected to one tail t-test analysis. The data obtained was presented in tabular form with an allowance of standard deviation values [3] to account for the precision of processed data. Data display and further presentation were by use of the bar and comparative bar and line graphs [3].

3 RESULTS AND DISCUSSION

3.1 Physicochemical Parameters

In this study, pH, total dissolved solids, electrical conductivity and temperature were determined and the results are showed in Table 1.

Temperatures of the samples were determined on site because the temperature is subject to significant changes with the environment. This is because it affects the dissolution of matter in water [3]. Low temperatures limit the dissolution while high temperature escalates dissolution. Optimum temperatures are conducive for moderate and allowable particle dissolution hence optimum water quality. Sampled water showed a small range in temperature between 22.9 and 23.3 °C. Previous studies carried out in Lake Victoria basin showed almost coinciding temperatures ranges of between 23.42 to 24.23 °C [3]. The temperature ranges in this study were within the WHO limits of 21 to 29 °C.

Electrical conductivity is attributed by the number of cations or anions present in a sample. Conductivity is proportional to the concentration of these particles and conductivity is temperature dependent. Increase in temperature increases conductivity [8,9]. In the study undertaken in the same region as this study, River Malakisi water conductivity was between 164 and 291 µS [5] while here, the conductivity ranges between 312.43 and 318.45 µS, slightly higher.

pH affects the composition of the water. Low pH encourages particles especially metal salts in water as indicated in previous studies of Osman and Kloas, 2010. Also, the river Malakisi study showed that water pH ranged between 6.8 and 7.3 [5]. In this river Kuywa study, it ranged between 7.19 and 4.34 on the downstream side of the river. This indicated pH out of the recommended range by WHO limits of between 6.5 and 8.5.

Table 1. Physicochemical parameters of samples from river Kuywa

Parameter	Sample		
	Mean values		WHO
	Upstream	Downstream	
Temperature (°C)	22.9 - 23.3		21 – 29 [8]
pH	7.19	4.34	6.5-8.5[8]
Conductivity (µS)	312.43	318.45	700 [8]
TDS (mg/L)	201	204	500 [8]

Total dissolved solids account for all particles soluble in water. Their concentration is proportional to the quantity of soluble particles in the sample. Total dissolved solids were found to be in the range of 201 and 204 mg/L. Temperature, conductivity and TDS were within WHO standards while pH values were not.

3.2 Heavy Metal

Metal traces are found in water due to their high solubility with water. They are mostly in form of metal salts and most metal salts are soluble in water [6,7]. Heavy metal is metal mineral with density above 3.5 to 7 g/cm³ [10]. Some of these metals are essential in the metabolism of biological organisms [10,11] like Zinc, Copper, and Iron among others. On the other hand, some of them are nonessential to biological organisms like Lead. In this study, metals determined were Chromium, Cadmium, Zinc, Lead and Copper.

3.2.1 Trend in heavy metal concentration

The results of the heavy metals were as shown in Table 2. Chromium had elevated concentrations followed by Zinc, Copper and Cadmium. Lead had concentrations below the detection limit. Concentration values were 0.2660 and 0.4276, 0.1369 and 0.1395, 0.1306 and 0.0855, 0.0684 and 0.0513 finally -0.3333 and -0.4486 ppm respectively. After performing the one tail t-test on two samples of means of water downstream and upstream, assuming the equal variance, t-statistical was found to be -0.029383601 while t-critical found to be 1.859548038, t-stat < t-critical, showing there is significant different between water upstream and downstream at P < 0.5.

The major contributing factor of this major increase of chromium concentrations could be weathering of the bed of the river rock and leaching of the soil on river banks [1,2]. Zinc metal, on the other hand, tends to be high than other metals except for chromium because zinc solubility in water increases with a decrease in pH of the water sample. Copper and cadmium solubility in low pH media is very lower respectively compared to Zinc [14,15]. Cadmium contributors in the environment are mostly phosphate minerals, fossil fuels and metal recycling especially zinc and also burning or incineration of municipal wastes [16] which is very limited in river Kuywa vicinity. The order of decreasing in concentration of the metals is chromium > zinc > copper > cadmium > lead is the same as shown in [17] where the order is

zinc > copper > cadmium > lead. The only difference is the position of the lead in the order [17]. In addition, copper ions are found to be competing ions of lead [18,19]. This could be the cause of less lead in the water sample collected. Cadmium is strongly adsorbed in mud [8,20] and river Kuywa has swamps and muds which could cause a low concentration of cadmium.

3.2.2 Comparison of heavy metals with WHO limits

In the study findings, copper and zinc were within the WHO allowable limits while Chromium and Cadmium were above the WHO allowable limits. Copper and zinc had values of 0.1306 to 0.0855 ppm and 0.1369 to 0.1395 ppm for upstream and downstream respectively. The WHO limits for copper and zinc are 1.0 ppm and 3.0 ppm respectively [13]. However, copper toxicity in surface water is greatly reduced when it is bound to particulate matter and also when water is hard [21]. On the other hand, chromium and cadmium concentrations were 0.2660 to 0.4276 ppm and 0.0684 to 0.0513 ppm respectively [12]. The WHO standards for chromium and cadmium are 0.05 ppm and 0.01 ppm respectively. Elevated levels of Cadmium above WHO standards may have resulted from inorganic farm fertilizers [1,6] used in the plantations around and also Cadmium is used as an antifriction in moving parts of the machines like the Nzoia sugar factory in the vicinity. Lead metal concentration was below the detection limit -0.3333 to -0.4486 ppm for upstream and downstream respectively, hence within WHO acceptable limits of 0.01 ppm [12].

3.2.3 Comparison of heavy metal concentration with other studies

In the study done on river Malakisi [5] which is in the same region as river Kuywa, both Copper and Zinc concentrations were in the range of 0.015 to 0.133 ppm and 0.161 and 0.621 ppm for Copper and Zinc respectively compared to this study with results of 0.1306 to 0.0855 ppm and 0.1369 to 0.1395 ppm respectively. In addition, studies done on copper in Lake Victoria, the concentration was in the range of 0.69 to 0.94 ppm [22]. Similar studies done on zinc in Lake Victoria showed the concentration not above 0.220 ppm. [13,23]. Chromium metal may also originate from municipal slugs [24]. Studies done on Lake Victoria basin showed chromium concentrations to be in the range of 0.23 to 0.79 ppm [22] and 0.025 to 0.188 ppm in Rift Valley Lakes [25].

Table 2. The concentration of metal ions (ppm)

Analyte	Sample		
	Mean concentration (ppm)		
	Upstream	Downstream	Allowed limits
Copper	0.1306 ±0.033	0.0855 ±0.065	1 mg/L [12,13]
Chromium	0.2660 ±0.071	0.4276 ±0.012	0.05 mg/L [12,13]
Cadmium	0.0684 ±0.035	0.0513 ±0.006	0.01 mg/L [12]
Zinc	0.1369 ±0.020	0.1395 ±0.028	5 mg/L [8]
Lead	-0.3333 ±0.118	-0.4486 ±0.033	0.01 mg/L [12]

River Kuywa being in the lake basin, chromium concentration was in agreement with those previously done. Studies already done on lead according to Muiruri et al. [26], on the surface of River Arthi showed a concentration range of between below detection limit to 0.047 ppm. Cadmium concentrations done by Kiema et al. [27] on Lake Victoria's sediments showed a range of 0.90 to 1.20 ppm. Which were also above the WHO recommended limits.

3.2.4 Comparison of metals concentrations in upstream and downstream regions

Chromium had a higher concentration both upstream and downstream while Cadmium had the least. Lead concentrations were below the detection limit. Copper concentrations decreased

at a noticeable margin downstream compared to all other metals. Copper mainly originates from the extensive use of sprays and pesticides for agricultural purposes [28]. Its solubility in water could have dropped which might have been caused by a low pH of the water [15]. Conversely, Chromium concentrations increased significantly downstream. Zinc concentration was almost retained in both upstream and downstream. Cadmium concentrations dropped downstream compared to other ions [5,15] Lead concentrations remained below detection limit both in upstream and downstream. This could have been contributed by the fact that zinc is a suppressor metal for lead [29,30]. It is noted that generally elevated concentrations of many metals are found downstream compared to the upstream region of the course of the river [31].

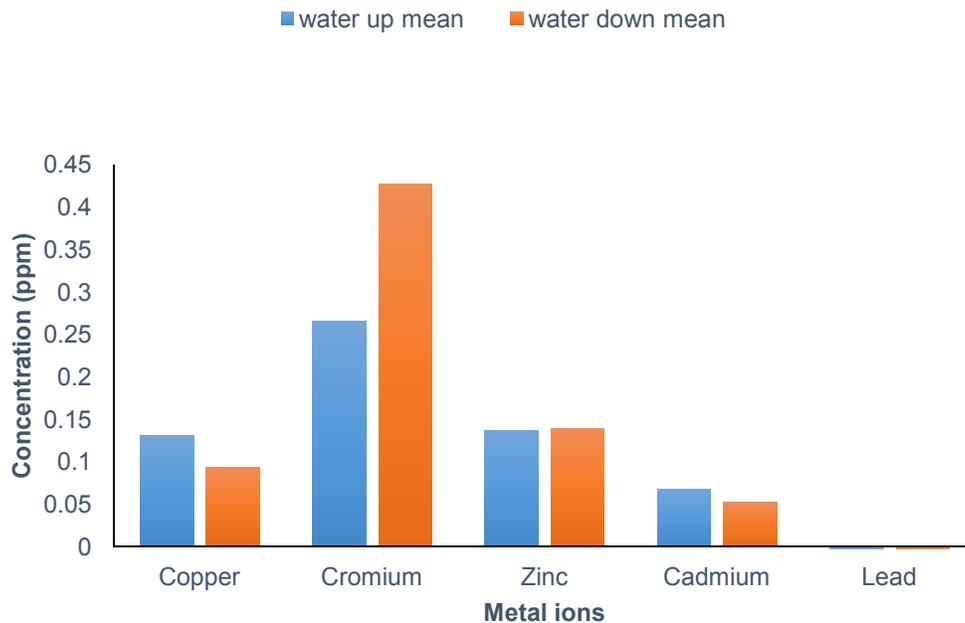


Fig. 2. Comparison of metal concentrations in the water upstream and downstream

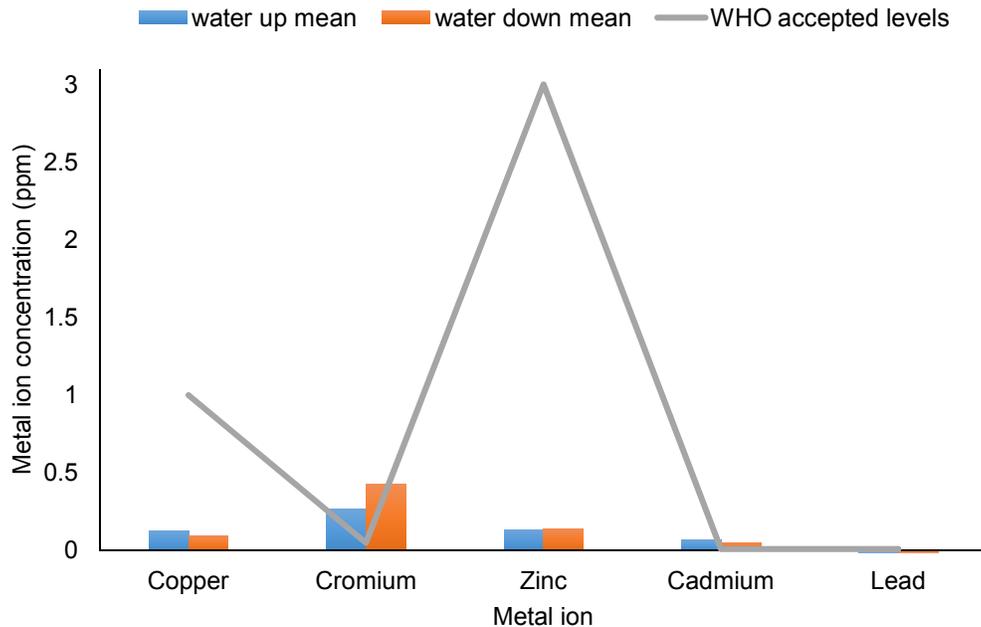


Fig. 3. Comparative line and bar graph of metals and standards

4. CONCLUSION

In the Nzoia area, near Nzoia Sugar factory, the population encounters a big problem of contamination from industrial, urban, agrochemical and geological origins. These led to variations in aspects like a relatively drop in pH [15]. The main source of water in the locality was River Kuywa. Water samples had suitable concentrations [12,13 and 20] of copper 0.0855 ppm and zinc 0.1395 ppm. Lead concentrations were below the detection limit. The river's downstream had relatively low pH of 4.34 which is not conducive for human domestic consumption [15]. There were elevated levels of Chromium 0.4276 ppm and Cadmium 0.0513 ppm, which were above the required concentrations [12,13]. Water from River Kuywa should not be consumed directly but should be treated first before consumption [5].

5. RECOMMENDATIONS

Water sources especially ground-water is supposed to be monitored to standardize its quality [7]. National Environmental Management Authority (NEMA) together with the Water Resources Management Authority (WARMA) should enforce the standard Quality Assessment procedures to be followed by the factories and

municipal management. Their effluents should be treated to the required standard levels before being released to the environment [1]. NEMA and WARMA should monitor the parameters caused by geological processes like rock weathering and leaching to minimize pollution. The population living in the affected area should be sensitized on causes, effects and mitigation of pollutants such as heavy metals. Also, more studies should be undertaken by environmental state agencies about the soil and air quality state in the area.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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