

Determination of Heavy Metals and Nutrients in Rivers Naka and Irigu, Chuka, (Kenya) Using Atomic Absorption Spectrometry and UV/Visible Spectrophotometry

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Abstract: Levels of concentration of heavy metals (lead, cadmium, arsenic and mercury) and nutrients in rivers Naka and Irigu were determined in the first three months (January, February and March, 2013) and variation downstream compared. Lead and cadmium were determined using Atomic Absorption Spectroscopy (AAS). Hydride generation method was used to determine concentration of arsenic while that of mercury was determined using cold vapour technique. Calorimetric methods were used to determine levels of nitrates and phosphates. Concentration levels of lead, cadmium and arsenic were found to be beyond the permissible levels stipulated by National Environment Management Authority (NEMA) and World Health Organisation (WHO) drinking water specifications. Lead had the highest concentration with a range of 0.0537 ± 0.103 parts per million (ppm) to 0.765 ± 0.782 ppm followed by cadmium with a concentration range of 0.035 ± 0.006 ppm to 0.24 ± 0.0084 ppm in both rivers Naka and Irigu. The high concentration levels of lead in River Naka could be attributed to disposal of wastes directly into the river from Chuka Town due to poor drainage systems. Mercury was found to be below the detection limit.

On the other hand, phosphate had a concentration range of 8.31 ± 0.429 ppm to 10.33 ± 0.189 ppm. This was above the specified level of 2.2 ppm in drinking water according to NEMA. Only nitrate was below the recommended levels of 50 ppm and 45 ppm NEMA and WHO guidelines respectively for drinking water.

Keywords: Water, Heavy Metals, Nutrients, AAS, UV/Visible Spectrophotometry, River Naka, River Irigu.

I. Introduction

Clean water is one of mankind's most precious gifts from nature. No other public or medical innovation comes close to having the importance of a safe clean supply of drinking water [Bunce, 1994]. Water quality is important in the health and sustenance of aquatic ecosystems and hydrology. Freshwater is used for drinking, irrigation, industrial uses, production of fish, recreation, transportation and waste disposal [Jackson *et al.*, 2001]. In addition, water plays a major role in the cycling of materials and can be a vector if it becomes [Olatunji and Osibanjo, 2012]. Water is classified as ground or surface water depending on its source. Apart from sustaining life, water is used in industries and pharmaceutical plants, mines, food processing, coolant, paper manufacturing, and so on. It is also used in agricultural irrigation and recreational purposes [Clair *et al.*, 1978]. The quality and stability of water from rivers depends on factors like lithology of the catchment, atmospheric and anthropogenic inputs and climatic conditions [Bricker and Jones, 1995; Markich and Brown, 1998; Bellos *et al.*, 2004; Olatunji and Osibanjo, 2012]. Heavy metals from weathered soils and rocks, mining and metallurgical releases and industrial emissions causes stress in water [Boari *et al.*, 1997; Adams, 2001], and this may expose microflora or microfauna, aquatic lives and humans who depend on such waters to contamination [Etorh, 2007]. Even though heavy metals do not remain in water for long, water catchments areas can become a source of concern if their levels exceed the recommended levels by both local and international bodies [Salomon and Forstner, 1984]. Water has been known to be the main source of human illness, such as cholera and typhoid. Fresh water habitats, like rivers, streams, swamps, marshes and lakes contain a wide variety of microorganisms [Daniel, 1998]. Water that contains a chemical or a biological contaminants is said to be polluted. It has an unpleasant smell, taste, colour and appearance [Alcarno, 2001]. Globally, food, water and the environment are all vulnerable to low level exposure to toxic metal ions. Heavy metals are elements with a density that is greater than five times that of water. They are normally present in natural waters in trace amounts. Their toxicity is attributed to their accumulation in body tissues and competitive interference with other essential elements [Carl, 1975]. On the other hand, nutrients like phosphates and nitrates cause algal-blooms if present in excess in a water body, a condition known as eutrophication. Nitrates in drinking water are of concern due to its toxicity in young children. Rivers Naka and Irigu are surface rivers running from the slopes of Mt. Kenya Forest. They are in Meru-South District, Chuka Division. River Naka passes next to Chuka Town located on a hilly slope of Mt. Kenya. Wastes from this town drain into the river in

form of surface run-offs. Along River Irigu are coffee factories that deposit coffee husks directly into the river. In this work, concentration levels of lead, cadmium, arsenic, mercury, nitrates and phosphates were determined in both rivers Naka and Irigu and compared. The concentration variation trend downstream was also evaluated in order to assess the suitability of the water for human consumption.

II. Materials and Methods

Materials

Analysis of lead and cadmium was done using Flame Atomic Absorption Spectrophotometer, Buck Scientific Model 210 VGP. HVG-1 Flame Atomic Absorption Spectrophotometer AA-62000, Buck Model Scientific 210 VGP was used to analyze arsenic, while mercury was determined using Buck Cold-Vapour Mercury Analyzer W/200A. Nutrients were analyzed using Visible Spectrophotometer. All reagents used were of analytical grade.

The study area of the two rivers is shown in the map below (Figure1)

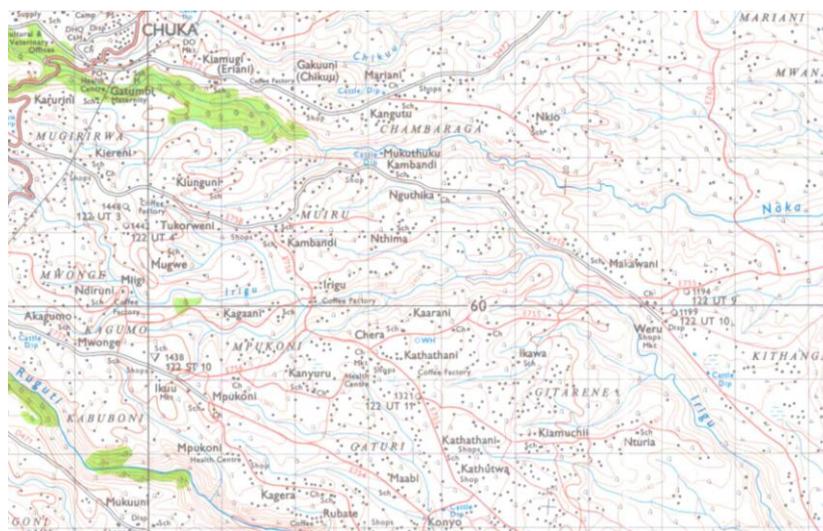


Figure 1: Map showing Rivers Naka and Irigu, in Chuka, Tharaka Nithi County

III. Methods

Flame atomic absorption spectrophotometer was used to determine the concentration of lead and cadmium at their respective wavelengths of 283.3 nm and 228.8 nm. To increase sensitivity, hydride generation and cold vapour techniques were used in the analysis of arsenic and mercury at 193.7 nm and 253.7 nm respectively. Brucine-Sulfanilic acid was used to determine the concentration of NO_3^- spectrophotometrically at a wavelength of 410 nm. Phosphate was determined at 660 nm. Essential physical water parameters such as pH, total dissolved solids, (TDS) and electrical conductivity were also determined.

Five samples from each river were collected in 500.0mL plastic bottles at intervals of 1 km and transported in a coolant box to the university laboratory for analysis on the same day.

Physical parameters, (TDS, conductivity, pH) were determined on the sampling sites using portable pH and TDS Meter. Two of the samples were collected on the upper part of the rivers, (with reference to Chuka Town for the case of R. Naka and coffee factory for R. Irigu) and three samples on the lower part of the rivers. 5mL nitric acid at a pH of 2-3 was then added to the samples and then preserved in polyethylene containers at 4°C.

Working standards were prepared from stock solutions of 1000ppm, (Pb, Cd, As and Hg). To analyse nitrate, 2.0mL of sample was measured into a 50.0mL beaker and then 1.0mL of Brucine-sulfanilic acid reagent added followed by 10.0mL sulphuric acid and mixed, as described by Brandford, (1993). A yellow coloured solution was formed, whose absorbance was determined at 410 nm. Phosphates on the other hand were analysed by adding 3.0ml molybdate solution to 3.0mL ascorbic acid solution in a 50.0mL volumetric flask and shaken well. 70.0mL of sample was then added and made to the mark with distilled water, and its absorbance measured at 660 nm.

0.1598g of lead nitrate, ($\text{Pb}(\text{NO}_3)_2$) and 0.2744g of cadmium nitrate, ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) salts were used in preparation of 1000 ppm stock solutions of lead and cadmium respectively, by dissolving each in 100.0mL of de-ionised water. Absorbencies were measured at 283.3 nm for lead and 228.8nm for cadmium using lead and cadmium hollow cathode lamps respectively. Analysis of arsenic was done by aspirating the samples through flow injection whereby they are mixed with NaBH_4 and HCl in the manifold and passed through a separator.

This separated the liquid and gaseous reaction products (volatile hydrides). Starting with the blanks, standards and then samples, 2.0mL of KI was added to 50.0mL of each. The standards and samples were allowed to react completely with 0.45% NaBH₄, 0.4% NaOH and 5.0% HCl for about 2 minutes after which absorbance was measured and recorded. Distilled water was run after every run of sample to prevent contamination. For the case of mercury, an aliquot (50.0mL) of the sample was measured into the reaction flask, into which 5.0mL of mixed acid solution of HCl/H₂SO₄ in the ratio 3:1 was added to the vessel, and the argon flow to the bubbler started. 10g of stannous chloride was added into an empty acid-cleaned 100.0mL plastic bottle, and then 20.0mL concentrated HCl, 2g of tin and 75.0mL de-ionised water added and swirled gently to dissolve. The energy was put to zero, and then slowly but steadily 5.0mL stannous chloride, (SnCl₂) reductant solution was injected into the septum of the flask stopper assembly with a syringe. Signal interactions were started at this time. The reading was allowed to get back or close to zero after which the argon bubbler flow was turned off and the reaction flask removed. The flask was then rinsed with 5.0% HCl/5.0% H₂O₂ and the bubbler soaked also in the same mixture to remove traces of the SnCl₂.

IV. Results and Discussion

Results

The Tables below show the results obtained for the various parameters.

Table 1: Physiochemical Parameters for River Naka

1st Sampling-January, 2013

Physiochemical Parameters	Sampling stations					
	NU1	NU2	NL3	NL4	NL5	NEMA
pH	6.7	6.3	6.4	6.5	6.8	6.5-8.5
EC, mS	0.06	0.06	0.06	0.06	0.07	
TDS, mg/L	26.5	24.5	25	26.6	26.9	1000

Table 2: Physiochemical Parameters for River Irigu

1st Sampling-January, 2013

Parameters	Sampling stations					
	IU1	IU2	IL3	IL4	IL5	NEMA
pH	7.2	7.4	7.3	7.5	6.5	6.5-8.5
EC, mS	0.06	0.06	0.06	0.06	0.06	
TDS, mg/L	22.9	23.5	23.2	22.1	22.2	1000

2nd Sampling-February 2013

Physiochemical

Parameters	Sampling stations					
	NU1	NU2	NL3	NL4	NL5	NEMA
pH	6.7	6.2	6.4	6.5	6.5	6.5-8.5
EC, mS	0.53	0.47	0.79	0.54	0.53	
TDS, mg/L	15.9	14.2	15.8	15.8	16.3	1000

Physiochemical						
Parameters	Sampling stations					
	IU1	IU2	IL3	IL4	IL5	NEMA
pH	6.2	7.2	6.3	7	7.2	6.5-8.5
EC, mS	0.4	0.42	0.66	0.6	0.5	
TDS, mg/L	11.6	11.8	12.6	12.8	13.2	1000

NB: TDS = Total Dissolved Solids

The pH value of water is an important indication of its quality and it is dependent on the carbon dioxide, carbonate-bicarbonate equilibrium. Acid-base reactions are important in ground water because of their influence on pH and the ion chemistry [Abida *et al*, 2009]. The pH value in the study areas varied between 6.2 and 7.5. The pH value of 7.5 to 8.0 usually indicates the presence of calcium and magnesium. Electrical conductivity is a useful parameter of water quality for indicating salinity hazards [Abida *et al*, 2009]. Electrical conductivity of Rivers Naka and Irigu was found to be varied from 0.06 mS to 0.79 mS.

Table 2: Concentration of Pb, Cd and As in Water Samples of river Naka

1 st Sampling-January 2013				
Sample No.	Pb	Cd	As	Hg
NU1	0.421 ± 0.064	0.103 ± 0.0036	0.0233 ± 0.979	BDL
NU2	0.0537 ± 0.103	0.0808 ± 0.0014	0.0287 ± 0.92	BDL
NL3	0.671 ± 0.078	0.0598 ± 0.0159	0.0215 ± 0.98	BDL
NL4	0.671 ± 0.14	0.0832 ± 0.006	0.0252 ± 0.52	BDL
NL5	0.233 ± 0.103	0.0686 ± 0.006	0.0337 ± 0.55	BDL
NEMA	0.01	0.003	0.01	0.001
WHO	0.01	0.005	0.05	0.001

Table 2: Concentration of Pb, Cd and As in Water Samples of river Irigu

1 st Sampling-January 2013				
Sample No.	Pb	Cd	As	Hg
IU1	0.765 ± 0.782	0.24 ± 0.0084	0.98 ± 0.0287	BDL
IU2	0.473 ± 0.0642	0.0861 ± 0.0059	0.0287 ± 0.922	BDL
IL3	0.452 ± 0.0531	0.0365 ± 0.0012	0.0205 ± 0.602	BDL
IL4	0.202 ± 0.053	0.035 ± 0.0006	0.0245 ± 0.715	BDL
IL5	0.141 ± 0.0545	BDL	0.0337 ± 0.549	BDL
NEMA	0.01	0.003	0.01	0.001
WHO	0.01	0.005	0.05	0.001

The results were then presented in bar graphs in order to view variation of analytes downstream and between the first and second sampling. These are shown below:

Fig 1: Bar Graph for Lead, Cadmium and Arsenic (1st Sampling)

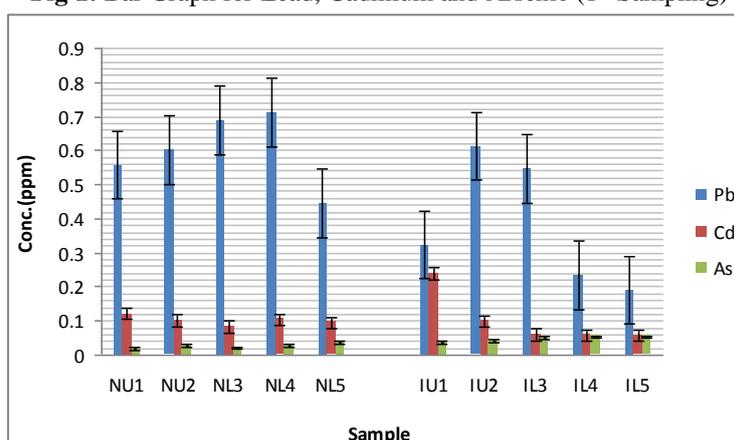


Fig 2: Bar Graph Lead, Cadmium and Arsenic (2nd Sampling)

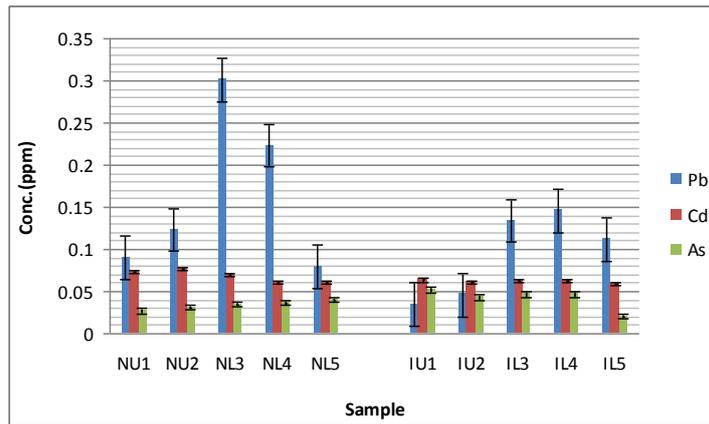


Table 3: Concentration of NO₃⁻ and PO₄³⁻ in water samples in River Naka

1 st Sampling-January 2013			2 nd Sampling-February 2013	
Sample No.	Nitrate	Phosphate	Nitrate	Phosphate
NU1	1.884 ± 0.049	9.605 ± 0.062	2.44 ± 0.048	8.66 ± 0.572
NU2	2.079 ± 0.049	9.675 ± 0.124	2.23 ± 0.082	8.66 ± 0.189
NL3	2.196 ± 0.037	9.625 ± 0.258	2.29 ± 0.06	8.87 ± 0.189
NL4	2.199 ± 0.051	8.917 ± 0.124	2.65 ± 0.033	8.36 ± 0.258
NL5	2.689 ± 0.102	9.524 ± 0.124	2.65 ± 0.066	8.61 ± 0.327
NEMA	50	2.2	50	2.2
WHO	45		45	

Table 3: Concentration of NO₃⁻ and PO₄³⁻ in water samples in River Naka

IU1	1.977 ± 0.054	10.03 ± 0.189	2.69 ± 0.062	9.78 ± 0.189
IU2	2.303 ± 0.116	10.33 ± 0.189	2.76 ± 0.029	8.56 ± 0.348
IL3	1.904 ± 0.085	9.928 ± 0.501	2.91 ± 0.082	8.31 ± 0.429
IL4	2.619 ± 0.151	9.979 ± 0.447	2.6 ± 0.65	9.94 ± 0.406
IL5	2.306 ± 0.135	10.13 ± 0.372	2.63 ± 0.08	8.92 ± 0.124
NEMA	50	2.2	50	2.2
WHO	45		45	

Figure 3: Bar Graph for Nitrate and Phosphate 1st Sampling

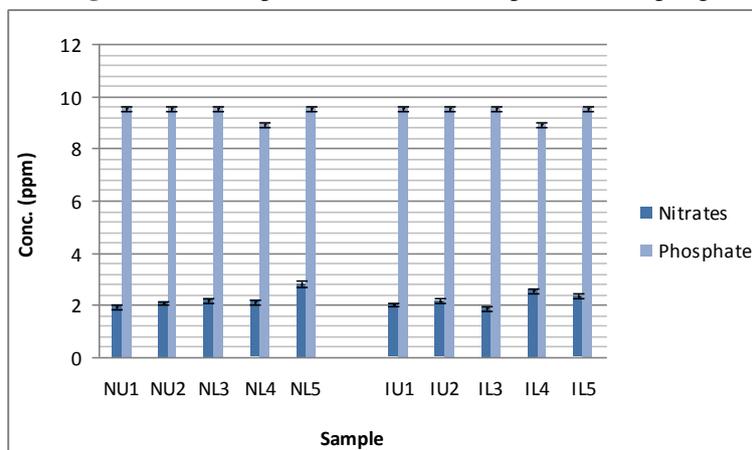
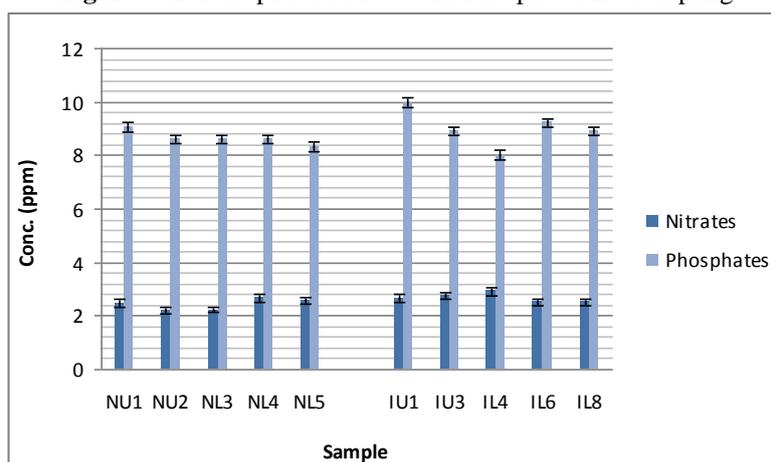


Figure 4: Bar Graph for Nitrates and Phosphates 2nd Sampling



V. Discussion:

From the findings of this research, it was found that the concentration of lead, cadmium and arsenic varied downstream in both rivers Naka and Irigu. Lead had the highest concentration followed by cadmium and finally arsenic. On comparison with the permissible levels of lead, cadmium and arsenic in drinking water according to KEBS and WHO standards, the three were found to be far much beyond these values (Table 2.1). Lead had the highest concentration, with a range of 0.0537 ± 0.103 ppm to 0.765 ± 0.782 ppm in the first sampling period (January) for the two rivers. In the second sampling (February), it had a range of 0.0354 ± 0.0146 ppm to 0.285 ± 0.015 ppm in both rivers. This shows a decrease in concentration from the first sampling. KEBS and WHO Standards has a value 0.001ppm. This high lead concentration can be attributed to the effluents from Chuka Town that empties into River Naka. These may be containing lead arising from petrol stations, soldering, plumbing, and also from exhausts of vehicles along the road. Corrosion from the metal linings of the pipes through which coffee berries pass may be the source of high levels of lead in River Irigu.

Cadmium was relatively lower than lead but still higher than the KEBS and WHO permissible levels of 0.003ppm and 0.005ppm respectively (Table 2.1). In both rivers the ranges were 0.035 ± 0.0006 to 0.24 ± 0.0084 ppm for the first sampling and 0.036 ± 0.0007 ppm to 0.054 ± 0.0119 ppm for the second sampling. Cadmium is usually associated with zinc in its occurrence. Hence corrosion of galvanized pipes and tanks can add cadmium to water which may be a contributing factor to the high levels of cadmium.

Arsenic was also found to be beyond the stipulated value of 0.01ppm according to KEBS, but below that given by WHO of 0.05ppm. However, it had the lowest concentration in comparison to lead and cadmium, with a concentration in the range of 0.0205 ± 0.602 ppm to 0.0337 ± 0.55 ppm in the first sampling and 0.0195 ± 0.419 ppm in the second sampling. Mercury was below the detection limit, (BDL) in both rivers. A slight increase in concentration up to sampling point three in River Naka can be attributed to the effect of direct entrance of waste from Chuka Town at this point. On the other hand, the level of phosphate was extremely high at some points, and far beyond the recommended level. Nitrate-nitrogen was found to be far much below the recommended value of 50mg/L. Both phosphate and nitrate concentration were found to be relatively constant down the two rivers under study. All The physical parameters, i.e. total dissolved solids (TDS), electrical conductivity and pH, (Table 4.5) were all found to be within the recommended values for drinking water by KEBS and WHO.

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