

**DETERMINATION OF LEVELS OF COPPER IN KAMITI RIVER ALONG COFFEE FARMS
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Abstract

Copper-based fungicides are extensively used in the control of coffee pests and diseases because they are relatively cheap and effective. This practice presents serious environmental implications owing to the toxic nature of copper. We report here an assessment on the effects of the use of copper-based fungicides on River Kamiti, which flows along coffee growing areas of Kiambu District, Kenya. The levels of copper in the river were determined using flame atomic absorption spectrophotometry (FAAS) and were found to range from 0.3 to $2.38 \times 10^{-2} \text{ mgL}^{-1}$. It was observed that high levels of copper coincided with coffee spraying seasons and a high amount rainfall, indicating that these contributed to increased seepage of copper in the river. Active pulping factories on both sides of the geographical regions were also found to be a source of the same. Statistical analysis on the experimental data of copper levels from the study sites showed that there was no significant difference between the regions implying that the sampling sites were not the source of variation. Although there is clear evidence that coffee farming introduces copper into the river, the levels of copper in Kamiti river were found to be within acceptable limits and this would be attributed to dilution effects. However, at specific points, the levels of copper were very high threatening the survival of aquatic animals, thus the use of copper compounds is of environmental concern.

Keywords: Copper, fungicides, river water

1.0 Introduction

Human activities such as mining, industrial processes, municipal wastes and farming have contributed to elevated levels of certain elements in the environment. This has resulted in contamination of the environment leading to serious health problems facing the world today. Presence of heavy metals in the environmental matrices is of particular concern because these may get incorporated into drinking water and various food chains (Kabata, 2007).

Coffee is one of the most important perennial cash crops in Kenya where it is grown in large and small scale farms. There are two major diseases of coffee of economic importance namely, coffee berry disease (CBD) caused by *Colletotrichum coffeanum* and leaf rust caused by *Hemileia vastatrix* that attack the crop leading to low yields (Water, 1952). The growth of these fungi is triggered by wet weather (Hindorf & Muthappa, 1974).

Coffee usually flowers at the same period when the fungus start to thrive and there is likelihood that the berries will be attacked at all stages of their growth (Fábio *et al.*, 2007). If this happens, the infected berries fall off before maturity. Effective control of these diseases is achieved by use of a good fungicide cover on the plant from a period before flowering to a period just before ripening and in Kenya these periods coincide with wet weather. Control of these diseases has been achieved through extensive use of organic and inorganic based fungicides. Unfortunately organic based fungicides do not offer adequate cover against coffee diseases as they undergo degradation (Masaba *et al.*, 1993). The fungicides of choice then are inorganic compounds, which are mainly copper based, or mixtures of the same with the organic fungicides (Masaba *et al.*, 1993). These come under trade names such as Nordox and Perenox to name a few.

Copper's fungicidal activity was first recognized in 1885 in France when Milladet reported that grapes along the road side sprayed with a mixture of copper sulphate and lime to make them less attractive to thieves were not defoliated by downy mildew (Hirst, 1970). This led to the development of a fungicide called Bordeaux. The effective compound was thought to be copper (II) hydroxide, $\text{Cu}(\text{OH})_2$ but latter was found to be a mixture of copper and calcium sulphates, whose composition depended on ratio, and age of the mixture (Van Alphan, 1957).

Huge amounts of these copper based fungicides are required to contain this coffee disease (Water, 1952). For example in Kenya alone, Perenox that contains 50% copper, is applied at a rate of 11 Kg per hectare implying an annual national requirement of 6,010 tonnes to cover 546,363.64 hectares, the area under coffee (Masaba *et al.*, 1993). Large quantities of copper from these fungicides find its way into the river through many ways. One among many is by runoff waters as application of the fungicides is during the rainy season. Another is during the coffee

processing, where the initial stage involves the removal of the beans from the berries in coffee pulping factories. This process requires a lot of water, which also inevitably washes off residue fungicides on the berries. This water also finds its way into the rivers, again contributing to the pollutant loading. The area under study has 12 such factories as indicated in the map, Figure 1.

Heavy metals tend to accumulate in various body organs and as a result, long-term exposure can lead to serious toxic effects when ingested (Bhunya, *et al.*, 1987). Widespread use of copper based fungicides in coffee growing regions is a concern as it introduces copper into the environment in rivers flowing through them (Potter, *et.al*, 1990). Even if copper is a necessary plant and animal nutrient, it is toxic to plants and other organisms at high levels (Hodgson *et.al.*, 1962). Therefore it should be monitored especially where there is a heavy agronomic use of copper compounds. Agricultural soils in such areas are reported to have average background levels of 20-30 $\mu\text{g ml}^{-1}$ (Baker, 1990), with average overall US level found to be 15.5- $\mu\text{g ml}^{-1}$ (Holmgren *et al.*, 1993). Some vineyard soils in Europe, which have seen intensive use of copper sulfate containing Bordeaux mixtures for 100 years, have soils with copper concentrations ranging from 100 - 1500 $\mu\text{g ml}^{-1}$ (Besnard *et al.*, 2001). In order to protect against phytotoxicity and negative impact on soil life, an investigation of the extent of pollution in rivers passing through coffee growing areas is necessary for purposes of pollution control. Kamiti River was chosen for a case study.

1.1 Study Area

The study area, was situated in Kiambu District Kenya which lies between $0^{\circ} 25'$ and $1^{\circ} 20'$ South of the equator and $36^{\circ} 31'$, $37^{\circ}15'$ East. Kamiti River from which the samples were collected runs through a topographic region of upper highland to lower midland zone whose altitude range from 1500-1800m above sea level (Kiambu DDP, 1996). The land is intensively utilised for agriculture because of the suitable soil and is located in a well-drained rugged terrain in the upper footridges and foot slopes of the Aberdares ranges. The main economic activity is a mixture of large scale and small-scale coffee farming, subsistence farming and small-scale tea farming.

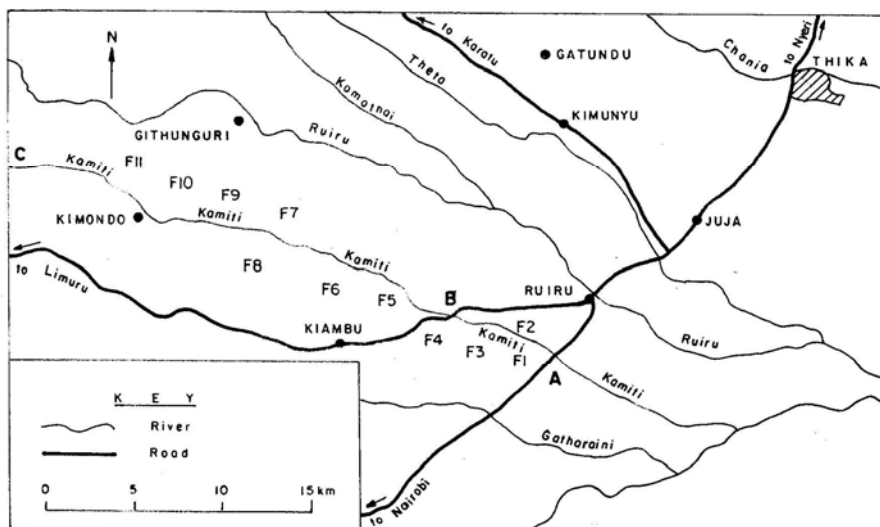


Figure 1 Map of a section Kiambu showing the factories sampling sites (surveys of Kenya)

The region **A- B** was given code TRB and region **B- C** given code KRB

Key Name of factories along Kamiti river

F1- Tatu	F5 – Gwa Thuo	F9- Ngurunga
F2- Munene	F6 - Gatamaiyo	F10- Lisura,
F3- Kiroeri	F7- Kamwaki	F11- Sasini
F4- Kwa Njoka	F8- Gwa Kenda	F12-Mbo-Kamiti

2.0 Materials and Methods

2.1 Sampling

Sampling was done during three different seasons, which were dictated by the weather and divided into two geographical regions. The first region starting from Thika Road bridge (**A**) to Kamiti/Ruiru Road Bridge (**B**) and the samples taken from selected sites between that region were labeled TRB (sample number). Similarly the others sampled between points (**B**) to Kamundung tea estate (**C**) and were labeled KRB (sample number). The total span of the sampling site was 30 km. The sampling seasons were; **1** (May)- after the long rains, **2** (August)- during the dry season and **3** (November)- during the short rain season. Therefore, the labeling of the samples was done to indicate the section of the river it was taken from and the season the sampling was done. A sample labeled 2KRB (sample number) means that the sample was done during the dry season (august) in the section between Kamiti river bridge and Kamundung.

Water was sampled using an extendable water-sampling scoop from the river. One liter of water was taken after thoroughly agitating the water at the sampling site and the pH monitored instantly using a Jenway potable pH meter model number 3071 which had been calibrated with pH buffers 4, 7 and 9. The samples were placed in 500 ml plastic containers that had previously been soaked in dilute nitric acid and later cleaned with de-ionized water and rinsed with the sample water five times to remove any trace of minerals. They were then transported to the laboratory.

2.2 Reagents

All the chemicals used were of analytical grade unless otherwise stated. Distilled and de-ionized water was used for making all dilutions and rinsing of glassware.

2.3 Standard Solutions

Copper standard solutions were prepared by weighing accurately 1.0000 ± 0.0005 g of copper powder in a clean beaker and 25 ml of concentrated nitric acid carefully added to dissolve all the metal weighed. The resulting solution was transferred into a 1-litre flask and made to the mark with distilled water. This solution contained 1000 mgL^{-1} of copper and was stored in a plastic container as a stock solution for a period not exceeding three months. Using the stock solution, subsequent dilutions were made to prepare standards.

The analysis was done using Buck scientific 210VGP Flame Atomic Absorption Spectrophotometer. Its operating parameters were set according to the specifications given by the manufacturer as shown in Table 1.

Table 1: Operating parameters of the Buck scientific 210VGP FAAS

Parameter	Wavelength	Slit-width	Lamp current	Fuel system	Sensitivity
Value	324.8 nm	0.7 nm	1.2 A	Air/acetylene	$2.0 \text{ Au} \cdot \text{mg}^{-1} \text{ L}$

Absorbance measurements were recorded for both standards and samples and a calibration curve from which the concentration of copper in water samples was then calculated was plotted.

3.0 Results and Discussion

The plot of calibration curve for copper was obtained and it is presented in the Figure 2. A similar calibration curve for determination of copper was prepared by Hasan (2003) who studied both sea and river waters. He had eight standard solutions containing $1\text{-}100 \text{ mgL}^{-1}$ for Mn(II), Cu(II), Cd(II) and Pb(II) which were the

metals of interest in river and seawater samples. This worker obtained a regression equation $Abs = 0.0747x + 0.0026$, $r^2 = 0.998$ which was within the acceptable limits. In this study the regression equation was $Abs = 0.0731x + 0.0007$, $r^2 = 0.9982$. The calibration was therefore valid for determination of copper. The correlation coefficient obtained in this work indicates that experimental points fitted in a straight line.

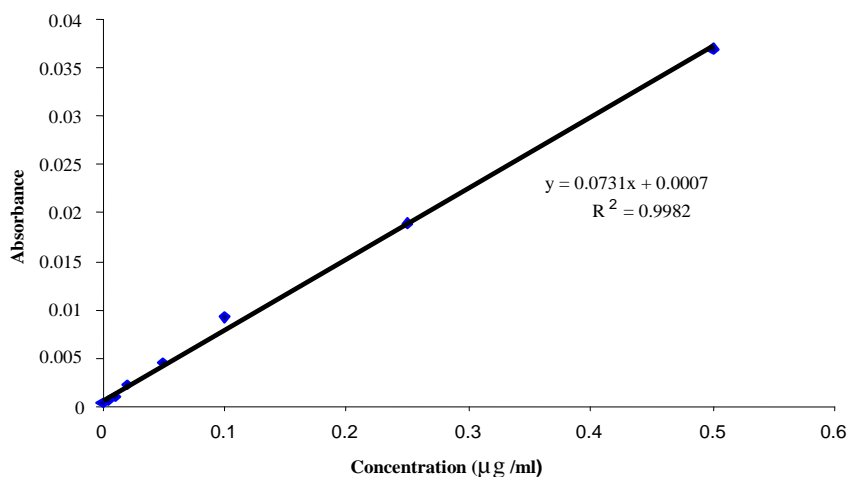


Figure 2 Calibration curve for determination of copper

The results of the FAAS analysis obtained are presented as shown in Table 2. The data gives a simple statistics such as ranges, mean and standard deviation for all the seasons sampled.

Table 2: Average concentration of copper in the water sampled in all the three seasons

	Copper levels (µg/ml)			
	KRB Range	Average	TRB Range	Average
May (After long rains)	0.8-1.38	0.98 ± 0.034	0.70- 2.2	1.01 ± 0.006
August (The dry season)	0.80-1.38	0.83 ± 0.046	0.75-0.82	0.77 ± 0.006
November (The short rains)	0.75-0.86	0.81 ± 0.006	0.00-1.89	0.76 ± 0.004

The average levels of copper were found to be low during the short rain season. This was attributed to the fact that runoff water was low coupled with the fact that there was less coffee harvesting in that period. As a result there was no migration (transfer) of copper from the fields to the river was low.

The distribution of copper along the profile of the river is presented graphically as shown in Figures 3 to 8. Sections TRB and KRB were considered separately when studying the variation of the levels with respect to sampling sites. This is because section TRB is an area with large scale farming only whereas the section KRB is of both subsistence and large-scale farming. In Figure 3, which represents the distribution of copper with respect to sample sites TRB after the long rains, the levels of copper remain fairly constant at about $0.83 \times 10^{-2} \text{ mgL}^{-1}$ but clear peaks were observed in various sites. These are sites 13, 20, 23-24 and 26-28. These correspond to sites with pulping factories, namely, Tatu, Munene, Kiroeri and Kwa Njoka.

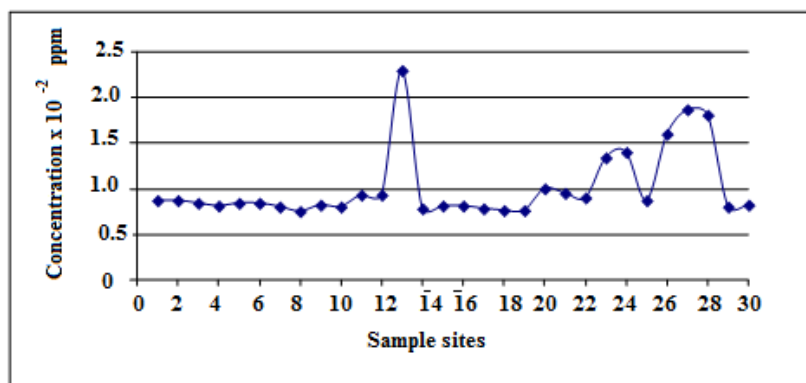


Figure 3: Concentration of copper from different sampling sites along TRB after the long rains.

Observations made at site 13, which show the point having highest concentration of copper at $2.3 \times 10^{-2} \text{ mgL}^{-1}$, correspond to the only site where the discharge was directly into the river. The other factories particularly Munene and Kiroeri had holding ponds spread over a large area but the effluent ultimately ended up in the river. A research study was carried out in Nigeria to determine concentration of various heavy metals in waste waters received in a treatment bond and compared to their respective concentration as the water exited. It was found out that there was a remarkable reduction in their levels and as such, treatment ponds served as a measure for control of heavy metals in waste waters (Ogunfowokan et al., 2007) Figures 4 below represent the distribution of copper with respect to sample sites during the dry season.

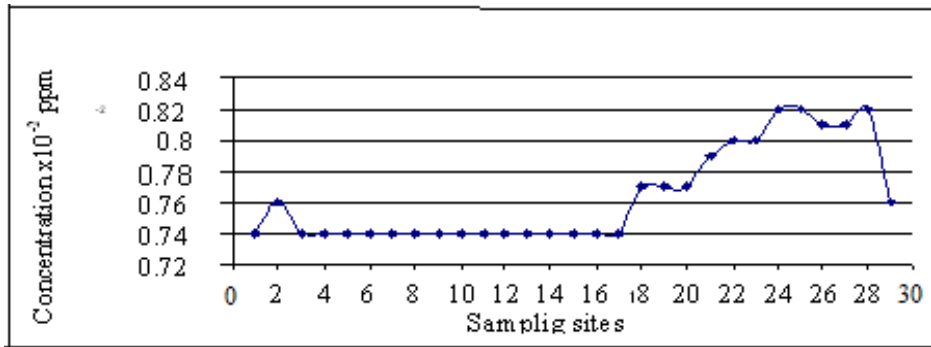


Figure 4 Concentration of copper from different sampling sites along TRB in the dry season

The levels are very low but the pattern appears to be similar to that of Figure 3 except for the absence of a peak at site 13. This is due to the fact that Tatu factory situated at that site, which discharges its effluent directly into the river, was not pulping during that period. The baseline was $0.74 \times 10^{-2} \text{ mgL}^{-1}$ close to what was observed after the rainy season. From sampling sites 17 to 30, a broad peak is observed which is as a result of introduction of copper by factories effluent, and the addition from the runoff water and some oozing from treatment ponds.

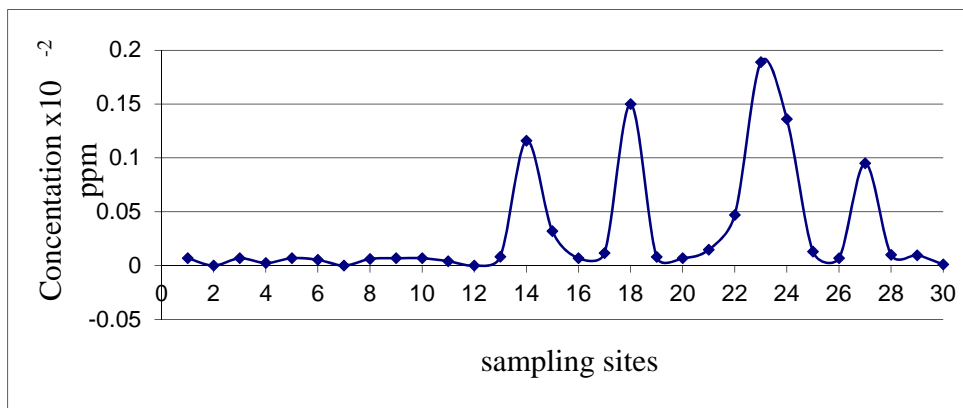


Figure 5: Represent the distribution of copper with respect to sample sites during the short rain season.

Figure 5 Concentration of copper in the water from different sampling sites along TRB during the short rains.

Four distinct peaks which are closely similar to those in Figure 2 are clearly visible. As expected the positions of these elevated points (peaks) correspond to sites where pulping factories are situated. The baseline is lower than for the other two seasons as this period corresponds to a low coffee harvesting season but there is emergence of sharp peaks at similar sample sites as in Figure 2, suggesting that copper in the river during this period is from factories alone.

It is observed that there are no peaks in the area between sites 1 to 12 in the figures above. This may be attributed to the fact that the area has neither a factory nor coffee farms on either side of the river and therefore no source of copper giving rise to that observation.. However a peak was observe at site 2 in Figure 4. This may have been as a result of introduction of copper in the fields by some subsistent farmers who use coffee husks as compost manure as they grow vegetables by irrigation.

The graphs in Figures 6 to 8 represent the area sample coded KRB where both subsistence and large-scale farming was practiced. It shows graphical representation of the distribution of copper along the profile of the river, in the upper region Kamiti road bridge to Kamundu tea estate.

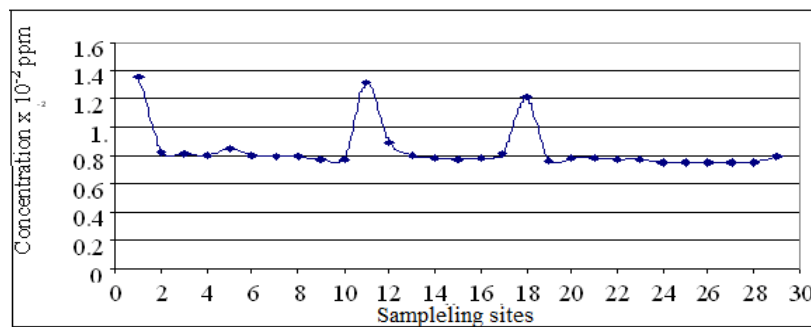


Figure 6: Concentration of copper from different sampling sites along KRB after the long rains.

Figure 6 represent samples taken after the long rains. This section has several factories. They are Kamwaki, Sasini, Kiroeri, Gitamaiyu, Kiroma, Mbo-Kamiti, Surwa, Ngurunga, Gatunda Katito, Muhunu and Migaa. However a close observation in the pattern of the graph show distinct peaks from sampling site 1, 11 and 18 only even though there are more than three factories in this region. Many factories like Gua Thuo, Gitamaiyu and Mboi-Kamiti, which occupies almost the entire sampling site in this region, and others were not actively pulping during the visit due to some misunderstandings among the owners.

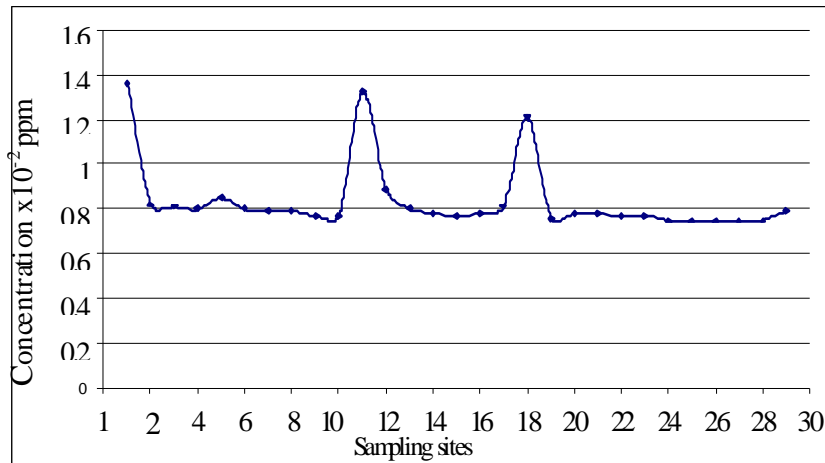


Figure 7: Concentration of copper in the water from different sampling sites along 2KRB in the dry season.

The representation of the above figure shows the variation of the levels of copper during the dry season, a period when coffee harvesting is on. The pattern of graphs in Figures 6 and 7 is similar indicating identical sources of copper for both seasons.

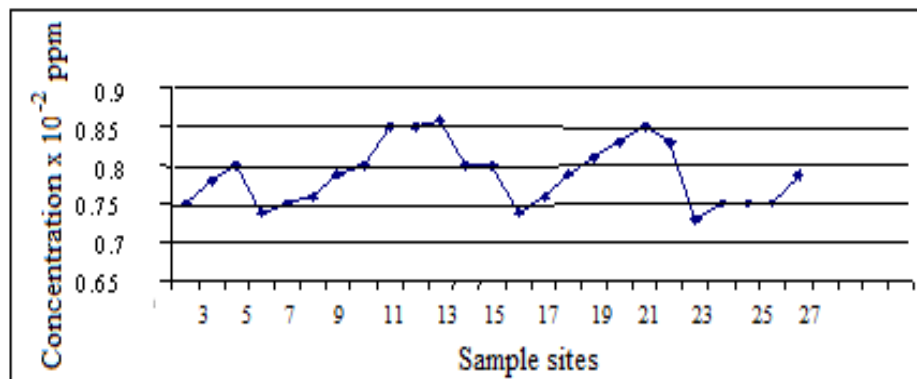


Figure 8: Concentration of copper in the water from different sampling sites along 3KRB during the short rains.

Figure 8 above shows that the levels of copper were very low since coffee was not being harvested. The pattern in Figure 8 does not appear similar with the other two in Figures 6 and 7 although sites with elevated levels agree in all the three. Coffee pulping also minimal during that season when sampling was done. Therefore the discharge points from the factories did not contribute copper into the river then.

It can be generally observed in all the cases that, a sharp rise in the content of copper in the river is occasioned by the presence of a coffee-pulping factory. One can estimate the number of factories by simply identifying the number of the high copper levels. It was observed that the concentration downstream falls to the

baseline level immediately after discharge points and this was attributed to high pH of the water which contribute to a decrease in the content of labile copper (Sheffrin *et.al.*, 1983).

The later was found to be generally above the neutral value leading to precipitation of any soluble copper salt introduced contributing to the low concentration.

The average levels of copper were found to be low during the short rain season and this was attributed to the fact that volume of runoff water was low and there was no coffee harvesting during that period. As a result the migration of copper from the fields to the river through runoff and by effluent was low.

These results agree with studies made by Payne (1986) that Mauree River that passes through an industrial complex and areas of high agriculture activity had similar values. The levels of copper in Kamiti river were found to be normal as with respect to WHO standards whose maximum allowable concentration in drinking water should not exceed a concentration of $\mu\text{g/ml}$ 1.0 copper ions (Maybeck *et al* 1990). Result of dilution effects of some several smaller streams joining the Kamiti river that do not have factories discharging into them, had no noticeable effects.

The results of total copper obtained in this study were subjected to ANOVA (one factor). Sampling was done in three different seasons. It was expected that the seasons would show variation in copper levels. ANOVA indicated there was indeed a significant difference in concentration between seasons based on F-test values.

During the rainy season there was a high concentration of copper compared to the dry season. High copper content during the rainy season may be attributed to surface runoff when fungicides from the field are swept to the river. It coincided with coffee harvesting and spraying season, which lead to high discharge of effluents and runoff to the river containing high levels of copper (Hindorf & Muthappa, 1974). During the dry season there was no surface runoff and the coffee processing was low hence less effluent discharges from factories. This can explain the low copper concentration reported in the water samples during the dry season.

Similar analysis was done to find out if there was a variation between the two regions where sampling was carried out. The statistical F-test showed that no significant difference between the regions implying that the sampling sites were not the source of variation.

4.0 Conclusions

The data obtained in this study showed dissolved copper to be present in Kamiti river water. However, the average content of copper in the water was lower than the maximum contaminant level and so is not a threat to aquatic life or community using this water except for possible accumulation of the element in the body on

prolonged use. However noticeably high levels were observed at effluent discharge points. The levels at those points were as high as $1.9 \times 10^{-2} \text{ mgL}^{-1}$ which is enough to threaten the survival of fish and other lower life forms in the river.

The study indicates that the copper in the river is mainly from effluents from the coffee pulping factories. Therefore coffee farming is the source of introduction of the vice into the river system by either factory effluents or run off water from the fields.

5,0 Recommendations

From the results of this research work, it is clear that treatment ponds should be encouraged. This should be done through the ponds to give ample time to have dissolved copper in the wastewaters to equilibrate with catechins found in coffee pulp such that copper is bound to safe complexes. A registration should be put in place such that no factory discharges effluent in the rivers directly but through the treatment ponds.

Content of copper in coffee products in the market should be carried out to find out if any trace of the vice finds it way in to those consumables.

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