

## JOURNAL ARTICLES

Sensing Gaseous Ammonia using Cation Exchanged Faujasite-X Zeolite

C.B.O. Kowenje and D.C. Doetschman

The Ft-Ir and Malarial Biological Studies of Copper (II) Complexes Containing Thiosemicarbazone and Semicarbazone Ligands Derived from Ferrocene and Pyridyl Fragments

L.S. Daniel, EMR Kiremire, H. Kambafwile, K. Chibale, P.J. Rosenthal, T.M. Kiratu, P.M. Guto, G.N. Kamau

Uptake and Distribution of Selected Heavy Metals by Sweet Potato Plant Varieties under Green House Conditions

J.K. Ndathe, F.B. Mwaura, J. Nsuba, L. Berga, P. Ndolo, S.L. Doty and G.N. Kamau

Correlation between Dissolved Oxygen and Total Dissolved Solids and their Role in the Eutrophication of Nairobi Dam, Kenya

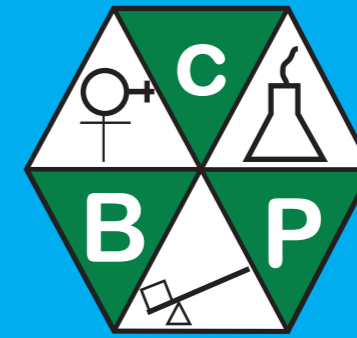
P. G. Muigai, P. M. Shiundu, F.B. Mwaura and G.N. Kamau

Phosphorous as the Limiting Nutrient Element for the Eutrophication of Nairobi Dam, Kenya

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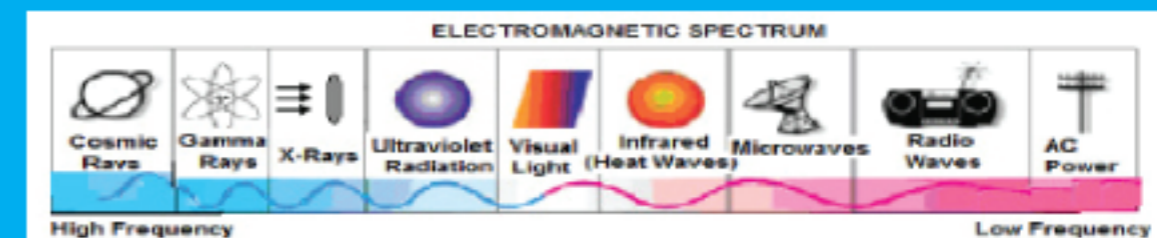
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## ELECTROMAGNETIC SPECTRUM



TREATED WITH RADIATION

## EDITORIAL

### **FOOD IRRADIATION: A possible option for food preservation in the developing nations**

You will agree with me that there are many times when we get angry when one goes to the kitchen only to find that the remaining fruit has gone bad, or even tomatoes, potatoes, cabbages and spinach have given in to new colour and sometimes accompanied with strange smell. In the developing countries there are a number of factors and scenarios, which need to be considered carefully. For example when the weather is good and plenty of rains, the harvests turn out to be at its best moment. In fact this is the scenario we have right now (May 2010). Due to heavy rains, starting towards the end of last year, the yields of most crops were quite attractive, thereby compelling farmers to think of extra storage facilities and effective methods for food preservation. This is also compounded by the fact that more pesticides are required to keep away the pests than during low harvest periods. Moreover, in the next one month we are going to have bounty harvest. I call vividly, seeing big loads of potato harvest from the gardens, only to find them rotting in two or so many weeks, due to lack of appropriate technology to preserve them and capable of prolonging their life time. It is true that some farmers and industries have been using the solar energy to dry the fresh vegetables, aimed at prolonging their life time on a small scale bases. This is particularly the case for beans, maize and related grains. Even after sun drying pesticides are still required to control the pest attacks if the grains are to be stored for a long time. Moreover, most of consumers would love to have potatoes and onions, which do not sprout within a short time and fruits that stay fresh longer than the natural expected life time.

On the other, there is another alternative, which is even more attractive. This refers to the use of ionizing radiation, which could be gamma rays from radioisotopes or X-rays from an appropriate generator. The gamma rays and X-rays are highly energetic, due to their short wavelengths, which fall in the range of  $10^{-9}$ - $10^{-12}$  and  $10^{-12}$ - $10^{-14}$ , respectively. Gamma and X-rays kill microorganisms, bacteria, viruses, insects and related pests, which are responsible for spoiling the food. Depending on the intensity or dose the high energy radiation destroys the living organisms by damaging their genetic material in such a way that they cannot reproduce effectively.

During the exposure of radiation to the appropriate target the food itself is also affected too, though to a small extent. This is because the harvested food materials are not expected to divide or grow with time. Definitely, sprouting of root crops, for example potatoes and onions, after harvest, is a factor that can be controlled by the energetic radiation. In addition, radiation can also be used to delay the ripening of fresh produce by modification of the metabolic processes of maturing fruits and vegetables. Following the ban on the use of ethylene dibromide, as a chemical fumigant, in 1984 in United States of America, farmers reverted to other alternatives, as well as use of radiation, to control insects after food harvest. It is clear that irradiated chicken can pose less of a risk from salmonella and other pathogens that cause food poisoning. Moreover, exposing pork to radiation can deactivate the parasite that causes trichinosis. Very high doses of radiation can completely destroy bacteria and mold on meat, fish and poultry so that when properly packaged they can survive for years without refrigeration. The

aflatoxin, which is common in harvested maize in this region, can be controlled by radiation.

Irradiation is a technology that can solve many other food related problems. It has been legal to use irradiation technology in the United States for over three decades. One of the short coming on the use of irradiation technology is the cost implication, which may not compare favorably with the chemical treatments and food processing. Another crucial factor to be considered in the developing countries is whether the consumer would be willing to have food exposed to high energy radiation (gamma rays and X-rays). Many individuals associate the term radiation to nuclear energy and nuclear weapons, as well as other accompanying fear and controversy. For the consumers to buy irradiated food they must be convinced that it is safe and has no side effects.

According to the International Consultative Group on Food Irradiation (ICGFI) and Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture International Atomic Energy Agency irradiated food is safe. Irradiation does not make food radioactive. Recall that everything in our environment, including food, contains trace amounts of radioactivity. This means that this trace amount (about 150 to 200 becquerels/kg) of natural radioactivity from elements such as potassium is unavoidable in our daily diets. For example, the maximum allowable energies for electrons and X-rays from the two machine-generated sources of radiation that can be used are 10 million electron volts (MeV) and 5 MeV, respectively. Even when foods are exposed to very high doses of radiation from these sources, the maximum level of radioactivity would be just one-thousandth of a becquerel per kilogram of food. This is 200,000 times smaller than the level of radioactivity naturally present in food. As per the ICGFI argument, food undergoing irradiation does not become radioactive any more than luggage passing through an airport X-ray scanner or teeth that have been X-rayed.

G.N. Kamau

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## TABLE OF CONTENTS

<b>Editorial</b> .....	i
<b>JOURNAL ARTICLES</b> .....	1-44
Sensing Gaseous Ammonia using Cation Exchanged Faujasite-X Zeolite <b>C.B.O. Kowenje and D.C. Doetschman</b> .....	1-7
The Ft-Ir and Malarial Biological Studies of Copper (II) Complexes Containing Thiosemicarbazone and Semicarbazone Ligands Derived from Ferrocene and Pyridyl Fragments <b>L.S. Daniel, EMR Kiremire, H. Kambafwile, K. Chibale, P.J. Rosenthal, T.M. Kiratu, P.M. Guto, G.N. Kamau</b> .....	8-19
Uptake and distribution of selected heavy metals by sweet potato plant varieties under green house conditions <b>J.K. Ndathe, F.B. Mwaura, J. Nsuba, L. Berga, P. Ndolo , S.L. Doty and G.N. Kamau</b> .....	20-34
Correlation between Dissolved Oxygen and Total Dissolved Solids and their Role in the Eutrophication of Nairobi Dam, Kenya <b>P. G. Muigai, P. M. Shiundu, F.B. Mwaura and G.N. Kamau</b> .....	35-43
Phosphorous as the Limiting Nutrient Element for the Eutrophication of Nairobi Dam, Kenya. <b>Peter G. Muigai, P.M. Shiundu, F.B. Mwaura and G.N. Kamau</b> .....	44-52
Information to Contributors .....	53-55
Publishing Agreements .....	55
Notices .....	56-67

# Sensing Gaseous Ammonia using Cation Exchanged Faujasite-X Zeolite

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## Abstract

This work presents a method that uses cheap, thermally stable and reusable cation exchanged solid zeolites to detect gaseous ammonia. Here, 24 separately exchanged Cu<sup>2+</sup> and Co<sup>2+</sup> cations per unit cell of 1.23 Si/Al Faujasite-X (as CuX and CoX, respectively), are used as sensors for the ammonia. Upon exposure of CuX to  $\geq 5$  ppm gaseous ammonia, the CuX showed a Diffuse Reflectance peak at 630 nm and an Infrared (IR) band at 1265 cm<sup>-1</sup> that are associated with characteristic interactions of ammonia with CuX framework. Both Diffuse Reflectance (DRS) and Infrared (IR) spectroscopic methods gave a linear detection range of about 25 ppm with attendant R<sup>2</sup>-value of 0.993 for DRS and 0.986 for IR. A similarly treated CoX upon exposure to ammonia gas showed “fingerprint” Diffuse Reflectance peak and IR band at 527 nm and 1312 cm<sup>-1</sup> respectively.

**Key words:** Ammonia, Cation-exchanged Zeolites, CuX, CoX, and Sensors.

## INTRODUCTION

Ammonia pollution is mainly from agricultural sources such as animal manure, forestry and fertilizers and it causes damage to sensitive habitats affecting plants and biodiversity including soils and water and upon accumulation in the atmosphere leads to long-range acidification [1,2]. Pollution by ammonia is, in addition, a recognized problem in mines, and marine environment [2]. The emissions of ammonia are somewhat more uncertain than those of SO<sub>2</sub> and NO<sub>x</sub>. However since gaseous pollutants inherently disperse into the atmosphere, ammonia eventually and synergically interacts with the SO<sub>2</sub> and NO<sub>x</sub> in the atmosphere leading to little overall impact of the legislative control of the latter two gases in several countries [2]. Up to date, little action has been taken by environmentalists to control the emission of ammonia that, ironically, upon decomposition in the environment has similar fate to those of NO<sub>2</sub> [3].

Therefore, without improvising how to effectively monitor the ammonia emissions, there may be no impetus for control measures to be instituted. The current methods of monitoring the environmental ammonia such as polymeric films [4] and by use of kjeldahl method [5] are less sensitive and cumbersome and therefore precludes the main producers of ammonia; the

rural poor farmers from monitoring their share of ammonia emission.

Spectroscopy is a very sensitive method and has been successfully used in the wet chemistry [6] to identify, characterize, and quantify the anion-cation ligation interactions [7]. In addition, a comparative study on methods of ammonia detection reports that photoacoustic and direct methods; such as the infrared, as used in this study, are of very fast response time in the range of few minute [8]. Differences in geometry, coordination, and the type of ligand or ligands around the central atom or ion is reflected in the intensity and wavelength of the spectral transition of the central ion [7]. Normally, the changes in electric field splitting like the  $\Delta_o$  changes in solid samples are monitored by Diffuse Reflectance spectroscopy (DRS) and the spectra recorded in Kubelka-Munk units (kmu) [6,7]. The ability of ligands to give rise to different crystal field splittings is expressed relatively in the ligand spectrochemical series [9,10]. The series gives rise to different wavelengths for a d-d transition in different ligand-metal cation combinations [7].

The infrared (IR) vibration frequencies of complexes formed in cation-exchanged zeolites are categorized into two main regions. The 4000 – 1000 cm<sup>-1</sup> region is associated with ligand vibrations in which changes provide

information on the perturbations caused by the cation-ligand interactions [11,12]. The region below  $1000\text{ cm}^{-1}$  provides information about the structure of the  $M^{n+}$  coordination sphere, the nature of the metal-ligand (M-L) bond and modes of zeolite matrix [12]. Thus, M-L vibrations would be affected by the strengths, covalency, ionicity of the bonds formed and the reduced mass of the entities involved [13]. The above effects on the vibration frequency, insofar as they affect the vibrational force constant ( $k$ ) and the effective reduced mass of the vibration, are quantitatively represented by the Equation (1) below for the case of a diatomic system.

$$\text{From, } \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \text{cm}^{-1}$$

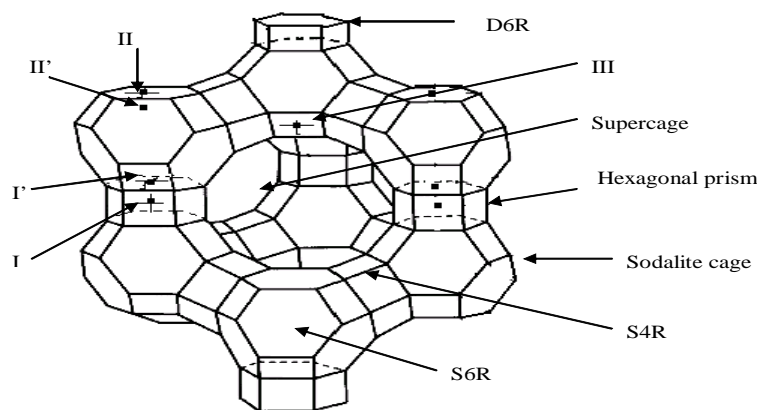
(1)

where  $\bar{\nu}$ ,  $c$ , and  $\mu$ , are the fundamental vibration frequency, velocity of light in a vacuum, and reduced mass respectively.

Therefore, such ligand specific transitions may be used to identify a particular

ligand or distinguish one from another, when other conditions are fixed. As a result, the presence of certain ligating agents in the environment may be detected by looking for the changes associated with their Cu(II) or Co(II) complex spectra when Cu(II) or Co(II) exchanged zeolites are exposed to the ligands [10,11]. Upon exchange into the zeolites (see Figure 1), the cations occupy the sites numbered I to III. Within these sites, ligations with adsorbates are possible [14].

The resulting coordination of the exchanged cation and the zeolites framework also affects the framework infrared vibration band positions [7]. Thus the groups of single four rings (S4R), single six rings (S6R), and double six rings (D6R) shall have distinct vibrational bands [12]. The relative ligand strengths are subtly reflected in their crystal field splittings and in the energies of their relative IR vibration modes [12].



**Figure 1: Faujasite-X cages and the cation exchange sites (I – III). Where S4R, S6R, and D6R stand for single-4-ring, single-6-ring, and double-6-ring structures respectively.**

Copper (II) and cobalt (II) were the first cations to be chosen for the study, because they form complexes that are easy to study by DRS and IR methods. This work may find relevance in qualitative monitoring of these adsorbates or their related functional groups in the environment. In addition, this is a novel attempt to use solid Zeolite support material in such monitoring applications. The characteristic electronic and bonding behavior for particular ligand-metal ion systems could be used by incorporation of tablets of variously exchanged zeolites into a multi-ligand array detector or sensor for the ligand agents.

## EXPERIMENTAL

### Materials used

Faujasite-X zeolite (NaX) (Si/Al = 1.23, *ca.* 2  $\mu\text{m}$  particle size, from Aldrich chemical company – United States of America (USA)), ammonium hydroxide (assay 29+%, from Fisher chemical company - USA), Cobalt (II) chloride (99+ % assay) and copper nitrate hydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 5/2\text{H}_2\text{O}$  (101.7 % by EDTA complexation, from J.T. Baker Chemical Company - USA) were used.

### Preparation of the Adsorbated-Cation Exchanged Faujasite Samples

The required concentration of  $\text{CoCl}_2$  or  $\text{Cu}(\text{NO}_3)_2 \cdot 5/2\text{H}_2\text{O}$  in the ratio of 1 g of zeolite to 20 ml of solution were mixed in an Erlenmeyer flask. The refluxing and other subsequent sample preparations and cation exchange level determinations followed the details as outlined by Kowenje et al. [14]. After which the required amount of ammonia (also referred to as an adsorbate) was put in the liquid transfer storage tube, and the adsorbate vapor allowed to vaporize over to the sample. The set-up was then allowed to stand for *ca.* 8 h at room temperature for complete and more homogeneous adsorption of the adsorbate into the exchanged zeolite. The above procedure was repeated for acetone, pyridine and water for comparison with the data from ammonia.

### Spectroscopic Measurements

Adequate amounts of the sample were packed in sealed quartz glass sample cuvettes and room temperature Diffuse Reflectance spectroscopy (DRS) measurements done from 200 to 1100 nm at a resolution of 2 nm using a 24 Cu/UC, the 24 Cu/UC sample was used in all Perkin-Elmer Lambda 2S UV-Vis spectrometer (Canada). subsequent studies.

For IR, a mixture of *ca.* 1% sample and *ca.* 99% KBr was ground in a glass mortar to fineness then pressed into a pellet. The resulting pellets were then fixed in FT-IR Bruker Equinox 55 spectrometer (Germany) at a nominal resolution of  $2\text{ cm}^{-1}$ . A total of 128 scans were collected for each sample and the spectrum was recorded over the  $4000 - 400\text{ cm}^{-1}$  range.

## RESULTS AND DISCUSSIONS

### Diffuse Reflectance Measurements

In Figure 2 below, the  $\lambda_{\text{max}}$  for all ranges of copper per unit cell (Cu/UC) samples peaked at 908 nm. Electronic transitions, such as the DRS peaks in this case, are metal-ligand specific [7]. Meaning that upto 24 Cu/UC, all the exchanged  $\text{Cu}^{2+}$  ions reside in similar chemical environments in the zeolites matrix. The  $\lambda_{\text{max}}$  peaking at approximately 500 nm indicated a different chemical environment and therefore the 38 Cu/UC may not be suitable for this study as the peak could introduce some interference. Since the highest sensitivity was shown by the 24 Cu/UC, the 24 Cu/UC sample was used in all subsequent studies.

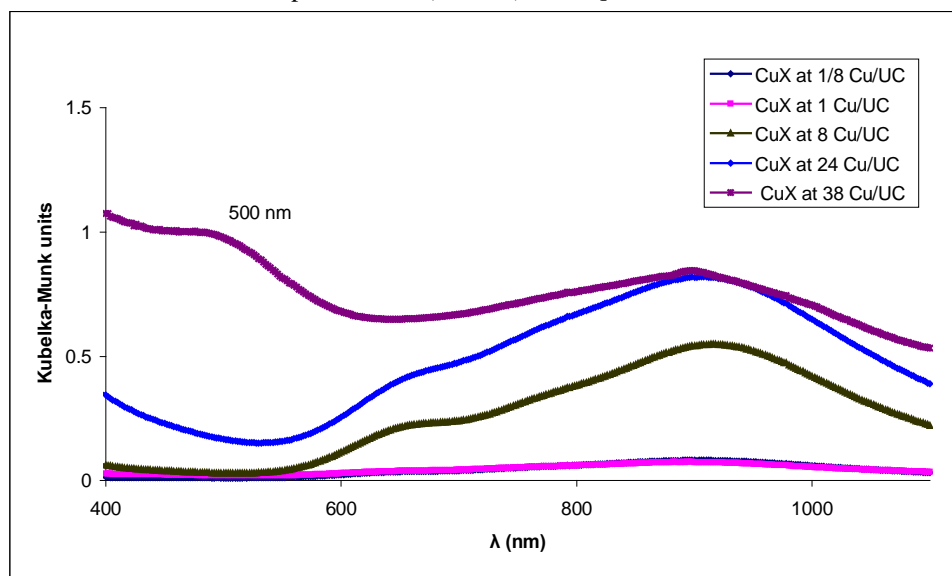


Figure 2: DRS of CuX at different concentration levels of Cu/UC.

Addition of ammonia to the dehydrated CuX (Fig. 3) reduced the intensity of the  $\lambda_{\text{max}}$  at *ca.* 908 nm and the  $\lambda_{\text{max}}$  position was shifted to *ca.* 630 nm. The amount of Cu/UC in the zeolites matrix did not interfere with the peaking position after the ammonia exchange. Figure 3 further shows a consistent increment in the intensity of the peak at 630 nm with the increase in both the amount of Cu/UC and the ammonia added. The shift was accompanied by a change from a greenish yellow to bluish color. The

intensification and the shifting of the  $\lambda_{\text{max}}$  are consistent with a less symmetric complex being formed [7]. In this case, it shows ammonia is reaching the copper ions. Such transitions are ligand-metal specific [15] and can therefore be used as a fingerprint peaks for the ammonia-copper complex. According to Delabie et al. [16], such a consistency is a manifestation of a specific metal-ligand interaction and represent a  $[\text{Cu}(\text{NH}_3)_4(\text{X})_2]^{2+}$ , with the extra coordinations



from oxygen bearing ligands ( $X = \text{H}_2\text{O}$ ,  $\text{OH}^-$ , or  $\text{O}_{\text{zeolite}}$ ).

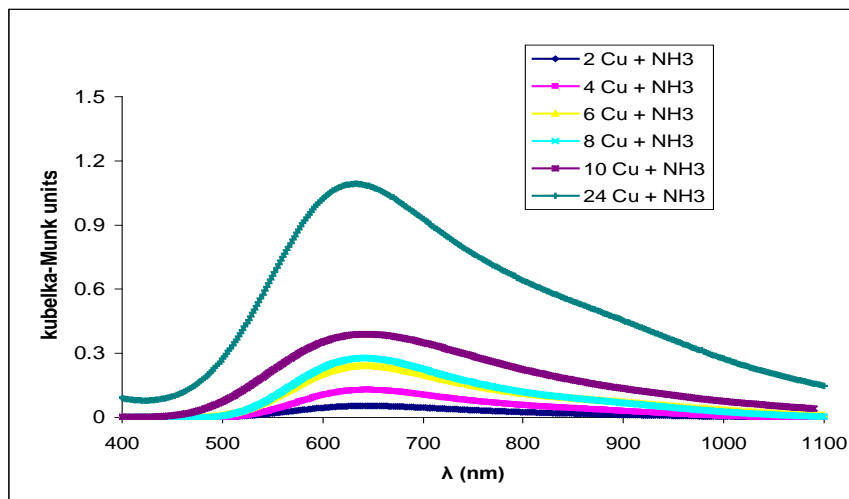


Figure 3: Diffuse reflectance spectra of CuX at various Cu/UC after ammonia addition.

Using Origin version 7 deconvolution program, the relative peak areas against the corresponding amount of ammonia applied were plotted in Figure 4. The quantification graph in Figure 4 was with the assumption that the geometry of the resulting metal-ligand complex

was consistent for all the amounts of adsorbate added [5,14]. A linear range from 5 to 25 ppm with  $R^2$  of 99.5% was obtained (Figure 4). Other workers have reported conflicting data depending on the method used [Ref.?].

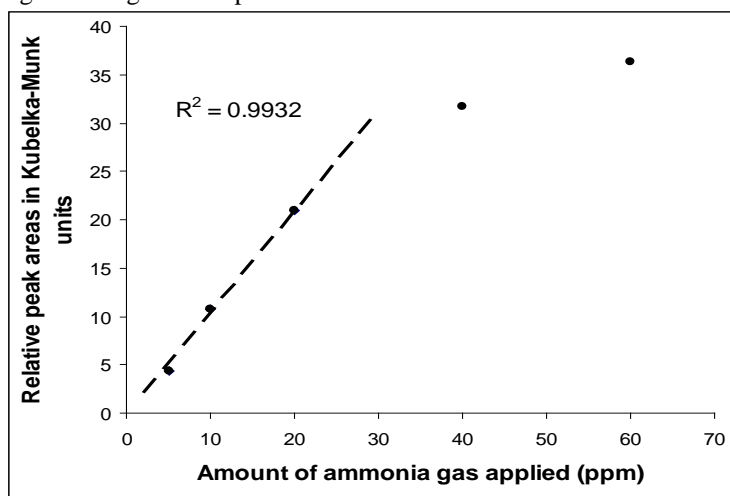


Figure 4: Correlation between Relative areas under the peak at 630 nm versus the amount of ammonia gas applied to 24 Cu/UC in relative Kubelka-Munk units.

Michael et al [17] used diode laser and photoacoustic spectroscopy to obtain detection limit of 8 ppm and a  $R^2$  value of 99.99%. Earlier, Diffuse Reflectance studies gave 80-1800 ppm [4] and 60 mM [6] linear ranges. The linear range ( $< 25$  ppm) obtained in Figure 4 could be linked to the amount of ammonia required to coordinate the exchanged cation sited in the major cavities of the zeolite in Figure 1. In addition, Figure 4 shows the limit to linearity for such a

method is ca. 25 ppm. The reasons for the limit are not yet clear, however, being in a porous medium a change in ligand adsorption isotherms mechanism is suspected. Such limitations impede the ability of cation exchanged zeolites to function as a quantitative sensor over larger adsorbate ranges.

To confirm that the specific DRS transitions are not unique to CuX, the same considerations were similarly performed for

Co/UC samples. The  $\lambda_{\max}$  for all the ranges of the Co/UC were at ca. 590 nm. The increase in the intensity of the  $\lambda_{\max}$  at ca. 590 nm with increasing amounts of  $\text{Co}^{2+}$  ions exchanged in was consistent with similar coordination for the resulting complex at a lesser symmetric site [11]. Similarly, as was the case with Cu/UC, all the

ranges for CoX up to 24 Co/UC may be used for this study. When the CoX at 24 Co/UC was exposed to ammonia, the results in Figure 5 were obtained. The shift in  $\lambda_{\max}$  to ca. 527 nm (Fig. 5), after the exposure to ammonia vapour is an indication that the ammonia has interacted with the  $\text{Co}^{2+}$  exchanged in to the Zeolite [7].

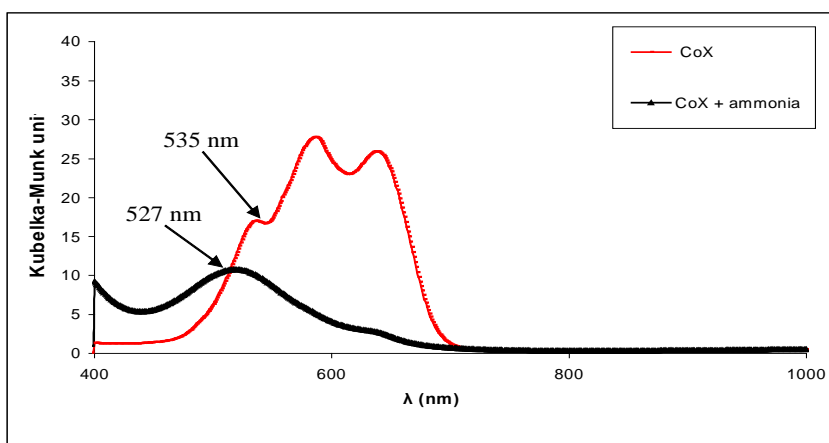


Figure 5: IR of CoX at 23 Co/UC before and after ammonia addition.

To exclude possible interferences from other environmental contaminants, the Cu/UC study included additional adsorbates with a similar functional group (such as pyridine), one abundant in the ambient atmosphere (such as water), and one abundant in organic environments (such as acetone) and the results

expressed in  $\text{cm}^{-1}$  energy units shown in Table 1 below. Spectroscopically, different ligand adsorbates show fingerprint DRS peaks and the peaks can be used to identify the individual molecules [18,19]. The differences in the energy values from the Table 1 are noteworthy.

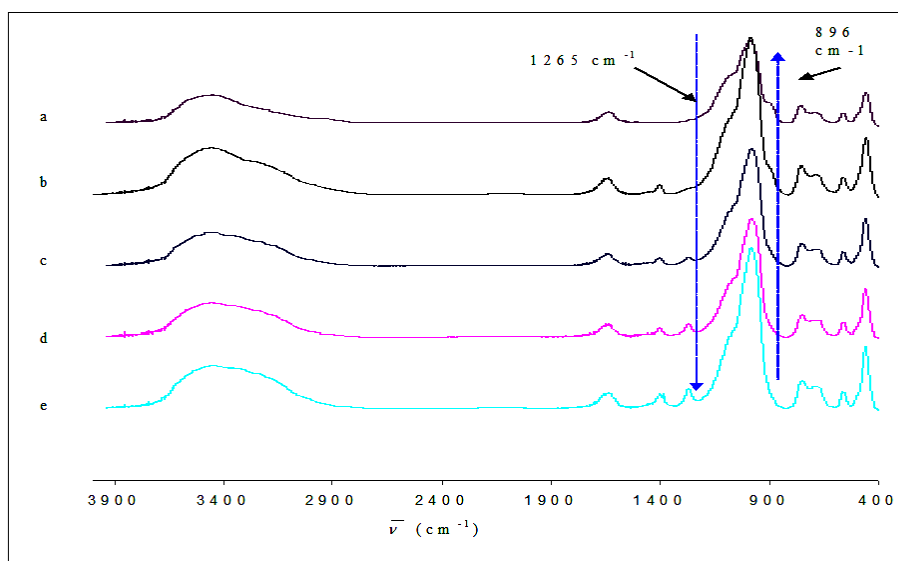
Table 1: The shifts in  $\lambda_{\max}$  for the various adsorbates in  $\text{cm}^{-1}$  energy units (The assumption is that the resulting complex after the exposure to the adsorbates have comparable geometry).

Sample	Changes in $\lambda_{\max}$ shifts from 908 nm of Cu/UC (converted to $\text{cm}^{-1}$ )
Ammonia	4860
Pyridine	3957
Acetone	1807
Water	1661

The  $\lambda_{\max}$  for ammonia is statistically different from the rest. Such differences show that ammonia is a stronger ligand compared to the

rest of the adsorbates [18,19] and can therefore be detected, without interferences, in the presence of the other adsorbates.

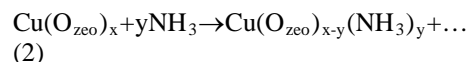
## Infrared measurements



**Figure 6: Infrared spectra of the 24 Cu/UC CuX exposed to different amounts of  $\text{NH}_3$  per  $\text{Cu}^{2+}$  exchanged in CuX. {From up, a) 0, b)  $\frac{1}{2}$ , c) 1, d) 2, and e) 4  $\text{NH}_3$  per Cu/UC}.**

Upon  $\text{Cu}^{2+}$  exchange, the Cu-Zeolite (Cu-Zeo) symmetric vibration band [20,21] forms at  $896\text{ cm}^{-1}$  (see Fig. 6 spectrum 'a'). In the Figure 6, the Cu-Zeo band at  $896\text{ cm}^{-1}$  is seen to disappear when the CuX is subsequently exposed to ammonia gas. In addition, Figure 6 shows the concomitant relative rise of the band at *ca.*  $1265\text{ cm}^{-1}$  and the demise of the shoulder at  $896\text{ cm}^{-1}$  with the increase in the amount of ammonia gas applied to the dehydrated 24 Cu/UC. The proportionate increase in the relative intensities of the  $1265\text{ cm}^{-1}$  band with the amount of ammonia absorbed into the dehydrated CuX indicates that ammonia directly controls this mode. Literature values for Hexamine-Copper Complex Cu- $\text{NH}_3$  symmetric stretching mode occurs in this neighborhood [22]. Thus we can assign the mode to Zeo-Cu-( $\text{NH}_3$ ) symmetric vibrations. As such, the accompanied decrease in the relative intensity of the  $896\text{ cm}^{-1}$  band is attributable to a reduced interaction of the Cu-Zeo bonding as ammonia

removes the  $\text{Cu}^{2+}$  from Zeolite framework [23] according to equation 2 below.



A correlated relative areas under the bands of the IR vibration modes with the amount of ammonia applied shows a shorter linear range of *ca.* 5 to 20 ppm and an  $R^2 = 0.986$ . In an additional experiment, when CoX was similarly treated with ammonia vapour a band at  $1312\text{ cm}^{-1}$ , similarly associated to Co- $\text{NH}_3$  symmetric vibration and one at  $918\text{ cm}^{-1}$  for Co- $\text{O}_{\text{zeolite}}$  was observed. Upon comparison to other adsorbates (pyridine, acetone and water vapour) on their ability to shift the Metal-Zeolite bands (at  $896\text{ cm}^{-1}$  for CuX and  $918\text{ cm}^{-1}$  for CoX), the band positions for each of the metal-adsorbate vibration was distinct (see Table 2).

**Table 2: Infrared fingerprint bands for ammonia, pyridine, acetone, and water when separately exposed to 24 Co/UC and 24 Cu/UC (designations w, and s refer to weak and strong bands respectively).**

Adsorbate	24 Co/UC	24 Cu/UC
Ammonia	1312 s	1265 s
Pyridine	1360 w	1250 s
Acetone	1400 s	1350 w

Water            1447 s            1280 s

---

A germane attempt to rank adsorbate ligands in terms of their Cu<sup>2+</sup> d-d splitting when the cation (Cu<sup>2+</sup>) was coordinated on a silica surface, had earlier been made by Trouillet *et al.* [24], in Cu/SiO<sub>2</sub> matrix. Trouillet and the co-workers applied the rule of ‘averaged environment’ to conclude that the order was ethylenediamine(en) > ammonia > water > silica (SiO<sub>2</sub>); a series similar to that is obtained from Table 2 but including pyridine and acetone.

### CONCLUSIONS

This work shows the spectroscopic characteristics of the ammonia in the presence of Cu<sup>2+</sup> and Co<sup>2+</sup> cations exchanged in the Faujasite-X zeolite and its ligand strength. This data may be used to identify and semi-quantify the presence of ammonia in the presence of pyridine, acetone, and water. Specifically both DRS and IR need to be merged together in any attempt to formalize the sensing of ammonia in the environment. Further research is, however, needed to quantify any highly varied concentrations of the ammonia in the environment.

### ACKNOWLEDGEMENTS

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# The FT-IR and Malarial Biological Studies of Copper(II) Complexes Containing Thiosemicarbazone and Semicarbazone Ligands Derived from Ferrocene and Pyridyl Fragments

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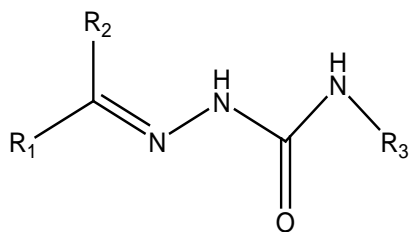
**The Fourier Transform Infrared (FT-IR) spectroscopic and malarial biological studies of complexes derived from the reactions of 2-acetylferrocenyl-4-phenylthiosemicarbazone, 2-acetylferrocenyl-4-methylthiosemicarbazone, 2-acetylpyridine-2-thiophenecarboxylsemicarbazone and 2-acetylferrocenyl-2-thiophenecarboxylsemicarbazone with copper(II) chloride are reported here. The ligands and complexes were synthesized using a method developed in our laboratory. The metal complexes and their corresponding ligands were tested against malaria parasites. It was found that in general the copper complexes synthesized are biologically more active than their corresponding ligands. In addition, detailed (FT-IR) studies of the ligands and complexes are reported here for the first time.**

## INTRODUCTION

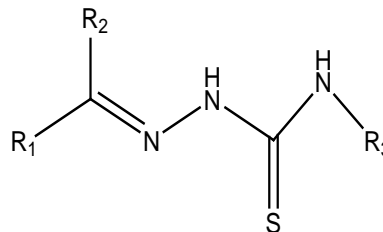
In recent years, metal complexes with sulfur ligands, such as thiosemicarbazide and its derivatives, have been the centre of attention because of their antitumor, antiviral, antibacterial, antifungal and antimalaria activities [1-2]. Acetylferrocenyl thiosemicarbazone metal complexes are able to suppress the proliferation of normal or transformed tumour cells [3]. It was discovered that numerous acetylferrocenyl thiosemicarbazone metal complexes inhibit the development of diverse experimental animals' tumour (e.g. Ehrlichascites tumour, sarcoma 180, B16 melanoma and colon 38 carcinoma) and the growth of human carcinomas [4]. Certain ferrocenium compounds were especially cytostatically found to be effective against human colorectal carcinomas [3-5]. Omote [6] reported copper complexes with a thiosemicarbazone-containing ferrocenyl group. Garg and Kapur [7] also prepared cobalt complexes with monoacetylferrocene thiosemicarbazone. Recently, Kiremire and his group [8] reported that the metal

complexes containing a dithio-based ligand were subjected to biological tests on falcipain-2 (FP-2) and falcipain-3 (FP-3) cystein protease enzymes from malaria parasite *P. falciparum*. The complexes exhibited high biological activity. Other biological studies of acetylferrocenyl metal complexes that are in the literature include those by Bakir and his group [9] and Soumitra *et al.* (1998) [10] who reported the biological studies of thiosemicarbazone containing ferrocene and their metal complexes against gram positive and gram negative bacterial species.

Although the synthesis and characterization of the ligands and their respective complexes using elemental analysis, <sup>1</sup>HNMR, <sup>13</sup>CNMR and Mass spectroscopic studies have already been reported, the biological studies against malarial parasites as well as the Fourier Transform-IR (FT-IR) studies of the complexes have not yet been reported. This paper describes the Fourier Transform Infrared (FT-IR) studies of metal-based thiosemicarbazone and semicarbazone-containing ferrocenyl group complexes and a brief report on the antimalarial activities of these complexes. The general structures of the ligands are shown below (Fig.1).



(a) Semicarbozone



(b)...Thiosemicarbazone

**Figure 1. General structures of (a) semicarbazone and (b) thiosemicarbazone ligands.** Where  $R_1$ ,  $R_2$  or  $R_3$  can be alkyl, aryl or H.

### EXPERIMENTAL

The synthetic methods of the ligands and their complexes mentioned in this paper were developed in our laboratory and have already been reported [8]. The samples of the purified ligands and their copper complexes synthesised were sent to the University of California, San Francisco, U.S.A. for testing the biological activities against malaria parasites. The antimalarial activity was evaluated against falcipain-2 and falcipain-3 of the

malaria parasite. The test was done *in vitro* against cysteine protease enzymes, *falcipain-2* and *falcipain-3* of the malaria parasite and against chloroquine resistant strain *W-2*. The results obtained showed the biological activity of each metal complex with chloroquine as a control.

FT-IR spectra were done at the University of Cape Town using the Perkin-Elmer spectrum One FT-IR spectrometer to record the spectra. The ligands under study are shown below (Fig.2).



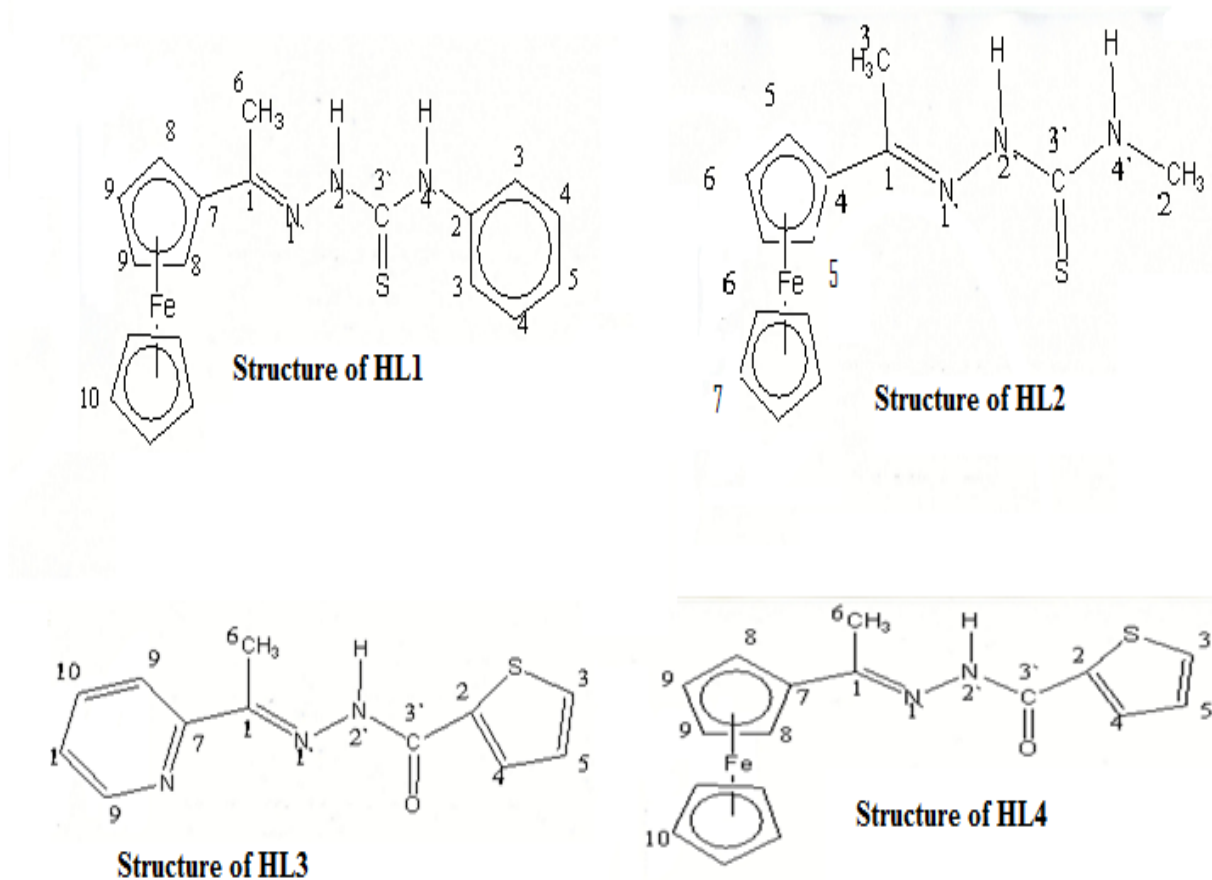


Figure 2: Structures of the ligands

## RESULTS AND DISCUSSION

### The Fourier Transform-Infrared spectra

The significant IR bands of the ligands, their metal complexes and their assignments are given in Table 1. Also the representative IR spectra of the ligand complexes HL<sup>1</sup>, HL<sup>2</sup>, HL<sup>3</sup> and HL<sup>4</sup> are

shown in figures 3, 4, 5 and 6 respectively. The chief IR bands of the ligands were identified by correlations of data for similar compounds. The IR spectrum of the ligands is almost identical in the region of 1002-1550 cm<sup>-1</sup> to those of their corresponding copper complexes whose proposed structures have already been reported [9].

**Table 1. Infrared absorption frequencies (cm<sup>-1</sup>) of HL<sup>1</sup>, HL<sup>2</sup>, HL<sup>3</sup> and HL<sup>4</sup> and their copper(II) complexes.**

Assign-ments	HL <sup>1</sup>	CuL <sup>1</sup> Cl <sub>2</sub>	HL <sup>2</sup>	CuL <sup>2</sup> Cl <sub>2</sub>	HL <sup>3</sup>	CuL <sup>3</sup> <sub>2</sub>	HL <sup>4</sup>	CuL <sup>4</sup> <sub>2</sub>
$\nu(\text{C-H})$	3018	3021	3019	3020	3020	3019	3020	3019
Ferrocenyl group	3099, 1498,410	3084, 1497, 410	3101, 1492, 410	3101, 1491, 410	-	-	3099, 1492, 410	3099, 1492, 410
$\nu(\text{C}=\text{N}^1)$	1595	1599	1580	1599	1595	1601	1638	1639
$\nu(\text{N}^1-\text{N}^2)$	1002	1002	1011	1034	1002	1002	1001	1001
$\nu(\text{N}^2-\text{H})$	3323	-	3346	-	3394	-	3349	3349
$\nu(\text{N}^4-\text{H})$	3413	3413	3412	3413	3413	3413	3413	3413
$\nu(\text{C}^3=\text{S})$	1414	-	-	-	1413	-	1414	-
$\nu(\text{C}^3=\text{O})$	-	-	1515	-	-	-	1516	1516
$\nu(\text{C}^3=\text{N}^2)$	-	1568	-	1528	-	1528	-	-
$\nu(\text{C}^3-\text{O})$	-	-	-	1210	-	-	-	1208
$\nu(\text{Cu-Cl})$	-	1187	-	1168	-	1185	-	1187

The spectra of all synthesized compounds show no broad band in the range 2500-3300 cm<sup>-1</sup> assigned to  $\nu(\text{OH})$ , suggesting the absence of water molecules [11]. Furthermore all ligands showed the absence of a band at ~1715 cm<sup>-1</sup> due to the characteristic carbonyl  $\nu(\text{C}=\text{O})$  stretching vibration of the respective starting acetylferrocene and acetylpyridine [12]. Instead, the appearance of a new

band at 1599 cm<sup>-1</sup> assigned to the  $\nu \text{C}=\text{N}^1$  linkage suggested condensation and formation of the proposed ligands [5].

Absorption bands occurring at *ca.* 3018-3021 cm<sup>-1</sup> for  $\nu(\text{C-H})$  is for methyl fragment present in all compounds [12]. According to Zahid and his group [13], the characteristic ferrocenyl group bands appear at *ca.* 3084-3101, 1492-1498 and 410 cm<sup>-1</sup>.

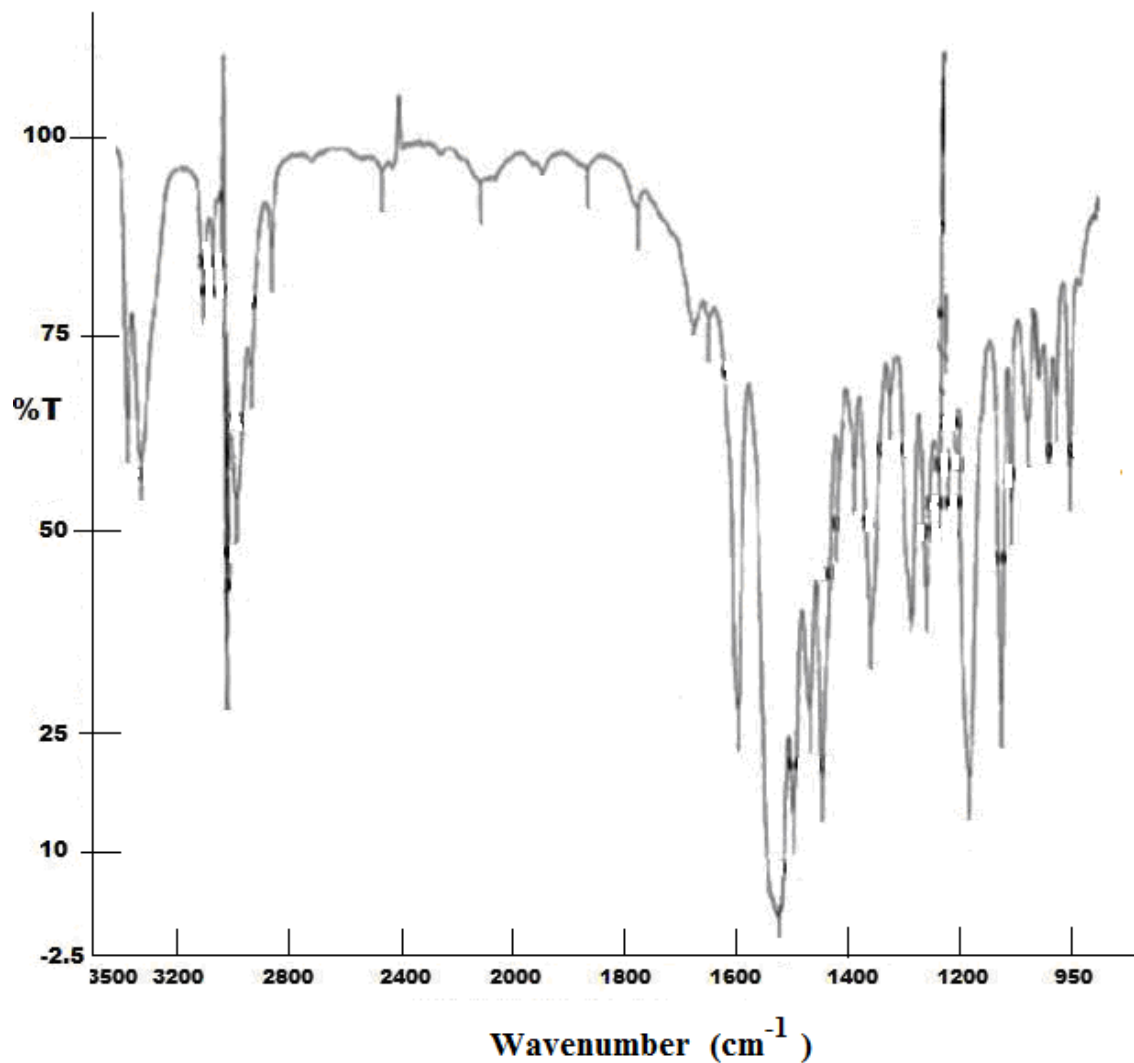


Figure 3. IR spectrum of HL<sup>1</sup>

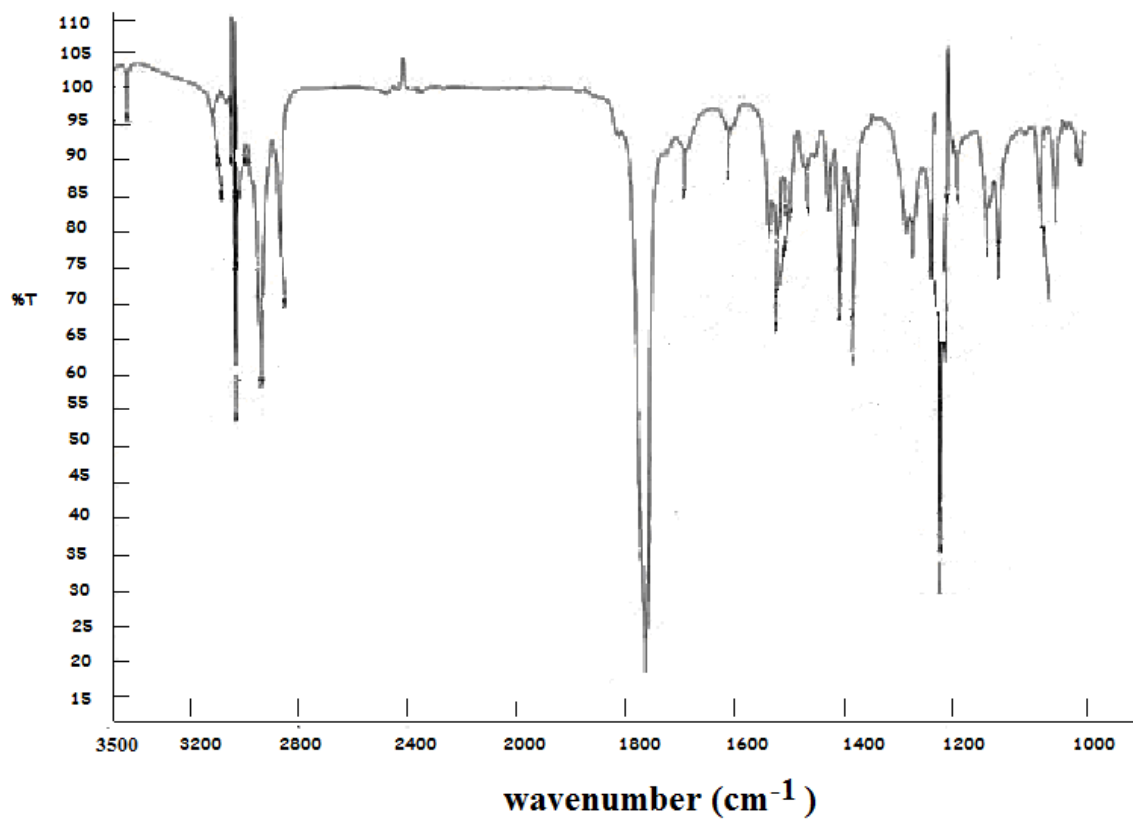


Figure 4: IR spectrum of HL<sup>2</sup>

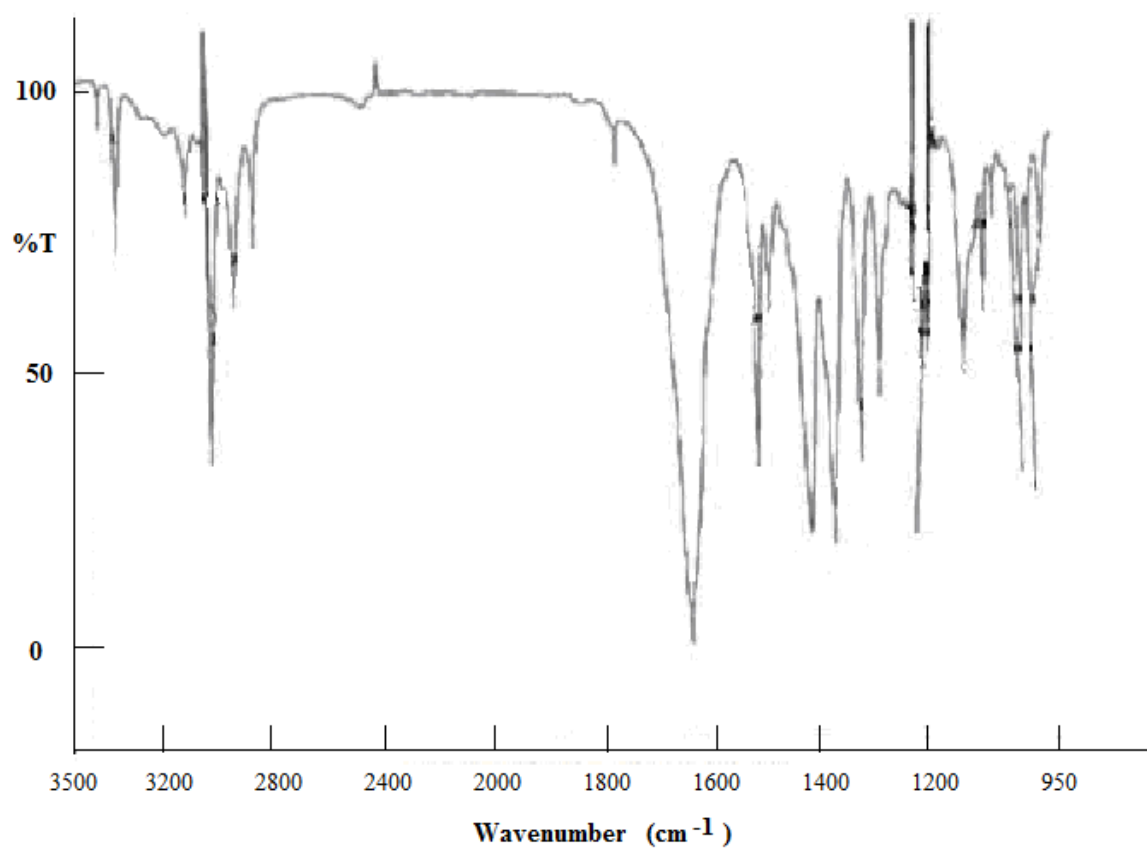
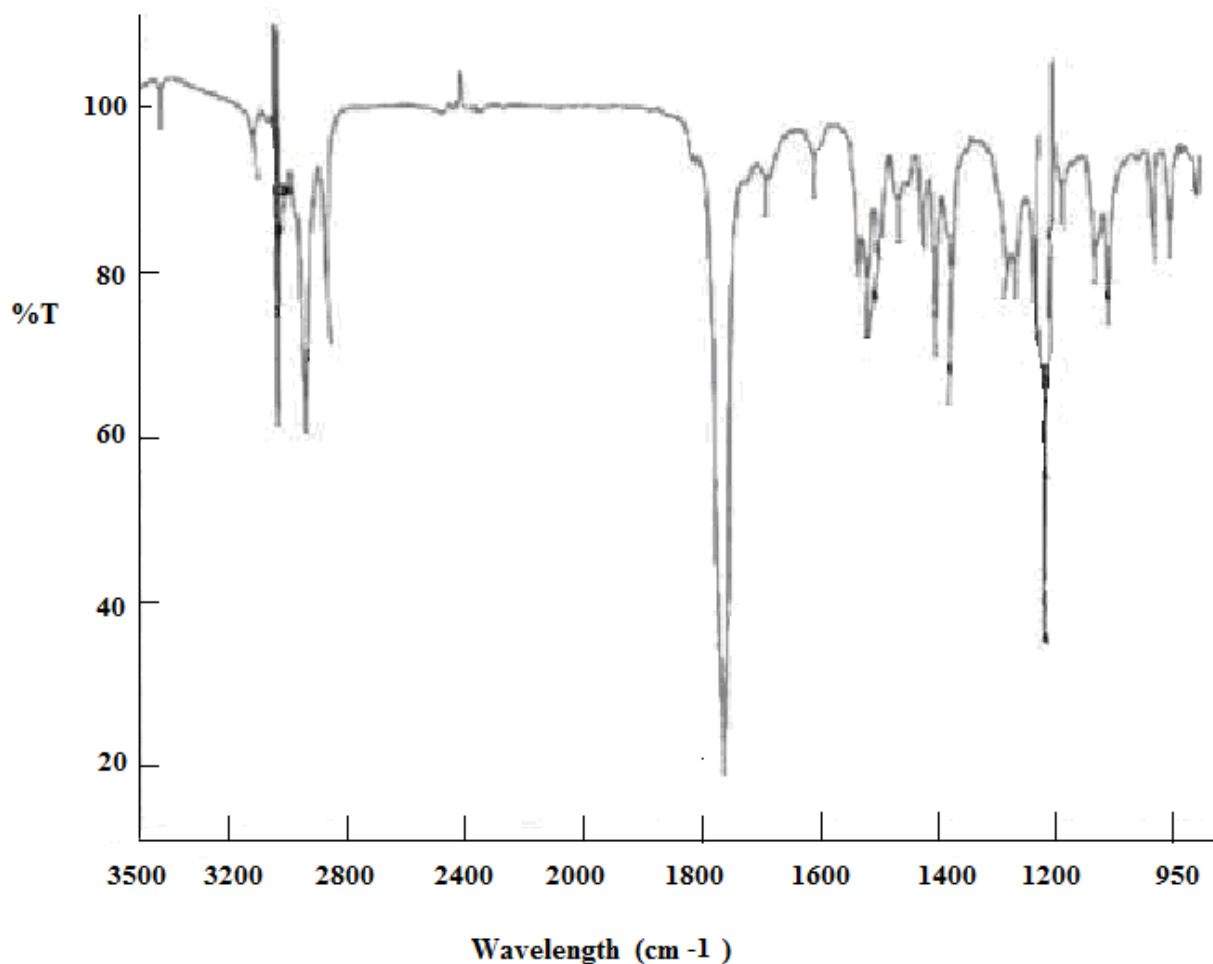


Figure 5: IR spectrum of HL<sup>3</sup>



**Figure 6: IR spectrum of HL<sup>4</sup>**

HL<sup>3</sup> does not show bands at 3084-3101, 1492-1498 and 410 cm<sup>-1</sup> indicating the absence of ferrocenyl group as expected. All ligand bands at around *ca.* 1595 cm<sup>-1</sup> for  $\nu(\text{C}=\text{N}^1)$ , *ca.* 1002 cm<sup>-1</sup> for  $\nu(\text{N}^1-\text{N}^2)$ , *ca.* 3349, and *ca.* 1038-1040 for  $\nu(\text{C}-\text{N})$  and *ca.* 3413 for  $\nu(\text{N}^4-\text{H})$  confirmed the suggested structures of the ligands shown above [5].

In all copper complexes, the band, *ca.* 1413 cm<sup>-1</sup> remain almost at the same position confirm that N<sup>4</sup>-H did not participate in chelation [12]. The band at *ca.* 3323-3349 for  $\nu(\text{N}^2-\text{H})$  is absent in all complexes; however, the band at *ca.* 1595 cm<sup>-1</sup> for  $\nu(\text{C}=\text{N}^1)$  is higher (*ca.* 1-9 cm<sup>-1</sup>) in the complexes indicate an interaction with the metal. It is known that if a metal coordinate bond is formed with a

nitrogen atom already bonded to a neighbouring N atom, a shift of the N-N stretching bands to higher frequencies occurs, probably due to the increase in the polarity of the N-N bond [5]. Absorption occurring at *ca.* ~1515 cm<sup>-1</sup> may be assigned to  $\nu(\text{C}=\text{O})$  in semicarbazone compounds [11]. In IR spectra, the band appearing at *ca.* ~1414 cm<sup>-1</sup> may be assigned to  $\nu(\text{C}=\text{S})$  [9] in thiosemicarbazone compounds

The IR spectra of the free ligands display a sharp band at *ca.* 3413 cm<sup>-1</sup>, assignable to N<sup>4</sup>-H group mode which remain at almost the same positions in the metal complexes, suggesting that the group is not involved in chelation [9]. In the IR spectra of the free ligands, bands at *ca.* 3323-3395 cm<sup>-1</sup> disappear in the corresponding copper(II)

complexes, indicating possible deprotonation of the ligands upon complexation [14].

The band at 1580-1595  $\text{cm}^{-1}$  and 1638  $\text{cm}^{-1}$  in HL<sup>1</sup> and HL<sup>2</sup> respectively, due to  $\nu(\text{C}=\text{N}^1)$ , are shifted to higher wave numbers ( $\nu$  10-20  $\text{cm}^{-1}$ ) in the copper complexes, suggesting coordination through the azomethine nitrogen [9]. The bands at 1413-1414  $\text{cm}^{-1}$  and 1515-1516  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}=\text{S})$ , respectively, are not observable in the complexes, indicating coordination of oxygen or sulfur to the central metal atoms and formation of Cu-O or Cu-S type of bonding. In addition, new weak to strong intensity bands are observed in the far IR spectra of the complexes. The band at ca 360-365, 305-315 and 422  $\text{cm}^{-1}$  may be assigned to  $\nu(\text{Cu}-\text{N})$ ,  $\nu(\text{Cu}-\text{S})$  and  $\nu(\text{Cu}-\text{O})$ , respectively [12]. The appearance of these bands further supports bonding of the ligands to the metal atom through nitrogen, sulfur and oxygen.

The coordination via the N<sup>1</sup> atom shifts  $\nu(\text{N}^1-\text{N}^2)$  to higher wavenumbers (0-33  $\text{cm}^{-1}$ ) than in the free ligands. The  $\text{C}=\text{N}^1$  stretching vibration also shifts to higher wavenumbers. This occurs due to the coordination of the ligand to the metal atom. The coordination process leads to withdraw of electron density in the  $\text{C}^3-\text{S}$ ,  $\text{C}^3-\text{N}^4$  and  $\text{N}^4-\text{H}$  bonds giving rise to a shift in  $\nu(\text{N}^4-\text{H})$  band position. However, the coordination does not significantly affect the ferrocenyl peaks at 3084-3101, 1492-1498 and 410  $\text{cm}^{-1}$  [5].

The disappearance of the  $\nu(\text{C}^3-\text{N}^2)$  band at ca. 1038-1045  $\text{cm}^{-1}$  provided further evidence in support of the involvement of this nitrogen in coordination to the copper atoms [12]. Furthermore, a characteristic band at 1528-1568  $\text{cm}^{-1}$  due to  $\nu(\text{C}^3-\text{N}^2)$  in the spectra of all the complexes suggest the formation of double bonds and the deprotonation of the N<sup>2</sup>-H [15]. The bands, at 1413-1414 and 1514-1516  $\text{cm}^{-1}$  assigned to  $\nu(\text{C}=\text{S})$  and  $\nu(\text{C}=\text{O})$  respectively, in the free ligands are either shifted, split, or weakened in all of the complexes indicating the participation of the S or O-atom in complex formation [11]. Moreover, in the far infrared region, the band at  $\sim 360$   $\text{cm}^{-1}$  attributed to  $\nu(\text{Cu}-\text{N})$  was observed for all the complexes, but was not found in the spectra of the free ligands as expected.

However, this implies that the formation of the (M-N) bond in the complexes [16 and 17].

The spectra of all studied complexes show no broad band in the range 3157-3500  $\text{cm}^{-1}$  assigned to  $\nu(\text{OH})$ , suggesting the absence of water molecules in the complexes [12]. CuL<sup>3</sup><sub>2</sub> and CuL<sup>4</sup><sub>2</sub> complexes show significant shift to lower frequencies for  $\nu(\text{C}-\text{O})$  band at ca. 1210 and 1208  $\text{cm}^{-1}$  respectively [15]. This probably due to the change of the double bond character of (C=O) to a mainly single bond character of the (C-O) in the complex. The presence of the peak in the region ca. 1413-1414  $\text{cm}^{-1}$  in Table 1 may tentatively be assigned to the C=S vibration [12].

### Antimalarial studies

The antimalarial activity of the copper(II) complexes synthesized together with their parent ligands has been screened against malaria parasite *Plasmodium falciparum*. The results (Table 2a and 2b) show that the complexes exhibit moderate activity against the cysteine protease enzyme, falcipain-2 (FP-2) and chloroquine-resistant (W-2) strain both from the malaria parasite, *Plasmodium falciparum*. The activities are provided in nanomolar (nM). It should be noted that the lower the reading of the complex (in nM) the higher the biological activity. Those complexes with the value of IC<sub>50</sub> (nM) greater than 20000 have negligible biological activity.

The results of the biological activities of ligands and their copper(II) complexes against malaria parasites are summarized in Table 2a and 2b. The data indicate that none of the ligands, HL<sup>1</sup>, HL<sup>2</sup>, HL<sup>3</sup> and HL<sup>4</sup> showed biological activities with W-2. However, HL<sup>1</sup> and HL<sup>4</sup> show modest biological active with FP-2. HL<sup>2</sup> and HL<sup>3</sup> showed no biological activities with either FP-2 or W-2. CuL<sup>1</sup>Cl<sub>2</sub> was the most biologically active against FP-2. The order of biological activity against FP-2 can be assigned as follows CuL<sup>1</sup>Cl<sub>2</sub> > CuL<sup>3</sup><sub>2</sub> > HL<sup>1</sup> > HL<sup>4</sup> > CuL<sup>4</sup><sub>2</sub>. On the other hand, the biological activity with respect to W-2 can be put in the order CuL<sup>2</sup>Cl<sub>2</sub> > CuL<sup>1</sup>Cl<sub>2</sub> > CuL<sup>3</sup><sub>2</sub>

Table2: Biological activities of metals complexes and			
Compounds tested	FP-2 average (nM)	Compounds tested	W-2 average (nM)
Control	9.5	$\text{CuL}^2\text{Cl}_2$	669.9
$\text{CuL}^1\text{Cl}_2$	473.65	Control	2482
$\text{CuL}^3_2$	4807	$\text{CuL}^1\text{Cl}_2$	11485
$\text{HL}^1$	5486.5	$\text{CuL}^3_2$	14580
$\text{HL}^4$	56400	$\text{HL}^1$	>20000
$\text{CuL}^4_2$	78775	$\text{HL}^2$	>20000
$\text{HL}^2$	>100000	$\text{HL}^3$	>20000
$\text{CuL}^2\text{Cl}_2$	>100000	$\text{HL}^4$	>20000

Comparing the biological activity of the ligands with their corresponding metal complexes with respect to FP-2, the following can be ascertained. The biological activity of  $\text{CuL}^1\text{Cl}_2$  complex is greater than the corresponding ligand  $\text{HL}^1$ . It is also observed that  $\text{CuL}^3_2$  complex is biologically active while its corresponding ligand  $\text{HL}^3$  is inactive. On the other hand, the  $\text{CuL}^4_2$  complex is less active than its corresponding ligand,  $\text{HL}^4$ .

The biological activity with respect to W-2, show the following sequence.  $\text{CuL}^2\text{Cl}_2$  complex is more biologically active than its corresponding ligand  $\text{HL}^2$ . Similarly,  $\text{CuL}^1\text{Cl}_2$  complex is more biologically active than its corresponding ligand  $\text{HL}^1$  and  $\text{CuL}^3_2$  complex is also more biologically active than its corresponding ligand  $\text{HL}^3$ . Both  $\text{CuL}^4_2$  complex and its corresponding ligand  $\text{HL}^4$  are biologically inactive. With the exception of  $\text{HL}^4$  and its corresponding complexes, it is quite clear that the complexes are more biologically active than their corresponding ligands. Similarly, the introduction of copper(II) to the thiosemicarbazone increases their biological activities as has been observed in the literature [10]. Generally, chelation/coordination reduces the polarity of the metal ion by partial sharing of its positive charge with the donor groups and possibly the pi-electron delocalization within the whole chelate ring [18]. This process tends to increase the lipophilic nature of the compound, which in turn, favors penetration through the membrane walls of the strains [4, 5]. In order to fully understand this phenomenon, the mechanisms of the biological activity need to be investigated. Furthermore, work is in progress to

conduct mass spectroscopy and x-ray structure analysis of the key complexes.

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# Uptake and distribution of selected heavy metals by sweet potato plant varieties under green house conditions

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The extent to which cadmium, chromium, lead and zinc ions were absorbed and trans-located into roots, stems and leaves of different sweet potato (*Ipomea batatas*) plant varieties from their respective metal solutions was studied. The five varieties used in this work were UP-A, UP-B, UP-C, UP-D and UP-16. The uptake and distribution of the respective ions depended not only on the type of metal ion but also on the type of sweet potato variety of interest. The levels of cadmium and chromium, obtained in the leaves ranged from 0 to 144.17 $\mu\text{g}$  and 2.81 to 100.63 $\mu\text{g}$ , respectively. On the other hand, the amount of lead and zinc in the leaves ranged from 0 to 13.80 $\mu\text{g}$  and 1.10 to 58.63 $\mu\text{g}$ , respectively. The amount of chromium and cadmium found in the leaves of sweet potato plant varieties was a bit higher than those obtained in the case of lead and zinc. In the case of zinc, the highest amount of metals in the leaves was found in 20ppm zinc solution rather than 50ppm zinc solution. For the other varieties, the highest amount of metal was found in 50ppm metal solutions as expected. Cadmium content obtained from sweet potato plant varieties grown in 10ppm cadmium solution ranged from 653.51 to 771.52  $\mu\text{g}/\text{gram dry weight (gdwt)}$  of the plant tissue while that from 20ppm solution ranged from 920.18  $\mu\text{g}$  to 1032.70  $\mu\text{g}/\text{gdwt}$ . Results of zinc content in the plant varieties grown in 10ppm zinc solution showed the range of 361.38 - 499.79  $\mu\text{g}/\text{gdwt}$  of the plant tissue and 505.44 - 601.67  $\mu\text{g}/\text{gdwt}$  for plants grown in 20ppm zinc solution. However, a lower range of between 308.63 and 370.42  $\mu\text{g}/\text{gdwt}$  was recovered from plants grown in 50ppm zinc solution. Plant varieties grown in lead solutions registered the highest lead content compared to the other metals used for the study. In case of 10ppm lead solution the plants accumulated a range of 7.14 - 108.10  $\mu\text{g}/\text{gdwt}$  lead, while the plants grown in 20ppm lead solution gave a range of 1389.41 - 1962.13  $\mu\text{g}/\text{gdwt}$  lead. On the other hand, plant varieties in 50ppm solution had lead content of between 2,800 and 3,570  $\mu\text{g}/\text{gdwt}$  of the plant tissue. Moreover, a 10ppm total chromium solution gave a range of 109.23 - 164.64 $\mu\text{g}/\text{gdwt}$ , while the plants grown in 20ppm chromium solution had chromium ranging from 159.13 to 240.7 $\mu\text{g}/\text{gdwt}$ . Total chromium content of the plants harvested from 50ppm solution ranged from 341.49 to 685.69 $\mu\text{g}/\text{gdwt}$  of the plant tissue.

The plants in hydroponics solutions containing cadmium survived for only 14 days, compared with other hydroponics containing other metals (chromium, lead and zinc), which continued to grow for additional days. The amount of each heavy metal in the roots, stem and leaves increased with the increase of ions in the metal solutions. However, the percentage of the metals in each part of the sweet potato plant variety decreased with the increase in metal ions in the hydroponics as expected. The variations in metal ion intake by different sweet potato varieties could not be fully explained.

## INTRODUCTION

Sweet potato plants were introduced in East Africa from Latin America by the Portuguese [1, 2]. Since the plants were first introduced in this region, there are currently about 100 varieties in Kenya and similarly related number of varieties in Tanzania and Uganda. In this region, generally, sweet potato vines are commonly grown in well-drained soils.

However, one of the objectives of the current research work was to determine whether the sweet potato varieties can grow in pure water and polluted water environment. If this is the case, then there is possibility of the pollutant being distributed in the different parts of the plant. Moreover, during the intake of water by plants various nutrients also end in the plant. For this reason plants can be used for environmental

remediation through a promising environmental technology called phytoremediation [3-8]. Phytoremediation is defined as the use of green plants to remove pollutants from the environment or to render them harmless [3]. The essential elements for the existence of the plants include carbon, hydrogen, oxygen, phosphorus, potassium, nitrogen and Sulphur (CHOPKNS). For plant growth, functions and maintenance of its structure certain minerals are required. All plants have the ability to accumulate from soil and water some metal ions, which are essential for growth and development. These metals include Fe, Mn, Zn, Cu, Mg, Mo and possibly Ni [9-16]. Certain plants also have the ability to accumulate heavy metals which have no known biological functions, which include Cd, Cr, Pb, Ag and Hg [3, 14]. In addition, some aquatic or semi-aquatic plants that have been used in phytoremediation include water hyacinth (*Eichonia crassipes*) which had been reported by Deierbug et.al., [5], Penny worth (*Hydrocotyle umbrellata*) as reported by Jain et al., [6] and water velvet (*Azolla pinnata*) as reported by Mo et al., [9,17] can take up Pb, Cu, Cd, Fe and Hg from contaminated solutions.

During the growth period of the plant some of the above heavy metals may be distributed in different parts of the plant, depending on the variety of interest. In the current research work, this distribution phenomenon of different heavy metals in certain varieties of sweet potato plants was to be investigated. It is important to note that in the current work the plants were grown in 'pure water' and water containing heavy metal ion pollutants. The relevant experiments were conducted in a special green house with stone walls, located in the School of Biological Sciences, University of Nairobi. The results obtained will go a long way in advising the farmers and consumers of possible accumulation

of pollutants by the sweet potato varieties, particularly if they are grown in heavy metal contaminated environment.

## EXPERIMENTAL

### Study design

The study was carried out at the University of Nairobi, Departments of Chemistry and Botany laboratories in the College of Biological and Physical Sciences, Chiromo campus. Planting and monitoring of plant growth took place at a special green house in the Department of Botany, while digestion of plant samples was carried out at the Department of Chemistry. Analysis of the digested samples using Atomic Absorption Spectroscopy (AAS) method was carried out at the Nairobi Water and Sewerage Services laboratory at Kabete, Nairobi.

### Sweet potatoes varieties

Five different varieties namely, UP-A, UP-B, UP-C, UP-D and UP-16 were provided by PRAPACE, Uganda and transferred to the University of Nairobi, Chiromo gardens, where they were grown for six months. After six months, cuttings of size 15-20cm long, containing 4 nodes, were obtained. Leaves were removed and the cuttings were then transferred into special open large plastic containers containing tap water and allowed to pre-root for four weeks (figure 1). Each of the pre-rooted sweet potato plant was transferred into a transparent plastic container containing water solutions of about 200ml (figure 2). The control experiment contained pre-rooted plants in 200ml of water, while each of the other containers had a specific heavy metal (Cd, Zn, Pb and Cr). The plants were then allowed to grow, either in blank solution or in heavy metal solutions, for a maximum of 21days.



**Figure 1: Pre-rooting of the sweet potato cuttings in an open plastic containers containing tap water in green house.**



**Figure 2: Growth of the pre-rooted sweet potato vines in water solutions with or without a specific metal of interest.**

### Stock solutions

The stock solutions of 1000ppm were prepared from cadmium nitrate, zinc nitrate, lead nitrate and potassium dichromate. Serial dilutions of the stock solutions into working concentrations of 10ppm, 20ppm and 50ppm were later prepared. Appropriate volumetric flasks and polypropylene or Teflon stoppers were used in the preparation.

### Harvesting

After 14 days, the sweet potato plant cuttings placed in cadmium ion solutions were harvested because they had dried up. Plant cuttings grown in zinc and lead ions solutions survived for a period of 21 days. However, the plant cuttings in 50ppm chromium ion solution dried before the end of the two weeks and were therefore harvested after 14 days. 10ppm and 20ppm solutions of chromium ions were monitored for 21 days.

The different parts of the plants were then separated by cutting, using clean stainless steel blades, into leaves, roots and stem during harvesting. The wet weights of the parts of the plants were then measured and stored in absorbent paper for air drying. The solutions that remained in the plastic container after harvesting were sealed with corks for metal ions analysis.

In all these experiments, water was taken to be the solvent and the respective metal

ions to be solutes, thereby giving an electrolyte in each experimental set up, as the metal salts used are soluble in water. This homogeneous solution was expected to transfer the metal ions to the different parts of the plant, during the growth period of the plant.

## RESULTS AND DISCUSSION

### Moisture content

The main different parts of the plant in this case were taken to be the roots, the stem and the leaves. When each of the plants were removed from the heavy metal solutions in which they were growing, it was held for about five minutes above the solution to allow excess water solution on the roots and the stem to dry up from the surface. Once the excess water was removed, the three different parts of the plants (roots, stem and leaves) were separated. Consequently, the roots, stems and leaves were weighed in the analytical balance to obtain the wet weights, aimed at establishing the moist content of each part of the plant (tables 1a, 1b and 1c). The three parts of the plant were dried in an oven to a constant weight at 105°C. The entries in the tables refer to the amount of water, which was originally in the plant part (leaves, stems and roots) for the plant grown in hydroponics containing a particular metal.

**Table 1a: Moisture content of different varieties of sweet potato vines grown in 10ppm solutions of different heavy metal ions.**

Sweet potato varieties	Plant parts	Cadmium: Water content/g	Zinc: Water content/g	Lead: Water content/g	Chromium: Water content/g
UP-A	Leaves	0.48	0.47	1.11	0.11
	Roots	0.55	0.28	0.55	0.21
	Stem	2.82	6.69	4.29	5.68
UP-B	Leaves	0.71	1.92	2.18	1.48
	Roots	1.75	1.67	2.29	1.30
	Stem	8.61	10.73	9.68	11.90
UP-C	Leaves	0.15	1.47	1.34	1.44
	Roots	2.37	1.12	2.19	1.46
	Stem	3.17	9.68	7.60	4.92
UP-D	Leaves	0.20	1.13	0.85	1.64
	Roots	1.35	0.86	2.23	1.77
	Stem	6.58	7.72	7.13	8.54
UP-16	Leaves	0.07	1.16	1.52	0.43
	Roots	0.93	0.80	2.59	1.18
	Stem	2.59	7.83	9.62	8.46

**Table 1b: Moisture content of different varieties of sweet potato vines grown in 20ppm solutions of different heavy metal ions.**

Sweet potato varieties	Plant parts	Cadmium: Water content(g)	Zinc: Water content(g)	Lead: Water content(g)	Chromium: Water content(g)
UP-A	Leaves	0.01	0.63	0.27	0.23
	Roots	0.65	0.27	0.43	0.42
	Stem	2.58	5.42	3.76	3.22
UP-B	Leaves	0.10	1.94	2.10	1.98
	Roots	1.31	1.18	3.20	1.69
	Stem	6.32	9.08	8.19	12.97
UP-C	Leaves	0.07	1.73	1.63	1.87
	Roots	0.68	1.18	2.53	1.33
	Stem	3.96	8.45	9.25	8.25
UP-D	Leaves	0.17	1.13	1.13	1.59
	Roots	1.16	0.92	2.66	1.56
	Stem	4.35	8.10	6.63	8.03
UP-16	Leaves	0.16	0.85	1.44	2.10
	Roots	1.04	0.76	2.02	1.83
	Stem	4.01	7.34	5.52	10.26

**Table 1c: Moisture content of different varieties of sweet potato vines grown in 50ppm solutions containing different heavy metal ions.**

Sweet potato varieties	Plant parts	Zinc: Water content	Lead: Water content	Chromium: Water content
UP-A	Leaves	0.48	0.54	0.65
	Roots	0.42	0.35	1.07
	Stem	2.72	2.61	6.40
UP-B	Leaves	1.94	1.73	1.36
	Roots	2.72	2.19	2.84
	Stem	8.79	9.31	9.68
UP-C	Leaves	1.07	0.96	1.60
	Roots	1.85	2.26	2.05
	Stem	8.72	5.92	8.88
UP-D	Leaves	1.03	1.66	1.08
	Roots	1.42	3.94	2.04
	Stem	6.46	7.65	7.20
UP-16	Leaves	0.99	1.53	0.66
	Roots	2.00	2.80	2.39
	Stem	7.81	7.39	5.96

In all cases it was noted that the stems had higher wet weights compared to the leaves and the roots.

The reason why the moist content was included in this section was due to the fact that the heavy metal uptake requires the presence of a

fluid or transfer media or phase, in this case water.

**Distribution of heavy metals in sweet potato plant varieties**

**Uptake of Cd ions**

Due to possible toxicity of the cadmium towards the plants, only concentration range of 0-20ppm was employed. At a concentration of

20ppm Cd solution the pre-rooted sweet potato plants did not produce any additional leaves and roots. However, the plants survived in these solutions for about 10 days but began drying up there after. What was interesting is that the 10 days exposure of the plants to the Cd solution enabled the metal ions to be absorbed into the plants (tables 2 and 3).

**Table 2: Amount of Cd in different parts of sweet potato plant varieties grown in 10ppm Cd solution.**

Variety	Plant part	Dry weight (g) A	Cadmium content ( $\mu\text{g}$ of dry weight) B	Cadmium content %* $C=B/2,000 \mu\text{g} \times 100$
UP-A	Leaves	0.118	$35.536 \pm 17.675$	1.78
	Roots	0.028	$348.723 \pm 20.275$	17.44
	Stem	0.811	$387.260 \pm 22.226$	19.63
	Total	0.958	771.520	38.58
UP-B	Leaves	0.428	ND	0
	Roots	0.054	$399.847 \pm 23.175$	19.99
	Stem	1.663	$287.327 \pm 27.684$	14.37
	Total	2.145	687.173	34.36
UP-C	Leaves	0.289	$1.323 \pm 0.415$	0.07
	Roots	0.051	$438.923 \pm 37.723$	21.95
	Stem	1.338	$213.263 \pm 44.545$	10.66
	Total	1.679	653.509	32.68
UP-D	Leaves	0.268	$2.970 \pm 0.120$	0.15
	Roots	0.038	$373.333 \pm 33.525$	18.67
	Stem	1.487	$289.746 \pm 2.456$	14.49
	Total	1.793	666.080	33.31
UP-16	Leaves	0.213	$1.633 \pm 0.190$	0.08
	Roots	0.049	$425.333 \pm 31.865$	21.27
	Stem	1.176	$298.293 \pm 28.666$	14.91
	Total	1.438	725.260	36.26

\*2,000  $\mu\text{g}$  is the total amount of Cd in the original solution.

In all the five different varieties, the roots appear to have the highest amount of Cd, except for the case of UP-A, due to the direct contact with Cd ion solutions (table 2). On the other hand, the leaves had the lowest amount of Cd, which was higher than that observed in the control experiment. The fact that there was significant amount of Cd in the leaves compared

to the control experiment signifies that truly the Cd was absorbed by the plant and trans-located into the leaves. It is worth noting that even though the roots had the largest amount of Cd in terms of percentage content; it had the lowest weight (table 2, column 3). In all the varieties, limited amounts of Cd (approximately 0.5  $\mu\text{g}$ ) were detected in the control experiments.



However, this amount was much lower (nearly 3 orders of magnitude) than that observed in Cd solutions. In summary, out of the 2,000 µg Cd initially in water, the levels of accumulation in the roots for all the varieties ranged from 348.723 to 438.923, whereas in the case of the leaves and the stem the range was from 0 to 35.5367 and 213.2633 to 387.2600, respectively. For 10 ppm Cd solutions the order of distribution was as follows:

**Leaves<Roots<Stem for UP-A variety**  
**Leaves<Stem<Roots for UP-B, UP-C, UP-D and UP-16 varieties**

When the concentration of Cd in the solution was increased from 10ppm to 20ppm, the amount of Cd in different parts of the plant also increased (table 3), but the percentage observed was lower than that in 10ppm Cd solution for all

the varieties (table 2 and 3). A possible explanation for this observation is that as the amount of non essential Cd ions is increased, the toxicity increases, implying that there might be inhibition of further uptake of the heavy metal. Furthermore, the adsorption of the cadmium ion on the surface of the roots inhibits the normal uptake of other additional nutrients, explaining the observed drying up of the plants in a lesser time than that observed in 10ppm Cd solution. For example, the amount of Cd in roots ranged from 430.583 to 486.613. It is important to note that the amount of Cd in the roots compares favorably to that in the stem (table 3), considering the fact that roots are directly in contact with the water and that the stem has a large surface area of contact.

**Table 3: Amount of Cd in different parts of sweet potato plant varieties grown in 20ppm Cd solution.**

Variety	Plant part	Dry weight(g) A	Cadmium content (µg of dry weight) B	Cadmium content in % C
UP-A	Leaves	0.182	144.170 ± 19.280	3.60
	Roots	0.036	430.583 ± 32.079	10.76
	Stem	1.050	457.950 ± 40.349	11.45
	Total	1.268	1032.7	25.81
UP-B	Leaves	0.302	4.233 ± 6.683	0.11
	Roots	0.056	452.233 ± 10.530	11.30
	Stem	1.526	463.7167 ± 13.897	11.59
	Total	1.884	920.183	23.00
UP-C	Leaves	0.308	ND	0
	Roots	0.063	486.613 ± 9.147	12.17
	Stem	1.424	448.963 ± 1.849	11.22
	Total	1.794	935.577	23.39
UP-D	Leaves	0.276	1.013 ± 0.967	0.03
	Roots	0.044	484.593 ± 19.301	12.11
	Stem	1.148	469.173 ± 11.722	11.73
	Total	1.468	954.780	23.87
UP-16	Leaves	0.252	4.463 ± 2.598	0.12
	Roots	0.0767	470.150 ± 49.130	11.75
	Stem	1.327	488.480 ± 8.704	12.21
	Total	1.656	963.093	24.08

The results obtained above for the absorption of cadmium and trans-location into the sweet potato plant varieties correlate well with what was reported earlier for absorption of Cd by *helianthus annuus* seedlings in soils [10,18]. For 20 ppm Cd solutions the order of distribution was as follows:

**Leaves<Roots<Stems for UP-A, UP-B and UP-16 varieties.**  
**Leaves<Stems<Roots for, UP-C and UP-D varieties.**

**Uptake of Zn ions**

When pre rooted plants were transferred to zinc solutions, and allowed growth to continue, the three main plant parts were found to contain zinc ions (table 4) after 21 days. In addition, the plants grew continuously throughout the experimental period with no signs of drying up, suggesting that Zn is a required nutrient by the plant.

**Table 4: Amount of Zn in different parts of sweet potato plant varieties grown in 10ppm Zn solution.**

Variety	Plant part	Dry weight (g) A	Zinc content ( $\mu\text{g}$ of dry weight) B	Zinc content % C
UP-A	Leaves	0.081	$1.102 \pm 0.178$	0.06
	Roots	0.0052	$85.790 \pm 26.413$	4.29
	Stem	1.032	$281.870 \pm 1.680$	14.09
	Total	1.118	368.761	18.44
UP-B	Leaves	0.237	$3.710 \pm 0.504$	0.19
	Roots	0.040	$215.010 \pm 36.638$	10.75
	Stem	1.421	$249.700 \pm 3.690$	12.49
	Total	1.699	468.420	23.43
UP-C	Leaves	0.173	$4.2900 \pm 1.330$	0.21
	Roots	0.0294	$257.560 \pm 36.740$	12.88
	Stem	1.527	$237.940 \pm 34.981$	11.90
	Total	1.730	499.790	24.99
UP-D	Leaves	0.140	$3.970 \pm 1.902$	0.20
	Roots	0.020	$130.203 \pm 11.050$	6.51
	Stem	1.260	$227.210 \pm 34.770$	11.36
	Total	1.420	361.383	18.07
UP-16	Leaves	0.103	$2.570 \pm 0.450$	0.13
	Roots	0.0118	$84.210 \pm 8.740$	4.21
	Stem	1.050	$323.353 \pm 34.375$	16.17
	Total	1.164	410.133	20.51

It was noted that the stems had higher levels of Zn than in the roots and the leaves for four varieties out of five varieties considered in this work. This suggests that Zn uptake by the sweet potato vines is more pronounced and may contribute to the large mass of the entire plant observed (table 4, column 3). For 10ppm zinc solutions the order of distribution was as follows: *Leaves<Roots<Stem for UP-A, UP-B, UP-D and UP-16 varieties*

*Leaves<Stem<Roots for UP-C variety*

As the concentration of Zn ions increased (from 10ppm to 20ppm), the amount of zinc in different parts of the plant varieties also increased (table 5). On the other hand, the total percentage uptake decreased with the increase in concentration of zinc ions.

**Table 5: Amount of Zn in different parts of sweet potato plant varieties grown in 20ppm Zn solution for a period of 21 days.**

Variety	Plant part	Dry weight (g) A	Zinc content ( $\mu\text{g}$ of dry weight) C	Zinc content % D
UP-A	Leaves	0.0779	$58.630 \pm 3.010$	1.47
	Roots	0.0043	$159.370 \pm 7.880$	3.98
	Stem	1.160	$325.770 \pm 30.809$	8.14
	Total	1.242	543.770	13.59
UP-B	Leaves	0.238	$27.850 \pm 5.754$	0.70
	Roots	0.0219	$282.270 \pm 30.447$	7.06
	Stem	1.301	$291.550 \pm 22.451$	7.29
	Total	1.561	601.670	15.05
UP-C	Leaves	0.1651	$54.200 \pm 26.190$	1.36
	Roots	0.0165	$214.060 \pm 41.226$	5.35
	Stem	1.465	$271.610 \pm 35.480$	6.79
	Total	1.647	539.870	13.50
UP-D	Leaves	0.130	$2.520 \pm 0.640$	0.06

	Roots	0.0212	241.600 ± 30.650	6.05
	Stem	1.034	261.320 ± 46.671	6.53
	Total	1.184	505.440	12.64
UP-16	Leaves	0.0952	4.800 ± 0.981	0.12
	Roots	0.0162	234.060 ± 44.466	5.85
	Stem	1.256	309.150 ± 21.510	7.73
	Total	1.368	548.010	13.70

Similar to the case of Cd, the stem registered higher amounts of Zn than the roots, which is a clear indication that the plants absorb and translocate the Zn ions into different parts of the plant. For 20ppm zinc solutions the order of distribution was as follows:

***Leaves<Roots<Stem for UP-A, UP-B, UP-C, UP-D and UP-16 varieties***

**The sweet potato varieties grown in 50ppm zinc solutions**

The amount of Zn registered in different parts of sweet potato varieties in 50ppm hydroponics were slightly lower than those

obtained in 20ppm Zn solutions (table 6). However, the amount of Zn in the roots was higher than that observed in the stem in four of the five varieties considered in this study. This observation may be attributed to the excessive amount of Zn adsorbed on the surface of the roots, which could not be taken up by the plant [15]. This explanation is further supported by the fact that in all the four heavy metals studied in this work the percentage metal content in the plant decreases as their original concentration in hydroponics increases.

**Table 6: Amount of Zn in different parts of sweet potato plant varieties grown in 50ppm Zn solution.**

Variety	Plant part	Dry weight (g)	Zinc content (µg of dry weight)	Zinc content %
		A	B	C
UP-A	Leaves	0.125	16.103 ± 1.483	0.16
	Roots	0.0120	123.697 ± 9.868	1.24
	Stem	1.640	168.830 ± 12.614	1.69
	Total	1.777	308.630	3.09
UP-B	Leaves	0.264	33.877 ± 2.265	0.34
	Roots	0.0991	171.717 ± 7.501	1.72
	Stem	1.642	164.830 ± 10.695	1.65
	Total	2.004	370.423	3.71
UP-C	Leaves	0.197	8.453 ± 0.441	0.08
	Roots	0.063	160.540 ± 9.656	1.61
	Stem	1.739	157.800 ± 8.089	1.58
	Total	1.999	326.793	3.27
UP-D	Leaves	0.1855	11.230 ± 2.082	0.11
	Roots	0.0571	166.987 ± 9.631	1.67
	Stem	1.338	161.347 ± 10.338	1.62
	Total	1.581	339.563	3.40
UP-16	Leaves	0.224	13.787 ± 1.237	0.14
	Roots	0.0746	165.000 ± 3.781	1.65
	Stem	1.388	160.903 ± 7.219	1.61
	Total	1.686	339.690	3.40

The uptake and translocation of zinc into the sweet potato plant can be related to previous work, which indicate that zinc accumulate in *Arabidopsis halleri* [11]. For 50ppm zinc solutions the order of distribution was as follows: ***Leaves<Roots<Stems for UP-A variety***

***Leaves<Stems<Roots for UP-B, UP-C, UP-D and UP-16 varieties***

**Behavior of sweet potato varieties subjected to hydroponic solution containing lead ions**

Lead is considered to be a heavy metal and is easily ingested by living things including

plants. Different parts of the sweet potato plant varieties exhibited varying amount of lead as indicated in table 7.

**Table 7: Amount of Pb in different parts of sweet potato plant varieties grown in 10ppm Pb solution.**

Variety	Plant part	Dry weight (g) A	Lead content ( $\mu\text{g}$ of dry weight) C	Lead content % D
UP-A	Leaves	0.142	$4.31 \pm 2.642$	0.22
	Roots	0.0246	$4.450 \pm 1.563$	0.22
	Stem	0.814	$0.980 \pm 0.170$	0.050
	Total	0.970	9.740	0.49
UP-B	Leaves	0.274	$5.51 \pm 0.659$	0.28
	Roots	0.100	$1.56 \pm 0.014$	0.08
	Stem	1.18	$121.85 \pm 17.89$	6.09
	Total	1.55	128.92	6.45
UP-C	Leaves	0.140	$3.32 \pm 0.835$	0.17
	Roots	0.088	$1.37 \pm 0.892$	0.07
	Stem	1.026	$90.32 \pm 31.50$	4.52
	Total	1.258	95.01	4.76
UP-D	Leaves	0.411	$1.89 \pm 0.57$	0.09
	Roots	0.100	$1.55 \pm 0.037$	0.08
	Stem	1.225	$150.69 \pm 28.63$	7.53
	Total	1.740	154.13	7.70
UP-16	Leaves	0.195	ND	0
	Roots	0.107	$1.53 \pm 0.022$	0.08
	Stem	1.356	$160.62 \pm 60.80$	8.03
	Total	1.659	162.15	8.11

Similar to the case of Zn, the stem had highest amount of Pb, ranging from 0.645 to 107.077, followed by roots and leaves, respectively, except for variety UP-A. No lead content was registered in leaves for variety UP-16, even though all other sweet varieties exhibited presence of lead in leaves, ranging from 1.26 to 3.673. For 10ppm lead solutions the order of distribution was as follows:

**Leaves < Roots < Stem for UP-16 variety**

**Stem < Leaves < Roots for UP-A variety**

**Roots < Leaves < Stem for UP-B, UP-C and UP-D**

As the initial concentration of lead was increased from 10 to 20 ppm the amount of lead

in each part of sweet potato variety increased considerably (table 8), signifying the direct relationship between the amount of metal content in hydroponics compared to that in the plant parts. However, the percentage of lead in each part of the plant increased compared to what was observed in the case of cadmium and zinc. It was noted that the plant varieties gave rise to more new roots than in other cases, which possibly presented additional surface area to which the plant could absorb and trans-locate the lead ions in the plant.

**Table 8: Lead levels in different parts of sweet potato plant varieties grown in 20ppm Pb solution for 21 days.**

Variety	Plant part	Dry weight (g) A	Lead content ( $\mu\text{g}$ of dry weight) C	Lead content % D
UP-A	Leaves	0.0409	$2.630 \pm 2.385$	0.07
	Roots	0.0143	$878.916 \pm 9.063$	21.97
	Stem	0.950	$679.677 \pm 58.949$	16.99
	Total	1.0048	1561.223	39.03
UP-B	Leaves	0.247	$0.740 \pm 0.364$	0.02
	Roots	0.138	$1752.370 \pm 135.831$	43.81
	Stem	1.428	$209.0167 \pm 20.6431$	5.23
	Total	1.813	1962.127	49.06

UP-C	Leaves	0.229	1.890	0.05
	Roots	0.0907	1544.307 ± 132.0477	38.61
	Stem	1.666	370.417 ± 26.0784	9.26
	Total	1.986	1916.613	47.92
UP-D	Leaves	0.180	0.950 ±	0.03
	Roots	0.1093	1443.423 ± 31.283	36.09
	Stem	1.5411	271.747 ± 4.416	6.79
	Total	1.8306	1716.120	42.91
UP-16	Leaves	0.1858	1.580	0.04
	Roots	0.0672	1138.153 ± 45.384	28.46
	Stem	1.154	249.673 ± 5.88	6.24
	Total	1.4072	1389.407	34.74

For 20ppm lead solutions the order of distribution was as follows:

**Leaves<Stems<Roots for UP-A, UP-B, UP-C, UP-D and UP-16 varieties**

Raising the hydroponics lead concentration to 50ppm increased the amount of lead in roots, stem and leaves significantly (table

9). On the other hand, the percentage lead ion in each part of plant decreased, compared to what was observed in 20ppm solution. This suggested that the excessive adsorption of lead ions on the surface of the roots inhibits further intake and trans-location of lead ions in the plant.

**Table 9: Lead uptake and distribution by sweet potato plants grown in 50mg/l lead solution for 21 days.**

Variety	Plant part	Dry weight (g) A	Lead content (mg of dry weight) C	Lead content % D
UP-A	Leaves	0.084	0.0003 ± 0.0004	0.003
	Roots	0.013	0.9306 ± 0.0223	9.31
	Stem	1.048	1.8704 ± 0.663	18.70
	Total	1.145	2.801	28.01
UP-B	Leaves	0.263	0.0138 ± 0.003	0.14
	Roots	0.081	2.727 ± 0.090	27.27
	Stem	1.651	0.658 ± 0.0152	6.58
	Total	1.996	3.398	33.99
UP-C	Leaves	0.135	0.0124 ± 0.0019	0.13
	Roots	0.068	2.834 ± 0.141	28.34
	Stem	0.684	0.484 ± 0.011	4.84
	Total	0.886	3.331	33.31
UP-D	Leaves	0.240	0.0019 ± 0.0006	0.02
	Roots	0.135	2.771 ± 0.115	27.71
	Stem	1.407	0.422 ± 0.015	4.22
	Total	1.782	3.195	31.95
UP-16	Leaves	0.239	0.0006 ± 0.0002	0.01
	Roots	0.075	2.934 ± 0.077	29.34
	Stem	1.237	0.636 ± 0.032	6.36
	Total	1.551	3.570	35.71

Significant lead uptake and translocation in corn was earlier reported by Huang [8]. These results compares favorably with the current work, which show that lead uptake by sweet potato plant varieties goes beyond 50 ppm. For 50ppm lead solutions the order of distribution was as follows:

**Leaves<Roots<Stem for UP-A variety**

**Leaves<Stem<Roots for UP-B, UP-C, UP-D and UP-16**

#### **Uptake and distribution of chromium in sweet potato plant varieties grown in 10ppm chromium solution**

The behavior of the sweet potato variety in hydroponics containing chromium was similar to that observed in the case of Zn. The roots, stems and the leaves of the different varieties indicated presence of Cr (table 10). The roots contained the highest amount of Cr ions for all

the varieties, except in variety UP-A, ranging from 9.463 to 114.533 µg.

For 10 ppm Chromium solutions the order of distribution was as follows:

*Leaves<Roots<Stem for UP-A and UP-16 varieties*

*Leaves<Stem<Roots for UP-B, UP-C and UP-D varieties*

**Table 10: chromium uptake and distribution by sweet potato plants grown in 10mg/l chromium solutions for 21 days.**

Variety	Plant part	Dry weight (g) A	Chromium content (µg of dry weight) C	Chromium content % D
UP-A	Leaves	0.022	3.250 ±	0.16
	Roots	0.007	9.463 ± 4.329	0.47
	Stem	0.880	147.89 ± 11.744	7.40
	Total	0.909	160.603	8.03
UP-B	Leaves	0.180	5.6500± 2.008	0.28
	Roots	0.082	77.837 ± 8.564	3.89
	Stem	1.219	40.737 ± 5.061	2.04
	Total	1.480	124.223	6.21
UP-C	Leaves	0.217	2.810 ± 2.807	0.14
	Roots	0.094	91.077 ± 9.825	4.55
	Stem	1.391	28.980 ± 6.161	1.45
	Total	1.703	122.867	6.14
UP-D	Leaves	0.210	12.645 ± 2.807	0.63
	Roots	0.113	114.533 ± 11.283	5.73
	Stem	1.518	37.457 ± 11.717	1.87
	Total	1.840	164.635	8.23
UP-16	Leaves	0.150	11.975 ± 3.260	0.60
	Roots	0.041	36.070 ± 13.950	1.80
	Stem	1.192	61.180 ± 12.229	3.06
	Total	1.384	109.225	5.46

Increasing the Cr concentration from 10ppm to 20ppm in the hydroponics raised the Cr concentration in each part of the sweet potato

variety (table 11). Similar to the case of Zn, the percentage of Cr in each part of the sweet potato variety decreased (table 11).

**Table 11: Total chromium uptake and distribution by sweet potato plants grown in 20mg/l chromium solutions for 21 days.**

Variety	Plant part	Dry weight (g) A	Chromium content (µg of dry weight) C	Chromium content % D
UP-A	Leaves	0.032	7.475 ± 3.727	0.19
	Roots	0.014	46.193 ± 16.193	1.15
	Stem	0.915	105.460 ± 24.156	2.64
	Total	0.961	159.128	3.98
UP-B	Leaves	0.257	44.543 ± 12.588	1.11
	Roots	0.074	124.660 ± 13.764	3.12
	Stem	2.016	61.363 ± 12.720	1.53
	Total	2.347	230.567	5.76
UP-C	Leaves	0.189	18.550 ± 7.156	0.46
	Roots	0.055	91.337 ± 14.601	2.28
	Stem	1.241	72.057 ± 13.084	1.80
	Total	1.485	181.943	4.54
UP-D	Leaves	0.186	11.050 ± 5.968	0.28
	Roots	0.079	142.955 ± 21.083	3.57
	Stem	1.289	86.750 ± 9.890	2.17
	Total	1.554	240.755	6.02

UP-16	Leaves	0.197	19.680 ± 12.680	0.49
	Roots	0.071	136.387 ± 22.045	3.41
	Stem	0.508	31.2167 ± 11.2686	0.78
	Total	0.777	187.283	4.68

For 20ppm Chromium solutions the order of distribution was as follows:

*Leaves<Roots<Stem for UP-A varieties*

*Leaves<Stem<Roots for UP-B, UP-C, UP-D and UP-16 varieties*

Hydroponics containing 50ppm Cr ions exhibited an increase in the amount of Cr in each

part of the sweet potato variety (table 12). The stem registered the highest amount of Cr in all the sweet potato varieties, except varieties UP-B and UP-C. On the other hand, the percentage Cr in different parts of sweet potato varieties decreased compared to that of 20ppm solutions.

**Table 12: Chromium uptake and distribution by sweet potato plants grown in 50mg/l chromium solutions for 14 days.**

Variety	Plant part	Dry weight (g) A	Chromium content (µg of dry weight) C	Chromium content % D
UP-A	Leaves	0.134	100.633 ± 18.375	1.01
	Roots	0.037	165.457 ± 29.138	1.65
	Stem	0.901	365.270 ± 56.519	3.65
	Total	1.071	631.360	6.31
UP-B	Leaves	0.243	24.977 ± 10.955	0.25
	Roots	0.134	289.437 ± 54.790	2.90
	Stem	1.849	256.183 ± 45.565	2.56
	Total	2.226	570.597	5.71
UP-C	Leaves	0.214	42.413 ± 13.268	0.42
	Roots	0.092	245.127 ± 54.005	2.45
	Stem	2.187	222.043 ± 43.656	2.22
	Total	2.493	509.583	5.09
UP-D	Leaves	0.206	19.930 ± 10.482	0.20
	Roots	0.084	193.513 ± 41.284	1.94
	Stem	1.025	128.043 ± 89.434	1.28
	Total	1.314	341.487	3.42
UP-16	Leaves	0.176	39.873 ± 5.970	0.40
	Roots	0.076	170.227 ± 31.780	1.70
	Stem	1.168	475.590 ± 72.581	4.76
	Total	1.418	685.690	6.86

It was noted that in case of chromium and zinc the amount of each found in the leaves of sweet potato plant varieties was a bit higher than those obtained in case of lead and cadmium. This similarity in the behavior of Cr and Zn can be attributed to their positions (first row of transition elements) in the periodic table. On the other hand, lead, [Xe]  $4f^{14}5d^{10}6s^26p^2$  and Cadmium, [Kr]  $4d^{10}5s^2$ , not only do they occur at different positions in the periodic table but also have different physical properties, like densities. Hence, the different behaviors observed for both Cd and Pb, compared to the other two elements (Cr and Zn). The type of distribution observed in this work differs from what was observed with regard to DDT absorption, which was found to be in high concentrations at the terminal zones [12].

### Conclusions

The present work indicated that significant amount of cadmium, lead, zinc and chromium was taken up by different sweet potato varieties. The heavy metal content absorbed by the sweet potato plant variety depended on the initial concentration of the metal, originally present in the hydroponics. Three main steps involved in uptake can be regarded as involving adsorption at the surface of roots, absorption and eventual trans-location into stem and leaves. This suggestion is supported by the fact that increased metal concentration in the hydroponic solutions led to an increase in amount of metal taken up and decrease in percentage intake and distribution. In all the observations for different concentrations of metals and different varieties, the leaves had the least amount of metal ions. The highest amounts of metal ions were recorded in either the roots or the stems. Only in the case of varieties UP-B, UP-C and UP-D at 10ppm lead solution whereby the leaves had more lead content than the stem. Considering the different distribution of the metal content in different parts of the plant, it is clear that metal contents in hydroponics are absorbed and trans-located in different parts of the plants. In this work, the temperature in the green house remained constant at about 24°C.

For the five varieties considered, lead exhibited the highest accumulation in roots, stem and leaves. This research finding compares favorably to cow peas plants, which were found to accumulate more DDT at the terminal zones (roots and leaves) than on the stem.

The above results demonstrates that the sweet potato plants could be used for phytoextraction, i.e., removing some of the metals from solution. Since much of the metal stays in the roots, these could be harvested and used for biofuel,

while the cuttings can be re-rooted (a trait for which this species excels!) and then placed back in the solution to remove more of the contaminant. Repeated planting of the sweet potato varieties will eventually remove all the pollutants.

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# Correlation between Dissolved Oxygen and Total Dissolved Solids and their Role in the Eutrophication of Nairobi Dam, Kenya

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**Research on Eutrophication of Nairobi Dam, Kenya and its tributaries has revealed fair negative correlation between Dissolved Oxygen (DO) and Total Dissolved Solids (TDS) Contents ( $y = -24.562x + 622.28$ ,  $R^2 = 0.6835$ ). This indicated that, sampling sites with low dissolved oxygen had high TDS, while those with high DO had low TDS. When the levels of these parameters in the aquatic environment studied were compared with other eutrophic aquatic systems of the world, it was found to be highly eutrophic. Thus, any of these two parameters could be used as an index of Eutrophication in a given water body suspected to exhibit Eutrophic activity. In the current study, it had been postulated that the major source of eutrophication could have been disposal of untreated raw sewage and use of phosphorous-containing surfactants.**

Key words: Dissolved Oxygen, Total Dissolved Solids, Eutrophication, Nairobi Dam.

## INTRODUCTION

Eutrophication is the enrichment of a water body (usually of still or slow-flowing fresh water) with plant nutrients (e.g., by the input of organic material or by surface run-off containing NITRATES and PHOSPHATES). Eutrophication may happen naturally but it is often a form of pollution. It leads to an increase in the growth of aquatic plants and often to algal blooms, which may smother higher plants; reduce light intensity; produce toxins which kill fish and through the aerobic decomposition of organic matter, deoxygenate the water, and thereby causing the death of many aquatic animals and higher plants. Eventually, the accumulation of organic matter may raise the bed of a lake until it becomes marsh, then dry land [1]. The history of Eutrophication studies and trophic state classification are well discussed in the literature [2-11].

**Dissolved Oxygen (DO)** is one of the best indicators of the health of a water ecosystem. Dissolved oxygen can range from 0 to 18 parts per million (ppm), but most natural water systems require 5-6 parts per million to support a diverse population [12].

Oxygen enters the water by direct absorption from the atmosphere or by plant photosynthesis. The oxygen is used by plants and

animals for respiration and by the aerobic bacteria which consume oxygen during the process of decomposition. When organic matter such as animal waste or improperly treated wastewater enters a body of water, algae growth increases and the dissolved oxygen levels decrease as the plant material dies off and is decomposed through the action of the aerobic bacteria [12]. Decreases in the dissolved oxygen levels can cause changes in the types and numbers of aquatic macro-invertebrates which live in a water ecosystem. Species which cannot tolerate decreases in dissolved oxygen levels include mayfly nymphs, stonefly nymphs, caddisfly larvae and beetle larvae [12]. As the dissolved oxygen levels decrease, these pollution-intolerant organisms are replaced by the pollution-tolerant worms and fly larvae [12].

Dissolved oxygen levels change and vary according to the time of day, the weather and the temperature. If yearly comparisons are made on dissolved oxygen levels, they should be done at the same time of day, during the same season and on a day with a temperature variation of only 10 degrees Celsius from the previous reading. A decrease in the dissolved oxygen levels is usually an indication of an influx of some type of organic pollutant [12]. Dissolved oxygen analysis measures the amount of gaseous oxygen (O<sub>2</sub>) dissolved in an aqueous solution. Oxygen gets into water by diffusion from

the surrounding air, by aeration (rapid movement) Total dissolved gas concentrations in water should not exceed 110 percent. Concentrations above this level can be harmful to aquatic life. Fish in waters containing excessive dissolved gases may suffer from "gas bubble disease"; however, this is a very rare occurrence. The bubbles or emboli block the flow of blood through blood vessels causing death. for good water quality. Oxygen is a necessary element to all forms of life. Natural stream purification processes require adequate oxygen levels in order to provide for aerobic life forms. As dissolved oxygen levels in water drop below 5.0 mg/l, aquatic life is put under stress. The lower the concentration of oxygen in an aquatic system, the greater the stress. Oxygen levels that remain below 1-2 mg/l for a few hours can result in large fish kills [12].

Oxygen depletion refers to low levels of DO and may result in fish mortality. A concentration of 5 mg/L DO is recommended for optimum fish health. Sensitivity to low levels of dissolved oxygen is species specific, however, most species of fish are distressed when DO falls to 2-4 mg/L. Mortality usually occurs at concentrations less than 2 mg/L. The number of fish that die during an oxygen depletion event is determined by how low the DO gets and how long it stays down. Usually larger fish are affected by low DO before smaller fish are. Dissolved oxygen (DO) is oxygen gas (O<sub>2</sub>) that is dissolved in water. Most DO in ponds is produced during photosynthesis by aquatic plants and algae. For this reason DO increases during daylight hours, declines during the night, and is lowest just before daybreak. Low levels of DO are most frequently associated with hot, cloudy weather, algae die-offs, or heavy thunderstorms. Dissolved oxygen can be monitored using an electronic oxygen meter or chemical test kit. Emergency aeration should be supplied whenever DO falls below 4 mg/L or environmental conditions favor an oxygen depletion event [13].

Water is a good solvent and picks up impurities easily. Pure water, which is tasteless, colorless and odorless, is often called the universal solvent. "Dissolved solids" refer to any minerals, salts, metals, cations or anions dissolved in water.

**Total Dissolved Solids** (TDS) comprise inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulfates) and some small amounts of organic matter that are dissolved in water. TDS in drinking-water originate from natural sources, sewage, urban runoff, industrial wastewater, chemicals used in the water treatment process and the nature of the piping or hardware used to convey the water, i.e., the

and as a waste product of photosynthesis.

External bubbles (emphysema) can also occur and be seen on fins, on skin and on other tissues. Aquatic invertebrates are also affected by gas bubble disease but at levels higher than those lethal to fish.

Adequate dissolved oxygen is necessary

plumbing. In the United States, elevated TDS has been due to natural environmental features such as: mineral springs, carbonate deposits, salt deposits, and sea water intrusion. But other sources may include salts used for road de-icing, anti-skid materials, drinking water treatment chemicals, storm-water and agricultural runoff and point/non-point wastewater discharges [13].

In general, the total dissolved solids concentration is the sum of the cations (positively charged) and anions (negatively charged) ions in the water. Therefore, the total dissolved solids test provides a qualitative measure of the amount of dissolved ions, but does not tell us the nature or ion relationships. In addition, the test does not provide us insight into the specific water quality issues, such as [elevated hardness](#), [salty taste](#) or [Corrosiveness](#). Therefore, the total dissolved solids test is used as an indicator test to determine the general quality of the water. Table 1 can be used to show the relationship of TDS to water quality problems

**Table 1: Dissolved solids and water quality.**

Cations combined with Carbonates: CaCO <sub>3</sub> , MgCO <sub>3</sub> and related salts	Associated with hardness, scale formation, bitter taste
Cations combined with Chloride NaCl, KCl	Salty or brackish taste, increase corrosivity

An elevated total dissolved solids (TDS) concentration is not a health hazard. The TDS concentration is a secondary drinking water standard and therefore is regulated because it is more of an aesthetic rather than a health hazard. An elevated TDS indicates the following:

- 1) The concentration of the dissolved ions may cause the water to be corrosive, salty or brackish taste, result in scale formation, interfere and decrease efficiency of hot water heaters and 2) Many contain

elevated levels of ions that are above the Primary or Secondary Drinking Water Standards, such as: an elevated level of nitrate, arsenic, aluminum, copper and lead [14].

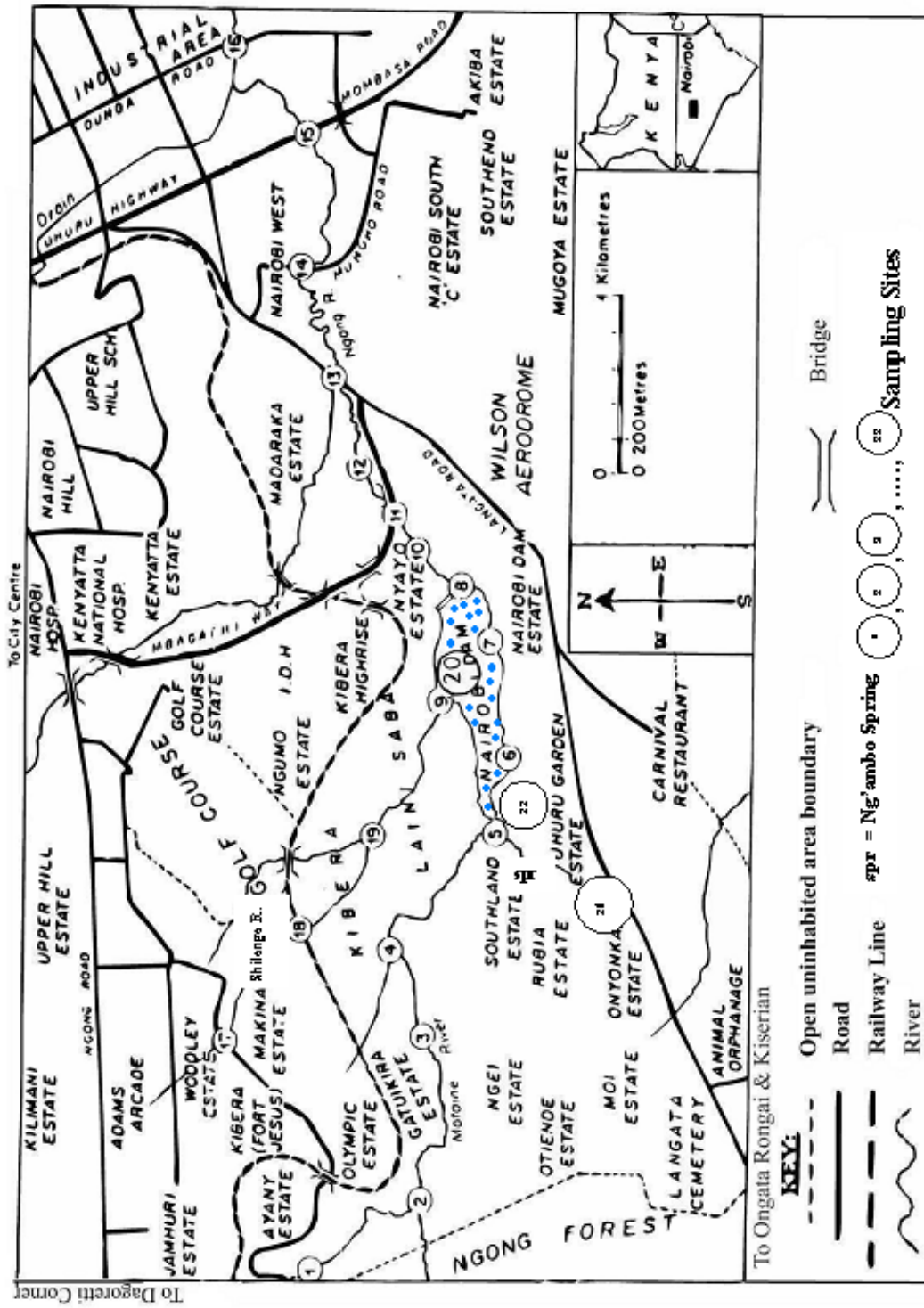
The principal application of TDS is in the study of [water quality](#) for [streams](#), [rivers](#) and [lakes](#), although TDS is generally considered not as a primary pollutant (e.g. it is not deemed to be associated with health effects), but it is rather used as an indication of aesthetic characteristics of [drinking water](#) and as an aggregate indicator of presence of a broad array of chemical contaminants. The term "settleable solids" refers to material of any size that will not remain suspended or dissolved in a holding tank not subject to motion, and exclude both TDS and total suspended solids (TSS) [15]. Settleable solids may include larger particulate matter or insoluble molecules. There is so much that has been written on TDS in the literature [16–21]. The maximum permissible level for TDS in drinking water in Kenya is 1500 mg/L while that for Dissolved Oxygen has not been specified [22].

Some decades ago, Nairobi Dam, Kenya, used to be a very attractive scene for recreation, as well as to offer certain services, such as domestic use and Church Baptism by immersion. As a result, tourists and local visitors would flock there. The water was then clear and plant growth minimal. In the closing years of the 20<sup>th</sup> Century, the dam was infested with aquatic weeds, especially the water hyacinth, leading to its imminent partial "death", and the former recreational activities were no more.

This was a probable consequence of Eutrophication. The current apparent Eutrophication in Nairobi Dam has been postulated to be mainly due to the abundance of phosphorous as a result of use and disposal of anionic surfactants, in domestic sewage effluents. The element, which is most essential for the growth of the (fresh-aquatic) water-hyacinth in the shallow dam, was therefore expected to be the limiting element in the growth and proliferation of the water hyacinth in the dam and its environs [23].

## EXPERIMENTAL SAMPLING

A map of part of the City of Nairobi showing Nairobi Dam, its tributaries and environs and the sampling points is shown in Figure 1, while the environmental information of all the sampling points, including their neighborhood vicinities is given in Table 2. The area of the dam is approximately 0.274 Km<sup>2</sup>. The water samples collected and analyzed were from Nairobi Dam and from its two main tributaries, Motoine and Ngong Rivers. Sampling was mainly done near the bridges, shores or where the dam and the rivers were easily accessible. Water samples were drawn in duplicate using cleaned High Density Poly-ethylene (HDPE) plastic Containe of 1L and 2L capacities, at the surface of various points of the dam and its two tributaries almost simultaneously. This was done by three well coordinated teams to avoid time-variation effects. The untreated samples were stored in the fridge at 4° C until the time of analysis.



**Figure 1.** Map of Nairobi Dam, its major tributaries and environs, showing the sampling points

TABLE 2: Environmental description of sampling points

SP No.	Description & Location	Notes (Activities)
1	First Sampling Point of Motoine River (Inlet), bordering Nairobi International Show.	Clean water. No slums in the vicinity. Middle-class area.
2	Second Sampling Point of Motoine River.	Beginning of slum, no proper sewage disposal.
3	Third Sampling Point of Motoine River.	Midst of slum, raw sewage.
4	Fourth Sampling Point of Motoine River.	End of slum, slight farming activities.
5	Dam Entrance from Motoine River (Inlet).	No water hyacinth growing during most of the sampling seasons.
6	On Nairobi Dam Shore.	Covered by water hyacinth.
7	On Nairobi Dam Shore.	Covered by water hyacinth.
8	At Exit of Nairobi Dam.	Covered by water hyacinth.
9	Dam Entrance from Shilanga River (Inlet).	Covered by water hyacinth.
10	First Sampling Point on outlet. No slum in the vicinity. A new modern middle class residential area (Nyayo Estate) on one side.	Small-scale farming belonging to Langata Prison on the other side. Domestic waste water from estate pouring into the river.
11	Second Sampling Point along the Ngong River Outlet. Middle class estate on one side.	Flower farming on other side, but sewage effluents from higher areas pouring into the river.
12	No residential area in the vicinity.	Small-scale and flower farming activities on either side.
13	Confluence with another stream passing through Kenyatta Hospital Estate.	Small-scale and flower farming and car-washing activities on either side.
14	Middle class residential areas on either side.	No slums, but slight agricultural activities.
15	Cemented river banks and bottom. No sediments available.	Flower farming, with a few middle-class residential areas and social amenities.
16	Final sampling point downstream at Mater Hospital bridge, after Uhuru Highway Drain confluence.	A few modern social and residential areas and the beginning of Industrial Area, with Lubrication and Metal Industries in place.
17	First Sampling Point upstream, along Shilanga River (Inlet), at Kibera DO's office.	Clean water, before slum, just after middle-class area.
18	Near the Railway Line.	Midst of slum, raw sewage.
19	At a confluence with river from Golf Course Estate.	End of slum, raw sewage.
20	Middle of Nairobi Dam.	Covered by water hyacinth.
21	First Sampling Point from Ng'ambo Spring (Inlet).	Clean (spring) water for domestic use, no slum. Middle-class area.
22	Dam Entrance from Ng'ambo Spring (Inlet).	No water hyacinth growing during most of the sampling seasons.

**KEY:** SP No. = Sampling Point Number

## SAMPLE ANALYSIS

### Determination of Dissolved Oxygen (DO)

Dissolved Oxygen (DO) of the water samples was determined directly using a Dissolved Oxygen Meter, model OXI 42 - Karl Kolb Scientific Technical Supplies, West Germany. The total dissolved solids content (TDS) of the water samples was determined using the recommended standard (gravimetric) method [24]. The un-acidified water samples (B) were filtered through numbers 40 or 540 filter papers. 100 ml of the filtrate was transferred into pre-weighed 100 ml

beakers and evaporated for about 12 hours in an air oven at  $105 \pm 2^\circ\text{C}$ . The beaker with TDS was cooled in a desiccator and weighed and the TDS content calculated from the formula shown below:  

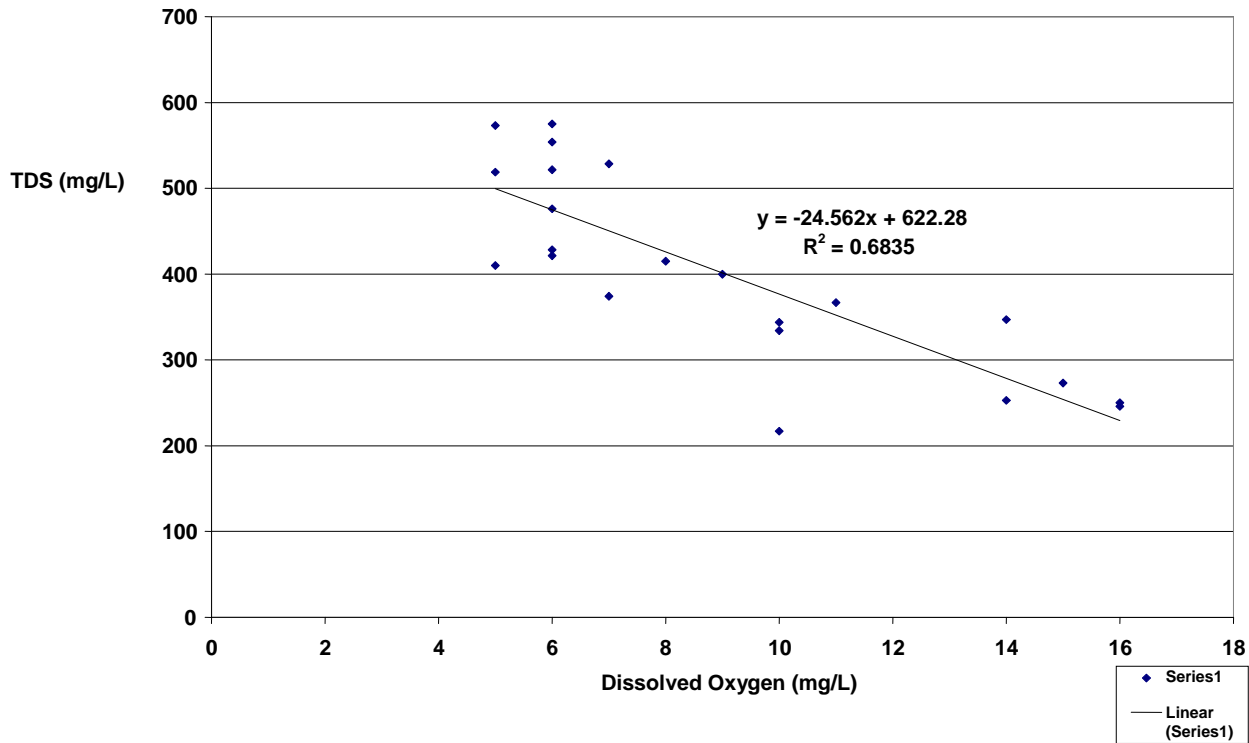
$$\text{TDS content, mg/l} = \frac{(\text{Wt. of beaker with TDS (g)} - \text{Wt. of empty beaker (g)}) \times 10^6}{\text{Sample Volume, in ml}}$$

## RESULTS AND DISCUSSIONS

Fairly good negative correlation was found between Dissolved Oxygen (DO) and Total Dissolved Solids (TDS) ( $y = -24.562x + 622.28$ ,  $R^2$

= 0.6835) in water sampled from various points along the Nairobi Dam Basin (Figure 2). The results for the two parameters (DO and TDS) at the

individual sampling points are depicted in Figures 3 and 4.



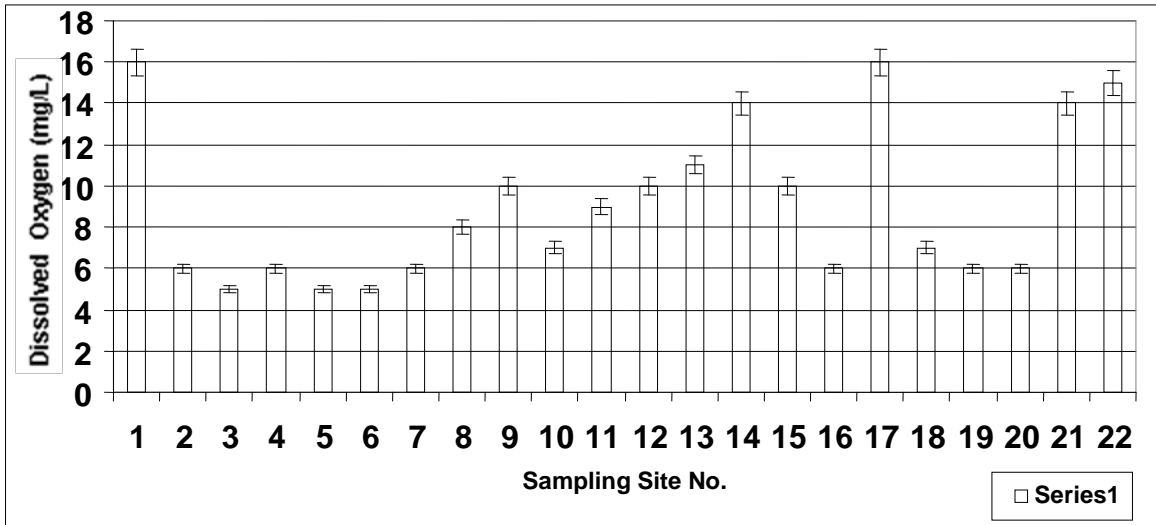
**Figure 2: Correlation Graph of Total Dissolved Solids (TDS) vs. Dissolved Oxygen for Water from Nairobi Dam Basin\***

\*This refers to Nairobi Dam, its two tributary inlets and one tributary outlet (Figure 1).

The negative correlation depicted in Figure 2 reveals that sampling points with low dissolved oxygen (DO) content had high Total Dissolved Solids (TDS) content. On the other hand, the sites which had high DO registered low TDS content. This was expected because low DO levels are associated with high organic matter contents [12]. This suggests that the most probable contributing factor was the untreated raw sewage containing both organic and inorganic matter emanating from

the informal residential settlements of the area studied. On the other hand, this shows that nearly saturated water solution with high nutrient levels (which is associated with high level of eutrophication) will have low Dissolved Oxygen content and may not support much aquatic life [12,13]. The detailed profiles of the two parameters for all sampling points are clearly illustrated in Figures 3 and 4.





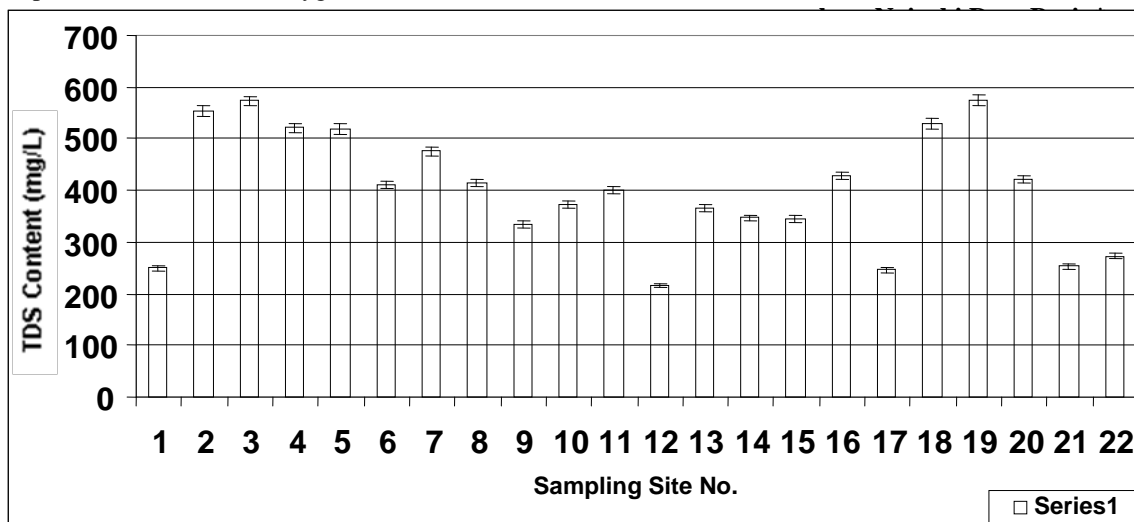
**Figure 3: Dissolved oxygen profile along Nairobi Dam Basin\***

\*This refers to Nairobi Dam, its two tributary inlets and one tributary outlet (Figure 1).

Close scrutiny of Figure 3 shows that sampling points along the two major inlet streams (Motoine and Shilanga Rivers) in the higher altitudes, far before the entrance to Nairobi Dam, i.e. Sites numbers 1 and 17 (Figure 1) registered the highest Dissolved Oxygen content (mean of 16 mg/L). These were closely followed by sampling sites 22 and 21 (along the shorter Ng'ambo Spring) and site number 14 (lower downstream, along the outlet, Ngong River) in that order (means ranging from 14 to 16 mg/L). On the other hand, those sites along the two major inlets just before the dam and most of those in the dam registered the lowest dissolved oxygen content in the following order: sites numbers 3, 5, 6, 2, 4, 7, 16, 19 and 20, whose means ranged from 5 to 6 mg/L. It is worth noting that in a pollution-free environment, it would be expected that Dissolved Oxygen level should

increase with decreasing altitude, i.e., downstream and that still water (such as the one in the dam) should register lower DO than the water which is constantly flowing. This may explain the gradual increase in DO along the relatively least polluted Ngong River outlet (sites numbers 10 to 14) and low DO in Nairobi Dam. However, this expected trend was not consistently observed along the main inlet streams (sites numbers 1 to 4 and 17 to 19), indicating gradual pollution along the inlet streams.

The above Dissolved Oxygen profile shows that the currently high extent of eutrophication in Nairobi Dam and its immediate vicinity could be associated with its diminished Dissolved Oxygen levels. This in turn explains the current disappearance of aquatic animals such as fish from Nairobi Dam.



**Figure 4: Total Dissolved Solids (TDS) Profile**

The profile depicted in Figure 4 shows that the total dissolved Solid content for the water sampled from sites numbers 12, 1, 17, 21 and 22 registered the lowest values in that order ( $> 200$  to  $< 300$  mg/L), while sites 3, 19, 2, 18, 4, 5, 7 had the highest TDS contents in that order ( $> 450$  to  $< 600$  mg/L), which is to a large extent the reverse of what was observed in Figure 3. This agrees with what was observed and reported under Figure 2 and the activities outlined in Table 1.

The TDS levels for all the sampling points were generally much higher than that reported for Eutrophic Lake Itasca waters (U.S.A) of about 185 mg/l [25], but lower than the maximum permissible limit of 1500 mg/L for drinking water specified in Kenya [22]. This maximum limit value for Total Dissolved Solids, allowed in the Kenya Standard for drinking water can therefore be associated with high Eutrophication activity and should therefore be revised downwards accordingly. Furthermore, it is far much higher than the maximum (secondary) limit of 500 mg/L specified in U.S.A. [16].

#### CONCLUSION AND RECOMMENDATIONS

The current research work on Nairobi Dam, Kenya, has revealed that there was fairly good negative correlation between dissolved oxygen (DO) and Total Dissolved Solids (TDS) ( $y = -24.562x + 622.28$ ,  $R^2 = 0.6835$ ) in water sampled from different points along the Nairobi Dam. The significant large gradient expresses the extent of eutrophication of the dam. In addition, the TDS levels for all the sampling points were somehow much higher than that reported for Eutrophic Lake Itasca waters (U.S.A) of about 185 mg/l [25], but lower than the maximum permissible limit of 1500 mg/L for drinking water specified in Kenya [22]. The maximum limit level of Total Dissolved Solids of 1500 mg/L, stipulated in the Kenya Standard [22] could therefore be associated with high Eutrophication activity.

Based on the results and conclusion indicated above, it is recommended that further research on the correlation between the parameters associated with Eutrophication and other physical parameters (such as dissolved oxygen) for Nairobi Dam and other aquatic bodies be carried out in order to determine the extent of eutrophication. Suitable measures should also be formulated to restore the original

condition of Nairobi Dam, Kenya in order to reduce total dissolved solid content and increase the level of dissolved oxygen and thus reduce or even eliminate the extent of Eutrophication of the dam and its environs. At the same time, the maximum limit of total dissolved solids of 1500 mg/L, stipulated in the Kenya Standard [22], should be revised downwards accordingly.

#### ACKNOWLEDGEMENTS

The authors wish to thank Kenya Bureau of Standards for allowing the main research analytical work to be conducted at their Laboratories. Our appreciations also go to Jomo Kenyatta University of Agriculture and Technology and the University of Nairobi for providing an enabling working environment and technical assistance. The authors also thank the individuals who assisted in field related technical activities.

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# Phosphorous as the Limiting Nutrient Element for the Eutrophication of Nairobi Dam, Kenya

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Research work on Nairobi Dam, Kenya and its tributaries revealed Poor negative correlation between Phosphorous (Hydrolysable +  $\text{PO}_4^{3-}$ ) and  $\text{NO}_3^-$  - Nitrogen, giving a regression line of  $y = -0.2176x + 2.1471$  with  $R^2 = 0.1876$  on water sampled over a period of one and half years. On the other hand, there was poor positive correlation between Phosphorous (Hydrolysable +  $\text{PO}_4^{3-}$ ) and Potassium ( $y = 2.142x + 32.964$ ,  $R^2 = 0.0815$ ) during the same sampling period. The positive phosphorous-potassium intercept, however, showed that phosphorous was more limiting than potassium. Overall, a pronounced positive correlation was found between Total Kjeldahl +  $\text{NO}_3^-$  - Nitrogen and Potassium contents in water sampled from the water hyacinth zone, giving a regression line of  $y = 0.6484x + 18.309$  with  $R^2 = 0.4801$ . This demonstrated that nitrogen was more limiting than potassium. Combining the two results suggested that the limiting element was either nitrogen or phosphorous. However, when the linear regression-correlation approach among the three nutrients (N, P, K) was employed, the best correlation was found between Hydrolysable +  $\text{PO}_4^{3-}$  - Phosphorous and Total Kjeldahl +  $\text{NO}_3^-$  - Nitrogen ( $y = 6.1118x + 8.424$ ,  $R^2 = 0.5244$ ). This final positive correlation and the corresponding regression equation both suggest that with respect to Nitrogen and Potassium, Phosphorous was the most limiting element, i.e., it gave a negative intercept. It got exhausted first and was responsible for the proliferation of the water hyacinth in the aquatic environment studied. Any future eradication and control of water hyacinth in the eutrophic Nairobi Dam will have to deal with phosphorous nutrient.

Key words: Limiting Element, Eutrophication, Nairobi Dam

## INTRODUCTION

Eutrophication is the enrichment of a water body (usually of still or slow-flowing fresh water) with plant nutrients (e.g., by the input of organic material or by surface run-off containing nitrates and phosphates). Eutrophication may happen naturally but it is often a form of pollution. It leads to an increase in the growth of aquatic plants and often to algal BLOOMS, which may smother higher plants; reduce light intensity; produce toxins which kill fish and through the aerobic decomposition of organic matter, deoxygenate the water and thereby causing the death of many aquatic animals and higher plants. Eventually, the accumulation of organic matter may raise the bed of a lake until it becomes marsh, then dry land [1]. The history of Eutrophication studies and trophic state classification are well discussed in the literature [2-11].

Phosphorous levels in the sediments are of considerable importance from the standpoint of Lake Eutrophication [12]. Much of the phosphorous is present in bound form and probably not available. Holdren *et al.* [13] presented data for inorganic phosphorous concentrations of the interstitial water of Lake Mendota (U.S.A.) sediments and for cores taken at different times of the year. Although there was some variation throughout the year, at the deeper location, this variation was not great. The average value for interstitial (soluble) phosphorous calculated from their data, 3.13  $\mu\text{g/ml}$ , is considerably higher at all times than the lake water concentration, showing that the sediments are a source of soluble phosphorous. Phytoplankton and other phosphorous-rich particles settle out of the water column into the surficial sediments and undergo decomposition processes, which lead to the release of soluble phosphorous. This soluble phosphorous can then move back into the overlying water by molecular diffusion or advection (Brock, 1985). Although

some phosphorous is adsorbed by Lake sediments [14, 15] a significant fraction of adsorbed phosphorous can be readily desorbed [12].

Phosphorous is present in lakes only in the form  $\text{PO}_4^{3-}$ , so that the complications regarding oxidation and reduction with Nitrogen do not arise. However, phosphorous is present in a number of different chemical forms such as orthophosphate, organic phosphates (including those present in organisms), metaphosphate, phosphorous adsorbed to mineral particles and calcium phosphate [12].

Nitrogen is one of the key nutrients in lake ecosystems. It is available to organisms in several forms, such as ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), and nitrite ( $\text{NO}_2^-$ ). Although all of these forms of Nitrogen are available to various organisms, ammonium and nitrate are the most important for phytoplankton and bacteria [12].

There are several definitions of 'limiting nutrient or element'. However, whichever definition is adopted, this would refer to the relatively most critical nutrient or element in whose absence the growth of a particular aquatic plant would be hindered or terminated altogether. In the current case study involving Nairobi Dam, Kenya, it was important to determine the limiting nutrient/element in order to solve the prevailing environmental problem using available knowledge and technology.

By plotting phosphorous versus nitrogen concentrations during various seasons, a straight-line relationship can usually be established. It is assumed that the limiting nutrient will be exhausted first, and will show as a negative intercept of the line on the axis of the limiting nutrient. The one which is not limiting will remain in solution, yielding a positive intercept of the line of best-fit [5]. Alternatively, the stoichiometric limiting nutrient uses the principles of conservation of mass and the stoichiometric composition of the algae biomass if that one nutrient is totally depleted. In order to calculate the stoichiometric limiting nutrient, one divides the concentration of each available nutrient in the water by the stoichiometric requirement of the algae (or other aquatic plants) for that nutrient, and states that the nutrient generating the lowest ratio is the "limiting nutrient" [16].

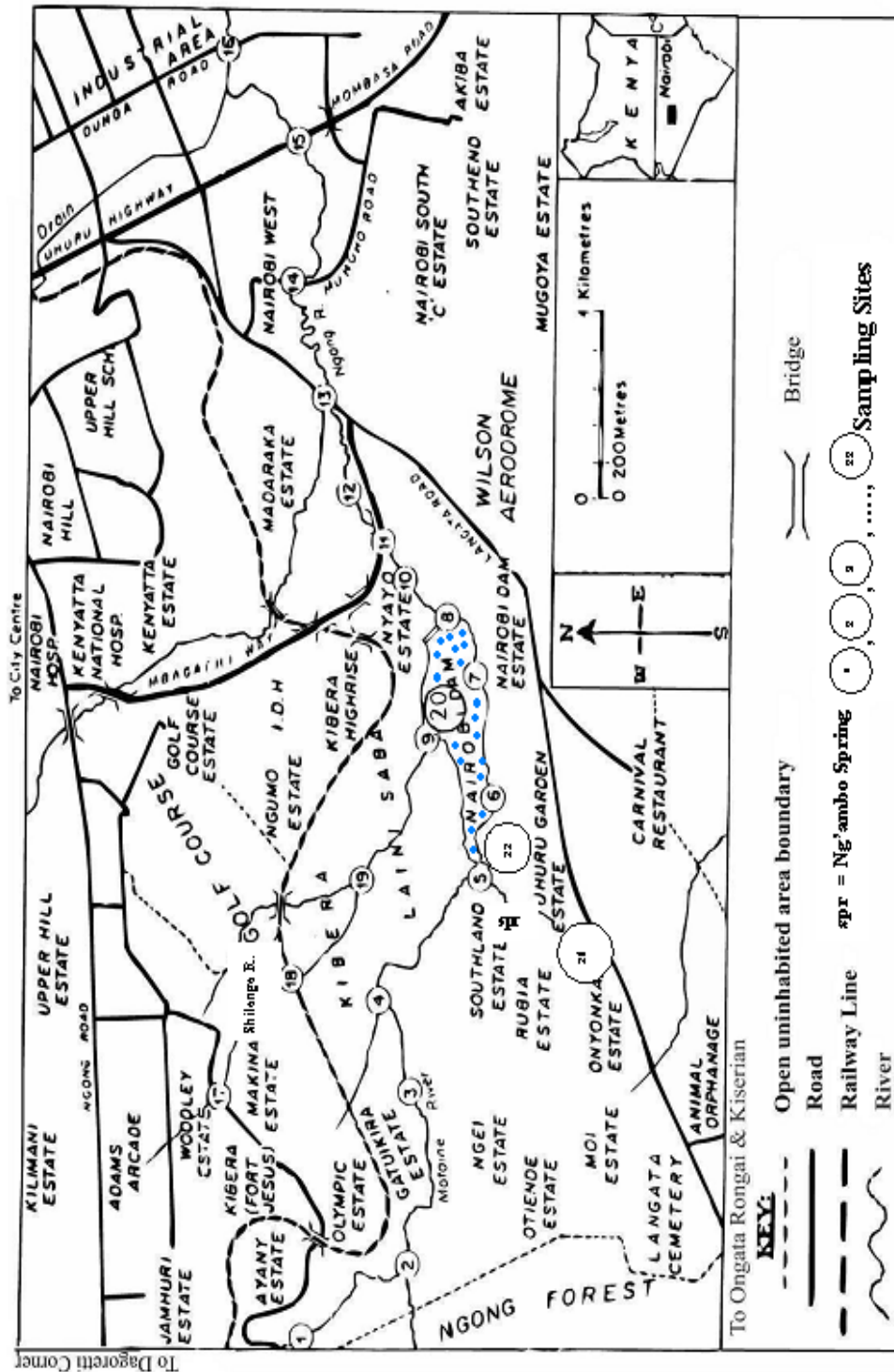
Phosphorous is a nutrient required by all organisms for the basic processes of life. Phosphorous is a natural element found in rocks, soils and organic material and it clings tightly to

soil particles and is used by plants, so its concentration in clean waters is generally very low. However, phosphorous is used extensively in fertilizer and other chemicals, so it can be found in higher concentrations in areas of human activity. Many seemingly harmless activities put together can cause phosphorous overloads [17].

Some decades ago, Nairobi Dam, Kenya, used to be very attractive scenery for recreation, as well as to offer certain services, such as domestic use and Church Baptism by immersion. As a result, tourists and local visitors would flock there. The water was then clear and plant growth minimal. In the closing years of the 20<sup>th</sup> Century, the dam was infested with aquatic weeds, especially the water hyacinth, leading to its imminent partial "death", and the former recreational activities were no more. This was a probable consequence of Eutrophication. The current apparent Eutrophication in Nairobi Dam has been postulated to be mainly due to the abundance of phosphorous as a result of use and disposal of soaps, detergents and related surfactants, in domestic sewage effluents. This element, which is most essential for the growth of the (fresh-aquatic) water-hyacinth in the shallow dam, was therefore expected to be the limiting element in the growth and proliferation of the water hyacinth in the dam and its environs [18]. Therefore, the current research work was aimed at establishing the limiting aspect of phosphorous in Nairobi Dam.

## EXPERIMENTAL

Twenty sampling points within Nairobi Dam and its immediate environment and tributaries were considered for this study (Figure 1). The area of the dam is approximately 0.274  $\text{Km}^2$ . The water samples collected and analyzed were from Nairobi Dam and from its two main tributaries, Motoine and Ngong Rivers. Sampling was mainly done near the bridges, shores or where the dam and the rivers were easily accessible. Water samples were drawn in duplicate using cleaned High Density Poly-Ethylene (HDPE) plastic containers of 1L and 2L capacities, at the surface of various points of the dam and its two tributaries almost simultaneously. This was done by three well coordinated teams to avoid time variation effects. For every pair of samples, one was acidified by addition of 2ml of conc.  $\text{H}_2\text{SO}_4$  (96-98% m/m) per litre of sample and stored at room temperature until the time of analysis. The untreated samples were stored in the fridge at 4° C until the time of analysis. The sampling covered different seasons experienced in the region, i.e., from 2<sup>nd</sup> October 2004 to 22<sup>nd</sup> April 2006.



**Figure 1.** Map of Nairobi Dam, its major tributaries and environs, showing the sampling points

Standard methods were used for the determination of phosphorous [19-21]. The acidified water samples were filtered through No. 40 or 540 filter papers. 40 ml of the water filtrate had its pH adjusted to 3-10, using 2 M sulphuric acid or sodium hydroxide. To this was added 1 ml of ascorbic acid solution (10 % (m/v)), followed by 2 ml of acid molybdate solution (13 g of ammonium heptamolybdate tetrahydrate  $\{(NH_4)_6Mo_7O_{24} \cdot 4H_2O\}$ ). The resulting solution was added to 0.35 g antimony potassium tartrate hemihydrate  $\{K(SbO)C_4H_4O_6 \cdot \frac{1}{2} H_2O\}$  in a clean glass container. To this final solution was added 200 ml of water followed by 300 ml of 9 M sulphuric acid with continuous stirring. This was diluted to the 50 ml mark with distilled water, mixed well and left to stand for at 30 minutes and diluted if necessary for a specified analysis. For calibration, 0.0; 1.0; 3.0; 5.0; 8.0; 10.0 and 15.0 ml of the orthophosphate standard solution (2 mg P/L) were transferred by means of pipette to a series of 50 ml volumetric flasks, diluted to about 40 ml with distilled water and the same reagents used in the colour development for the samples added before diluting to 50 ml with distilled water and treated as for the samples. The absorbance for the standards and sample solutions were read at 880 nm with CADAS 100 UV / Visible Spectrophotometer. A calibration graph of absorbance against the phosphorous content, in mg/l, of the calibration solutions was plotted and linear correlation coefficient ascertained to be  $\geq 0.99$  and sample phosphorous contents calculated. Spiked water was treated in the same way for Quality Control checks.

***Determination of Total Kjeldahl (Proteinaceous and Ammoniacal) Nitrogen – (TKN):***

***Automated Distillation & Titration***

For the determination of Total Kjeldahl Nitrogen (TKN), 30 ml of liquid (water, liquid blank and recovery) samples were weighed into clean dry digestion tubes. 0.8 g of  $CuSO_4 \cdot 5H_2O$  and 7 g of  $K_2SO_4$  were added to each of the digestion tubes. 10 ml of 96% concentrated Sulphuric acid was added from a dispenser and mixed carefully by swirling the tube by hand. The rack with digestion tubes containing the samples was placed besides the automated digester and fitted with the exhaust manifold on top. The vacuum source scrubber was turned on to maximum air flow rate. The tubes and exhaust manifold were placed in the pre-heated digester at  $420^\circ C$  and the heat shields hooked on the stand. The tube contents were digested for 3-5

minutes with maximum air flow rate through the manifold. The flow was then adjusted until the fumes were just contained. The digestion was continued until all samples were clear with a blue green solution. This process took an average of 30 minutes, depending on sample type. The stand with the tubes and exhaust manifold were removed and the entire assembly cooled sufficiently at room temperature, but avoiding solidification. However, if formed, any solid was dissolved by placing the digestion tube in the pre-heated digester for a short time.

The Automated Distillation / Titration – 2300 Kjeltex Analyzer Unit, Foss Tecator (Computerized) was started up (according to the instrument's operating manual). Boric acid solution (1% (m/v) containing 0.0007% methyl red indicator, 0.001% bromocresol green indicator, 1.7% methanol (m/v) and 0.0005 M NaOH) was used as receiver solution. The suitable Kjeldahl programme was selected for reading the nitrogen content in %, m/m. One or two blanks were run, their display noted and their value recorded. The prepared digestion tube was placed in position and the safety door closed. When the cycle was over, the results were noted and the safety door opened to remove the digestion tube ready to insert the next sample digestion tube and the cycle repeated. These included the liquid and solid spikes and in-House Reference Materials (HRM) [22, 23].

**Calculation of results:**

$$\text{Total Kjeldahl Nitrogen (TKN), \% , m/m} = \frac{1.401 \times (V_2 - V_1) \times N}{B}$$

B

Where  $V_2$  = Volume of hydrochloric acid required for the sample;

$V_1$  = Volume of standard hydrochloric acid required for the blank;

N = Normality of hydrochloric acid used in titration;

B = Mass in grams of the sample taken for determination.

***Determination of Nitrate - Nitrogen***

50 ml of the calibration standard solutions and acidified water samples, including their respective blanks and spiked Quality Control sample solutions were transferred into 100 ml plastic beakers. 2 ml of sodium salicylate solution (0.5% (m/v)) was added and evaporated to near dryness in the air oven at  $105 \pm 2^\circ C$ . The residue was cooled at room temperature. 2 ml of concentrated Sulphuric acid was added and the



solution allowed to stand for about 10 minutes. 15 ml of distilled water was added followed by 15 ml of mixed solution containing sodium hydroxide (400 g/L) and potassium sodium tartrate (16 g/L). This was cooled to room temperature and transferred to 100 ml volumetric flask and made to the mark with distilled water. These were stirred and mixed well. The absorbance of the calibration standard (0.0, 1.0, 3.0, 6.0, 9.0 and 12.0 mg/l) and sample solutions, their respective blanks and recovery spikes were measured, using a calibrated CADAS 100 UV / Visible Spectrophotometer at 420 nm after taking the zero reading using a blank test solution and operated as per manufacturer's instructions. A calibration graph of absorbance against the concentration was plotted and its linear correlation coefficient, i.e.  $r$  ascertained to range from 0.99 to 1.00. Using the linear regression equation, the sample nitrate was calculated. This value was multiplied by the stoichiometric conversion factor of 0.226 to obtain the corresponding  $\text{NO}_3^-$ -N concentration [24].

The total amount of nitrogen was estimated by the following formula:

$$\text{'Total' Nitrogen content} = \text{Total Kjeldahl Nitrogen (TKN)} + \text{Nitrate - Nitrogen}$$

#### *Determination of Potassium in Water from Nairobi Dam Basin*

This was done using Corning 400 Flame Photometer. Calibration was done using 0, 1, 2, 4, 6, 8 and 10 mg/l potassium standards. The filtered water samples were aspirated directly into the flame and diluted if necessary, using distilled water. Their emission intensities were read using a potassium filter at 766.5 nm and their potassium concentrations calculated from the calibration graph.

#### RESULTS AND DISCUSSIONS

Poor negative correlation was found between (Hydrolysable +  $\text{PO}_4^{3-}$ ) - Phosphorous and ( $\text{NO}_3^-$ ) - Nitrogen, giving a regression line of  $y = -0.2176x + 2.1471$ ,  $R^2 = 0.1876$  (figure 2) on average in water sampled during the entire period between 2<sup>nd</sup> October 2004 and 22<sup>nd</sup> April 2006. On the other hand, there was also poor positive correlation between (Hydrolysable +  $\text{PO}_4^{3-}$ ) - Phosphorous and Potassium, with a regression line of  $y = 2.142x + 32.964$  with  $R^2 = 0.0815$  during the same sampling period (figure 3). The positive potassium-intercept however shows that phosphorous was more limiting than potassium.

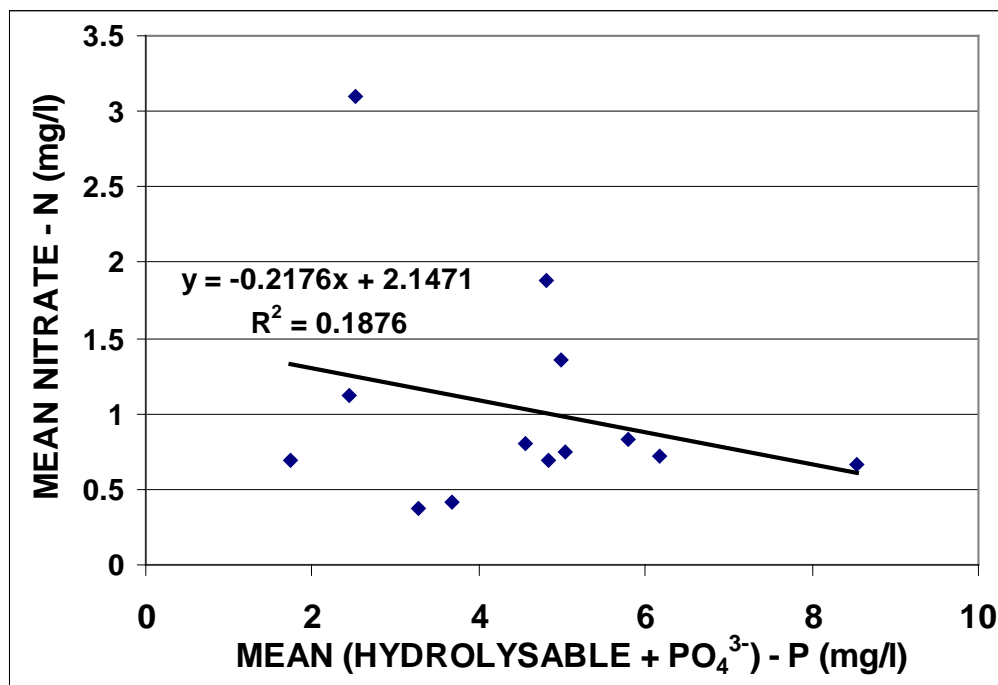
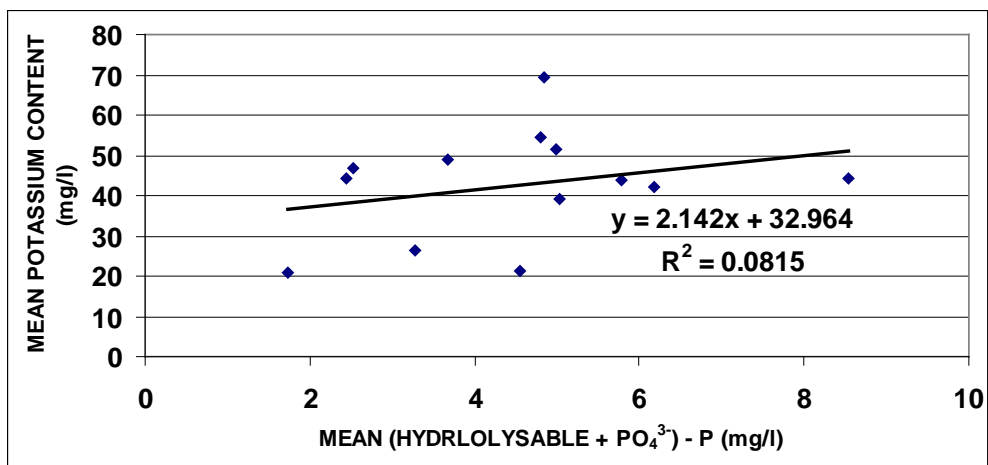


Figure 2: Mean Nitrate – Nitrogen Concentration vs. Mean 'Total' Phosphorous Concentration in Water from Nairobi Dam Basin.\*

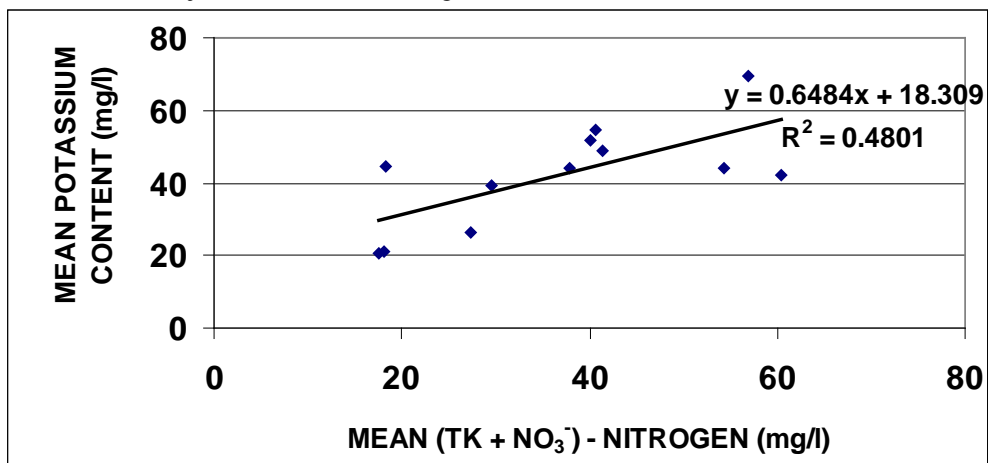


**Figure 3: Overall Mean Concentration of Potassium vs. Mean Concentration of 'Total' Phosphorous in Water from Hyacinth Zone of Nairobi Dam Basin.**

Results of figure 3 refers to Nairobi Dam, its two tributary inlets and one tributary outlet (figure 1).

Potassium contents in water sampled from the water hyacinth zone. This gave the following line of  $y = 0.6484x + 18.309$  with  $R^2=0.4801$ (figure.4).

However, a better positive correlation was found between (Total Kjeldahl + NO<sub>3</sub><sup>-</sup>) - Nitrogen and



**Figure 4: Overall Mean Concentration of Potassium vs. Mean Concentration of 'Total' Nitrogen in Water from Hyacinth Zone of Nairobi Dam Basin.**

Results of figure 4 refer to sampling points 5 – 14, 20 and 22

This regression equation shows that nitrogen was more limiting than potassium. At this juncture, the limiting element was either nitrogen or phosphorous. Furthermore, using the linear regression-correlation approach among the three nutrients (N, P, K), the best correlation was found between Phosphorous (Hydrolysable + PO<sub>4</sub><sup>3-</sup>) and Nitrogen (Total Kjeldahl + NO<sub>3</sub><sup>-</sup>) - (y

$= 6.1118x + 8.424$ ,  $R^2 = 0.5244$ ), as shown in Figure 5. This final positive correlation and the corresponding regression equation both suggest that with respect to Nitrogen and Potassium, Phosphorous was the most limiting element, i.e., it had negative intercept. It got exhausted first and was responsible for the proliferation of the water hyacinth in the aquatic environment studied. Any future eradication and control of this weed will have to deal with this nutrient element.

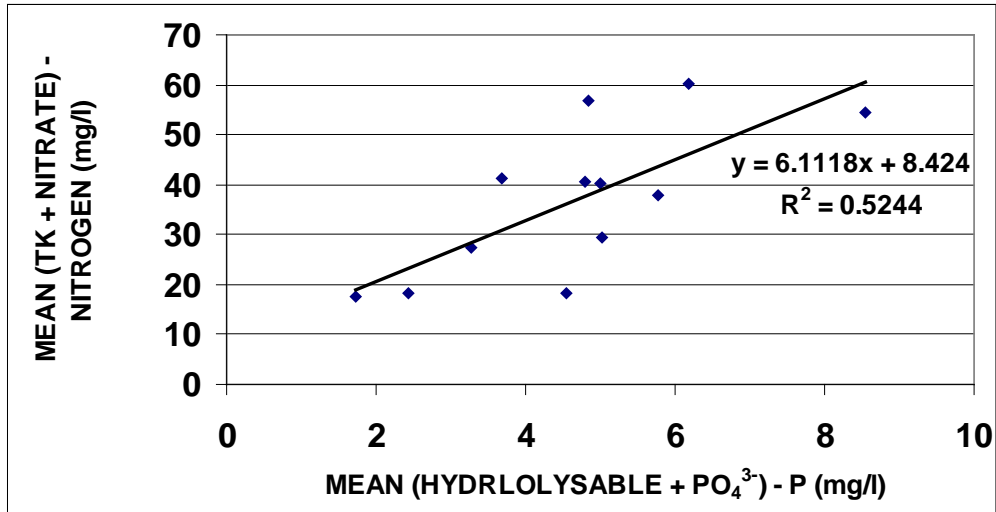


Figure 5: Overall Mean Concentration of 'Total' Nitrogen vs. Mean Concentration of 'Total' Phosphorous in Water from Hyacinth Zone of Nairobi Dam Basin.

## CONCLUSIONS

The current research work on Nairobi Dam, Kenya has revealed that there was poor negative correlation ( $R^2 = 0.1876$ ) between Phosphorous (Hydrolysable +  $PO_4^{3-}$ ) and nitrogen ( $NO_3^-$ ) in water during the entire sampling period. Among the three major nutrients (Nitrogen, Phosphorous and Potassium) for plant growth, the best correlation was found between Phosphorous (Hydrolysable +  $PO_4^{3-}$ ) and Nitrogen (Total Kjeldahl +  $NO_3^-$ ), with  $R^2 = 0.5244$ . In addition, among the three elements, phosphorous was found to be the most limiting nutrient element, i.e., gave negative intercept, relative to either total nitrogen or potassium. The implication here is that it got exhausted first and was responsible for the proliferation of the water hyacinth in the aquatic environment studied. Any future eradication and control of this weed will have to deal with this nutrient.

The limiting nutrient, Phosphorous must have originated from anthropogenic activities. These are mainly the untreated (raw) sewage from the surrounding informal, low-income settlements and use of phosphorous-containing soaps and detergents. Based on the above results, it is clear that with reference to nitrogen, it is the total Kjeldahl + Nitrate which is important when it comes to consideration of correlation with other nutrients and eutrophication aspects. This was particularly exemplified in the current case study involving Nairobi Dam, Kenya.

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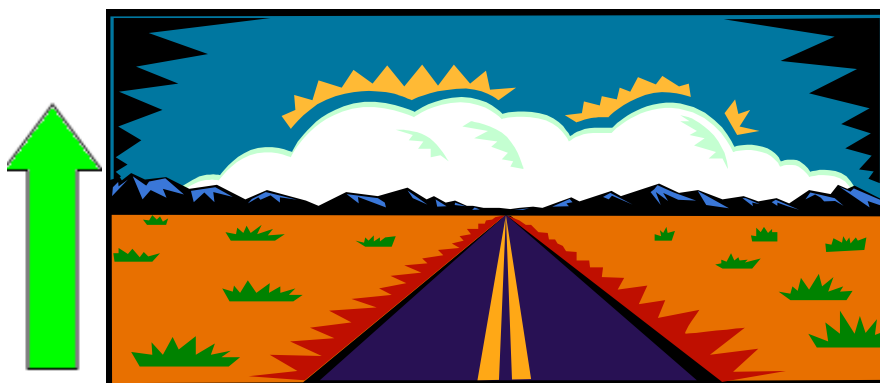
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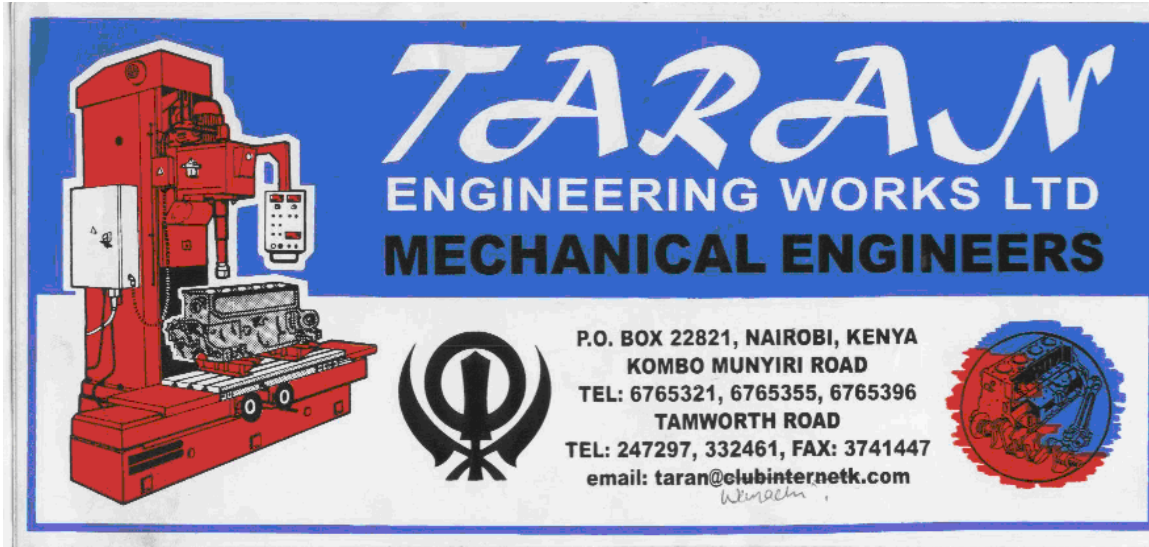
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For further details, visit the conference website at <http://www.esalama.org>

Or

<http://www.esalama.org>



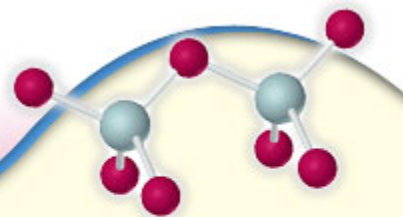
Sohag University



AAPAC

**The 11<sup>th</sup> International Chemistry Conference and Exhibition in Africa  
(11 ICCA)**

**The Role of Chemistry in Development of Africa**



**Egypt, Luxor**

**20<sup>th</sup>-23<sup>th</sup> November 2010**

-Complete registration form (one copy per participant) should be received by the organizing committee not later than **1/8/2010**:

**Registration Form**

<b>Title</b>	<input checked="" type="checkbox"/> Prof. <input type="checkbox"/> Dr. <input type="checkbox"/> Mr. <input type="checkbox"/> Ms. <input type="checkbox"/> Miss
<b>Family Name</b>	
<b>Given Name(s)</b>	
<b>Sex</b>	<input checked="" type="checkbox"/> Male <input type="checkbox"/> Female
<b>Institution/Company</b>	Department of Chemistry, University of Nairobi, Kenya
<b>Mailing address</b>	Chiromo Campus, P.O. Box 30197, 00100
<b>City</b>	Nairobi
<b>Zip Code</b>	00100
<b>Country</b>	KENYA
<b>Phone</b>	254 20 4440164 or 254 722822196
<b>Fax</b>	254 20 4440164
<b>E-mail</b>	<a href="mailto:genkamau@hotmail.com">genkamau@hotmail.com</a> or <a href="mailto:gnkamau@uonbi.ac.ke">gnkamau@uonbi.ac.ke</a>
<b>Field of Presentation*</b>	Chemical Education
<b>Type of Presentation</b>	<input checked="" type="checkbox"/> Oral presentation <input type="checkbox"/> Poster presentation <input type="checkbox"/> Accompanying Person

\* Field of talk or presentation is, e.g., Physical, Inorganic, Organic, Analytical, Biochemistry...

**Registration Fees\***

	Before 1/8/2010	After 1/8/2010
<b>For Egyptian participants** (L. E.)</b>		
<input type="checkbox"/> Registration & accommodation*** fees	2500	2600
<input type="checkbox"/> Accompanying person fees.	1000	1100

<b>For non-Egyptian participants* (€)</b>		
□ Registration & accommodation*** fees for non-African applicant.	<b>600</b>	<b>650</b>
□ Registration & accommodation*** fees for African applicant.	<b>350</b>	<b>400</b>
□ Registration & accommodation*** fees for student/younger chemist****	<b>350</b>	<b>400</b>
□ Accompanying person fees.	<b>500</b>	<b>550</b>
<b>For Exhibition</b>	<b>L.E. 500 per m2</b>	

\* The fees do not include the transportation or return fly tickets fees to Luxor and Egypt.

\*\* 50% discount for members of Egyptian Universities and Research Centers.

\*\*\* Accommodation will be in five stars hotel (double room). Single occupancy is available at extra cost.

\*\*\*\* Young chemist who is a student or did not get PhD.

Registration is only confirmed after receiving the conference fees.

The fees cover the participation in the scientific programs, the conference materials, a half board accommodation for 4 nights in 5 stars hotel (double room) and coffee breaks.

The registration fees should be paid in one of the following ways:

**i) By bank transfer (for outside Egypt, for non-Egyptian):**

Bank Name: Arab African International Bank (Cairo – Egypt)

Swift Bank Code: ARAIEGCXXXX

Account Number: 6003364021.

Beneficiary's Bank Name: Central Bank of Egypt (54 EL GAMOHRIA ST., Cairo-Egypt)

Swift Bank Code: CBEGEGCXXXX

Beneficiary Account Number for \$: 4082176602,

for € 4082190264

Beneficiary Cust Name: Sohag University - Private Boxes

Please write **your name** and "**11 ICCA**" on your bank transfer

**ii) By bank transfer (for egyptian):**

يرصملا ءتين جلاب 27808 / 501 / 650 :باسحلا مقر - جاهوسب ءعماجلا عرف - ءراهقلا كنب  
ايقيرفأ ءيمنت رمتؤم هولعلا ءيلك تارمتؤم: ءباتك ءاجرلا (11ICCA)

**iii) By bank draft or check:**

*For the benefit of:* Chemistry Department, Faculty of Science, Sohag University, Sohag-82534, Egypt.

Please write **your name** and "**11 ICCA**" on your bank draft.

If payment is being made by an institution, please make sure that the **participant's name** is indicated.

**Please send a copy of your bank transfer or draft to**

**E-mail: [conf11icca@sohag-univ.edu.eg](mailto:conf11icca@sohag-univ.edu.eg)**

**[africa11icca@sohag-univ.edu.eg](mailto:africa11icca@sohag-univ.edu.eg)**

**[africaconf2010@yahoo.com](mailto:africaconf2010@yahoo.com)**

**[conf11icca@yahoo.com](mailto:conf11icca@yahoo.com)**

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or **Fax: +20934601159**

## PAN AFRICA CHEMISTRY NETWORK

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Web: [www.panafricanchemistrynetwork.com](http://www.panafricanchemistrynetwork.com)

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## GC-MS WORKSHOP

Jomo Kenyatta University of Agriculture & Technology, Kenya  
23<sup>rd</sup> – 27<sup>th</sup> August 2010

### GC-MS: A versatile technique for qualitative and quantitative mixture analysis

Applications are invited from researchers, lecturers and those students pursuing PhD in relevant topics for the above workshop which will cover mainly basic aspects in theoretical and practical aspects of Gas Chromatography, Electron Impact (EI) Mass Spectrometry and applications of GC-MS.

Applications giving detailed description of teaching and current research work, CV and letters of introduction from one referee (in case of students) should reach the PACN Kenya office by **31<sup>st</sup> May, 2010**. Opportunities are limited to 15 positions only. Those who qualify will be informed by **10<sup>th</sup> June 2010**. Limited travel allowances will be provided by PACN Kenya for those who request and are deemed deserving.

The workshop will be facilitated by Dr. Mathias Schäfer and Professor Anthony Gachanjah. Dr. Mathias Schäfer works as a senior scientist at the University of Cologne, Germany where he heads the Mass Spectrometry facility in the Department of Chemistry. His research interests comprise basic aspects of gas-phase chemistry, infrared multiphoton dissociation (IRMPD) spectroscopy and the structure elucidation of natural and synthetic compounds.

Prof. Anthony Gachanja is an Associate Professor in Analytical/Environmental Chemistry at the Jomo Kenyatta University of Agriculture and Technology with research interests in analytical instrumentation, natural pesticides, water research, and air quality. He is actively engaged in analytical equipment validation and maintenance, waste water treatment and also attached to National Environment Management Authority (NEMA) as an expert.

Resource persons:

**Dr. Mathias Schäfer and Prof. Anthony Gachanjah**

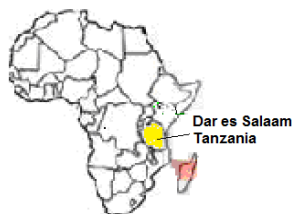
Enquiries and applications may be sent to:

Mrs Ruth Odhiambo  
Administrator, PACN Kenya Office  
Department of Chemistry  
University of Nairobi  
P.O. Box 30197, 00100 Nairobi  
Email: [pacn@uonbi.ac.ke](mailto:pacn@uonbi.ac.ke)



**9<sup>th</sup> East and Southern Africa Environmental Chemistry and Theoretical  
Chemistry in Africa Forum**  
October 3<sup>rd</sup> – 7<sup>th</sup> 2011

East and Southern Africa Environmental Chemistry and Theoretical Chemistry in Africa Forum will be hosting the 6th International conference from 5<sup>th</sup> to 9<sup>th</sup> October, 2009 in Dar es Salaam, Tanzania.



**FIRST ANNOUNCEMENT AND CALL FOR ABSTRACTS**

**THE 9<sup>TH</sup> EAST AND SOUTHERN AFRICA ENVIRONMENTAL CHEMISTRY  
(ESAEC)  
AND  
THE 9<sup>TH</sup> THEORETICAL CHEMISTRY IN AFRICA  
CONFERENCE**

**VENUE:** Dar es Salaam, Tanzania

**DATES:** October 3<sup>rd</sup> – 7<sup>th</sup>, 2011

**THEME**

**SCIENCE AND TECHNOLOGY: SOLUTIONS FOR DEVELOPMENT AFRICA.**

**Objectives**

To bring together scientists, particularly from Africa, for exchange of ideas and research results in the fields of theoretical chemistry, environmental chemistry and related fields.

To foster collaboration among scientists from Africa and also enhance collaboration among scientists at international level.

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**2011 is the year dedicated to Chemistry and its applications.**

How can science community join the Chemists to celebrate the year 2011? For those of us who are chemists let us start planning ahead of time, by possibly coming up with ideas on how to go about it. Individual or group ideas are welcome.

Below see what ACS is planning May/June 2010 ACS Office of International Activities. In collaboration with the American Chemical Society Committee on International Activities, the ACS Office of International Activities publishes ACS International News in electronic form on a bimonthly basis. It is designed to provide information on activities, networks, resources, products and services related to international aspects of chemical sciences, technology, engineering and innovation.

For information on international meetings and conferences, we invite you to visit [www.acs.org/meetings](http://www.acs.org/meetings) to search and view opportunities in the US and internationally. We also encourage you to join the ACS Network, which allows you to stay current in the scientific industry and network with ACS Members and partners from around the world. Visit [www.acs.org/network](http://www.acs.org/network) to register.

Please share this email with your colleagues, and we also hope you will consider contributing content for future editions. Send your ideas and suggestions to [intfacts@acs.org](mailto:intfacts@acs.org).