CLEAN WATER FOR TODAY AND TOMORROW

Water is a finite and life sustaining resource and covers about 70% of the physical environment of the planet Earth. Fresh water resources are scarce and unevenly distributed. The amount of water available globally is about 1.4 billion cubic meters. Of this amount, 97% is saline, and is in seas and oceans and is a habitat to diverse marine ecosystems. Of the remaining 3% fresh water, only less than 1% is found in lakes and rivers, supporting all our developmental activities. About 2% of the available fresh water resources is locked up in glacial ice at the poles. The fresh water in rivers and lakes thus needs to be managed well for our sustenance and that of future generations.

A wide range of human and natural processes affect the biological, chemical, and physical characteristics of water, and thus impact water quality. Contamination by pathogenic organisms, trace metals, human-produced and toxic chemicals, introduction of non-native species, changes in the acidity, temperature, and salinity of water can all harm aquatic ecosystems and make water unsuitable for human use. Numerous human activities like agriculture, industry, mining, disposal of human waste, population growth, urbanization and climate change impact water quality significantly. Agriculture can cause nutrient and pesticide contamination and increase in salinity. Nutrient enrichment has become one of the planet Earth’s most widespread water quality problems. Industrial activity releases about 300-400 million tons of heavy metals, solvents, toxic sludge, and other waste into the world’s waters each year. Mining and drilling create large quantities of waste materials and by-products and large-scale waste-disposal challenges. Widespread lack of adequate disposal of human waste leads to contamination of water worldwide, as water knows no boundaries. Over 80 percent of the sewage in developing countries is discharged untreated in receiving water bodies. Meanwhile, growing populations will potentially magnify these impacts, while climate change will create new water quality challenges.

Water contamination weakens or destroys natural ecosystems that support human health, food production and biodiversity. Studies have estimated that the value of ecosystem services is double the gross national product of the global economy, and the role of freshwater ecosystems in purifying water and assimilating wastes has been valued at US$

400 billion. Most polluted freshwater ends up in the oceans, damaging coastal areas and fisheries. Every year, more people die from the consequences of unsafe water than from all forms of violence. Women, children, and the economically disadvantaged are the most affected by water quality impacts. Over 90 percent of those who die as a result of water-related diseases are children under the age of five. Women are forced to travel long distances to reach safe water. The poor are often forced to live near degraded waterways, and are unable to afford clean water. Livelihoods such as agriculture, fishing, and animal husbandry all rely on water quality and quantity.

Effective solutions to water quality challenges exist and have been implemented in a number of places. It is time for a global focus on protecting and improving the quality of the world's freshwater resources. Among the fundamental solutions to water quality problems are: prevent pollution, treat polluted water and restore ecosystems. Each of this solution will be discussed in our next issue.

Peterson M. Guto

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SORGUM VULGARE AND PENNISETUM TYPHOEDUM AS USEFUL BIOSORBENTS FOR THE REMOVAL OF HEAVY METAL IONS FROM WATER SOLUTION

Manju Chaudhary and Mukesh Kumar

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ABSTRACT

Sorgum Vulgare (oat) husk and Penisetum Typhoedeum (millet) husk have been found useful for the removal of heavy metal ions from water or waste water. Divalent ions of copper, lead and cadmium can be efficiently removed from waste water streams using low cost and widely available biosorbents sorgum vulgare and pennisetum typhoedeum husk. Maximum adsorption of the divalent copper, cadmium and lead at pH 7 and room temperature on a column of 10 inches height and 2 inches diameter are found in the order $Pb^{+2} > Cu^{+2} > Cd^{+2}$ for pennisetum typhoedeum(millet) husk and $Cu^{+2} > Pb^{+2} > Cd^{+2}$ for sorgum vulgare(oat) husk.

Key Words: *Biosorption, millet husk, oat husk, low cost biosorbent.*

1. INTRODUCTION:

Growing industries gave good job opportunities and pace to the economic growth of India and at the same time pose serious threat to the environment. Water being most important part of industries and environment has been affected most. Quality of water in the nearby areas of the industrial growth is facing problem of heavy metal contaminations. Surface water as well as underground water is equally affected. About 20 metals have identified as toxic to human health and out of this half are emitted into the environment in quantities that pose risk to human health.

A number of chemical and physical processes are available for the removal of these toxic ions from the water samples. Of all the available processes which can remove these toxic ions from water have some or the other technical or economical problem. A study of such systems and their difficulties has been studied and reported[1]. Therefore some methods which are environment friendly and low cost are desirable. A study on different types of biosorbents and their probable use has been reported by researchers [2]. Here is a useful method which in recent years has gained a lot of attention ‘the biosorption’.

Biosorption can be defined as a non directed physico-chemical interaction that may occur between metal/radionuclide species and microbial cells [3]. A variety of micro organisms as biosorbents have been identified and reported [4-7] for the removal of heavy metal ions. Some plant wastes like those obtained from agriculture farms have also been reported to be efficient biosorbents [8-15]. Removal of chromium [16-18], iron [16-19], lead [19-21] have also been studied and reported.

In the present paper the biosorption of lead, copper, and cadmium on the two biosorbents that are available in plenty in southern Rajasthan are reported.

2. EXPERIMENTAL

2.1 Preparation of the biosorbent.

The biowaste that is the husk of millet and oat have been procured from the nearby village. The husk was washed thoroughly with water to remove the sand etc. then it was treated with dilute HCl to remove natural colour of the husk and again washed with demineralised water. Thoroughly washed husk was dried in a hot air oven at about 60 ^{o}C for 24 hours. The properly dried husk is now ground to a fine powder and kept in air tight jars and taken as and when required.

A steel column of 20 inches height and 2 inches diameter was taken. The biosorbent was filled into the column till a height of 10 inches only. All the experiments have been carried out using this column only.

2.2 Preparation of solutions.

Standard solutions (1000mg/L) of copper (II), lead(II) and cadmium(II) were prepared in the laboratory by dissolving copper sulphate, lead nitrate and cadmium chloride in doubly distilled water. Stock solutions were kept in covered and labeled bottles. These stock solutions were used after further dilution according to the requirement. The pH of the solutions was adjusted using NaOH and HCl.

2.3 Method

The test solution containing metal ions was allowed to flow through the prepared column of 12 inches height and 2 inches diameter. The flow of test solution was maintained by using burette. The flow rate was mentained 3 ml/min for all the experiments except when effect of variation of the rate of flow was studied.

A clean tumbler properly washed with deionised water was used to collect the percolated water. All the test solutions were examined before and after the treatment using atomic absorption spectrophotometer.

Sorption efficiency (%) of the biosorbent was calculated in terms of metal ion adsorbed per gram of the biomass using following formula.

$$Q = \{[C_0\text{-}C] \times V\}/M$$

$$\text{Sorption efficiency (\%)} = [\ (C_0 - C) \div C_0] \times 100$$

Where Q is the amount of metal ion biosorbed per gram of the biomass and is expressed in mg/g. C_0 and C are the initial and final concentrations(mg/L) of the test solutions, V is the volume of the test solution and M is the mass of biomass (g).

3. RESULTS AND DISCUSSIONS

3.1 Effect of pH on the sorption capacity of the biosorbent

Biosorption of metal ions on to the surface of the biosorbent is greatly influenced by the pH of the solution. At higher pH the biosorbent which naturally contain anionic surface (due to the presence of OH^- and COO^- depending upon the variety of plant species) is further enriched by OH^- ions which lead to enhanced adsorption properties of the biosorbent. It is therefore suggested that if the water sample contain higher amount of these ions (heavy metals) than adsorption should be carried out at higher pH and after the removal process is over the pH of purified water be adjusted accordingly. As expected the sorption of metal ions increase with increase in the pH of the solution. The possible reason may be that at lower pH; H^+ and H_3O^+ ions compete with the metal ions for adsorption on to the surface of biosorbent. At higher pH less number of H^+ ions are there to occupy the adsorbent sites available for the metal cations. The pH of the solution was varied from 2to 7. The pH of the normal water is around 7(in most cases about 8) and therefore pH 7 is chosen to conclude the adsorbent capacities of the biosorbent.

It is clear from the following tables that the extent of adsorption increases with increase in the pH of the solution. Same trend is observed in both the cases. The results are shown in table1 (for millet husk) and table 2(for oat husk).

Table 1. Effect of pH on adsorption capacity of millet husk.

Ph	Pb^{+2}(% removal)	Cd^{+2}(% removal)	Cu^{+2}(% removal)
2	56	19	48
3	55	35	58
4	60	40	60
5	72	52	68
6	75	58	68
7	78	59	72

Table 2. Effect of pH on adsorption capacity of oat husk.

Ph	Pb^{+2}(% removal)	Cd^{+2}(% removal)	Cu^{+2}(% removal)
2	30	18	53
3	33	22	58
4	48	25	63
5	65	25	63
6	68	27	65
7	72	28	80

3.2 Effect of rate of flow of solution through column.

Rate of flow of solution through the biosorbent column effect the net percentage removal of metal ions from the solution. If the solution travels quickly down the column then the metal ions get less time to adhere to the surface of the biosorbent. Therefore the effect of rat**e** of flow on the percentage removal of the ions from the test solutions must be considered and studied. Following figures illustrates that with the increase in the contact time between the adsorbent and the metal ions from test solutions percentage removal of the ions is also increased. The results are shown in table 3(for millet husk) and table 4(for oat husk).

Table 3. Effect of rate of flow of solution on adsorption capacity of millet husk.

Rate of flow of solution through the column(ml/min)	Pb^{+2}(% removal)	Cd^{+2}(% removal)	Cu^{+2}(% removal)
2	78	59	72
4	72	48	68
6	62	34	50
8	50	18	38
10	20	7	3

Table 4. Effect of rate of flow of solution on adsorption capacity of oat husk.

Rate of flow of solution through the column(ml/min)	Pb^{+2}(% removal)	Cd^{+2}(% removal)	Cu^{+2}(% removal)
2	72	28	80
4	65	20	76
6	42	13	58
8	22	5	33
10	8	1	11

3.3 Effect of height of column.

Keeping the diameter of the column fixed and varying the height of the column it is seen that the sorption of ions is greatly influenced. Increase in the height of the column means increase in the number of adsorption sites. Therefore the extent of sorption is to increase with the increase in the height of the column. Height of the column is varied from 8 inches to 14 inches. Results are shown below in table 5(for millet husk) and table 6(for oat husk).

Table 5. Effect of height of column on the percentage removal on millet husk.

Height of column(inches)	Pb^{+2}(% removal)	Cd^{+2}(% removal)	Cu^{+2}(% removal)
8	63	48	65
10	78	59	72
12	81	65	85
14	85	70	89

Table 6. Effect of height of column on the percentage removal on oat husk.

Height of column(inches)	Pb^{+2}(% removal)	Cd^{+2}(% removal)	Cu^{+2}(% removal)
8	66	22	77
10	72	28	80
12	78	30	84
14	83	35	89

The results show that oat husk is better adsorbent for the copper than millet husk.

Preference of Cu^{+2} ions shows that there is some specialty in the cell wall structure of oat husk which attract copper ions more than other ions. This preference might be due to the presence of some copper binding enzymes in the oat husk. In case of lead and cadmium millet husk is preferred more than oat husk. Also the results show that cadmium is least adsorbed ion.

3.4 Effect of initial concentration of the metal ion solutions

Initial concentration of metal ions in the solutions affects the rate of sorption of ions on the sorbent surface. Initially the rate of adsorption increase with increase in initial concentration of the ions in solution. This is due to large number of adsorption sites available for few metal ions in the solution. On further increase in the concentration the rate of adsorption nearly become stable when number of metal ions and number of adsorption sites become equal. Beyond this concentration there is no increase in the rate of adsorption. The initial concentration of metal ions taken for the study is 20 mg/L each. The equilibrium is reached at about 160mg/L and then no further increase in the rate of adsorption is noticed. The results are shown below in table 7 (for millet husk) and table 8 (for oat husk).

Table 7. Effect of initial concentration of solution on adsorption capacity of millet husk.

Initial concentration of metal ions(mg/L)	Pb^{+2} (mg/g)	Cd^{+2}(mg/g)	Cu^{+2}(mg/g)
20	3.12	2.2	2.8
40	4.8	2.8	3.6
80	5.4	3.0	5.2
120	6.8	3.5	6.8
160	7.2	3.6	6.8
200	7.2	3.6	6.9

Table 8. Effect of initial concentration of solution on adsorption capacity of oat husk.

Initial concentration of metal ions(mg/L)	Pb^{+2} (mg/g)	Cd^{+2}(mg/g)	Cu^{+2}(mg/g)
20	2.8	1.1	3.2
40	3.5	1.4	3.5
80	4.2	2.2	4.2
120	4.8	2.8	4.8
160	5.2	2.8	5.2
200	5.4	2.8	5.2

Here again the adsorption rate of cadmium is very slow as compared to the other two caions. Cadmium therefore can be concluded to have least affinity for the adsorption sites on the biosorbents. The reason for this behaviour of cadmium is unknown. But as majority of polluted water samples contain contamination of other two mentioned cations so we can suggest the use of millet husk(penistum typhoideum)and oat husk(sorgum vulgare) for the removal of copper and lead cations.

CONCLUSION

Biosorption capacities of penisetum typhoideum (millet husk) and sorgum vulgare(oat husk) are studied for the bivalent cations of copper, lead and cadmium. It is found that the sorption capacity of millet husk is better than that of oat husk. The three understudy ions showed preference for one adsorbent over the other. The order of adsorption on millet husk has been found like this Pb^{+2}(78%)> Cu^{+2}(72%)> Cd^{+2}(59%). For oat husk the order of adsorption has been Cu^{+2}(80%)>Pb^{+2}(72%)>Cd^{+2}(28%). After studying and analyzing the results it has been concluded that millet and oat husk can be used for the removal of divalent copper, lead and cadmium ions from their aqueous solutions. Widely available and ecofriendly biowaste like husk of millet and oat can serve the purpose of water purifier in rural areas.

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AN INVESTIGATION OF THE TRANSPORT AND DISPERSION OF ATMOSPHERIC POLLUTANTS OVER EAST AFRICA DURING THE OL DOINYO LENGAI VOLCANIC ERUPTION IN JULY 2007 AND MARCH 2008

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ABSTRACT

Explosive volcanic eruptions affect climate by injecting gases and aerosol particles into the troposphere and stratosphere. Only if the eruption cloud is rich in SO_2 will the eruption produce a long-lived aerosol cloud, in response to the sulfate aerosols that form over the next few weeks. The eruption of Ol Doinyo Lengai Tanzania, July 2007 and March 2008, injected pollutants into the atmosphere with potential impacts on the air quality and climate over East Africa. This work simulated the spatial and temporal distribution of the volcanic gases and particulate matter emitted after the eruption. The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, which is a complete system for computing simple air parcel trajectories to complex dispersion and deposition simulations, was used for the analysis. The dispersion of pollutant was calculated by assuming either puff or particle dispersion. The results indicated that the effluents were largely spread and eventually deposited around northern Tanzania and along the Kenya - Tanzania border. A relatively small concentration of pollutants was transported to Lake Victoria within 48 hours.

1.0 INTRODUCTION

Volcanic eruptions are caused by plate motions through the theory [1] of plate tectonics (IJBCP, 2006). Volcanic eruptions affect climate by injecting gases and aerosol particles into the stratosphere. Only if the eruption cloud is rich in SO_2 will the eruption produce a long-lived aerosol cloud, in response to the sulfate aerosols that form over the next few weeks. Otherwise, explosive eruptions that only produce large ash particles, such as the 1980 Mount St Helen's eruption, can produce a large local weather perturbation, but do not have long-lasting climatic effects. Some volcanoes, such as Kiluaea and Etna, produce large quiescent tropospheric emissions of sulfate precursors, but only if there is a dramatic change in these emissions will climate be changed.

Stratospheric aerosol clouds last for several years, reflecting sunlight and cooling the surface. These clouds also absorb both solar (near infrared) and terrestrial radiation, heating the lower stratosphere.

Volcanic aerosols also serve as surfaces for heterogeneous chemical reactions that destroy stratospheric ozone, which lowers ultraviolet absorption and reduces the radiative heating in the lower stratosphere, but the net effect is still heating. As this chemical effect depends on the presence of anthropogenic chlorine, it has only become important in recent decades. Tropical eruptions produce asymmetric stratospheric heating, producing a stronger polar vortex and associated positive mode of the Arctic Oscillation in tropospheric circulation. This pattern is one of enhanced warm advection over Northern Hemisphere (NH) continents in winter, producing winter warming after large tropical eruptions. There is no evidence that volcanic eruptions can produce El Nino events, but El- Nino Southern Oscillation (ENSO) variations must be considered when searching the climatic record for volcanic signals, as they have similar amplitudes and time scales.

Volcanic eruptions and gaseous emissions

Volcanic eruptions typically also emit gases, with H_2O, N_2 and CO_2 being the most abundant gas emitted (Figure 1). Over the lifetime of the Earth, these gases have been the main source of the planet's atmosphere and ocean, after the primitive atmosphere of hydrogen and helium was lost to space. The water has condensed into the oceans, the CO_2 has been changed by plants into O_2 or formed carbonates that sink to the ocean bottom, and some of the C has turned into fossil fuels [2, 3]. Human beings and animals eat the plants, drink the water and breathe the oxygen. It should also be noted that the atmosphere is mainly composed of N_2 (78%) and O_2 (21%), both of which had sources in volcanic emissions. Out of these gases, both H_2O and CO_2 are important greenhouse gases, but their atmospheric concentrations are so large (even for CO_2 at only 372 ppm) that individual eruptions have a negligible effect on their concentrations and do not directly impact the greenhouse effect. Rather the most important climatic effect of explosive volcanic eruptions is through their emission of sulfur species to the stratosphere, mainly in the form of SO_2, but possibly sometimes as H_2S [4]. These sulfur species react with H_2O to form H_2SO_4 on a time scale of weeks, and the resulting H_2SO_4 aerosols produce the dominant radiative effect from volcanic eruptions. The 1982 El Chicho´n eruption injected 7 megatons of SO_2 into the atmosphere, and the 1991 Pinatubo eruption injected 20 megatons.

Ol Doinyo Lengai Vocano

Ol Doinyo Lengai is a unique volcano that is located in the Rift valley bout 120 km NW of Arusha, Tanzania. It is located at an altitude of 2886 meters. It is the only volcano in the world that erupts natrocarbonatite lava, highly fluid lava that usually contains almost no silicon. Natrocarbonatite lava is also much cooler than other lavas, being only about 510^o C compared to temperatures over 1100^o C for basaltic lavas [5, 6, 7].

Natrocarbonatite lava glows orange at night, but is not nearly as bright as silicon-based lavas since it is not as hot. During the day it is not incandescent; most flows look like very fluid black oil, or brown foam, depending on the gas composition. In the past, some visitors to the crater believed they were seeing mud flows. Most newly solidified lava is black and contains crystals that sparkle brightly in the sun (Figure 2).

Since the late 1980's, activity at Ol Doinyo Lengai has been witnessed by many observers. The activity is usually centered in one or more of the small cones that have been formed on the crater floor by previous eruptions of lava (Figure 2). Eruptions have typically taken the form of open lava pools or lakes that may or may not be overflowing, lava flows issuing from holes or cracks inside or near the base of the cones, or lava splashes or fountains from the summit vents of the cones. The activity is not well understood but is believed to be connected with the plumbing of the crater, the level of the lava within the plumbing and the gas content of the lava. Our scientific understanding about the causes of the lava to flow out at any particular time or how the various vents in the crater are interconnected is very limited. Additionally, no one has any idea when the present pattern of frequent small lava flows will give way to explosive activity like that seen in 1966 and to a lesser extent in 1993.

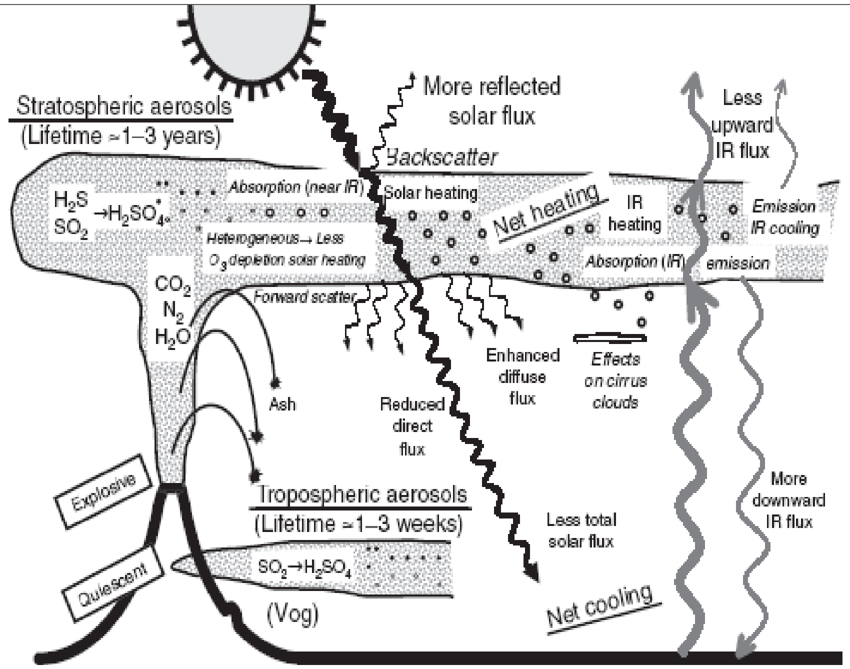


Figure 1 : Schematic diagram of volcanic inputs to the atmosphere and their effects. (Adapted from Plate 1 of Robock (2002), owned by the American Geophysical Union).

Figure 1:

2.0 EXPERIMENTAL

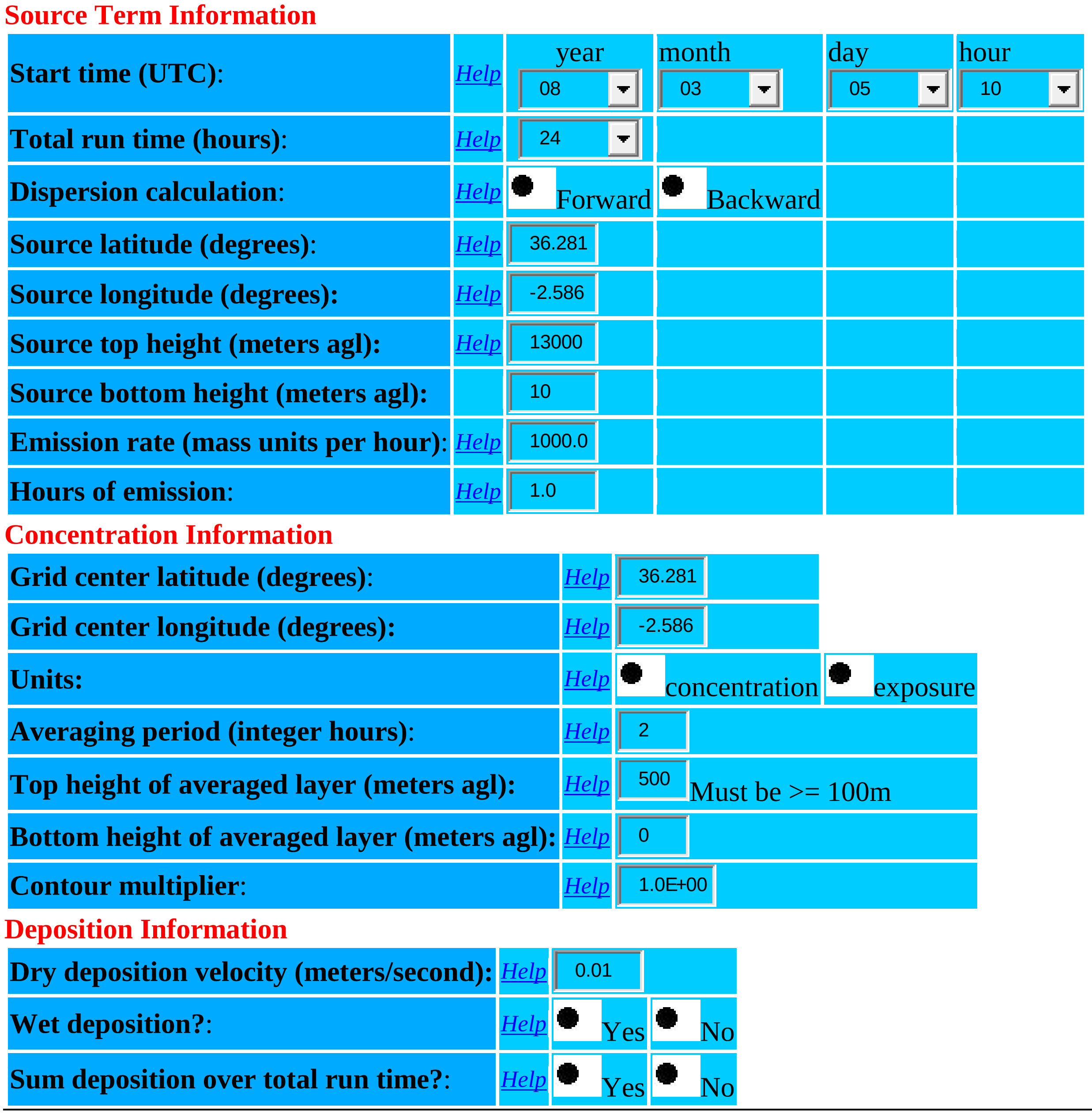
Remotely sensed Sulphate aerosol and temperature data over East Africa was collected for the period January 2007 to February 2008 from the Global Chemical Weather Forecast System (GCWFS) model of Japan. The Ol Doinyo Lengai Mountain erupted two times during July 2007 emitting aerosols into the atmosphere. In March 2008 the volcanic eruption reached a column of about 16km.

The spatial and temporal patterns of the sulphate aerosols were analysed using the GCWFS. A comparison was made of the same period in 2008 and in previous years of 2001-2007.

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, a system for computing simple air parcel trajectories to complex dispersion and deposition simulations, was used for simulating the transport and dispersion of the volcanic ash. The dispersion of the ash was calculated by assuming both puff or particle dispersion [10].

The data in this research work was obtained from GDAS. Simulation experiment was performed by using HYSPLIT model.

Table 1: HYSPLIT model setting for the 5th march 2008 eruption of Ol Doinyo Lengai



Source Term Information

Start time (UTC):	Help	year 08	month 03	day 05	hour 10
Total run time (hours):	Help	24			
Dispersion calculation:	Help	● Forward	● Backward		
Source latitude (degrees):	Help	36.281			
Source longitude (degrees):	Help	-2.586			
Source top height (meters agl):	Help	13000			
Source bottom height (meters agl):		10			
Emission rate (mass units per hour):	Help	1000.0			
Hours of emission:	Help	1.0			

Concentration Information

Grid center latitude (degrees):	Help	36.281	
Grid center longitude (degrees):	Help	-2.586	
Units:	Help	● concentration	● exposure
Averaging period (integer hours):	Help	2	
Top height of averaged layer (meters agl):	Help	500 Must be >= 100m	
Bottom height of averaged layer (meters agl):	Help	0	
Contour multiplier:	Help	1.0E+00	

Deposition Information

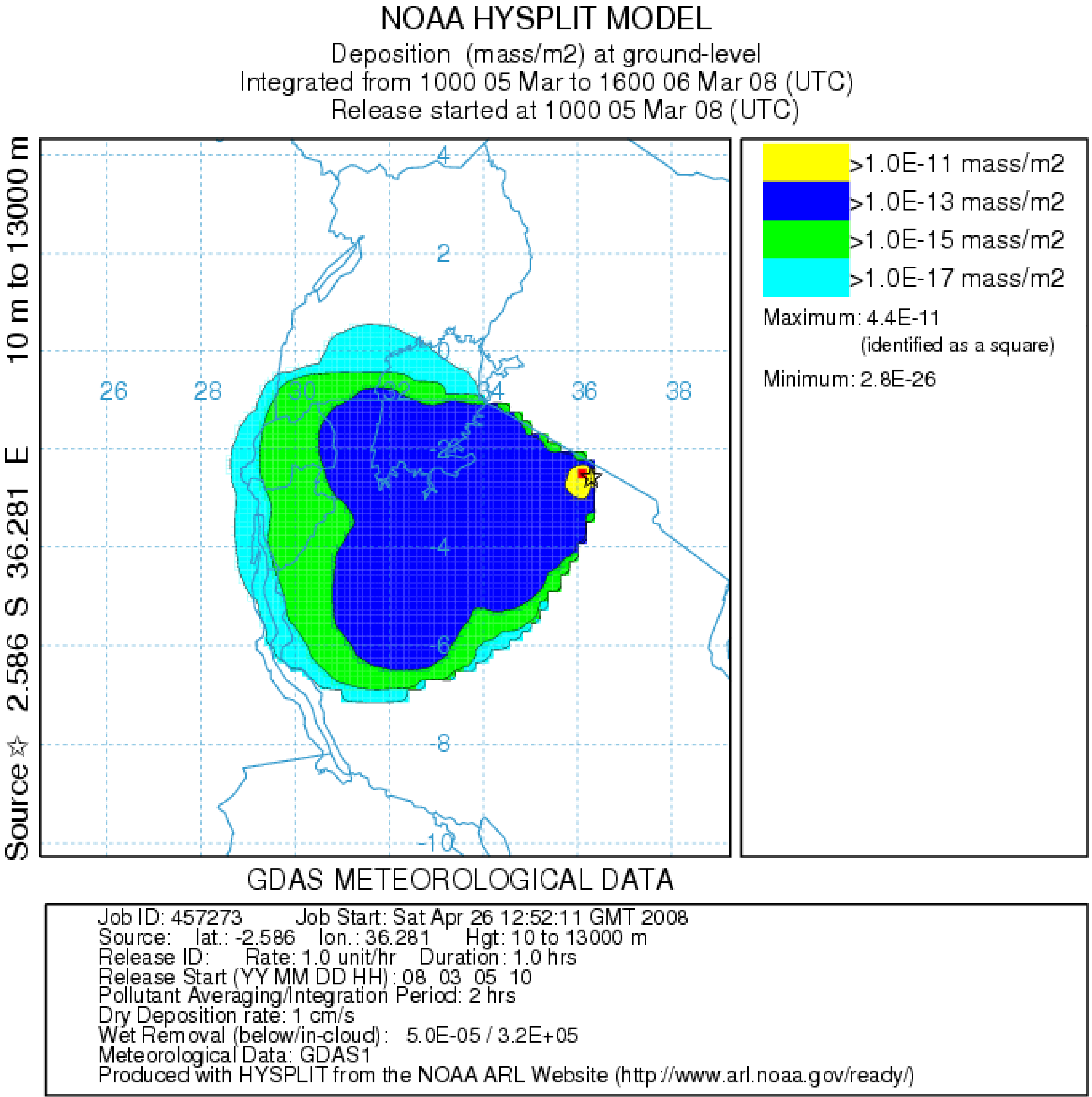
Dry deposition velocity (meters/second):	Help	0.01	
Wet deposition?:	Help	● Yes	● No
Sum deposition over total run time?:	Help	● Yes	● No

Global Data Assimilation System (GDAS) data was used as the meteorological data input into the HYSPLIT model. Forward trajectories were simulated from 10.00 am on 5th March 2008 up to the next 24 hours. The source strength was assumed to be 1000 kt/m3 (Table1). The source top and bottom heights were taken as 13,000 m and 10 m above ground level, respectively. The source top height was taken so because it was reported that the eruption reached about 16 km above sea level (2008). More details of the model setting are shown in Table 1.

The Hysplit model was run using the input data indicated in Table 1. The model output produced both forward and backward trajectories, together dispersion plots. All the outputs were generated from the model in graphical form.

3.0 RESULTS AND DISCUSSION

The lower stratosphere is largely stable, experiencing minor variability. Figure 4 depicted a typical lower stratospheric sulphate aerosol pattern. It shows that East Africa is largely characterised by almost similar concentrations. However, the coastal region experiments have slightly higher concentration of the sulphate aerosols.



Job ID: 457273 Job Start: Sat Apr 26 12:52:11 GMT 2008
Source: lat.: -2.586 lon.: 36.281 Hgt: 10 to 13000 m
Release ID: Rate: 1.0 unit/hr Duration: 1.0 hrs
Release Start (YY MM DD HH): 08 03 05 10
Pollutant Averaging/Integration Period: 2 hrs
Dry Deposition rate: 1 cm/s
Wet Removal (below/in-cloud): 5.0E-05 / 3.2E+05
Meteorological Data: GDAS1
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

Figure 2 : Dispersion plot of emissions on 5th March 2008

The dark shade indicates the highest concentration. It is clear that it was more dispersed towards Tanzania side and Lake Victoria which encroaches Rwanda and Rwanda, with no significant encroachment to the Kenya and Uganda side. It is interesting to note that the highest and lowest concentration shift to the western side, which is attributed to the direction of the wind moving from the East.

The Southern side of the Lake Victoria basin was affected the most (Figure 3). The deposition in the lake may give rise to additional pollutants into the basin. Although the volcanic eruption occurred in the Northern Tanzania, atmospheric distribution of the air mass affected about 5 countries: Tanzania, Uganda, Rwanda, Burundi and Kenya.

Further work should involve the chemical composition of the lake. Geological investigation should have also been done to indicate

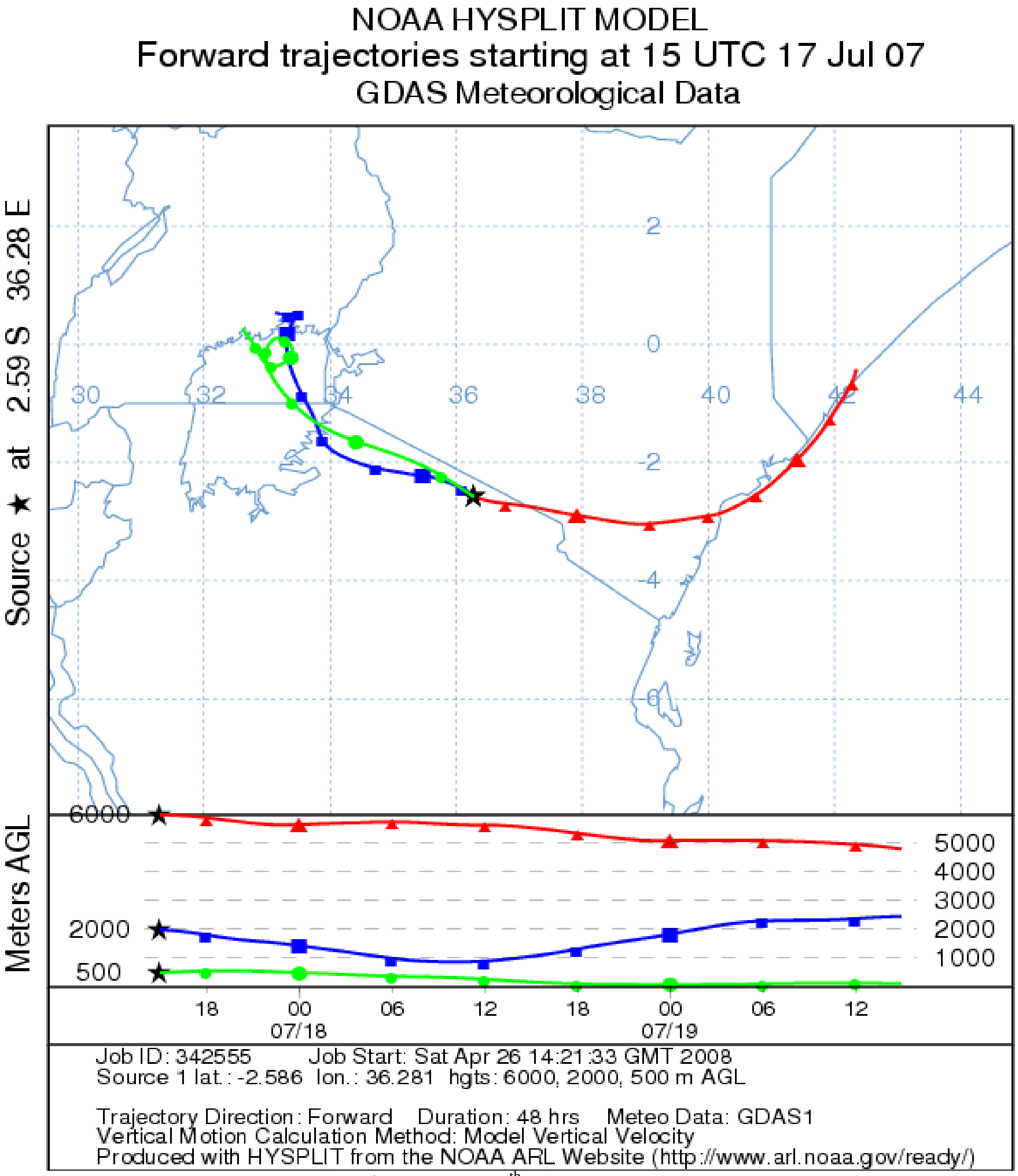


Figure 3 : Trajectory plot of emission on 7th July 2007

Analysis of the Spatial patterns of sulphate aerosols during march 2008 and March 2007 revealed that significantly higher concentrations of aerosol load was present in the upper troposphere/lower stratosphere (Figures 3 and 4). It is important to note that this pattern may significantly affect air quality and even climate at least in the short term. Further studies will bring more light about the matter.

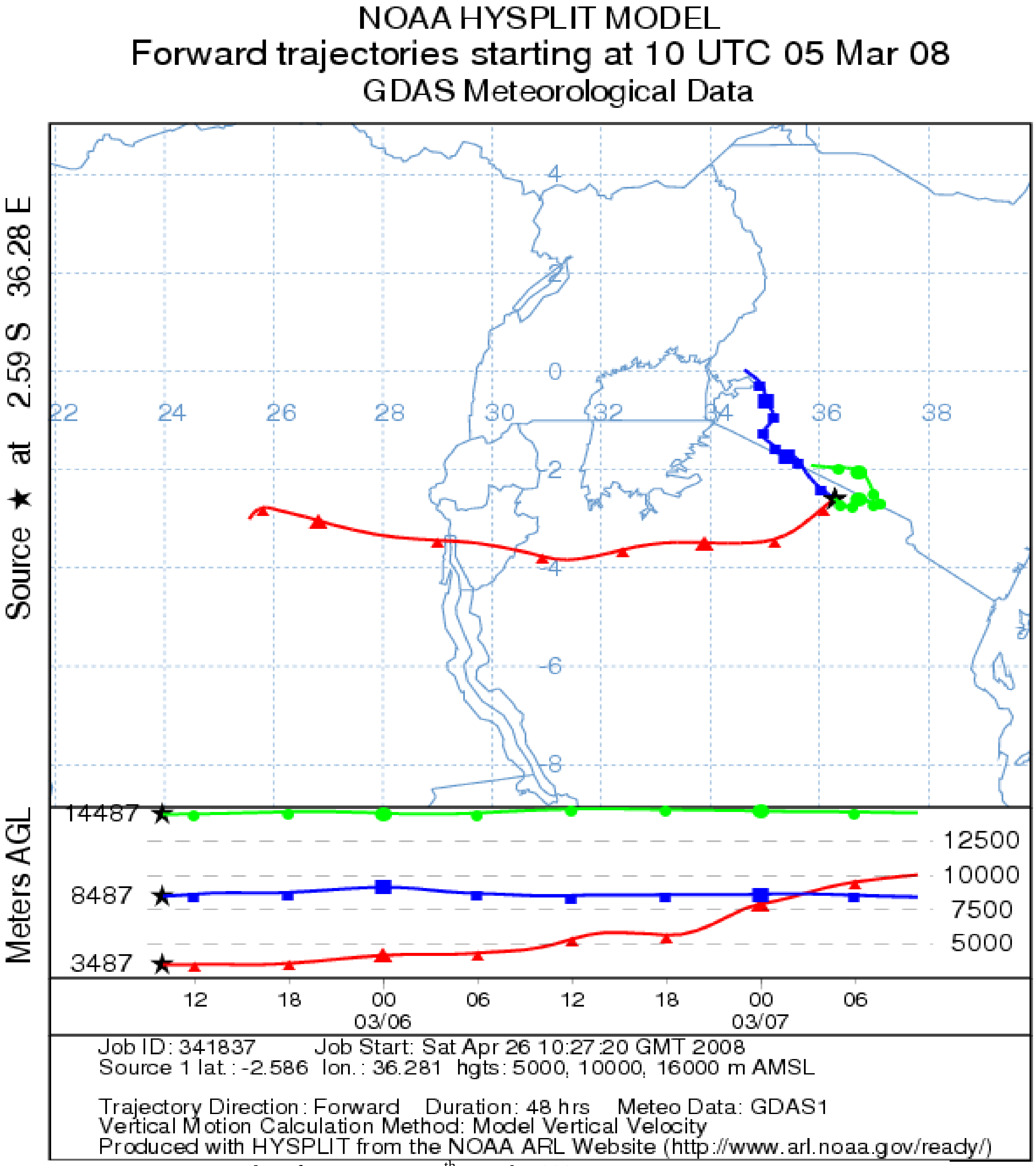


Figure 4 : Trajectory plot of emissions on 5th March 2008

The results indicated that the effluents were largely spread and eventually deposited around northern Tanzania and along the Kenya-Tanzania border for the case of July 2007. Figure 5 illustrates that in 6 hours volcanic ash was transported to Lake Victoria within 48 hours. At upper air level volcanic ash was transported to Kenyan coastal region.

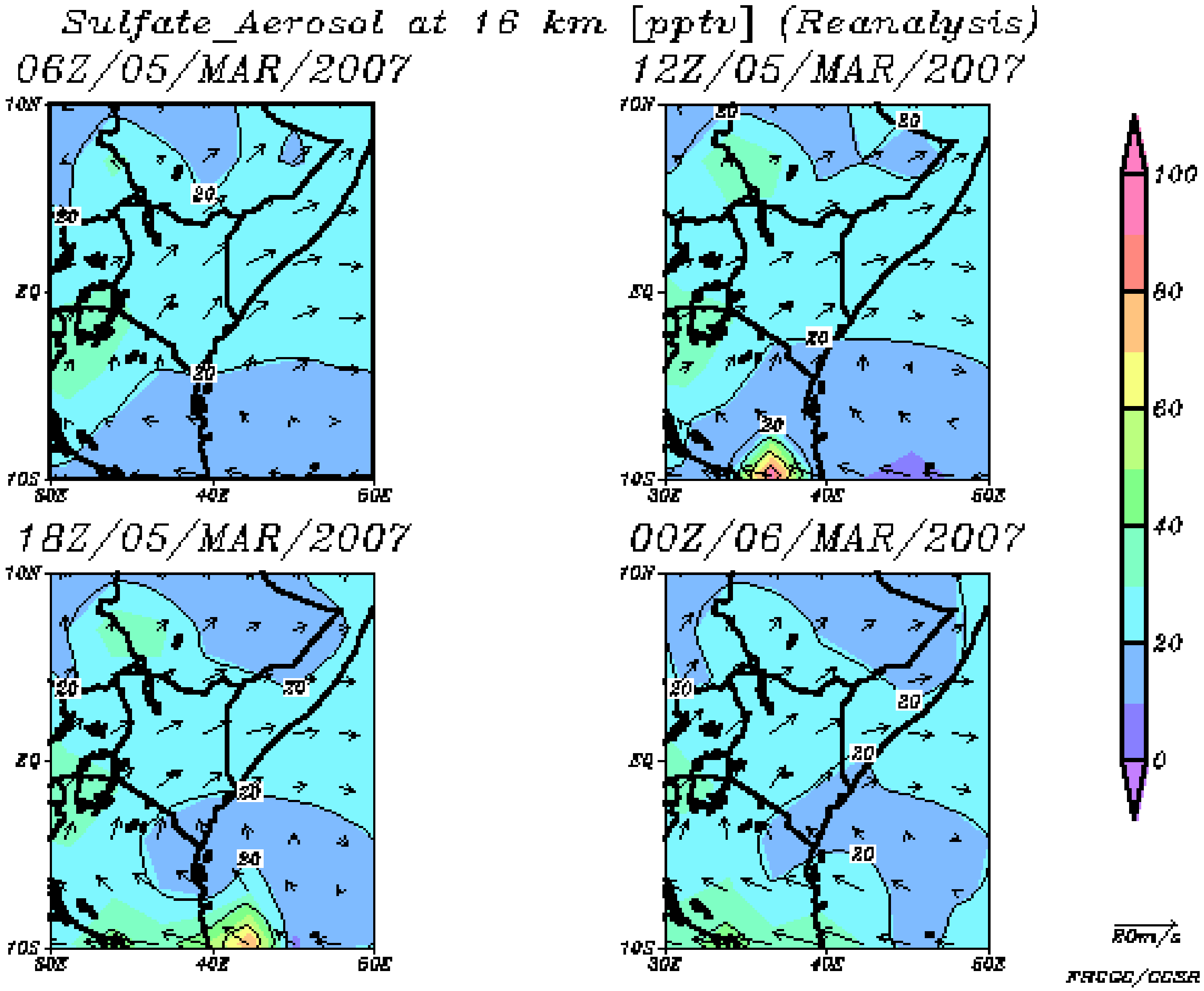


Figure 5 : Spatial distribution of sulphate aerosols in March 2007

Simulation results of transport of volcanic ash in March 2007 indicate that Tanzania, Kenya and Burundi were affected in terms of transport of the volcanic ash. However, Uganda remained largely unaffected (Figure 6). The effect was dependent on the source height. The simulation utilized three arbitrary heights as shown in figure 6.

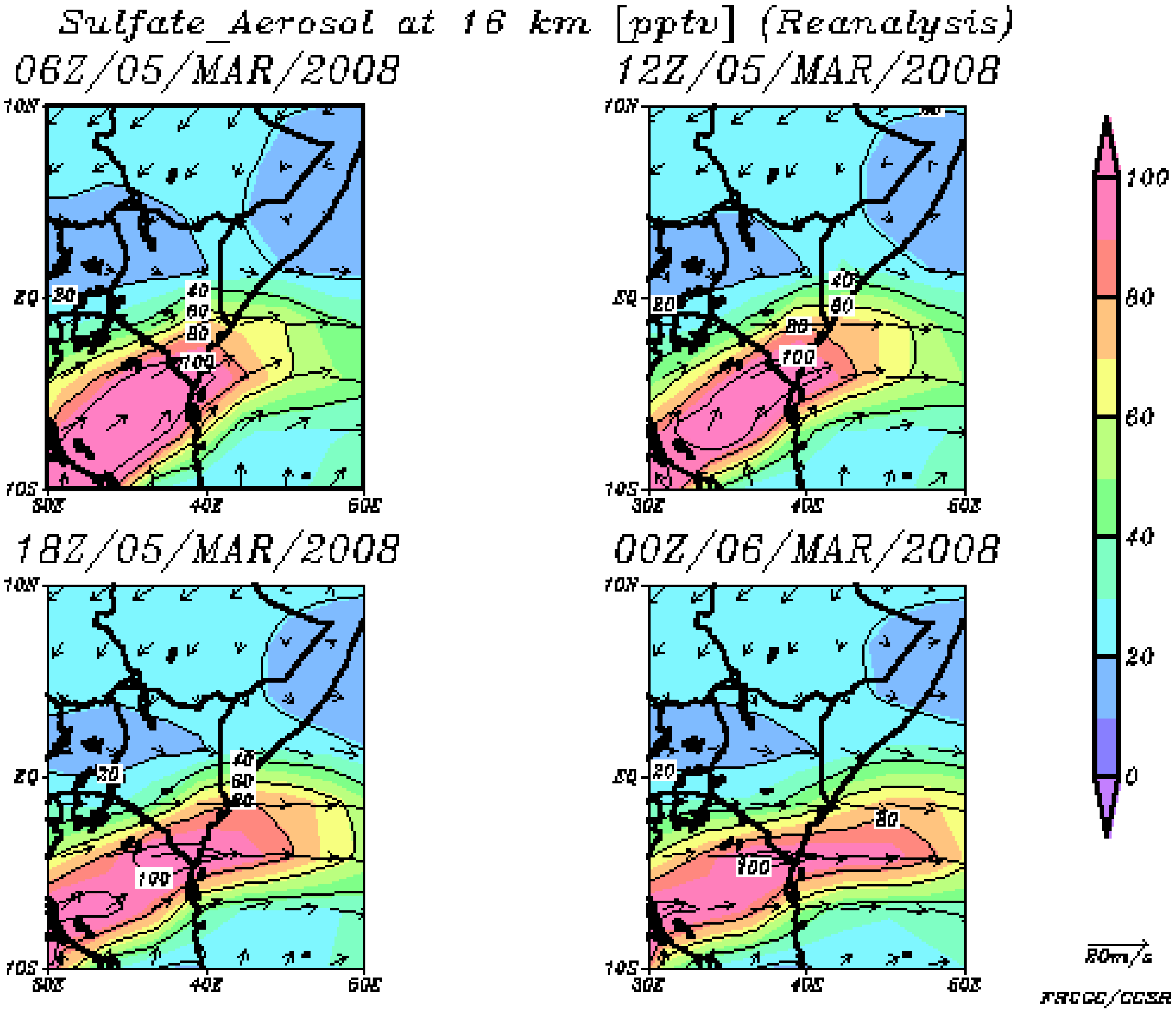


Figure 6 : Spatial distribution of sulphate aerosols in March 2008

Simulation results of dispersion of volcanic ash in March 2008 indicate that Tanzania, Uganda, Rwanda and Burundi were affected in terms of deposition of the volcanic ash. However, Kenya remained largely unaffected (Figure 7).

4.0 CONCLUSION

The Ol Doinyo Lengai eruptions in July 2007 and March 2008 affected the atmospheric integrity of all the east African countries. Most East African Countries, apart from Kenya were affected by the volcanic ash of Ol Doinyo Lengai eruptions of July 2007 and March 2008.

Lake Victoria experienced deposition of the volcanic ash with implications on aquatic ecosystem. This requires further studies in view of the importance of the Lake as resource and as a component of the climate system

There is need for regional efforts in the systematic monitoring of the volcano in the interest of air quality climate over East Africa.

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DIRECT SYNTHESIS OF SH/NH_2-BI-FUNCTIONALIZED MESOPOROUS SILICA USING CARDANOL AS A TEMPLATE

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ABSTRACT

The preparation and characterization of SH/NH_2-bi-functionalized mesoporous silicas are reported. The materials were prepared via a one-pot simultaneous condensation of (3-mercaptopropyl)-trimethoxysilane (MPTMS), 3-aminopropyltrimethoxysilane (APTES) and tetraethyl orthosilicate (TEOS) using cardanol or *n*-dodecylamine as templating agents. The materials were characterised by diffuse reflectance Fourier Transform Infrared (FTIR), nitrogen physisorption, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). Results indicated that the amino and the thiol groups were successfully incorporated into the silica matrix and their distribution was homogeneous. It was further observed that the average pore diameters and the BET surface areas for the cardanol-templated and *n*-dodecyalamine-templated silicas were 18 nm and 238 m^2/g, and 3.2 nm and 773 m^2/g, respectively.

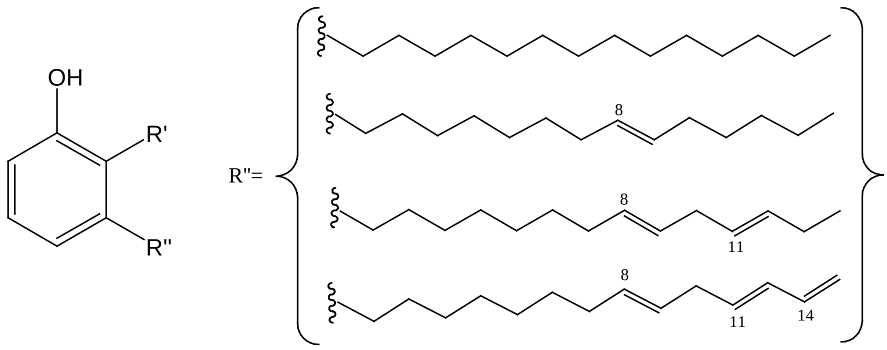
INTRODUCTION

The template-directed synthesis of mesoporous organosilicas has opened up almost unlimited possibilities for the chemical design of novel nanomaterials [1]; with a possibility of controlling not only structural ordering but also surface chemistry [2,3]. Indeed a lot of mesoporous organosilica materials have been prepared for various applications including catalysis [4-6], separation [7], optical activities [8], nanoscience [9], drug delivery [10] and toxic metal adsorption [11-15]. The application versatility of these materials derives from their high surface area, tunable pore sizes, ability to attach functional group of interest, and good mechanical and thermal stability.

So far most of the developed organosilica materials have been monofunctional, i.e., they contain only one type of functional group. A number of such groups that have found various applications include amines [4,16,17], thiols [12-14], sulfonic acids [18], carbonyls [19], just to mention a few. Normally such organosilicas are developed either through grafting of the organic group onto pre-formed silica or by a co-condensation of a silica precursor and an organic group precursor in the presence of a neutral surfactant as a template [20].

Similar preparation procedures have been applied to a few bi-functional organosilicas that are reported in the literature [21-25]. The latter materials were tested successfully as selective adsorbents for toxic heavy metals [24-26] or in controlling the selectivity of competitive nitroaldol condensation [27]. In general the bi-fuctionalised silica shows promise in processes requiring controlled confinement such as when the channel reactivity needs to be coupled with hydrophobic/hydrophilic balance of the localised environment. For instance, in a study by Sepehrian *et al*. [24] it was observed that aminopropyl ligands attracted ‘hard’ metal ions such as Ni, Cr, Mn and Fe whereas mercaptopropyl ligands attracted ‘soft’ metal ions such as Pd and Hg as per Pearson’s Hard-Soft Acid Base (HSAB) theory [28].

Most of the reported monofunctional organosilica materials that were developed by the co-condensation method used neutral commercial templates such as *n*-dodecylamine [17], polyethylene oxide [29] or triblock copolymer P123 [30]. However, the achieved pore diameters hardly reached 10 nm. Organosilicas with about 17 nm have previously been prepared using cashew nut shell liquid (CNSL) as a template [16]. CNSL is a natural agricultural by-product obtained from cashew nut processing. The major components of CNSL (Fig. 1) are phenolic compounds, anacardic acid (**1**) and cardanol (**2**) [31]. The organosilicas developed over CNSL as a template were successfully applied in the immobilization of invertase enzyme [32] as well as in supporting copper Schiff base catalyst [6]. In a different study Msigala and Mdoe [5] established that, of all the components of CNSL, it is cardanol that produces the highest yield of organosilica when used as a template. As a follow up of the latter work, we hereby report the synthesis of a bi-functionalized mesoporous silica using cardanol, a component of the CNSL, as a template.



1: R' = CO_2H, anacardic acid

2: R' = H, cardanol

Figure 1: Major components of cashew nut shell liquid.

EXPERIMENTAL

Materials and Reagents

Chemicals used in the co-condensation process, namely, (3-mercaptopropyl)-trimethoxysilane, MPTMS, (assay ≥ 98%), 3-aminopropyltrimethoxysilane, APTES, (assay 97%) and tetraethyl orthosilicate, TEOS, (assay ≥ 98%) were purchased from Fluka Chemie. Other standard laboratory grade reagents and chemicals were purchased from Aldrich. All chemicals were used as received without further purification. In addition, CNSL was extracted from cashew nut shells that were collected from Mtwara region in Tanzania using a procedure explained elsewhere [5].

Isolation of Cardanol from CNSL

Isolation of anacardic acid from CNSL was done using a procedure reported by Paramashivappa *et al.* [31]. Thereafter the isolated anarcadic acid was hydrogenated in the presence of 5% Pd/C catalyst at room temperature for 24 h. This was followed by decarboxylation of the saturated anarcadic acid through heating in a furnace at 200°C for 4 h in order to achieve cardanol. The saturation and decarboxylation were proved by Fourier Transform Infrared (FTIR) spectroscopy.

Synthesis of SH/NH_2-Bi-functionalised Mesoporous Silica

The synthesis was carried out through a one-pot co-condensation technique following a procedure by Hilonga *et al.* [16] with minor modifications. A typical preparation involved preparing a solution of cardanol (2.5 g) in aqueous ethanol (46 ml of absolute ethanol and 53 ml of distilled water) at ambient temperature and pressure. To a stirred solution of the latter TEOS (18.89 g), 3-aminopropyltrimethoxysilane (0.96 g) and mercaptopropyl triethoxysilane (1.19 g) were added separately but simultaneously. The mixture was aged for 18 h, followed by vacuum filtration and ethanol washing of the resulting product. The template was then removed by a Soxhlet extraction for 10 h using ethanol as a solvent. The final solid was dried in an oven at 110°C for 8 h. The same procedure was repeated using *n*-dodecylamine (DDA) as the template for comparison purposes.

Characterization of the Bi-functionalised Mesoporous Silica

The porosity characteristics of the bi-functionalised mesoporous silicas were measured by nitrogen adsorption isotherm at 77 K using a Quantachrome® ASiQwin™ (version 2.0)-automated gas sorption instrument. Scanning electron microscopy (SEM) and electron-dispersive X-ray (EDX) spectroscopy were performed on a Zeiss Supra 55 instrument at 5.0 and 20 kV, respectively. Analyses were performed on powder samples that were previously dried. For EDX spectroscopy the contents of elements on the surface were calculated based on the means of six different single-point analyses. Diffuse reflectance Fourier Transform Infrared (FTIR) spectroscopy to confirm the functional groups present in the materials was performed on a Perkin-Elmer 2000 FTIR spectrophotometer. The spectra were recorded from 4000 to 600 cm^{-1}.

RESULTS AND DISCUSSION

The synthesis of SH/NH_2-bi-functionalised mesoporous silica was carried out using cardanol as a template. A commercial surfactant *n*-dodecylamine which has been used before as a template was also used in this study for comparison purposes [4,17]. The method was simple and the recovery of the template was more than 95%. The functional groups contained in the bi-functionalized mesoporous silica were identified by FTIR and EDX. Figure 2 shows the FTIR spectrum of a typical bi-functionalised material. From the figure, vibration signals at around 1000-1200 cm^{-1} are observable. These are due to Si-O-Si symmetric and asymmetric stretching vibrations typical of condensed silica network. The strong peak around 1620 cm^{-1} was mainly from the bonding vibration of adsorbed water. The band around 2900 cm^{-1} was assigned to C-H stretching vibrations due to the presence of propyl groups from both 3-aminopropyltrimethoxysilane and mercaptopropyl triethoxysilane. The vibration band of C-N is usually observed at 1000 - 1300 cm^{-1}. However, the peak is hardly seen due to its overlap with other peaks. The OH stretching band of the silanol groups was also observed at 3200 -3600 cm^{-1}. The N-H stretching band appears in a similar region but it was masked by the Si-OH band. N—H bending mode was observed at 1550 cm^{-1}. The weak S-H stretching peak which normally appears at around 2550 cm^{-1}, was not observable, probably due to the small amount of thiol groups present in the sample.

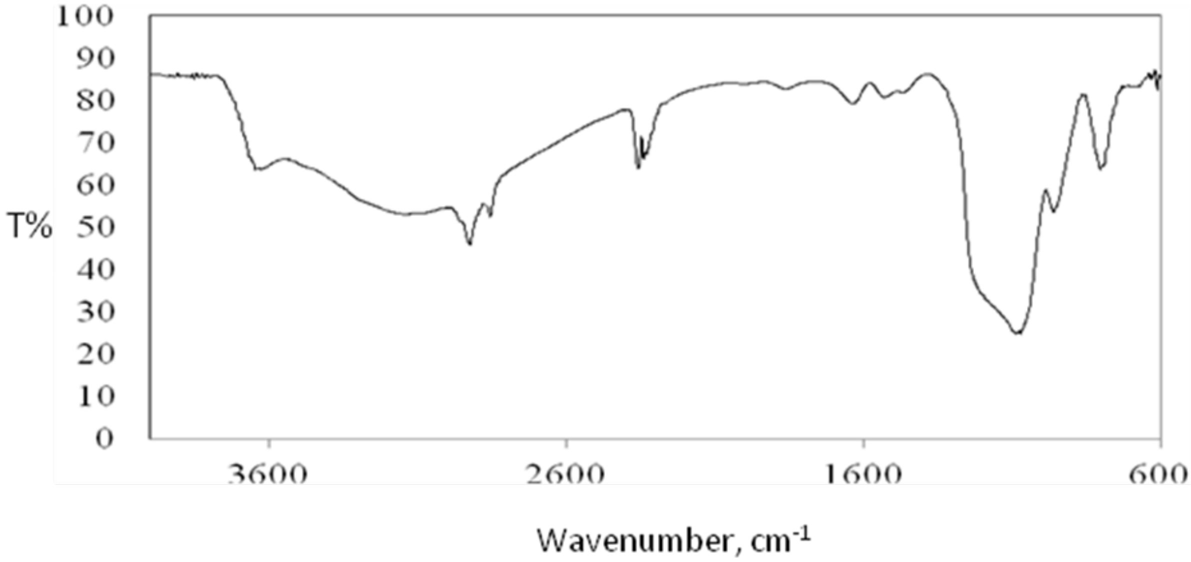
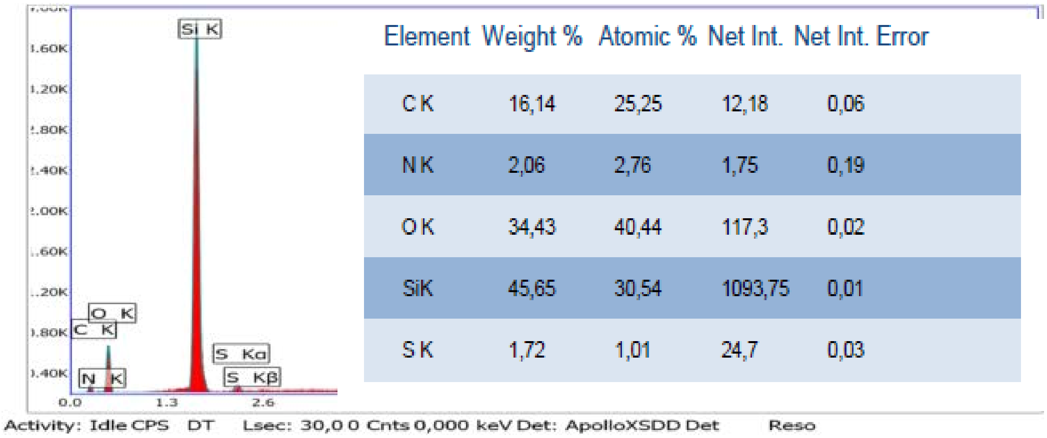


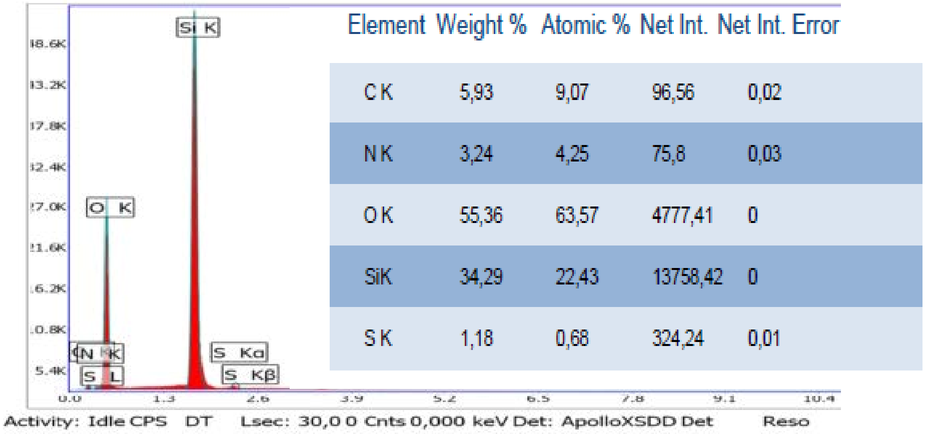
Figure 2: FTIR spectrum of SH/NH_2-bifunctionalised mesoporous silica prepared using cardanol as a structure director.

The inclusion of thiol and amino groups into the mesoporous silica matrix was further confirmed by EDX analysis. The compositional information of the EDX analysis in Figures 3 and 4 exhibits the presence of silicon, oxygen, nitrogen, sulphur and carbon elements in the prepared bi-functionalised mesoporous silica. The signals of nitrogen and sulfur elements provide a powerful evidence for the successful incorporation of the organic groups into the silica mesophases. Furthermore, analysis at different points on the organosilica sample indicated that the thiol and amino groups are homogeneously distributed. The compositional information also indicated equal silicon/sulfur atomic ratios for the materials templated by cardanol and *n*-dodecylamine. However, the silicon/nitrogen atomic ratios for the cardanol- and *n*-dodecylamine-templated materials were 11 and 5, respectively. This indicates that there were more nitrogen atoms than sulfur on the surface of the *n*-dodecylamine-templated bi-functionalised silica matrix. This suggests that there was a secondary source of nitrogen elements apart from the aminopropyltrimethoxysilane, which is attributed to traces of remaining *n*-dodecyalmine template.



Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	16,14	25,25	12,18	0,06
N K	2,06	2,76	1,75	0,19
O K	34,43	40,44	117,3	0,02
SiK	45,65	30,54	1093,75	0,01
S K	1,72	1,01	24,7	0,03

Figure 3: EDX data for SH/NH$_2$-bifunctionalised mesoporous silica prepared using cardanol as a template.



Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	5,93	9,07	96,56	0,02
N K	3,24	4,25	75,8	0,03
O K	55,36	63,57	4777,41	0
SiK	34,29	22,43	13758,42	0
S K	1,18	0,68	324,24	0,01

Figure 4: EDX data for SH/NH$_2$-bifunctionalised mesoporous silica prepared using *n*-dodecylamine as a template.

The morphology at the nanometer length scale of the bi-functionalised mesoporous silica was observed using SEM (Figure 5). The morphology of the cardanol-templated as well as the *n*-dodecylamine-templated materials showed an aggregation of fluffy primary particles of nearly spherical to irregular shapes. A closer look reveals that the primary particles of the cardanol-templated silica are roughly spherical and they contain some pores. The *n*-dodecylamine-templated silica, on the other hand, does not show any kind of porosity at the given scale. Their texture is fluffier, showing a continuous aggregation of indistinguishable primary particles.

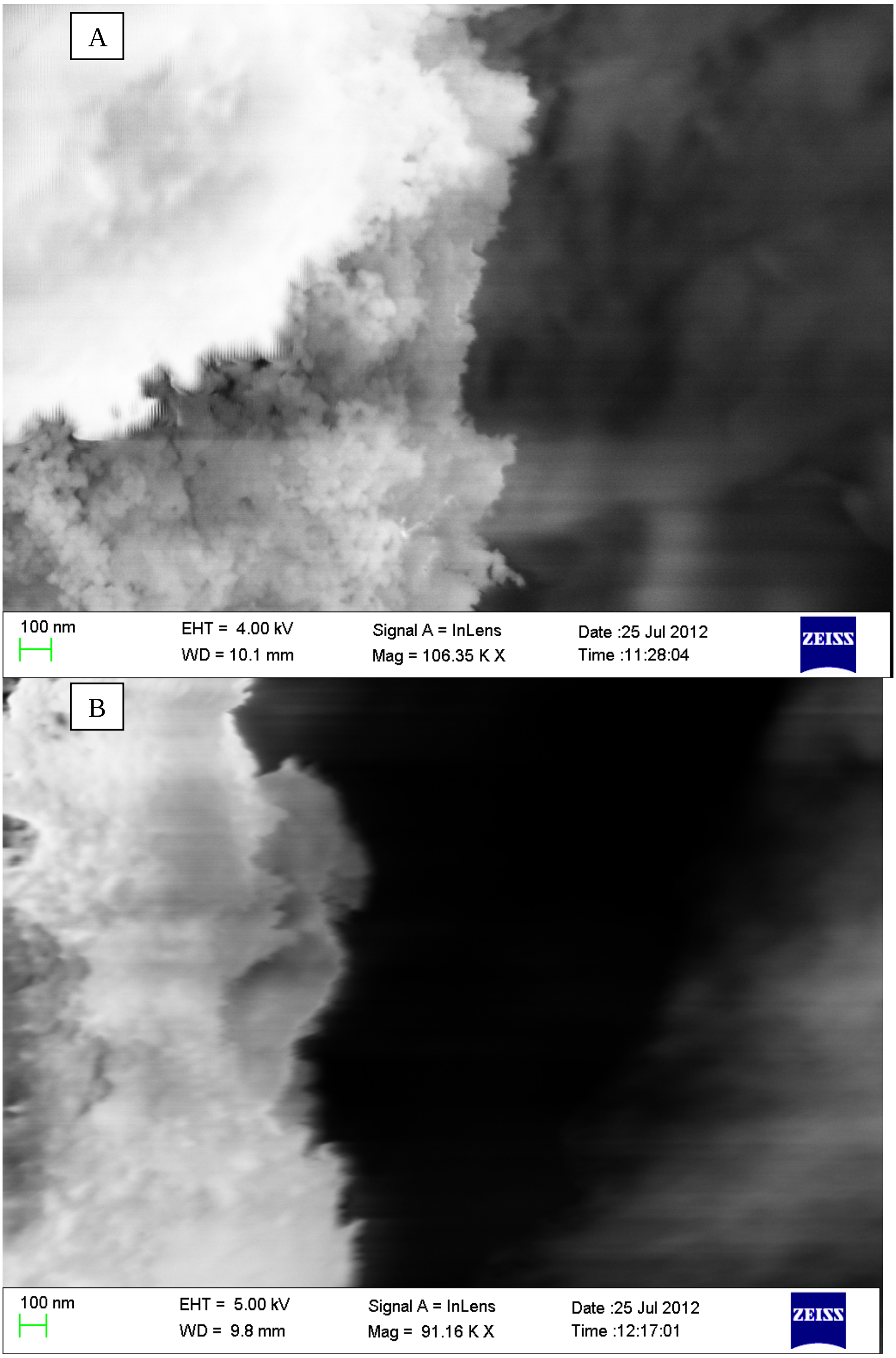


Figure 5: SEM images of bi-functionalised silica using A) cardanol B) *n*-dodecylamine as templates.

Adsorption–desorption isotherms of the SH/NH_2-bifunctionalised mesoporous silicas prepared using cardanol and *n*-dodecylamine as surfactants are shown in Figure 6. In accordance with the International Union of Pure and Applied Chemistry (IUPAC) classification both isotherms are type IV, indicating that the materials are mesoporous [33]. The isotherms show an initial gradual increase of nitrogen uptake at low relative pressure (< 0.1). Above that, the isotherms form a plateau followed by another sharp rise of nitrogen uptake starting from about relative pressure of 0.8 units. The initial gradual increase of nitrogen uptake at low relative pressure (< 0.1) observed in the isotherms was ascribed to a gradual microporous filling by the nitrogen and the formation of a monolayer of nitrogen on the walls of the mesopores. This was followed by formation of multilayer of the adsorbate and ultimately capillary condensation in the pores [34]. The cardanol-templated material showed a well pronounced hysteresis loop above relative pressure 0.4, whereas that of DDA-templated material was relatively small and it was found above relative pressure 0.8. This implies that the majority of pores in DDA-templated material are framework confined compared to those of cardanol-templated material.

The nitrogen adsorption analysis also gave some information on the pore size, pore size distribution and BET surface areas. Results indicated that cardanol template produced a material with larger pore diameter and smaller surface area than DDA template. The observed average pore diameters were 17.8 and 3.2 nm for the cardanol-templated and DDA-templated materials, respectively. On the other hand, the Brunauer-Emmett-Teller (BET) surface areas for the cardanol-templated and DDA-templated materials were 238.0 m²/g and 773.2 m^2/g, respectively. In a template-directed synthesis normally the packing parameter and hence the resulting material are dependent on the alkyl chain length and the head group area of the templating agent [35]. In that case the difference in pore diameters and surface areas observed between the cardanol- and the *n*-dodecylamine-templated silicas might be due to the large phenolic head group in cardanol compared to the amine head group in DDA. A similar observation is also reported for CNSL-templated materials elsewhere [32].

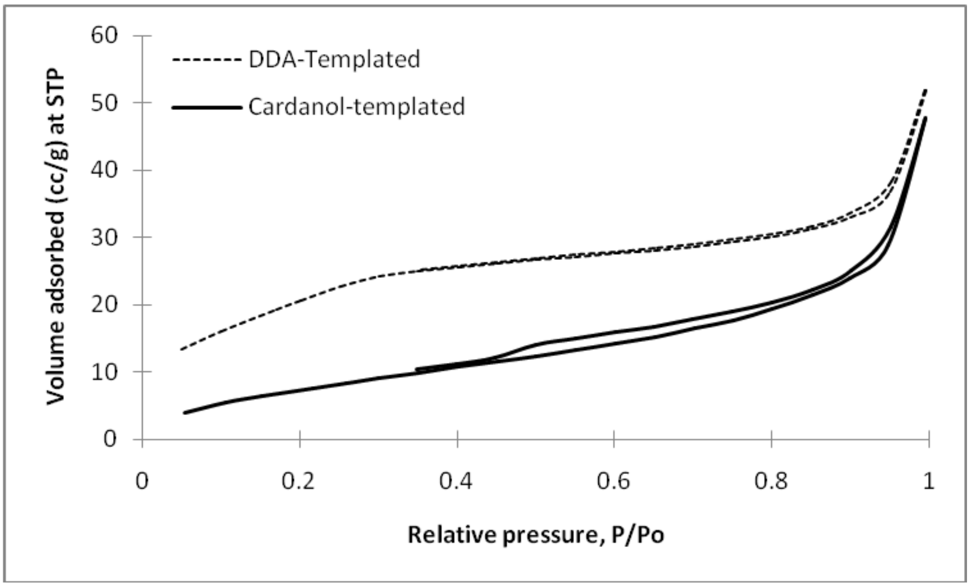


Figure 6: Adsorption-desorption isotherms for the bi-functionalised mesoporous silica.

CONCLUSION

SH/NH_2-bi-functionalised mesoporous silica have been prepared through a one-pot co-condensation of APTES, MPTMS and TEOS using cardanol and *n*-dodecylamine as templates. The preparation technique has enabled a direct functionalization of the silica surface with a homogeneous distribution of the functional groups. Furthermore, our results show that cardanol as a template produces materials with pore diameters up to 18 nm, a size that is larger than that obtained for materials templated by *n*-dodecylamine, which was 3.2 nm. The materials have BET surface areas of 238 m^2/g and 773 m^2/g for the cardanol- and the *n*-dodecylamine-templated materials, respectively.

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ADSORPTION OF 2, 4, 5, 6-TETRACHLOROISOPHTHALONITRILE (CHLOROTHALONIL) BY NAIROBI RIVER SEDIMENTS: ADSORPTION CHARACTERISTICS AND RELATED THERMODYNAMIC DATA

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ABSTRACT

The adsorption\desorption of chlorothalonil by suspended Nairobi river sediment particles in an aqueous solution was studied in terms of a model which assumes the adsorption/desorption reaction: $n X + S \Leftrightarrow S X_n$ and $K = [S X_n]/[X]^n[S]$, where X is the chemical species of interest and S is the substrate. K is the adsorption/desorption equilibrium constant, S denotes adsorption site in the sediment and SX_n is the particle-pesticide complex. The apparent adsorption/desorption equilibrium constant K is given by: *$\ln[X]_{ads} = \ln(nK) + n\ln[X]_e + [SX_n]_w$*, where $[X]_{ads}$ is the concentration of X in the adsorbed state in suspension. $[X]_e$ is the concentration of X in solution at equilibrium. $[SX_n]_w$ is the pesticide adsorption site complex in the suspension at equilibrium. The calculated values of the apparent K' and $\Delta G'$ were 80 and -9.9×10^3 kJ/mol, respectively, for the adsorption of chlorothalonil by Nairobi river sediment. The negative value for $\Delta G'$ confirmed the fact that adsorption reaction occurs spontaneously as expected. Moreover, adsorption of chlorothalonil onto suspended/dissolved sediment particles decreased with increase in mass of the substrate.

Key words: *Adsorption, pesticide, chlorothalonil, adsorption equilibrium constant*

INTRODUCTION

Chlorothalonil (tetrachloroisophthalonitrile) is a broad spectrum non-systematic fungicide. Its trade names include; Bravo, Chlorothalonil, Daconil 2787, Isotherm Termil, Forturf, Mold-Ex, Nopcocide N-96, Pillarich and Tuffcide [1]. The compound can be found in formulations with many other pesticide compounds. Chlorothalonil is a broad-spectrum organochlorine pesticide (fungicide) used to control fungi that threaten vegetables, trees, small fruits, turf and other agricultural crops [2]. It also controls fruit rots in cranberry bogs, and is used in paints as an additive. Chlorothalonil is an aromatic halogen compound and a member of the chloronitrile chemical family, see Fig. 1. It is a grayish to colorless crystalline solid with an odorless to slightly pungent smell. It is non-corrosive, stable in moderately alkaline or acidic aqueous solutions and has a molecular weight of 265.89 g/mol. At high temperatures, Chlorothalonil may decompose producing hydrochloric acid [3]. It boils and melts at 350.0 and 250.5 degrees Celsius respectively and exhibits low water solubility (0.6mg/liter). It is however more soluble in organic solvents such as acetone, hexane and cyclobutanone.

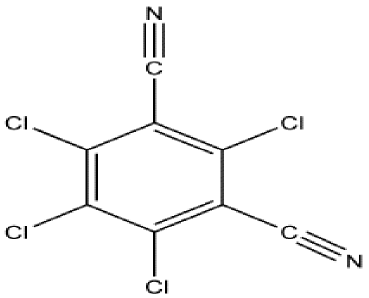


Figure 1. Chlorothalonil structure

Though not considered acutely toxic by ingestion (oral LD_{50} is greater than 10000mg/kg) Chlorothalonil is very toxic on inhaling (World Health Organization, 1996) [4]. Long term exposure to Chlorothanil through inhalation leads to kidney damage, loss of muscle coordination, rapid breathing, nose bleeding, vomiting, hyperactivity, dermatitis, vaginal bleeding, bloody urine followed by death.

Also although Chlorothalonil is practically non-toxic to birds (with the mallard ducks for example exhibiting an LD_{50} of nearly 5000 mg/kg) and does not significantly affect most avian wildlife; its metabolites are dangerous to most aquatic life. Chlorothalonil metabolites are found to be highly toxic to fish, aquatic invertebrates, and marine organisms. Fish, such as rainbow trout (LC_{50} of 0.25 mg/l), bluegills (LC_{50} of 0.3 mg/l) and channel catfish (LC_{50} of 0.43 mg/l) are noticeably affected even when chlorothalonil levels are low (less than 1 ppm). Chlorothalonil does not accumulate in the fatty tissues (its bioaccumulation factor being about 425 times the background water concentration and thus quite low) and is rapidly excreted from the body primarily in an unchanged form [5].

In aerobic soils, the half-life for chlorothalonil ranges from between one to three months. Chlorothalonil degradation is found to increase with increase of soil moisture and/or temperature. It is also known not to undergo surface degradation owing to sunlight [6]. It has high binding and low mobility in silty loam and silty clay loam soils, and has low binding and moderate mobility in sand [3]. In studies conducted in water over a ten week's period, Chlorothalonil, at low and neutral pH levels, was found to be generally stable. However, in very basic water (pH 9.0), about 65% of the Chlorothalonil was degraded into a major metabolites, 4-hydroxy-2,5,6-trichloroisophthalonitrile. In areas where this fungicide is used, it and/or its metabolites have been fairly persistent in the environment- its degree of pollution depending on the rate of application. For instance, in one surface water location in Michigan, Chlorothalonil concentration was reported to be 6.5 mg/L. Similarly, its residues may remain on above-ground crops and small amounts of one or more of its metabolites have been found on the harvested crop. In another study, Chlorothalonil has been detected in ambient air in Minnesota, USA, and Prince Edward Island, Canada [6]. In both cases, the contamination was presumed to have come from potato farms in the area. The main metabolite of chlorothalonil DS-3701 (4-hydroxy-2,5,6-trichloroisophthalonitrile), has been shown to be 30 times more acutely toxic than chlorothalonil and more persistent in the environment [7]. Laboratory experiments have shown that it can thin the eggshells of birds, though there is no evidence that this is happening in the environment.

Chlorothalonil can be produced by the direct chlorination of isophthalonitrile or by treating tetrachloroisophthaloyl amide with phosphoryl chloride [8]. It breaks down under basic conditions but is stable in neutral and acidic media. Technical chlorothalonil contains traces of dioxins and hexachlorobenzene, a persistent organic pollutant banned under the Stockholm Convention, (World Health Organization, 1996) [4]. It is against this wide ranging background that we got interested in this pesticide and therefore decided to study its environmental behavior, particularly with respect to its adsorption on sediments in River beds, which are disposal outlets for most of the pesticides and related pollutants.

Theory of adsorption phenomenon

The theory behind the adsorption process has been reported earlier by Zaranyika and Mandizha, 1998[9]. Here we present the adsorption kinetics of Chlorothalonil onto Nairobi river sediments based on the adsorption model of a binary dilute solution [10]. The apparent thermodynamic data is also calculated.

The characteristic adsorption of pesticide by soils or sediments can be described by the Freundlich empirical isotherm [11]:

$$C_{ads} = k_F C_e^n \quad \ldots \ldots \ldots \ldots \ldots 1).$$

Where k_F the Freundlich constant, C_{ads} is the concentration (mg/ml) of the pesticide adsorbed by the soil/sediment in suspension and C_e is the concentration of the pesticide in the solution (mg/ml) at equilibrium, Bowman and Sans, 1977 [12]. By taking batches of known mass of sediments (adsorbent), and mixing with solutions of known initial concentration of pesticides, followed by shaking and equilibration, the concentration of the adsorbed pesticide (Cads) and that at equilibrium (Ce) can be estimated. The Freundlich factor k_F is a constant for a given system and therefore may be used to compare the degree of adsorption of different solutes onto various sediments. On the other hand, n is regarded as a measure of adsorption non-linearity between solution solute concentration and adsorption. The adsorption process of pesticides on soils was reviewed by Burchill et al., [10]. Several factors need to be considered in conducting adsorption studies. Firstly, what is the kinetics involved, particularly the magnitude of the adsorption and desorption rate constants and also the energies involved. Do the latter depict weak or strong nature of interaction between the solute and the adsorbents? Secondly, what are the initial and equilibrium conditions and how do the chemical composition and/or structure of both the adsorbent and the pesticide affect the results?

In order to obtain the adsorption/desorption, equilibrium, thermodynamic and kinetic data, there is need to come up with a functional adsorption/desorption equilibrium model, from which the apparent equilibrium constant and kinetic information can be calculated. Assuming that the adsorption of pesticide solute by the colloidal/sediment or both particles occurs during the shaking period, implying when the sediment is in suspension, then the adsorption/desorption equilibrium can be described as follows [9.13]:

$$nX + S \Leftrightarrow SX_n \text{..(2)}$$

$$K = [SX_n]/[X]^n[S] \text{.................................(3)}$$

On re-arrangement;

$$[SX_n] = K[X]^n[S] \text{..................................(4)}$$

Where X is the pesticide molecule of interest; S is the adsorbent/substrate or adsorption site on the sediment or colloidal particle in solution and K is the adsorption/desorption equilibrium constant. SX_n is the particle-pesticide adsorption complex. Also, one notes that S is a solid whose mass is very large compared to that of the solute. Therefore, the $[S]$ can customarily be taken to be unity thereby reducing equation 4 to;

$$[SX_n] = K[X]^n \text{.......................................(5)}$$

And on taking logs we have;

$$\log[SX_n] = \log K + n\log[X] \text{....................(6)}$$

It means, since equation (6) is linear, the value of K, the equilibrium constant, and n, the number of pesticide molecules adsorbed, can be obtained from the slope and intercept of the $\log[SX_n]$ versus $\log[X]$ plots respectively. In addition, the standard Gibbs free energy of activation ΔG, can be estimated by use of the conventional equation [9,14]:

$$K = e^{-\Delta G/RT} \text{..(7)}$$

Assuming the assumption that the adsorption of chlorothalonil by colloidal and/or sediment particles occurs during the shaking (on suspended particles) and also that all the adsorbed pesticide goes to the sediment on settling, then the concentration of pesticide adsorbed to the suspended particles $[X]_{ads}$ can be obtained using equation 8 below;

$$[X]_{ads} = [X]_i - [X]_e \text{..................................(8)}$$

Where $[X]_i$ represents the initial pesticide concentration before a known mass of sediments is added, and $[X]_e$ is the equilibrium pesticide concentration in solution. Also, agitation facilitates the settling down of the sediments and thus the separation of dissolved and adsorbed pesticides. Since n molecules of pesticide are associated with a single adsorption site, then [SX_n] is given by;

$$[SX_n] = \tfrac{1}{n}\left([X]_i - [X]_e\right) \text{. . .. .(9)}$$

$$[SX_n] = \tfrac{1}{n}[X]_{ads} \text{.. .. .. (10)}$$

Nomura and Hilton [15] and later Zaranyika et. al., [16,17] demonstrated the existence of a colloidal bound fraction when a pesticide is shaken with water containing sediment. They also showed that the colloidal bound fraction in suspension after settling was significantly small compared to the bound fraction in the sediment thus justifying the assumption made regarding the determination of [SX_n] using $[X]_{ads}$ above. Note that [SX_n] is the concentration of the colloidal bound fraction in suspension at settling equilibrium, since not all the pesticide is adsorbed. Therefore, on modifying equation 10 to show the total adsorbed pesticide we have;

$$[X]_{ads} = nK'([X]_e + [SX_n]_w)^n \text{....................(11)}$$

where K' is the apparent adsorption equilibrium constant and $[SX_n]_w$ is the concentration of the colloidal bound fraction in suspension at settling equilibrium. On taking logarithm equation 11 yields a linear expression;

$$\ln[X]_{ads} = \ln(nK') + n\ln\left([X]_e + [SX_n]_w\right) \text{...(12)}$$

Assuming that equilibrium exists between the colloidal bound fraction in the sediment and that in the suspension, then equation 2 becomes:

$$nX + S \leftrightarrow (SX_n)_w \leftrightarrow (SX_n)_{sediment} \text{............(13)}$$

It is apparent from equation 13 that a steady state exists with respect to $[SX_n]_w$ at settling equilibrium. Moreover, a plot of $\ln[X]_{ads}$ versus $\ln([X]_e + [SX_n]_w)$ in equation 12 will not affect the value of n in equations 6 and 10, but will affect the value of nK. Therefore, the value of K obtained is not a true equilibrium constant, but rather an apparent equilibrium constant (K').

EXPERIMENTAL SECTION

Materials and Reagents

Chlorothalonil (IOBA Chemie, 99% pure), acetone (Panreac quimica, 95%) and Acetonitrile (HPLC analytical grade 85% from Fisher Scientific Co. (Fairlawn, NJ). were used as received. An orbital shaker fitted stopwatch was used for all timing purposes. Distilled water was used for all preparations. The sediments used in these experiments were collected from the Nairobi River which is about 200 m from the Department of Chemistry, University of Nairobi. The sediments were characterized with respect to pH, % organic carbon, % sand, % silt, % clay, and CEC using standard methods, Table 1.

Instrumentation

All UV-Visible spectrophotometric measurements were taken on UV-Visible spectrophotometer (1700 model, Shimadzu Corporation, Kyoto Japan). All reversed phase chromatographic measurements were done using a HPLC instrument (Shimadzu Corporation, Kyoto Japan) fitted with a tunable SPD-20A Prominence UV-Vis detector and a Prominence LC and CTO-10-AS VP Shimadzu column oven. A 15cm MCH-5-N-CAP C18 column was employed. A Fischer scientific A-160, analytical balance was used for all weight measurements.

PROCEDURE

Solutions of chlorothalonil in acetone in the concentration range 0-100 ppm were prepared. Each of the 20, 40, 60, 80, 100 ppm solutions prepared was scanned using the UV-Vis spectrophotometer on a wavelength range of between 200-900nm. The resultant absorbance curves can be seen in Fig. 2.

In order to demonstrate the existence of the adsorption/desorption equilibrium, 0.1, 0.5, 1.0, 1.5 and 2.0g of the dried sediment were shaken with 10ml of 2mg of chlorothalonil aqueous solution for 60 minutes. The sediment was then allowed to settle for 12 hrs, after which the water phase was decanted, and then filtered through Whatman A40 filter paper. The concentration of chlorothalonil in the clear aqueous solution $[X]_e + [SX_n]_w$ was determined by reversed phase HPLC as discussed above. Determinations were made using the 15cm MCH-5-N-CAP C18 column and 85% HPLC grade acetonitrile in distilled water as the mobile phase. The data obtained is recorded in Table 2. Figure 3 shows the typical HPLC chromatograms obtained, while Figure 4 shows the resultant adsorption isotherm.

In order to determine the values of *n* and K', 0.5g of the dried sediment was shaken with 10ml distilled water spiked at 10, 20, 30, 40 and 50mg/ml levels of chlorothalonil. Each of the samples in quadruplicate was shaken for 15, 30, 45 and 60 minutes using an Orbital shaker. The concentration of the chlorothalonil in clear solution was determined as described above. The results are presented in Table 4. Figure 5 shows typical chromatograms obtained.

Figure 6 shows the plots obtained when the log of the total concentration of chlorothalonil in water, $[X]_e + [SX_n]_w$, was plotted against the concentration of chlorothalonil adsorbed to suspended colloidal and/or sediment particles, $[X]_{ads.}$ The values of the apparent adsorption/desorption equilibrium constant, K' and apparent free energy $\Delta G'$, for the adsorption of chlorothalonil obtained are shown in Table 5. An assumption made in arriving at the values in Table 5 was that the addition of sediment to the solution does not alter the volume of the solution significantly.

RESULTS AND DISCUSSION

In order to gain more insight with respect to the type of Nairobi river sediments used it was found necessary to determine the physical properties and composition of the sediment (Table 1). The nature of the sediments can greatly influence its adsorption characteristics. According to Table 1 the texture grade of the sediment is clay. The pH of the sediment approximates that of water, whereas the small percentage of organic carbon (0.85%) may explain the negligible adsorption of the organohalide compound, chlorothalonil, onto the sediment.

Table 1: Properties of the sediment used in chlorothalonil adsorption experiments.

Properties	
pH(0.01M $CaCl_2$)	6.86
Organic carbon (%)	0.85
Sand (%)	20
Silt (%)	14
Clay (%)	66
CEC (Cation exchange capacity)	3.36meq/100g

Clear solutions of chlorothalonil exhibited the expected characteristic UV-Visible spectra (Figure 2). The characteristic absorption band for chlorothalonil occurred at λ_{max} of 324 nm. A distinguishable blue shift peak was also observed at ca. 200nm which has also been reported for chlorothalonil by other authors, e.g., Kutty, et.al. 2012 [18]; Armbrust et. al., [19]. A plot of the chlorothalonil absorbance versus concentration at this wavelength yielded a linear relationship (Figure 3). It means the system adhered to the Beer Lambert's Law at the concentration range of 0-100 ppm used in this work.

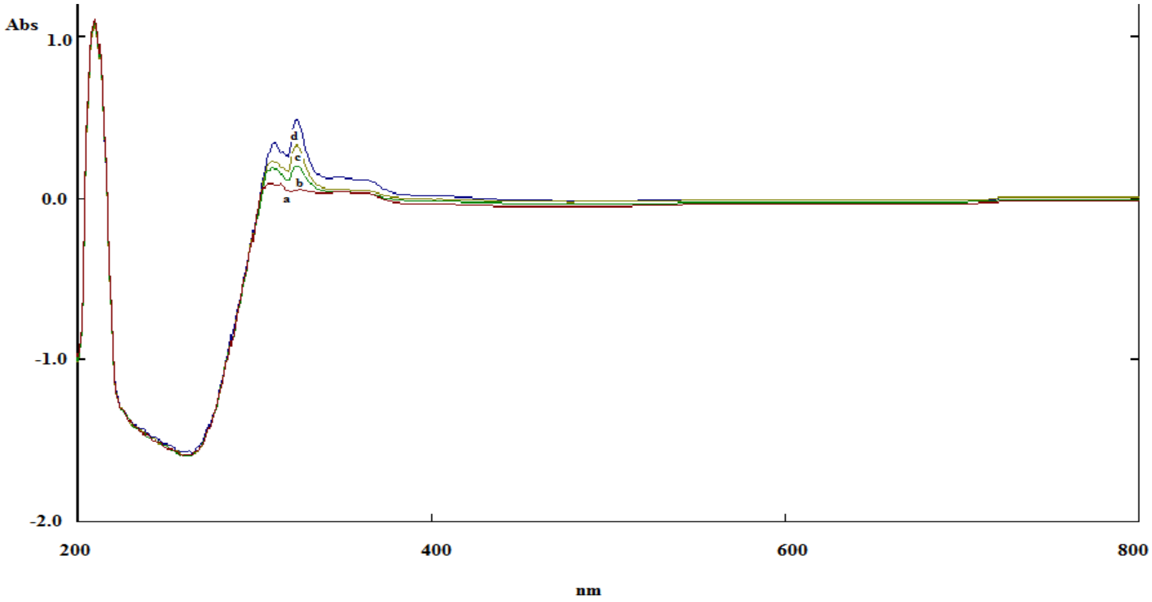


Figure 2: Spectra for different concentrations (20ppm,40ppm,60ppm,80ppm,100ppm) of chlorothalonil.

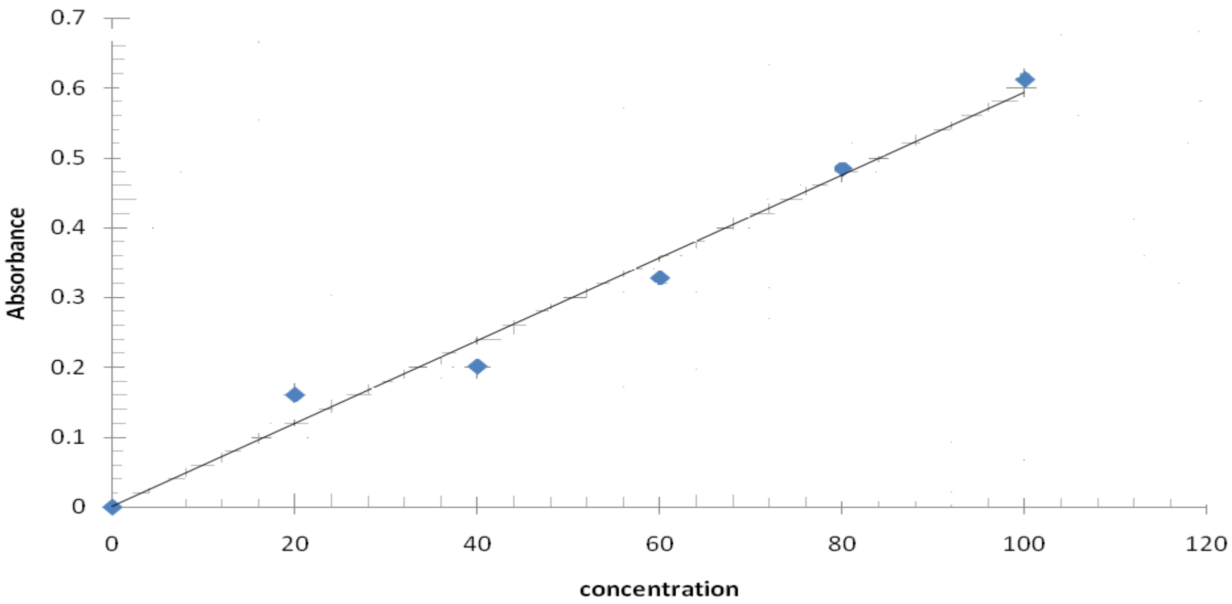


Figure 3: A plot of absorbance versus concentration at λ_{max} (324nm).

In Table 2, the data of the absorption of chlorothalonil as a function of amount of sediment added is presented. It was found that as the amount of sediments in the experimental solutions increased, the concentration of chlorothalonil in solution, $([X]_e + [SX_n]_w)$, decreased. This was because, the increase in the amount of sediments meant increased concentration of the pesticide adsorption sites and thus more and more pesticide being removed from solution.

The highest value of $([X]_e + [SX_n]_w)$, had a relative standard deviation of 9.6%, suggesting relatively good precision of the experiments. Overall, when a 0.2mg/ml chlorothalonil solution was equilibrated with increasing amounts of sediment, the amount of the chlorothalonil remaining in solution and/or suspension showed an exponential drop as the amount of sediment was increased (Figures 4 and 5). This is consistent with equation 11 above, and confirms the existence of an adsorption/desorption equilibrium in the system, in agreement with the predictions of the adsorption/desorption equilibrium model presented above.

With the increase with the number of adsorption site as the quantities of the sediments were increased, the amount of chlorothalonil adsorbed $[X]_{ads}$ is expected to increase. Table 2 and Figure 5 show that as the mass of the sediments increased from 0.1 - 2.0g, the concentration of the chlorothalonil in the adsorbed state increased from 182.26 - 194.3g, a 6.6% increase which, albeit small, is significant.

Table 2: Adsorption of chlorothalonil as a function of the mass of the sediments added.

Mass of Sediment(g)	$[X]_e + [SX_n]_w$ (µg/ml) Trials			$[X]_e + [SX_n]_w$ (µg/ml) Mean
	1st	2nd	3rd	
0.1	17.87	15.12	20.25	17.74 ± 1.71
0.5	12.56	13.95	11.2	12.57 ± 0.92
1.0	9.60	8.28	10.11	9.33 ± 0.61
1.5	7.23	6.04	7.38	6.88 ± 0.45
2.0	6.49	5.43	5.16	5.69 ± 0.48

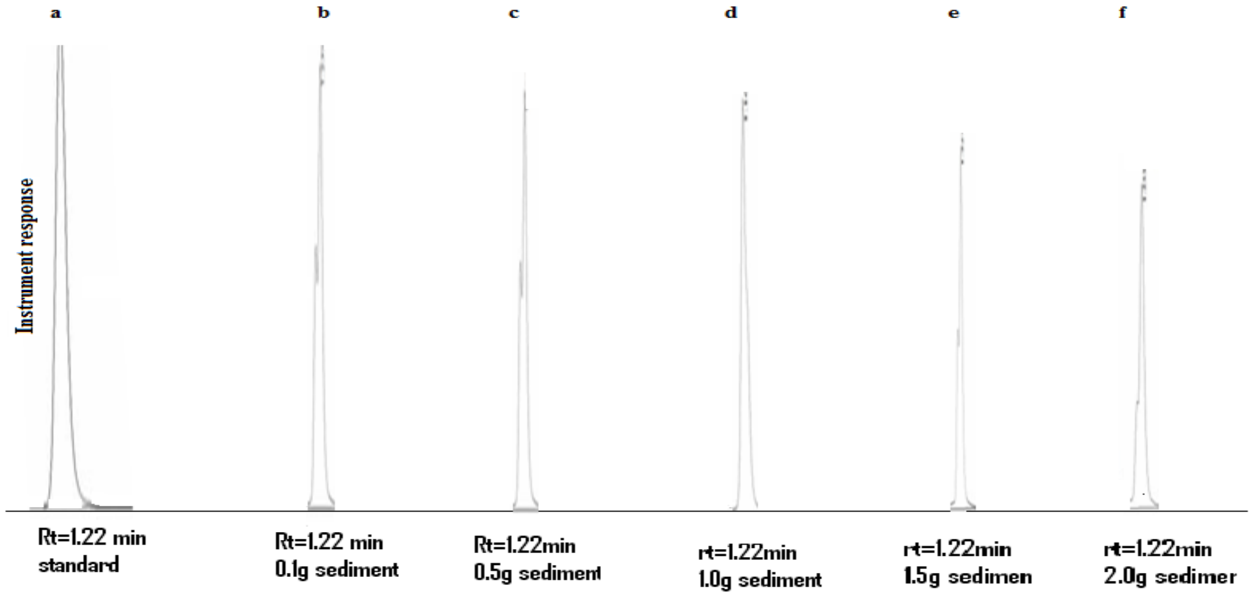


Figure 4: Typical HPLC chromatograms obtained for 2mg/ml chlorothalonil standard solution following the equilibration for 60 minutes of 0.1g (b), 0.5g (c), 1.0g (d), 1.5g (e) and 2g (f) sediment in 10ml distilled water.

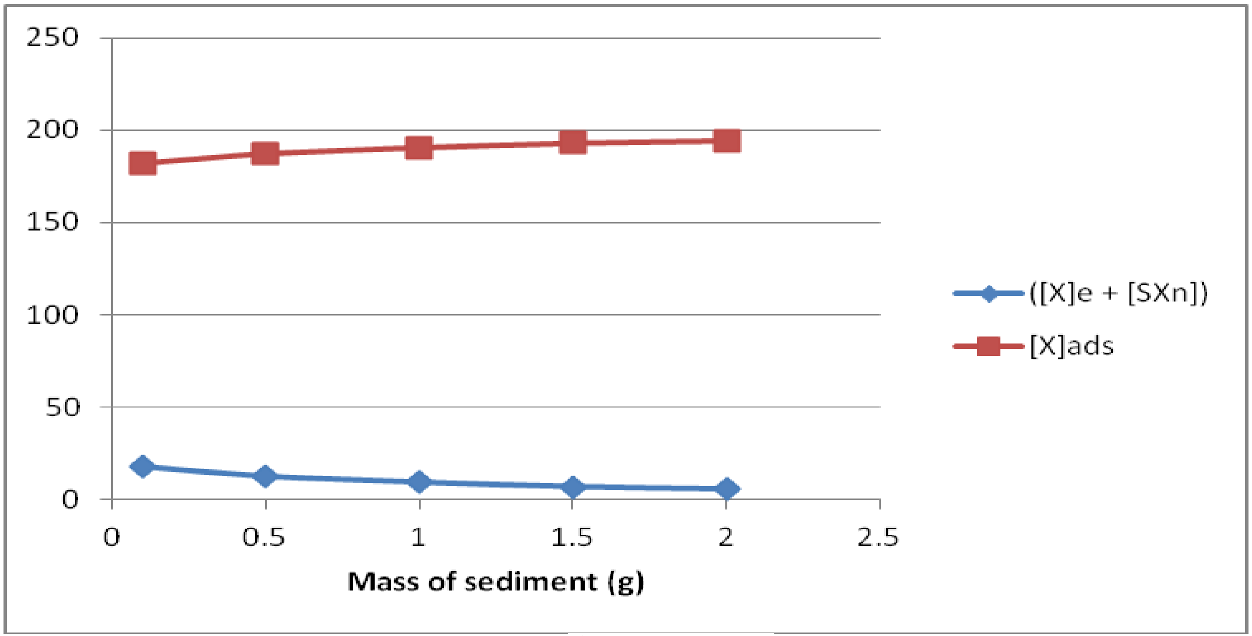
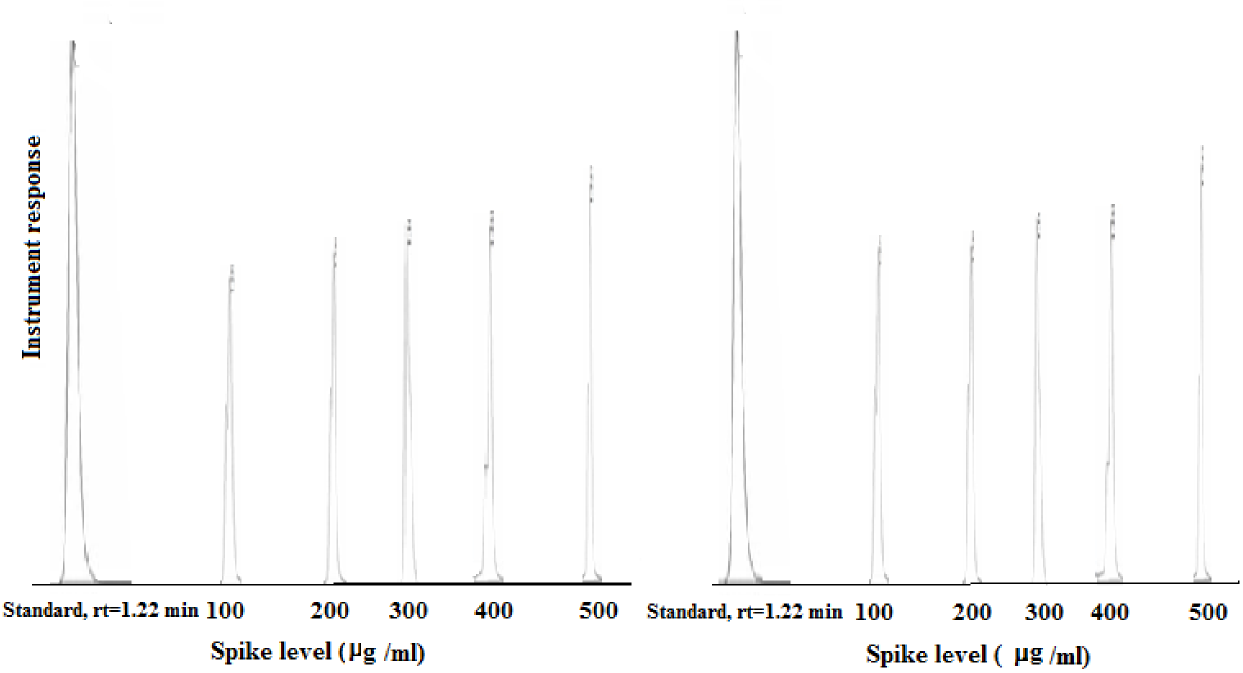


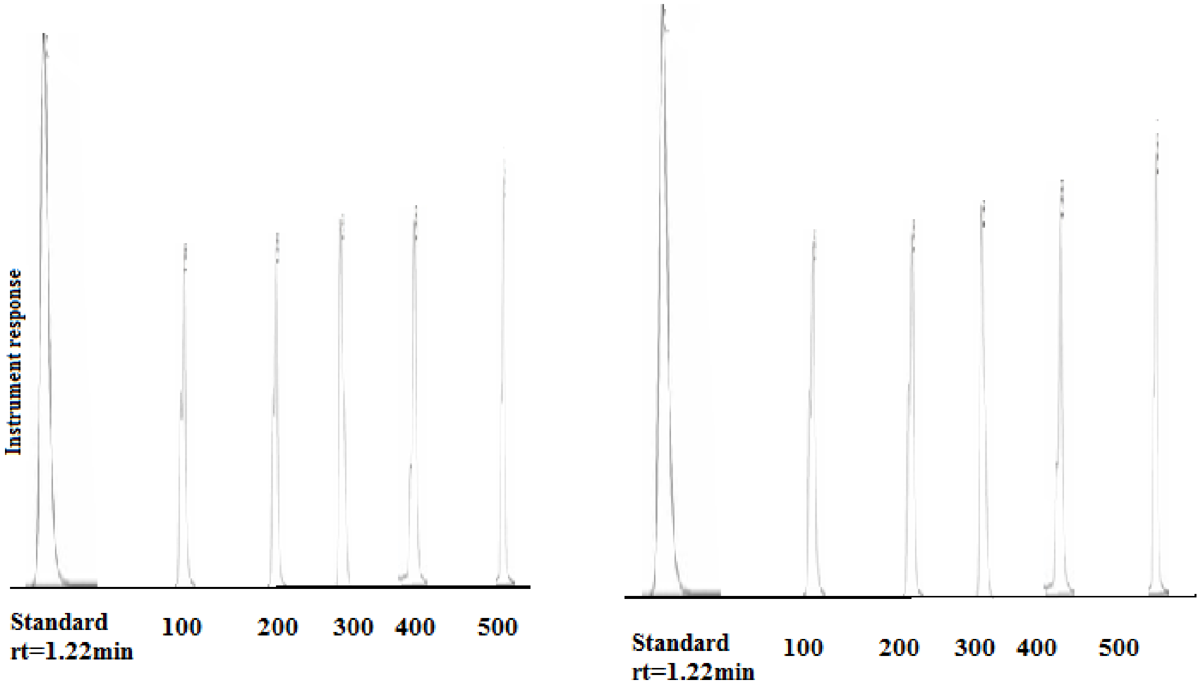
Figure 5: Adsorption of chlorothalonil by sediment: $([X]_e + [SX_n]_w)$ versus mass of sediment.

Similarly, spiking aqueous solutions with chlorothalonil, containing 0.5g sediments and equilibration at different times, gave chromatographic peaks which were dependent on spiking level and shaking periods (Fig. 6). The data shows that upon spiking, the levels of $[X]_{ads}$ increased at all spiking levels, reaching peak values within the first 15 min after which it starts to fall. It means the system reaches equilibrium within the first15 minutes after which the backward process (desorption) begins as is evidenced by the fact that after 30 min., the solution concentration of chlorothalonil ($[X]_e + [SX_n]_w$, (µg/ml), reaches peak values. This re-triggers the adsorption process and values of $[X]_{ads}$ begins to build up as the cycle repeats. Figure 6, gives a more indicative picture of this dependence of chlorothalonil adsorption on the spiking levels and equilibration time.



15 minutes

30 minutes



45 minutes

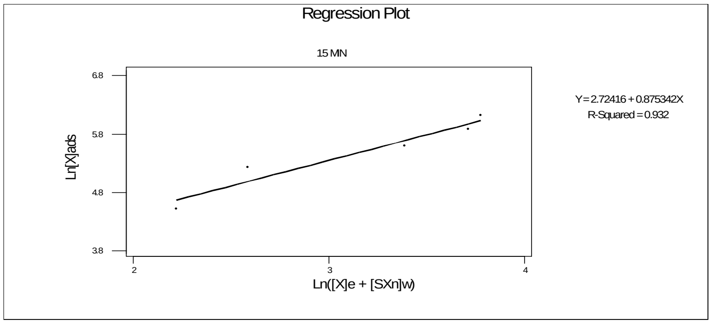
60 minutes

Figure 6: Typical chromatograms for standard solutions of chlorothalonil in water, equilibrated for different periods.

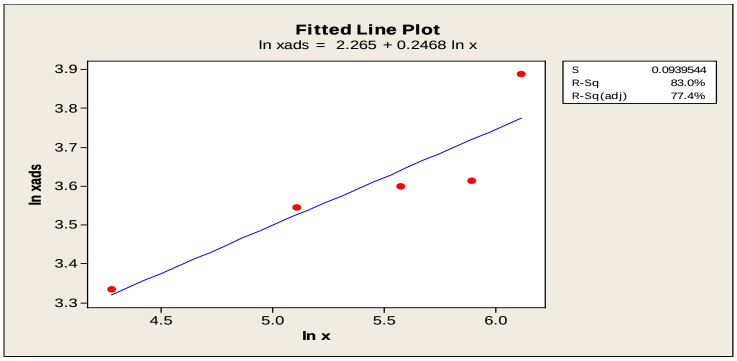
Table 3: Aqueous phase concentration of chlorothalonil following equilibration of 0.5g sediment aqueous suspension in water, spiked with different concentrations of chlorothalonil, for different periods.

Shaking time(min)	Spike level(μg/ml)	$[X]_e + [SX_n]_{w)}$ (μg/ml)	$[X]_{ads}$ (μg/ml)
15	100	9.20	90.8
	200	13.29	186.71
	300	29.59	270.41
	400	40.90	359.10
	500	43.56	456.44
30	100	32.59	67.41
	200	43.34	156.66
	300	47.78	252.22
	400	45.39	354.61
	500	48.02	451.98
45	100	22.07	77.93
	200	27.31	172.69
	300	31.84	268.16
	400	41.47	358.53
	500	46.53	453.47
60	100	34.95	65.05
	200	40.96	159.04
	300	42.54	257.46
	400	45.87	354.13
	500	47.23	452.77

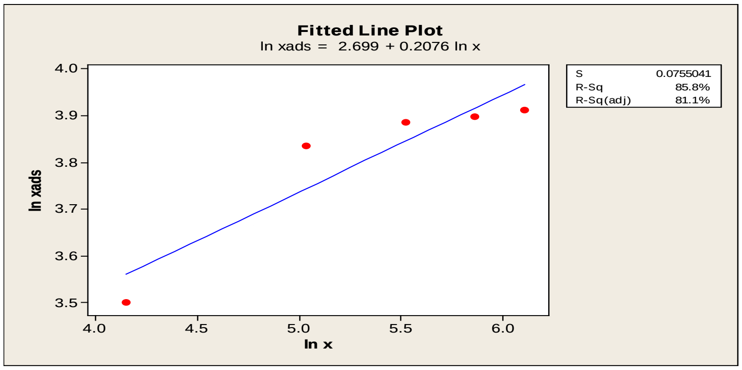
On applying equation 12 onto the data in Table 4, for 15, 30, 45 and 60 minutes shaking times and a 0.5 g sediment quantity, linear relationships were obtained. From the straight lines (Figure 7.), the values of n, the number of adsorbed molecules and the apparent equilibrium constants were estimated and collected in Table 5. In the linear plots, the y-intercept and the slope gave the values of ln (n$K^{'}$) and n respectively. Other thermodynamic data are also given in Table 5. An average value of the apparent equilibrium constant $K^{'}$ of 80.0124 was obtained. The values of $\Delta G^{'}$ calculated is -9.9 x 10^3 kJ/mol. The negative apparent Gibb's free energy value depicts a spontaneous adsorption process. Since the value is below 20 kJ/mol, expected for cases where strong interaction forces are involved, one may conclude that the adsorption of chlorothalonil in the sediments involves a physisorption process. The values of $K^{'}$ obtained for chlorothalonil differs slightly from that reported for amitraz [9]. Such differences may be attributed to the different chemical structures of the pesticide involved, differences in the nature of sediment particle and morphology of the sediment.



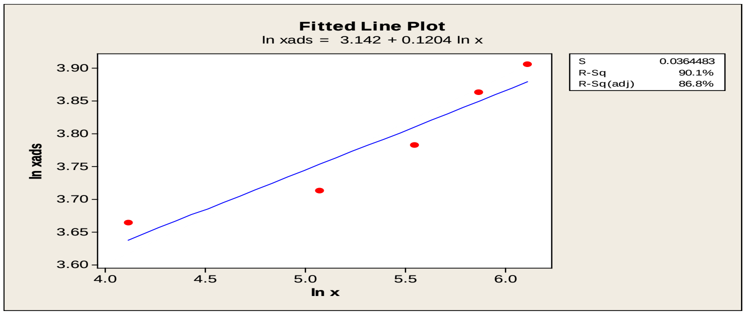
15 min



30 min



45 min



60 min

Figure 7: Adsorption of chlorothalonil by Nairobi river sediment: In[x]$_{ads}$ $_{versus}$ In [X]$_e$ + [SX$_n$]$_{w)}$ regression curves..

Table 4: Adsorption/desorption Parameters of Chlorothalonil by Nairobi river sediment.

Equilibration	n	ln(nK')	K'	ΔG (kJ/mole)
15	0.8753	2.724	17.145	$-7.040\text{x}10^3$
30	0.2468	2.265	39.024	$-9.078\text{x}10^3$
45	0.2076	2.699	71.603	$-10.583\text{x}10^3$
60	0.1204	3.142	192.012	$-13.030\text{x}10^3$
Mean			80.012	$-9.933\text{x}10^3$

As explained earlier, the exponent n is the number of pesticide molecules associated with a single adsorption site, S, to give the pesticide-site complex $SX_{n.}$ The value of n ranges from 0.854 at 15 min. equilibration time, to 0.1204 at 60 min equilibration time, suggesting that each molecule of chlorothalonil is initially associated with a single adsorption site, and that the number of adsorption sites increases up to 10 at 60 min equilibration time, possibly as a result of aggregation of colloidal particles about the pesticide molecule as a function of time. The major adsorption interactions which bind small organic molecules in the soil particles of colloidal dimensions range from 1nm to 1mm, according to Burchill et al., [10]. In addition, combining equations 9 and 10 we obtain equation 14 which gives the relationship between the apparent equilibrium constant, K', and the true equilibrium constant, K;

$$K' = K[X]_e / [X]_e + [SX_n]_w \text{.........................(14)}$$

It is apparent that the extent to which K' deviates from K depends on the value of $[SX_n]_w$ and the value of n.

Desorption is a special case of thermal dissociation, hence we can use transition state theory to obtain the apparent desorption rate constant, $k_d{}'$, in terms of the apparent adsorption/desorption equilibrium constant, K', thus [20]:

$$k'_d = \frac{k\,T}{h} K' \quad \text{…………………………..(15)}$$

where, k is the Boltzmann constant, T is the absolute temperature, and h is the planks constant.

The mean lifetime of a molecule of chlorothalonil in adsorbed state, is given by $1/k_d$ [21a]. Substitution of the appropriate values in equation 15 yields a value of $3.91\text{x}\ 10^{-12}$ s for the apparent lifetime of a molecule of chlorothalonil in the adsorbed state. Such apparent life time of the adsorbed state points to physisorption, rather than chemisorption for which room temperature lifetimes as long as 3000 s has been predicted [21b].

The value of K' is a measure of how tightly the pesticide binds/sticks to sediment particles. The greater the K' value, the less likely a chemical will leach or contribute to runoff. A very high value means it is strongly adsorbed onto soil and organic matter and does not move with the river running water. In this case, the sediment acts a sink for the pesticide residues and thus reduces the extent of pesticide contaminant down- stream. Pesticides are less likely to leach out or occur as surface runoff when the K' is greater than 5, as suggested by Burchill et. al. [10].

CONCLUSION

From the above experiments there is existence of adsorption/desorption processes of chlorothalonil by Nairobi river sediments. The adsorption of chlorothalonil onto suspended/dissolved particles decreases with increase in mass of the substrate (sediment). In this study, it was found out that several factors affect the chlorothalonil adsorption/desorption processes. These factors include the spiking levels, contact time amongst others. The longer the contact time the higher the rate of adsorption. A negative ΔG' was obtained in this study indicating a spontaneous adsorption process but at the same time the low free energy values indicates the chlrothalonil molecules were simply physisorbed onto the sediment adsorption sites. The high clay content coupled with the small amount of organic carbon in the sediment may account for the observed adsorbed chlorothalonil.

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COMPOSITIONAL AND STRUCTURAL CHARACTERIZATION OF INDIGENOUS SALTS IN KENYA: A CASE STUDY OF 'PARA', 'MAGADI' AND 'LEBEK' CRYSTALLINE SALTS.

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ABSTRACT

Compositional analysis was carried out on three indigenous basic salts from Lake Magadi, Shores of Lake Victoria and the Hot Springs of the Kerio Valley which are different parts of Kenya. All treatments were done in triplicate in complete randomized block design. Fresh and dry weights were recorded at the end of the experiment and analysed for K, Na, Ca, Mg, Co, Fe, Mn, Cu, Pb, Cd , Zn cations and CO_3^{2-}, and HCO_3^- anions. The three different indigenous basic salts are commonly refered as 'magadi', 'Para', and 'Lebek' respectively from the three areas. pH, quantitative and qualitative analysis was done using Atomic Absorption Spectroscopy, Flame Photometry, FTIR and the wet methods; Gravimetry and titrimetry. A wet digestion procedure was adopted to dissolve the salts. In general, the concentration of heavy metals in the salts followed the order: magadi; Fe > Co > Pb > Cd Mn> Zn > Cu; Para; Fe > Mn > Co > Zn> Pb > Cu>Cd; Lebek; Fe > Mn > Zn > Co> Cu > Pb>Cd. Sodium, Potassium and calcium content was found to be very high in all the samples. Sodium concentration was recorded to be 71.52 mg/g in 'Magadi', Potassium concentration was found to be 2.69 mg/g in 'Para', and calcium concentration was found to be 166.09 mg/g in 'Lebek'. Samples of 'Para' and 'Lebek', contained comparatively higher amounts of Fe as compared to 'magadi'. Lead is present in higher levels in all the samples than minimum levels. The pH values ranged from 9.98±0.01 to 11.26±0.03, an indication of the alkaline nature of these salts.

Key words: *Indigeneous salts; Composition; Characterisation; Heavy metals; Hydrolysis*

INTRODUCTION

Magadi, Para and Lebek are commonly used salts in several countries in East, West, and Central Africa homes (1,2). The main use of these indigenous salts is cooking tough food materials such as beans and maize utilising their ability to fasten the softening and the digestive property of the food. In addition , the salts are used as prophylactic agents and feed supplements to cattle and goats (1). In some places, 'magadi' is ground with tobacco in the preparation of snuff (*2*).

In in the alkaline lakes of Eastern Rift Valley, 'magadi' is formed in the crystalline form ($Na_2CO_3.NaHC0_3.2H_2O$), due to chemical weathering of rock minerals and high evaporation of the lake waters. Magadi is also formed, as the so-called scooped magadi, on the surface soil due to capillary evaporation of soil water (3).

Analyses of both crystalline and scooped magadi from Nigeria and Ghana have shown that crystalline magadi consists essentially of trona mixed with minor contents of halite (NaCl). The scooped magadi is rich in trona but it also contains admixtures of quartz, clays, chlorides, and sulphates (3,4).

The main objective of this study was to determine the differences in metallic ions (Zn, Li, Na, K, Ca, Mg, Pb, Cu, Mn, Cd, Co) and carbonate (CO_3^{2-} ,HCO_3^-) concentration in Magadi, Para and Lebek from the Eastern, Western, North Rift and Kendu-bay parts of Kenya. The differences in the mineralogical composition caused by the differences in structure will also be discussed.

EXPERIMENTAL

Instrumentation and wet chemistry methods of Analysis

Buck Scientific Model 210VGP Atomic Absorption Spectroscopy and Corning Flame 840 photometry were used to analyse the metallic ion composition of the salts. FTIR spectroscopy and potentiometry were used to identify the structure of each salt using carbonates and bicarbonates in them and measure pH respectively. Gravimetry and titrimetry were used for the quantification of CO_3^{2-} , HCO_3^- and pH measurement.

Sample Collection and Analysis

Magadi samples from Lake Magadi, ($n = 15$), Para samples from Kendu-bay at the shores of Lake Victoria ($n = 30$), Lebek samples from Kerio-valley ($n = 30$) and market places (n=3) were collected, packaged dry in paper bags and taken to the laboratory. In the laboratory ,each sample was crushed and homogenized in a mortar. About 10.00-20.00 grams of each salt sample was oven dried in a 100.00 mL beaker at a temperature of 110^{o}C for 2.0 hours. A triplicate mass of 2.000 grams of each of the cooled dried salt sample were weighed and dissolved in 100.00 mL beaker with 50.0 mL of de-ionized water. The solution was then filtered using Whatman filter paper No. 42 (5,6).

The pH of the clear filtrate was measured after which the filtrate solution was acidified with 1.0 mL 0.1M HNO_3 , placed into a 100.0 mL volumetric flask and filled to the mark with more de-ionized water. The solutions were corked and mixed thoroughly and were ready for metallic ions analysis using AAS and Flame photometry .

For quantification of CO_3^{2-} and HCO_3^- , a triplicate mass of 0.700 grams of each of the cooled dried salt sample was weighed and dissolved in 100.00mL beaker with 50.00mL of de-ionized water. The solution was then filtered using Whatman filter paper No. 42. The end point titration method according to the standard methods where the end point of pH = 4.5 was used. An aliquot of 5.00 ml of the magadi solutions (2.00 g/100.0 ml) was diluted to 50.0 ml and titrated automatically with 0.1 N HCl (3,4).The samples were categorized as**:**MS100 series, samples of mineral salts (‘Magadi’), PS200 series, samples of mineral salts (‘Para’), and LS300 series, samples of mineral salts (‘Lebek’)

Results and Discussion

From table 1.0, the pH values recorded for MS100, PS200 and LS300 oven dried were 11.26±0.03, 10.88±0.06 and 10.85±0.06 respectively. The pH values of non-oven dried samples were 9.98±0.01, 10.08±0.02 and 10.09±0.02 respectively for the three salt types. Magadi salt recorded the least pH in its raw form because of the acidic hydrogen in the CO-H bicarbonate. The large difference between oven dried and non-oven dried clearly indicates the decomposition and loss of most of acidic hydrogen during the drying stage, increasing the pH proportionately with HCO_3^-. Magadi salt had the highest amounts of hydrogen carbonates as compared to both para and lebek salts. These findings correlate well with earlier studies (7,8) which recorded similar observations of pH increase wherever HCO_3^- decomposed.

Table 1.0: The pH of the salts (1% wt/v solution)

Salt sample	Sample treatment	
	Oven dried (OD)	Non-oven dried
MS100	11.26±0.03	9.98±0.01
PS200	10.88±0.06	10.08±0.02
LS300	10.85±0.06	10.09±0.02

Functional group analysis of the salts using FTIR.

Figures one to three below show the functional group analysis of the salts using FTIR

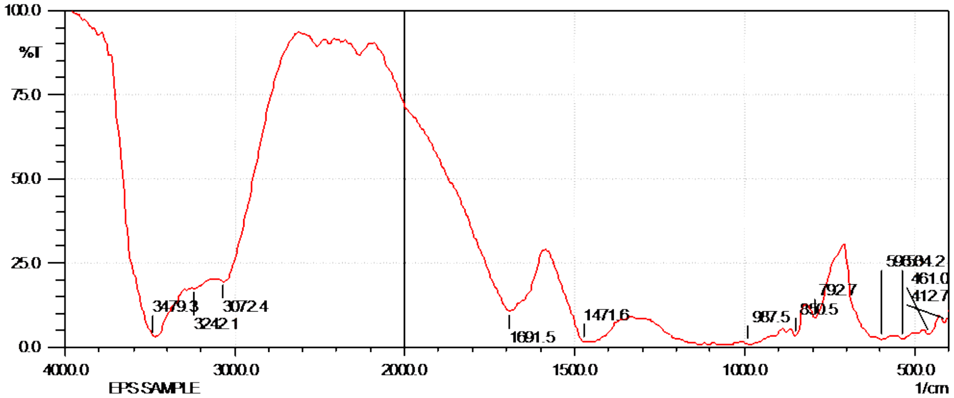

Figure 1: FTIR spectrum of PS200-salt

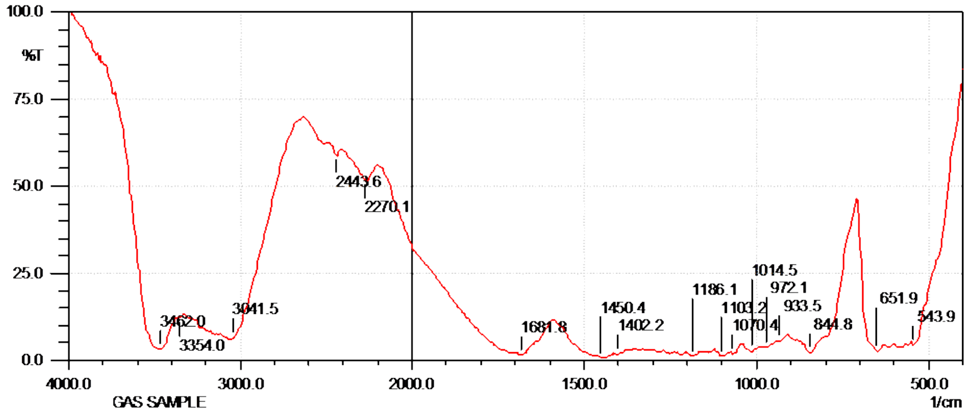

Figure 2: FTIR spectrum of MS100-salt

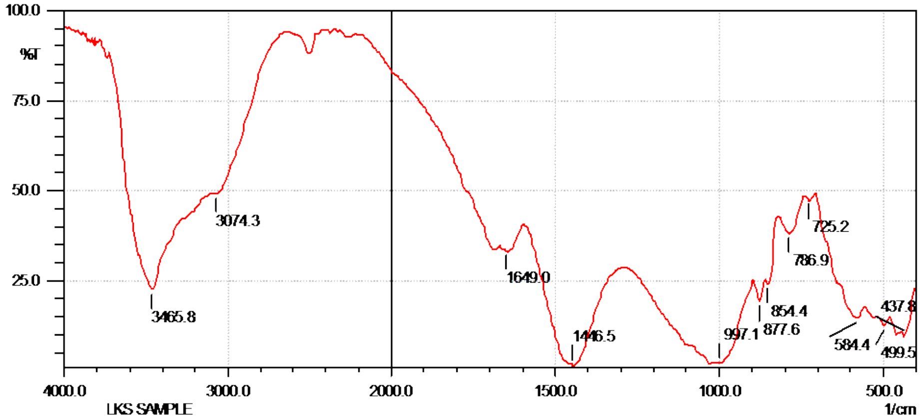

Figure 3: FTIR spectrum of LS300-salt

From figures one to three ,it was observed that all the salts showed FTIR major peaks at 3479-3482cm^{-1} , 1650-1690cm^{-1} and 950-1000 cm^{-1} ranges due to the –O-H , C=O and C-O stretches respectively. This is an indication of the presence of a carbonate and bicarbonate anions in the salts (9). The salts contain the two anions. This is in agreement with studies earlier done on metal carbonates and bi-carbonates. In the FTIR transmission spectra of metal bi-carbonate salts, bands for free HCO_3^- ion in aqueous solution were assigned as follows: stretching of C-OH at 1010 cm^{-1}, symmetric stretching of CO_2 at 1360 and 1310 cm^{-1}, asymmetric stretching of CO_2 at 1668 and 1605 cm^{-1}, and out-of-plane bending of CO_3^{2-} at 843 cm^{-1}. The rest of the fundamental vibration modes, (symmetric in-plane bending of CO_3^{2-}) and (asymmetric in-plane bending of CO_3^{2-}) should appear below 800 cm^{-1}, a spectral region which could not be observed. This is correlates well with earlier studies (7,8,10)

Major elements composition levels

Table 2 below shows the composition of alkali and alkaline earth metals in dry salt samples

Table 2.0: Composition in mg/g of alkali and alkaline earth metallic elements in dry salt

Samples	Alkali and Alkaline earth Metal Composition in mg/g				
	Na	K	Li	Ca	Mg
MS100	71.52±1.96	0.31±0.04	0.21±0.02	0.25±0.12	0.02±0.00
PS200	27.23±0.87	2.69±0.41	0.29±0.02	52.56±8.03	2.89±0.13
LS300	25.83±0.38	1.37±0.05	0.15±0.02	166.09±6.55	0.16±0.00

Sodium concentration in MS100, PS200 and LS300 salts was 71.52±1.96, 27.23±0.87 and 25.83±0.38 respectively. Most of the magadi minerals were sodium based. (11,12). LS300-salt had the highest Calcium concentration amounts with a mean concentration of 166.09±6.55 mg/g .This could be attributed to the calcite rock source from which the hot spring bines originate. This is in line with other studies done on Lake Brines in Africa (4, 13, 14). Potassium concentration in PS200-salt had the highest amounts with a mean concentration of 2.69±0.41 mg/g . The concentration of potassium ions in all the three salts was less than 3.00 mg/g. This is in line with studies done in Lake Magadi (11) and Lake Albert (7) which showed that potassium is in low concentration because of leaching during salt precipitations. Magnesium concentration in PS200-salt was highest amounts with a mean concentration of 2.89±0.13 mg/g .The concentration of magnesium ions in all the three salts was low, as compared to studies done in Lake Magadi (11). Lithium concentration in PS200-salt had the highest amounts with a mean concentration of 0.29±0.02 mg/g .These results were comparable to those obtained (5,15) and reported that this could be due to the trace nature of lithium in mineral rocks.

Major anions content

Table three below shows the percentage anionic radical content in dry salt samples.

Table 3.0: Percentage (%) Anionic radical Content wt/wt in dry salt sample

Samples	Anionic radicals Content % wt/wt		
	Carbonate CO_3^{2-}	Hydrogen carbonate HCO_3^{-}	Total Carbonate CO_3^{2-} & HCO_3^{-}
MS100	21.9±0.5	25.3±0.3	47.2±0.2
PS200	6.5±0.4	7.3±0.2	13.9±0.3
LS300	5.5±0.1	6.2±0.1	11.8±0.4

The percentage concentration of CO_3^{2-} ranged from 5.5±0.1% to 21.9±0.5%. MS100-salt recorded the highest percentage of total carbonate with a mean percent concentration of 47.2±0.2%, with the mean percent CO_3^{2-} of 21.9±0.5% and hydrogen carbonate (HCO_3^{2-}) 25.3±0.3%. PS200-salt recorded the second highest percentage of total carbonate (13.9±0.3%) of the salt samples analyzed; with the percent carbonate (CO_3^{2-}) being 6.5±0.4% and hydrogen carbonate (HCO_3^{2-}) 7.3±0.2%. LS300-salt recorded the third highest percentage of total carbonate (11.8±0.4%) of the salt samples analyzed; with the percent carbonate (CO_3^{2-}) being 5.5±0.1% and hydrogen carbonate (HCO_3^{2-}) 6.2±0.1%. This conforms to the earlier studies (11,15) which recorded similar results. This could be due to the fact that, the final major reaction that could influence the HCO_3^- contents in the deep aquifer is the addition in the system of CO_2 of deep origin (5,10).

Trace elemental content

Table four below shows the composition of trace metallic elements in dry salt samples.

Table 4.0: Composition in µg/g of trace metallic elements in dry salt samples

Samples	Trace Metallic elements in µg/g						
	Zn	Co	Cu	Pb	Cd	Fe	Mn
MS100	9.06±2.73	20.69±1.02	2.91±0.38	16.16±0.43	11.15±1.20	214.79±16.63	10.21±2.97
PS200	15.33±2.43	15.74±0.60	8.44±0.32	12.83±1.30	2.87±0.27	1650.63±133.89	396.90±35.72
LS300	23.01±3.09	20.49±1.49	10.07±1.04	9.50±1.37	2.24±0.15	5068.59±460.97	346.81±0.47

Iron concentration in LS300-salt had the highest amount with a mean concentration of 5068.6±461.0 µg/g. It was followed by PS200-salt with a mean concentration of 1650.6±133.9 µg/g, while MS100-salt had a mean concentration of 214.8±16.6 µg/g. The salts PS200 and LS300 showed quite significant amounts as compared to MS100. The same trend was reported (5,6), in which in which it was attributed to the salts rock of origin, clay rock which is rich in iron and manganese .

Manganese concentration in PS200-salt had the highest amount with a mean concentration of 396.90±35.72 µg/g. It was followed by LS300-salt with a mean concentration of 346.81±0.47 µg/g, while MS100-salt had a mean concentration of 10.21±2.97 µg/g. The salts PS200 and LS300 showed quite significant amounts as compared to MS100. These can be attributed to the salts rock of origin, (5,6).

Zinc concentrations in KS300-salt had the highest amount with a mean concentration of 23.01±3.09 µg/g .It was followed by PS200-salt with a mean concentration of 15.33±2.43 µg/g; while MS100-salt had a mean concentration of 9.06±2.73 µg/g. Zinc in the salts generally recorded substantial amounts considering its trace nature. These could be due to the rock source (15).

Lead concentrations in MS100-salt had the highest amount with a mean concentration of 16.16±0.43 µg/g). It was followed by PS200-salt with a mean concentration of 12.83±1.30 µg/g, while LS300-salt had a mean concentration of 9.50±1.37 µg/g. Lead levels in the salts falls beyond the normal minimum levels in residues. This was attributed to the underlying rock source, and the conditions of the underground brine fluids (14).

Copper concentration LS300-salt had the highest amount with a mean concentration of 10.07±1.04 µg/g . It was followed by PS200-salt with a mean concentration of 8.44±0.32 µg/g, while MS100-salt had a mean concentration of 2.91±0.38 µg/g. Copper levels in the salts falls beyond the reported values 4.0-6 µg/g in residues (5,6,15), which was attributed to the underlying rock source, and the conditions of the underground brine fluids.

Cadmium concentration in MS100-salt had the highest amount with a mean concentration of 11.15±1.20 µg/g . It was followed by PS200-salt had a mean concentration of 2.87±0.27 µg/g and LS300-salt had a mean concentration of 2.24±0.15 µg/g. Cadmium concentration levels in the salts falls within the normal minimum levels of 2-5 µg/g in residues for samples PS200 and LK300 but remained high in MS100 this correlates well by studies done earlier (6,13). This could be attributed to the underlying rock source, and the conditions of the underground brine fluids (14).

Cobalt concentration in MS100-salt had the highest amounts of Cobalt with a mean concentration of 20.69±1.02 µg/g (table 4.0), while LS300-salt had a mean concentration of 20.49±1.49 µg/g and PS200-salt had a mean concentration of 15.74±0.606 µg/g. Lead levels in the salts falls beyond the normal minimum levels 5-10 µg/g in residues as reported (16). This could be due to the underlying rock source, and the conditions of the underground brine fluids (14).

Conclusion

The three salts differ in their percent elemental compositional levels greatly (MS100 had 71.53 mg/g Na, and 0.25 mg/g Ca; PS200 had 27.23 mg/g Na and 52.56 mg/g Ca and LS300 had 25.83 mg/g Na and 166.09 mg/g Ca). The salts have the same carbonate and bi-carbonate structure which only differs in percent concentration levels (MS100 had 47.2%; PS200 had 13.9% and LS300 had 11.8% total carbonate).

Magadi salt is basically a sodium carbonate-sodium bi-carbonate. The bicarbonate content is slightly higher than the carbonate. Para and Lebek salts have small amounts of carbonates and bi-carbonate and they are more of calcium and iron salts. All the three salts were found to be alkaline salts with pH values greater than 9.8. FTIR spectra showed that all the three salts had bicarbonate in their structure.

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ASSESMENT OF THE EFFECTS OF TOBACCO FARMING ON SOIL NUTRIENTS IN MIGORI COUNTY, KENYA

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ABSTRACT

Assessment of heavy metal pollution due to tobacco farming: Cd, Pb, Co, Cu, Cr, Mn, Ni and Zn was conducted in Migori county, Kenya using Atomic Absorption Spectrometry (AAS). Grid sampling was employed in which 50 m^2 of land was randomly selected in each of two sampling areas and was divided into ten equally sized grid cells of 5 m^2. The study also investigated the effects of these heavy metals on the fertility indices of the soil such as PH, nitrogen, available nitrogen, phosphorous, available phosphorous and organic carbon. Data obtained was subjected to analysis of variance (ANOVA) and correlation analysis using the Pearson moment correlation coefficient technique. The mean concentrations of heavy metals was 14.5 µg/g for Pb, 9.2 µg/g for Cd, 99.7 µg/g for Zn, 33.4 µg/g for Cu, 25.0 µg/g for Cr, 43.6 µg/g for Ni and 14743 µg/g for Mn. The Contamination Factor revealed that the sites were moderately contaminated, the Pollution Load Index showed Mabera to be more contaminated with PLI = 1.15 while Masaba had 1 .05 and finally Geoaccumulation Index showed the two regions to be moderately contaminated. Significantly positive correlation was found to exist between nitrogen, potassium, total organic matter, nitrates and total phosphorus at P = 0.01. Significantly positive correlation was also found to exist between lead and nitrogen; nitrates and copper; chromium and cobalt; potassium and manganese, TOC; nitrogen and nitrates, TOC and total phosphorus. Chromium and zinc; manganese and total phosphorous, TOC; potassium and total phosphorous. The findings in this study will serve to create awareness of the extent of heavy metal pollution to Kenyan policy makers in the mitigation of heavy metal pollution, as it is barely monitored.

Key words: *Heavy Metal Contamination, Soil Fertility, Migori County, Contamination Factor (CF), Pollution Load Index(PLI), Geoaccumulation Index (Igeo), Total Organic Carbon (TOC)*

INTRODUCTION

The metals found in the environment come from natural weathering process of earth's crust, soil erosion, mining, industrial discharge, urban runoff, sewage effluents, air pollution fallout and pest or disease control agents. Over recent decades an annual worldwide release of heavy metals reached 22,000 T (metric ton) for cadmium, 939,000 T for copper, 783,000 T for lead and 1,350,000 T for zinc (1). Elemental pollutants are particularly difficult to remediate from soil, water, and air because, unlike organic pollutants that can be degraded to harmless small molecules, toxic elements such as mercury, arsenic, cadmium, lead, copper, and zinc are immutable by all biochemical reactions and hence remain in ecosystem (2).

Heavy metals namely; aluminium (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) are the major environmental pollutants and their phyto-toxicitty is well established (3). Bio-concentrations of heavy metals in agricultural, horticultural plants, weeds and in aquatic macrophytes are of great concern to human life. Hence heavy metal pollution is gaining importance. The ingestion of heavy metals via food intake is an important non-occupational source of human exposure to toxic metals. The amount of metals taken in via this pathway varies from food to food, since various plants accumulate heavy metals at different levels. Food plants that tolerate relatively high concentration of potentially hazardous metals are likely to create a greater health risk than those that are more sensitive and show definite symptoms of toxicity.

A precise knowledge of heavy metals concentration and the forms in which they are found, their dependence on soil's physico-chemical properties provide a basis for careful soil management, which will limit as far as possible, the negative impact of heavy metals on the ecosystem (4). The concentrations of heavy metals in soil solution depend on the equilibrium between soil solution and the solid phase, with pH playing a decisive role (5). In addition to pH, other soil key parameters such as cation exchange capacity, organic matter content, quantity and type of clay minerals, oxides of Fe, Al and Mn; and the redox potential of the soil, all play various roles in determining the soil's ability to retain and immobilize heavy metals. These heavy metals may adversely affect the soil eco-system safety, not only agricultural product and water quality, but also the human health (6).

Heavy metals tend to form complexes with organic matter in the soils which are different for each metal. In addition to forming complexes, organic matter also retain them in exchangeable forms. These two properties affect each heavy metal differently. For example copper is bound and made unavailable chiefly through the formation of complexes, while cadmium is retained in an exchangeable form and is more readily available (4). The paper discusses the effects of heavy metals on the fertility indices of the soil.

EXPERIMENTAL

The Study Area (Location and Environment)

The area chosen for study was Southern Nyanza, about 400 km South West of Nairobi. The area covers Migori County (Figure 1) which is located in south western Kenya, along Lake Victoria region (7). The altitude is roughly 1500 meters above sea level. The soils are well drained and tending to loamy. This favors the cultivation of tobacco.

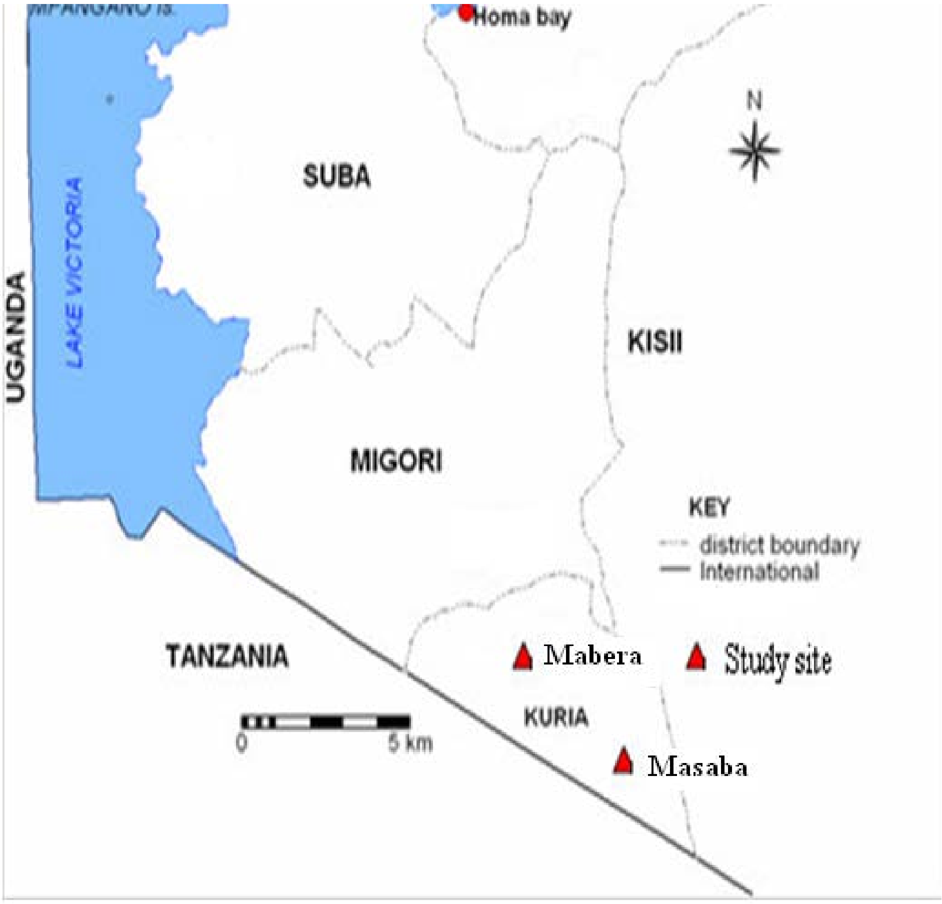


Figure 1: Study area sites in Southern Nyanza. Source: Adapted from (7).

Sample Collection

There were two sampling fields, one in Mabera and another from Masaba. Eleven samples were taken from each field. Nine of the samples were from spots where tobacco was planted while two were from a virgin land. Grid sampling (8) was employed in which 50 m^2 of land was randomly selected in each of the two sampling areas and was divided into ten equally sized grid cells of 5 m^2. Using a soil auger, 15-20 cores (a core is an individual boring or coring at one spot in the field) were collected at random. Testing of soil was done in August before planting and February after harvesting. The method was chosen due to its uniform soil characteristics. The cores were collected from between the rows of row crops. Samples were collected from the surface layer to a depth of 6 inches. The cores were mixed thoroughly in a clean plastic pail which formed a composite sample. The sample boxes or bags were filled to the fill line (9). All samples were kept cool until delivered to the soil testing laboratory at Jomo Kenyatta University of Agriculture and Technology. Tobacco seedlings were planted on sites where soil was tested; the two leaves close to the shoot were collected every month for testing until the crop was harvested. Such a strategy was adopted since heavy metals tend to accumulate more on the active sites of a plant (8).

Laboratory Analyses

Six parameters affecting fertility were determined namely; total organic carbon; available phosphorus; nitrates; potassium; total nitrogen; electrical conductivity and pH. In addition eight heavy metals namely lead, copper, cadmium, nickel, cobalt, manganese, zinc and chromium were analyzed. Organic carbon was determined using the Degtjaroff Method (10). Phosphorus (P) content determination was done using the colorimeter method using sodium hydrogen carbonate extraction (8). The total nitrogen was determined using the Kjeldal Method while pH was determined using 1:2.5 $CaCl_2$ dilution method (8). The double acid digestion technique was used in sample extraction using HCl and HNO_3 to digest the soils for heavy metals analysis. The concentration of the metals was determined using Shimadzu Spectrophotometer (Model, UV – 1800). The instrument was set up at a wavelength for each analyte; Cu (324.7 nm); Cd (228.8 nm); Zn (334.5 nm); Ni (341.5 nm); Co (345.35 nm); Mn (280.11 nm); Cr (425.55 nm) and Pb (217.0 nm).

RESULTS AND DISCUSSION

The mean values, standard error of mean (SEM) for the selected physicochemical properties and the concentration of basic fertility elements of the surface soil for the tobacco fields in the two localities used in this study are shown in Tables 1 below.

Table 1: Phytochemical properties of soils from Migori County, n = 3

Field No/ID---2012	MABERA	MABERA CONTROL	AMASABA CONTROL	MASABA
pH- H_2O (2:5)	6.10	6.70	6.60	6.10
Ec-H_20 (2:5)	0.01	0.12	0.12	0.11
% N (total)	0.20	0.23	0.20	0.17
% P (total)	0.48	0.72	0.56	0.46
% p (Avail.)	0.45	0.56	0.11	0.07
Ppm NO_3^-	2.02	3.30	1.34	0.26
% K	0.20	0.80	0.67	0.23
% TOC	0.02	0.04	0.04	0.03

The pH values ranged from 6.10 – 6.70 for the soil at Mabera locality and 6.10 - 6.60 for the surface soil at Masaba locality. The electrical conductivity values ranged from 0.01 – 0.12 mmho/cm showing the fields to be non saline (11). The organic carbon present was higher for the two control sites which had never been cultivated with the values of 0.04 %, the cultivated fields of Masaba and Mabera had 0.03 % and 0.02 % respectively. The nitrogen content for the sites ranged from 0.17 % to 0.23 %. For the subsoil considering the carbon and total nitrogen values, the nitrogen: carbon ratio ranged from 5 for the Masaba control to 10 at Mabera. The mean concentrations of heavy metal in soils after harvesting of tobacco is shown in table 2 below.

Table 2 The mean concentrations (in µg/g) of heavy metal in soils after harvesting of tobacco, n = 3

Locality	Pb	Cd	Cr	Zn	Ni	Cu	Co	Mn
Mabera	36.03 ± 0.00	9.02 ± 0.01	32.77 ± 0.014	48.92 ± 0.08	33.50 ± 0.01	26.14 ± 0.00	36.03 ± 0.00	14761.5 ± 0.01
Masaba	31.00 ± 0.07	8.33 ± 0.01	38.90 ± 0.01	58.37 ± 0.00	42.70 ± 0.02	21.09 ± 0.04	47.00 ± 0.01	14743.5 ± 0.08

The values obtained suggest that the pH of the soil samples were slightly acidic. The pH values obtained showed cultivated sites to be slightly higher than that of the uncultivated. This means that the tobacco planted fields are slightly more acidic than the uncultivated soil. The soil net ability to hold nutrients and water is higher with increasing pH. This is especially true with soils with high organic matter content and also certain types of clays. The values for potassium are less than the 0.2 mol/kg soil values (12). The soil pH, organic carbon, total nitrogen, carbon: nitrogen ratio, available phosphorus, exchangeable and potassium, all declined after cultivation of tobacco. With the low to moderate fertility status of the studied soils, amelioration of the physicochemical properties of the soil and fertilization especially with nitrogen and potassium carriers are necessary to boost crop production.

Assessment of metal contamination

Contamination Factor (CF)

The level of contamination of soil by metal is expressed in terms of a contamination factor (CF) calculated as, (13)

$$CF = (C_m \text{ Sample}/C_m \text{ Background})$$

where C_m Sample is the concentration of the samples while C_m background is the concentration of the control sites.

Table 4 Contamination factors for heavy metals in soils for each sampled zone.

	Cd	Pb	Cr	Zn	Mn	Ni	Cu	Co
Masaba	1.50	1.30	0.76	1.02	0.87	0.86	1.30	1.02
Mabera	1.50	1.60	0.64	0.98	1.02	0.95	1.50	1.34

where the contamination factor CF < 1 refers to low contamination; $1 \leq CF < 3$ means moderate contamination; $3 \leq CF \leq 6$ indicates considerable contamination and CF > 6 indicates very high contamination. From table 4 above, the two sites range from low to moderate contamination

Pollution Load Index(PLI)

Each site was evaluated for the extent of metal pollution by employing the method based on the pollution load index (PLI),

$$PLI = (CF_1 \times CF_2 \times CF_3 \times CF_4 \ldots CFn)^{1/8}$$

$$\text{Mabera, } (1.5 \times 1.6 \times 0.64 \times 0.98 \times 1.02 \times 0.95 \times 1.5 \times 1.34)^{1/8} = 1.16$$

$$\text{Masaba, } (1.5 \times 1.3 \times 0.76 \times 1.02 \times 0.87 \times 0.86 \times 1.3 \times 1.02)^{1/8} = 1.05$$

where *n* is the number of metals studied (eight in this study) and *CF* is the contamination factor calculated. This type of measure has however been defined by some authors in several ways, for example, as the numerical sum of eight specific contamination factors whereas, (14) assessed the site quality as the arithmetic mean of the analysed pollutants. In this study, the authors found it appropriate to express the *PLI* as the geometric mean of the studied pollutants since this method tends to reduce the outliers, which might bias the reported result. The PLI provides simple but comparative means for assessing a site quality, where a value of PLI < 1 denote perfection; PLI = 1 present that only baseline levels of pollutants are present and PLI > 1 would indicate deterioration of site quality (15).

To effectively compare whether the two stations suffer contamination or not, the pollution load index, PLI, was used. The PLI was aimed at providing a measure of the degree of overall contamination at a sampling site. Based on the results presented above, Mabera is more contaminated with a PLI of 1.16 than Masaba which has a PLI of 1.05. The two sites show strong signs of pollution or deterioration of site quality since their PLI is > 1 (15). Relatively high PLI values suggest input from anthropogenic sources attributed to increased human activities

Geoaccumulation Index (Igeo)

Enrichment of metal concentration above baseline concentrations was calculated using Geoaccumulation Index *(I*geo*)* (16). This method assesses the metal pollution in terms of seven (0 - 6) enrichment classes ranging from background concentration to very heavily polluted, as follows:

$$\text{Sample} = \log_2 (C_m \text{ of sample} / 1.5 \times C_m \text{ Background})$$

The factor 1.5 is introduced in this equation to minimise the effect of possible variations in the background values, *C*m Background, which may be attributed to lithogenic variations in soils. Table 5 below shows the *I*geo values from Masaba and Mabera

Table 5 *I*geo values from Masaba and Mabera

	Cd	Pb	Cr	Zn	Mn	Ni	Cu	Co
Masaba	0.000	-0.19	-0.9	-0.55	-0.78	-0.8	-0.16	-0.55
Mabera	0.000	-0.15	-1.22	-0.6	-0.54	-0.6	-0.2	-0.16

The seven proposed descriptive classes for *I*geo values are given in table 6 below (16).

Table 6 The *I*geo classes with respect to soil quality.

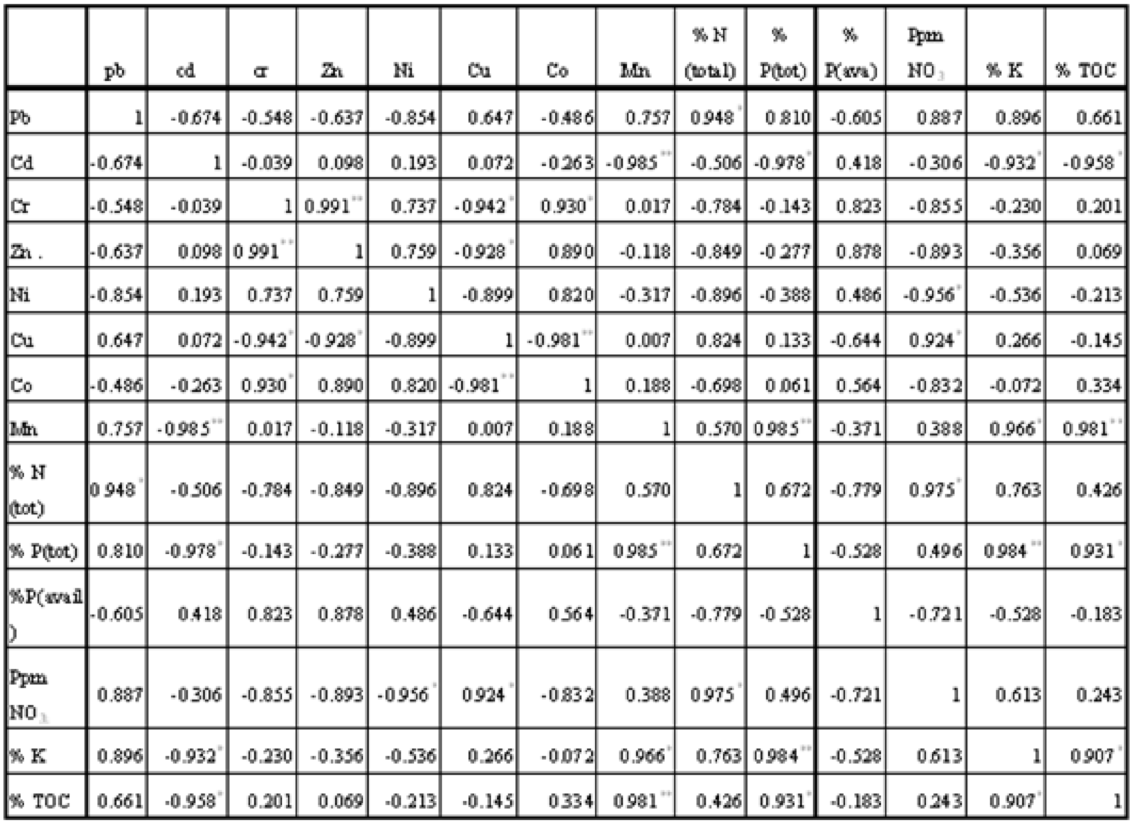
Igeo value	**Igeoclass**	**Designation of soil quality**
> 5	6	Extremely contaminated
4 - 5	5	Strongly to extremely contaminated
3 - 4	4	Strongly contaminated
2 - 3	3	Moderately to strongly contaminated
1 - 2	2	Moderately contaminated
0 - 1	1	Uncontaminated to moderately contaminated
0	0	Uncontaminated

The calculated geoaccumulation (*I*geo) values are presented in table 5. It is evident that the regions are uncontaminated *I*geo value of <0 is observed. As revealed from the three pollution assessment methods; *I*geo showed the sites to be uncontaminated, PLI revealed strong signs of pollution or deterioration of site quality since their PLI is > 1(15), and CF confirmed that the two sites range from low contamination to moderately contaminated.

Statistical Techniques

The data obtained was subjected to correlation analysis using the Pearson moment correlation coefficient technique as is found in the Statistics for Physical and Social Sciences (SPSS 11) software package and the results are shown in table 7

Table 7: Correlation between and among heavy metals and fertility indices



	pb	cd	cr	Zn	Ni	Cu	Co	Mn	% N (total)	% P(tot)	% P(ava)	Ppm NO$_3$	% K	% TOC
Pb	1	-0.674	-0.548	-0.637	-0.854	0.647	-0.486	0.757	0.948*	0.810	-0.605	0.887	0.896	0.661
Cd	-0.674	1	-0.039	0.098	0.193	0.072	-0.263	-0.985**	-0.506	-0.978*	0.418	-0.306	-0.932*	-0.958*
Cr	-0.548	-0.039	1	0.991**	0.737	-0.942*	0.930*	0.017	-0.784	-0.143	0.823	-0.855	-0.230	0.201
Zn .	-0.637	0.098	0.991**	1	0.759	-0.928*	0.890	-0.118	-0.849	-0.277	0.878	-0.893	-0.356	0.069
Ni	-0.854	0.193	0.737	0.759	1	-0.899	0.820	-0.317	-0.896	-0.388	0.486	-0.956*	-0.536	-0.213
Cu	0.647	0.072	-0.942*	-0.928*	-0.899	1	-0.981**	0.007	0.824	0.133	-0.644	0.924*	0.266	-0.145
Co	-0.486	-0.263	0.930*	0.890	0.820	-0.981**	1	0.188	-0.698	0.061	0.564	-0.832	-0.072	0.334
Mn	0.757	-0.985**	0.017	-0.118	-0.317	0.007	0.188	1	0.570	0.985**	-0.371	0.388	0.966*	0.981**
% N (tot)	0.948*	-0.506	-0.784	-0.849	-0.896	0.824	-0.698	0.570	1	0.672	-0.779	0.975*	0.763	0.426
% P(tot)	0.810	-0.978*	-0.143	-0.277	-0.388	0.133	0.061	0.985**	0.672	1	-0.528	0.496	0.984**	0.931*
%P(avail)	-0.605	0.418	0.823	0.878	0.486	-0.644	0.564	-0.371	-0.779	-0.528	1	-0.721	-0.528	-0.183
Ppm NO$_3$	0.887	-0.306	-0.855	-0.893	-0.956*	0.924*	-0.832	0.388	0.975*	0.496	-0.721	1	0.613	0.243
% K	0.896	-0.932*	-0.230	-0.356	-0.536	0.266	-0.072	0.966*	0.763	0.984**	-0.528	0.613	1	0.907*
% TOC	0.661	-0.958*	0.201	0.069	-0.213	-0.145	0.334	0.981**	0.426	0.931*	-0.183	0.243	0.907*	1

*Significant at 0.05 ** Significant at 0.01

Table 7 shows the correlation between some of the fertility indices and the heavy metals on one hand; and among the metals and fertility indices themselves on the other. Correlation was tested at two levels, P = 0.01 and P = 0.05. The values are considered for the two sampling areas in bulk. Significantly positive correlation was found to exist between nitrogen, potassium, total organic matter, nitrates and total phosphorus at P = 0.01. Significantly positive correlation was also found to exist between lead and nitrogen; nitrates and copper; chromium and cobalt; potassium and manganese, TOC; nitrogen and nitrates, TOC and total phosphorus. Chromium and zinc; manganese and total phosphorous, TOC; potassium and total phosphorous. Correlation between total phosphorous and organic matter, organic matter and potassium and phosphorus has been established by so many researches and documented works. Significantly positive relationship has been shown by the works of (17, 18) at the Sokoto-Rima valley. It has also been asserted by (19) that organic matter is an important source of soil nitrogen and phosphorus while (20) has shown that the contribution of organic matter to the CEC of soil is several times higher than that of clay, per unit weight. The impact of the heavy metal concentration on the soil fertility is very significant, so far. The correlation was found to exist between lead and nitrogen; chromium and cobalt; copper and nitrates; chromium and zinc; manganese and TOC, potassium and total phosphorous both at P = 0.05 and P = 0.01. The greater impact could probably be attributed to the much high concentration of the metals in the soil. The work of (21) has shown that at much higher concentration (0.2 –1.0 mg/kg for Cd, 15

– 25 mg/kg for Pb and Cu) and much higher CEC (30 – 35 cmol/kg); heavy metals such as copper and zinc have been shown to affect the concentration of beneficial metal such as calcium and magnesium. Their works also has however not established any relationship between lead and organic matter. The significant relations shown by lead to nitrogen is an indicator of the masking effect the former could have on the latter as shown by (22), much like the relationship shown by copper and lead to phosphorous . The ability of these metals to form complexes with other ions at certain pH has already been shown by various authors (22, 23, 4). The high concentration of phosphorus in the soil has encouraged presumably, the formation of phosphate of lead and copper which may probably explain the correlation shown by these two metals to phosphorus.

Conclusion

It was concluded that heavy metals contamination in soil is moderate. Solubility of these contaminants plays a vital role in their availability to plants; hence toxicity is also affected by solubility. The values obtained suggest that the pH of the soil samples were slightly acidic ranging between 6.1 and 6.7. The pH values for cultivated sites were slightly higher than those of the uncultivated sites. This means that the tobacco planted fields are slightly more acidic than the uncultivated soil. The soil net ability to hold nutrients and water is higher with increasing pH.

The results obtained in the study showed that the soil supporting the growth of tobacco in these localities were slightly acidic, and low in carbon content, nitrogen and phosphorus. The concentrations of available phosphorus is low when compared with the values that have been considered optimal for tobacco cultivation. The soil pH, organic carbon, total nitrogen, carbon: nitrogen ratio, available phosphorus, exchangeable and potassium, all declined after cultivation of tobacco.

4.2 Recommendations

With the low to moderate fertility status of the studied soils, amelioration of the physicochemical properties of the soil and fertilization especially with nitrogen and potassium carriers are necessary to boost crop production.

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RATE OF UPTAKE OF CADMIUM, CHROMIUM, LEAD AND ZINC IONS BY ROOTS, STEMS AND LEAVES OF DIFFERENT *IPOMOEA BATATAS* PLANT VARIETIES UNDER *IN VITRO CONDITIONS*

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ABSTRACT

Five sweet potato plant varieties grown in water solutions, containing varying amount of metal ions (Cd, Zn, Pb and Cr), demonstrated different rates of up take of the ions and distribution in leaves, roots and stems. Cadmium hydroponics exhibited high rates of metal intake into sweet potato plant varieties and could not tolerate concentrations exceeding 20 ppm of Cadmium. The five sweet potato plant varieties were Up-A, UP-B, UP-C, UP-D and UP-16. The rates of metal ion uptake increased with the increase in initial metal ion concentration of the hydroponics, but were independent of the amount of leaves, roots and stems. Overall, for the four metal ions and the five varieties considered, the lowest rates were recorded in leaves, whereas the highest rates were registered by roots or stems. For example, in case of 10 ppm Cd^{2+} ions solutions, the rates for the uptake by leaves, roots and stems increased as follows UP-B<UP-C<UP-16<UP-D<UP-A; UP-A<UP-D<UP-B<UP-16<UP-C; UP-C<UP-B<UP-D<UP-16<UP-A, respectively. Similar behavior was observed for other hydroponics containing different metal ions. This research work demonstrated ability of the sweet potato (SP) varieties to absorb and translocate heavy metal to roots, stems and leaves. The sp exhibited phyto-filtration (rhizofiltration) process, capable of cleaning up an environment contaminated with heavy metal pollutants. The rate of heavy metal uptake can be used to determine the plant varieties that are suitable to absorb high amounts of metal ions within a short time.

INTRODUCTION

Pollution of the biosphere with toxic metals has accelerated with increase in industrialization. The primary sources of this pollution include burning of fossil fuels, mining, municipal wastes, fertilizers, pesticides and sewerage (Kabata and Pendias, 1989). Toxic metal contamination of soil, streams and ground water pose a major environmental and human health problem. There is a need for an effective and affordable method for the removal or reducing the toxic metals from environment. Various physical, chemical and biological processes are already in use to remediate contaminated soil. These processes either decontaminate the soil or 'stabilize' the pollutant within it (Cunningham *et al.*, 1995).

Plants can be used for environmental remediation through a promising environmental technology called phytoremediation. Phytoremediation is defined as the use of green plants to remove pollutants from the environment or to render them harmless (Raskin *et al.*, 1997). All plants have the ability to accumulate metal ions which are essential for growth and development from soil and water. These metals include Fe, Mn, Zn, Cu, Mg, Mo and possibly Ni. Certain plants also have the ability to accumulate heavy metals which have no known biological functions which include Cd, Cr, Pb, Co, Ag, and Hg (Baker and brooks, 1989; Raskin *et al.*, 1994).

Sweet potato (*Ipomoea batatas*) is a hardy stress-tolerant, fast growing plant that grows well in almost every part of eastern and central Africa. It has an extensive, branching root system that is well suited for phytoremediation application. Sweet potato plant is tuberous rooted perennial, usually grown as annual herbaceous, stems forming a running vine up to 4m long. It is usually prostrate and slender, with milky juice, lateral stem and branches arising from the short term and usually not branched. The current study is intended to investigate the rate of uptake of selected heavy metals in different varieties of sweet potato plant (*Ipomoea batatas*) sub immersed in heavy metal ion containing solutions. The heavy metals selected for this study include cadmium, chromium, lead and zinc.

There are different mechanisms of heavy metal ion uptake by plants. These include phytoextraction, phytofiltration (rhizofiltration**)** and phytostabilization. In case of Phytoextraction process, the optimum plant for the Phytoextraction process should be able to tolerate and accumulate high levels of heavy metals in its harvestable parts as well as having a rapid growth rate and the potential to produce a high biomass in the field (Salt *et al.*, 1995). The high biomass metal accumulating plants and appropriate soil amendments are used to transport and concentrate metals from the soil into the above ground shoots (Raskin *et al.*, 1997). Phyto filtration (rhizofiltration**)** process takes place in the soil immediately surrounding plant roots which absorb, precipitate and concentrate toxic metals from polluted effluents (Dushenkov *et al.*, 1995). An ideal plant for rhizofiltration should have rapidly growing roots with the ability to remove toxic metals from solution over extended period of time. On the other hand, Phyto-stabilization process involves a case whereby heavy metal tolerant plants are used to reduce the mobility of heavy metals, thereby reducing the risk of further environmental degradation by leaching into the ground water or by air borne spread. A good phytostabilizing plant should tolerate high levels of heavy metals and immobilize these metals in the soil via root uptake, precipitation or reduction. The plants produce chemical compounds to immobilize contaminants at the interface of roots and soil (Raskin *et al.*, 1997).

The rate of uptake of the heavy metal ions was determined by dividing the heavy metal content accumulated in the plant parts (roots, stems and leaves) by the number of days in which the plant varieties were submersed in aqueous solutions.

METHODOLOGY

Apparatus and Equipments

Portable conductivity meter model H1991300 (Hanna Instruments) was used to measure conductivity in µS/cm with a range of 0-3999, temperature in ^{o}C with a range of 0-60^{o}C and pH with a range of 0.00-14.00. Analytical balance model Sartorius 2463 (±0.001g) was used to weigh standard salts, dry plant parts and soil samples.

Sweet potatoes varieties

Five different sweet plant varieties, namely UP-A, UP-B, UP-C, UP-D and UP-16, were obtained locally and the cuttings planted in the Chiromo gardens, where they were grown for six months.

Chemicals

Both analytical and general purpose reagents were used in the study, depending on the required analytical work. The analytical grade reagents used were concentrated nitric acid, hydrochloric acid and perchloric acid (Fluka Chemeka Switzerland). Standard solutions used for Atomic Absorption Spectroscopy (AAS, Shimadzu AA-6300) analysis of cadmium, zinc, lead and chromium ions were obtained from Spectrosol BDH chemicals ltd Poole England in 1000ppm stock solutions.

Calibration solutions

The standard calibration solutions used for conductivity measurements, 1413 µS/cm at 25°C, were from Hanna Instruments. For pH calibration, standard buffer solution of pH of 7.01 at 25°C was first used, followed by pH 4.01 buffer solutions at 25°C. The general purpose grade reagents included hydrated cadmium nitrate, hydrated zinc nitrate, lead nitrate and potassium dichromate, which were supplied by different manufacturers highlighted below.

Laboratory preparation of standard heavy metal solutions

Stock solutions

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

Preparation of cadmium (Cd^{2+}) ion solution

$Cd(NO_3)_2.4H_2O$ reagent was obtained from Fluka Chemeka Switzerland with purity of 99% and molecular weight of 308.47. The cadmium ions stock solution was prepared by weighing accurately 2.7721g of $Cd(NO_3)_2.4H_2O$ and placing in a 1000ml volumetric flask. Distilled water was then added while shaking the mixture up to the 1L mark to make 1000ppm solution of cadmium ions. The prepared solution was stored in 1 L plastic container.

Preparation of zinc (Zn^{2+}) ion solution

$Zn(NO_3)_2.6H_2O$ reagent was obtained from LOBA Chemie PVT LTD Mumbai, India. Its purity was 99% with molecular weight of 297.48. The zinc ions stock solution was prepared by weighing accurately 4.5960g of $Zn(NO_3)_2.6H_2O$ and placing in a 1000ml volumetric flask. Distilled water was then added while shaking the mixture up to the 1L mark to make 1000ppm solution of zinc ions. The prepared solution was stored in 1 L plastic container.

Preparation of lead (Pb^{2+}) ion solution

$Pb(NO_3)_2$ was obtained from LOBA Chemie PVT LTD Mumbai, India. Its purity was 99% with a molecular weight of 331.21. The lead ions stock solution was prepared by weighing accurately 1.6147g of $Pb(NO_3)_2$ and placing in a 1000ml volumetric flask. Distilled water was then added while shaking the mixture up to the 1L mark to make 1000ppm solution of lead ions. The prepared solution was stored in 1 L plastic container.

Preparation of chromium (Cr^{6+}) ion solution

$K_2Cr_2O_7$ was obtained from BDH chemicals Ltd Poole England. Its purity was 99.9% and the molecular weight was 294.18. The chromium ions stock solution was prepared by weighing accurately 2.8431g of $K_2Cr_2O_7$ and placing in a 1000ml volumetric flask. Distilled water was then added while shaking the mixture up to the 1L mark to make 1000ppm solution of chromium ions. The prepared solution was stored in 1 L plastic container.

Preparation of working solutions

In order to obtain the working hydroponic solutions of 10ppm, 20ppm and 50ppm cadmium, zinc, lead and chromium solutions, serial dilutions was done from the 1000ppm stock solution of each metal ion.

Experimental set up

The prepared metal ion solutions in plastic containers (200ml) were allowed to equilibrate for 24 hours, after which the initial conductivity, pH and temperature measurements were taken. After taking the above measurements, the pre-rooted sweet potato plants were submersed in the prepared solutions. Each experimental set up was in triplicate. A 24 hour equilibration time was allowed after which measurements were taken daily during the experimental period which ranged from 0 to 14 days for cadmium ion solutions and 0 to 21 days for zinc, lead and chromium ion solutions.

Monitoring

Conductivity meter, Hanna Instrument model 991300, was used to measure the electrical conductivity (µS/cm), temperature (^{0}c) and pH. Physical changes of plant parts (leaves, roots and stems) were noted and recorded. Measurements of electrical conductivity, pH and temperature were recorded daily for a period of 0-21 days, depending on the period the plants survived in the test solutions.

Control Experiment

Each heavy metal ion solutions of zinc, lead, cadmium and chromium had concentrations of 0ppm, 10ppm, 20ppm and 50ppm without plants. The pre-rooted plants of the sweet potato varieties were placed in distilled water only as a control measure.

Sweet potato plants for the experimental work.

The sweet potato plant cuttings used in this study were obtained from varieties grown in a garden at the University of Nairobi, College of Biological and Physical Sciences (CBPS). The cuttings were 15-20cm long (4 nodes). Leaves were removed and the cuttings placed in large plastic containers with tap water. They were left to pre root for four weeks. The pre-rooted sweet potato plant varieties were then submersed in metal ion solutions, containing either zinc, lead, cadmium or chromium of concentrations 0ppm, 10ppm, 20ppm and 50ppm. A control experiment had only distilled water and the selected pre-rooted plant. There were three replicates for each experimental set up, corresponding to a specific metal ion. The plants were harvested, separated into three parts (roots, stem and leaves) and then dried to a constant weight in an oven. The dried plants parts were digested and then analyzed for metal ion contents using atomic absorption spectrophotometer (AAS).

The plant varieties exhibited different growth behaviors in the different solutions. In Cd-containing solutions, the plant varieties dried within the first 10 days of planting and therefore were harvested after 14days. The plant varieties sub immersed in Zn and Pb-containing solutions tolerated the presence of metal ions for more than 14 days but were harvested after 21days. Plants in Cr-containing solutions survived for 21days for 10ppm and 20ppm but in 50ppm Cr-containing solutions they dried up before 21 days and therefore harvested after 14days. After harvesting, the plants were separated into three plant parts, namely roots, stems and leaves. These parts were dried and weighed to a constant weight. The samples were then acid digested and analyzed for respective heavy metal contents using the AAS technique. The results of the heavy metal contents were calculated in µg of dry weight. The rate of uptake of the heavy metal ions in the different plant parts was obtained by dividing the metal content accumulated in the plant part by the number of days the plant variety was submersed in the metal ion containing solution.

RESULTS AND DISCUSSIONS

The tables presented in this section show the results of the rate of uptake of cadmium, zinc, lead and chromium in the plant roots, stem and leaves of different sweet potato plant varieties. The constant dry weight of the plant parts were recorded, the metal uptake in µg of dry weight noted and their rate of metal uptake calculated. The rate of uptake of the metal was obtained by dividing the metal content in the particular plant part in µg by the number of days in which the plant varieties were immersed in a known concentration of the metal ions.

As per table 1, the lowest rates were recorded in leaves, whereas the highest rates were registered by roots, except for the case of UP-A, where stem had the highest rate. Overall, for the 10 ppm Cd^{2+} ions, the rates for the leaves, roots and stem uptakes increased as follows UP-B<UP-C<UP-16<UP-D<UP-A; UP-A<UP-D<UP-B<UP-16<UP-C; UP-C<UP-B<UP-D<UP-16<UP-A, respectively. This demonstrates that the variety UP-A had the highest rates for the leaves and the stems. On the other hand, for the 20 ppm Cd^{2+} the rates the leaves, roots and the

stems were as follows UP-C<UP-D<UP-B<UP-16<UP-A; UP-A<UP-B<UP-16<UP-D<UP-C; UP-C<UP-A<UP-B<UP-D<UP-16, respectively (table 2). Moreover, apart from the case of UP-A and UP-16, the rate of uptake decreased for the leaves as the applied Cd^{2+} increased from 10 to 20 ppm. As expected, the uptake rates for the roots and stem increased as the applied amount Cd^{2+} increased from 10 to 20 ppm.

Table 1: The rate of uptake of Cd in sweet potato plant varieties immersed in 10ppm Cd^{2+}-containing solutions over a 14 day period.

Variety	**Number of days in solution**	**Plant part**	**Dry weight (g) of plant? A**	**Cadmium content (µg of dry weight in column A) B**	**Rate of Cd uptake (µg/day) C**
UP-A	**14**	**Leaves**	0.12	35.54 ± 17.68	2.54
		Roots	0.03	348.72 ± 20.28	24.91
		Stem	0.81	387.26 ± 22.23	27.66
UP-B	**14**	**Leaves**	0.43	ND	-
		Roots	0.05	399.85 ± 23.18	28.56
		Stem	1.66	287.33 ± 27.68	20.52
UP-C	**14**	**Leaves**	0.29	1.32 ± 0.42	0.09
		Roots	0.05	438.92 ± 37.72	31.35
		Stem	1.34	213.26 ±44.55	15.23
UP-D	**14**	**Leaves**	0.27	2.97 ± 0.12	0.21
		Roots	0.04	373.33 ± 33.53	26.67
		Stem	1.49	289.75 ± 2.46	20.70
		Total	1.80	666.08	47.58
UP-16	**14**	**Leaves**	0.21	1.63 ± 0.19	0.12
		Roots	0.05	425.33 ± 31.87	30.38
		Stem	1.18	298.29 ± 28.67	21.31

Roots had the lowest mass and yet showed the highest uptake of Cd^{2+} ions in all the varieties except variety UP-A.

Table 2: The rate of uptake of Cd in sweet potato plant varieties immersed in 20ppm Cd^{2+}-containing solutions over a 14 day period.

Variety	Number of days in solution	Plant part	Dry weight (g) A	Cadmium content (μg of dry weight in column A) B	Rate of Cd uptake (μg/day) C
UP-A	**14**	**Leaves**	0.18	144.17 ± 19.28	10.30
		Roots	0.04	430.58 ± 32.08	30.76
		Stem	1.05	457.95 ± 40.35	32.71
UP-B	**14**	**Leaves**	0.30	4.23 ± 6.68	0.30
		Roots	0.06	452.23 ± 10.53	32.30
		Stem	1.53	463.72 ± 13.90	33.12
UP-C	**14**	**Leaves**	0.31	ND	-
		Roots	0.06	486.61 ± 9.15	34.76
		Stem	1.42	448.96 ± 1.85	32.07
UP-D	**14**	**Leaves**	0.28	1.01 ± 0.97	0.07
		Roots	0.04	484.59± 19.30	34.61
		Stem	1.15	469.17 ± 11.72	33.51
UP-16	**14**	**Leaves**	0.25	4.46 ±2.60	0.32
		Roots	0.08	470.15 ± 49.13	33.58
		Stem	1.33	488.48 ± 8.70	34.89

The results in table 2 demonstrated that the sweet potato plant varieties submersed in 20ppm Cd-containing solutions generally showed higher rate of uptake of Cd than the plants submersed in 10ppm Cd- containing solutions. The results in the tables 1 and 2 demonstrated that the cadmium was absorbed and translocated into the stems and the leaves. This observation is similar to the results obtained by Dicagno *et al.*, (1999), These researchers found out that Cd accumulated in the roots of *Healinthus anuus* exceeded those in the shoots.

Zinc is an essential nutrient for plant growth when accumulated in small quantities. However, high amounts may affect the growth of plants. The dry weight mass of the stems were higher than those of leaves and the roots in all the set ups. However, there was no correlation between changes in mass of dry weight with increase in concentration of zinc solutions. According to table 3, the stems registered the highest rate of zinc uptake, but leaves gave the lowest zinc uptake rate, as expected, considering the fact that stem acts as the storage part of the plant. This trend stayed put as the applied zinc content was increased to 20 ppm (table 4). However, when the applied zinc was increased to 50 ppm, roots gave the highest rates of zinc uptake for all the sweet potato varieties, except for the UP-A variety (table 5). Overall, for the 10 ppm Zn^{2+} ions, the rates for the leaves, roots and stem uptakes increased as follows UP-A<UP-16<UP-B<UP-D<UP-C; UP-16<UP-A<UP-D<UP-B<UP-C; UP-D<UP-C<UP-B<UP-A<UP-16, respectively. It is not clear why this variation takes place, however, the observed randomness in uptake rates for different plant varieties could be attributed to natural distribution of absorbed metal ions.

Table 3: The rate of uptake of Zn in sweet potato plant varieties immersed in 10ppm Zn^{2+}-containing solutions over a 21day period.

Variety	Number of days in solution		Plant part	Dry weight (g) A	Zinc content (µg of dry weight in column A) B	Rate of Zn uptake (µg/day) C
UP-A	**21**		**Leaves**	0.08	1.10 ± 0.18	0.05
			Roots	0.01	85.79 ± 26.41	4.09
			Stem	1.03	281.87 ± 1.68	13.42
UP-B	**21**		**Leaves**	0.24	3.71 ± 0.50	0.18
			Roots	0.04	215.01 ± 36.64	10.24
			Stem	1.42	249.70± 3.69	11.89
UP-C	**21**		**Leaves**	0.17	4.29 ± 1.33	0.20
			Roots	0.03	257.56 ± 36.74	12.26
			Stem	1.53	237.94 ± 34.98	11.33
UP-D	**21**		**Leaves**	0.14	3.97 ± 1.90	0.19
			Roots	0.02	130.20 ± 11.05	6.20
			Stem	1.26	227.21 ± 34.77	10.82
UP-16	**21**		**Leaves**	0.10	2.57 ± 0.45	0.12
			Roots	0.01	84.21 ± 8.74	4.01
			Stem	1.05	323.35 ± 34.38	15.40

Table 4: The rate of uptake of Zn in sweet potato plant varieties immersed in 20ppm Zn^{2+}-containing solutions over a 21day period.

Variety	Number of days in solution		Plant part	Dry weight (g) A	Zinc content (µg of dry weight in column A) B	Rate of Zn uptake (µg/day) C
UP-A	**21**		**Leaves**	0.08	58.63 ± 3.01	2.79
			Roots	0.01	159.37 ± 7.88	7.59
			Stem	1.16	325.77 ± 30.81	15.51
UP-B	**21**		**Leaves**	0.24	27.85 ± 5.75	1.33
			Roots	0.02	282.27 ± 30.45	13.44
			Stem	1.30	291.55 ± 22.45	13.88
UP-C	**21**		**Leaves**	0.17	54.20 ± 26.19	2.58
			Roots	0.02	214.06 ± 41.23	10.19
			Stem	1.47	271.61 ± 35.48	12.93
UP-D	**21**		**Leaves**	0.13	2.52 ± 0.64	0.12
			Roots	0.02	241.60 ± 30.65	11.50
			Stem	1.03	261.32 ± 46.67	12.44
UP-16	**21**		**Leaves**	0.10	4.80 ± 0.98	0.23
			Roots	0.02	234.06 ± 44.47	11.15
			Stem	1.26	309.15 ± 21.51	14.72

Table 5: The rate of uptake of Zn^{2+} ions in sweet potato plant varieties submersed in 50ppm Zn^{2+}-containing solutions over a 21day period.

Variety	Number of days in solution		Plant part	Dry weight (g) A	Zinc content (µg of dry weight in column A) B	Rate of Zn uptake (µg/day) C
UP-A	**21**		**Leaves**	0.13	16.10 ± 1.48	0.77
			Roots	0.01	123.70 ± 9.87	5.89
			Stem	1.64	168.83 ± 12.61	8.04
UP-B	**21**		**Leaves**	0.26	33.88 ± 2.26	1.61
			Roots	0.10	171.71 ± 7.50	8.18
			Stem	1.64	164.83 ± 10.69	7.85
UP-C	**21**		**Leaves**	0.20	8.45± 0.44	0.40
			Roots	0.06	160.54 ± 9.66	7.66
			Stem	1.74	157.80 ± 8.09	7.51
			Total	2.00	326.79	15.57
UP-D	**21**		**Leaves**	0.19	11.23 ± 2.08	0.53
			Roots	0.06	166.99 ± 9.63	7.95
			Stem	1.34	161.35 ± 10.3	7.68
UP-16	**21**		**Leaves**	0.22	13.79 ± 1.24	0.66
			Roots	0.08	165.00 ± 3.78	7.86
			Stem	1.39	160.90 ± 7.22	7.66

The rate of uptake of Zn in the plant varieties immersed in 50ppm Zn-containing solutions was lower than those immersed in 20ppm Zn-containing solutions. These results may be attributed to the increase in concentration of zinc content in the plant, which may have contributed to higher toxicity of zinc, thereby slowing the growth and hence the low uptake rates. It is worth noting that the rate of uptake of Zn^{2+} ions in the stems and roots in varieties UP-C, UP-D and UP-16 were relatively equal.

The toxicity of zinc in plants has been reported to be caused by interactions with other elements like phosphorus and iron. Toxicity arising from excess zinc is seen in chlorosis of leaves and production of stunted growth (Dowdy, 1975). This observation agrees with the observations made on the leaves of varieties UP-C, UP-D and UP-16 immersed in 50ppm zinc-containing solutions, thereby showing evidence of toxicity in plants. Sweet potato plant varieties however, showed tolerance in 10ppm and 20ppm zinc-containing solutions.

Results of the rate of uptake of lead in the sweet plant varieties immersed in Pb-containing solutions in different concentrations for 21days period are shown in tables 6 to 8. For the 10 ppm Pb^{2+} solutions, the rates for the leaves, roots and stem uptakes increased as follows UP-16<UP-D<UP-C<UP-A<UP-A; UP-B=UP-C=UP-D=UP-16<UP-A; UP-A<UP-C<UP-B<UP-D<UP-16, respectively (table 6). Except for the leaves, an interesting scenario was observed when the concentration of the Pb^{2+} ions was increased from 10 to 50 pm (tables 7 and 8). For all the sweet varieties, when the initial lead concentration was increased from 10 to 20 ppm the uptake rates in roots and stem increased by factor ranging from about 2 to 1,000 times. Moreover, when the initial concentration of the solution was increased from 20 to 50 ppm, the rates of uptake by roots and stem increased by factor ranging from 1 to 16 times (tables 6, 7 and 8).

Table 6: The rate of uptake of Pb in sweet potato plant varieties immersed in 10ppm Pb^{2+}-containing solutions over a 21day period.

Variety	Number of days in solution	Plant part	Dry weight (g) A	Lead content (μg of dry weight in column A) B	Rate of Pb uptake (μg/day) C
UP-A	**21**	**Leaves**	0.14	4.31± 2.64	0.21
		Roots	0.02	4.45 ± 1.56	0.21
		Stem	0.81	0.98 ± 0.17	0.05
UP-B	**21**	**Leaves**	0.27	5.51 ± 0.66	0.26
		Roots	0.10	1.56 ± 0.01	0.07
		Stem	1.18	121.85 ± 17.89	5.80
UP-C	**21**	**Leaves**	0.14	3.32 ± 0.84	0.16
		Roots	0.09	1.37 ± 8.92	0.07
		Stem	1.03	90.32 ± 0.32	4.30
UP-D	**21**	**Leaves**	0.41	1.89	0.09
		Roots	0.10	1.55 ± 0.04	0.07
		Stem	1.23	150.69 ± 28.63	7.18
UP-16	**21**	**Leaves**	0.20	ND	0
		Roots	0.11	1.53 ± 0.02	0.07
		Stem	1.36	160.62 ± 60.80	7.65

Table 7: The rate of uptake of Pb in sweet potato plant varieties immersed in 20ppm Pb^{2+}-containing solutions over a 21day period.

Variety	Plant part	Dry weight (g) A	Lead content (μg) of dry weight in column A) B	Rate of Pb uptake (μg/day) C
UP-A	**Leaves**	0.04	2.63 ± 2.39	0.13
	Roots	0.01	878.92 ± 9.06	41.85
	Stem	0.95	679.67 ± 58.95	32.37
UP-B	**Leaves**	0.25	0.74 ± 0.36	0.04
	Roots	0.14	1752.37 ± 135.83	83.45
	Stem	1.43	209.02 ± 20.64	9.95
UP-C	**Leaves**	0.23	1.89	0.09
	Roots	0.09	1544.31 ± 132.05	73.54
	Stem	1.67	370.42 ± 26.08	17.64
UP-D	**Leaves**	0.18	0.95	0.05
	Roots	0.11	1443.42 ± 31.28	68.73
	Stem	1.54	271.75 ± 4.42	12.94
UP-16	**Leaves**	0.19	1.58	0.08
	Roots	0.07	1138.15 ± 45.38	54.20
	Stem	1.15	249.67 ± 5.88	11.89

Overall, the data obtained indicate that with the increase in the concentration of Pb-containing solutions, in which the plant varieties were submersed, the rate of uptake of Pb increased as well. Roots though having least mass compared to the stems and the leaves showed highest rate of Pb uptake.

Table 8: The rate of uptake of Pb in sweet potato plant varieties immersed in 50ppm Pb^{2+}-containing solutions over a 21day period.

Variety	Plant part	Dry weight (g) A	Lead content (µg of dry weight in column A) B	Rate of Pb uptake (µg/day) C
UP-A	**Leaves**	0.08	0.30 ± 0.40	0.01
	Roots	0.01	930.6 ± 22.30	44.31
	Stem	1.05	1870.44 ± 662.90	89.07
UP-B	**Leaves**	0.26	13.8 ± 2.6	0.66
	Roots	0.08	2726.60 ± 90.0	129.84
	Stem	1.65	657.81 ± 15.22	31.32
UP-C	**Leaves**	0.13	12.40 ± 1.97	0.59
	Roots	0.07	2833.81 ± 140.90	134.94
	Stem	0.68	484.33 ± 10.62	23.06
UP-D	**Leaves**	0.24	1.90 ± 0.61	0.09
	Roots	0.14	2771.2 ± 115.11	131.96
	Stem	1.41	421.64 ± 15.00	20.08
UP-16	**Leaves**	0.24	0.60	0.03
	Roots	0.07	2934.20 ± 76.77	139.72
	Stem	1.24	635.50 ± 32.10	30.26

The low lead uptake behaviors by the plant varieties, submersed in 10ppm Pb^{2+}-containing solutions, could not be explained (table 6). Maina (1984) reported that lead was taken up in very low concentration by cowpeas, tomatoes, sugar loaf and spinach planted in Kariobangi sewage works soils. However, the current work indicates high uptake of lead ions as the initial solution concentration is increased. This is supported further by the appearance of healthy-like sweet potato varieties in lead containing solutions. Research work by Goyer and co-workers had indicated that high calcium intake inhibits lead absorption (Goyer, 1977), suggesting the solutions used in the current work did not have significant amount of calcium.

Chromium metal was also tested for the uptake by the five sweet potato varieties. The plant varieties were submersed in different Cr-containing solutions (10 and 20 ppm) for 21 days and 50 ppm Cr solution for 14 days. The reason for the reduced time was that the plants submersed in the more concentrated solution dried up before 14 days period and were therefore harvested. For the 10 ppm Cr solutions roots registered highest uptake rates, except for varieties UP-A and UP-16. To a first approximately, the same trend was observed for the 20 and 50 ppm Cr solutions. In addition, as the initial concentration of Cr was increased the rates of Cr uptake by leaves, roots and stems increased similarly. This is the expected trend and the increment ratio could be used to estimate the concentration of the initial concentration of the solution. The significant increase in rates of Cr uptake by the leaves with the increase in initial solution concentration suggests uptake and translocation of the metal ion to different parts of the plant.

In summary, for the 10 ppm Chromium ions, the rates for the leaves, roots and stem uptakes increased as follows UP-C<UP-A<UP-B<UP-16<UP-D; UP-A<UP-16<UP-B<UP-C<UP-D; UP-C<UP-D<UP-B<UP-16<UP-A, respectively(table 9). In addition, for the 20 ppm Cr^{3+} the rates the uptake by the leaves, roots and the stems were as follows UP-A<UP-D<UP-C<UP-16<UP-B; UP-A<UP-C<UP-B<UP-16<UP-D; UP-16<UP-B<UP-C<UP-D<UP-A, respectively (table 10). Moreover, for the 50 ppm chromium, the rates for the uptake by the leaves, roots and the stems were as follows UP-D<UP-B<UP-16<UP-C<UP-A; UP-A<UP-16<UP-D<UP-C<UP-B; UP-D<UP-C<UP-B<UP-A<UP-16, respectively (table 11). From these results it is clear that different varieties have different behavior towards uptake of pollutants.

Table 9: The rate of uptake of Cr in sweet potato plant varieties submersed in 10ppm Cr-containing solutions over a 21day period.

Variety	Plant part	Dry weight (g) A	Chromium content (µg of dry weight in column A) B	Rate of Cr uptake (µg/day) C
UP-A	**Leaves**	0.02	3.25	0.15
	Roots	0.01	9.46 ± 4.33	0.45
	Stem	0.88	147.89 ± 11.74	7.04
UP-B	**Leaves**	0.18	5.65 ± 2.01	0.27
	Roots	0.08	77.84 ± 8.56	3.71
	Stem	1.22	40.73± 5.06	1.94
UP-C	**Leaves**	0.21	2.81 ± 0.81	0.13
	Roots	0.09	91.08 ± 9.83	4.34
	Stem	1.39	28.98 ± 6.16	1.38
	Total	1.70	122.87	5.85
UP-D	**Leaves**	0.21	12.65 ± 2.81	0.60
	Roots	0.11	114.53 ± 11.28	5.45
	Stem	1.52	37.46 ± 11.72	1.78
	Total	1.84	164.64	7.83
UP-16	**Leaves**	0.15	11.98 ± 3.26	0.57
	Roots	0.04	36.07 ± 13.95	1.72
	Stem	1.19	61.18 ± 12.23	2.91

Overall these results demonstrated that the rate of uptake increased in the different parts of the plant with the increase in initial concentration of metal ion.

Table 10: The rate of uptake of Cr in sweet potato plant varieties immersed in 20ppm Cr-containing solutions over a 21day period.

Variety	Plant part	Dry weight (g) A	Chromium content (µg of dry weight in column A) B	Rate of Cr uptake (µg/day) C
UP-A	**Leaves**	0.03	7.48 ± 3.73	0.36
	Roots	0.01	46.19 ± 16.19	2.20
	Stem	0.91	105.46 ± 24.16	5.02
UP-B	**Leaves**	0.26	44.54 ± 12.59	2.12
	Roots	0.07	124.66 ± 13.76	5.94
	Stem	2.02	61.36 ± 12.72	2.92
UP-C	**Leaves**	0.19	18.55 ± 7.16	0.88
	Roots	0.06	91.34 ± 14.60	4.35
	Stem	1.24	72.06 ± 13.08	3.43
UP-D	**Leaves**	0.19	11.05 ± 5.97	0.53
	Roots	0.08	142.96 ± 21.08	6.81
	Stem	1.29	86.75 ± 9.90	4.13
UP-16	**Leaves**	0.20	19.68 ± 12.68	0.94
	Roots	0.07	136.39 ± 22.04	6.49
	Stem	0.51	31.22 ± 11.27	1.49

Table 11: The rate of uptake of Cr in sweet potato plant varieties immersed in 50ppm Cr-containing solutions over a 14day period.

Variety	Number of days in solution	Plant part	Dry weight (g) A	Chromium content (µg of dry weight in column A) B	Rate of Cr uptake (µg/day) C
UP-A	**14**	**Leaves**	0.13	100.63 ± 18.38	7.19
		Roots	0.04	165.46 ± 29.14	11.82
		Stem	0.90	365.27 ± 56.52	26.09
UP-B	**14**	**Leaves**	0.24	24.98 ± 10.96	1.78
		Roots	0.13	289.44 ± 54.79	20.67
		Stem	1.85	256.18 ± 45.57	18.30
UP-C	**14**	**Leaves**	0.21	42.41 ± 13.27	3.03
		Roots	0.09	245.13 ± 54.00	17.51
		Stem	2.19	222.04 ± 43.66	15.86
UP-D	**14**	**Leaves**	0.21	19.93 ± 10.48	1.42
		Roots	0.08	193.51± 41.28	13.82
		Stem	1.03	128.04 ± 89.43	9.15
UP-16	**14**	**Leaves**	0.17	39.87 ± 5.97	2.85
		Roots	0.08	170.23 ± 31.78	12.16
		Stem	1.17	475.59 ± 72.58	33.97

It is clear that the rate of uptake of Cr in plant varieties immersed in the 50ppm Cr-containing solutions as shown in table 11 was higher than in the same plant varieties immersed in 10ppm and 20ppm Cr-containing solutions respectively. The plant varieties immersed in 50mg/l chromium solutions was harvested after 14day period because the plants could not tolerate the high concentrations of chromium. This observation was attributed to increase of toxicity of chromium in more concentrated solutions which could have inhibited chromium uptake by the plant. Chromium has not been shown to be essential for plant growth and phytotoxicity due to high concentration in soils has been reported (Bott and Bruggenwert, 1976).

Table 12 shows comparison results of rate of uptake of metals in different plant parts from the plants immersed in the 10ppm metal containing solutions.

Table 12: Comparison of rates of uptake of heavy metal ions in different parts of sweet potato varieties immersed in 10ppm metal containing solution.

Variety	Plant part	Rate of Cd uptake (14)	Rate of Zn uptake (21)	Rate of Pb uptake (21)	Rate of Cr uptake (21)
UP-A	**Leaves**	2.54	0.05	0.21	0.15
	Roots	24.91	4.09	0.21	0.45
	Stem	27.66	13.42	0.05	7.04
UP-B	**Leaves**	-	0.18	0.26	0.27
	Roots	28.56	10.24	0.07	3.71
	Stem	20.52	11.89	5.80	1.94
UP-C	**Leaves**	0.09	0.20	0.16	0.13
	Roots	31.35	12.26	0.07	4.34
	Stem	15.23	11.33	4.30	1.38
UP-D	**Leaves**	0.21	0.19	0.09	0.60
	Roots	26.67	6.20	0.07	5.45
	Stem	20.70	10.82	7.18	1.78
UP-16	**Leaves**	0.12	0.12	0	0.57
	Roots	30.38	4.01	0.07	1.72
	Stem	21.31	15.40	7.65	2.91

Brackets indicate the number of days the sweet potato plants were submersed in solutions containing metal ions.

The comparative data presented in table 12 indicates that the rate of uptake of Cd in the plant varieties immersed in 10ppm solutions of different metals had the highest rate of uptake.

This rapid uptake of Cd suggests significant accumulation within a short time for a given sweet potato variety. Thus sweet potato varieties could be used to remove cadmium contaminated environment like swamps, soils, pools and related areas.

Similar comparison was made in the plant varieties immersed in 20ppm metal containing solutions as indicated in table 13.

Table 13: Comparison of rate of uptake of heavy metal ions in different parts of sweet potato varieties immersed in 20ppm metal containing solution.

Variety	Plant part	Rate of Cd uptake (14)	Rate of Zn uptake (21)	Rate of Pb uptake (21)	Rate of Cr uptake (21)
UP-A	**Leaves**	10.30	2.79	0.13	0.36
	Roots	30.76	7.59	41.85	2.20
	Stem	32.71	15.51	32.37	5.02
UP-B	**Leaves**	0.30	1.33	0.04	2.12
	Roots	32.30	13.44	83.45	5.94
	Stem	33.12	13.88	9.95	2.92
UP-C	**Leaves**	-	2.58	0.09	0.88
	Roots	34.76	10.19	73.54	4.35
	Stem	32.07	12.93	17.64	3.43
UP-D	**Leaves**	0.07	0.12	0.05	0.53
	Roots	34.61	11.50	68.73	6.81
	Stem	33.51	12.44	12.94	4.13
UP-16	**Leaves**	0.32	0.23	0.08	0.94
	Roots	33.58	11.15	54.20	6.49
	Stem	34.89	14.72	11.89	1.49

The results on table 13 indicate that the rate of uptake in the plants immersed in 20ppm Pb-containing solutions was the highest compared to those of the plants immersed in 20ppm Cd and Cr-containing solutions. Plant varieties immersed in Cd-containing solutions though immersed for 14 days showed highest rate of uptake compared with other metals, hence anticipated high toxicity. Leaves generally showed lower uptake of Pb in all the plant varieties immersed in the metal solutions in which they were immersed. Generally, the rate of uptake of Cr was lowest compared to other metals.

Table 14 shows the comparison results of the rate of uptake of metal ions immersed in 50ppm metal containing solutions. There were no 50ppm Cd-containing solutions because the sweet potato plant varieties could not tolerate even the 20ppm Cd-containing solutions as they dried before the 14th day.

Table 14: Comparison of rate of uptake of heavy metal ions in different parts of sweet potato varieties immersed in 50ppm metal containing solution.

Variety	Plant part	Rate of Zn uptake (21)	Rate of Pb uptake (21)	Rate of Cr uptake (14)
UP-A	**Leaves**	0.77	0.01	7.19
	Roots	5.89	44.31	11.82
	Stem	8.04	89.07	26.09
UP-B	**Leaves**	1.61	0.66	1.78
	Roots	8.18	129.84	20.67
	Stem	7.85	31.32	18.30
UP-C	**Leaves**	0.40	0.59	3.03
	Roots	7.66	134.94	17.51
	Stem	7.51	23.06	15.86
UP-D	**Leaves**	0.53	0.09	1.42
	Roots	7.95	131.96	13.82
	Stem	7.68	20.08	9.15
UP-16	**Leaves**	0.66	0.03	2.85
	Roots	7.86	139.72	12.16
	Stem	7.66	30.26	33.97

The plant varieties immersed in the metal ion containing solutions of 50ppm showed that the plant varieties immersed in Pb-containing solutions had the highest uptake compared to the rate of uptake in plants immersed in the same concentration solutions of Zn and Cr. Zinc uptake was lowest in all the varieties. The results also indicate that the rate of uptake in the leaves was lowest in all the plant varieties in the different heavy metal solutions in which the plants were immersed.

CONCLUSION

The results demonstrated that the sweet potato plant varieties used for this work absorbed and translocated significant amounts of cadmium, zinc, lead and chromium in their roots, stems and leaves. The rate of uptake of heavy metal absorbed by the sweet potato plant variety depended on the initial concentration of the metal ion, originally present in the heavy metal-containing solutions.

The results indicated that the rate of uptake of heavy metals ions were not dependent on the mass of the plant parts in which they accumulated. In all the plant varieties, roots weighed the least but showed the highest rate of uptake compared to the stems and the leaves in most plants. However, in a few varieties stems had the highest rate of metal uptake though the stems weighed more than the roots like in the case of zinc. The rate of heavy uptake can therefore be used to determine the plant varieties that are suitable to absorb high amounts of metal ions within a short time.

Three main steps involved in uptake can be regarded as involving adsorption on the surface of roots and the part of the stem submersed in the solution, absorption by the roots and eventual trans-location into the stems and the leaves. This suggestion is supported by the fact that increased metal-containing solutions concentration resulted in an increase in the rate of heavy metal uptake in different plant variety tissues. Only in the case of varieties UP-B, UP-C and UP-D at 10ppm lead-containing solution where the leaves had more lead uptake than the stem. Considering the different distribution of the metal content in different parts of the plant, it is clear that metal contents in solutions are absorbed and translocated in different parts of the plants.

For the five varieties considered, lead exhibited the highest rate of uptake in roots, stem and leaves. In most of these varieties, highest accumulation of the heavy metals was recovered in the roots followed by the stems and then the leaves. In some cases the stems had higher rates of uptake than roots. The high rate of uptake of lead in the roots was possibly due to growth of new roots as observed in the sweet potato varieties submersed in the lead-containing solutions. Moreover, plants in lead containing solutions looked healthy, suggesting lead to be a nutrient, which calls for further investigation.

The results obtained from the experiments demonstrated that the rate of uptake of the heavy metals was highest in the roots in most varieties, although in some cases stems also, showed the highest rate of uptake. However, in all the plant varieties submersed in concentrations of Cd, Cr, Pb and Zn-containing solutions, leaves showed the least rate of metal ions uptake. This was attributed to slow translocation of the metal ions within the plant to the leaves as the days progressed. The plant varieties submersed in 10ppm Cd-containing solutions showed higher rate of uptake in its plant parts compared to similar varieties submersed in 10ppm Cr, Pb and Zn-containing solutions. Lead, on the other hand, showed highest rate of uptake in the plant varieties submersed in 20ppm Pb-containing solutions compared to the other metals submersed in their respective 20ppm solutions. There were no 50ppm Cd-containing solutions as the plants could not tolerate 20ppm Cd concentration.

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SEANAC
African
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SOUTHERN AND EASTERN AFRICAN NETWORK OF ANALYTICAL CHEMISTS (SEANAC)

TO BE HOSTED BY: *DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NAIROBI, KENYA*

VENUE: *REEF HOTEL, MOMBASA - KENYA*

Dates: *22nd June 2014 – 28th June 2014*

1. BACKGROUND

The African continent is poverty stricken partly because of droughts, poor management of resources by governments and also lack of technical expertise to prepare nations for unforeseen disasters. If the capacity is enhanced in the basic sciences, particularly Analytical Chemistry, the quality of life can be improved significantly.

For example a good knowledge of the quality of water can help reduce unnecessary expenditure that could be incurred by the medical care sector as a result of high levels of toxic elements in the water.

Since most of the nations in Africa rely on unprocessed river water or portable water, the availability of expertise to examine and define the characteristics of such water is important for the inhabitants and their livestock. The many rivers and lakes in the African continent provide a good source of nutrition in fish, hence monitoring pollution can reduce the metal uptake by fish.

Therefore there is a need for a pool of expertise in Analytical Chemistry not only to service the industry but also to add value to the quality of people's lives. During a Sida funded workshop in February 2002, held in Gaborone, Botswana that led to the formation of the Southern and Eastern African Network for Analytical Chemists (SEANAC) it was agreed that such a pool of expertise should be familiar with issues relating to the continent.

2. OBJECTIVES

SEANAC has three main objectives:

(1) To promote analytical chemistry in the region through collaboration, research, research training, teaching and information sharing.

(2) To facilitate inventory, access, operation, maintenance and repairs of analytical equipment.

(3) To collaborate with organisations of similar aims.

3. WORKSHOP TRAINING AND CONFERENCE PROGRAMMES

To be uploaded soon

4. IMPORTANT DATES

(a) SEANAC TRAINING WORKSHOP:

- Venue: *Department of Chemistry, University of Nairobi*
- Dates: *1st July 2013 – 10th July 2013*

(b) SEANAC PRE-CONFERENCE:

- Venue: *Reef Hotel, Mombasa - Kenya*
- Dates: *20th June 2014 – 22nd June 2014*

(c) SEANAC CONFERENCE:

- Venue: *Reef Hotel, Mombasa - Kenya*
- Dates: *22nd June 2014 – 28th June 2014*

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12TH AFRICALMA/EAST AND SOUTHERN AFRICA LABORATORY MANAGERS ASSOCIATION (E-SALAMA) WORKSHOP

To be hosted tentatively by the University of Botswana

02-06 December 2013

E-SALAMA

Background

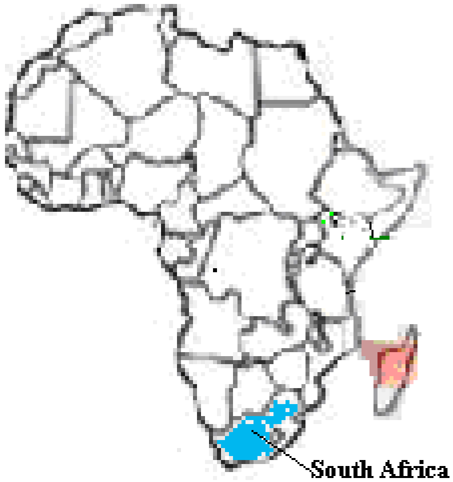
The East and southern Africa laboratory Managers Association (E-SALAMA) was established in 2002 with members from Kenya, Tanzania and Uganda. Since then others countries have joined and these include Zimbabwe, Botswana, Lesotho, Ethiopia and Sudan.

E-SALAMA was established with the aim of training laboratory managers in member countries towards achieving accreditation for their laboratories. To this end, the workshop is held annually and rotates from one member country to another. Prior to 2007, the workshop was held in Kenya, Tanzania and Uganda. In 2007 Zimbabwe hosted the workshop that was held 8 – 11 December 2007 at Victoria Falls. Subsequently the workshop was held in Kenya (2008), Ethiopia (2009) and Sudan (2010), Zimbabwe (2011), Lesotho (2012), while this year's workshop will be held in Botswana.

10th East and Southern Africa Environmental Chemistry and Theoretical Chemistry in Africa Forum

October 07th – 11th 2013

East and Southern Africa Environmental Chemistry and Theoretical Chemistry in Africa Forum will be hosting the 10th International conference from 07th to 11th October, 2013 tentatively at the University of Venda, South Africa.



Preamble: East and Southern Africa Environmental Chemistry (ESAEC) and Theoretical Chemistry in Africa (TCA) Forum is held bi-annually, but rotate among the countries in the region. The overall objective of this forum is to address issues related to environment and theoretical chemistry in the region.

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An investigation of the transport and dispersion of atmospheric pollutants over east Africa during the Ol doinyo lengai volcanic eruption in July 2007 and march 2008. *N. J. Muthama, E.M. Mathu and G. N. Kamau*

Direct synthesis of SH/NH_2-bi-functionalized mesoporous silica using cardanol as a template. *J. E. G. Mdoe*

Adsorption of 2, 4, 5, 6-tetrachloroisophthalonitrile (chlorothalonil) by Nairobi River Sediments: Adsorption Characteristics and Related Thermodynamic Data. *J. K. Mbugua, I. N. Michira, S. M. Kagwanja, V. O. Madadi, M. F. Zaranyika and G. N. Kamau*

Compositional and Structural Characterization of Indigenous Salts in Kenya: A Case study of ‘para’, ‘magadi’ and ‘lebek’ Crystalline Salts. *O. A. Mosima, O. E. Rangondi, O. Nathan and K. Jackson*

Assesment of the Effects of Tobacco Farming on Soil Nutrients in Migori County, Kenya., *K.E. Omayo, J.S. Chacha, E.R. Okongo and A. M. Salim*

Rate of uptake of cadmium, chromium, lead and zinc ions by roots, stems and leaves of different *ipomoea batatas* plant varieties under *in vitro conditions. J. K. Ndathe, F. B. Mwaura, J. Nsuba, L. Berga, P. Ndolo, S. L. Doty and G.N. Kamau*

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