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Assessment of nutrient and heavy metal concentrations in sediments and macrophytes of the Oroma wetland, Nigeria

Проценка на концентрацијата на минерални материи и тешки метали во седименти и макрофити во мочуриштето Орома, Нигерија

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Abstract

This study assessed the nutrient and heavy metal concentrations in sediments and macrophytes of the Oroma wetland, University of Port Harcourt, Nigeria. A map representation of the wetland was assigned North-South (N-S) grid lines and six numbers were randomly selected to represent the six sampling points – SS1, SS2, SS3, SS4, SS5 and SS6. Sediment and three macrophytes (*Alchornea cordifolia*, *Sacciolepis africana*, and *Harungana madagascariensis*) that were present in each grid were collected and analyzed. Results showed that the wetland sediment was polluted with cadmium (4.80-54.10 mg/kg) and lead (98.60-175.30 mg/kg) whereas, only the sediment obtained from SS1 was polluted with nickel (75.9 mg/kg). In the sediment, cadmium posed a very high ecological risk; lead posed a considerable ecological risk whereas, the other heavy metals analyzed in this study posed low ecological risks. SS5 and SS6 had very high ecological risks whereas, the other sampling sites had moderate ecological risks. Cadmium, cobalt, copper, iron, zinc and arsenic were in same cluster in sediment based on cluster analysis while, chromium and nickel were assigned a separate cluster. The macrophytes collected from each site bioaccumulated the heavy metals from the sediment albeit at varying levels. Major sources of the nutrient and heavy metal burden in Oroma wetland were identified as runoffs and effluents from the adjoining University, residential areas, farmlands, car wash centers, generator houses, slaughter houses, metal dump sites, automobile maintenance shops, and vehicle exhaust. This study has highlighted the pollution status of the Oroma wetland sediment, the heavy metal burden of its macrophytes and the ecological risks posed by these heavy metals which have serious public health and ecological consequences.

Key words: Heavy Metals, Macrophytes, Sediments, Oroma, Wetland

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Апстракт

Во оваа студија се прикажани концентрациите на минералните материи и тешките метали во седименти и макрофити во мочуриштето Орома, Универзитет на Порт Харкорт, Нигерија. Мочуриштето беше претставено на карта со нанесени линии во правец север-југ и шест полигони (SS1, SS2, SS3, SS4, SS5 и SS6, кои ги претставуваат точките за собирање примероци) беа одбрани по случаен избор. Од сите точки беше собиран седимент и три макрофитски растенија (*Alchornea cordifolia*, *Sacciolepis africana*, and *Harungana madagascariensis*) .

Резултатите покажаа дека седиментот беше загаден со кадмиум (4,80–54,10 mg/kg) и олово (98,60-175,30 mg/kg), додека само седиментот од SS1 беше загаден со никел (75,9 mg/kg). Кадмиумот во седиментите преставува висок еколошки ризици. Оловото претставува значаен еколошки ризик, додека останатите анализирани метали претставуваат низок еколошки ризик.

SS5 и SS6 се со висок еколошки ризик, додека останатите точки се со умерен еколошки ризик. Кадмиумот, кобалтот, бакарот, железото, цинкот и арсенот се групирани во заеднички кластер, додека хромот и никелот се во одделна група.

Макрофитите од различните точки биоакумулираа тешки метали од седиментот, но со различен интензитет. Главни извори на минерални материи и тешки метали во мочуриштето Орома се површинскиот истек и ефлуентите од Универзитетот во непосредна близина, станбените населби, фармите, инсталации за миење автомобили, генераторски станици, кланици, депонии за метали, автомобилски сервиси и издувните гасови од автомобилите. Со оваа студија е дефиниран статусот со загадување на мочуриштето Орома, оптоварувањето на макрофитите со тешки метали, како и еколошкиот ризици кој произлегува од тешките метали со сериозни последици по јавното здравје и животната средина.

Клучни зборови: тешки метали, макрофити, седименти, мочуриште Орома

Introduction

Wetlands are unique areas that display attributes of land and water. They are distinguished by the presence of saturated soils and/or standing water for a certain duration of time during the rainy season, a condition that facilitates the development of hydric soils and aquatic vegetation. They cover 6% of the world's land surface and are found everywhere, in all climates and countries, from the tundra to the tropics (Maltby 2013). In Nigeria, most wetlands occur in the Niger Delta region and represent 2.6 % of the country's total area of about 923,768 km^2 making it the largest in Africa and the third largest in the world (Nwankwoala 2012).

Wetlands are of great value to humans as they assist in the production of food, especially the cultivation of swamps for rice (rice paddies), fish, cranberries, salmon etc. Wetlands provide humans with commercial animal populations and are also a commercial source of timber. Wetlands are also valued for their ability to take up and remove nutrients and heavy metals, provide fibre and food resources, sustain biodiversity and provide protection from flood. Wetlands are the only ecosystem type that has their own international convention – the Ramsar convention of 1971 (Maltby 2013) which defined wetlands as areas where water is the primary factor controlling the environment and the associated plant and animal life. Hence, any change in water volume poses a threat to the area and integrity of wetlands since wetlands are defined by hydrologic conditions. An increase in the nutrient loadings usually poses a threat to the integrity of the wetland since wetlands are defined by their water quality.

For centuries, natural wetlands have been a sink for waste since they have the ability to absorb large quantities of environmental pollutants (Groudev *et al*. 2001). This is facilitated by some fundamental purification processes such as sedimentation, oxidation of contaminants and bacterial degradation, uptake of nutrients by plants, adsorption of dissolved substances and particles in the waste on to the substrate.

Wetlands and aquatic systems are more readily polluted by nutrients and heavy metals as a result of industrial, agricultural, municipal, and residential waste water streams that are discharged into it. Nutrient losses from

agricultural activities enter wetland systems basically as excess runoff which flows over or under farmland. Heavy metal pollution is also common in aquatic and wetland systems (Ayeni *et al*. 2010). However, only a small portion of free metal ions could be taken away by water flows (e.g. flooding or rainfall runoff) leaving a large quantity that gets deposited in the sediment due to co-precipitation, adsorption and hydrolysis (Gaur *et al*. 2005), and which may endanger human health when acquired through the food cycle. Numerous researches have shown that crops grown on soils that are highly polluted by heavy metals have greater concentrations of heavy metals than those grown on unpolluted soils (Nabulo 2006).

The fate of pollutants (excess nutrients and heavy metals) in wetland sediments is a subject of study because of the direct potential toxicity to biota and the indirect threat it poses to the wellbeing of humans via storage of toxicants in food crops and groundwater pollution. Heavy metals have the tendency to bio-accumulate (i.e., assimilated by organisms like macrophytes at a rate greater than the ability of the organism to get rid of it) and are therefore, considered dangerous. When heavy metals accumulate in wetland soil, it will directly (or indirectly) through plants enter food chains and endanger herbivores, indirectly carnivores and ultimately humans. More so, plant uptake of heavy metals results in accumulation in the tissues of plant and eventually phytotoxicity and change of plant community (Gimmler *et al*. 2002).

Hence, in this study, the nutrients and heavy metal sources in Oroma wetland, Port Harcourt, and the accumulation of these heavy metals in sediments and macrophytes were studied. This is aimed at having a good understanding of the nutrient and heavy metal status of the Oroma wetland which will help in determining the capacity of the wetland to act as filters of pollutants and thus, encourage the effective management of the wetland ecosystem and mitigation of human activities that are negatively impacting the wetland.

Study area

The Oroma wetland of the University of Port Harcourt is situated in Port Harcourt metropolis within Obio-Akpor Local Government Area of Rivers State. The Oroma wetland is approximately 1.7 km^2 and stretches within Latitude 4°53´31.99"N through Latitude 4°5´449.16"N and Longitude 6°54´06.12"E through Longitude 6°56´11.03"E. It is located along the Aluu-Rumuekini axis in the northwest, to the heart of the University Park of the University of Port Harcourt.

The climate over the wetland is a tropical monsoon consisting of long and heavy rainy seasons and few months (December and January) of dry seasons (harmattan). The heaviest precipitation (an average of 414 mm of rain) occurs in the city in the month of September whereas January is the driest month of the year with an average of 36 mm rainfall. The average temperatures in Port Harcourt are typically between 25-28 °C and these values remain relatively constant with little variation throughout the course of the year (The Weather Network 2014).

Generally, in Port Harcourt, drainage is poor as the topography is low lying with lots of surface water and a high rainfall of approximately 2780 mm per annum (The Weather Network 2014). The source of water in the Oroma wetland is precipitation that falls on the wetland directly, surface water runoff during rainfall, groundwater in-flow, and periodic flooding caused by increased water levels of surface water bodies nearby. The Oroma wetland also has additional water in-flow from Aluu, Rumuekini and Alakahia communities, University of Port Teaching Hospital, Rumuosi community, Choba Park and University Park of the University of Port Harcourt. The wetland drains as a seasonal stream (channel) into the New Calabar River system. There is a slight variation in the duration of flooding in the wetland; some areas are slightly permanently flooded while others are seasonally flooded and have more species density than the others.

Materials and method

Collection of Samples

Samples for this study were collected from the Oroma wetland in the month of August, 2015. A map representation of the wetland was assigned North-South (N-S) grid lines and numbers (Fig. 1). Six numbers were randomly selected to represent the six sampling points. Tab. 1 shows the coordinates and altitudes of the randomly selected points.

A soil sample and three macrophyte samples were collected in replicates from each of the six N - S transects in the month of August to ensure reproducibility. The composite sediment

Table 1. Sample Sites and Coordinates

Sampling site	Northings	Eastings	Altitude (m)
SS1	N04°54'07.0''	E006°54'49.3''	24
SS2	N04°53'56.0''	E006°54'54.7''	15
SS3	N04°53'49.0''	E006°54'59.6''	17
SS4	N04°53'39.4''	E006°55'39.0''	18
SS5	N04°53'20.6''	E006°55'21.6''	11
SS6	N04°53'45.0''	E006°55'51.2''	19

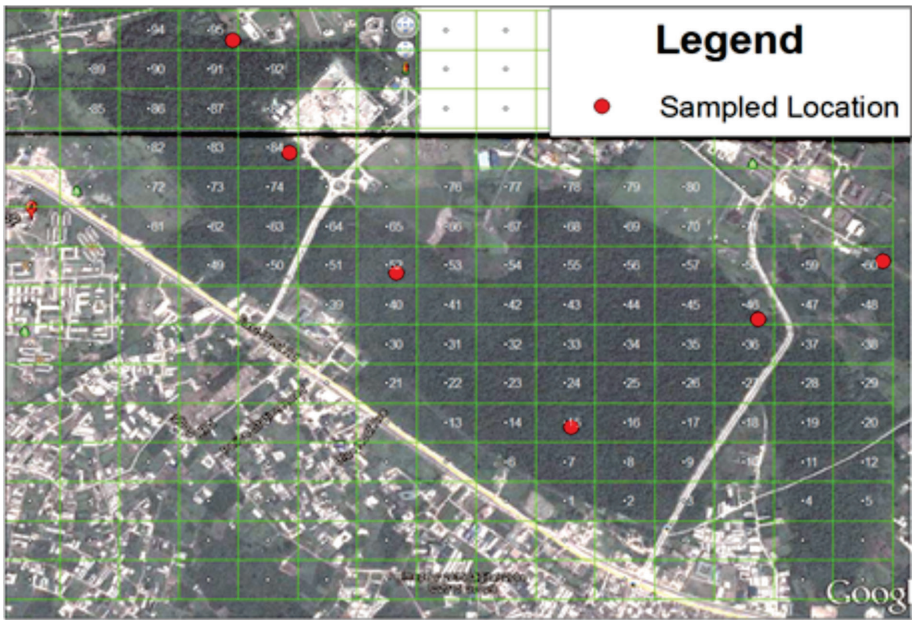

Figure 1. Gridded Study Area Showing Sampling Points

samples (0-20 cm depth) were collected using a Dutch soil auger into a clean, sterile polythene bag and thereafter, sent to the laboratory for nutrients and heavy metal analyses in an ice box maintained at a temperature of about 4 ^{0}C. Three plant species namely: *Alchornea cordifolia*, *Sacciolepis africana* and *Harungana senegalensis* were handpicked for this study being the most common plant species in the six wetland transects.

Analysis of pH and Nutrients

The pH was determined by the use of a pH meter (Mettler delta). The available total nitrogen was determined by the alkaline permanganate method described by Subbaiah & Asija (1956) whereas, the estimation of available total phosphorus in soil was carried out using the ascorbic acid method (Olsen *et al*. 1954). The available total potassium ion in soil was estimated using a flame photometer (Jackson 1967).

Heavy Metal Analyses

The plant and soil samples were desiccated in 24 hours at 600 °C and 700 °C respectively before they were washed. The solid samples were crushed to fine powder and weighed for digestion after desiccating. Hydrogen peroxide (30% Fluka), nitric acid (65% Aldrich), potassium chloride (Aldrich) and hydrochloric acid (37% Fluka) were used for digestion. Sample dilution was done using distilled water with a resistivity greater than 17.5 MΩcm.

The desiccated plant samples were digested in an acid solution using the Berghoff MWS-2 microwave digestion system. Hydrogen peroxide (10 ml) and nitric acid (8 ml) were added to 200 mg of desiccated samples that had been placed in the digestion vessels. The vessels were allowed to cool at room temperature after 30 minutes' digestion time, each solution volume was then topped up to 50 ml for each sample using distilled water. The values obtained were verified using the Certified Standard Reference Material SRM

1515 from the National Institute of Standards and Technologies.

Desiccated soil samples (500 mg) were placed in different digestion vessels and 9 ml hydrochloric acid (aqua regia) and 3 ml nitric acid were added to each vessel. The vessels were cooled to room temperature after 60 min digestion. For each sample, the solution volume was topped up to 50 ml using distilled water. For soil samples, the Certified Standard Reference Material SRM 2711 and 2710 was used for verification of the values obtained.

Flame Atomic Absorption Spectrometry

The Flame Atomic Absorption Spectrometry (FAAS) was employed to determine the elements present in the samples. The AVANTA GBC flame atomic absorption spectrometer with hollow cathode lamps that needs less volume of sample and proffers a good sensitivity was used to determine the Zn, Cu, Co, Ni, Pb, As, Cd, Fe, Mn and Cr elements from samples.

Calibration curve based on the absorber concentration was developed to determine the concentration of elements present in plant samples. Different known concentrations of various solutions were prepared with the concentration of elements in unknown sample determined via extrapolation from the calibration curve. The solutions used for Flame Atomic Absorption Spectrometry (FAAS) calibration were prepared from standard solution (Merck) of the elements being studied. The concentrations of all samples were recorded as mg/kg dry weight of material.

Duplicate samples were analyzed and the instruments used for several measurements were calibrated using standard and blank solutions. Heavy metal concentration in plant samples were measured using a set of standard calibration curves with relatively better standard deviations and good linear regression. The reliability of the measuring apparatus was verified by periodic testing of standard solutions and quality control test was used to check for accuracy and the degree of agreement between the measured and standard values in the plants; the difference was less than 5%. The limit of detection (LOD) for all the metals analyzed in this study is 0.001 mg/kg except for lead that has a LOD of 0.01 mg/kg. The limit of quantification (LOQ) for Cu, Ni, Mn and Co is 0.003 mg/kg, whereas LOQ for Pb, Fe and Zn are 0.04 mg/kg, 0.001 mg/kg and 0.0006mg/kg respectively. LOQ for Cr, Cd and As is 0.005 mg/kg.

Potential ecological risk index (PERI) was used to determine the degree of ecological risk of heavy metals present in sediments (Hakanson 1980). PERI integrates the heavy metal concentration with environmental effect, ecological effect, and toxicology and was used to evaluate the ecological hazard and heavy metal pollution for sedimentology. The calculated mathematical formula for PERI is expressed as:

$$RI = \sum_{i=1}^{n} E_i$$

$$E_i = T_i \frac{C_i}{C_0}$$

Where,

RI is the sum of all risk factors for heavy metals in sediments; $E_r i$ is the monomial potential ecological risk factor for a given substance; *Ti* represents the metal toxic factor of a certain metal;

C_i is the metal content in the sediments and C_0 is the regional background value of heavy metals in the sediments.

The metal toxic factor and background values for metals in sediments are presented in Tab. 2.

The following values as proposed by Håkanson (1980) were used in the interpretation of ecological risks in sediments: RI <150, low ecological risk for the sediment; 150 ≤ RI <300, moderate ecological risk for the sediment; 300 ≤ RI <600, considerable ecological risk for sediment; RI ≥ 600, very

Table 2. Reference C_n^i and toxic coefficient T_r^i of different heavy metals

Heavy metals	Cd	As	Cu	Pb	Co	Zn	Ni	Cr	Fe	Mn
C_0 (mg/kg)	0.5	15	30	25	12.7	80	26.9	61	Not determined	Not determined
Ti	30	10	5	5	5	1	5	2		

Sources: Hilton *et al.* (1985), Jiao *et al*. (2015) and Pérez *et al*. (2002)

high ecological risk for the sediment.

Results obtained were subjected to cluster analysis in order to categorize heavy metals in groups or clusters so that heavy metals in a particular group are more alike in one way or another when compared to heavy metals in another group.

Results and discussion

In this study, nutrients (nitrogen, phosphorus and potassium) and heavy metals (copper, cadmium, iron, manganese, chromium, cobalt, nickel, zinc, lead and arsenic) loads in Oroma wetland sediment and macrophytes from all six sampling points were determined and results obtained are presented in Figs. 2-14.

The concentration of total nitrogen in sediments ranged from 0.033-1.844 mg/kg (Fig. 2). The highest concentration of total nitrogen was obtained in SS1 while the least concentration of total nitrogen was obtained in SS3. The high nitrogen content in SS1 sediment may be due to the active agricultural activities going on around SS1 when compared to the other sampling sites. Jarvie *et al*. (2006) had earlier stated that agricultural and urban areas account for most of the nutrients (especially nitrogen) causing eutrophication. Furthermore, the high concentration of nitrogen in SS1 might be due its high altitude (*ca*. 24 m), which predisposes this wetland region only to seasonal flooding during the rainy season. Nutrients in sediment usually dissolve in water during floods and disturbance and dissipate by horizontal and vertical transport.

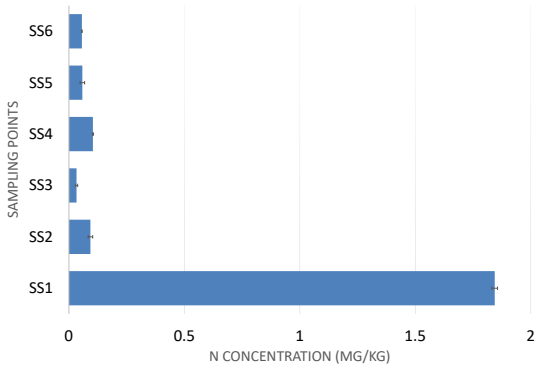

Figure 2. Nitrogen concentration profile of sediment samples obtained from Oroma wetland

However, since SS1 is seasonally flooded, nitrogen would be trapped in the sediment (instead of dissolving in water and flowing out) during a greater part of the year when floods in the area recede due to its high altitude. Moreover, it has been reported that gaseous losses of nitrogen through denitrification is the most significant nitrogen removal mechanism in natural as well as constructed freshwater wetlands (DeBusk 1999). The ability of denitrification to permanently remove nitrogen from the system as dinitrogen gas makes it one of the few processes capable of counteracting eutrophic conditions. High nitrate availability and bioavailable organic carbon are some factors that favor denitrification rates. Since SS1 is not always flooded, its sediment may not be anoxic and hence, will not encourage denitrification. This may have accounted for the high nitrogen concentration in SS1. Other sampling points are inundated with water most of the year thus, rendering the underlying sediment anoxic. This may explain the lower nitrogen concentrations obtained at those sampling points which may have been facilitated by denitrification. Nevertheless, the water chemistry and other wetland conditions, such as climate, vegetation, water depth and water flow determine how much nitrogen that is removed (*i.e.* transformed or removed from the water phase) in a wetland and which nitrogen processes or fluxes are prominent.

The total phosphorus in sediment samples ranged from 0.246-6.066 mg/kg (Fig. 3). SS1 had the highest phosphorus concentration whereas the least concentration was obtained from SS3 sediment. It is expected that since total nitrogen was highest in SS1, total phosphorus will also occur at a relatively high concentration in SS1 considering its altitude as previously stated and the common source of both nutrients – inorganic fertilizer. This is in line with Garn (2002) that stated that increased phosphorus delivery occurs in areas where soil fertilizer is delivered to water bodies and where human and animal waste are carried in runoff into water bodies. Phosphorus does not remain dissolved in water during flood episodes since it forms insoluble precipitates with calcium, iron, and aluminum, in addition to plant uptake. Moreover, phosphorus will more likely leach to the groundwater or be lost to runoff if the soil's capacity to hold phosphorus by adsorption is exceeded (Nasir 2010). The most common limiting nutrients in wetlands are nitrogen and phosphorus.

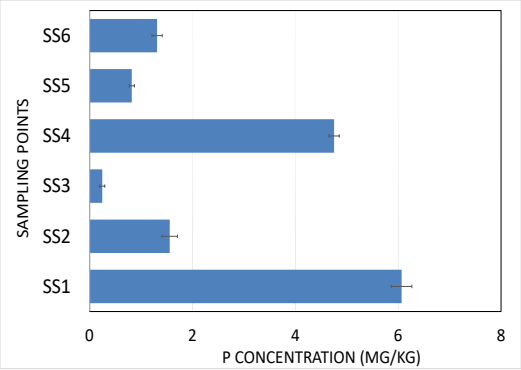

Figure 3. Phosphorus concentration profile of sediment samples obtained from Oroma wetland

Total potassium content of sediment samples ranged from 376.0-788.0 mg/kg (Fig. 4). SS5 sediment had the highest total phosphorus concentration whereas the least concentration was obtained in SS1 sediment. Although nitrogen, phosphorus and potassium are the major constituents of inorganic fertilizer, potassium has other major sources (e.g. detergent). Hence, SS5 had the highest concentration of potassium probably due to the presence of car wash facilities close to the sampling point. This is in concordance with report of Nguyen et al. (2006) which that stated that the major inputs of potassium in sediments are from fertilizer, irrigation water, detergents, outputs or removal via harvested products, residues, leaching, erosion and water runoff. In addition, the decrease in the concentration of potassium outward of SS5 is probably due to the non-proximity of the sampling points to the car wash.

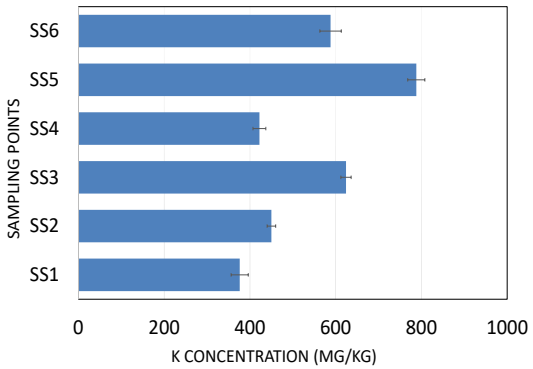

Figure 4. Potassium concentration profile of sediment samples obtained from Oroma wetland

The pH of sediment samples ranged from 4.55-5.90 (Fig. 5) with SS2 having the highest value and SS4, the least pH value. Our pH data is in accordance with the fact that wetland soils are usually acidic. Various processes are responsible for this acidity with the uptake of ammonium (NH_4^+) by plant roots being the main mechanism. Decreased acidity is usually obtained in swamps and fens due to the buffering of pH by groundwater and riverine water which are often alkaline in nature whereas, in bogs, rainwater has little ability to buffer increases in H^+ concentrations hence, resulting in the surface remaining generally acidic as reported by Sorrell & Gerbeaux (2004). Since pH was lowest in SS4 and highest in SS2, there is a tendency that heavy metals will be less available for plant uptake in SS4 and more available for plant uptake in SS2. Generally, as the pH reduces, heavy metals become more mobile and available for plants which are dependent on the actual combination of physical and chemical properties of soil.

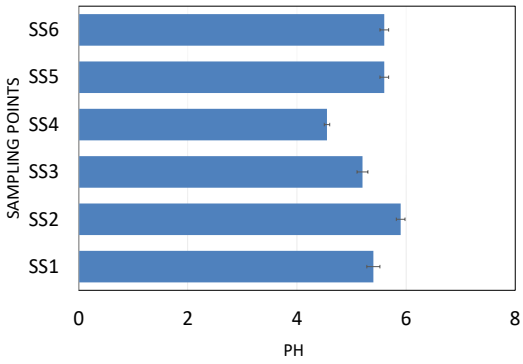

Figure 5. pH profile of sediment samples obtained from Oroma wetland

The cadmium load in sediments ranged from 4.80-54.10 mg/kg (Fig. 6). The highest concentration of cadmium in the sediments was obtained in SS5 and the least concentration in SS4. The concentration of cadmium in the plant tissues ranged from < 0.001-57.80 mg/kg. *A. cordifolia* from SS6 had the highest concentration of cadmium while the least concentration of cadmium in plant tissues was obtained from all the three plant species in SS4 and also in the tissues of *A. cordifolia* and *S. africana* in SS5. The tissue of *S. africana* in SS1 had a higher concentration of cadmium than the cadmium concentration obtained from its sediments. Similarly, the tissue of *A. cordifolia* in SS6 also had a higher concentration of cadmium than its sediment.

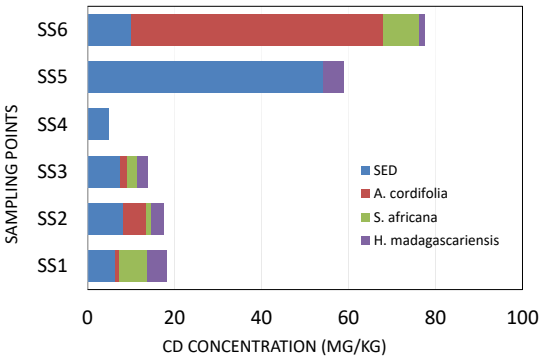

Figure 6. Cadmium concentration profile of sediment and macrophyte samples obtained from Oroma wetland

The concentration of cadmium in all the sediments exceeded the effects range low (ERL) limits of 1.2 mg/kg as specified in the ecologically-based guidelines for metals and organic toxicants (USEPA 2002) implying that the sediment is laden with cadmium. Cadmium hence, poses a very high ecological risk for sediments in Oroma wetland based on the interpretation of ecological risks for sediments proposed by Håkanson (1980). The highest concentrations of cadmium, cobalt, copper, iron, manganese and zinc were observed in SS5 and SS6 which is likely the reason why they all fell within cluster one in the cluster analysis (Fig. 7).

The high concentration of cadmium in the sediment sample obtained from SS5 accentuates the high potassium content obtained from same sample as cadmium and potassium are components of fertilizer used for agricultural activities and detergent used in car washes. Relatively high concentrations of heavy metals such as lead, mercury, arsenic, cadmium, uranium and chromium are found in phosphate rock commonly used in fertilizers. Amongst these heavy metals, the often considered worst for human and environmental health are cadmium and uranium (Roy 2001). Since the technologies needed to remove cadmium from superphosphate fertilizer are yet to be implemented globally, cadmium can be used as an indicator of fertilizer inputs (Roy 2001). Nevertheless, the uptake of cadmium by plants to a significant degree depends on the bioavailability of the introduced cadmium.

Cadmium is known to accumulate in pastures' foliage and lead to animal toxicity (Roberts & Longhurst 2002). The concentrations of cadmium in normal plants from uncontaminated soils usually range from 0.05 to 0.2 mg/kg (Peng *et al*. 2008), but this range was exceeded in all the sampling stations where cadmium was available for plant uptake implying that the sediments are laden with cadmium. Other authors have reported the accumulation of metals in tissues of other macrophytes such as duckweed salix, cattail (*Typha latifolia*) and common reed (*Phragmites australis*) (Ye *et al*. 2001). If metals are accumulated in above ground tissues, they may pass on the contaminants to herbivores. The application of sewage sludge, manure and limes also results in enrichment of cadmium in soil and sediment. Cadmium was not available for plant uptake in SS4. This may be as a result of the low pH (4.55) value of the sediment obtained from SS4 since Maiti & Jaiswal (2008)

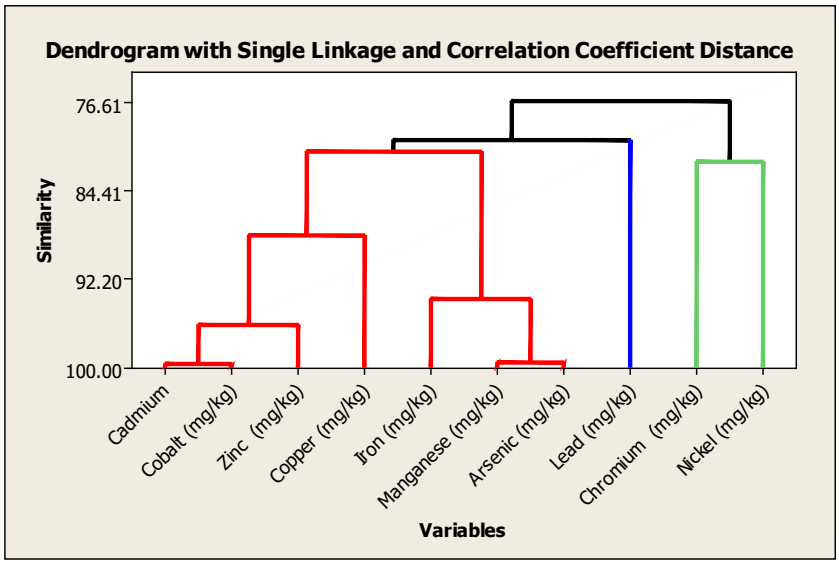

Figure 7. Heavy metal clusters in Oroma wetland Sediments

had stated that metal accumulation in plants depends on various factors such as type of plant, age, pH, form and type of available metals in substrate and climatic conditions.

The relatively higher concentration of cadmium in the tissue of *A. cordifolia* in SS6 (which was higher than that obtained in SS6 sediment) is most likely due to cadmium pollution that occurred in the past and was taken up by the plant, *A. cordifolia,* which appears to be an accumulator of cadmium. Ravera (2001), reported that while the pollutant concentrations in the water only indicate the situation at the time or seasons of sampling, pollutant concentrations in sediments and organisms are due to the past as well as recent pollution status of the organism's environment or habitat.

Cobalt concentration in all the sediments ranged from <0.001-5.70 mg/kg (Fig. 8). The sediment from SS5 had the highest concentration (5.70 mg/kg) of cobalt whereas, this heavy metal was not detected in sediment samples obtained from other sampling points. The concentration of cobalt in the plant species from all the sampling stations ranged from < 0.001-7.90 mg/kg. *A. cordifolia* from SS1 had the highest concentration of cobalt in its tissue despite being non-detectable in SS1 sediment whereas, cobalt was not detected in most of the tissues obtained from other sampling stations except in SS4 and SS5. In SS4, cobalt was not detected in the sediment but was found in tissues of *S. africana* obtained from SS4.

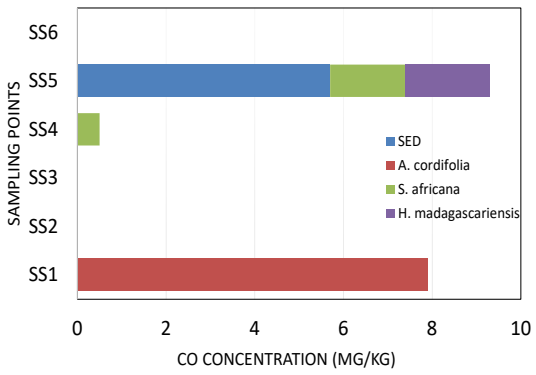

Figure 8. Cobalt concentration profile of sediment and macrophyte samples obtained from Oroma wetland

The absence of cobalt in all the sediments except the SS5 sediment may be attributed to its sorption capacity. Reactions occur between metal contaminants, ligands in water and surface sites on the solid matrices in contact with the water. In these sorption reactions, the metal is bound to the solid matrix and is referred to as being sorbed. In an earlier study by Jerry & Terry (2005), the following patterns of decreasing metal partition coefficient (K_d) in sediments was observed: Pb> Hg > Cr^{3+}> Cu > Ni > Zn > Cd > Ag > Co > As. Thus, the low sorption capacity of cobalt to solid matrix (in this case, sediment particle) may be the reason why it was not detected in sediment samples obtained from most of the sampling points. This may also be the same reason why arsenic was not detected in sediment samples from all six sampling stations in this study. Episodes of floods, sediment disturbance, water flow and turbulence may affect cobalt retention in sediment and result in its removal from the sediment. The retention processes of trace metals by soils can be noticeably shifted by alterations in soil solution chemistry, like ionic strength, pH, and redox potential (Gerringa *et al*. 2001). The presence of cobalt in the sediment obtained from SS5 may most likely be due to the presence of the scrap metal dump adjacent to SS5 which provided a constant supply. Cobalt metal is usually combined with other metals to make alloys that are resilient or more resistant to corrosion and wear in machines. The corrosion of the alloys in the open scrap metal yard may have facilitated the leaching of cobalt from the scrap alloys and its eventual discharge into SS5 of the Oroma wetland through run-offs/storm water. Based on the interpretation of ecological risks in sediments proposed by Håkanson (1980), cobalt poses a low ecological risk for sediments of the Oroma wetland. This implies that a significant increase of cobalt sediment concentration due to human activities has not occurred though it may have been introduced into the wetland prior to this study. This is envisioned in its presence in plant tissues obtained from 'cobalt-free' sediments in this study implying that prior bioaccumulation of this metal had occurred when cobalt was present in the sediment in the past. The concentration of cobalt in the tissues of *S. africana* and *H. madagascariensis* further alludes to the fact that plants take up heavy metals when present in sediments. High concentrations of metals can be accumulated from the water column by aquatic plants and/or from sediments. In the cluster analysis performed, the accumulation of cobalt, cadmium, lead and chromium in the macrophytic tissues were relatively low and did not occur in all the sampling stations hence they were grouped in cluster one (Fig. 7). This could be as a result of their non-bioavailabity to macrophytes.

Sediments in all sampling points had chromium concentrations ranging from 14.10-37.10 mg/kg (Fig. 9). The highest concentration of chromium was obtained in sediment of SS1 whereas SS4 had the least concentration. In plant tissues, chromium was only detected in *A. cordifolia* (0.6 mg/kg) and *H. madagascariensis* (0.6 mg/kg) obtained from SS1 which also had the highest chromium load in sediment. Chromium was not detected in plant tissues obtained from other sampling points despite its presence in sediments of the area.

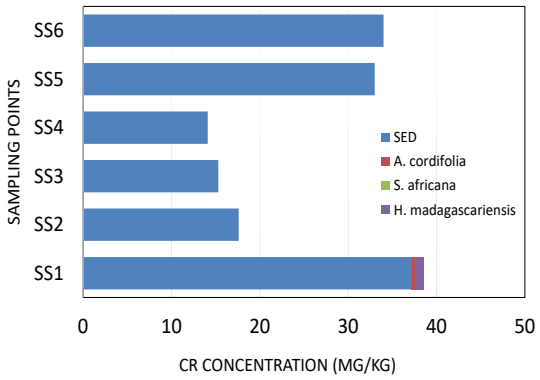

Figure 9. Chromium concentration profile of sediment and macrophyte samples obtained from Oroma wetland

Chromium concentration in all sediments were lower than the ERL of 81 mg/kg as specified in the ecologically-based guidelines for metals and organic toxicants (USEPA 2002) thus, implying that the sediments of Oroma wetland are not contaminated with the heavy metal, chromium. However, the relatively higher concentration of chromium in the sediment obtained from SS1 is probably due to the site's relatively higher altitude and the agrochemical application of fertilizer near the site. In the cluster analysis (Fig. 5), chromium and nickel were in the same cluster (cluster two) most likely because SS1 and SS6 had the highest concentrations of both metals thus, suggesting that either both metals have the same flow dynamics or might have entered the wetland from a common source.

The copper load in sediment from the various sampling points ranged from 4.80-22.70 mg/kg (Fig. 10). SS5 sediment had the highest copper concentration while the least concentration was obtained in SS3 sediment. In the three plant tissues, various copper concentrations ranging from 3.0-28.0 mg/kg were obtained. However, the highest tissue concentration of copper was obtained in *H. madagascariensis* from SS3 whereas *A. cordifolia* obtained from SS1 gave the least concentration of copper in its tissue. The plants from all the sampling stations except SS5 had higher concentrations of copper in their tissues than the sediments from where they were obtained.

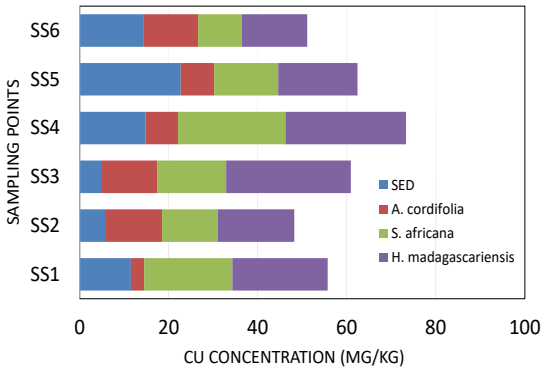

Figure 10. Copper concentration profile of sediment and macrophyte samples obtained from Oroma wetland

Copper concentration values in all sediments were lower than the ERL of 34 mg/kg as specified in the ecologically-based guidelines for metals and organic toxicants (USEPA 2002) and hence, poses a low ecological risk in sediments of Oroma wetland (Håkanson 1980). However, the relatively higher copper concentration in SS5 sediment could be due to input from the scrap metal dump and adjoining maintenance outfits.

The relatively higher concentration of copper in the tissues of the wetland plants when compared to the copper load in respective sediments is an indication that copper was available for plant uptake and accumulation although, *S. africana* and *H. madagascariensis* appear to be better accumulators of copper than *A. cordifolia*. Copper, manganese and zinc were grouped in cluster two due to their relatively high capacity to bioaccumulate in plant tissues in all the sampling stations. The fact that the concentration of heavy metals in tissues of macrophytes can be many times higher than is obtained in the host aquatic environment makes aquatic flora very influential in heavy metal accumulation (Samecka-Cymerman *et al*. 2005).

The iron content ranged from 1194.0-7918.0 mg/kg and from 83.40-280.40 mg/kg in sediment and plant tissues respectively (Fig. 11). SS6 sediment had the highest concentration of iron whereas the SS2 sediment had the least concentration. The tissue of *S. africana* obtained from SS4 had the highest concentration of iron whereas, *A. cordifolia*

tissue from SS1 had the least concentration. In all sampling points, the concentration of iron in sediment was higher than the concentration of iron obtained in tissues of the plants.

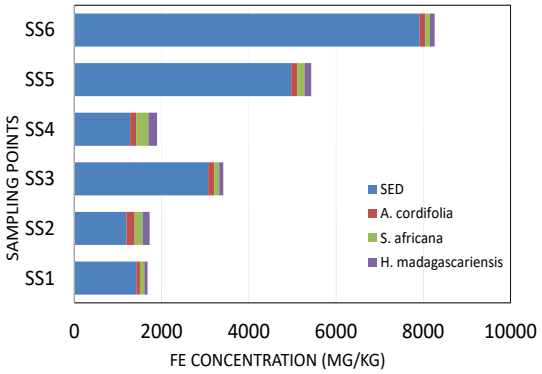

Figure 11. Iron concentration profile of sediment and macrophyte samples obtained from Oroma wetland

Generally, the concentration of iron in Oroma wetland sediment was quite high when compared to other metal concentrations in sediment. This observation had earlier been corroborated by Inengite *et al*. (2010) that recorded high values of iron ranging from 552 -15,379.50 mg/Kg in their study. The relatively higher concentration of iron in SS6 sediment may be because it is seasonally flooded and not inundated with water most part of the year. The dense plant litter and dense vegetation on its surface may slow down precipitation effects and thus, attenuate vertical transport of iron leading to increased concentration. The iron that has been deposited overtime had remained trapped in the sediment instead of being dissolved and carried away by flood. The solubility of Fe^{3+} and Fe^{2+} amorphous hydrous oxides largely controls the mobility of iron in soil, though iron solubility may also be greatly modified by the formation of other iron compounds, such as carbonates, sulphides and phosphates (Kabata-Pendias & Pendias, 2001). In general, Fe^{3+} has a very low mobility whereas Fe^{2+} ion is moderately mobile in secondary environments. Flood inundation events in soil result in the reduction of Fe^{3+} to Fe^{2+} which increases iron solubility. SS6 is seasonally flooded and hence, iron solubility in its sediment may not be very active. Although the source of iron in SS6 is not clear, Reimann *et al*. (2003) had reported that iron sulphate is used as a fertilizer and herbicide which could be a possible source of iron in SS6. Other anthropogenic sources of iron in the wetland could have been the deposition of sewage and the small-scale iron and steel works outfits around the area. Sewage from Alakahia and Rumuosi catchment area may have contributed to the iron load since SS6 is the first point of entry of runoffs from Alakahia and Rumuosi prior to discharge into the wetland.

The concentration of iron obtained in the plant tissues suggests that iron was not very available for plant uptake despite its very high concentration in sediment of Oroma wetland. This inference is supported by Micó *et al*. (2006) who had stated that an elevated soil content of total iron does not suggest that it is available to plants. For instance, iron deficiency in plants may not be due to insufficient total soil iron content but to the formation of insoluble compounds since iron is mainly found in precipitated forms (such as oxides and hydroxides) in these soils. Hence, the availability of iron to plant roots is very low despite the fact that iron is one of the most abundant metals in the earth's crust. However, *A. cordifolia* and *S. africana* were better assimilators of iron when compared to *H. madagascariensis*. Iron and nickel occurred in cluster three due to their relatively high capacity to bioaccumulate in macrophytic tissues in all the sampling stations.

Nickel was only detected in sediment samples obtained from SS1 and SS6, with SS6 having a higher concentration of 75.90 mg/kg (Fig. 12). However, nickel was detected in all plant tissues from all six sampling points with concentrations ranging from 0.20-24.20 mg/kg. The highest and least nickel concentrations were obtained in the tissue of *A. cordifolia* from SS4 and SS5 respectively. Plant tissues from SS2, SS3, SS4 and SS5 had appreciable nickel loads despite the dearth of nickel in corresponding sediments harboring the macrophytes. However, *S. africana* and *A. cordifolia* appear to be better accumulators of nickel when compared to *H. madagascariensis*.

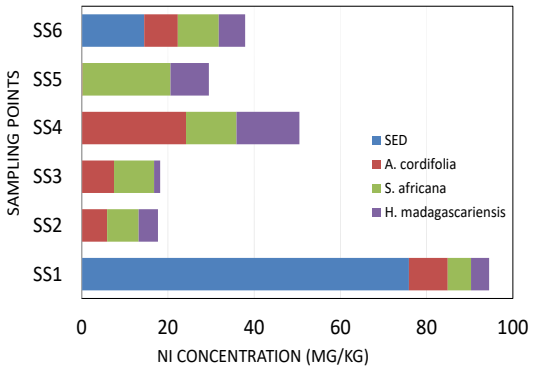

Figure 12. Nickel concentration profile of sediment and macrophyte samples obtained from Oroma wetland

The nickel burden in all sediment samples except SS1 was lower than the ERL of 21 mg/kg as specified in the ecologically-based guidelines for metals and organic toxicants (USEPA 2002). This implies that SS1 sediment is highly contaminated with nickel and this is most likely due to the site's close proximity to several power generating plants as petroleum products generally contain nickel. SS6, where nickel was also detected but in a lower concentration, is in the vicinity of a generator plant. Nickel found in the plant tissues obtained from SS2, SS3, SS4 and SS5 may remotely be due to atmospheric deposition arising from generator plant exhaust. Osuji & Onojake (2004) had reported that nickel was the highest trace heavy metal associated with crude oil. Nickel is released into the atmosphere through the exhausts of power plants and municipal refuse incinerators and its removal from the air usually takes a long time. However, nickel may settle to the ground with precipitation after undergoing atmospheric reactions and can also end up in surface water through the discharge of untreated wastewater streams. Eventually, most of the nickel compounds released to the environment will end up being adsorbed to soil particles or sediment where they become immobile. However, when soil or sediment pH becomes acidic, nickel compounds regain their mobility and often leach down to the underlying groundwater (Raymond & Felix 2011) which may explain its non-detection in most sediment samples from the Oroma Wetland. Nickel poses a low ecological risk in sediment of Oroma wetland based on the interpretation of ecological risks in sediments proposed by Håkanson (1980).

The concentration of nickel obtained from plant tissues is an indication that nickel was available for plant uptake and that bioaccumulation took place in the plants. Nickel could have accumulated from the water column and/or from sediments which may result in macrophytic tissues bearing heavy metal concentrations several times higher than concentrations in aquatic environment according to Samecka-Cymerman *et al*. (2005).

The lead burden in the sediments ranged from 98.60-175.30 mg/kg for various sampling points (Fig. 13). The sediment in SS6 had the highest concentration of lead whereas, the least was obtained from SS4. Among the plant tissues, lead was only detected in *S. africana* obtained from SS2 and *A. cordifolia* obtained from SS1, SS3 and SS6 with *A. cordifolia* tissue from SS6 having the highest lead burden of 35.30 mg/kg. No lead was detected in *H. madagascariensis* in all sampling stations. Plant tissues obtained from SS4 and SS5 showed no lead burden despite the presence of lead in the sediment of those sampling points. The lead burden in the plant tissues indicates that lead was not readily available for plant uptake in most sampling points albeit, *A. cordifolia* showed potentials for lead uptake from sediment.

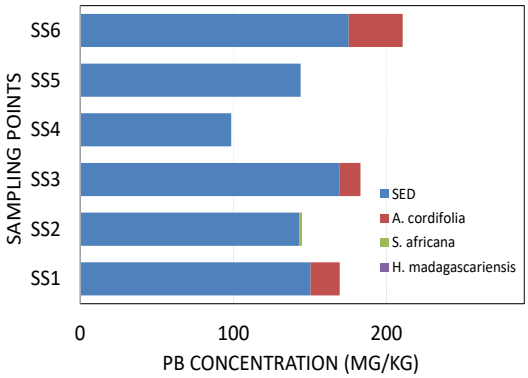

Figure 13. Lead concentration profile of sediment and macrophyte samples obtained from Oroma wetland

The lead burden in sediment of all the sampling points exceeded the ERL of 47 mg/kg as specified in the ecologically-based guidelines for metals and organic toxicants (USEPA 2002) implying that the sediment of Oroma wetland is highly polluted with lead. The concentration of lead in all sampling points were within a proportionately narrow range of 98.60-175.30 mg/kg compared to the concentrations of other metals that varied widely across the sampling sites, this could be the rationale behind lead been in cluster three alone in the cluster analysis (Fig. 7). Judith *et al*. (2013) had attributed lead burden in sediment to evaporative concentrations and point and diffused inputs from industrial, farms and urban associated activities like garages and car wash. The high concentration of lead in SS6 sediment could have been due to urban runoff from Alakahia and Rumuosi communities. Its low solubility in water may also have exacerbated this high burden in SS6 since that area of the wetland is not susceptible to constant flooding unlike other stations. The dense plant litter and dense vegetation in SS6 may also impair rapid vertical migration of lead into the subsurface strata leading to increased lead burden in the surface strata.

Based on the interpretation of ecological risks in sediments (Håkanson 1980), lead poses a moderate ecological risk in sediments in Oroma wetland.

In the case of arsenic, it was not detected in the sediments and plant tissues obtained from all six sampling stations. Thus, arsenic concentration in sediment of all sampling points was lesser than the LOD value of 0.001 mg/kg. This implies that the sediment of Oroma wetland is not polluted with arsenic. Though, it was not ascertained if arsenic is part of the pollutant load entering the wetland from adjoining settlements, its scarcity in the wetland sediment may be attributed to its very low affinity/sorbtion for sediment particles compared to other heavy metals. Jerry & Terry (2005) had observed the following patterns of decreasing metal partition coefficient (K_d) in sediments Pb> Hg > Cr^{3+} > Cu > Ni > Zn > Cd > Ag > Co > As which may suggest that arsenic is highly mobile resulting in its rapid transfer from sediment into the overlying surface water during flood events in Oroma wetland. In the study carried out by Jerry & Terry (2005), arsenic was also not detected in sediment samples. Based on the data obtained in this study and the ecological risks interpretation in sediments, arsenic poses a low ecological risk for sediments in the Oroma wetland (Håkanson 1980). Very low accumulation of arsenic in the tissues of macrophytes could be the reason behind arsenic occurring in cluster four alone in the cluster analysis (Fig. 7). However, its non-accumulation could be attributed to its scarcity in the sediment.

The manganese load of sediment samples and plant tissues from Oroma wetland is shown in Fig. 14. Sediment concentrations ranged from 50.30-311.60 mg/kg while tissue concentrations ranged from 6.10-160.90 mg/kg. The highest manganese concentration in sediment was obtained in SS6 while the lowest concentration was obtained in SS2. As for the plant tissues analyzed, the highest concentration was obtained in the tissue of *S. africana* from SS1 whereas the least concentration was obtained in *S. africana* tissue from SS5. Manganese concentrations in plant tissues obtained from SS1, SS2, SS3 and SS4 were higher than were obtained in their respective sediment samples.

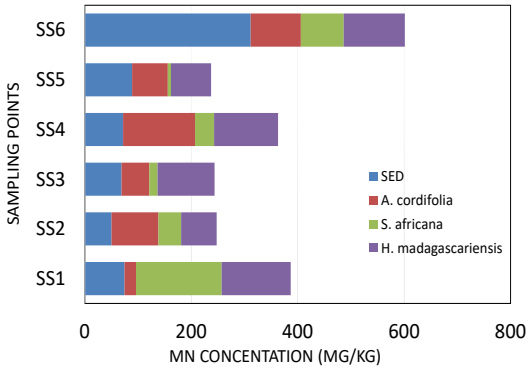

Figure 14. Manganese concentration profile of sediment and macrophyte samples obtained from Oroma wetland

Zinc concentration in sediment samples from various sampling points ranged from 24.80-52.90 mg/kg (Fig. 15). SS5 sediment had the highest concentration of zinc whereas SS1 sediment had the least concentration. For the plant tissues, the concentration of zinc ranged from 7.10-58.20 mg/kg. Generally, *H. madagascariensis* tissues had the highest concentration of zinc among plant tissues. The least zinc load was obtained from *S. africana* derived from SS6. Zinc load in plant tissues (especially *H. madagascariensis*) was higher than the load in corresponding sediment at SS3 and SS4 suggesting active accumulation of zinc by these macrophytes.

The zinc burden in all sediment samples was lower than the effects range low (ERL) limits of 150 mg/kg as specified in the ecologically-based guidelines for metals and organic toxicants (USEPA 2002) implying that the sediment of Oroma wetland is not polluted with zinc. However, the relatively high concentration of zinc in sediment of SS5 is an indication of an appreciable introduction of zinc into the wetland through anthropogenic activities in the catchment area. Inputs from the scrap metal dumps, animal husbandry and farming activities are likely to contribute to enhanced zinc concentration in the sediment of SS5. Some soils are heavily contaminated with zinc and this phenomenon is common in areas where zinc has been refined or mined, or where sewage sludge from industrial areas has been applied in farms as organic fertilizer (Lenntech 2008). Another possible source of zinc is the close promixity of automobile maintenance workshops to SS5. There is also a possibility that sources of zinc are likely from eroded motor vehicle tire rubber exacerbated by poor road surfaces and the indiscriminate

disposal of spent lubricating oils in which zinc (as zinc dithiophosphates) is present as part of its many additives (Bai *et al*. 2008). Based on the interpretation of ecological risks in sediments proposed by Håkanson (1980), zinc poses a low ecological risk in sediments of Oroma wetland.

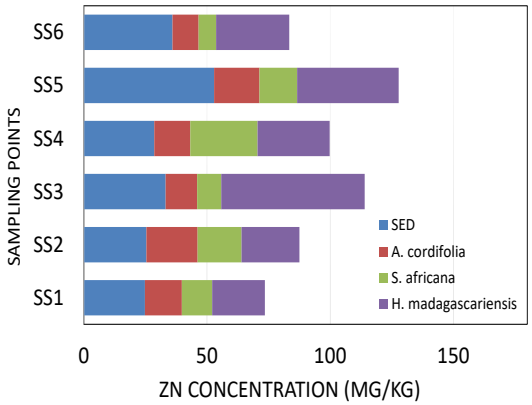

Figure 15. Zinc concentration profile of sediment and macrophyte samples obtained from Oroma wetland

The zinc burden in plant tissues is an indication that zinc was available for plant uptake in all the sampling points of the Oroma wetland. However, *H. madagascariensis* and *A. cordifolia* seem to be better accumulators of zinc than *S. africana*. The relatively higher concentration of zinc in plant tissues when compared to corresponding sediment samples obtained from SS3 and SS4 is an indication that the older a plant is the more concentration of a pollutant it is expected to have taken up from the soil. Samecka-Cymerman *et al*. (2005) had espoused that the concentration of heavy metal in aquatic environment may be several ten to several thousand times lesser than in macrophytic tissue.

The heavy metal load obtained in various sediment samples of the Oroma wetland is an indication that the uncontrolled ongoing anthropogenic activities taking place in the vicinity of the wetland is negatively impacting the wetland. The results also show that the macrophytes in Oroma Wetland have varying potentials to accumulate in their tissues certain metals present in sediment and this may have far reaching public health and ecological consequences.

Conclusion and recommendation

The results obtained from this study show that the sediment samples obtained from each of the six sampling sites of the Oroma wetland were highly polluted with cadmium and moderately polluted with lead as a result of the uncontrolled anthropogenic activities taking place in the catchment area of Oroma wetland. The heavy metal burden in sediment was of decreasing ecological risk in the following order: Cd > Pb > Ni > Cu > Cr > Zn > Co > As whereas, the order of decreasing ecological risk with regards to the sampling sites is as follows: SS5 > SS6 > SS2 > SS3 > SS1 > SS4. The heavy metal load in SS5 and SS6 sediments posed a very high ecological risk in those stations while the heavy metal burden in sediments of other sampling sites posed a moderate ecological risk.

Anthropogenic activities like the use of agrochemicals on farmlands, generator houses, discharge of untreated sewage from catchment areas, release of effluents from slaughter houses, car wash centers, metal dumpsites, automobile maintenance shops, fast food centres, etc. into the wetland and the discharge of runoffs and chemical leaks into the wetland were identified as sources of the high nutrient and heavy metal content of the wetland sediment.

Hence, adequate impact mitigation measures should be put in place to protect the health of the wetland and ensure its preservation considering the many ecological and hydrologic functions it performs and the diversity of life forms it sustains.

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