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Energy Dispersive X–ray fluorescence (EDXRF) and Chemometric Analysis of Shore Sediment Heavy Metal Characteristics at Port Victoria, Kenya.

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Background*: Lake Victoria basin is characterized by increased human and industrial activities due to high population density. Due to these activities, effluents containing heavy metals are discharged directly or indirectly onto land and in water bodies within the basin which are then ferried by river Nzoia into Port Victoria shoreline.*
Materials and Methods*: In this study, bottom sediments being sinks for the heavy metals, were sampled and analyzed for heavy metal concentration using EDXRF and chemometric techniques; principal component analysis (PCA) and hierarchical cluster analysis (HCA).*
Results*: The mean concentration levels of Ti, Zn, Cu, Mn, Rb, Sr and Zr were 1915.05±103.92, 43.33±5.32, 27.15±4.91, 682.86±21.21, 39.41±1.04, 162.95±5.22 and 113.63±1.18 µg/g which were found to be below their natural background levels of 4400, 132, 170, 950, 90, 370 and 220 µg/g. However, the mean concentration of Pb was 29.0216±2.41 µg/g which was above its natural background level of 16 µg/g. PCA results indicate strong correlation among Mn, Cu, Zn and Zr in cluster one, Ti and Rb in cluster two and Pb and Sr in cluster three. HCA apportioned all heavy metals to result from agricultural activities, municipal waste water discharges and sewage sludge from the industries in the lake basin.*
Conclusion: *It is on this basis that urgent measures should be put in place to control pollution by heavy metals in the Lake Victoria basin.*
Key Word*: **Heavy metal, EDXRF, Chemometrics, PCA, HCA***

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I. Introduction

Heavy metals occur naturally due to weathering of rocks or may be immobilized through human activities [1, 2] hence elevating natural levels in the environment [3]. Lake Victoria basin is characterized by high population and many industries [4]. Effluents from natural sources, atmospheric pollutants, pesticides and fertilizer applications discharge heavy metals into rivers, estuaries and lakes directly or indirectly [5, 6]. Extensive utilization of land has led to washouts that ease transportation of effluents containing heavy metals into river Nzoia which is the largest river in the basin that facilitates deposition of effluents in the bottom sediments at Port Victoria shoreline [7, 8, and 9]. Surface bottom sediments are usually a good source of sedimentation and remobilization processes of heavy metals **[1**0, 11 and 12]. Through biomagnifications and the associated food chain the health of the population in the lake basin is put to risk [13, 14 and 15].

Studies elsewhere and in Kenya have been carried out about heavy metal concentration in the environment. For instance, in China, concentration of As, Hg, Cr, Pb, Cd and Cu in sediments of Lake Tahiu were measured using ICP-AES, Agilant-7500. The mean concentration were found to be greater than the natural background levels in Lake Tahiu basin. The principal component analysis (PCA) and hierarchical analysis (HCA) associated Mn, Cd and As to natural weathering of natural sources whereas Hg and lead Pb were associated with anthropogenic activities [16]. In Indonesia, the concentration and pollution level of heavy metals Mn, Fe Co, Ni, Cu and Zn in the surface sediments of Kendari bay were measured by inductively coupled plasma mass spectrometry (ICP-MS) Fe had the highest concentration of 1100-29800 µg/g followed by Mn (34.39-399.59 µg/g), Zn (2.58 -129.7 µg/g), Ni (1.14-15.34 µg/g), Cu (0.6-15.81 µg/g) and Co (0.24 -7.33 µg/g). PCA suggested similar distinctions of Fe, Ni and Co in 25 sampled sites. Geochemical index suggested that the Kendari Bay surface sediment is unpolluted for each heavy metals investigated [17]. In Pakistan**,** heavy metal contamination and ecological risk assessment in surface sediments were measured by inductively coupled plasma optical emmission spectrometry (ICP-OES). Only Al had average concentration lower than the average value of the upper continental crust (UCC). Pollution indices indicated contamination of sediments with As, Cd and Ni. PCA, HCA and correlation coefficients suggested the origin of heavy metal to both anthropogenic and natural sources [18]. In Bangladesh, concentration levels of Cd, Cr, Cu, Mn, Fe and Pb were measured in ten

sediment samples of major canals in Dhaka City by Flame Emission Atomic Absorption Spectrophotometer (FL-AAS). Cr, Cu and Pb were found to be major pollutants while Cd, Mn and Fe were found to be minor pollutants. PCA and HCA showed strong interrelationship between Pb and Cu and Mn and Fe in the study [19]. In South Africa, concentrations of Cr, Pb, Zn, Ti, Mn, Sr, Cu and Sn in sediments taken along a section of the Swart kops river and its estuary were measured using a Shimadzu sequential plasma spectrometry (ICPS-1000II) and the calibration curve method. Elevated concentrations were measured in areas where storm surface runoff from informal settlement and industry entered both the river and the estuary [20].

In East Africa, concentration of heavy metals in Winam and Mwanza gulfs of Lake Victoria were determined using AAS. In the study, Zn was found to have high values of (1.019 ppm) and (0.889 ppm) at Winam and Mwanza gulfs respectively **[**21**]**. Still in the Lake Victoria basin, trace metal concentration in the sediments of Lake Kanyaboli were investigated for Ag, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn and Zn. The levels were compared with standard levels of unpolluted fresh water provided by the world health organization (WHO) and it was found out that Lake Kanyaboli was unpolluted except for the metal (Mn) which is a result of natural geochemical weathering within the basin [22]. Distribution of trace metals Cu, Cd, Zn, Fe and Pb in sediment of rivers; Sio, Nyando, Nyamasaria and Sondu miriu as well as on four beaches; Port Victoria, Hippo point, Dunga and Kisumu car wash along Lake Victoria, Kenya was investigated. The concentration of the metals in sediment was found to accumulate downstream and this was attributed to increased deposition by the slowing rivers as they enter a large water body (Lake Victoria). It was also found out that Kisumu car wash area recorded elevated concentration levels of all the metals while the Hippo point, Dunga Beach and Port Victoria Beach recorded low concentrations of all the metals [23].

Few studies carried out on heavy metal concentration in the Lake Victoria region by using univariate techniques are inefficient in analyzing environmental data. This has led to inadequate knowledge about environmental impact due to pollution by immobilized heavy metals in the Lake Victoria Basin [24]. Therefore the aim of this study was to sample, measure the levels of (Ti, Mn, Zn, Cu, Pb, Rb, Zr, Sr) and analyze the complex environmental data using EDXRF spectrometry technique in combination with multivariate chemometric techniques; principal component analysis (PCA) and the hierarchical cluster analysis (HCA). The PCA was used to study patterns of heavy metals immobilized in the lake basin while the HCA apportioned the sources of the heavy metals. In this way, the available information will be reference to future studies on pollution management of the lake basin.

II. Materials And Methods

1.1 Study area and Sampling

The shoreline of Port Victoria was chosen in this study because it is where the largest river Nzoia draining from the lake basin discharges effluents through three tributaries. The global positioning system (GPS) was used to locate the selected sampling points at intervals of about 1 km along a shoreline of 10 km as shown in Fig 3.1. Each sampling point was reached by boat and two bottom sediments samples of at least 200g were scooped by a corer at a depth ranging between (0-4cm) within a sampling area of 1 m^2. The samples were then put in well labeled polythene bags and then transported to the laboratory for preparation and analysis.

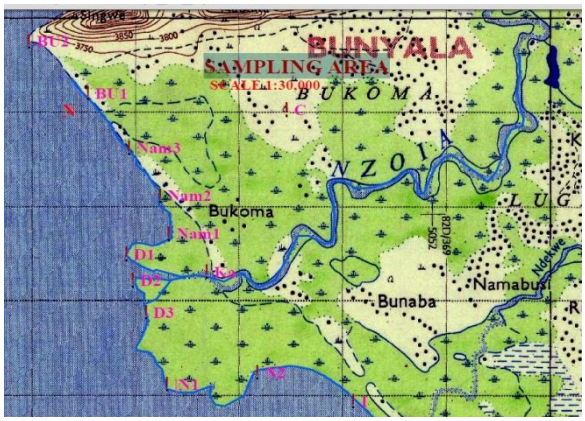

Figure 3.1: Map of Port Victoria shoreline. (Map drawn to scale by the Institute of Survey Nairobi, Kenya). Ka= Kabras, D1, D2 and D3= Active deltas of River Nzoia, N1and N2= Nanganda, I= Indufu, Nam1, 2, 3= Namugerwa (blocked deltas of River Nzoia), Bu1, 2= Bukoma beaches. Also note River Ndekwe discharging at site I.

2.2 Sample preparation

Sediment samples from each site were oven dried at 100^{o}C for 48 hrs to a constant weight and then each sample was ground into fine powder using a mortar and a pestle [25]. Approximately 1 g of the sample was then stored in clean Petri dishes and then diluted using cellulose (starch binder) in the ratio 7:3 to reduce matrix effects and improve pellet formation [26]. The diluted samples were then pressed into pellets of diameter 2.5 cm by the hydraulic press and thereafter labeled in readiness for analysis.

2.3 Spectral data and analysis

The spectrometer used in this work was the lithium drifted silicon Si (Li) detector (EG & G Ortec, 30 mm^2 x 10 mm sensitive volume, 25 μm Be window) with an energy resolution of 180 eV at 5.9 keV Mn Kα line. Cd-109 radioisotope source was used to excite and eject electrons in the inner energy levels of the metal atoms in the samples. The spectral data and analysis was done by using computer based multi-channel analyzer (MCA) and quantitative X-ray Fluorescence Analysis software (AXIL-QXAS) with an acquisition time of 2000 s [27]. The energies of the photo peaks on the X-ray spectrum was compared with tables of X-ray energies to identify the metals in the samples while the intensity of the photo peaks was used to determine concentration of the identified metals according to (3.3).

$$I_i = G_o K_i \rho_i d \left[\frac{1 - e^{a\rho d}}{(a\rho d)} \right] \qquad (3.3)$$

Where, G_O is the geometric factor for calculation of fluorescence intensity, K_i is the constant of the analyte element 'i' in the sample, a_i is the average mass absorption constant, ρ_i is the sample mass density and d is the thickness of the sample.

2.4 Limits of detection in XRF spectrometry

The below detection limit (BDL) for measured metals in the analytical method was determined by using (3.4). Where, *C*, is the concentration of the sample, N_b is the net background intensity and N_p is the net peak intensity. I_b and N_P are the net background and peak intensities while,C, is the elemental concentration of the five determinants.

$$DL = 3C \frac{\sqrt{N_b}}{N_p} \qquad (3.4)$$

2.5 Analysis of Certified Reference Material (IAEA SOIL-7)

For quality assurance in the analytical method, the dispersion $(C_i)_{disp}$ of measured elemental concentration values $(C_i)_m$ from the certified values $(C_i)_c$ were calculated using equation 3.5.

$$(C_i)disp = \frac{(C_i)m - (C_i)c}{(C_i)c} \times 100 \quad \% \qquad (3.5)$$

Where, $(C_i)_m$ is the measured value of the element, i, in the sample, $(C_i)_c$ is the certified value of the element ,I, in the reference sample and $(C_i)_{disp}$ is the dispersion of the measured value from the certified values calculated using equation 3.5. The detector performance was found to be good during measurement as the dispersion of measured values from the true values were within the accepted limits of ± 10 %.

2.*6 Multivariate Chemometric Analysis of the measured data*

Due to complexity of environmental data, multivariate techniques; principal component analysis (PCA) and hierarchical cluster analysis (HCA) are suitable in analyzing such kind of data [28]. Both mathematical and statistical methods are employed to evaluate and interpret data by extracting maximum information from the measured data [29, 30]. PCA manipulates complex raw data and extracts principal components in the sequence of decreasing variance with the first few principal components carrying a lot of information while the rest are regarded as noise in data [31, 32, 33, 34]. The original data matrix is transformed into a product of two matrices, one of which contains the information about the sites and the other about concentration [35, 36] as shown in (3.6a).

$$X = T.P^t + E \qquad (3.6a)$$

where, X is the original data matrix (m x n) with m in this work representing sampling sites and n representing measured elemental concentrations in bottom sediment samples collected from Port Victoria shoreline. T is the score matrix (m x a) with, a, representing the necessary number of principal components (Pcs) containing maximum information. This matrix characterizes the sampling sites by the new transformed coordinates of the data in space and it has the same number of rows as the original data matrix.

The score matrix describes the data in terms of similarities/ differences as well as the identification of the outliers. In this work, P^t is the square matrix
(a x n) called the loading matrix which has the same number of columns as the original data matrix and it contains a set of weights and loadings of the original features in each principal component. This loading matrix describes the data structures in terms of the contribution of the observed variables on the principal components. The matrix E is the error matrix (m x n) which contains no significant information about the original data and in this work it was discarded to simplify the analysis as well as to avoid random errors in the analysis [37].
HCA technique examines inter point distances between all sampling sites and measured elemental concentrations of bottom sediment samples and presents that information in the form of a two dimensional plot called the dendrogram that facilitates the use of human pattern recognition abilities. First, each heavy metal is regarded as a cluster before a similarity distance (Euclidean) is determined between all the clusters. For example, if two clusters of heavy metals are taken to be i and i′, then the similarity distance $d_{ii'}$ exists only if $d_{ii'}=d_{i'i}<0$ where $d_{i'i}=1$ when $X_i=X_{i'}$. The row vectors in the data matrix X are given as X_i and $X_{i'}$ as in (3.6b)

$$d_{ii'} = \sum_{j=1}^{j} \left(x_{ij} - x_{i'j}\right)^2 \qquad (3.6b)$$

Where, j is the number of repetitive measurements between the clusters. Nearest clusters are linked together until only one cluster remains making the measured data more interpretable [38].

$$d_{mj} = \frac{n_i + n_j}{n + n_j} d_{ij} + \frac{n_{i'} + n_j}{n + n_j} d_{i'j} - \frac{n_j}{n + n_j} d_{ii'} \qquad (3.6c)$$

Where, m is the new formed object or cluster, i, i′ and j are the previously clustered objects, n_i is the number of objects in cluster i, $n_{i'}$ is the number of objects in cluster i′, $n = n_i + n_{i'}$, while d_{ij}, $d_{i'j}$ and $d_{ii'}$ are the squared Euclidean distances.

III. Results and Discussion

3.1 Heavy metal concentration in bottom sediments

The concentrations levels of Ti, Mn, Cu, Zn, Pb, Fe, Rb, Sr and Zr from bottom sediment samples were measured in (μg/g) using Energy dispersive X-ray fluorescence technique and are presented in Table 3.1. The concentrations for all metals measured in this work varied from one sampling site to another. This may be due to non homogeneous distribution of metals at the shoreline [39] as a result of unsystematic dispersal of the heavy metals by tides which vary in magnitude at different times, grain size distribution and the hydraulic processes in the riverine system [40]. Pb at all sampled sites was above the natural background levels of 16 μg/g [42] an indicator that it may be anthropogenic at Port Victoria shoreline [43, 44]. Its sources may be traffic fuels, Old paint from households and from the applied fertilizers in Lake Victoria catchment areas [45]. Mn and Zr measured elevated levels than their natural background values of 950 and 220 μg/g only at the discharge points of river Nzoia (Ka) and river Ndekwe (I). This indicates that the riverine system in the lake basin is the major transporter of effluents into Lake Victoria [46, 47]. The rest of the metals (Ti, Cu, Zn, Rb and Sr) had levels that were nearly equal to their natural background levels and this indicates their source as being either naturally occurring or anthropogenic [48]. The concentration levels measured in this work were found to be comparable with other findings elsewhere [9, 16, 20, 22, 23, 38, 39].

Table 3.1: Concentration of heavy metals

	Ti	Mn	Cu	Zn	Pb	Rb	Sr	Zr
Site								
Ka	4975±140	955±36	BDL	68±4	31±2	66±1	152±3	266±4
D1	1735±135	274±26	BDL	44±4	24±2	39±1	174±4	92±7
D2	1755±104	405±27	BDL	37±3	32±3	44±1	175±3	73±1
D3	1261±111	216±22	BDL	31±5	21±1	30±1	138±2	63±1
N1	1495±99	264±18	BDL	39±2	29±1	31±1	135±2	79±1
N2	2071±176	248±31	BDL	41±6	28±2	26±2	139±4	79±2
I	3493±102.3	5105±100	79±4	89±3	34±1	44±1	179±3	281±3
Nam1	962±113.7	147±16	BDL	38±3	28±1	26±1	149±2	80±1

Nam2	1764±99	289±23	BDL	41±3	33±1	40±1	226±5	123±2
Nam3	1205±113	105±10	BDL	30±3	26±1	40±1	163±4	95±2
Bu1	953±78	BDL	BDL	BDL	24±1	44±1	157±3	64±1
Bu2	1312±137	BDL	BDL	31±6	32±2	38±1	162±4	59±1

3.2 Principal component analysis (PCA)

PCA was performed on eight measured heavy metals to explore the relationships among them [40]. The measured data was rotated by varimax method and normalized by applying the Kaiser method. Varimax rotation was used to recalculate the results in order to enhance their interpretation [41]. Normalization was used to reduce the influence of some measured heavy metals (eg extreme levels) over others before the principal components and the percent of variance explained by each of them were calculated [34]. Table 3.2 shows factor loadings on the principal components. PCs with eigen values higher than one explaining 89.58 % of total variance were considered for analysis [42]. The first PC explains 61.40 % of total variance and loads heavily on Mn (0.96), Cu (0.94), Zn (0.86), Zr (0.72) and moderately on Ti (0.52). The second PC explaining 15.97 % of the total variance is dominated by Ti (0.80) and Rb (0.93).

The loading of Ti on both PC1 and PC2 indicate the metal as having mixed sources of origin in the lake basin [16]. The third PC accounting for 12.21 % of total variance is dominated by Pb (0.76) and Sr (0.91). Relationships among these heavy metals are given in a three dimensional space plot in Fig 3.1.

Table 3.2: Factor loadings

Element	Loadings on principal components		
	PC1	PC2	PC3
Ti	0.52	0.80	0.46
Mn	0.96	0.10	0.20
Cu	0.94	0.21	0.48
Zn	0.86	0.44	0.15
Pb	0.31	0.16	0.76
Rb	0.10	0.92	0.21
Sr	-0.02	0.10	0.91
Zr	0.72	0.65	0.18
Eigen Value	4.91	1.28	1.03
% explained variance	61.40	15.97	12.21
% cumulative	61.40	77.37	89.58

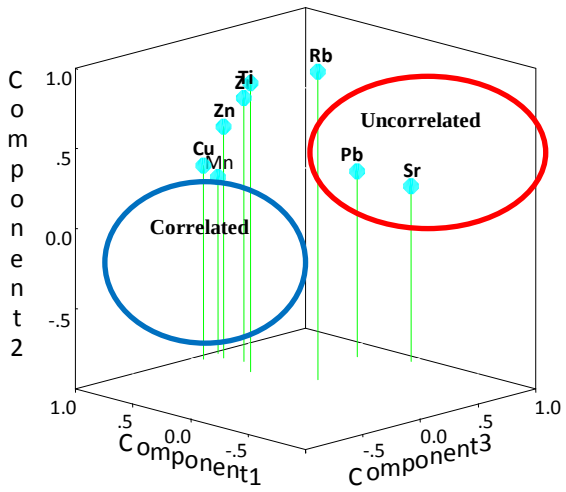

Fig 3.1: PCA plot

In the above Plot, Ti, which loads heavily on PC2 is classified together with (Mn, Cu, Zn and Zr) on PC1. This indicates that Ti has multiple sources in the Lake basin [41]. Rb loads only on PC2 indicating that it has one source. Pb and Sr load heavily on PC3 indicating that both have a common source different from that of Ti, Mn, Cu, Zn and Zr.

3.2 Hierarchical cluster analysis (HCA)

In this work, the concentration data of the measured heavy metals was standardized by means of Z scores and Euclidean distances calculated before applying the Ward's method. The results in Fig 3.2 present three main clusters which are consistent with PCA interpretations. Cluster A (Mn, Cu, Zn, Zr,Ti) have both agricultural and industrial sources in the lake basin [44]. Mn is associated with phosphatic fertilizers as well as from steel and iron used in industry. Cu is commonly used as a fungicide in the rich agricultural basin [46, 47] as well as a lubricant in industry hence its composition in the industrial sludge [29]. Ti is attributed to the paper pulp industry in Webuye as it is commonly used because of its high resistance to organic acid, sulfides and strong bleaches [51]. Zr and Zn being good resistance to corrosion are often used as alloys during galvanization of other metals such as steel and iron. Their sources may be due to wear and tear of steel and iron that is widely used by artisans in the lake basin [49]. Cluster B has only Rb which was found to be with moderate loadings on PC1 (0.5) and PC2 (0.47). It is attributed to industrial, agricultural and natural sources (weathering of rocks and soils) in the catchments of Lake Victoria. Cluster C (Pb and Sr) with high loadings on PC2 were found to be uncorrelated to each other and to all other metals measured in this work ($r<0.5$). The uncorrelation was attributed to their high enrichment factors than all the other metals measured in this work. The enrichment is mostly naturally occurring from the underlying Lake rock. The sources of Pb in the lake basin may be attributed to old paint and traffic emissions [36], from filling materials in vehicle tyres [48] and agricultural pesticides used in the farms in the Lake Victoria basin [51]. Sr is attributed to the spill oil transported from deports in Eldoret and Kisumu and from incinerator ashes in the Lake Basin [44].

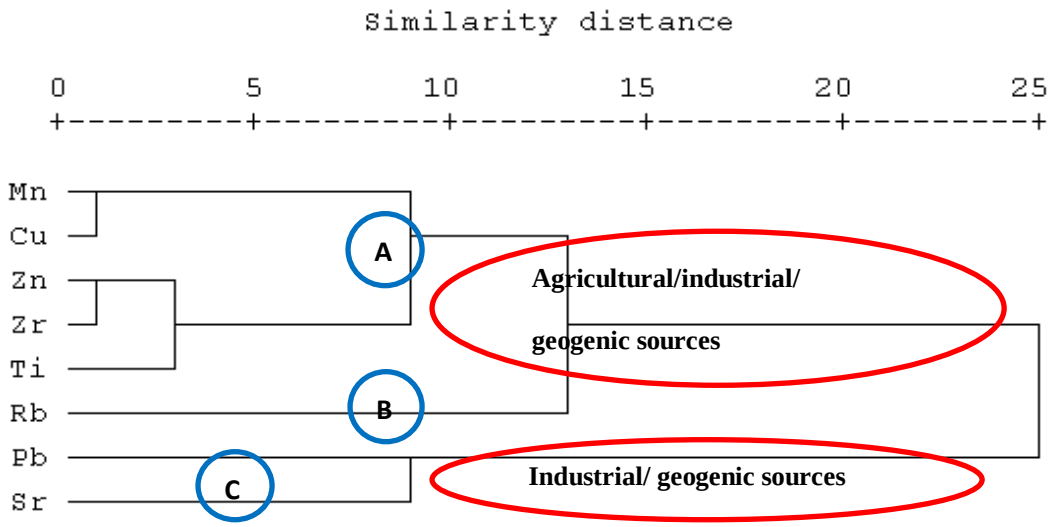

Figure 3.2: Hierarchical analysis of heavy metals

IV. Conclusion

Increased human and agricultural activities in the Lake Victoria basin have discharged effluents containing heavy metals hence increasing their natural background levels in the lake basin. PCA and HCA have identified relationships and sources of these heavy metals in the Lake basin. The major findings in this study are;

1. The mean concentration levels of Ti, Zn, Cu, Mn, Rb, Sr and Zr were found to be below their natural background levels except for Pb which had concentration of 29.0216±2.41 µg/g which was above its natural background level of 16 µg/g.
2. Principal component analysis (PCA) showed strong correlation ($r>0.5$) for Ti, Mn, Zn, Cu and Zr while Pb and Sr were found to be uncorrelated ($r<0.5$) to each other and to all other heavy metals in this work at all sampled points along the Port Victoria shoreline.
3. HCA apportioned all heavy metals to result from agricultural activities, municipal waste water discharges and sewage sludge from the industries in the lake basin.

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