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# Geochronological and spatial distribution of heavy metal contamination in sediment from Lake Naivasha, Kenya

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#### ABSTRACT

Sediment cores hold large information on the history of human interactions with lakes and surrounding environments. Hence, this study investigated the geochronological and heavy metals characteristics of sediment from Lake Naivasha, Kenya. Geochronological characteristics were established from sediment cores, using <sup>210</sup>Pb and <sup>137</sup>Cs. On the other hand, heavy metals; Al, As, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were analyzed using Inductively Coupled Plasma - Optical Emission Spectrometer (ICP – OES). Their probable sources were predicted using Pearson's correlation and Principal Component Analysis (PCA) while heavy metal contamination levels were assessed using geoaccumulation Index (Igeo), Contamination Factor (CF) and Enrichment Factor (EF) pollution indices. Results showed that the cores were about 140 years old with an estimated average mass sedimentation rate of 0.32 g/cm<sup>2</sup>/yr. Vertical fluctuations of heavy metal contamination were observed along the sediment cores with high values recorded near the surface. Further, PCA and pollution indices showed that Al, Cr, Cu, Ni, and Pb were from natural sources while, Zn, Mn, Fe, and As, (in order of contamination levels), were both from natural and anthropogenic sources. Therefore, this study showed the geochronological trends of sedimentation and impacts of human activities on Lake Naivasha.

#### **KEYWORDS**

Sediment; Lake Naivasha; heavy metals; geochronology; mass sedimentation rate; pollution indices (l<sub>geo</sub>; CF and EF)

#### 1. Introduction

Lake sediments record a large volume of information about changes in the lakes and their catchment giving rich history of human-nature interactions with the waterbody (Al-Mur, Quicksall, & Al-Ansari, 2017; Ntakirutimana, Du, Guo, Gao, & Huang, 2013; Sahli et al., 2017; Yanhong, Sumin, Barttarbee, & Yuxin, 2004). The information, largely include; land use, climatic, and environmental changes, which can be used to reconstruct the pollution history of a lake (Al-Mur et al., 2017; Skordas, Kelepertzis, Kosmidis, Panagiotaki, & Vafidis, 2015). Further the sediment cores provide chronologies of sediment contamination in aquatic environment (Al-Mur et al., 2017). The concentration of metals in sediments acts as an accurate indicator of aquatic system contamination. According to Bing, Wu, Liu, and Yang (2013) and Purushothaman, Mishra, Das, and Chakrapani (2012) the lake sediments are useful in assessing the health status of aquatic ecosystems. Also, the assessment of lake sediments is used during environmental surveys to aid in establishing changes in sediment characteristics input with time (Dai et al., 2007). Assessment of sediment geochemistry is, thus, directly relevant to assessing the possibility of toxic effects of heavy metal contamination (Ntakirutimana et al., 2013; Seshan, Natesan, & Deepthi, 2010; Tarras-Wahlberg, Everard, & Harper, 2002).

Investigations of geochemical changes with depth can be used in determining sediment contamination and, in cases where sedimentation rates are known, changes in contaminant loading with time can be assessed (Tarras-Wahlberg et al., 2002). Changes in sediment contamination with depth also aids in studying the impacts of anthropogenic activities on aquatic system (Wang et al., 2016; Zanjani-Jamshidi & Saeedi, 2017). The sediments can also be used in understanding the spatial and seasonal variation of contaminant concentration levels (Lau & Chu, 1999). According to Al-Mur et al. (2017); Zanjani-Jamshidi and Saeedi (2017) and Sahli et al. (2017) study of sediment core vertically provides a reliable historical natural and anthropogenic metal record together with accumulation of various elements over time. In aquatic system, most metals are predominantly associated with the deposited sediment. They occur as sediment bound metals but have a potential of changing to ionic state (Purushothaman et al., 2012) further affecting heavy metal distribution along the sediment core.

The lake sediments play a key role in internal cycle of the metals where sediments either acts as a permanent or temporary sink of metals (Bing, Wu, Nahm, & Liu, 2013; Elkady, Sweet, Wade, & Klein, 2015). The trace metals can be introduced in the lake environment from natural and

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anthropogenic sources (Rejomon, Martin, Nair, Thomas, & Sini, 2016; Seshan et al., 2010). These trace metals have low solubility and are not biodegradable but usually interact with organic and inorganic matters later settling to the water body bottom sediments (Al-Najjar, Rasheed, Ababneh, & Al-Omarey, 2011). Though sediments act as a sink of heavy and trace metals, some metals are not permanently bound on them, but they can be recycled into the overlying water column (Hu, Deng, Xie, Chen, & Li, 2015; Seshan et al., 2010; Wu, Wang, Wu, Fu, & Liu, 2014). This occurs when the sediments experience physical and biological disturbance or in cases where the environmental change is experienced for instance the fluctuation of temperature and pH (Hu et al., 2015).

In investigating the environmental changes and anthropogenic impact on the lake, various proxies are used (Bhuiyan, Dampare, Islam, & Suzuki, 2015; Stoof-Leichsenring, Junginger, Olaka, Tiedemann, & Trauth, 2011; Yang et al., 2014). The proxies include, relating time with sediment in the lake to understand the variation of sediment concentration with time. This can be achieved by dating of sediment core using the natural or artificial Fallout Radionuclides (FRNs). The most common FRNs used in assessing recent sedimentation of reservoirs through dating of the sediment core include Cesium-137 (<sup>137</sup>Cs), Lead-210 (<sup>210</sup>Pb), and Beryllium-7 (<sup>7</sup>Be) nuclides (Maina, Sang, Mutua, & Raude, 2018; Yang Hong Wu et al., 2010). The use of <sup>210</sup>Pb radionuclide in sediment dating along the core aids in characterizing changes of sediment input for a period of 100–150 years back (Dai et al., 2007; Yang & Turner, 2013; Yusoff, Zulkifli, Ismail, Abd, & Mohamed, 2015; Zalewska, Woroń, Danowska, & Suplińska, 2015). According to Yang and Turner (2013) various lakes in China, for instance Qinghai, Gaihai, Nam Co lakes among others have successfully applied <sup>210</sup>Pb and <sup>137</sup>Cs radiometric chronologies in assessing the recent environmental changes. The combined analysis on chronology and heavy metal assessment on lake sediments aids in environmental management (Zalewska et al., 2015). The findings from these analyses inform the environment managers on historical impact of anthropogenic activities on the lake and aids in assessing effectiveness of conservation practices adopted within the lakes catchment.

Further, analysis of the lakes sediment can aid in understanding the sources of pollutants within aquatic ecosystems. The surface water runoff, agricultural fertilizer leaching, anthropogenic activities such as disposal of untreated industrial effluents and domestic sewage leads to increased nutrients, trace, and heavy metals concentration in lake sediment (Bing et al., 2013). One such lake that could be affected by lake sediment pollution is Lake Naivasha, Kenya. According to Harper and Mavuti (2004) the lake is of great importance in local and national socio-economic development. As a result, it was declared a wetland of international importance in 1995 under the Ramsar Convention (Becht, Odada, & Higgins, 2005). The lake has been reported by Stoof-Leichsenring et al. (2011) to be threatened by sediment pollution resulting from anthropogenic activities.

According to Tarras-Wahlberg et al. (2002) human activities that greatly impact Lake Naivasha include; clearance of natural vegetation for agriculture (floriculture and horticulture) and interference with fringing papyrus swamps along the perennial inflow rivers (Malewa and Gilgil). According to Everard, Vale, Harper, and Tarras-Wahlberg (2002) these rivers carry a significant amount of sediment load into the lake. This is the case for Lake Naivasha since the rivers pass through areas with extensive agriculture. On the other hand, papyrus fringe on the inflow point into the lake have been tampered with (Boar & Harper, 2002). The increase in sediment load from Gilgil and Malewa Rivers have led to an increased input of nutrients such as phosphorus and nitrogen into the lake. These have resulted to growth of phytoplankton further raising turbidity levels of Lake Naivasha water (Boar & Harper, 2002; Kitaka, Harper, & Mavuti, 2002). Hence, there is need to understand the geochronological changes of sediment flow in Lake Naivasha. Further, this study sought to investigate the accumulation history of heavy metal contaminants in sediments of Lake Naivasha over the past 50 years. This aided in establishing the recent spatio-temporal distribution of the contaminants in the lake and identifying their potential sources.

#### 2. Materials and methods

#### 2.1. Study area

The study was conducted in Lake Naivasha covering the Main and Crescent Island Lakes (Figure 1) located about 100 km northwest of Nairobi (Hickley et al., 2002; Njuguna, 1988). It is located approximately 0°10' to 1° 00'S, and 36°10' to 36°45'E (Yihdego & Becht, 2013). Lake Naivasha is a fresh water lake that has no surface outlet but its freshness results from the lakes interaction with ground water (Bergner, Trauth, & Bookhagen, 2003; Everard et al., 2002). The lake has a surface area of about 150km<sup>2</sup> which fluctuates from 100 to 200 km<sup>2</sup> (Becht et al., 2005) with an average elevation of 1890 m above sea level (Becht & Harper, 2002).

The lake water balance largely benefit from Malewa River, which drains Kinangop Plateau (Harper & Mavuti, 2004; Kitaka et al., 2002). Extensive agriculture takes place within Lake Naivasha basin and has led to more areas being converted into farmlands even on steep slopes (Hickley et al., 2004). Because of these changes in land use within the basin; the lake is threatened by sedimentation (Stoof-Leichsenring et al., 2011).

### 2.2. Sediment collection

Sediment cores were collected from preselected locations of Lake Naivasha (Figure 1). This ensured that



Figure 1. Location of Lake Naivasha, Kenya showing distribution of core sampling points and other dated cores S1 (Stoof-Leichsenring et al., 2011) with V1 by Verschuren (2001).

the different sections of the lake (at inlet, middle, furthest from inlet, deepest parts) were covered during sampling. Toward the inlet of the lake, this was captured at the Malewa site where M1, M2, M3 cores were collected while the deepest part of the Main Lake (Hippo point) was catered for by HP core. At the middle of the lake, ML core was retrieved while the deepest area that was sampled was at Crescent where CR core was collected (Table 1).

A Vibe coring device which consisted of a vibrating core head with weight rig, check valve, and core tube was used in collecting the sediment cores. The Vibe core was vertically lowered using a winch into the sediment, until the point where the core could not progress because of sediment compaction or in some cases especially at Crescent site the length of the core was controlled by the length of core tubes. The core was then retrieved using the winch, capped, stored, and transported to the laboratory in an upright position. The procedure of retrieving and handling the core had previously been applied by Dunbar, Allen, and Higley (1999) and Sang, Raude, Mati, Mutwiwa, and Ochieng (2017). Upon transportation to the laboratory, the cores were longitudinally split into two, then sliced into layers according to visually identified stratigraphic changes. To have manageable samples within the available budget, only one sediment core was analyzed for every site. Samples for bulk density, geochronological and geochemical analysis were picked. During sampling from the core tube for geochemical analysis samples, sediments near the wall of the core tube were discarded to avoid cross contamination from the core tube. In ensuring the analyzed sample was free from walls contamination, Wu, Lücke, and Wang (2008) had followed a similar

 Table 1. Sediment core information and location in Lake Naivasha.

S/N	Site	Core ID	Longitude	Latitude	Core length (cm)	Water depth (m)
1	Malewa	M1	36.339670	-0.728278	129.5	4.2
2		M2	36.339696	-0.752069	135	6.3
3		M3	36.309121	-0.752459	109	6
4	Hippo point	HP	36.318199	-0.788416	144	7.8
5	Middle lake	ML	36.363285	-0.788127	113	6
6	Crescent	CR	36.408070	-0.763718	181	16.3

procedure. The bulk density (ρ) was estimated using standard ASTM method (D 2937–04) while radioiso-topes <sup>137</sup>Cs and <sup>210</sup>Pb was used in analyzing sediment chronology with depth.

#### 2.3. Geochronological analysis

Geochronological analysis involved sample preparation followed by radioisotope activity measurement. In sample preparation, the samples were oven dried for about 24 h at 50°C, disaggregated using a rubber mallet and then passed through a 2 mm mesh sieve. The samples were then filled in a Marinelli beaker, weighed, and sealed using an aluminum composite foil. The sealed sample was stored for minimum 21 days; a period which was more than five times <sup>222</sup>Rn half-life to attain radioactive equilibrium as described by Putyrskaya, Klemt, Rollin, Astner, and Sahli (2015), Wu et al. (2010) and Yang and Turner (2013).

The radioisotopes activity was measured by gammaspectrometry, using Broad Energy Germanium detectors (BEGe-5030) of Canberra. The samples were placed in detector and activity of <sup>40</sup>K, <sup>210</sup>Pb, <sup>214</sup>Pb, <sup>214</sup>Bi, and <sup>137</sup>Cs determined for a count of 86,000 s. The <sup>40</sup>K, <sup>137</sup>Cs, and total <sup>210</sup>Pb activities were measured at 1461, 662,, and 46.5 keV, respectively. In addition, other activities; <sup>214</sup>Pb and <sup>214</sup>Bi aiding in calculation of excess <sup>210</sup>Pb from total <sup>210</sup>Pb (Sikorski & Bluszcz, 2003) were detected at wavelengths 352 keV and 609 keV, respectively. From the detected activities, the dates were assigned on excess <sup>210</sup>Pb using Constant Rate of Supply-Piece Wise (CRS-Pw) model where <sup>137</sup>Cs was used as the independent time marker as described by Appleby (1998) and Putyrskaya et al. (2015).

#### 2.4. Geochemical analysis

This involved sediment sample preparation, digestion and analysis of heavy metals using Inductively Coupled Plasma Optical Emission Spectrometer (ICP - OES). To avoid possible contamination, all glassware and equipment used were acid washed by soaking them in Nitric acid-HNO<sub>3</sub> (10%) for at least 24 h and rinsed repeatedly with distilled water. Sediment sample was air dried and, in some cases, oven drying was undertaken where the sample was dried at 40°C. The sediment samples were then pre-sieved (2 mm) to eliminate shells, gravel, and roots. The samples were then homogenized using a Porcelain mortar and pestle to obtain fine powder. A 0.25 g of ground samples was added into Teflon lined high pressure tubes, for heavy metal digestion using Aqua regia (HCl + HNO<sub>3</sub>, volume ratio of 3:1). The samples in Teflon tubes were then placed in a microwave (Berghof MWS-3 Digester), and digested for about 15 min at 200°C. The solution was left to cool, filtered, and then diluted to 50 ml using distilled water.

The analysis of heavy metals (Al, As, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in sediment samples was then performed using ICP OES (ICP OES Avio 200) following digestion of sediment. For analytical quality control; standard reference materials (GBW 07402 and GBW 07404), reagents blanks and randomly selected sample replicates were analyzed. The blanks did not indicate any contamination and the standards confirmed the accuracy of analysis in ICP OES. A similar procedure was followed by Hseu et al. (2002) and Islam, Ahmed, Raknuzzaman, Habibullah -Al- Mamun, and Islam (2015) while digesting and analyzing sediments for heavy metal concentration.

# 2.5. Identifying sediment sources in lake Naivasha

Multivariate statistical techniques which included Pearson correlation and Principal Component Analysis (PCA) were used in investigating the potential sources of heavy metals in sediment samples. The Analyse-it 4.92 extension in Excel software was used for PCA and correlation analyses. To assess the relationship between heavy metals in sediment, Pearson correlation analysis was used. From Pearson correlation, the values above 0.65 were taken to be strongly correlated while those less than 0.4 signified a weak correlation between the heavy metals. A similar classification procedure had been previously followed by Bhuiyan et al. (2015); Ghandour, Basaham, Al-Washmi, and Masuda (2014) and Lim, Aris, and Ismail (2013) while investigating the sources of various heavy metals in water and sediment.

On the other hand, PCA was performed on the heavy metal concentration in sediments of different sites within the lake to further understand the heavy metals that can be grouped to be from the same source. The eigenvectors in PCA analysis were used to determine the sites that had common pollution sources. The Principal Components (PC) with Eigen values greater than one were considered to be relevant as reported by Venkatramanan, Chung, Ramkumar, Gnanachandrasamy, and Kim (2015); Yang et al. (2014) and Yuan et al., 2014). To consider the heavy metals contribution to a given group, the components that were found to have a factor loading of >0.6, 0.4-0.6, and 0.3-0.4 were classified to be strongly, moderately or weakly, associated with elements in that class, respectively. Similar classification procedure had been used by Wu et al. (2014) in a study that focused on determining the source of heavy metals in Sediment. The resulting clusters from the different components aided in establishing the groups of elements that may be classified to be homogeneous. A Similar procedure of using Pearson correlation and PCA in assessing sources of contaminants had successfully been applied by Yuan, Shen, Liu, Wang, and Meng (2011).

# **2.6.** Pollution assessment of heavy metal in sediment

To assess the degree of sediment contamination with heavy metal; different indices such as geoaccumulation index ( $I_{geo}$ ), Contamination Factor (CF) and Enrichment Factor (EF) were used. For a reliable finding from the pollution indices like CF,  $I_{geo}$ , and EF, selection of correct background values for different metals plays a significant role (Liaghati, Preda, & Cox, 2003).

In this study, the global average for shale values reported by Turekian and Wedepohl (1961) were selected as the background values for the metals studied. The number of times heavy metal concentration in the sediment exceeded the background concentration was determined using the CF. In calculating the CF, Equation 1 was used as presented by El-Sayed, Moussa, and El-Sabagh (2015) and Wang et al. (2016).

$$CF = \frac{C_{metal}}{C_{background}}$$
(1)

where, C<sub>metal</sub> is the total metal concentration and C <sub>background</sub> represents the average background value of the metal in sediment.

The CF was then classified into four grades as given by Al-Mur et al. (2017); El-Sayed et al. (2015) and Sabo, Gani, and Ibrahim (2013). Another index that was used in determining the contamination level was  $I_{geo}$ . The  $I_{geo}$  is useful in assessing the extent of anthropogenic input in sediment and its calculation follows Equation 2 (Bhuiyan et al., 2015; Elkady et al., 2015; Gupta, Jena, Matic, Kapralova, & Solanki, 2014; Sabo et al., 2013; Seshan et al., 2010; Shafie et al., 2013).

$$I_{geo} = Log_2 \left(\frac{C_n}{1.5B_n}\right)$$
(2)

where;  $C_n$  is the measured concentration of specific heavy metal,  $B_n$  is the geo- chemical background of the heavy metal in consideration and 1.5 is the correction factor due to lithogenic influence.

On the other hand, EF is a powerful tool that is useful in regional comparison of heavy metals in sediments (El-Amier, Elnaggar, & El-Alfy, 2017; El-Sayed et al., 2015). The EF is useful in assessing the chances of human influence on heavy metal concentrations in the sediment (Al-Mur et al., 2017). The use of EF requires a selection of a normalizing metal which is not easily affected by anthropogenic activities. Hence, to further understand the possibility of anthropogenic impact on heavy metals concentration in sediment cores, the metals were normalized using Al (Equation 3) as a conservative element.

$$EF = \frac{\left(\frac{C_{m}}{C_{AI}}\right) \text{sediment}}{\left(\frac{C_{m}}{C_{AI}}\right) \text{ background}}$$
(3)

where,  $\binom{C_m}{C_{Al}}$  sediment is the ratio of metal and Al concentrations in the sediment sample, and  $\binom{C_m}{C_{Al}}$  background is the ratio of metal and Al concentrations considering the background values.

Since Al has relative stability in sedimentation, it has been used as the conservative element (Hyun, Lee, Lee, & Choi, 2007; Yao & Xue, 2016; Yuan et al., 2011) that aids in differentiating the natural and anthropogenic sources input in the investigated heavy metals. In this study, the procedure followed in normalization was adopted from Al-Mur et al. (2017) and Bhuiyan et al. (2015). The EF values were classified using categories described in Bhuiyan et al. (2015) and Ghrefat, Abu-Rukah, and Rosen (2011).

### 3. Results and discussion

# **3.1.** Distribution of artificial and natural radionuclides in sediments

The multiple radionuclides detected in Crescent (CR) and Malewa (M1) Cores within a single measurement in the detectors were <sup>137</sup>Cs, <sup>40</sup>K, <sup>210</sup>Pb <sup>214</sup>Bi, and <sup>214</sup>Pb, and their activities are presented in Figure 2(a,b). The <sup>137</sup>Cs activities were found to be at a range of 1.44-8.77 Bg/kg and 1.01–10.99 Bg/kg for CR and M1 cores, respectively. This was in agreement with reports by Maina et al. (2018) and Matisoff (2014) that there is low <sup>137</sup>Cs activities in the southern hemisphere. Comparing the <sup>137</sup>Cs activities of Lake Naivasha sediment with those recorded by Jeff and Shepherd (2009) for soils in Saiwa River watershed, Western Kenya, it was noted that the concentration of <sup>137</sup>Cs activities measured for the soils were also low, and they ranged from 0.00 to 4.28 Bg/kg in both depositional and disturbed sites. Further, in this study, <sup>137</sup>Cs peak activity was well defined at the deeper layers corresponding with 72 and 52.5 cm depth for CR and M1 cores, respectively. These peak activities were considered to mark a period when there was high <sup>137</sup>Cs deposit from the nuclear weapon testing (Apostu, Radulescu, Margineanu, Ionita, & Popescu, 2012; IAEA, 1998; Mabit et al., 2014; Putyrskaya & Klemt, 2007; Ruecker, Park, Brunner, & Vlek, 2008). It was difficult to detect any <sup>137</sup>Cs activity beyond 83 and 69 cm for CR and M1 cores, respectively. This could have indicated that depth 83 and 69 cm marked the emerging of nuclear weapon testing which corresponds with early 1950s. On the other hand, <sup>214</sup>Bi and <sup>214</sup>Pb activities along the sediments cores were observed to be closely related (Figure 2).

The <sup>214</sup>Bi and <sup>214</sup>Pb activities aided in calculating the excess <sup>210</sup>Pb in the studied cores. The maximum value of unsupported <sup>210</sup>Pb did not exist at the surface of the cores in layers along the profiles as shown in Figure 2. Further an irregular decline of the <sup>210</sup>Pb for Crescent and Malewa core was noted. A similar trend was observed in a dated sediment core of Lake Naivasha by Stoof-Leichsenring et al. (2011). Putyrskaya et al. (2015) had also observed cases where <sup>210</sup>Pb activity was maximum in subsurface layers for sediment cores collected in Lakes Brienz, Thun, Lucern and Prealpine Lake Meggione of Switzerland. A similar observation had been made by Wang et al. (2016) where they assesed sedimentation rate using <sup>210</sup>Pb chronology on Karnaphuli River estuary, Chittagong, Bangladesh.

The low values of <sup>210</sup>Pb activity recorded at the upper sections of sediment core could be due to mixing of sediments experienced because of wind wave action (Appleby, 1998). The sediment mixing may lead to post depositional redistribution (Verschuren, 2001). Miguel, Bolıvar, and Garcia-Tenorio (2003) had also reported that activities of unsupported <sup>210</sup>Pb are largely affected by rapid mixing experienced at the upper layers of sediment cores.



**Figure 2.** Distribution of <sup>137</sup>Cs, <sup>40</sup>K, <sup>210</sup>Pb <sup>214</sup>Bi and <sup>214</sup>Pb radionuclides activities together with bulk density (ρ), sediment age along the cores collected in Lake Naivasha, Kenya (a) Crescent site – CR core and (b) Malewa site – M1 core.

Further the fluctuation of <sup>210</sup>Pb vertical sediment profile could be because of impacts of growing plants for instance papyrus and water hyacinth in Lake Naivasha. According to Putyrskaya et al. (2015) and Yang and Turner (2013) a high sedimentation rate could be reported when the vegetation dies off leading to fluctuations along the vertical sediment core profile. To cater for these impacts the <sup>210</sup>Pb chronology was validated using<sup>137</sup>Cs an independent time marker. Miguel et al. (2003) and Putyrskaya et al. (2015) had also successfully used <sup>137</sup>Cs as an independent marker while using CRS-Pw model in dating cores collected from different lakes in Switzerland.

### 3.2. Geochronology of sediment cores

The <sup>137</sup>Cs was found useful as an independent marker to correct <sup>210</sup>Pb chronology. However, in using <sup>137</sup>Cs, it was possible to assign only one date corresponding to year 1963 the layer which peak <sup>137</sup>Cs was measured unlike in northern hemisphere where year 1986 is used as a reliable marker due to Chernobyl accident effect. Since <sup>7</sup>Be was not measured for the top sediment layer, surface of sediment core was assumed to correspond to the date of sampling. The CR and M1 core were dated up to 140  $\pm$  10 and 81  $\pm$  7 years, respectively (Figure 2). The period was found to be within the acceptable application period of <sup>210</sup>Pb dating.

According to Steiner, Hanselmann, and Krähenbühl (2000) application of <sup>210</sup>Pb sediment core dating, is limited to spans of about 100–150 years which is approximately 5 to 7 times its half-life (22.6 years). Further, the corrected <sup>210</sup>Pb CRS-Pw model was found to be a useful tool in determining the recent sedimentation rates. This agreed with reports by Miguel et al. (2003) who indicated that despite <sup>210</sup>Pb limitations, the nuclide has been used extensively in estimating the sedimentation processes and rates.

### 3.3. Mass sedimentation rate

Using CRS-Pw model for <sup>210</sup>Pb, the average mass sedimentation rate of Lake Naivasha was established to be approximately 0.32 g/cm<sup>2</sup>/yr. Toward the inflow represented by M1 core, the average mass sedimentation rate was found to be 0.40  $\pm$  0.04 g/cm<sup>2</sup>/yr while at the Crescent Island Lake a lower mass sedimentation rate of 0.26  $\pm$  0.15 g/cm<sup>2</sup>/yr was recorded from the CR core. A fluctuation in sediment accumulation rates along the cores was noted where a general increase of sedimentation rate in the recent years was observed (Figure 3).

It was noted that Malewa has a higher sedimentation rate compared to Crescent which could be explained by the fact that M1 core was collected near the inflow part of the lake while Crescent is located far from the inflow. Further, the great fluctuation of sedimentation rate along M1 core could be attributed to the core being collected close at the inflow part of the lake an area that can be highly affected by changes in sediment inflow. On the other hand, CR core was collected in part of the lake that deep, shielded from the wind and far from the inflow. The sediment received at Malewa may be distributed to various parts of the lake but the sediment that finds its way to Crescent majorly settles there hence the gradual accumulation rate experienced at the site.

Considering the <sup>137</sup>Cs a constant sedimentation rate of 0.21 and 0.3 g/cm<sup>2</sup>/yr was recorded in CR and M1 core, respectively. Comparing results of the current study with those of previous studies, it was found that the mid lake as presented by Stoof-Leichsenring et al. (2011) experiences the least sedimentation rate of 0.08 g/cm<sup>2</sup>/yr compared to Malewa and Crescent. The current sedimentation rate at Crescent Island Lake was found to be comparable to what was reported by Verschuren (2001).

From the dating and sedimentation rate results of Lake Naivasha, it was found that approximately 72 and 52.5 cm core length of Crescent and Main Lake would account for the past 50 years. As a result, the impact of recent environmental change on the lake, which was assessed from the sediment core was limited to about 53 cm core length for the main lake while at Crescent Island Lake the core was analyzed for geochemical analysis up to 72 cm depth.

# 3.4. Variation of heavy metals along sediment cores

The variation of heavy metal concentration at different depths for the six sediment cores from Lake Naivasha is shown in Figure 4. Study of vertical sediment profiles in a core aids in establishing historical sequence in pollution and contamination of sediment (Al-Mur et al., 2017). In the current study, it was found that most heavy metals in the cores studied, had their own distribution characteristics.

For some cores, it was noted that at the surface of the core the metal concentration was slightly lower than that of the immediate second top layer. This could be an indicator that the adopted conservation measures in the catchment have had an impact on the sediment quality (Seshan et al., 2010). Chen, Liang, Xu, Huang, and Li (2012) reported that the sediment core holds history of sediment contamination and in most cases the surface of the sediments to a few centimeters below, reflects the continuous change in level of contamination.

It was noted that the surface of sediments for HP and CR core collected at Hippo point and Crescent sites, (representing the deep parts of the Lake Naivasha) Al and Fe were found to be highest at the top of the core. At Hippo point (HP core) large fluctuations of Fe was noted affecting the core up to 20 cm depth. This suggested that there could be an increase in metal delivery into the lake in recent years. Similar observation had been made by Al-Mur et al. (2017) on core sediments collected from Red Sea, Saudi Arabia. A study conducted by Wang, Hu, Xiong, Huang, and Duan (2012) on distribution of heavy metals in core sediments of Baihua Lake, also observed that the top 10 cm of the core had high mean



Figure 3. Sedimentation rate at Crescent (CR core) and Malewa (M1 core) sites in Lake Naivasha derived from <sup>137</sup>Cs and CRS-Pw <sup>210</sup>Pb models.



Figure 4. Depth wise distribution of heavy metal concentration of six sediment cores collected from Lake Naivasha, Kenya.

concentration of the studied metals. In the rest of cores studied for the current study, Al and Fe were found to increase on the second layer and then in deeper layers a general reduction in concentration was noted.

On the other hand, Mn was found to have a significant vertical fluctuation for all cores studied especially from layers between 20 and 50 cm. This could be due to the diagenetic processes that affect Mn leading to metal's remobilization (Elkady et al., 2015). Since Crescent followed by Hippo Point are less affected by wind action in the lake compared with other sites, the less oxygen available in these sites could have led to increase of reduced Mn hence high values on Mn measured. In addition, it was found that the Mn concentration is higher in the deeper layers of the core than at the surface. Further, the vertical profiles for Mn and Zn in all the six cores were found to have different patterns which indicated that the Zn availability was not affected by the Mn cycling in the cores. A similar finding of Zn movement not being coupled with Mn was reported by Steiner et al. (2000) in a study conducted on an alpine lake in Switzerland. The difference in Zn and Mn movement in the sediments could indicate that these metals are from diverse sources within the catchment.

Further, Pb was found to vary with depth in all sites, for instance M1 core showed a great variation between the surface and the layer immediately below it. Studies conducted in Red sea and Tanjung Pelepas harbor in Malaysia, on heavy metal distribution along the sediment cores by Al-Mur et al. (2017); Al-Najjar et al. (2011) and Yusoff et al. (2015) attributed the vertical fluctuations of metal concentration to changes of anthropogenic input with time. The variation in Pb concentration could also arise from indirect sources such as atmospheric deposition. According to Fu et al. (2014) the Cr, Co, and Pb can be related to changes in traffic or agricultural activities. In Lake Naivasha the increase of these metals at the upper part of sediment cores could be indicating a chance that the increased use of pesticides and fungicides within the catchment is impacting metal concentration in the lake.

At 20 cm depth to the surface of the sediment cores, the As concentration was shown to have increased in five cores except in M1 core. The increase of As, serves as an indicator of anthropogenic impact in the water body since its major source is from agricultural input.

Further, the fluctuations of metals along the core depth could also occur in Lake Naivasha due to remixing of sediments caused by wind turbulence that the lake experiences. In variation of heavy metal concentration with depth, it was also noted that lately mid lake is receiving more heavy metal loading than before since in all metals studied, the surface of sediment core has higher concentration than the deeper parts of the core other than that of Mn metal only. The information gathered from the down core variation of geochemical behavior of elements and heavy metals further aids in assessing the impacts of human activities to the water body and in quantifying the impact of different conservation (Liaghati et al., 2003; Zanjani-Jamshidi & Saeedi, 2017)

# **3.5.** Concentration and distribution of heavy metals in Lake Naivasha

The mean concentration of heavy metals in Lake Naivasha sediment for Al, As, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were found to be 44,457.07, 13.05, 15.03, 14.95, 46,566.43, 1233.07, 14.61, 7.00, and 178.29 mg/kg, respectively. Further, the heavy metal spatial distribution within the lake is presented in Table 2.

The mean concentration of heavy metals in the studied sediment cores varied significantly from each other. The M2 core was found to record highest mean concentration of Al, As, Cr, Fe, and Zn. This core was collected about 3 km from the inlet of River Malewa. The high concentration recorded could be due to compounding effect on combination of inflow from River Malewa, Gilgil, Karati, and the effluent of domestic waste water treatment site (Njogu, Keriko, Wanjau, & Kitetu, 2011). On the other hand, it was observed that CR core recorded the lowest mean concentration of Cr, Cu, and Ni. This was in agreement with the findings reported by Njogu et al. (2011) in an earlier

study investigating the distribution of heavy metals in soils, sediment, and fish from Lake Naivasha basin.

In studying the heavy metal distribution, elevated mean concentrations of various heavy metals were also found in the Mid Lake as measured in ML core. Similar findings where middle sections of lake, registered high heavy metal contamination than inflow parts, had been reported by Yuan et al. (2011) in a research conducted in Taihu Lake, China.

Further, the mean concentration of Zn in the Lake Naivasha sediment varied from 140.41 to 178.3 mg/kg for all the six cores with the highest mean concentration recorded in M2 core closely followed by ML core. It was found that the Zn levels in all sites are already elevated since the threshold effect level of sediment quality criteria according to Tarras-Wahlberg et al. (2002) is set at 123 mg/kg. It is also noted that the Zn concentration in the sediments were all higher than the background value (95 mg/kg) presented by Turekian and Wedepohl (1961).

According to Zahra, Hashmi, Malik, and Ahmed (2014) Zn is mainly from direct input of municipal effluents, and geochemical weathering of parent rock material. Tarras-Wahlberg et al. (2002) had previously reported concentration of 88-190 mg/kg within Lake Naivasha Catchment, and it was found that a relatively high concentration of zinc in Naivasha catchment could be attributed to natural source. According to Nzeve, Kitur, and Njuguna (2014) the sources of Zn in reservoirs and Lake sediments can be from waste water, alloys of brass, and bronze, batteries, fungicides, and pesticides. Zeng and Wu (2013) reported that Zn, Pb, and Cu in aquatic ecosystems can be from industrial wastewaters. This could not be the case in this study since Lake Naivasha is not largely surrounded by industries (Tarras-Wahlberg et al., 2002) and the waste water directed into the lake is majorly from domestic sewage.

On the other hand, As concentration was found to range from 8.7 to 14.4 mg/kg in all cores studied. Comparing this with the background value for As (13 mg/kg) it was found that the sediment in Lake Naivasha can be considered to be lowly contaminated with As. On the other hand, comparing the As concentration with the recommended values in sediment quality criteria; Threshold Effect Level (5.9 mg/kg) in

Table 2. Mean concentration and spatial distribution of heavy metals in Lake Naivasha and their background values, together with sediment quality criteria Threshold Effect Level.

Variable/Site	Al	As	Cr	Cu	Fe	Mn	Ni	Pb	Zn
CR	39,463.17	11.68	12.36	12.98	40,551.23	1458.62	11.73	7.42	171.98
M1	35,867.95	8.68	14.14	13.16	40,143.63	1086.15	12.33	9.79	140.41
M2	52,217.32	16.19	17.72	14.62	54,096.05	1116.56	16.41	7.99	178.30
M3	47,129.10	14.18	15.81	14.28	46,723.98	1056.22	17.59	5.87	169.46
ML	49,259.60	14.16	16.61	14.02	49,544.05	1232.74	15.80	5.14	173.05
HP	42,805.25	13.42	13.52	20.67	48,339.66	1448.16	13.83	5.77	159.04
Mean	44,457.07	13.05	15.03	14.95	46,566.43	1233.07	14.61	7.00	165.37
Background values for shale <sup>a</sup>	80,000	13	90	45	47,200	850	68	20	95
Sediment quality criteria <sup>b</sup>	-	5.9	37	36	-	-	18	35	123

<sup>a</sup> Background values adopted from Turekian and Wedepohl (1961)

<sup>b</sup> Sediment Quality Criteria for protection of aquatic life. Threshold Effect Level adopted from Tarras-Wahlberg et al. (2002)

Table 2; Lake Naivasha can be said to be contaminated with As. According to Shrivastava, Ghosh, Dash, and Bose (2015) As in the environment is mostly from natural and anthropogenic sources. The anthropogenic source of As is mainly from agricultural activities while its natural source is atmospheric emission.

Further, it was observed that the lowest and highest mean concentration of Al was recorded in CR and M2 cores, respectively. Since Al is an abundant conservative element that is not easily affected by anthropogenic activities (Yang et al., 2014) the source of Al in CR core and other parts of Lake Naivasha can be attributed to lithogenic sources. Another heavy metal concentration that is largely controlled by lithogenic sources is Iron (Fe). In Lake Naivasha, it was observed that Fe was highest in M2 core with a mean concentration of 54,096.05 mg/kg while the lowest Fe was measured in CR core. There are low chances of pollution from agricultural activities at Crescent where CR core was collected. On the contrary, CR core was found to record a high concentration of Mn.

The high Mn concentration recorded in CR and HP core could be attributed to remobilization of Mn in deeper layers. A Similar observation, of Mn being high in deeper parts of the lake, was made by Elkady et al. (2015) who had studied heavy metal concentration in sediment samples of Lake Manzala, Egypt. Zeng and Wu (2013) reported that Fe and Mn are more sensitive to redox-reactions than the other elements. In some cases, reduced Mn remobilization takes place, and it is redeposited near the surface under oxidizing conditions (Elkady et al., 2015). According to Yang and Sañudo-Wilhelmy (1998) geogenic sources of Mn are considered to have greater impact on soils than the anthropogenic sources. However, the anthropogenic sources of Mn may affect the concentration of this metal in the sediments. From the analysis of heavy metal, it was found that their distribution and concentration in Lake Naivasha sediment can be attributed to geogenic and anthropogenic sources.

#### 3.6. Sediment source identification

The PCA and Correlation analysis aided in distinguishing the sources of heavy metals in Lake Naivasha sediment. In this study, the results from PCA showed that the first three components accounted for about 97% of the total variance in the data. The PC1 was dominated by Al, As, Cr, Fe, and Ni accounting for about 67.1% while Mn and Pb were dominant in PC2 that explained about 19.0% variance. Further, Zn and Cu were represented in PC3 which catered for 11% variance (Table 3).

According to Fu et al. (2014) the metals clustered in one component indicates that they could have similar distribution patterns and source. The heavy metals in PC1were highly associated with Al and Fe hence the metals in this group are largely associated to geogenic or lithogenic sources. On the other hand, heavy metals in PC2 and PC3 were classified to be from both

**Table 3.** Variance, eigenvalues, and eigenvectors on Principal Component Analysis matrix of heavy metals in Lake Naivasha sediment.

	Principal Components (PC)						
Parameter	1	2	3	4	5	6	
Al	0.401	0.105	0.082	0.051	0.090	0.233	
As	0.316	0.143	0.544	0.612	0.382	0.209	
Cr	0.389	0.195	0.083	0.058	0.355	0.389	
Cu	0.235	0.218	0.579	0.377	0.576	0.146	
Fe	0.395	0.070	0.177	0.237	0.298	0.361	
Mn	0.029	0.715	0.276	0.569	0.275	0.099	
Ni	0.387	0.189	0.119	0.306	0.234	0.387	
Pb	0.258	0.704	0.190	0.034	0.411	0.452	
Zn	0.159	0.080	0.398	0.050	0.016	0.486	
Eigen Values	6.037	1.708	1.041	0.108	0.084	0.022	
Proportion (%)	0.671	0.190	0.116	0.012	0.009	0.002	
Cumulative	67.077	86.057	97.619	98.816	99.751	1.000	
proportion (%)							

anthropogenic and natural sources. The heavy metals in these two components could also be affected by the diagenic processes involved. Chen et al. (2012) had reported almost similar metal classification in three different PCs that explained the mixed sources of the metals to river sediments. In some cases, the PCA and Correlation results were found to agree on the metals grouped in each category. Al-Mur et al. (2017) and (Yuan et al., 2011) had successfully used Correlation and PCA in distinguishing sources of metals in sediments of Red sea, Saudi Arabia, and Taihu Lake in china, respectively.

While considering Pearson's correlation in most sediment cores studied, Al and Fe were found to be strongly correlated (0.6–0.987) and this was an indicator that there was no major change in metals from geogenic source in Lake Naivasha. A similar observation had been made for sediment cores collected in Malaysia by Yusoff et al. (2015). In the current study, a strong negative correlation of Mn with Al (Table 4) in five (CR, M1, HP, ML, and M2 core) of the cores studied was observed. This implied that Mn could be from anthropogenic input or affected by diagenetic processes. According to Elkady et al. (2015) the strong negative correlation between these two metals could be as a result of geochemical processes acting on sedimentary Mn.

In Crescent it was found that Al, As, Cr, Fe, and Ni had a strong positive relationship a fact that supported the PC1 group results. Further, Cu and Zn were also found to have a strong positive correlation with Pb while Zn and Mn had a strong negative correlation (Table 4). These findings closely agreed with the classes from PCA results. Relating Al and Fe at Hippo point (HP core), it was observed that a negative relationship existed which indicated that Fe in Hippo point could be from both natural and anthropogenic source. This was further supported by the finding that Fe and Mn at Hippo point had a strong relationship (0.8) a region where Mn had been found to be of high quantity.

On the other hand, in Crescent (CR core) and the inflow part of the lake (M1, M2, and M3 cores), Fe and Mn, were found to have a negative relationship. This

	Al	As	(r		Fe	Mn	Ni	Ph	 7n
<i>(</i> )	7.4	113	Ci	Cu				15	20
	1 000								
AI	1.000								
AS Cr	0.525	0.636							
Ci Cii	0.021	0.030	0.254						
Cu Fo	0.053	-0.360	-0.254	0 207					
re	0.888	0.302	0.80/	-0.397	0 2 2 7				
	-0.304	-0.500	-0.303	-0.592	-0.527	0.479			
INI Dh	0.739	0.730	0.750	-0.065	0.001	-0.476	0.024		
PD 7n	-0.160	0.110	-0.532	0.517	-0.595	-0.555	-0.024	0.409	1 000
Z11 M1	0.200	-0.095	-0.065	0.002	-0.156	-0.546	0.070	0.496	1.000
	1 000								
Δς	-0.067								
rs Cr	-0.007	0 751							
Cu	0.450	-0.265	-0.256						
Eu Fo	0.430	0.205	0.230	0313					
Mn	-0.579	-0.234	-0 724	-0.028	-0 343				
Ni	0.876	-0.168	0.236	0.020	0.686	-0.423			
7n	0.670	0.100	0.549	0.623	0.500	-0.414	0 312		
Ph	-0.477	0.379	-0.259	-0.157	0 3 2 7	0.567	-0.230	-0.267	1 000
M2	0.177	0.575	0.235	0.157	0.527	0.507	0.250	0.207	1.000
Al	1 000								
As	0.780								
Cr	0.970	0.654							
Cu	0.450	0.472	0.360						
Fe	0.987	0.814	0.926	0.455					
Mn	-0.034	0.356	-0.182	0.650	0.040				
Ni	0.984	0.735	0.954	0.333	0.986	-0.118			
Pb	0.526	0.159	0.613	0.695	0.457	0.081	0.451		
Zn	0.968	0.646	0.980	0.521	0.927	-0.069	0.935	0.707	1.000
M3									
Al	1.000								
As	0.954								
Cr	0.927	0.891							
Cu	0.979	0.980	0.897						
Fe	0.930	0.844	0.800	0.933					
Mn	0.911	0.805	0.947	0.875	0.895				
Ni	0.857	0.920	0.809	0.841	0.629	0.633			
Pb	0.848	0.872	0.682	0.823	0.686	0.563	0.944		
Zn	0.788	0.652	0.650	0.666	0.664	0.630	0.744	0.844	1.000
ML									
Al	1.000								
As	0.762								
Cr	0.987	0.675							
Cu	0.831	0.382	0.825						
Fe	0.382	0.873	0.247	0.053					
Mn	-0.274	0.396	-0.404	-0.504	0.784	0.000			
NI	0.995	0.755	0.991	0.793	0.355	-0.300	0.167		
Pb Zu	0.129	-0.382	0.281	0.176	-0./28	-0.829	0.167	0 704	1 000
Zn	0.092	-0.390	0.231	0.122	-0.738	-0.840	0.165	0.726	1.000
	1 000								
AI Ac	1.000								
AS Eo	0.901	0 100							
re Cu	-0.433	-0.192	0.066						
Cu Cr	-0.100	-0.455	0.000	0.060					
CI Mn	-0.500	0.044	-0.4/0	-0.002	-0 500				
Ni	0.052	0.555	_0.210	0.240	0.550	-0.308			
Ph	0.482	0.752	_0.135	<b>–0 740</b>	0.356	-0.619	0 268		
7n	0.801	0.855	-0 357	-0 323	0.692	-0.816	0.633	0.841	1 000
	0.001	0.035	0.557	0.525	0.072	0.010	0.035	0.071	1.000

Table 4 Correlation coefficient for boow motals in six sodiment cores from Lake Naivasha, Kenya

indicated that the two metals (Fe and Mn) could be from various sources or the processes affecting their distribution are not similar. These findings were different from those reported by Bhuiyan et al. (2015) who found that Fe and Mn had moderate positive relationship 0.494 in sediment while in water almost no correlation existed between the two metals. Lack of Fe and Mn correlation could be an indicator that various sources of these metals exist.

Further a strong negative relationship between Al and Mn, Pb was noted in M1 core. Having found that Al was from natural sources, the Mn and Pb were classified to have been influenced by anthropogenic activities. On the other hand, at hippo point (HP core) Zn and Mn were found to have a strong Negative relationship (-0.816) while Fe and Cu still had a negative relationship with Zinc. This was an indicator that these metals could have been from diverse sources. In CR and M1 core, Cu and Zn were found to have strong positive correlation of 0.882 and 0.623, respectively. This might have suggested that these heavy metals in both sites could be from the same anthropogenic source. In HP,

M3, ML, and M2 core, Zn and Pb were found to have a strong positive correlation (>0.7) which could be an indicator that the factors affecting distribution of these metals are the same. The source of Cu and Pb could be from domestic wastewater or agricultural sources especially from fungicides and other agrochemicals used in the farms surrounding the lake.

The significant positive correlation among heavy metal in the sediment were considered to suggest common source or geochemical activities while those metals that had significant negative correlation were attributed to having various sources and geochemical activities. According to Bhuiyan et al. (2015) and Ghrefat et al. (2011), strong positive correlation between elements indicates that the elements are from the same source and that their transportation process is similar. The also reported that metals which had no significant correlation with Al, would be suggesting that they are from anthropogenic sources. However, in some cases, significant correlation does not always indicate a common source of metals. This was demonstrated by Zhou, Liao, Shu, Yang, and Lan (2015) where they found that Ni in the study area was 2 times higher than the background value of the metal but from correlation results, the metal was classified to be influenced by natural sources. From these multivariate analysis, Al in Lake Naivasha was found to be majorly from lithogenic source as a result it was the most suitable metal for normalization procedure. This followed a requirement that the normalizing metal should not be dependent on anthropogenic inputs. Further, normalization of metals aids in understanding the level of pollution in the heavy metal under consideration.

### 3.7. Pollution of lake sediments

It was noted that most values from pollution indices (CF, EF, and  $I_{geo}$ ) had increased slightly from the past to recent years (Figures 5 and 6) for As, Zn, Cu, and Fe. Figures 5 and 6 represents chronological variation of pollution level in the cores collected at Malewa and Crescent site. Yusoff et al. (2015) reported similar



**Figure 5.** Pollution levels for various heavy metals in sediment in Crescent site of Lake Naivasha derived from contamination Factors (CF), geoaccumulation Index (I<sub>geo</sub>) and Enrichment Factors (EFs).

there has been an increasing trend of metal pollution. Further, Figure 7 presents the spatial distribution of the pollution indices for various heavy metals studied which indicates that various parts of the lake experience distinct pollution levels.

Hippo Point is highly contaminated with Fe and Cu while crescent is largely affected by Mn, Zn as shown in Figure 6. The  $I_{geo}$  values were found to vary from one metal to another in the different sites of the lake. Most metals in the Lake were found to have  $I_{geo}$  values being less than zero other than the values for Zn in all sampling sites and Mn in hippo point and Crescent. The  $I_{geo}$  values of Zn ranged from 0.0 to 0.3 with the lowest value being in M1 while the high values were recorded

in M2, ML, and CR cores. Considering  $I_{geo}$  classification, Lake Naivasha is classified in class zero signifying that the sediments are uncontaminated (Table 5). This suggests that the metals in the lake are mainly from natural sources and that the lake was only polluted with Zn and Mn metals.

The trend of Lake Naivasha metal contamination using CFs index was the same with that of  $I_{geo}$ . The Al, Cr, Cu, Ni, and Pb in all cores had CF values less than one (< 1). Similar low values had been reported by Goher, Farhat, Abdo, and Salem (2014) in a study conducted on surface sediments of Lake Nasser Egypt. On the other hand, Fe in M2, M3, and HP core, As in M2, M3, ML, and HP together with Zn and Mn for all sites had CF values greater than one. This indicated that the heavy metal concentration in the sediments is not only dependent on geogenic sources but also was polluted from anthropogenic activities.



Figure 6. Pollution levels for various heavy metals in sediment at Malewa site of Lake Naivasha derived from contamination Factors (CF), geoaccumulation Index (I<sub>geo</sub>) and Enrichment Factors (EFs).



Figure 7. Spatial distribution of Contaminant Factor (CF), Enrichment Factor (EF) and geoaccumulation Index (I<sub>geo</sub>) values for various heavy metals in Lake Naivasha sediment.

To establish the heavy metals pollution, Enrichment Factors (EFs) of the sediments were calculated. The order of the mean EFs for sediment in Lake Naivasha was Zn >Mn >Fe (As) >Pb >Cu >Ni >Cr with values of 3.2, 2.7, 1.8, 0.68, 0.6, 0.4, and 0.3, respectively. Considering the studied metals, it was established that the lake is highly polluted with Zn, Mn Fe, and As where the range of enrichment factors (EFs) for As (1.5-1.9), Fe (1.7-1.9), Mn (2.0-3.5), and Zn (2.9-3.7) in all sites were found to be >1.5 (Table 5). According to El-Amier et al. (2017); El-Sayed et al. (2015) and Zahra et al. (2014) EF values > 1.5 indicate that these metals have been impacted by anthropogenic input. The difference in EF values for metals along the profile may be due to varied concentration of input to the sediment depending on their source. It can also be because of the different diagenic processes involved for each metal. The highest pollution of As, Fe, Mn, and Zn was found to be in M2, both M1 and HP (for Fe), CR and CR cores, respectively. In the study, it was noted that Enrichment Factor of Zn in all sites is  $\geq$  3 which was classified as having moderate enrichment (Table 5). Moderate enrichment of Zn to sediment had also been reported by Kouidri et al. (2016) in a study conducted in Ain Tomouchent, Algeria.

From the EF results, it was observed that the metals in the lake could be from two sources, the anthropogenic and lithogenic sources. Zn could originate from anthropogenic activities for instance disposal of municipal waste water and agricultural inputs like fertilizers and pesticides. Comparing the EFs of the heavy metals in Lake Naivasha sediment with those of Taihu Lake, China as presented by Yuan et al. (2011) it was noted that the mean EF values in Lake Naivasha ranged from 0.3 to 3.7 while those of Taihu Lake were 0.4–3.7, respectively. Like Lake Naivasha, Taihu Lake is a fresh water lake that is also surrounded by agricultural activities and receives effluent from domestic wastewater.

**Table 5.** Classes of pollution indices (adopted from El-Amier et al., 2017; El-Sayed et al., 2015; Zahra et al., 2014) and contamination categories of heavy metal in Lake Naivasha sediment based on Contamination Factor (CF), Enrichment Factor (EF) and Geoaccumulation Index ( $I_{geo}$ ).

	Index	Class/	Sediment	
Indices	Value	Level	description	Current study (avg)
CF	<1		Low	Al (0.55), Cr (0.17),
			Contamination	Cu (0.33), Ni (0.21), Ph (0.25)
	1 < (F		Moderate	As (1.00). Fe (1.01).
	< 3		contamination	Mn (1.45), Zn (1.73)
	3 ≤ CF		Considerable	
	< 6		contamination	
	$CF \ge 6$		Very high	
			contamination	
EF		Level		
	< 1	Ι	No enrichment	Cr (0.30), Cu (0.61),
				Ni (0.39), Pb (0.66)
	1-3	Ш	Minor	As (1.79), Fe (1.80),
	2 5		enrichment	WIN (2.71)
	3-5	111	Moderale	Zh (3.23)
	5 10	NZ	Modoratoly	
	J-10	IV	sovere	
			enrichment	
	10-25	v	Severe	
		-	enrichment	
	25–50	VI	Very severe	
			enrichment	
	>50	VII	Extremely severe	
			enrichment	
l <sub>geo</sub>		Class		
	< 0	0	Uncontaminated	Al (-1.46), As (-0.64), Cr
				(–3.21), Cu (–2.25), Fe
				(-0.62), Mn (-0.09), Ni
	0 < 1	1	Uncontaminated	(-2.84), PD $(-2.20)$
	0 < 1	1	to moderately	211 (0.19)
			contaminated	
	1 < 2	2	Moderately	
	2	-	contaminated	
	2 < 3	3	Moderately to	
			strongly	
			contaminated	
	3 < 4	4	Strongly	
			contaminated	
	4 < 5	5	Strongly to	
			Extremely	
	_	-	contaminated	
	≥ 5	6	Extremely	
			contaminated	

Though the other metals studied in the current study showed no impact of anthropogenic activities, it was noted that the As, Fe Mn, and Zn metals in most lake sites had been affected by anthropogenic sources. This was established from all pollution indices which showed that the metals could be classified in lowly contaminated to moderately contaminated classes depending on the various groupings of the indices. The findings of this study agreed with the report by Rabee, Al-Fatlawy, Abd, and Nameer (2011) that CF, I<sub>geo</sub> and EF indices aid in distinguishing natural and anthropogenic input on heavy metals.

## 4. Conclusions

In this study, vertical distributions of natural and artificial radionuclides (<sup>40</sup>K, <sup>210</sup>Pb, <sup>214</sup>Bi, <sup>214</sup>Pb, and <sup>137</sup>Cs) in two cores from Lake Naivasha were analyzed using gamma

spectrometry. The <sup>137</sup>Cs was successfully used as an independent time marker and aided in establishing depth age relationship using excess <sup>210</sup>Pb. From the dated cores, the average mass sedimentation rate at Malewa (near the inflow) and Crescent sites of Lake Naivasha was found to be 0.40  $\pm$  0.04 and 0.26  $\pm$  0.15 g/cm<sup>2</sup>/yr, respectively. Further considering the past 50 years, sediments of Lake Naivasha was found to have an average heavy metal concentration of 44,457.07, 13.05, 15.03, 14.95, 46,566.43, 1233.07, 14.61, 7.00, and 178.29 mg/kg for Al, As, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, respectively.

From multivariate analysis, it can be concluded that Al, Cr, Pb, Cu, and Ni availability in the sediment core was mainly due to lithogenic control while Zn, Mn As, and Fe are controlled by both natural and anthropogenic sources. Pearson's correlation and Principal Component Analysis (PCA) aided in assessing the sources of contaminants/pollutants in sediment.

It was noted that most heavy metals had low  $I_{geo}$  (geoaccumulation Index) and CF (Contamination Factor) values which varied along the core depth. Lake Naivasha sediment was classified to range from uncontaminated to moderately contaminated class using the CF and  $I_{geo}$  indices. Further, the average Enrichment Factor (EF) values ranged between 0.3 and 3.2, with the highest EFs registered by Zn and Mn metals. Lake Naivasha sediment was found to have no enrichment with Cr, Cu, Ni, and Pb metals while a minor to moderate enrichment was recorded for As, Mn, Fe. Further the lake was found to be moderately enriched with Zn metal.

The values recorded for I<sub>geo</sub>, CF, and EF indicate that Lake Naivasha sediment quality has not been greatly affected by anthropogenic activities. However, caution should be practiced since it can be noted in most heavy metals studied, the pollution indices were increasing on the upper section of the cores compared to the lower layers. This could be an indicator that recent human activities are impacting on the sediment quality. From the findings of this study, the information on dating derived from <sup>210</sup>Pb together with <sup>137</sup>Cs and sediment contamination with heavy metals aided in understanding the impacts of human activities to Lake Naivasha with time.

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