

Potentially Toxic Elements and Some Major Elements Occurrences and Distribution in Surficial Sediments Under The Expanding Aquaculture Operations within The Littoral and Limnetic Areas of Lake Victoria (Kenya)

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Citation: Job Mwamburi (2026). Potentially Toxic Elements and Some Major Elements Occurrences and Distribution in Surficial Sediments Under The Expanding Aquaculture Operations within The Littoral and Limnetic Areas of Lake Victoria (Kenya). *Environmental Reports; an International Journal*. DOI: <https://doi.org/10.51470/ER.2026.8.2.74>

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Received 03 July 2026 | Revised 05 August 2026 | Accepted 07 September 2026 | Available Online October 03 2026

ABSTRACT

Sediments contamination and remobilization of adsorbed contaminants increases their potential transfer along the trophic levels and exposure risks to the benthic dwelling communities. However, metal availability and toxicity is inherently related to metal speciation. Shallow littoral, deep and very deep limnetic areas within the Winam Gulf and the open lakes zones were sampled and analysed for major and trace elements. Spatially, the lake sediments reveal variable characteristics when moving from the littoral to the deeper zones. The elemental concentrations, sedimentary organic matter, carbonate and water contents were compared across the lake and water zones. The organic matter and carbonate contents revealed significant variation across the lake zones, but with no significant relationships ($p < 0.05$) with the elements. Sediment water contents in littoral and very deep sediments showed significant ($p < 0.05$) differences. The iron (Fe) lead (Pb), nickel (Ni) and copper (Cu) contents varied significantly between the sediment fractions (un-fractionated and finer fraction). Magnesium, silver, nickel and iron concentrations exhibited significant differences between the water and lake zones. The sediment were enriched with Ag and Cu, but the geo-accumulation index shows uncontaminated sediments, except for silver. This implies lithological sources for the major elements and anthropogenic sources for silver, copper and lead. The bioavailability of the minor potentially toxic elements is controlled by their association with the surface sediments. Evaluations for lead, copper and nickel levels are a concern due to their exceedance of the threshold effect levels, and probable adverse effects to bottom dwelling organisms.

Keywords: Surficial sediments; Lake Victoria; Trace elements; Ecological risks; Spatial distribution; Geochemical accumulation.

INTRODUCTION

Globally, trace metal pollution is an environmental problem mainly associated with key natural sources (volcanism, crude oil drilling and operation; mineral weathering processes); human activities and manufacturing industries, mining activities, solid and liquid effluent discharges, vehicle and industrial emissions; and other widespread and diverse anthropogenic sources. Artisanal gold mining areas are of concern due to the potential release of lead, cadmium, mercury, nickel, arsenic, copper and chromium from mining and processing of gold ore [1]. Metal tolerant or metal accumulating plant species, especially hyperaccumulators can accumulate high metal levels (Copper, iron, manganese, molybdenum, nickel and zinc) without showing toxicity, and hence their potential use as phytoremediators of contaminated soils or phyto-mining of economically valuable metals and restoration of ecosystems. However, there are concerns on the potential health risks on the use of these plants by humans and wildlife as food and medicine [2]. Investigations on trace elements in large rivers and natural lakes [3-9] reports on the distribution levels and sources, while other recent findings by Rosca et al. [10] show the use of catchment lithology and sediment Pb and Zn isotopes in documenting landuse changes and chronology of anthropogenic pollution in a Kenyan rift valley lake. In Lake Victoria (East Africa) low levels of methyl mercury were

reported in lake water at a few sites, but total mercury was detectable with an average content of 220 ng/g [11] in the top 10 cm of the lake core sediments, with a total Hg rise since 1960. Elements such as mercury can also undergo microbial methylation [12] in the anaerobic environments in bottom water, sediments and soils; and therefore we need to understand the rates of mercury methylation, since the methyl mercury species is the most toxic.

Environmental factors and compositional variability of aquatic sediments have a significant influence on metal speciation and retention within the ecosystems. Sediment organic carbon adsorbs organic contaminants and enhances their retention in soils and sediments. However, data on the environmental fate of contaminants within the catchment area is limited. Cyanide speciation in seepage water, surface water, wastewater and sediments around artisanal gold mining areas [13] revealed exceedance of regulatory thresholds. Residues of agricultural chemicals such as organochlorine pesticides are still detectable in sediments and water of one of the urban river, and increased downstream [14]. Around the Winam gulf catchment, random forests modelling has also been used in prediction and uncertainty evaluation of the total concentrations of the soil iodine, selenium, zinc and soil pH in western Kenya [15] as a means to guide farmer fertilizer application and agricultural policy.

High bioaccumulation affinities of Cu, Zn, Pb, Cd, Fe and Al were found between crab tissues (*Cardisoma armatum*, Herkiots, 1851) and heavy metals in sediments [16]. Fish ingest heavy metal and pesticide contaminants residues accumulated in food items, or absorb them from suspended particulate matter through their respiratory gills, causing oxidative stress. However, documented studies linking effects of metal toxicity to fish species from the lake with metal intoxication a few. Potentially toxic elements such as Pb, Ni, Cu, As, Zn, Hg, Cd and Cr accumulate in soils, biota and sediments posing serious environmental concerns. Uptake of the major (Na, K, Mg, Fe, P, Ca) and minor (Mn, Cu, Zn, I, Se, Zn) trace elements in the correct proportions serve as vital minerals [2,17-18] in diets of cage cultured fish and other wild species. As cage culture of tilapia expands within the relatively shallow bays and open lake areas [19-21], there are potential concerns on the potential ecological impacts on the benthic areas of the lake. Wastewater treatment plants are point sources of high volumes of treated effluents and together with urban surface runoffs and other untreated waste discharges contribute to the discharge of organic and inorganic contaminants into the riverine and lentic ecosystems. There is no clear evidence on the synergistic effects of heavy metals and antibiotics on the propagation of antibiotic resistant genes [22] in the aquatic environment. Besides this, improved diets of Nile tilapia in cages around L. Victoria is a priority for reducing the environmental impacts from P and N loading [19] in feed wastes. Currently, there is a growing need to mitigate the recent reports of fish kills in the shallow bays [23-24] which were due to hypoxic underwater conditions around cage operations, most probably as a result of the limited water exchanges around the cage structures. Fish kills led to total economic losses of \$7.7 million, with Kisumu County incurring 95.35% of the losses, with high-density cage farms experiencing severe losses due to overcrowding, degraded water quality and nutrient accumulation [24].

High loadings of eroded soils within Lake Victoria (Kenya) river drainage basins is due to increasing precipitation [25-26], and this may lead to increased mobilization of elements in lake and river ecosystems. Trace metals studies along the river drainage basin have revealed the presence of Pb, Zn, Fe, Mn, Cd, Cu, Cr in the surficial sediments and water of River Yala [27]. Similarly, detailed investigations on the sediment trace elements mapping within the Winam gulf delineated trace metal accumulation around the river mouths, littoral and limnetic sites [20,28], human body tissues, and other environmental matrices within the lake basin [29-30]. Ecological and public health risks associated with some of the toxic and commonly encountered chemical residues in drinking water sources and wastewater effluents, is a concern and is often prioritized for monitoring by both the national [31-32] and other international [33-36] environmental management agencies, but there is little information on contaminant levels in benthic and core sediments, aerial deposits, and tissues of different aquatic biota. Several other ongoing studies have reported presence of contaminants of emerging concerns (CECs) and different organic contaminant residues at varying concentrations [37-39] as a result of the uncontrolled discharge of untreated and partially treated wastewaters directly into surface river and lake waters. This has elucidated concerns due to the potential development of antibiotic resistance [40-42] within the aquatic ecosystem.

Safe recycling and re-use of nutrient rich biosolids from wastewater treatment plants is also a concern due to potential transfer of the potentially toxic elements (Pb, Hg, Zn, Mo, Se, Cd, Cr, As, Cu and Ni) and persistent organic pollutants in biosolids for agricultural use when they occur in levels above the recommended limits [38, 43-44].

Increasing sediment deposition also affects both coastal marine and freshwater maritime operations around shallow harbours; and this often calls for remediation measures to effectively manage disposal of dredged materials; and reclamation of waterways and channels to allow boating and shipping. Both the sand and surficial sediments are useful for the socio-economic benefits of surrounding communities in construction and agriculture, besides providing unique benthic habitats. Sediment dredged from rivers, waterways, and harbours have a beneficial value, although there are barriers of social acceptance when contaminated sediments are used on land and attract extra cost of disposal [45]. Locally available sands from the littoral areas are sources of sand, which is also utilized in large amounts for construction, besides forming suitable fish nursery grounds. However, not much information is provided on post degradational effects. Of concerns is the contamination of sediments from the different sources around urbanizing shorelines, wastewater discharges, and expanding population; and accompanied land use and land cover changes. Surrounding landscape gradients, crop cultivation, pesticide use, and extraction of minerals are contributing factors to the anthropogenic loading of elements into lake and river channels, but variations across the wider Nyanza gulf zones are not well mapped in detail when compared to recent efforts by Aura et al., [20] in spatial mapping of surface sediments within the Winam gulf zone. Uncontrolled disposal and chemical degradation of solid materials and plastics and low recycling potential continues to be a challenge in lake environmental management, and contributes to the pollution of sediments and remobilization of inorganic and organic elements into the lake ecosystem. The study objectives were to determine the lake-wide spatial distribution of trace elements in the uppermost layer of lake bottom sediments in order to identify the elements accumulation levels, potential sources; evaluate the degree of trace element contamination and the ecological risks using some of the relevant sediment pollution indices.

MATERIALS AND METHODS

Environmental changes in Lake Victoria (East Africa)

Lake Victoria is a wide and relatively deep shallow basin which was formed about 0.4Ma ago [46]. From the littoral to the deep bottom zone, the surface is an important habitat, known for its high fish species diversity and high productivity levels as indicated by the well documented eutrophic conditions. Lake sedimentation is a continuous process known to modify the bottom habitat as a result of deposition of in-lake and other external materials through active transport of erosional and weathered rock and soil formations. Verschuren et al [47] described the 180 years environmental history (1820-1996) of the lake based on deep water (67-68m) sediment core (V96-5MC), and sediments were reportedly to have accumulated at a relatively constant rate of $0.032 \pm 0.001 \text{ g/cm}^2/\text{year}$ or 2.3mm per year [48]. All previous deep coring data in the main lake reported a mass accumulation rate (based on the ^{210}Pb activity) ranging from 0.01 to $0.032 \text{ g/cm}^2/\text{yr}$ [11,47,49].

The lakes ecology has changed over time as due to increasing human activities [50] which are depicted in a century chronology (1901-2006) on changes on the lake fisheries, fish introductions, lake level changes, water hyacinth invasions, eutrophication events, dominance of cyanobacteria and onset of fish cages around the year 2006. Several studies have quantified soil erosion [25-26]; water and sediment flows, which contributes to the remobilization of terrestrial elements and materials transport into lake ecosystems. These studies and information are required to design better watershed management actions and reduce sediment contamination.

Study area

Lake Victoria (East Africa) lies in a relatively low depression between the Eastern and Western arms of the East African Rift system [51], and it is among the great lakes of the White Nile basin [52]. The lake has a mean and maximum water depth of 40m and 80m, with a total surface area of 68,800 Km². The lake catchment area covers about 195,000Km² and extends South-western into Rwanda and Burundi. The lake dried at about 17300 years ago and refilled beginning about 14,700 years ago. The catchment area supports a high population of about 40 million people and a mean population density of about 250 persons per Km² which is growing at a rate of 3.55 per year. The Kenyan section of Lake Victoria (Nyanza Gulf, surface area of 4,113 Km²) is an eastwards extended gulf (Winam Gulf 1,493 Km²) and the open lake area (Fig. 1), with several inhabited small and large islands. The Winam Gulf (mean depth of about 6m) is a relatively shallow semi-enclosed embayment which deepens westwards from Kisumu to Mbita (about 65 - 70 Km horizontal) Water.

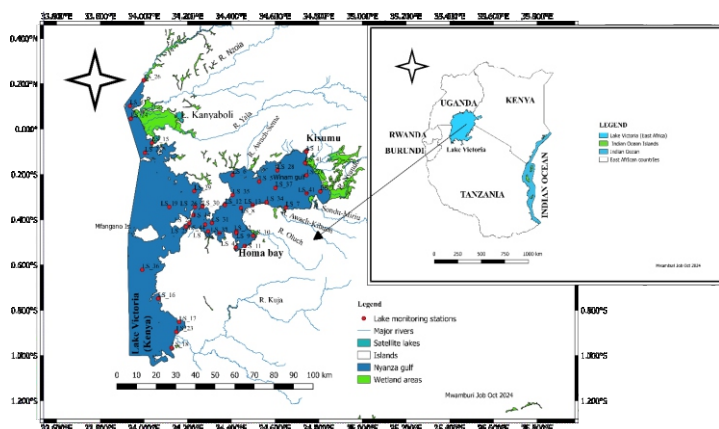


Fig. 1 A map showing the sampling stations within the Winam gulf and open lake areas of Lake Victoria (Kenya) depth of greater than 10m [52] are found beyond Ndere Islands, with the very deep areas in the open lake. Rusinga Island forms a barrier to the open lake which exchanges water through the southern (Mbita channel) and the northern passages (Rusinga Channel). The watershed around the Winam Gulf receives riverine materials through major inflowing rivers (Oluch, Sondu-Miriu, Awach-Kibuo, Nyando, Awach-Seme and key urban rivers (Kibos, Kisat and Kisan). Re-opening of the Mbita causeway restored the restricted open lake-Winam Gulf water exchange. Recent developments in cage aquaculture operations from 2006 [20-21,24,53] and associated fish kills, the persistent remnants of the invasive water hyacinth (*Eichhornia crassipes*) since its invasion in 1988-1990 [54-57], are still a concern due to potential impacts on the lake benthic habitats and fisheries.

Artisanal gold mining, quarrying and sand harvesting are some of the major mining activities [58] associated with environmental degradation. Several previous and recent water quality surveys documented a gradient in water quality and nutrients from Winam gulf towards the main lake [59-61].

Sampling

The sampling survey was conducted in June 2012 (Fig. 1) at littoral and limnetic sites within the Winam gulf and open lake areas as follows:-Winam gulf sites: LS_1 (Kisumu Pier); LS_2 (Maboko Is.); LS_3 (Off Nyando river mouth); LS_4 (Off Sondu Miriu); LS_6 (Asembo bay); LS_7 (Off Awach River mouth); LS_8 (Gingra rock); LS_34 (Mitimbili); LS_35 (Achieng Oneko); LS_13 (Balarawi); LS_28 (Off Kibos RM); LS_5 (Off Ndere Isl.); LS_9 (Soklo); LS_10 (Oluch RM); LS_11 (Homabay); LS_12 (Kopiata); LS_14 (Utajo); LS_15 (Luanda Gembe); LS_24 (Mbita East); LS_37 (Mid gulf); LS_33 (Mirunda bay); LS_30 (Luanda Kotieno); LS_26 (Rusinga channel); LS_31 (Madundu); LS_32 (Kowuor). The open lake (OPL) sites included: LS_16 (Matara bay); LS_17 (Sori-Karungu); LS_18 (Muhuru bay); LS_25 (Mbita west); LS_36 (Remba); Northern section LS_19 (Bridge Is.); LS_20 (Off Yala RM); LS_21 (Off Nzoia RM); LS_22 (Off Sio RM); LS_23 (Off Kuja RM);

Surficial sediments were collected using a pre-cleaned ponar grab sampler. The innermost portions of sediments were used for gravimetric determinations and trace metal chemical analysis, to avoid portions in contact with the grab sampler. The field samples were kept frozen in pre-cleaned high density polythene bags in the field, prior to initial sample preparation in the laboratory. The sediments were characterized by determination of the percentage water, carbonate and organic matter contents. The water content was determined by oven - drying about 5.0g of the wet sediment at 105 °C for 6 hours and to constant weight. About 1.0g of the dry sediment was used to determine the carbonate and organic matter contents. The percentage Loss on Ignition (% L.O.I) was also determined by heating about 1.0g of the dry sediment at 550 °C [62] in a furnace and determining the weight loss. All determinations were made in triplicates. To ensure quality of data, all dried samples were cooled in a desiccator and gravimetric measurements were made inside the laboratory using sensitive analytical balances. This ensured all possible contamination from the air was avoided.

About 1.0 g of the sediment was digested with 10ml (3:1 v/v ratio) of conc. HCl - HNO₃ mixture at 90 °C for 60 minutes. Acid blanks together with the digested sample solutions were diluted to mark in 50ml volumetric flasks. All glassware used in the extractions were soaked in 10% HNO₃ v/v, rinsed with deionized water. All reagents used were of analytical grade to check for possible contamination, and blanks were carried through the same procedures. Replicates were included in all analyses.

Sediment accumulation and enrichment indices of elements

A geo-accumulation index (I_{geo}) value was calculated according to Muller [63],

$I_{geo} = \log_2[(C_n) / (B_n \times 1.5)]$ (1), where C_n = measured concentration of element in the surficial sediments; 1.5 = a correction factor to cater for the influence of the natural geochemical variation; and B_n = the shale rock background concentration value according to [64] and crustal average [65].

The evaluation of metal pollution was done using the seven categories, which ranges from class zero (uncontaminated, I_{geo} value = less than or equal to zero) to class six (extremely contaminated, I_{geo} value = greater than or equal to 5).

The sediment enrichment factor (SEF) index of measured levels of metal elements in sediments was used to understand their sources (anthropogenic and natural or geogenic) in the surficial sediments. The SEF [66] was calculated as follows:-

$SEF_{element} = [(C_{es}/C_{rs})_{sample}] / [(C_{ebk}/C_{rbk})_{background}]$ (2), where C_{es} and C_{ebk} = the measured element concentration in surficial sediments and its background levels; C_{rs} and C_{rbk} = the reference conservative element concentration in the sample and its background levels [67]. The evaluation of elemental enrichment in the sediments was done using the five categories, which ranges from class one (depletion to minimal enrichment, SEF value = < 2) to class 5 (extremely high enrichment, SEF value = > 40). The contamination factor (CF) for each of the determined PTE was calculated as follows:

$$CF_{element} = (C_i/C_{rf}) \text{ (3)},$$

Where: C_i = PTE concentration in the sample and C_{rf} = the reference background value of the PTE. The categories of CF range from a value of < 1 (low contamination) to 6 ≥ (very high contamination). The ecological risk factor was applied to evaluate the potential ecological risk of a specific PTE (Hakanson 1980), where Tr^i values used were as proposed by Hakanson [68]

$$Er^i = Tr^i (CF) \text{ (4)}$$

The Tr^i and CF are the toxic response factors and contamination factor values respectively. A Tr^i value ranges from < 40 (low potential ecological risk) and > 320 (very high ecological risk). The PTE potential ecological risk index (PERI) was applied to evaluate the sum of the potential risk factors where:- risk of a specific PTE [68], where Tr^i values used were as proposed by Hakanson [68].

$$PERI = \sum(Er^i) \text{ (5)}$$

The PERI categories range from low ecological risk (, 150) to very high ecological risk (PERI > 600).

Chemical and statistical analysis

Elemental concentrations in both samples were determined using flame and graphite Atomic Absorption Spectrophotometer (Varian Techtron Spectra AA-10, Varian Techtron PTY Ltd. Varian Associates Inc.), according to the manufacturer's conditions with appropriate standard solutions. Although recovery studies were not conducted, all samples were analysed together with batches of blank samples, to check for any contamination.

Table 1: Major and minor elements concentrations in surface sediments (% and µg/g dry weight). (Arithmetic mean ± Standard deviation; Gm = Geometric mean)

Elements		Mean (±SD)	Sediment fraction			
			Un-fractioned	Fractioned	Un-fractioned (Gm)	Fractioned (Gm)
Major (%)	Fe	5.524 (±1.994)	4.988 (±2.194)	6.080 (±1.619)	5.858	4.225
	Ca	0.861 (±0.784)	0.947 (±0.916)	0.774 (±0.623)	0.676	0.613
	Mg	0.229 (±0.097)	0.227 (±0.099)	0.232 (±0.096)	0.203	0.026
	Mn	0.112 (±0.085)	0.092 (±0.046)	0.133 (±0.110)	0.081	0.106
Minor (µg/g)	Pb	29.72 (±29.56)	30.45 (±13.01)	28.96 (±40.40)	26.60	20.64
	Co	8.56 (±3.20)	9.19 (±2.97)	7.91 (±3.35)	8.71	7.08
	Ag	7.53 (±14.92)	9.78 (±21.42)	5.74 (±5.97)	4.16	2.90
	Ni	33.16 (±44.48)	44.06 (±60.28)	21.88 (±8.67)	33.52	19.98
	Cu	98.63 (±163.73)	168.09 (±213.08)	31.49 (±16.98)	113.76	28.14

Statistical data description and the type of distribution of the variables was checked using Shapiro-Wilk normality test in R software [69]. Where appropriate, significant correlations and spatial differences between zones (at 0.05 level of significance) were determined using parametric and non-parametric tests, to understand any associations and spatial variations. Multivariate statistical analysis was done using the R software packages after data was checked for normality and standardized.

RESULTS

Non-parametric statistical test were used to test significant variations between group medians for non-normal parameters. There was a significant ($p < 0.05$) increase in water depth across the lake zones and water zones, except for the river mouth sites in both the open lake and Winam gulf areas. Spatially, the lake sediments reveal variable characteristics when moving from the littoral sites to the deeper zones of the lake (Fig. 2a). The characteristics of the surficial sediments (i.e sedimentary organic matter OM, carbonate and water contents) were compared across the lake (Winam gulf area-WG; River mouth areas of the Winam gulf-RM_WG; Open lake areas-OPL and River mouth areas in the open lake-RM-OPL) and water zones (Littoral, deep limnetic and very deep limnetic). The percentage OM and carbonate content revealed significant variation across the lake zones, except for the OM and water contents between the river mouth sediments in the gulf and open lake; and the WG vs OPL sediments. Water contents also showed no significant difference between the WG vs OPL; RM_WG vs RM_OPL and RM_WG vs OPL Water contents in littoral and very deep sediments also showed significant ($p < 0.05$) differences (Fig. 2b). Significant variations were evident between the carbonate Lake zones revealed no significant variation in sediment carbonate. However, significant ($p < 0.05$) OM variations emerged between deep and very deep limnetic sites, and water contents in sediments from deep littoral and limnetic zones.

Similarly, the major and trace elements concentrations in the top surface bottom sediments were compared between the three different lake and water zones of the Kenya part of Lake Victoria. The results show the spatial variability of the elements in un-fractioned and finer surface sediments. The mean (arithmetic) contents of the major and minor elements decreased from Fe > Ca > Mg > Mn and Ag > Co > Pb > Ni > Cu (Table 1). The range and median values of Fe, Ca, Mg, and Mn contents varied from 0.52 - 9.25 (5.70) % dry wt., 0.193 - 4.145 (0.576) % dry wt., 0.026 - 0.485 (0.225) % dry wt. and 0.018 - 0.548 (0.087) % dry wt.

There were no significant variations observed in Mg, Ca, Mn, Ag and Co concentration between the two sediment fractions analyzed. The mean Fe contents were significantly ($p = 0.031$, T-test) higher in the finer sediments than the un-fractionated bottom. A Wilcoxon test also revealed much higher median Pb, Ni and Cu contents in the un-fractionated compared to the finer sediments. The surficial sediments contents of the major and minor elements varied spatially; and between the lake and water zones (Figs 3a-c; 4a and 4b). There were no significant variations between un-fractionated and finer sediments Mg, Ca, Mn Co, Ag, except for Fe, Pb, Ni and Cu concentrations. The levels of Fe, Ca and Ni in littoral and deep limnetic sediments showed significant variations (Table 2), when compared to the contents of Mn, Mg, Ca, Pb, Co, Ni and Cu. Between the lake zones significant variations were evident for Ni, Ag, Mg and Fe (Fig. 4a-4b). In general, the spatial Fe contents increased from the Winam gulf zone and the river mouths into the open lake zone,

but levels appear to decrease towards the deeper limnetic zones. Nickel levels show a slight and gradual decrease from littoral areas into the deeper limnetic basin areas. Significant inter-elemental correlations coefficients ranged from weak to strong (0.362 to 0.701) associations. The associations between the sediment metal contents (Table 3 a and b) shows a significant relationship between the major elements in both the sediment fractions, and non with the sediment components, except for un-fractionated Ca and Mg with carbonates, and between un-fractionated Fe versus water contents and Fe versus water depth. Cobalt, lead, nickel and copper also exhibited significant associations in the un-fractionated sediments, whereas Co, Ni and Cu were more associated in the finer sediments. Organic matter did not show any significant associations with the trace elements, whereas Co and Ag contents revealed significant relationships.

Table 2: A comparative evaluation of the significant variations ($p < 0.05$ bold) of the major and minor elements concentrations in surface sediments (Wilcoxon test p values) collected from the different lake (Winam gulf = WG; WG river mouth = RM_WG, OPL = open lake; OPL river mouth = RM_OPL) and water zones (Littoral, L; Limnetic_deep, LD; Limnetic_very deep LVD)

Major & trace elements	Lake zones						Water zones		
	WG vs RM_WG	WG vs RM_OPL	WG vs OPL	RM_WG vs OPL	RM_WG vs RM_OPL	RM_OPL vs OPL	L vs LD	L vs LVD	LD vs LVD
Fe	0.137	0.044	0.288	0.852	0.662	0.279	0.041	0.328	0.626
Mn	1.000	0.295	0.445	0.477	0.605	0.753	0.051	0.501	0.066
Ca	0.960	0.064	0.116	0.573	0.345	0.959	0.139	0.056	0.011
Mg	0.463	0.001	1.000	0.491	0.001	0.002	0.925	0.437	0.658
Pb	1.000	0.343	0.428	0.948	0.651	0.636	0.682	0.562	0.556
Co	0.387	0.469	0.626	0.945	0.990	0.969	0.669	0.690	0.515
Ag	0.0127	0.028	0.472	0.018	0.082	0.154	0.655	0.615	0.243
Ni	0.007	0.921	0.329	0.272	0.017	0.721	0.016	0.102	0.690
Cu	0.959	0.812	0.357	1.000	0.491	0.916	0.857	0.914	0.816

NB: SG= significant in bold

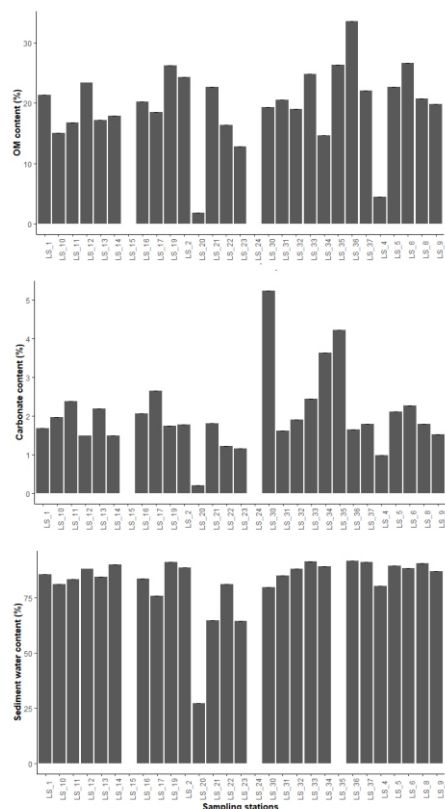


Fig 2a: The spatial variations in sediment organic matter, carbonate and water contents characteristics in surficial sediments

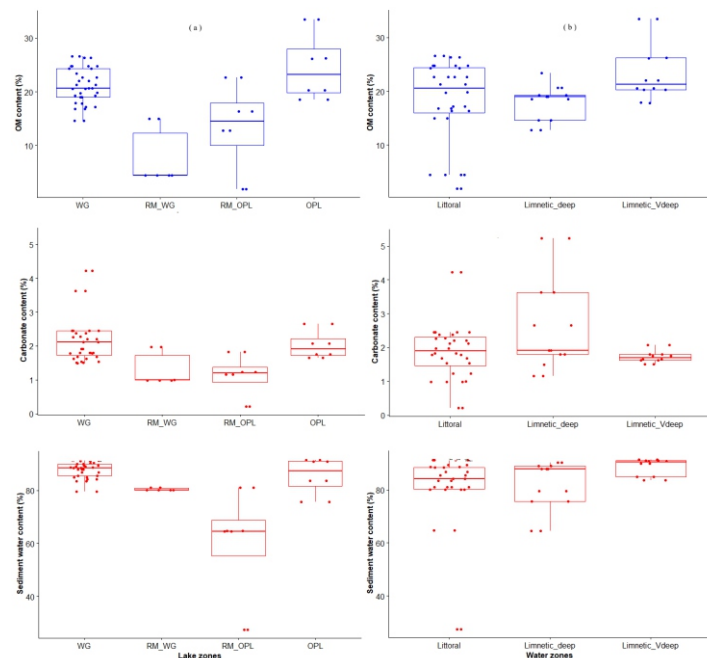


Fig 2b: The variations in sediment organic matter, carbonate and water contents characteristics by lake (a) and water (b) zones

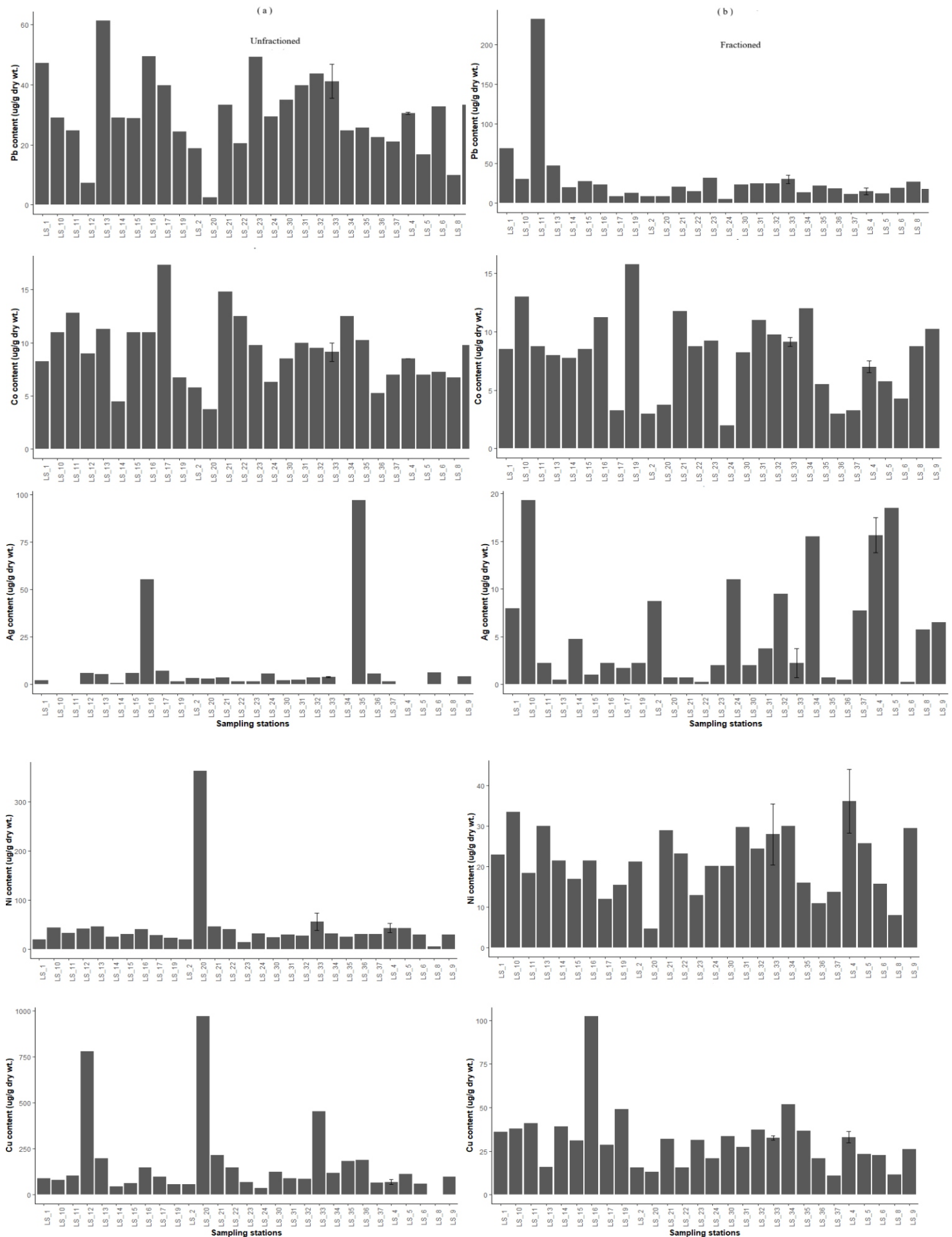


Fig. 3a: The spatial variations in sediment Pb, Co, Ag, Ni and Cu contents in surficial sediments.

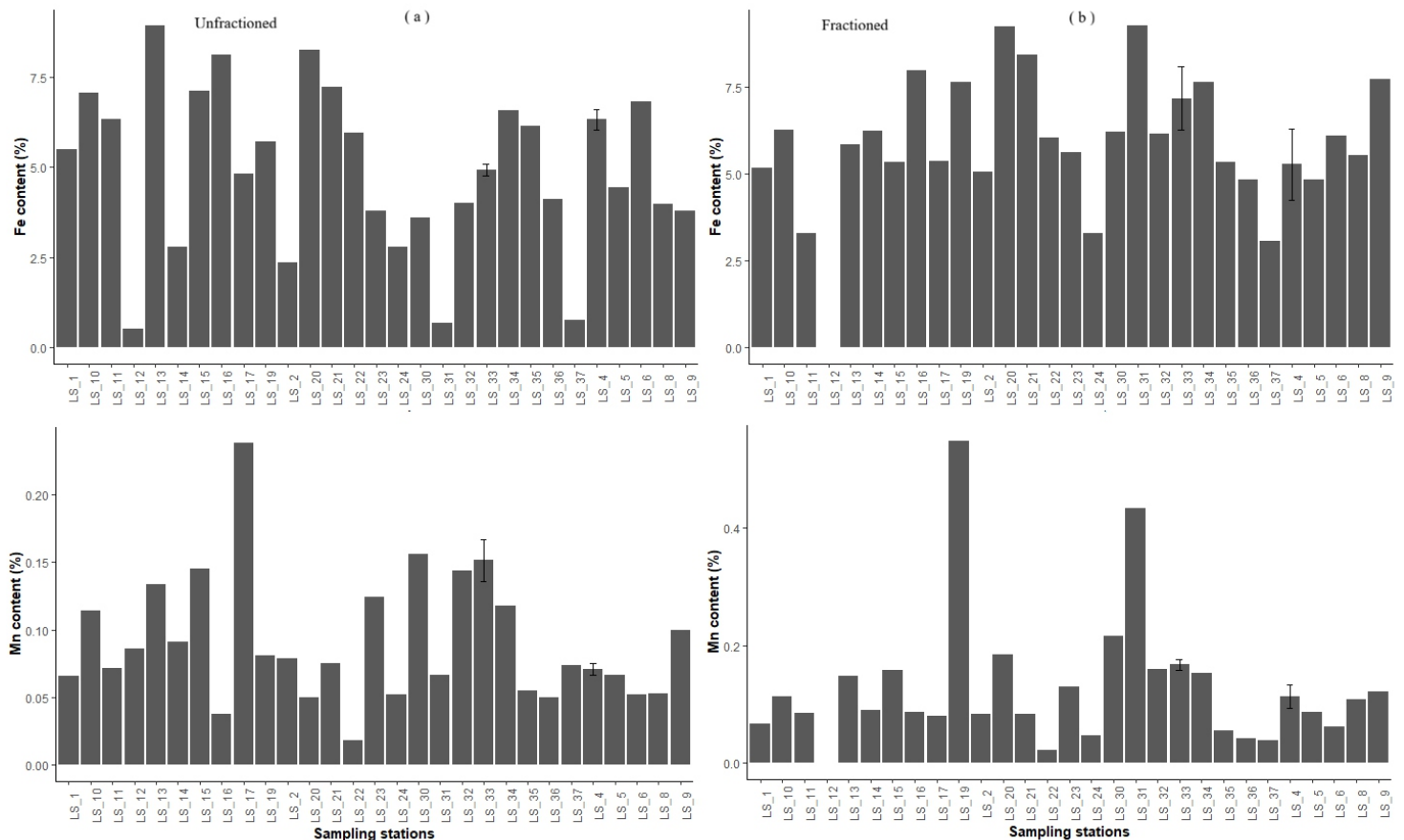


Fig. 3b: The spatial variations in sediment Fe and Mn contents in surficial sediments

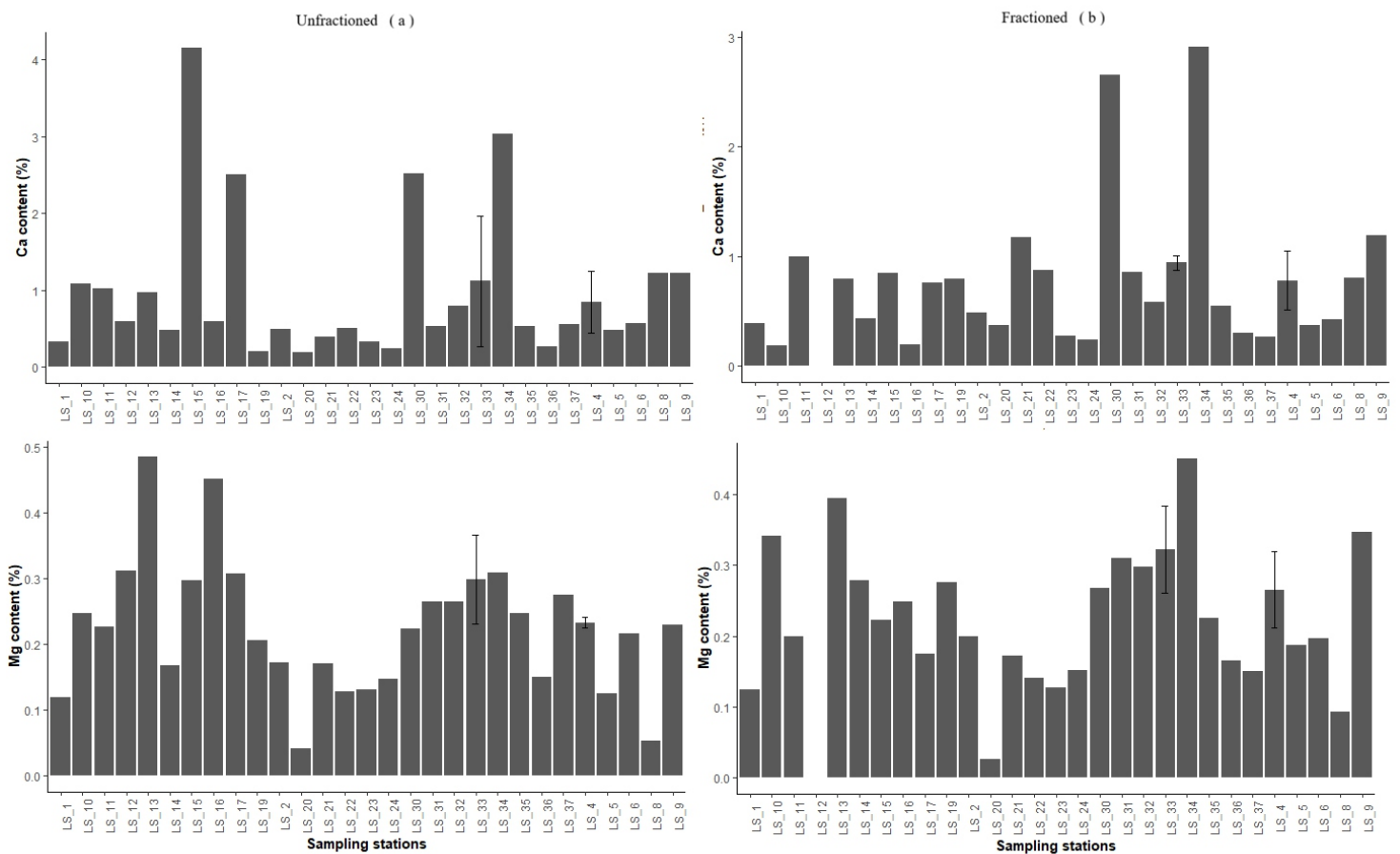


Fig. 3c: The spatial variations in sediment Ca and Mg contents in surficial sediments

Table (3a and b): Spearman's rank correlation coefficients of the relationship between major and minor elements in the un-fractioned (a) and finer sediments (b) (CO_3 = carbonates OM = Organic matter; H_2O = Water content; Dep = Water depth; Bolded and italicized coefficients are significant at 0.05* and 0.01** level of significance)

(a) Un-fractioned sediments

	Fe	Mn	Ca	Mg	Pb	Co	Ag	Ni	Cu	OM	CO_3	H_2O	Dep
Fe	1.000												
Mn	-0.121	1.000											
Ca	0.099	0.496**	1.000										
Mg	0.133	0.509**	0.607**	1.000									
Pb	0.138	0.391*	0.137	0.372*	1.000								
Co	0.414*	0.325	0.541**	0.561**	0.396*	1.000							
Ag	0.312	-0.018	0.391	0.512*	0.109	0.352	1.000						
Ni	0.518**	-0.080	0.050	0.282	-0.042	0.266	0.355	1.000					
Cu	0.296	-0.091	0.022	0.133	-0.037	0.309	0.262	0.495**	1.000				
OM	-0.276	-0.126	-0.226	0.009	-0.094	-0.283	0.380	-0.211	0.084	1.000			
CO_3	0.172	0.360	0.468*	0.422*	0.254	0.384	0.490*	-0.039	0.192	0.345	1.000		
H_2O	-0.378*	-0.002	-0.083	0.077	-0.226	-0.455*	0.029	-0.179	-0.167	0.701**	0.225	1.000	
Dep	-0.468*	0.082	0.020	0.183	-0.021	-0.197	-0.087	-0.449*	-0.252	0.205	0.070	0.387*	1.000

(b) Finer sediments

	Fe	Mn	Ca	Mg	Pb	Co	Ag	Ni	Cu	OM	CO_3	H_2O
Fe	1.000											
Mn	0.616**	1.000										
Ca	0.383*	0.409*	1.000									
Mg	0.469**	0.544**	0.431	1.000								
Pb	0.048	0.257	0.138	0.200	1.000							
Co	0.636**	0.514**	0.377	0.457*	0.483**	1.000						
Ag	-0.108	0.109	-0.130	0.253	-0.147	0.112	1.000					
Ni	0.388*	0.246	0.362	0.698**	0.190	0.441*	0.445*	1.000				
Cu	0.316	0.302	0.176	0.504**	0.338	0.584*	0.213	0.309	1.000			
OM	-0.124	-0.259	-0.085	-0.090	0.018	-0.144	-0.269	-0.241	-0.123	1.000		
CO_3	-0.065	-0.004	0.247	0.292	0.261	0.074	0.136	0.023	0.282	0.345	1.000	
H_2O	-0.160	-0.045	-0.047	0.175	0.020	-0.051	0.119	-0.057	-0.069	0.701**	0.225	1.000
Dep	-0.049	0.087	-0.328	0.015	-0.052	0.041	-0.006	-0.367	0.004	0.205	0.387*	1.000

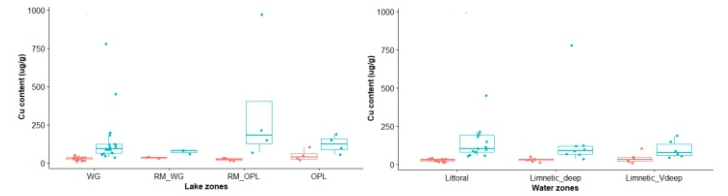
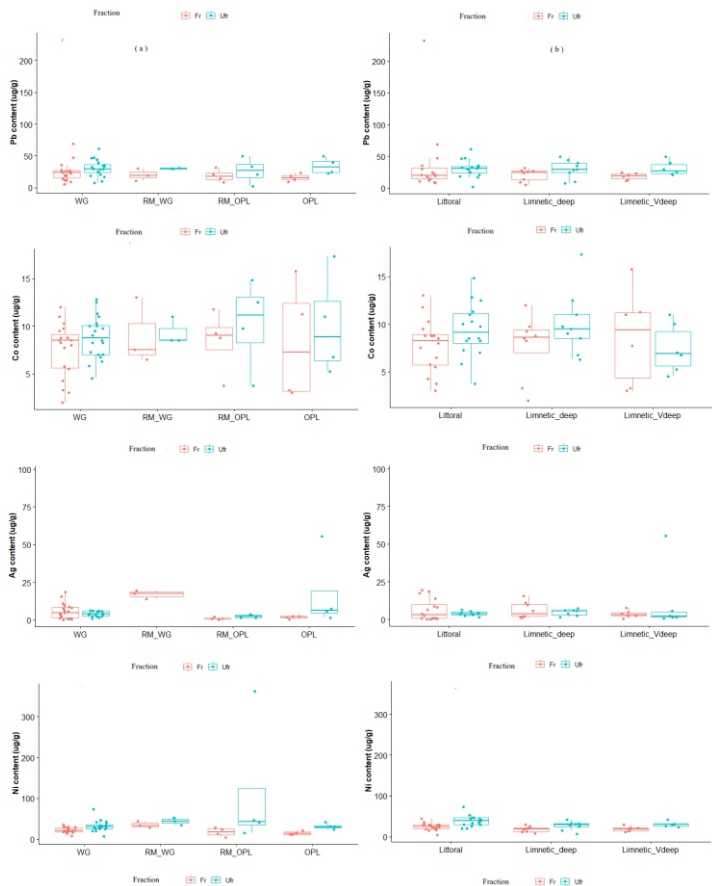
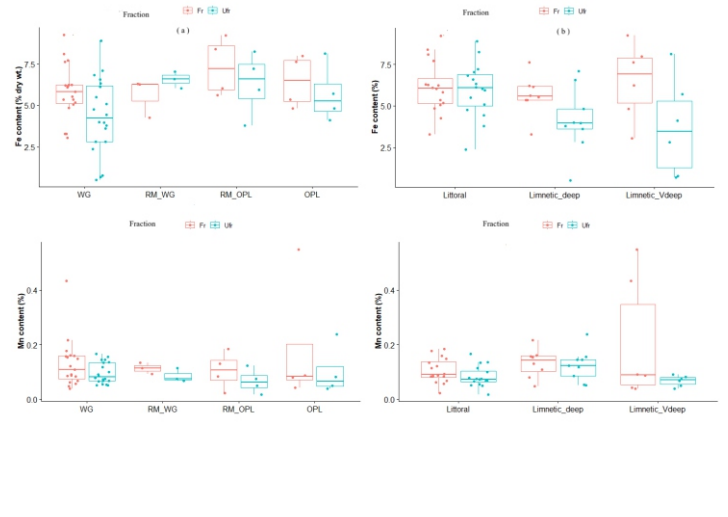


Fig. 4(a): The elemental variations (minimum, Q1, Q2, Q3 and maximum values) grouped by lake (a) and water (b) zones and colored by sediment fractions (Ufr = un-fractioned; Fr = finer sediments)



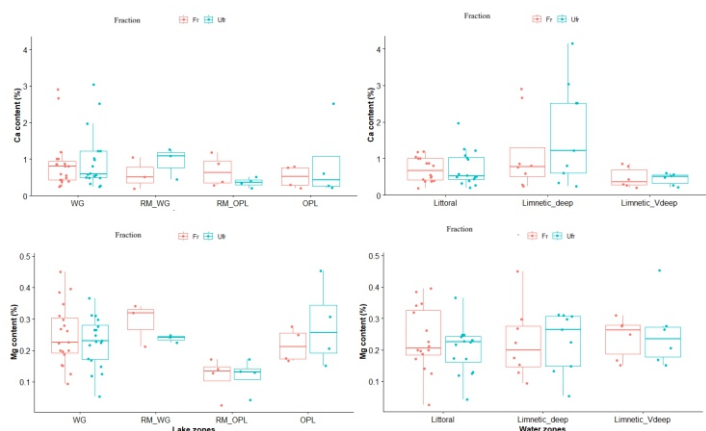


Fig. 4(b): The elemental variations (minimum, Q1, Q2, Q3 and maximum values) grouped by lake (a) and water (b) zones and colored by sediment fractions (Ufr = un-fractionated; Fr = finer sediments)

Single pollution indices of geo-accumulation (I_{geo}), enrichment factor (EF), contamination factor (CF) and ecological risk factor (Er) were calculated for some of the elements. The finer sediment accumulation was assessed using the I_{geo} index (Muller 1969) which is based on 7 categories. Silver exhibited the highest positive values (mean=5.21, range = 1.74 - 8.0), whereas Ni and Co showed negative and lower maximum values. The mean EFs for Cu, Co, Ni, Pb, Mn, Fe and Ag were as follows: -2.46 (Ni), -1.95 (Cu), -1.08 (Co), -0.46 (Pb), -0.31 (Mn), and -0.24 (Fe). Geo-accumulation values above zero were found for Pb (Site LS_10), Mn (Site LS_11, 33, 13, 19, 15), and Fe (Sites LS_11, 33, 31, 16, 19, 20, 21). Sediment enrichment factors were also calculated for the finer sediments. The calculated sediment enrichment factors for Pb, Co, Fe, Mn and Ni were much lower than those for Ag, Cu and Pb. The sediment EFs at each site were highly variable for both sediment fractions and ranged from 0.07 - 16.52 (Pb), 4.1 to above 40 (Ag), 0.1 - 3.5 (Co), 0.04 - 5.5 (Ni), 0.22 - 48 (Cu), 0.2 - 9.1 (Mn), 0.1 - 5.7 (Ca), and 0.1-7 (Mg) (Fig. 5a & b). A Spearman's correlation plot (Fig. 4c) shows a significant positive association between un-fractionated Co, Mn, Pb and Ni.

Silver contents in the finer sediment exhibited the highest contamination factors compared to Fe, Mn, Pb, Cu, Ni and Co. The CFs ranged (mean CF values) from 0.66 - 1.98 (1.28, Fe), 0.27 - 6.45 (1.56, Mn), 0.25 - 11.6 (1.15, Pb), 0.11 - 0.83 (0.41, Co), 0.07 - 0.65 (0.32, Ni), and 0.02 - 2.27 (0.68, Cu). The sediment CF was indicative of moderate contamination for Fe, Mn, Pb, whereas Cu, Ni and Co contents were of low contamination. The potential ecological risk factor was calculated for Cu and Pb contents in the finer sediment fraction according to Hakanson (1980). Lead and copper showed a range and mean of 1.3 - 5.8 (7.3 ± 10.1 , Pb) and 1 - 11.4 (3.4 ± 1.98 , Cu), which implies a low potential ecological risk for these elements respectively.

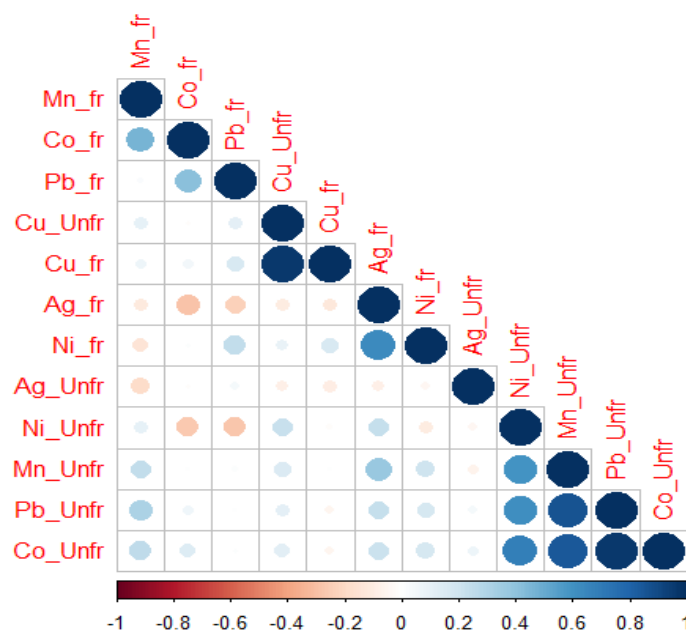


Fig. 4c: A Spearman's correlation plot showing the relationships inter-elemental between the enrichment factors

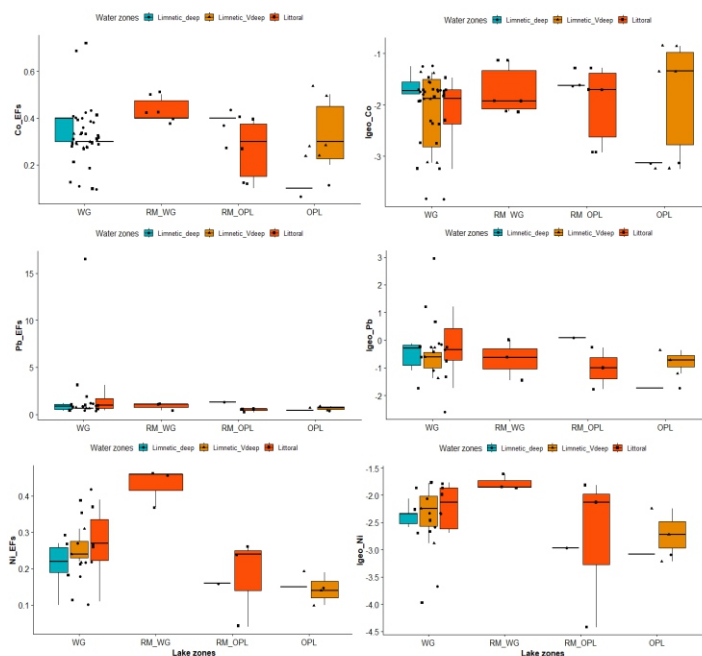


Fig. 5(a): The Co, Pb and Ni enrichment factors and geo-accumulation indices in the finer surficial sediment fraction grouped by lake zones and colored by water zones.

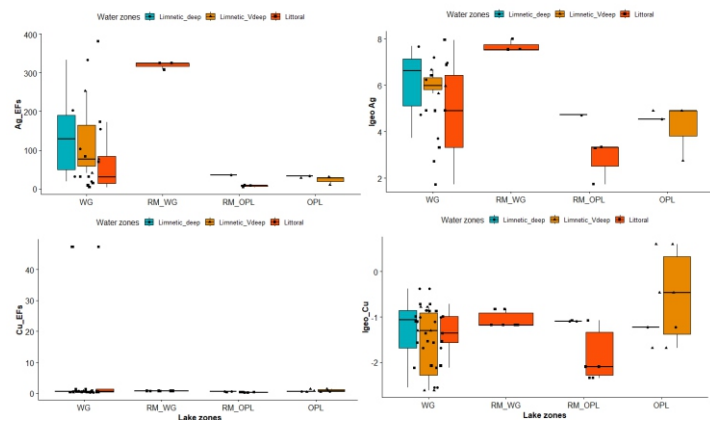


Fig. 5(b): The Ag and Cu enrichment factors and geo-accumulation indices in the finer surficial sediment fraction grouped by lake zones and colored by water zones.

A multivariate PCA analysis (Table 4, Fig. 6) revealed a good representation using four principal components (with greater than 10 % of the explained variance), which cumulatively explained about 64.7 % of the variance. The 2 axes projected explained 25% (PC 1) and 18% (PC 2) of the variance. Calcium (Ca), magnesium (Mg), nickel (Ni), copper (Cu), iron (Fe) and manganese (Mn) elements, together with sediment organic matter (% OM), carbonate (% CO₃) and water (% H₂O) contents were all well represented, when compared to silver (Ag) and lead (Pb). Positive and negative loadings on the first principal (PC1) were associated with Mg, %H₂O, %CO₃, and Cu, Ni respectively. Principal component 2 revealed positive loadings for Ca, Co, Fe and Mn, whereas water depth and %OM showed negative loadings. The remaining axes (PC 3, PC4 and PC5) which were not projected on the 2D, showed significant loadings for water depth, Pb, Ag and Pb. The four sampling sites in the river mouth areas within the open lake (OPL and RM-OPL) were associated with PC1, whereas the sites in clear open lake (OPL), Winam gulf (WG) and RM-WG were more associated with both axes (PC1 and PC2). Limnetic_deep and very deep) water zones were associated with PC2 and littoral zones with PC1.

Table 4: A principal component analysis extraction of the eigen values and the percentage variation for each dimension

Dimensions	Eigen values	Variation (%)	Cumulative variation (%)
1	3.253	25.02	25.02
2	2.337	17.98	43.00
3	1.467	11.28	54.28
4	1.349	10.38	64.66
5	1.239	9.53	74.19
6	0.982	7.55	81.74
7	0.690	5.31	87.05
8	0.568	4.37	91.42
9	0.417	3.21	94.63
10	0.291	2.24	96.87
11	0.180	1.38	98.25
12	0.126	0.97	99.22
13	0.102	0.78	100

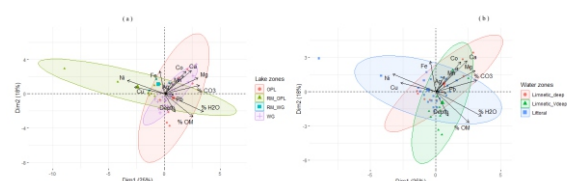


Fig. 6: A principal component analysis (PCA) biplot showing the correlation and ordination of samples by lake (a) and water (b) zones

DISCUSSION

Nyanza gulf forms the north eastern section which deepens towards the central basin of the lake. Both Winam gulf and open lake deposits reflect the high in-lake primary productivity, resulting in organic rich sediments towards the deeper basin. The past Holocene description of deep core sediments of Lake Victoria [46] are indicative of organic rich sediments (bulk TOC ranging from less than 4 to 20 weight %) and of high hydrogen index values. Similar observations from deep sediment cores of Lake Victoria reported presence of flocculent muds with high organic matter and total organic carbon [48]. The gulf surface sediments exhibited a similarly high content of organic matter, low and less variable carbonate contents. The OM levels were only significantly different in areas of the gulf which are considered relatively shallow and hydrologically active with regards to new materials inputs and remobilization (RM vs WG; RMOPL Vs OPL).

Total concentrations have provided initial information on extents of metal contamination of environmental samples and sediments. Nevertheless, more information for assessment of potential environmental effects on sediments is from a metals bioavailability and toxicity is assessed from geochemical fractionation studies [70-71]. Exchangeable and non-residual metal species are more mobile and bioavailable to aquatic organisms. Therefore, the distribution of the sediment texture, organic carbon and chemical composition offers significant geochemical controls on metal accumulation in bottom sediments. This study used the un-fractionated and fractionated sediments (less than 63 µm grain size) metal differences to understand the spatial distribution over different water and lake zones. Significant differences were evident for Fe Pb, Ni and Cu, but the approach of the study did not separate the fine fraction into clay and silt components. Significant variations in accumulated contents across different sediment grain sizes occur, and in most cases, much higher contents emerge in the fine sediment grain size.

Major, minor and trace elements occur in the earth crust in concentrations of about or greater than 10%, 0.01% - 10% and up-to 0.01 % respectively. The calcite, dolomite and apatite (Ca-phosphate mineral) are the main Ca containing rock forming minerals, and the iron ore deposits and laterite formations are oxides of Fe. Weathering of rock minerals and erosion of highly weathered rocks and clay soils (mostly of clay minerals rich in aluminosilicates) results in accumulation and redistribution of major elements encountered in bottom sediments. Occurrences of carbonatites ore deposits are major sources of rare earth elements and host different mineral deposits [72]. The weathering of carbonatite bodies around the region contributes to total P increases in lake sediments [73-74]. Guya [75] also reported high apatite phosphorus (136.7 – 1511.3 mg/Kg) and sediment total phosphorus (512.5 – 2,254.4 mg/Kg) within the littoral sites compared to the limnetic sites in Winam gulf. Therefore, intrusive igneous carbonatite formations in the southern parts of the gulf are potential sources of carbonate and iron minerals, depending on the predominant carbonate mineral.

At each representative locality, the surface sediments reflect the recent deposits and activities from previous processes within the basin together with materials transported through river channels, urban surfaces and terrestrial runoffs. Soil erosion is a major contributor of new deposits around the river mouth and littoral zones.

This is reflected in the high turbidity of rivers and areas around the river mouths and shoreline or littoral zones. However, compositional characteristics of the surface sediments is also highly heterogeneous, and mostly modified by slow settling organic matter. Sediments normally accumulate relatively higher amounts of metallic elements than the ambient aqueous medium of lakes. Increasing presence of suspended sediments and particulate matter in water acts as a physical pollutant to fish by clogging the gill structure. However, adsorbed PTEs can have adverse effects to aquatic organisms, when toxic elements are in high concentrations. The accumulated mean concentrations of the major elements (Fe, Mg and Mn), in fractionated sediments were much higher, except for Cu which showed higher levels in un-fractionated portion of the sediments. It is well known that the finer sediments are collectors of metals, and hence the surface area property of sediment grains results in higher adsorption and accumulation. However, only Fe contents appeared significantly elevated in the finer fraction, whereas Pb, Ni and Cu were significantly more in the un-fractionated sediments. This is explained also by the low and insignificant negative correlation of elements with OM and sediment carbonates, yet most of the elements remained well correlated with each other, except for silver (which was mostly negatively correlated with the rest of the elements, except Ni). This implies most of the elements are from lithological sources, except Ag, Cu and Pb which are from anthropogenic sources. The first principal of the PCA biplot revealed that positive and negative loadings were associated with Mg, %H₂O, %CO₃, and Cu, Ni respectively. The second principal component revealed positive loadings for Ca, Co, Fe and Mn, whereas water depth and %OM showed negative loadings. The four sampling sites in the river mouth areas within the open lake (OPL and RM-OPL) were associated with PC1, whereas the sites in clear open lake (OPL), Winam gulf (WG) and RM-WG were more associated with both axes (PC1 and PC2). Limnetic_deep and very deep water zones were associated with PC2 and littoral zones with PC1.

The key point sources are located at Kisumu and Homa bay where waste treatment and storm water discharges occur. Most inflowing rivers feed the southern littoral zones of the Winam bay when compared to the northern side. Therefore, the Winam gulf (WG) is an active zone where materials transported from the basin by surface runoffs and rivers are remobilized before settling out in the deeper basin towards the open lake (OPL) areas. The westward gradients in suspended solids, nutrient elements, and ionic contents in the lake water is well described from several surveys (59-61,53). Using surficial lake sediments, Gikuma-Njuru et al [76] reported a longitudinal gradient of the sediment total phosphorus and its fractions within the gulf as a result of the high rates of terrigenous input and resuspension and transport of the light, P rich inorganic and organic matter towards the main lake. The results found sediment Ca was to be strongly associated with sediment total P and apatite-P [76]. We observed no significant spatial variations in most of the elemental levels across the zones (littoral to limnetic), except for Fe and Ni (between Littoral vs Limnetic deep) and Ca (between Limnetic deep vs very deep) only. However, differences across lake zones could possibly be due to the differences in terrestrial sources at the localities and in-lake productivity levels and settling and depositional differences for Mg and Fe. For Ag variations in between lake zones could possibly be due to other unidentified sources mostly associated with both diffuse and point waste water discharges.

It is expected that increasing dilution occurs towards the open lake with increasing amounts of terrigenous materials closer to the shoreline and littoral sites. Trace elements are often remobilized from such diffuse sources and accumulate in soils and translocated into the surface water and lake sediments. Sediment grain size, redox conditions, pH, and high contents of iron oxyhydroxides exert a control on the concentration of elements in sediments. The finer sediment grain size provides a higher surface area and concentrated trace elements. The high lake water pH means that most of the Fe is complexed and exists as inorganic precipitates. This also explains the low and insignificant association of the elements with the sediment organic carbon proxy.

In comparison, these concentrations are lower but close to the recent detailed geochemical data of Winam gulf surficial sediments. The mean concentrations of the PTEs (Pb, Ni-un-fractionated, Cu -un-fractionated and Ag) were found to be slightly higher than the levels from the detailed geochemical data, which did not include the open lake sediments. Variations as a result of locality differences and sediment extraction techniques were observed when these Pb, Cu and Ni contents are compared with data from Uganda. Lower pseudo-total (sum from the BCR sequential extraction of 60 cm long sediment cores) mean and range (n=18) concentrations of Pb, Cu and Ni 17 (10-25) mg Pb/Kg; 39 (21-121) mgCu/Kg and 29 (19-56) mg Ni/Kg [77] were reported, where main lake offshore and inner bay sites were sampled. Decadal changes within the Nyanza gulf surface and core sediments (Table 5) shows a wide range in concentrations with a decreasing trend over the years. However, there are concerns on the wide variations in Cu and Ag concentrations over the years since the studies incorporated different areas and number of sites during the surveys.

There are concerns on the finer grain size sediments contents of Pb, Cu and Ni (Table 5) which show high exceedances of the sediment quality threshold levels for the freshwater sediments. High sediment enrichments were observed for un-fractionated elements (Ag, Mn, Pb, Ni, Cu and Co) when compared to the finer sediment fractions. However, the sediment geo-accumulation indices calculated for Pb, Cu, Co, Ni, Fe and Mn were mostly below zero, an indication of uncontaminated sediments, except for the high index for Ag. Bioturbation and sediment resuspension can facilitate metal transfer from bottom sediments to overlying water. The extents of metal releases or remobilization will be controlled by sediment properties and overlying and pore water environmental conditions of the oxic-anoxic layer at the bottom. The effects of species-specific bioturbation on sediment metal remobilization were quantified via release flux analysis experiments [78]. Both benthic species (representing distinct bioturbation functional groups *Limnodrilus hoffmeisteri*-upward conveyor, *Cipangopaludina cathayensis*-sediment regenerator, *Corbicula fluminea*-biodiffuser) exhibited significant metal accumulations, and sediment bioaccumulation factors revealed species-specific uptake of heavy metals by benthos. Several species of freshwater bivalves accumulate a wide range of essential elements (Na, K, Mg, Ca), non-essential (Co, Ba, Sr) and toxic elements (As, Pb, Hg) at concentrations above those measured in natural waters [79-80]. Mean concentrations of Cu (16.7±0.55 and 90.0±2.97 mg/Kg dwt.) and Zn (685±8.30 and 158±1.91mg/Kg dwt.) in benthic invertebrate species (Mussel, *Anodonta woodiana* and Pond snail, *Bellamya aeruginosa*) from Dianshan Lake (China) revealed substantial accumulation respectively [81].

Bivalves also grow a shell of calcium carbonate (precipitation of CaCO_3 , of either aragonite or calcite structure) in sequential layers through biomineralization in the extrapallial fluid. Even though bivalves tissue metal burdens and elemental concentrations in aqueous phase were not incorporated in this study, the threshold, midrange and extreme effects values of the sediment quality guidelines (Table 6) were used to evaluate the potential risks to the benthic dwelling organism. The samples with elemental concentration values below the threshold values are considered safe with no adverse toxic effects. Therefore, sediments should incorporate monitoring of the effects of these elements on the benthic fauna of the lake to understand any potential ecological effects.

Table 5: Decadal spatial changes in the concentrations of the potentially toxic elements in the bottom lake sediments of the Nyanza gulf at different survey periods ($\mu\text{g/g}$ dry weight; mean $\pm$ standard deviation; OPL = open lake)

Year of survey	Lake area		Pb	Co	Cu	Ni	Ag
2022 ^a	Winam gulf (173 sites)		23.5 $\pm$ 5.0	19.8 $\pm$ 7.2	45.1 $\pm$ 15.9	36.5 $\pm$ 11.0	-
2018 to 2019 ^b	Winam gulf (14 sites) & OPL (4 sites)	North (6 sites)	24 $\pm$ 11	-	50 $\pm$ 27	35 $\pm$ 10	0.25 $\pm$ 0.18
		South (5 sites)	34 $\pm$ 20	-	39 $\pm$ 22	40 $\pm$ 19	0.24 $\pm$ 0.06
		Strait (3 sites)	20 $\pm$ 5.0	-	74 $\pm$ 24	39 $\pm$ 12	0.23 $\pm$ 0.05
		OPL (4 sites)	17 $\pm$ 2.9	-	66 $\pm$ 22	34 $\pm$ 20	0.2 $\pm$ 0.0
2016 to 2017 ^c	Winam gulf (4 sites) OPL (1 site)	Winam gulf	6.82 $\pm$ 3.4 to 195 $\pm$ 273	-	23.7 $\pm$ 11 to 60.1 $\pm$ 63	15.9 $\pm$ 7.1 to 29.0 $\pm$ 11	0.031 $\pm$ 0.01 to 1.36 $\pm$ 1.7
		OPL	13.3 $\pm$ 7.5	-	46.9 $\pm$ 35	17.3 $\pm$ 6.9	0.023 $\pm$ 0.01
2012 ^d	Winam gulf (23 sites) & OPL (8 sites)		30.45 $\pm$ 13.01**	9.19 $\pm$ 2.97**	168.09 $\pm$ 213.08**	44.06 $\pm$ 60.28**	9.78 $\pm$ 21.42**
			28.96 $\pm$ 40.40*	7.91 $\pm$ 3.35*	31.49 $\pm$ 16.98*	21.89 $\pm$ 8.67*	5.74 $\pm$ 5.97*

(NB: a = [82]; b = [28] values are mean 95% confidence interval; c = [83]; d = This study; ** = Un-fractioned; * = Fractioned)

Table 6: The evaluation of the sediment quality in terms of the percentage of sediment samples exceeding the specific element sediment quality guidelines (SQG) values (mg/Kg dry weight) specified for threshold, mid range and extreme effects on the benthic dwelling organisms.

SQG Thresholds	Pb			Cu			Ni		
	SQG value	Un-fractioned (%)	Fractioned (%)	SQG value	Un-fractioned (%)	Fractioned (%)	SQG value	Un-fractioned (%)	Fractioned (%)
Threshold effect									
TEL	35	25.8	13.3	35.7	90.3	38.3	18	93.5	66.7
ERL	35	25.8	13.3	70	64.5	3.3	30	58.1	10
LEL	31	41.9	16.7	16	93.5	80	16	93.5	70
CB(TEC)	35.8	25.8	10	31.6	96.7	43.3	22.7	87.1	43.3
Mid range effect									
PEL	91.3	0	3.2	197	16.1	0	36	32.3	3.3
ERM	110	0	3.2	390	9.7	0	50	9.7	0
EC(PEL)	112	0	3.2	108	38.7	0	42.8	19.4	3.3
Extreme effect									
TET	170	0	3.2	86	54.8	3.3	61	6.5	0
SEL	250	0	0	110	38.7	0	75	3.2	0
CB(PEC)	128	0	3.2	149	22.5	0	48.6	9.7	0

NB: TEC/L and PEC/L = Threshold and Probable effect (level) concentration [84-85]; CB = Consensus based ERL and ERM = Effect range low and median [86]; LEL and SEL = Lowest and severe effect level (ANZECC 1997); TET = Toxic effect threshold [87].

Geochemical partitioning of elements in sediments has been used to understand the potential mobility of sorbed metals on sediments, potential bioavailability and toxicity, using selective extractant and at specific conditions of temperature and pH. However, the fate of engineered nanoparticles in aquatic ecosystems and sediments is still unclear. This study documented much higher Ag levels than more recently reported by Marriot et al [28] and Outa et al [83] a sign of decreasing silver contents in sediments. However, sediment core results of Outa et al [83] reported increasing levels of Cu, Zn, Cd, Pb and Ag on the surface than downcore area, especially at the Kisumu bay site. The maximum un-fractionated sediment Pb contents (61.3 $\mu\text{g/g}$) are lower than those recently reported within the southern and northern sites (105 and 86 mg/Kg) of the Winam gulf by Marriot et al [28]. The mean Pb levels from this study are similar to the maximum levels around the strait area (36 mg/Kg) and open lake sites (23 mg/Kg).

Presence of accumulated Ag may originate from its historical use and current industrial applications. Silver nanoparticles have beneficial uses in consumer products due to its microbial properties, and its silver colloidal solutions containing silver have previously been used in photography and microbiology. Free dissolved Ag can bind to natural OM and form less soluble chloride complexes, and result in accumulation in sediments. Marriot et al [28] found lower Ag in the northern section of the Winam gulf (maximum of 1.1 mg/Kg) than the strait, southern Winam section and the open lake sites. Using a different background value for Ag, the silver geo-accumulation indices [28] were positive and much lower (0.93 to 1.28) in sampling sites around river mouth, beaches and selected areas with cage operations, than this study. Outa et al [83] also reported lower mean contents (0.031 $\pm$ 0.01 to 1.36 $\pm$ 1.7 mg/Kg) in short sediment cores (25cm) during an 8 month repeated sampling at selected sites of Kisumu bay, Asembo bay, Kibos river mouth,

Gingra rock area (n= 38, Winam gulf), and one site off Rusinga Island (0.023 ± 0.01 mg/Kg, n=11) in the open lake. Therefore, surface bottom sediments can serve as a sink for silver containing wastes besides other mineralogic sources. Extra follow-up studies on Ag distribution may be necessary due to the anomalous values found.

There were no significant differences in accumulated metals found in the un-fractioned portion of surface sediments when compared to the finer fraction, except for Fe, Pb, Ni and Cu elements. Mg, Ag, Ni and Fe elements concentrations exhibited significant differences. between the water and lake zones. The calculated sediment enrichment factors revealed enrichments in Ag and Cu, but the geo-accumulation index shows uncontaminated sediments, except for the high silver index. This implies lithological sources for the major elements and anthropogenic sources for silver, copper and lead, although the bioavailability of the minor potentially toxic elements is controlled by their association with the surface sediments.

CONCLUSIONS

Decadal changes within the Nyanza gulf surface shows a wide range in Pb, Cu, Co, Ni and Ag concentrations, with a decreasing trend over the years. This study documented much higher Ag levels than more recently reported data, a sign of decreasing silver contents in sediments. However, there are concerns on the wide variations in Cu and Ag concentrations over the years since the studies incorporated different areas and number of sites during the surveys. There were no significant differences in accumulated metals found in the un-fractioned portion of surface sediments when compared to the finer fraction, except for Fe, Pb, Ni and Cu elements. Mg, Ag, Ni and Fe elements concentrations exhibited significant differences. between the water and lake zones. The calculated sediment enrichment factors revealed enrichments in Ag and Cu, but the geo-accumulation index shows uncontaminated sediments, except for the high silver index. This implies lithological sources for the major elements and anthropogenic sources for silver, copper and lead. The concentrations of lead, copper and nickel levels are a concern due to their exceedance of the threshold effect levels, and probable adverse effects to bottom dwelling organisms. Bivalve species (benthic filter feeders) have a high bioaccumulation potential, but they have not been adequately utilized as biomonitors of trace metal toxicants. Therefore, the study recommends the monitoring of the PTEs and effects of these elements on the benthic fauna of the lake to understand any potential ecological effects. An extended grid sampling of the remaining portion of the lake will greatly support detailed spatial mapping of the lake bottom sediments, for better management of potential impacts from the expanding cage aquaculture.

ACKNOWLEDGEMENTS

We acknowledge the Kenya Marine and Fisheries Research Institute for the support during field sampling activity.

FUNDING

The work received no funding apart from logistical support.

CONFLICT OF INTEREST

The author declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data supporting the findings of this study are available upon reasonable request.

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