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Levels and Spatial Distribution of Heavy Metals in Lake Chilwa Catchment, Southern Malawi

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ABSTRACT

The aim of this study was to assess the levels and distribution of heavy metals in Lake Chilwa and its catchment, and to understand the associated level of pollution. Water and sediment samples were collected from the lake and main inflowing rivers. A total of 23 surface water samples were sampled and analysed for pH, EC, Cu, Cr, Zn, Cd, Pb, As and Hg. Conductivity and pH were measured on-site with a Hanna portable multi meter, while metals were analysed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The pH was found within the alkaline range (7.87-10.13), while conductivity ranged from 97-390µS/cm. The following metals were detected in the water samples; Zn (6.24–1168.70 µg/L), Cu (BDL–47.83 µg/L), Pb (BDL–49.94 µg/L), Cr (0.22–33.05 µg/L), Ni (0.40–8.20 µg/L) and Cd (BDL–0.53 µg/L). Hg and As were not detected in all sampling locations. Strong positive correlations were observed between Cd and Pb (r = 0.70), Cu and Zn (r = 0.70), while Cd and Ni (r = 0.50), Pb and Ni (r = 0.41) showed mild correlations, suggesting similar sources of input. Sediments were sampled from 2 locations in the lake and the following metals were detected; Zn (66.13 mg/Kg), Pb (7.74 mg/Kg), Ni (35.39 mg/Kg), Cu (20.02 mg/Kg), Cr (54.81 mg/Kg) and As (1.0 mg/Kg). Mercury and arsenic were not detected from both sampling locations. The heavy metal pollution index ranged from 2.24 to 114.45. All points except Kachulu harbour had values far below the critical pollution index value of 100. The values observed were well below the tolerable limits recommended by the World Health Organisation (WHO) standard for potable water, except for Pb at Kachulu Bay (P19) which was above the limit. Concentrations of the metals in the rivers were low upstream and increased downstream. Highest values for most of the elements were observed from the lake. Though levels are low now, the persistent and cumulative properties of these elements would render them unsafe in the near future if proper controls are not enforced.

Keywords: Heavy metals, Lake Chilwa, Water pollution, Water quality

INTRODUCTION

Water resources are vital in providing ecosystem services. They supply products, possess attributes that are beneficial to almost all forms of life and hence are a very important part of our natural heritage (Manahan, 2000). Pollution of these resources occurs because human activities have altered the structure of rural landscapes and increased the quantity of substances that are loaded into the rivers and lake systems. Studies elsewhere have shown elevated levels of chemical pollutants such as heavy metals in streams and rivers passing through urban areas and farmlands (Mortvedt, 1996; Woitke *et al.*, 2003). For instance, agrochemicals and waste from industries, institutions and residential areas may contain heavy metals. The transport of such pollutants to water bodies through erosion and direct disposal contributes to their presence in rivers and lakes. Due to their persistence in nature, heavy metals have the potential to bio accumulate and cause toxic effects in organisms high in the food chain (Paul, 2017). Some heavy metals such as copper (Cu), manganese (Mn), nickel (Ni) and zinc (Zn) are essential to plants and animal life as micronutrients, while many other metals such as cadmium (Cd), chromium (Cr) and lead (Pb) have no known physiological activity (Mandal, 2008). Chromium, for example is known to cause allergenicity, perforation in nasal septum and some cases of lung cancer (Saha & Nandi, 2011). In plants Cr affects the growth of roots, stems and leaves, which may affect total dry matter production and yield (Shanker *et al.*, 2005).

Though important for microorganisms, plants and animals, Zn at higher doses than optimal, produces toxic effects on various tissues and organs including the hematopoietic system, cytogenetic, biochemistry and endocrine system functions (Osman *et al.,* 2000). In soils and water, the metals exist either as separate entities or in combination with other components such as ions, metal compounds, metal complex or organic materials and metals attached to minerals (Marques *et al.*, 2009). In the water column they can be removed and transferred to the sediment phase through a number of complex processes that include precipitation of insoluble oxy-hydroxide compounds or sorption onto particulate material (Woods, 2009). Adsorption by or co-precipitation with hydrous iron and manganese oxides forming in the water column can scavenge metals from solution, while clay and organic particles already present in the water column can also bind and remove metals (Peltier *et al.*, 2003). Sediments are therefore considered the ultimate sink of the metals. Contaminated sediments can threaten creatures in the benthic environment, exposing worms, crustaceans and insects to hazardous concentrations of toxic metals (Egbenni *et al.,* 2011). These toxic elements may be lethal to some forms of benthic organisms, reducing food available to larger animals such as fish. As the benthic organisms feed on the contaminated sediments, the metals bioaccumulate in their tissues. When larger animals feed on these contaminated organisms, the toxic elements are taken into their bodies, moving up the food chain in a process known as biomagnification. As a result, fish and shellfish, waterfowl, and freshwater and marine mammals may accumulate hazardous concentrations of these toxic elements. Metals in the sediments do not always remain at the bottom of the water body. Anything that stirs up the water can resuspend the sediments. Resuspension may mean that all of the animals in the water, and not just the bottom dwelling organisms, will be directly exposed to the toxic elements.

MATERIALS AND METHODS

Study area

A location map of the study area is shown in Fig. 1. Lake Chilwa and its catchment is an important ecosystem in Malawi providing ecosystem services that include, water purification and storage, fertile lands for agriculture, settlements and maintenance of biodiversity (EAD, 2010). The lake is an endorheic Lake with 8 main inflowing rivers, viz; Likangala, Sombani, Naisi, Domasi, Thondwe, Mulunguzi, Namadzi and Phalombe. The catchment is also of international importance as a RAMSAR site, seasonally hosting migratory birds that fly from the northern hemisphere escaping the cold winters. (Mvula & Haller, 2009). Despite the benefits the catchment provides, it is threatened by pollution from several activities and processes likely to results in the accumulation of heavy metals and these include; indiscriminate disposal of waste, sewage effluent and agrochemicals washed to water resources (Kafumbata *et al*., 2014; Vunain *et al*., 2019). Therefore, this research sought to study the levels and distribution of heavy metals in this catchment. The results generated will be useful to formulate holistic management strategies for the sustainable utilization and conservation of this catchment and provide a baseline for future research.

Sample collection

A total of 23 sites were purposively selected and sampled along the main rivers in the study area (Fig 1). Sampling points were selected to represent the upper, lower and wetland catchment areas. Sites P01, P05, P07 and P08 located in the upper catchment area constitute mountains, upland fields, and human settlements which are sparsely distributed. Sites P01 and P07 are located in the heart of the mountains within the forest reserve. These two points were selected to represent areas with less anthropogenic disturbance. Sites P02, P03, P06, P09, P10, P22, P23, P14, P13, P18, P15, P16, P04 and P11 lie in the lower catchment areas where human settlements, farming and other anthropogenic activities are prevalent. Sites P03, P12 and P17 are located within the wetland where rice, maize and vegetable cultivation are dominant. Three sites, P19, P20 and P21 were selected from the lake to understand levels of heavy metals in the lake. Both water and surface sediments were sampled from these lake locations. Site P19 represent the harbour, where a majority of activities along the lake take place including, trading, boat loading and offloading among others.

Physico-Chemical Analysis of Water and Sediment samples

pH and conductivity were measured on-site with a digital multi-meter with electronic glass electrode (Model no. 59, MARTINI instruments, USA). Water samples were filtered through cellulose acetate membrane filters (0.45 µm, Whatman) into an acid washed polyethylene 200mL volume bottle. Preservation of the metals was done by acidifying the water samples to $pH < 2$, using nitric acid and stored at 4 ^oC until analysis. Sediments were sampled using a sediment corer which was drilled through the sediment bed to a depth of 0–20 cm. The sediments were dried in an oven at 105 ^oC and ground with a pestle and mortar. Digestion was performed by the *aqua regia* microwave digestion method. 1 g of the ground sample was placed in a Teflon beaker, then 10 ml HNO_3 and 3 mL HCl were added then digested in a microwave digestion unit. Digested samples were then filtered and diluted to 100 mL with distilled water and kept in plastic bottles until metal analysis. Extraction was done in triplicate and blanks were included for quality control.

Metals (Cd, Pb, Zn, Cr, As, Hg, Ni and Cu) were analysed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Perkin–Elmer Optima 5300 DV). The obtained data were statistically analysed using analysis of variance (ANOVA) at 5% significance level. PAST 3.25 data analysis package produced the correlation data among all the parameters.

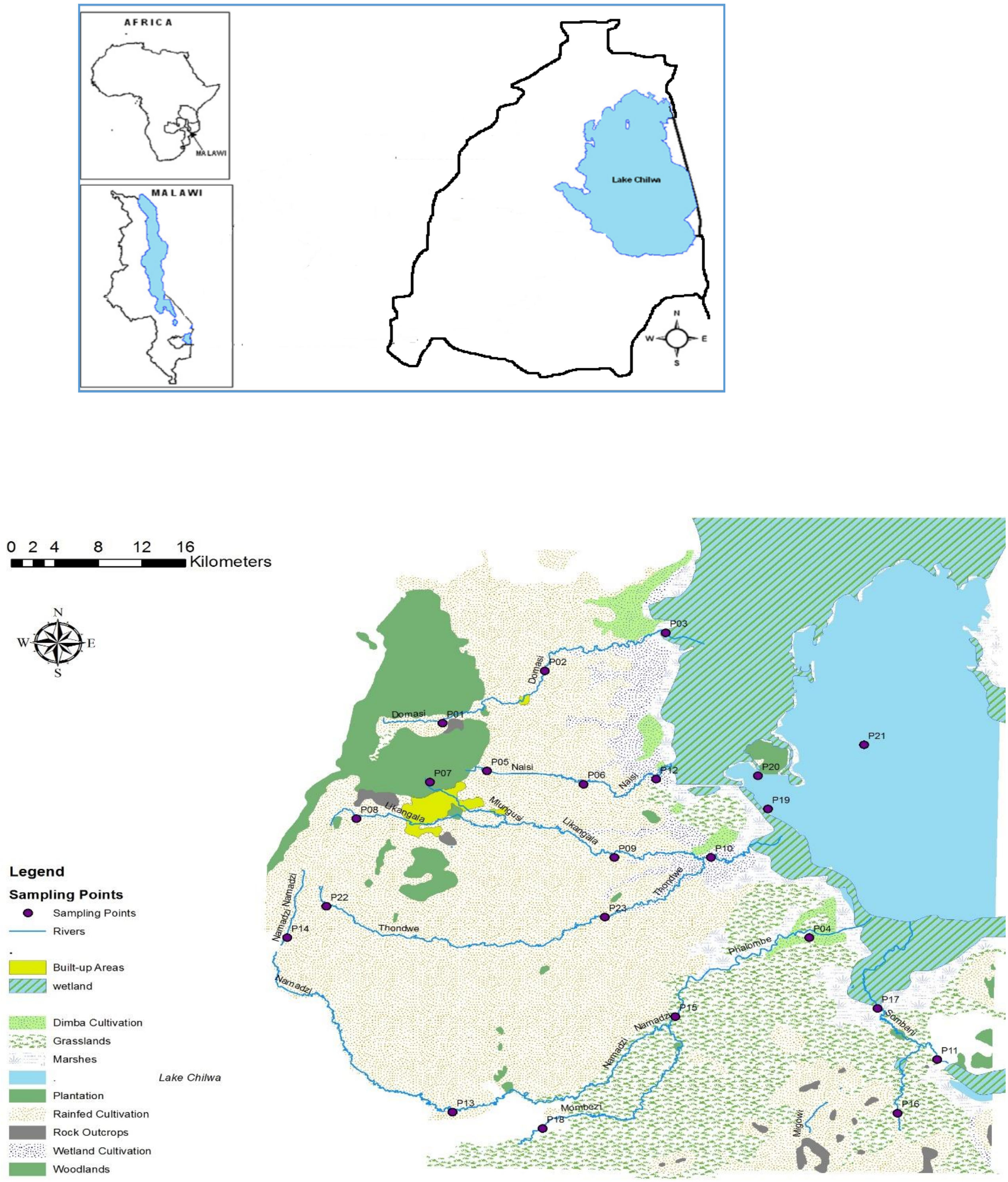

Fig 1: Lake Chilwa catchment and sampling locations

Determination of the Heavy Metal Pollution Index (HPI)

The quality of the water with respect to the heavy metals was determined using the heavy metal pollution index (HPI). HPI is a method of rating the heavy metal pollution proposed by Prasad and Bose (2001) that shows the composite influence of individual heavy metals on the overall quality of water.

The HPI method was developed by assigning a rating or weightage (Wi) for each chosen parameter. The rating is an arbitrary value between zero and one and its selection reflects the relative importance of individual quality considerations. It can be defined as inversely proportional to the standard permissible value (Si) for each parameter (Prasanna *et al.,* 2012). In this study, the concentration limits (i.e., the standard permissible value (Si) and highest desirable value (Ii) for each parameter) were taken from the WHO standard. The uppermost permissive value for drinking water (Si) refers to the maximum allowable concentration in drinking water in absence of any alternate water source. The desirable maximum value (Ii) indicates the standard limits for the same parameters in drinking water. The HPI, is determined using the equation (1):

$$HPI = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi} \quad (1)$$

Where Qi and Wi are the sub-index and unit weight of the inth parameter, respectively, and n is the number of parameters considered. The sub index (Qi) is calculated from equation (2):

$$Qi = \sum_{1=1}^{n} \frac{\{Mi(-)Ii\}}{Si - li} x100 \quad (2)$$

Where MI, Ii, and Si, are monitored metals, ideal and standard values of the inth parameter, respectively. The sign indicates numerical difference of the two values, ignoring the algebraic sign (Prasanna *et al.,* 2012). The water is considered not polluted if the HPI value is less than 100 (Reza & Singh, 2010).

RESULTS AND DISCUSSION

Water within the catchment exhibited an alkaline pH ranging from 7.87 to 10.17 with an overall mean of 8.57. The highest pH was observed from the lake, especially the Lake harbour. The alkaline pH in the lake is attributed to high levels of carbonates (Chidya *et al.*, 2011). Furthermore, there was a significant difference in pH from the sampling locations. Values observed from the rivers were well below the critical limits recommended WHO (Table 1). pH has an implication on metal speciation and affects the partitioning between the sediment and water column phases (Malinowska, 2017). In alkaline conditions, the metals are enriched in the sediments by adsorption, complexation, flocculation, and sedimentation (Manahan, 2000). If the pH changes and becomes acidic, the dynamic equilibrium will be broken, and the heavy metals in the sediments will be transferred and transformed, and released to the overlaying water, which will lead to secondary pollution.

Table 1: A Summary of the pH, Electric Conductivity (EC) and Metals Concentrations (µg/l) in the Water Pitched against the WHO (2008) Standard Limit Values.

	Average	Min	Max	WHO
pH	8.57	7.87	10.17	6.5–8.5
EC (µS/cm)	193	97	390	N/A
Cd	0.10	BDL	0.526	3
Cr	3.36	0.22	33.05	50
Cu	8.07	BDL	47.83	2000
Ni	3.03	0.40	8.29	70
Pb	3.30	BDL	49.94	10
Zn	119.03	6.24	1168.70	10,000
As	BDL	BDL	BDL	10
Hg	BDL	BDL	BDL	1

Conductivity values on the other hand ranged from 97 to 390 µS/cm. The rivers showed the lowest values compared to the lake (348-390 µS/cm). The endorheic property of the lake allows accumulation of the metal ions from the inflowing rivers thereby increasing the ionic strength of the water. The river points located in the upstream locations, especially in the mountain locations (P01 and P07), showed the lowest values of conductivity (Table 4). The upstream locations are characterized by sparsely distributed rural settlements and less farming activities while downstream locations comprise intensive farmlands, a sewage treatment facility, settlements, markets and areas where waste is disposed of indiscriminately. This trend was also observed by earlier studies along Likangala river where levels were attributed to human activities such as farming and waste management (Chidya *et al*., 2011; Pullanikkatil *et al.*, 2015). Six metal elements in order of decreasing concentration, were detected in the waters; Zn > Cu > Pb > Cr > Ni > Cd (Table 1). Mercury and arsenic were not detected in all sampling locations. Similar to conductivity, the lake had an overall high concentration of the metal elements compared to the rivers (Table 3). This could also be attributed to the endorheic nature of the lake which allows concentration of the metal elements. Significant spatial variation was observed on all metals studied. The levels observed for all metals except Pb, were below the WHO critical limits. However, at Kachulu bay, Pb was above the guideline limit (49.94 µg/L).

Correlation analysis was computed to examine the relationship among the metals and the results are presented in Table 2. There was significant positive correlation between Cd and Pb (0.70), Cd and Ni (0.50) and Pb and Ni (0.41). This can be used to understand inter elemental association and hence determine the sources of the metal elements.

Table 2: Correlation analysis of the metals

	Cd	**Cr**	**Cu**	**Ni**	**Pb**
Cd	1				
Cr	-0.09				
Cu	-0.12	-0.1			
Ni	0.48	0.12	0.4		
Pb	0.69	-0.07	0.26	0.42	
Zn	-0.22	-0.16	0.7	-0.2	0.12

The elemental association may signify that each paired element has an identical source (Sekabira *et al.,* 2010). Nickel and cadmium are used in rechargeable batteries; lead and cadmium are used in vehicle acid batteries; copper and nickel are used in stainless steel products that include iron sheets and cooking utensils. Improper waste management within the catchment could facilitate the transport of these elements from their associated wastes.

Table 3: Mean concentration values for pH, Electric Conductivity (µS/cm) and metals (µg/l) measured in the water

Sample ID	Sample Description	GPS coordinates (UTM)	pH	EC	Cd	Cr	Cu	Ni	Pb	Zn	As	Hg
P01	Domasi Upstream	749864, 8306620	8.03	110	BDL	0.685	0.056	0.478	1.013	25.804	BDL	BDL
P02	Domasi Middle stream	759263, 8312213	8.22	170	0.061	0.388	BDL	1.164	0.178	31.110	BDL	BDL
P03	Domasi Downstream	770392, 8316327	8.44	190	BDL	0.267	10.794	0.826	2.637	829.815	BDL	BDL
P04	Namadzi Downstream	783600, 8283567	8.15	160	0.018	0.820	4.211	1.388	0.766	30.706	BDL	BDL
P05	Naisi Upstream	753934, 8301485	8.08	102	BDL	0.592	0.032	0.398	1.109	28.873	BDL	BDL
P06	Naisi Midstream	762822, 8300057	8.83	110	0.135	2.727	1.088	2.774	BDL	24.012	BDL	BDL
P07	Mulunguzi upstream	748688, 8300270	8.07	97	BDL	0.224	0.047	0.421	0.970	25.493	BDL	BDL
P08	Likangala Upstream	741894, 8296343	8.43	140	0.119	0.331	3.154	2.927	0.373	6.244	BDL	BDL
P09	Likangala Midstream	765671, 8292193	8.67	130	0.125	2.467	1.348	2.805	0.021	11.429	BDL	BDL
P10	Likangala Downstream	774559, 8292195	8.81	220	0.131	3.158	2.071	4.200	BDL	15.926	BDL	BDL
P11	Mpoto outlet	795401, 8270457	8.78	190	0.090	0.687	15.932	3.576	1.144	143.645	BDL	BDL
P12	Naisi Downstream	769498, 8300603	8.31	180	BDL	0.388	47.831	2.091	8.394	1168.706	BDL	BDL
P13	Namadzi Mid-stream	750763, 8264806	8.75	250	0.037	2.771	2.412	3.378	BDL	9.773	BDL	BDL
P14	Namadzi Upstream	735524, 8283569	8.13	120	0.068	3.232	2.012	3.954	0.250	18.936	BDL	BDL
P15	Phalombe Midstream	771292, 8275075	8.73	239	0.148	4.207	2.113	3.928	BDL	14.993	BDL	BDL
P16	Sombani midstream	791760, 8264718	8.8	170	BDL	33.050	1.002	2.436	0.097	17.543	BDL	BDL
P17	Sombani Downstream	789925, 8275949	8.22	160	BDL	0.736	4.719	1.544	0.711	91.863	BDL	BDL
P18	Mombezi Upstream	759056, 8263043	7.87	260	0.345	3.597	0.265	3.516	0.394	21.802	BDL	BDL
P19	Lake Chilwa Harbour	779816, 8297378	10.17	390	0.526	2.131	12.745	7.134	49.938	76.914	BDL	BDL
P20	Lake Chilwa	778879, 8300974	9.48	350	0.071	5.827	24.545	8.290	1.741	25.708	BDL	BDL
P21	Lake Chilwa	788677, 8304276	9.41	348	BDL	3.721	26.201	6.983	2.736	31.219	BDL	BDL
P22	Thondwe Upstream	739157, 8286938	8.37	170	0.153	2.634	0.504	2.794	BDL	15.595	BDL	BDL
P23	Thondwe Midstream	764798, 8285771	8.26	180	0.173	2.650	0.440	2.674	0.008	15.356	BDL	BDL

**BDL = below detection limit*

Copper and zinc are often added to livestock feed due to their anti-microbial and growth promoting properties, with significant concentrations ending up in manure. The high association between copper and zinc could be attributed to manure usage within the agricultural fields (Mantovi *et al*., 2003). Poor farming practices that include farming along the river banks could facilitate the transport of these metals to the water resources.

Table 4 shows the levels of the metals in the sediments from the two sampling stations (P20 and P21). Levels of metals from the two points did not show any significant difference (p>0.05). Zinc seems to be the dominating element in this catchment, with the highest proportion in both water and sediments. The concentration of the elements observed followed a similar trend as that observed in the river Ganga in Asia where zinc was detected with the highest concentration and cadmium with the lowest concentration, attributed to industrial and agricultural waste (Paul, 2017). Metals such as arsenic which were absent in the water column were detected in the sediments, while cadmium which was detected in the water, was absent in the sediments.

Table 4: Concentrations of Metals in sediments in mg/Kg

	P20	**P21**
As	1.27±0.38	0.73±1.02
Cd	0.00±0.0	0.0±0.0
Cr	53.72±3.67	55.89±9.31
Cu	24.04±1.35	24.17±0.44
Hg	0.00±0.0	0.00±0.0
Ni	35.03±2.70	35.74±6.83
Pb	7.36±0.52	8.13±0.74
Zn	64.15±5.28	68.11±10.35

The absence of cadmium in sediments could be attributed to the low levels detected and its high water solubility, similar to that observed in the Ebute Ogbo river in Nigeria (Adeniyi *et al.*, 2011). Arsenic which was absent in the water column was detected in the sediments. It implies that the conditions in Lake Chilwa promote complexion of arsenic to sediments. Additionally, the endorheic nature of the lake and low turbulence limits resuspension of the metals to the water column.

CONCLUSION

The levels of heavy metals observed in this study do not pose serious harm to the environment, except for lead at Kachulu bay. However due to their persistent and cumulative property the low levels now would pose a great threat in the near future if proper measures to control their levels are not put in place. The high pH observed from the surface waters favours fractionation of the heavy metals to the sediment phase and this could be attributed to the low levels in the water column.

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