Research Article

Occurrence and ecological risk assessment of heavy metals in agricultural soils of Lake Chilwa catchment in Malawi, Southern Africa

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Abstract
Understanding the levels and associated ecological risk caused by heavy metals is important for the sustainable management and utilization of Lake Chilwa catchment, an important ecosystem in Malawi providing fertile lands for agriculture and a designated wetland ratified by the Ramsar convention in 1997. Concentrations of chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), arsenic (As), mercury (Hg) and cadmium (Cd) were analyzed from 22 soil sampling locations. Extraction and quantification were achieved by microwave digestion and Inductively Coupled Plasma Optical Emission Spectrometer, respectively. Mean values were detected in the following order; Zn > Cr > Ni > Cu > Pb > As. Strong correlations were observed between As and Pb (r = 0.85), Cr and Ni (r = 0.82), Cu and Ni (r = 0.81), Cr and Cu (r = 0.8), and Pb and Zn (r = 0.73) suggesting similar sources of input. Principal component analysis revealed that Cu, Pb, Zn and As originate from anthropogenic activities, while Cr and Ni were geogenic. The ecological risk caused by these metals, calculated by the Ecological Risk Index (RI) method, showed a low to moderate ecological risk. The wetland areas had higher overall concentrations and RI values compared to the rest of the catchment. It is therefore important to enforce measures to manage and control these levels to avoid their damaging effects.

Keywords Heavy metals · Soil pollution · Ecological risk · Soil · Lake Chilwa catchment · Malawi

1 Introduction

Soil pollution by heavy metals is an important environmental concern causing grave and irreparable damage to ecosystems. Rapid population growth, high urbanization rates, poor planning of cities, poor agricultural practices and lack of enforcement of environmental laws and regulations, among others, have been consistently associated with the accumulation of heavy metals in soils [1, 2]. Studies have been carried out to understand the levels of the metals in agricultural soils within the African continent. Elevated levels of Cd, Cr, Cu, Ni, Pb and Zn in agricultural soils have been reported in Egypt [3], Nigeria [4], Kenya [5, 6], South Africa [7] and Zambia [8]. The concentrations were mainly attributed to mining activities, waste disposal, application of organic manure, inorganic fertilizers, herbicides and pesticides. Heavy metals accumulate in surface soils and migrate to crops by plant root respiration. Humans and animals are exposed directly or indirectly through consumption of contaminated food plants [9, 10]. Some metals such as Zn and Ni are essential for cell metabolic processes and are required within specified

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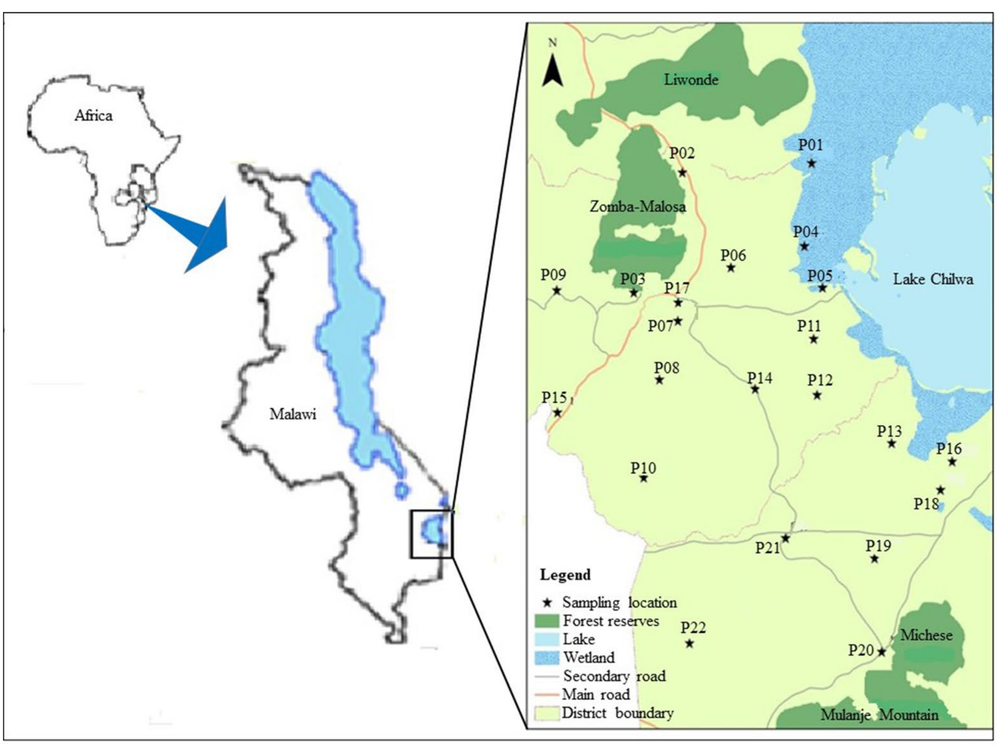
amounts. Other heavy metals such as Pb, Cd, Hg and As have no beneficial effects in plants and animals and are considered toxic [11].

To the best of our knowledge, limited studies have been carried out on heavy metals in Malawi, mostly on the levels of heavy metals in surface water from different parts of the country. For example, Cu and Pb were detected in Mudi River, a river that passes through the industrial areas of Blantyre, the commercial city of Malawi [12]. Another study reported on the presence of Cr, Pb and Zn in the waters of Likangala River, which passes through Zomba city, the old capital of Malawi [13]. A recent study about Lake Chilwa, reported on the presence of Cu and Zn in the sediments of the lake and attributed this to fertilizer usage and indiscriminate disposal of metal products within the catchment [14]. Our previous study also reported the presence of Pb, Zn, Cu, Cd, Cr, and Ni in Lake Chilwa and influent rivers [15]. The only study that has reported on heavy metals in soils was carried out in riverbank soils along Mudi River, which passes through the industrial area of Blantyre city. The results showed the following average concentrations; Cr (8.19 mg/kg), Cu (10.13 mg/kg), Ni (4.32 mg/kg), Pb (3.49 mg/kg), Zn (17.45 mg/kg) and Cd (0.18 mg/kg) and this was attributed to industrial effluents [16].

Lake Chilwa catchment is an important ecosystem in Malawi providing ecosystem services beneficial to all forms of life. However, intensification of agricultural enterprises coupled with improper farming practices, insufficient waste management facilities and lack of enforcement of environmental laws and regulations have the potential to elevate the concentrations of heavy metals to toxic levels in agricultural soils of the catchment. This research was therefore carried out to determine the concentrations of heavy metals in the agricultural soils, identify the possible sources and to evaluate their ecological risk. The study is significant as it informs communities and policy about the ecological risks associated with levels of the studied elements in the area. It further adds valuable data to our basic knowledge that are needed to understand the area and stimulate future research on soils and related segments of the catchment. Also, the results will be useful to formulate holistic management strategies for the sustainable utilization and conservation of this important catchment and provide a baseline for future research.

1.1 Setting

Lake Chilwa catchment is located in the southern part of Malawi bordering Mozambique to its eastern side (Fig. 1). The catchment covers three districts, namely Machinga, Zomba and Phalombe. Main crops grown in the catchment are maize and rice. Other crops include cassava, groundnuts, millet, sweet potatoes, vegetables, sugar cane and bananas. The common practice of farming, especially for



Sampling points and their coordinates

ID	Easting	Northing
P01	773054	8316136
P02	754122	8314874
P03	747010	8298799
P04	772002	8304987
P05	774690	8299439
P06	761249	8302157
P07	753503	8294947
P08	750778	8287117
P09	735742	8299096
P10	748443	8273958
P11	773388	8292543
P12	773895	8285071
P13	784795	8278605
P14	764787	8285853
P15	735821	8282690
P16	793693	8276134
P17	753507	8297430
P18	791991	8272335
P19	782309	8263128
P20	783360	8250630
P21	769272	8265861
P22	755191	8251776

Fig. 1 Map of the Chilwa catchment located in Malawi within the Southern African region showing the sampling points

maize, is the ridge and furrow system using a hand hoe. The wetland area close to the lake constitutes fertile soils and is dominated by rice and maize fields.

Most of the Chilwa basin is underlain by ancient metamorphic and igneous rocks of the Malawi Basement complex represented by a group of high-grade metamorphic rocks, mostly chamokitic granulites of quartz and feldspar. South of the Lake, there is a complex of alkaline silicate rocks, carbonates, rocks rich in sodium and calcium carbonates. Major soil groups include calcimorphic alluvial soils, hydromorphic soils, latosols and lithosols (young 1960).

2 Materials and methods

2.1 Sampling and heavy metal extraction

A total of 22 soil samples were purposively sampled in the dry season (Fig. 1). The samples represent the different parts of the catchment including, the upland fields (P03 and P02), wetland fields (P01, P04, P05, P18 and P13), semi intensive fields within estates and farmer schemes (P08, P10, P11 and P15), fields within the city and towns (P14, P21, P17 and P20) and fields located in the rural areas (P06, P07, P09, P12, P16, P19 and P22). The soil samples were collected from a depth of 0–10 cm using a stainless-steel shovel and stored in polyester bags. The samples were dried and ground to powder using a pestle and mortar before sieving them through a 60-mesh. Heavy metal extraction was achieved by the *aqua regia* microwave digestion method where 1 g of the sample was placed in a Teflon digestion tube together with 10 mL HNO_3 and 3 mL HCl. The solution was filtered through a 0.45 µm membrane and the concentrations of the heavy metals were determined on Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) at the University of Tubingen in Germany. Blanks and standards were also performed for quality control.

2.2 Potential ecological risk index of heavy metals

The ecological risk index (RI) was used to quantify the potential environmental and human health hazard from heavy metal contamination in the soils. The RI represents the toxicity of heavy metals and the response of the environment [17].

The potential ecological risk is defined as follows:

$$C_f^i = C^i_{\text{surface}} / C^i_{\text{reference}} \; C_f^i = C^i_{\text{surface}} / C^i_{\text{reference}} \tag{1}$$

$$E_f^i = C_f^i \times T_f^i E_f^i = C_f^i \times T_f^i \tag{2}$$

$$RI = \sum\nolimits_f^i E_f^i RI = \sum\nolimits_f^i E_f^i \tag{3}$$

where C_f^i is the contamination factor that describes the contamination of a given toxic metal in the soil. $C^i_{surface}$ is the measured concentration of heavy metals in soils. $C^i_{reference}$ is the background reference values of the metals in soils (Table 1). T_f^i is the toxic response factor for a given substance provided by Hakanson, also given in Table 1. E_f^i is the potential risk index for a single heavy metal. RI is the sum of individual potential risk factors E_f^i for heavy metals in soils. The following terminologies are used to describe the risk factor: RI ≤ 50 suggest low ecological risk; 50 ≤ RI < 100, moderate ecological risk; 100 < RI ≤ 150, considerable ecological risk; and RI ≥ 150, high ecological risk [17].

2.3 Statistical analysis

Data entry and statistical analysis were performed using MS Excel (Microsoft 2010) and PAST 3 statistical software. Pearson correlation, Principal Component Analysis (PCA) and Eigenvector analysis were used to determine the relationship among the heavy metals and apportion the sources.

3 Results and discussion

Tables 2 and 3 present a summary of results of all metals measured in the soils from all sampling sites. The average concentrations decreased in the following order Zn > Cr > Ni > Cu > Pb > As. Hg and Cd were not detected from all sampling locations. Due to the absence of standards for heavy metals in soils in Malawi, the United States Environmental Protection Agency standards [18] were used in this study. The average concentrations were all

Table 1 Background reference levels (mg/kg) and toxic response factors by [17]

	Hg	Cd	As	Cu	Pb	Cr	Zn
Background reference levels	0.02	0.1	12.7	22.5	21.00	67.3	65.4
Toxic response factor	40	30	10	5	5	2	1

Table 2 Concentration (mg/kg) of heavy metals and ecological Risk Index (RI) values

ID	Cr	Cu	Ni	Pb	Zn	As	Hg	Cd	RI
P01	26.16	20.97	16.29	16.81	99.21	5.11	BDL	BDL	7.89
P02	27.90	5.70	14.53	4.11	15.21	BDL	BDL	BDL	1.58
P03	3.12	4.08	3.83	7.00	22.92	BDL	BDL	BDL	1.11
P04	52.04	28.92	34.14	7.52	61.47	1.36	BDL	BDL	5.84
P05	63.13	33.57	21.98	5.42	79.14	BDL	BDL	BDL	5.60
P06	21.01	11.11	15.79	5.00	22.19	0.68	BDL	BDL	2.51
P07	31.99	8.02	17.11	4.99	13.56	0.43	BDL	BDL	2.34
P08	7.11	11.98	18.20	5.66	17.01	0.27	BDL	BDL	2.04
P09	31.14	12.43	16.66	4.60	22.70	0.55	BDL	BDL	2.76
P10	8.08	13.13	15.22	5.87	16.01	0.21	BDL	BDL	2.14
P11	20.62	6.36	9.14	4.25	23.48	0.72	BDL	BDL	2.01
P12	7.11	12.01	14.11	5.76	18.00	0.55	BDL	BDL	2.24
P13	31.15	33.79	43.18	8.14	60.81	2.07	BDL	BDL	6.38
P14	65.87	11.26	17.66	3.37	27.51	BDL	BDL	BDL	2.99
P15	41.20	22.57	16.53	9.29	37.12	0.92	BDL	BDL	4.66
P16	29.77	10.19	14.33	4.92	26.39	0.66	BDL	BDL	2.64
P17	2.83	4.12	2.52	8.96	92.85	4.20	BDL	BDL	4.44
P18	29.09	12.15	14.68	8.87	45.13	2.25	BDL	BDL	4.25
P19	26.78	12.02	14.28	7.43	45.43	1.91	BDL	BDL	3.86
P20	3.00	5.78	4.07	6.89	21.64	0.67	BDL	BDL	1.71
P21	38.84	8.99	20.05	4.56	23.74	0.51	BDL	BDL	2.57
P22	21.07	6.77	14.81	4.55	16.09	0.83	BDL	BDL	2.11

BDL, Below detection limit

Table 3 Summary statistics of heavy metal concentrations in mg/kg in comparison with the maximum allowed levels for [18]

	Cr	Cu	Ni	Pb	Zn	As	Hg	Cd
Min	2.83	4.08	2.52	3.37	13.56	BDL	BDL	BDL
Max	65.87	33.79	43.18	16.81	99.21	5.11	BDL	BDL
Mean	26.77	13.45	16.32	6.54	36.71	1.09	NA	NA
SD	18.06	8.91	8.90	2.86	25.96	1.33	NA	NA
CV	67.45	66.21	54.50	43.77	70.71	122.52	NA	NA
USEPA (2010)	250.00	1500.00	420.00	300.00	2800.00	41.00	17.00	39

SD, Standard deviation, *CV,* coefficient of variation, *BDL,* below detection limit, *NA,* not applicable

below the threshold limits of USEPA. However, heavy metals are persistent and bioaccumulate and magnify high in the food chain causing health implications to higher trophic level organisms. Therefore, it is of great importance to monitor their levels to avoid detrimental environmental and health effects.

Significant spatial variation was observed in this study. The wetland points, P01, P04, P05 and P13 had the highest levels of Pb, Zn, As, Cr, Cu and Ni as shown in Table 2. The wetland area is dominated by intensive rice and maize fields and therefore application of fertilizers, pesticides and manure in these fields could be attributed to these levels [19, 20]. Agricultural enterprises, especially within the lower catchment, have increased rapidly, replacing much of the natural vegetation [21]. Figure 2 shows land use change within the catchment, highlighting increased agricultural activities (shown in pink color). It should be noted that there are no industrial activities on a scale that can have significant impacts on the levels of elements in the area apart from agriculture and fishing related activities.

Fields located within the city and trading centers (P14 and P17) showed high levels of Cr, Pb, Zn and As. Vehicular emissions, poor waste management and agrochemicals could be associated with the levels. Fields located in the rural areas and upland sparsely populated mountain areas, dominated by maize subsistence fields (P06, P07, P09, P12, P16, P19 and P22), had the lowest concentrations.

A comparison of heavy metal studies in agricultural soils elsewhere are summarized in Table 4. The results show varied findings across the continent. Levels above our findings were observed from areas with either mining or industrial activities.

The Pearson correlation matrix shows significant positive correlations between Cr and Cu, Cr and Ni, Cu and Ni, Cu and Zn, Pb and As and Zn and As (Table 5). Strong correlations can indicate that each paired element has an identical source [30].

To further pin out the elemental associations and tease out the probable sources, Principal Component Analysis (PCA) was computed and the results are presented in Table 6 and illustrated in Fig. 3. Two principal components (PC) were extracted, and the cumulative variance contribution rate was 84.17%. PC 1 accounts for 49.27% of the total variance, while PC 2 accounts for 34% of the total variance. Cu, Pb, Zn, As have high loadings on PC 1 suggesting an identical source. These elements are commonly associated with agrochemicals, mainly from pesticides, manure and inorganic fertilizers. Zn and Pb have been reported as impurities in inorganic fertilizers

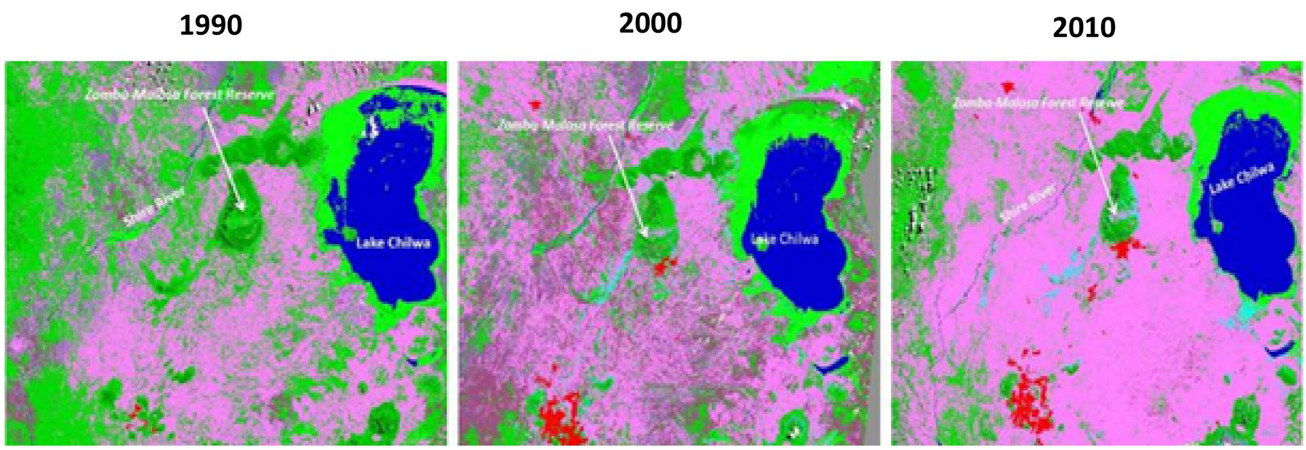


Fig. 2 Intensification of agricultural activities in Lake Chilwa catchment from 1990 to 2010

Table 4 Heavy metals in agricultural soils (mg/kg) from other studies

City/Country	Cr	Cu	Pb	Zn	Ni	Cd	Hg	As	Reference
Zomba, Malawi	26.77	13.45	6.54	36.71	16.32	–	–	1.09	This study
Egypt	8.42	3.82	0.24	21.87	10.28	0.09	–	–	[8]
Lusaka, Zambia	39.00	343.00	48.00	147.00	20.00	0.11	0.02	4.00	[11]
Nigeria	0.26	20.52	15.00	27.70	0.05	0.02	0.02	–	[1]
Kunshan, China	87.73	34.27	30.48	105.93	31.08	0.2	0.2	8.15	[22]
Spain	63.48	107.65	213.93	427.8	34.75	1.42	–	–	[23]
America	–	95.00	23.00	–	57.00	0.78	–	–	[24]
Korea	–	2.98	5.25	4.78	–	0.12	0.05	0.78	[25]
Slovakia	–	65.00	139.00	140.00	29.00	–	–	–	[26]
USA	48.5	48.00	55.00	88.5	29.00	13.5	–	–	[27]
India	2.19	1.2	0.95	28.24	4.34	0.82	–	–	[28]
Iran	10.36	9.62	5.17	11.56	11.28	0.34	–	–	[29]

Table 5 Correlation matrix of the heavy metals in agricultural soils of Lake Chilwa catchment ($P < 0.05$)

	Cr	*Cu*	*Ni*	*Pb*	*Zn*	*As*
Cr	1					
Cu	0.80	1				
Ni	0.82	0.81	1			
Pb	0.02	0.34	0.04	1		
Zn	0.35	0.54	0.21	0.73	1	
As	−0.01	0.16	0.00	0.85	0.80	1

Table 6 Matrix of PCA

Parameter	PC 1	PC 2
Cr	0.37	0.75
Cu	0.77	0.54
Ni	0.53	0.72
Pb	0.77	−0.54
Zn	0.90	−0.24
As	0.73	−0.62
Eigenvalue	2.96	2.09
% variance	49.27	34.90

[31], Cu and Zn are highly associated with farmyard manure [32], Lead arsenate (acid—$PbHAsO_4$ or basic—$Pb_4(PbOH)\,(AsO_4)^3)$) and Zn arsenate ($As_2O_8Zn_3$) are used as pesticides, especially in vegetable gardens and rice fields [33, 34]. It follows that application of fertilizers, pesticides and manure in the fields and gardens are a probable source of these elements. As stated earlier, metals and related industrial activities in the area are insignificant compared to agriculture activities. Possible sources of metals are remnants of agricultural tools such as hoes and sporadic remains of old metals from cars and other small materials. As such these may not contribute significant amounts of these elements. Concentrations of Ni did not vary much across the catchment, an indication that the source could be geogenic. Therefore, the second PC with high loadings of Cr and Ni could be attributed to leaching and weathering of the parent rock material, more, especially from the igneous rocks. Contribution from various sources including (for Cr) vehicular sources such as road dust from catalytic converter erosion and asbestos brakes and (both Ni and Cr) waste incineration are perceived minimal in this area due to low activities of such nature.

The potential Ecological Risk Index ranged from low ecological risk (6.09) at P03 to moderate ecological risk (71.17) at P13 (Fig. 4). The wetland locations (P01, P13, P16) with intensive cultivation show a moderate ecological risk compared to the rest of the catchment. This is in tandem with the observed levels and the PCA, suggesting a link between intensified agricultural activities and associated levels. There is therefore a need for monitoring and enforcement of measures to control the levels of heavy metals in this catchment and avoid their detrimental effects.

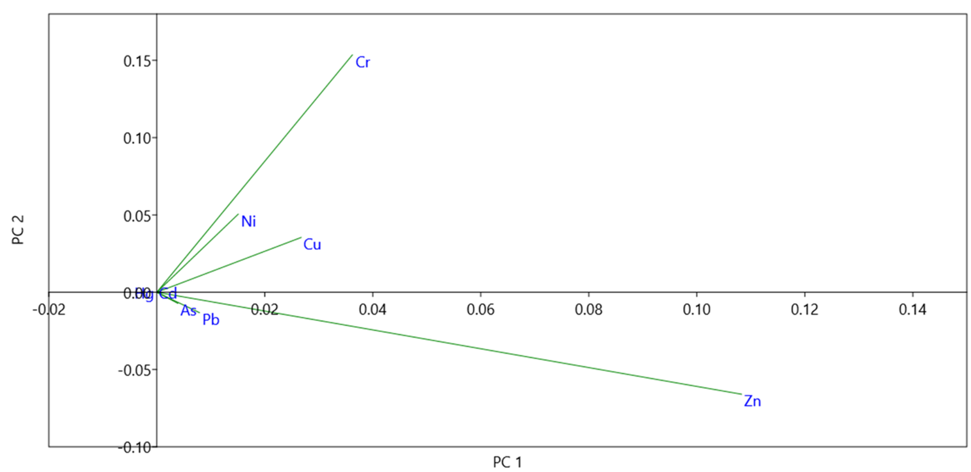


Fig. 3 Two dimensional PCA loading plot for heavy metals in agricultural soils of Lake Chilwa catchment

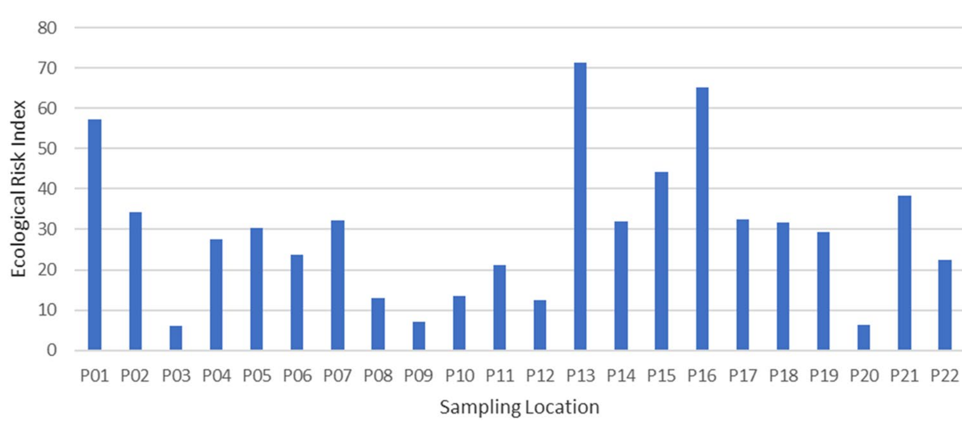


Fig. 4 Potential ecological risk index across the catchment

4 Conclusion

Concentrations of heavy metals in the Lake Chilwa catchment in southern Malawi were measured, and the associated ecological risk was determined. Highest concentrations were observed in the lower catchment, within the wetland areas that are dominated by rice and maize fields, while lowest values were observed from upland soils located in the mountain areas. Concentrations from all sampling locations were well below the threshold limits by USEPA guidelines. Correlation analysis and principal component analysis revealed that anthropogenic activities constitute the main sources of the metals to the soils. The ecological risk index showed levels ranging from low risk to moderate environmental and human health risk. It is important to note that heavy metals are persistent and bioaccumulate and magnify in organisms high in the trophic levels, causing irreparable damage. It is therefore imperative to monitor the levels and apply all necessary precautionary measures to manage the levels within acceptable limits for the sustainable utilization of the catchment.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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