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Contamination Levels and Ecological Risk Assessment of Potentially Toxic Metals in Sediments of Eleyele Lake and Odo-Iyaalaro River, Nigeria

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ABSTRACT: Increasing anthropogenic activities due to rising global human population and urbanization have resulted into contamination of many urban lakes and rivers with potentially toxic metals (PTMs). This study investigates the contamination levels and ecological risk assessment of selected PTMs (Fe, Cu, Zn, Cr, Pb and Cd) in sediments of Eleyele Lake in Ibadan and Odo-Iyaalaro River in Lagos, Nigeria using appropriate standard methods after nitric acid/perchloric acid digestion and analyzing with atomic absorption spectrophotometer (Buck 210 Model). Results show that the highest concentrations, among the analyzed PTMs, were measured for Fe in the ranges of 51-143.7 mg kg^{-1} and 177.4 – 344.2 mg kg^{-1} for Odo-Iyaalaro River and Eleyele Lake sediments, respectively. Only Cd concentrations exceeded the toxicity reference value and sediment quality guidelines, showing that the sediments may be contaminated with Cd. Contamination factor and geo-accumulation index show that all studied PTMs had low contamination in the sediments except Cd which had a moderate pollution in sediments of Odo-Iyaalaro River and considerable pollution in Eleyele Lake sediments. Extreme enrichment was observed for Pb and Cd in Odo-Iyaalaro River sediments and for Cd in Eleyele Lake sediments, indicating anthropogenic influences. Cd also presented moderate and considerable ecological risks in sediments of Odo-Iyaalaro River and Eleyele Lake, respectively while other studied PTMs showed low ecological risks in sediments of both water bodies. Periodic monitoring of Odo-Iyaalaro River and Eleyele Lake sediments for PTMs (particularly Cd) is, therefore, advocated to protect the aquatic and benthic/pelagic organisms.

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Due to rapid growth in human population worldwide coupled with increasing domestic activities, industrial and agricultural production, large amounts of hazardous chemicals including potentially toxic metals (PTMs) are being discharged into the aquatic ecosystems (Islam *et al*., 2015). Sediment is regarded as a sink for PTMs in rivers and lakes (Oyeyiola *et al*., 2014). Contamination of water and sediment material by PTMs is an environmental concern in aquatic ecosystems (Ndhlovu *et al.*, 2023). PTMs are considered as serious contaminants in marine sediments as a result of their stability against degradation, potential toxicity and bioaccumulation (Pejman *et al.*, 2015); and their concentrations in sediments could serve as an indicator of contamination status and conditions of marine ecosystems (Kumar *et al.*, 2020). Although certain heavy metals in low amounts are needed for the survival of aquatic organisms, their elevated concentrations are toxic and could affect the aquatic organisms and humans (Kumar *et al.*, 2020). Anthropogenic factors have been identified as primary drivers for sediment pollution in rivers and lakes (Botle *et al*., 2024; Chang *et al*., 2024). PTMs can be released into the aquatic environment

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through the discharge of effluents from households, industries and wastewater treatment plants (WWTPs), as well as leaching of fertilizers, herbicides and pesticides; vehicular exhaust and mining activities (Kumar *et al.*, 2020). PTMs may pose significant adverse and deleterious health effects to invertebrates, fish, and humans (Ali *et al.*, 2016). For example, PTMs, especially cadmium and lead have carcinogenic effect, result into chromosomal abnormalities, and cause damage and dysfunction of the liver, spleen and blood (Ndhlovu *et al.*, 2023). Therefore, regular environmental monitoring of PTMs in rivers and lakes is imperative as this can present early warning of pollution for adequate proactive and preventive measures to be taken in order to protect the health of aquatic dwelling organisms.

Although PTMs contamination of Eleyele lake in Ibadan, Nigeria, which has threatened the integrity of the ecosystem of the lake, has been linked to anthropogenic activities in the catchment area (Utete and Fregene 2020), most existing published research work on the composition and effects of PTMs in Eleyele Lake focused on its water quality and rarely on sediments (Ayomide *et al.*, 2023). There is therefore insufficient information regarding PTMs contamination in the sediment of Eleyele Lake. Furthermore, the catchment area of Odo-Iyaalaro River in Lagos, Nigeria witnesses the presence of many industries, a wastewater treatment plant (WWTP) as well as many residential and office buildings. Alongside other anthropogenic activities, these industries, WWTP, offices and households discharge their treated and untreated wastewater, which may have a wide composition of PTMs, into this river, making it vulnerable to contamination with PTMs and become harmful to the aquatic organisms and humans. Hence, the objective of this work is to investigate the contamination levels and ecological risk assessment of potentially toxic metals in sediments of Eleyele Lake and Odo-Iyaalaro River, Nigeria.

MATERIALS AND METHODS

Description of sampling locations: Eleyele Lake is situated in the north-west of Ibadan, Oyo State, Nigeria at an altitude of 125 m above sea-level and between 7°25'00' and 7°26'30'N latitudes and 3°51'00' and 3°52'30'E longitudes (Adeogun *et al.*, 2015). During early period of rainy season, occurrence of flooding at Eleyele Lake is usually observed with an accompanied rising in the water level. Predominant human activities in the area include fishing, car washing, block making, clothes washing, automobile repairing, farming, agro-processing and boat trafficking (Utete and Fregene 2020). Odo-Iyaalaro River is situated in Lagos State, Nigeria and it is a sub-catchment of the Ogudu River, which discharges into the Lagos lagoon. Odo-Iyaalaro River spans about 15.8 km in length, flowing through densely populated areas of about 2.5 million (Ogunbanwo *et al.*, 2022). The catchment area of Odo-Iyaalaro River contains significant sources of pollution from wastes and effluents discharged from households, various industries and a sewage treatment plant. The maps showing the sampling locations are presented in Figure 1 and Figure 2.

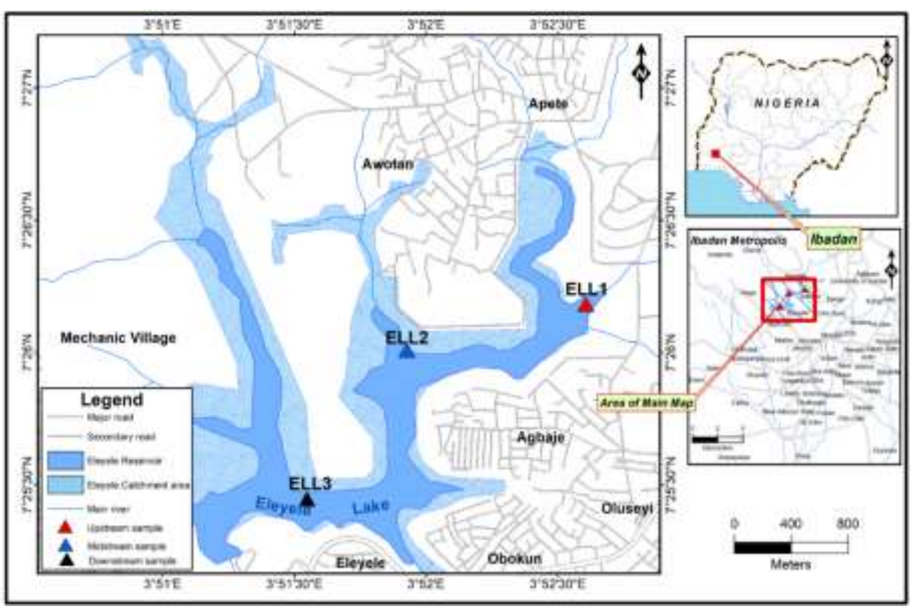

Fig. 1: Map showing the sampling locations in Eleyele Lake in Ibadan, Nigeria

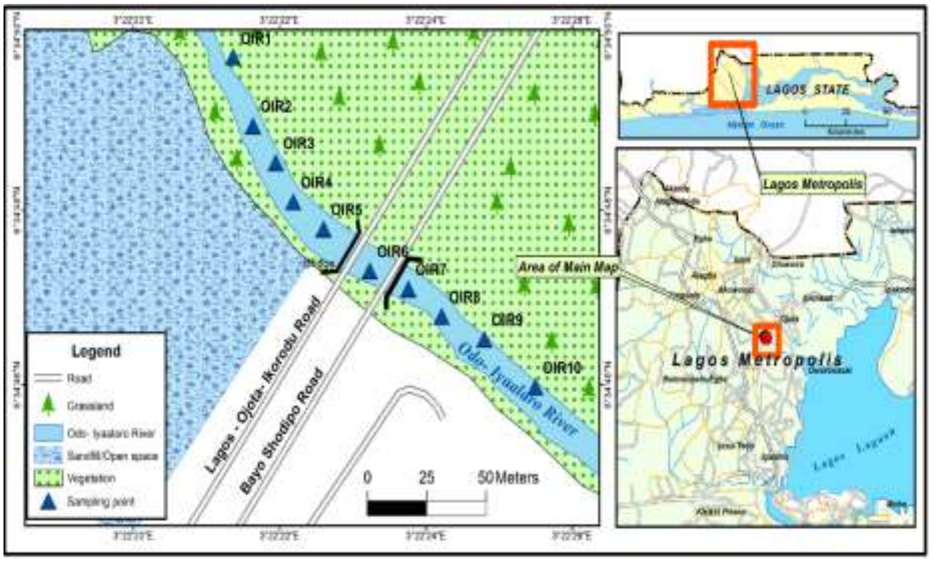

Fig. 2: Map showing the sampling locations in Odo-Iyaalaro River, Nigeria

Sample digestion and heavy metals analysis: 0.5 g sediment sample was weighed into a conical flask. 5 mL nitric acid was added, followed by the addition of 1 mL perchloric acid. The sample was digested for about 2 hours and allowed to cool, after which 5 mL of dilute HCl in H_2O (1:1, *v/v*) was added. The solution was then made up to 25 mL with deionized water and filtered. The heavy metals (Fe, Cu, Zn, Cr, Pb and Cd) concentrations were determined using atomic absorption spectrophotometry (Buck 210 Atomic Absorption Spectrophotometer). Quality assurance measures such as procedural blanks, replicate analyses and recovery studies were taken. Recoveries of the heavy metals ranged from 65% (Cr) to 102% (Cu).

Contamination factor (CF): This factor represents contribution of human activities to heavy metals pollution (Kumar *et al.*, 2020) and is calculated by following Hakanson (1980) according to equation (1):

$$CF = \frac{MC}{BC} \text{……… (1)}$$

Where MC is the concentration of heavy metal in the sediment sample analyzed and BC is the concentration of heavy metals in the background environment obtained from Taylor and McLennan (1995) and Kumar *et al.,* (2020). The background values used in this study were 25 (Cu), 0.098 (Cd), 35 (Cr), 20 (Pb) and 30890 (Fe). CF was classified according to Hakanson (1980) and Kumar *et al.,* (2020): CF < 1 as low, 1 ≤ CF < 3 as moderate, 3 ≤ CF < 6 as considerable and CF ≥ 6 as high contamination.

Pollution Load index (PLI): Pollution load index indicates the contamination load of evaluated heavy metals in the sediments and is related to contamination factor as follows in equation (2):

$$PLI = (CF_1 \times CF_2 \times CF_3 \times CF_4 \times \ldots CF_n)^{1/n} \text{……..(2)}$$

Where CF is the contamination factor of individual heavy metal and n is the number of assessed heavy metals in the sediment. Categorization of PLI was according to Ndhlovu *et al.*, (2023): PLI <1 indicates no metal pollution and PLI >1 indicates pollution.

Enrichment factor (EF): used to identify the content of heavy metals in the sediment (Kumar et al. 2020) by following Muller et al. (1979) and was computed by equation (3):

$$EF = \frac{MC/MC(Fe)}{BC/BC(Fe)} \text{………(3)}$$

Where MC and BC are the concentrations of heavy metal in the sediment sample analyzed and in the background environment, respectively while MC (Fe) and BC (Fe) are the concentrations of iron in the sample and background environment, respectively. EF was classified according to Sutherland (2000) and Kumar *et al.,* (2020) as follows: EF < 2 as minimum enrichment, 2 ≤ EF < 5 as moderate enrichment, 5 ≥ EF < 20 as significant enrichment, 20 ≥ EF ≤ 40: high, and > 40 as extreme enrichment in sediment.

Geoaccumulation index (I_{geo}): provides required information about the extent of contamination by heavy metals in a porous medium and was computed according to Muller *et al.,* (1979) in equation 4:

$$I_{geo} = \log_2\left(\frac{MC}{1.5 \times BC}\right) \text{………..(4)}$$

where MC and BC are the concentrations of heavy metal in the sediment sample analyzed and in the background environment, respectively. Categorization of pollution level by the heavy metals follows Muller et al. (1979). $I_{geo} < 0$ implies practically unpolluted, $0 < I_{geo} < 1$ means slightly polluted, $1 < I_{geo} < 2$ signifies moderately polluted, $3 < I_{geo} < 4$ refers to severely polluted, $4 < I_{geo} < 5$ implies severe to extremely polluted and $I_{geo} > 5$ shows extreme pollution.

Ecological risk assessment of heavy metals in sediment: The potential ecological risk of individual heavy metal (ER) was calculated using equation 5:

$$ER = CF \; x \; Tr \; \ldots\ldots (5)$$

Where CF and T_r are the contamination factor and toxicological response factor, respectively of individual heavy metal. T_r values were taken from Duodu *et al.,* (2016) and Kumar *et al.,* (2020) and were as follows: 5 (Cu & Pb), 1 (Zn), 2 (Cr) and 30 (Cd). Ecological Risk Index (RI) was then computed as the summation of potential ecological risk (ER) values of the heavy metals as depicted in equation 6:

$$\text{RI} = \sum_{i=1}^{n} (Tr^i \; x \; CF^i) \ldots\ldots (6)$$

Similarly, the modified potential ecological risk of individual heavy metals (MER) and modified potential ecological risk index (MRI) were calculated from the corresponding enrichment factor using the following equations 7 & 8:

$$MER = EF \; x \; Tr \ldots\ldots\ldots (7)$$

$$MRI = \sum_{i=1}^{n} (Tr^i \; x \; EF^i) \ldots\ldots (8)$$

The categorization of potential ecological risk factors was according to Hakanson (1980) and Kumar *et al.,* (2020): ER < 40 as low, 40 ≤ ER < 80 as moderate, 80 ≤ ER < 160 as considerable, 160 ≤ ER < 320 as high, and ER > 320 as very high ecological risk. The categorization of risk index (RI) and modified risk index (MRI) is as follows: RI or MRI <150 as low, 150 ≤ RI or MRI < 300 as moderate, 300 ≤ RI or MRI <600 as considerable, and RI or MRI > 600 as high ecological risk.

RESULTS AND DISCUSSION

PTMs composition in sediments: The measured concentrations of heavy metals in the sediments of Odo-Iyaalaro River and Eleyele Lake are presented in Table 1. The ranges of heavy metals concentrations in the sediments of Odo-Iyaalaro River were 51-143.7 mg kg^{-1}, 0.8 -2.6 mg kg^{-1}, 0.25-1.73 mg kg^{-1}, n.d -2.9 mg kg^{-1}, 1.0 -15.6 mg kg^{-1} and n.d. – 0.8 mg kg^{-1} for Fe, Cu, Zn, Cr, Pb and Cd, respectively while the concentration ranges in the sediments of Eleyele Lake were 177.4 – 344.2 mg kg^{-1}, 1.7 – 4.6 mg kg^{-1}, 0.84 – 1.22 mg kg^{-1}, n.d. – 2.9 mg kg^{-1}, 0.08-1.3 mg kg^{-1}, 0.08- 1.3 mg kg^{-1} for Fe, Cu, Zn, Cr, Pb and Cd, respectively. The highest concentrations were measured for Fe among the analyzed heavy metals in the sediments collected from both water bodies. Eleyele Lake sediments had higher concentration levels of Fe and Cu than in the sediments of Odo-Iyaalaro River, the highest concentration of Fe was recorded in sediments collected upstream of the lake. Pb was, however, present in higher amounts in the sediments of Odo-Iyaalaro River than in the sediments of Eleyele Lake.

Table 1: Concentration profiles of PTMs (mg kg^{-1}) in sediments from Odo-Iyaalaro River and Eleyele Lake, Nigeria*

	Sampling Point[a]	Fe	Cu	Zn	Cr	Pb	Cd
Odo-Iyaalaro River	OIR1	85.9±8.1	1.7±0.1	0.54±0.01	n.d.	10.8±3.5	0.5±0.2
	OIR2	57.1±4.3	0.8±0.1	1.14±0.02	n.d.	15.6±0.9	n.d
	OIR3	94.1±7.2	2.6±0.1	1.73±0.01	n.d.	5.9±1.4	0.13±0.08
	OIR4	52.0±3.8	1.7±0.1	0.55±0.01	n.d.	9.7±3.2	n.d
	OIR5	60.0±7.6	0.8±0.1	0.56±0.03	n.d.	1.0±0.1	n.d
	OIR6	61.5±4.7	1.7±0.1	0.25±0.01	n.d.	6.1±1.9	n.d
	OIR7	143.7±11.2	1.7±0.1	0.84±0.01	2.9±0.1	10.8±0.9	0.23±0.03
	OIR8	66.1±7.9	0.8±0.1	1.44±0.02	n.d.	8.3±1.7	n.d
	OIR9	51.0±8.3	1.7±0.1	1.45±0.04	n.d.	2.9±0.7	0.13±0.03
	OIR10	57.0±9.6	0.8±0.1	1.13±0.01	n.d.	5.1±4.3	0.8±0.1
Eleyele Lake	ELL1 (upstream)	344.2±13.4	4.6±0.1	0.84±0.01	n.d.	1.3±0.6	1.3±0.6
	ELL2 (midstream)	305.7±15.9	2.5±0.2	1.22±0.13	2.9±0.1	0.08±0.03	0.08±0.03
	ELL3 (downstream)	177.4±12.5	1.7±0.1	0.85±0.02	n.d.	0.8±0.7	0.15±0.01
USEPA TRV[b]		n/a	16	110	26	31	0.6
SQGs[c]		n/a	34	150	81	46.7	1.2

**PTMs - potentially toxic metals; [a]-specific sampling points are shown in Fig. 1; [b]–TRV-Toxicity Reference Value (USEPA, 1999); n.d.- not detected; n/a-not available; c- sediment quality guidelines (NOAA, 1999).*

This may not be unconnected to the fact that the river (Odo-Iyaalaro River) flows through a typical urban area where high vehicular emission of exhaust containing lead is expected and also numerous industries and a WWTP situated around the area discharge their effluents into the river (Oyeyiola *et al.*, 2014). Chromium was detected and measured in samples collected from only one location at Odo-Iyaalaro River, and also only in the samples collected midstream of Eleyele Lake. Oyeyiola *et al.,* (2013) determined much higher concentrations of the PTMs (Cd, Cr, Cu, Pb and Zn) in the sediments of Odo-Iyaalaro River, up to 1040 mg kg^{-1} for Zn. In comparison with the study by Utete and Fregene (2020) who obtained concentrations up to 98.85 mg kg^{-1} for Zn in the sediments of Eleyele Lake much lower levels of the heavy metals ((Zn, Cu, Cd, and Pb) were measured in this study. Sources of heavy metals into the Eleyele Lake have been alluded to run-off from highly polluted and open sewer drainage systems and leachates from solid waste dumps in the Eleyele catchments (Utete and Fregene 2020). In comparison with the toxicity reference values (TRV) of the USEPA (1999) and sediment quality guidelines (NOAA 1999), only Cd concentrations (in few sediment samples) exceeded the TRV and sediment quality guidelines (NOAA 1999) indicating that the sediments may be contaminated with Cd. This was further established subsequently considering some other pollution indices.

Contamination level of PTMs in sediments: The results of contamination indices for the evaluation of PTMs pollution are presented in Table 2.

Table 2: Contamination factor, Enrichment factor and Geo-accumulation Index of PTMs in sediments*

	Contamination Factor		Enrichment Factor		Geo-accumulation Index	
	Odo-Iyaalaro River	Eleyele Lake	Odo-Iyaalaro River	Eleyele Lake	Odo-Iyaalaro River	Eleyele Lake
Fe	0.002	0.01	n.c.	n.c.	-9	-7
Cu	0.06	0.12	26	13	-5	-4
Zn	0.01	0.01	6	2	-7	-7
Cr	0.01	0.03	2	3	-4	-4
Cd	1.76	5.02	776	496	1	2
Pb	0.38	0.04	172	4	-2	-5

**PTMs- potentially toxic metals; nc- not calculated*

In terms of contamination factor, all studied heavy metals (except Cd) had low contamination in the sediments of both Odo-Iyaalaro and Eleyele Lake. Cd had moderate pollution in the sediments of Odo-Iyaalaro but considerable pollution in Eleyele Lake sediments. Pollution load index which indicates contamination load of all studied heavy metals was less than 1 for both Odo-Iyaalaro and Eleyele Lake sediments, indicating no apparent heavy metal pollution in the sediments of both water bodies (Ndhlovu *et al.*, 2023). Considering the enrichment factor (EF), moderate enrichment was observed for chromium in the sediments of both water bodies as well as for Zn and Pb in only Eleyele Lake sediments. Significant enrichment was observed for Zn and Cu at Odo-Iyaalaro sediments and for Cu in Eleyele sediments. Extreme enrichment of Pb in Odo-Iyaalaro sediments and Cd in both Odo-Iyaalaro and Eleyele sediments was observed, indicating anthropogenic influences. In terms of geo-accumulation index, all studied heavy metals, except Cd, exhibited practically no pollution. The sediments were, however, moderately polluted for Cd.

Risk of PTMs in sediments: The values for the potential ecological risk of individual PTM and ecological risk indices are shown in Table 3. Considering the potential ecological risk (ER) of individual PTM, all studied PTMs (except cadmium) posed low ecological risk in the sediments of both water bodies. Cd posed moderate ecological risk and considerable ecological risk in the sediments of Odo-Iyaalaro River and Eleyele Lake, respectively. A previous study also showed that Cd posed the highest ecological risk in the sediment of Odo-Iyaalaro River (Oyeyiola *et al.*, 2014). Risk index (RI) indicates there was a low risk of the combined heavy metals in Odo-Iyaalaro River sediments while a moderate ecological risk was observed for Eleyele Lake sediments, apparently due to Cd contributions. Olayinka and co-workers also found out in their study that Cd had the highest toxic concentration in Eleyele Lake (Olayinka *et al.*, 2017). Kumar *et al.* (2020) equally observed that Cd, among other heavy metals, showed the highest ecological risk in the sediments of certain Indian rivers and was the major contaminant responsible for ecological risks. Chang and co-workers recently identified Cd as one of the two heavy metals posing the greatest threats in the sediments of Chaohu Lake, China over the past 50 years (Chang *et al.*, 2024). The human health effect of Cd may include kidney dysfunction, skeletal damage, and reproductive deficiency. Furthermore, the digestive, immune and reproductive systems of fish may also be affected by Cd (Olayinka *et al.* 2017; Jona and Ayodele-Olajire 2022). Due to the potential ecological risk of Cd in the sediments of Odo-Iyaalaro River and Eleyele Lake in this study, the regular monitoring of the two water bodies should be prioritized and appropriate mitigation strategies should be developed to protect the freshwater ecosystems from potential adverse effect s of PTMs.

Table 3: Ecological and modified ecological risk of PTMs in sediments

	Potential Ecological Risk of Individual PTMs (ER)					Ecological Risk index (RI)
	Cu	Zn	Cr	Cd	Pb	
Odo- Iyaalaro River	0.29	0.01	0.02	52.81	1.90	55.03
Eleyele Lake	0.59	0.01	0.06	150.51	0.18	151.35
	Modified Potential Ecological Risk of Individual PTMs (MER)					Modified Ecological Risk Index (MRI)
	Cu	Zn	Cr	Cd	Pb	
Odo Iyaalaro River	128	6	4	23269	858	24265
Eleyele Lake	65	2	6	14886	22	14981

**PTMs- potentially toxic metals*

Conclusions: Among the PTMs investigated, only Cd concentrations exceeded the toxicity reference values and sediment quality guidelines, indicating that sediments of Eleyele Lake and Odo-Iyaalaro River may be contaminated with Cd. All studied heavy metals had low contamination in the sediments of both Odo-Iyaalaro River and Eleyele Lake, except Cd which had a moderate pollution in the sediments of Odo-Iyaalaro River and considerable pollution in Eleyele Lake sediments. Extreme enrichment of Pb and Cd in the sediments indicates anthropogenic influences. While all PTMs (except cadmium) posed low ecological risk in the sediments of both water bodies, Cd presented moderate ecological risk and considerable ecological risk in the sediments of Odo-Iyaalaro River and Eleyele Lake, respectively. This study suggests the need for regular monitoring of Eleyele Lake and Odo-Iyaalaro River for PTMs (especially Cd) to protect the aquatic and benthic organisms living in or near the water bodies.

Declaration of Conflict of Interest: **T**here is no conflict of interest.

Data Availability Statement: Data are provided by the first author upon request.

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