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Heavy metal mobility, bioavailability, and potential toxicity in sediments of the Korle lagoon in Ghana

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ABSTRACT
This study aimed to identify the mobility, bioavailability, and potential toxicity of heavy metals (HM) in sediments of the Korle lagoon using metal partition. Sediments were analysed using the BCR (Bureau of reference) method. As (60%), Pb (50%), Zn (57%) and Fe (40%) were found in high concentration in the ion exchangeable fraction. The oxidisable fraction was dominated by Cu (51%), Cd (95%), Cr (61%), Ni (63%), As (35%), Fe (21%), Hg (30%), Pb (19%) and Zn (11%). The reducible fraction was dominated by Zn (29%), Pb (24%) and Hg (19%). The residual fraction was dominated by Hg (49%) and Fe (34%). PCA was used to identify pH and organic matter as the most important factors controlling the mobility and bioavailability of HM in the sediments. Arsenic, Pb, Zn and Fe were found to have the highest mobility. Chromium, Cu and Ni have medium mobility. Hg has low mobility. Most of the HM show potential bioavailability and toxicity.

KEYWORDS
Heavy metals; mobility; toxicity; bioavailability; risk

Introduction

Pollution by HM in aquatic environments has become a major concern globally. This is largely caused by the increase in the use and processing of HM during various activities to meet the needs of the increasing population [1,2]. In aquatic environments, sediments serve as a reservoir for metals and play a major role in the distribution and storage of metals [3]. The Korle Lagoon stands out as one of the most polluted water bodies on earth [4]. The Korle Lagoon, however, used to be a freshwater ecosystem with an abundance of fishes, crabs, and other aquatic life forms that contributed to food security for the local residents [5]. The land uses within the fringes of the lagoon include settlements, the large concentration of industries such as textile factories and Ghana Breweries Ltd, vehicle repair shops, market, E-waste sites; and there is uncontrolled and unplanned urbanisation with many slums and squatters [6].

The Korle lagoon thus receives metals in untreated or inadequately treated wastewater from domestic, industrial, and agricultural sources. Previous studies recorded high concentrations of metals in and around the lagoon. Clottey [7] reported very high concentration for Cd (1.10–54.50 mg/kg), Pb (42.92–112.45 mg/kg), Cr (0.3–50.6 mg/kg) and Cu (5.15–29.38) in the sediments of the Korle Lagoon. Aboagye [8] showed that the concentration of Cd and Pb in fishes obtained from the estuary of the Korle lagoon

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exceeded the WHO recommended level and so was not safe for human consumption. Fosu-Mensah *et al.* [9] also reported that the concentration of Pb (84.44 mg/kg), Cd (103.66 mg/kg), Cu (202.99), Ni (72 mg/kg) and Sn (705.32 mg/kg) in lands and vegetation around the Korle lagoon exceeded the WHO/FAO levels for agricultural soils.

Although there are many studies on the HM pollution of the Korle Lagoon, they have mainly focused on the total concentration of metals in the sediments. The total concentration of metals in sediments can be used as an indicator for the assessment of sediment contamination. But, this cannot provide sufficient information for tohe assessment of environmental impact [10]. This is because the environmental behaviour of metals in soils and sediments depends on their chemical forms that influence their mobility, bioavailability, and potential toxicity [11–13]. Thus, there is a need for environmental impact and risk assessment studies on the different chemical forms of HM in the Korle Lagoon.

Heavy metal speciation using sequential extraction procedures is necessary. The principle of sequential extraction is based on selective extraction of HM in different fractions using specific solvents [14]. This has been successfully applied to partition HM in sediments into different binding forms; ion exchangeable and carbonate bound (F1), Fe-Mn oxide bound (F2), organic matter/sulphide bound (F3), and residual (F4) [14,15]. The most reactive and bioavailable fraction is the exchangeable and carbonate bound fractions that are weak structures that are easily broken down by ion-exchange mechanism [16]. The oxidisable and reducible fractions are potential mobility fractions whose structure can be broken down as a result of a changes in pH, redox, and decomposition. The residual components comprise the non-mobile fraction that can only be disrupted by strong acids [16]. Thus, the sum of the metals associated with exchangeable and carbonate-bound, reducible, and the oxidisable fractions determine the mobile fraction (MF) and the most bioavailable metals [10].

High mobility of metals in the Korle lagoon may have an impact on major economic activities around it. These include fishing at the estuaries of the lagoon, farming, and residential activities. Fishes and food products can accumulate heavy metals introducing them into the food chain. But, accumulation of these metals in organic tissues is highly dependent on metal mobility since non-mobile metals (metals associated with F4) do not pose a major environmental risk. Since most studies have focused on the total metal concentration, it is not possible to ascertain if these metals pose a major risk. It is necessary to determine the chemical forms of the metals to determine their risk to the environment. In this study, the concentrations of heavy metals (As, Cu, Hg, Pb, Cd,, Zn, Fe, Ni) in surface sediments of the Korle lagoon were analysed to determine their different chemical forms in order to assess their mobility, bioavailability and potential toxicity.

Methodology

Study location

The study focuses on the Korle lagoon and its catchment area. The Korle Lagoon is in Accra, the capital of Ghana and stretches to the west of the city centre within longitude 05°35′N and latitude 00°06′W. It has an estimated catchment of 400 km^2 and covers a surface area of about 0.6 km^2 [6]. The Korle Lagoon is fed by the Odaw River which flows through Accra with a catchment area of about 60% of Accra metropolitan area [6]. This catchment serves as the location for storm water runoff resulting in the transport of pollutants to various areas such as farms and residential areas.

Sampling and chemical analysis

The sampling location was divided into four quadrants and three surface sediments (1–15 cm) were randomly collected from each quadrant (Figure 1) making a total of 12 samples. Sediments were sampled with a Van Veen grab sampler into plastic bags and transported to the laboratory in coolers containing ice packs. In the laboratory, samples were air-dried and ground into fine particles using a mortar and pestle and sieved through a 2 µm mesh and analysed for pH, Total organic carbon (TOC), and metals.

Sequential extraction

The sediment samples were analysed according to the BCR three-step sequential extraction procedure described by Rauret *et al.* [17]. Fraction 4 was analysed according to the US EPA method 3050 B [18].

Exchangeable and carbonate-bound fraction (F1): 40 ml of 0.11 mol/ L acetic acid were added to 1 g of sample in a 50 mL centrifuge tube and extracted for 16 h at 25°C using a mechanical shaker followed by centrifugation at 3000 g for 20 min. The residue was washed with deionised (DI) water by shaking for 15 min, centrifuged and the supernatant discarded.

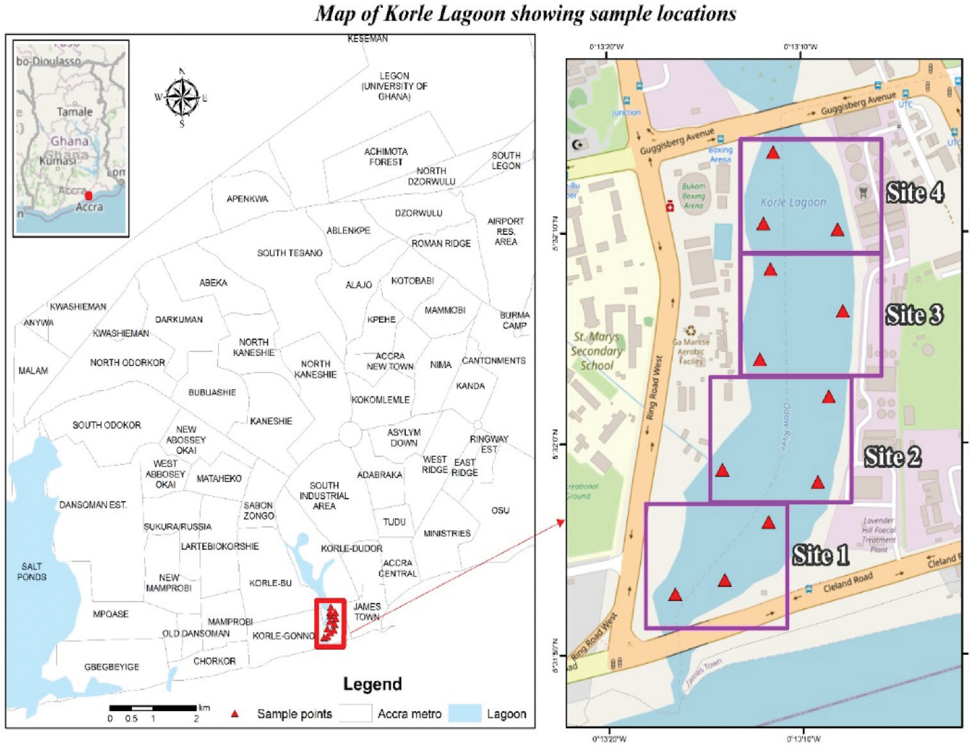

Figure 1. Map of study area showing sampling location.

Reducible fraction (Fe-Mn Oxide bound) (F2): 40 ml of 0.5 mol/L hydroxylamine hydrochloride, pH = 2, adjusted with 2.5% (v/v) nitric acid were added to the residue from the first step and extracted at room temperature using a mechanical shaker for 16 h. The extract was separated, and the residue was washed with deionised water as described in the first step.

Oxidisable fraction (Organic matter and sulphide bound) (F3): 10 ml of Hydrogen peroxide were added in small aliquots to the residue from the second step. This was digested at room temperature for 1 h and further digested at 85°C for another hour. The volume was reduced to about 2 ml by heating the uncovered tube before adding another 40 ml of hydrogen peroxide. This was digested for 1 hr at 85°C to reduce the volume to about 1 ml. Samples were cooled to room temperature and 50 ml of 1 mol/L ammonium acetate, pH = 2, adjusted with nitric acid were added and extracted for 16 h. The residue was separated and washed as described in the previous step.8

Residual (F4): The residue from step 3 was then digested with Aqua Regia solution. One (1) ml of conc HCl and 1 ml of conc HNO_3 was added to the residue and digested on a digestion block preheated to 110 ± 4°C for 40 minutes. After 40 mins, the tube was removed from the block, 10 ml of deionised water was added and digested for a further 20 mins. Samples were allowed to cool and topped up to the 50 ml mark.

Heavy metal determination

Nexion 2000- ICP-MS equipped with a micro mist nebuliser and microarray spray chamber was used to determine the concentration of metals. Calibration standards were prepared from a 500 mg/L multielement standard solution using a 1% (v/v) nitric acid solution. The instrument was calibrated from 1 to 100 μg/L using dwell times of 60, 25, 25,15,50,25,25,10,25 milliseconds for As, Cd, Cr, Cu, Hg, Ni, Pb, Fe and Zn respectively. Before analysis, samples were diluted at least 1:10 with 1% (v/v) HNO_3 to reduce the high matrix. All the relative standard deviations of the replicate samples were <20%. Reagent blanks, duplicates, and certified reference material (SCP science Enviromat SS-2 soil standard) were used for quality control and accepted with recovery percentages >90%.

pH

Forty (40) ml of deionised water were added to 10 g of sample in a 50 ml tube. The mixture was placed on a mechanical shaker and mixed for 30 min at room temperature. After 30 min, samples were allowed to stand for 1 hour and pH was measured using a TPS Smartchem electrode probe and metre.

Organic matter content

An aliquot of dried sediments (0.35 g) was weighed into a carbon-free combustion boat and loaded onto an autosampler rack of LECO analyser and analysed for Total carbon. Another 0.35 g of dried sediments were weighed into a carbon-free combustion boat and treated with phosphoric acid until bubbling stops. The sample was dried in an oven pre-heated at 40°C for 24 hours and transferred to another oven preheated at 105°C. The boat was loaded onto the autosampler rack of a LECO analyser after drying and analysed for total inorganic carbon. Total organic carbon was calculated using equation 1. Organic matter was calculated by multiplying TOC with the convenience/conversion factor of 1.724 [19].

$$\text{TOC}(\%) = \text{Total carbon} - \text{Inorganic carbon} \tag{1}$$

$$\text{Organic matter}(\%) = \text{TOC}(\%) \times 1.724 \tag{2}$$

Risk assessment code (RAC)

The Risk Assessment Code (RAC) was used to assess the contamination and potential toxicity of HM in the sediments of the Korle Lagoon. According to the RAC, HM in the sediments can thus be classified as no risk ($\text{RAC} \leq 1$), low risk (LR) ($1 < \text{RAC} \leq 10$), medium risk (MR) ($10 < \text{RAC} \leq 30$), high risk (HR) ($30 < \text{RAC} \leq 50$), and very high risk (VHR) ($\text{RAC} > 50$) [20].

The RAC was calculated as follows:

$$\text{RAC} = \text{F1}/\text{TM} \times 100 \tag{3}$$

F1 – ion exchangeable fraction and carbonate bound fraction (mg/kg)
TM – total concentration (mg/kg).

Statistical analysis

Exploratory data analysis to determine the mean, standard deviation, and percentages were done in Excel 2013. Results were expressed as mean ± Standard deviation. Principal Component Analysis (PCA) was used to reduce the dimensionality of data to make the data more interpretative and Correlation analysis was performed to determine the relationship between the variables. Both PCA and correlation were done using SPSS 24. Prior to statistical analysis, normality of data was checked using the Shapiro–Wilk test and data were found to have a normal distribution.

Results

Sediment properties and physicochemical characteristics

Table 1, below, shows the basic physicochemical properties of the sediments. The sediments were alkaline with a pH range of 8.12–8.30. The concentration of organic matter (OM) in the bottom sediments from the Korle Lagoon was high and ranged from 6.5% to 7.6% (Table 1). A significant difference was observed in the concentrations from the different sampling sites for pH ($P = 0.0021$: $P < 0.05$) and organic matter ($P = 0.037$: $P < 0.05$) indicating that the pollutants were not evenly distributed in the sediments.

Table 1. Mean organic matter and pH in surface sediments from the Korle lagoon.

Site	OM (%)	pH
1	6.5 ± 0.06	8.13 ± 0.05
2	6.8 ± 0.01	8.30 ± 0.05
3	7.1 ± 0.41	8.30 ± 0.03
4	7.6 ± 0.03	8.21 ± 0.03

Speciation of heavy metals

Metal speciation was used to assess the heavy metal mobility and bioavailability in the Korle lagoon. Generally, heavy metals in the Korle lagoon were highly mobile as higher percentages were found in the mobile fractions; F1+ F2+ F3. Figure 2 shows the extractable percentages of heavy metals. Tables 2–10 illustrate the percentages of the metals in each fraction for the sediment samples. Arsenic was present in a higher percentage in the ion exchangeable fraction (60%). A little over one-third (35%) of As was found in the oxidisable fraction indicating that As is bound to organic matter and sulphides that are easily oxidised. The total mobile fraction of As (F1+ F2+ F3) was also high (96%) (Figure 2). But, As was hardly detected in the reducible fraction (0.3%) implying that there were low levels of As bound to Mn and Fe Oxides.

Cadmium was present in higher concentrations in the oxidisable fraction F3 which is equivalent to 95% of the total Cd (10.15 mg/kg) concentration. This means that a high percentage of Cd is bound to organic matter and sulphides. The total mobile fraction for Cd was 96.11% indicating the Cd was highly mobile in the Korle Lagoon. It was hardly detected in F1 (0.9%), F2 (0.2%), and F4 (3%).

Cu associated with F1, F2, and F3 constituted 36%, 5%, and 51% respectively. Cu was relatively high in F3 followed by F1 which indicates high mobility. The residual fraction represented 8% of the total Cu (18.75 mg/kg) content in the sediments.

Ni was highly dominant in the oxidisable fraction (63%) followed by the ion-exchangeable and carbonate-bound fraction F1 (21%). F2 and F4 had extraction percentages of 5 and 11% respectively. The results show that the mobility of Ni was high. Similarly, Hg and Fe showed a high affinity for organic matter (F3 = 30% and 21% respectively). But, Fe was found to be dominantly associated with F1 (40%). Although Fe was high in the residual fraction F4, the total mobile fraction, F1+ F2+ F3 (66%) indicates that Fe is highly mobile in the Korle lagoon. Hg is highly associated with residual fraction F4 (49%) and may be less mobile compared to the other metals. It is, however, highly mobile in the Korle lagoon with the percentage mobile fraction of F1+ F2+ F3 being 50%.

Pb and Zn are highly mobile elements in the Korle lagoon and are mostly associated with the ion-exchangeable and carbonate-bound fraction (50% and 57%, respectively). They are also highly associated with the reducible fraction (24 and 29%, respectively) and are bound to Fe and Mn oxides. They are present in high levels in the oxidisable fraction (19 and 11%) and are less associated with the residual fraction (5 and 4%).

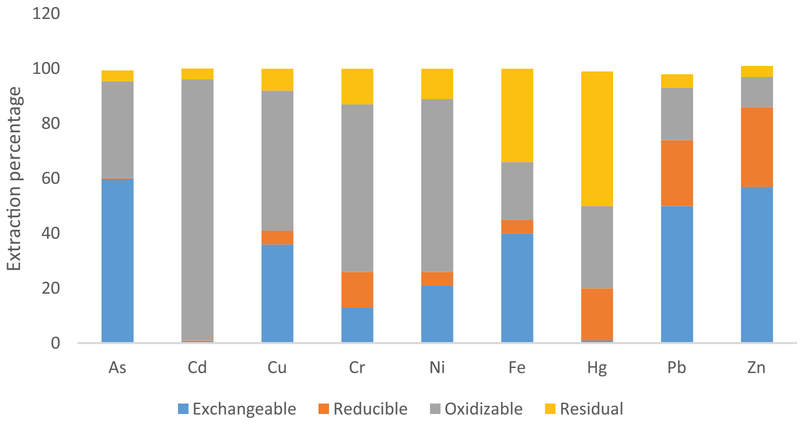

Figure 2. Extraction percentages of As, Cd, Cu, Cr, Ni, Fe, Hg, Pb, and Zn in sampling sites in the Korle lagoon.

Table 2. Distribution of Arsenic in sediment fraction (mg/kg).

		Exchangeable F1		Acid reducible F2		Oxidisable F3		Residual F4		
	Total As	Conc	%	Conc	%	Conc	%	Conc	%	F1+ F2+ F3 (%)
1	3.09 ± 0.86	1.33 ± 0.07	42.94	0.01 ± 0.04	0.36	1.69 ± 0.16	54.64	0.06 ± 0.02	2.05	97.95
2	1.98 ± 0.56	1.25 ± 0.04	63.11	0.02 ± 0.04	1.06	0.63 ± 0.07	32.09	0.07 ± 0.02	3.74	96.26
3	1.84 ± 0.59	1.29 ± 0.07	69.87	0.00 ± 0.01	0.00	0.48 ± 0.14	26.28	0.07 ± 0.02	3.85	96.15
4	2.16 ± 0.62	1.38 ± 0.07	64.09	0.00 ± 0.08	0.00	0.62 ± 0.15	28.78	0.15 ± 0.04	7.14	92.86
Mean	2.27 ± 0.56	1.31 ± 0.06	60.00	0.01 ± 0.01	0.35	0.86 ± 13.02	35.45	0.09 ± 0.04	4.20	95.80

Table 3. Distribution of Cd in sediment fraction (mg/kg).

		Exchangeable F1		Acid reducible F2		Oxidisable F3		Residual F4		
	Total Cd	Conc	%	Conc	%	Conc	%	Conc	%	F1+ F2+ F3 (%)
1	10.35 ± 4.89	0.00 ± 0.01	0.01	0.02 ± 0.003	0.17	9.92 ± 0.21	95.86	0.41 ± 0.05	3.96	96.04
2	9.97 ± 4.65	0.10 ± 0.03	0.97	0.03 ± 0.01	0.28	9.47 ± 0.60	95.01	0.37 ± 0.04	3.73	96.27
3	9.99 ± 4.64	0.13 ± 0.04	1.26	0.02 ± 0.01	0.19	9.46 ± 0.23	94.67	0.39 ± 0.02	3.88	96.12
4	10.31 ± 4.77	0.13 ± 0.01	1.29	0.03 ± 0.01	0.31	9.73 ± 0.35	94.43	0.41 ± 0.02	3.97	96.03
Mean	10.15 ± 0.2	0.09 ± 0.06	0.88	0.02 ± 0.01	0.24	9.65 ± 0.22	94.99	0.39 ± 0.11	3.89	96.11

Table 4. Distribution of Cu in sediments fraction (mg/kg).

		Exchangeable F1		Acid reducible F2		Oxidisable F3		Residual		
	Total Cu	Conc	%	Conc	%	Conc	%	Conc	%	F1+ F2 + F3 (%)
1	9.09 ± 3.12	1.18 ± 0.022	12.93	0.09 ± 0.05	0.98	6.91 ± 0.55	75.98	0.92 ± 0.22	10.11	89.89
2	21.65 ± 4.51	9.51 ± 0.70	43.92	1.38 ± 0.12	6.36	9.13 ± 2.28	42.16	1.64 ± 0.35	7.56	92.44
3	20.21 ± 4.10	9.24 ± 0.68	45.69	1.29 ± 0.13	6.38	7.90 ± 1.66	39.08	1.79 ± 0.20	8.85	91.15
4	24.06 ± 5.28	10.06 ± 0.18	41.81	1.41 ± 0.03	5.86	11.08 ± 2.83	46.07	1.51 ± 0.05	6.26	93.74
Mean	18.75 ± 6.64	7.50 ± 4.23	36.09	1.04 ± 0.64	4.89	8.75 ± 1.8	50.82	1.46 ± 0.38	8.20	91.80

Table 5. Distribution of Cr in sediments fraction (mg/kg).

		Exchangeable F1		Acid reducible F2		Oxidisable F3		Residual		
	Total Cr	Conc	%	Conc	%	Conc	%	Conc	%	F1+ F2 + F3 (%)
1.00	41.48 ± 10.28	4.34 ± 0.11	10.45	4.34 ± 0.03	10.45	25.67 ± 2.03	61.89	7.14 ± 2.18	17.20	82.80
2.00	45.39 ± 11.41	5.79 ± 0.69	12.76	5.79 ± 0.24	12.76	28.46 ± 1.93	62.71	5.35 ± 0.50	11.78	88.22
3.00	45.68 ± 11.49	6.04 ± 0.42	13.22	6.02 ± 0.19	13.19	28.64 ± 1.52	62.70	4.98 ± 0.17	10.89	89.11
4.00	46.85 ± 11.13	6.80 ± 0.57	14.50	6.78 ± 0.06	14.48	28.36 ± 0.37	60.54	4.91 ± 0.44	10.48	89.52
Mean	44.85 ± 2.33	5.74 ± 1.03	12.73	5.73 ± 1.02	12.72	27.78 ± 1.41	61.96	5.59 ± 1.05	12.59	87.41

Table 6. Distribution of Ni in sediment fraction (mg/kg).

		Exchangeable F1		Acid reducible F2		Oxidisable F3		Residual		
	Total Ni	Conc	%	Conc	%	Conc	%	Conc	%	F1+ F2+ F3 (%)
1	11.55 ± 3.24	1.85 ± 0.08	16.01	0.54 ± 0.53	4.66	7.68 ± 0.24	66.45	1.49 ± 0.34	12.87	87.13
2	12.29 ± 3.00	2.96 ± 0.22	24.05	0.79 ± 0.23	6.46	7.35 ± 0.88	59.81	1.19 ± 0.22	9.68	90.32
3	11.14 ± 2.88	2.53 ± 0.08	22.74	0.47 ± 0.15	4.22	6.92 ± 0.24	62.09	1.22 ± 0.16	10.95	89.05
4	11.85 ± 3.16	2.62 ± 0.16	22.12	0.43 ± 0.07	3.65	7.51 ± 0.26	63.40	1.28 ± 0.13	10.84	89.16
Mean	11.71 ± 0.48	2.49 ± 0.46	21.23	0.56 ± 0.16	4.75	7.36 ± 0.33	62.94	1.30 ± 0.13	11.08	88.92

Table 7. Distribution of Fe in sediment fraction (mg/kg).

		Exchangeable F1		Acid reducible F2		Oxidisable F3		Residual		
	Total Fe	Conc	%	Conc	%	Conc	%	Conc	%	F1+ F2+ F3 (%)
1	8476.52 ± 62	1965.12 ± 62	23.18	354.70 ± 29	4.18	4177.25 ± 504	49.28	1979.46 ± 159	23.35	76.65
2	11,067.35 ± 388	5098.57 ± 162	46.07	649.99 ± 138	5.87	1096.46 ± 659	9.91	4222.32 ± 163	38.15	61.85
3	11,032.52 ± 57	5188.54 ± 107	47.03	504.57 ± 76	4.57	778.63 ± 233	7.06	4560.78 ± 699	41.34	58.66
4	11,709.14 ± 101	5490.48 ± 101	46.89	584.78 ± 46	4.99	1900.32 ± 872	16.23	3733.56 ± 640	31.89	68.11
Mean	10,571.38 ± 1430	4435.68 ± 1655	40.79	523.51 ± 127	4.91	1988.17 ± 1533	20.62	3624.03 ± 1147	33.68	66.32

Table 8. Distribution of Hg in sediment fraction (mg/kg).

		Exchangeable F1		Acid reducible F2		Oxidisable F3		Residual		
	Total Hg	Conc	%	Conc	%	Conc	%	Conc	%	F1+ F2+ F3 (%)
1	0.21 ± 0.05	0.009 ± 0.002	4.37	0.03 ± 0.004	15.53	0.04 ± 0.02	18.93	0.13 ± 0.05	61.17	38.83
2	0.19 ± 0.04	0.00 ± 0.001	0.00	0.03 ± 0.005	16.15	0.08 ± 0.02	39.58	0.09 ± 0.01	44.27	55.73
3	0.19 ± 0.04	0.002 ± 0.001	0.00	0.02 ± 0.002	12.50	0.08 ± 0.01	40.10	0.09 ± 0.08	47.40	52.60
4	0.20 ± 0.04	0.003 ± 0.002	1.02	0.06 ± 0.029	32.49	0.04 ± 0.01	21.83	0.09 ± 0.08	44.67	55.33
Mean	0.20 ± 0.01	0.004 ± 0.002	1.35	0.04 ± 0.02	19.17	0.06 ± 0.02	30.11	0.10 ± 0.02	49.38	50.62

Table 9. Distribution of Pb in sediment fraction (mg/kg).

		Exchangeable F1		Acid reducible F2		Oxidisable F3		Residual		
	Total Pb	Conc	%	Conc	%	Conc	%	Conc	%	F1+ F2 + F3 (%)
1	16.83 ± 1.91	6.28 ± 0.28	37.31	3.91 ± 0.22	23.21	4.91 ± 0.21	29.16	1.74 ± 0.61	10.32	89.68
2	30.96 ± 6.03	15.51 ± 2.51	50.09	8.79 ± 0.33	28.41	5.43 ± 0.27	17.54	1.23 ± 0.04	3.96	96.04
3	34.37 ± 8.05	19.91 ± 3.11	57.94	8.07 ± 1.08	23.48	5.13 ± 0.31	14.94	1.25 ± 0.08	3.65	96.35
4	37.64 ± 8.24	21.78 ± 0.90	57.85	8.97 ± 0.45	23.83	5.62 ± 0.20	14.94	1.28 ± 0.08	3.39	96.61
Mean	29.95 ± 9.16	15.87 ± 6.91	50.80	7.44 ± 2.38	24.73	5.27 ± 0.32	19.14	1.37 ± 0.24	5.33	94.67

Table 10. Distribution of Zn in sediment fraction (mg/kg).

		Exchangeable F1		Acid reducible F2		Oxidisable F3		Residual		
	Total Zn	Conc	%	Conc	%	Conc	%	Conc	%	F1+ F2+ F3 (%)
1	118.87 ± 21	38.93 ± 0.42	32.75	55.59 ± 7.14	46.76	18.20 ± 2.64	15.31	6.16 ± 1.49	5.18	94.82
2	242.24 ± 57	102.26 ± 23.89	42.21	118.19 ± 96.22	48.79	16.35 ± 2.91	6.75	5.44 ± 6.15	2.25	97.75
3	142.66 ± 50	110.99 ± 16.95	77.80	12.22 ± 5.64	8.57	13.84 ± 1.52	9.70	5.61 ± 0.57	3.93	96.07
4	171.32 ± 57	128.99 ± 7.86	75.29	19.40 ± 8.92	11.32	17.34 ± 2.18	10.12	5.60 ± 0.36	3.27	96.73
Mean	168.77 ± 53	95.29 ± 39	57.01	51.35 ± 48	28.86	16.43 ± 1.89	10.47	5.70 ± 0.33	3.66	96.34

Correlation analysis

To identify common characteristics, sources of metals, and to evaluate the potential of organic matter and pH to influence metal mobility, Pearson correlation analysis was performed. Strong linear correlation was found in As vs Hg (0.983), Fe vs Cu (0.997), Fe vs Cr (0.997), Fe vs Pb (0.986), Cr vs Pb (0.995), Cr vs Cu (0.989) and Pb vs Cu (0.995). In addition, As, Cd and Hg had a significant negative correlation ($P < 0.05$) with pH ($-0.940 < r < -0.983$). Similarly, a moderate correlation was observed between Cu, Cr, Fe, Pb, Zn, and pH ($0.629 < r < 0.722$) at a 0.05 significant level. Organic matter correlated positively with Cu, Cr, Fe, and Pb.

Principal component analysis (PCA)

Principal Component Analysis (PCA) was applied to the total metals and mobile fraction in the sediments. PC1 accounts for 72.7% of the total variance suggesting that PC1 is the important factor controlling the source and distribution of metals in the sediments. PC 2 accounts for 14.7% and PC 3, 12.6% of the total variance (Table 11). PC1 is highly loaded with Cu, Cr, Pb, Fe, As, MFCu, MFCr, MFPb, MFFe, HgMF, AsMF, and organic matter and PC2 is loaded with As, Cd, Hg, and pH (Table 12). Figure 3 shows the loading plot of the first three PCs. Here may be seen the characteristics and spatial distribution of the metals in space with the contribution of variables in the sample. The closeness of variables signifies the strength of their correlation.

Table 11. Correlation between heavy metals (As, Cd, Cu, Cr, Ni, Fe, Hg, Pb, Zn) and pH and organic matter.

	As	Cd	Cu	Cr	Ni	Fe	Hg	Pb	Zn	pH	OM
As	1										
Cd	.779	1									
Cu	−.889	−.455	1								
Cr	−.886	−.411	.989*	1							
Ni	−.081	−.073	.321	.190	1						
Fe	−.903	−.459	.997**	.997**	.246	1					
Hg	.983*	.872	−.828	−.804	−.151	−.834	1				
Pb	−.890	−.409	.970*	.995**	.090	.986*	−.800	1			
Zn	−.567	−.572	.630	.510	.843	.574	−.648	.431	1		
pH	−.940*	−.945*	.715*	.686*	.112	.722*	−.984*	.683*	.629*	1	
OM	−.581	.056	.812*	.871*	−.015	.833*	−.431	.886*	.122	.269	1

*. Correlation is significant at the 0.05 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 12. Principal component analysis of heavy metals.

	Component		
OM	0.969		
Pb	0.947	0.303	
PbMF	0.944	0.311	
Cr	0.934		
CrMF	0.924	0.338	
Fe	0.904	0.334	
CuMF	0.888		0.354
Cu	0.884	0.321	0.34
HgMF	0.833	0.348	0.429
FeMF	0.761	−0.534	0.369
AsMF	−0.748	−0.647	
As	−0.701	−0.701	
Cd		−0.981	
pH	0.417	0.891	
Hg	−0.567	−0.797	
Ni			0.997
NiMF			0.981
Zn		0.426	0.877
ZnMF	0.497	0.451	0.741

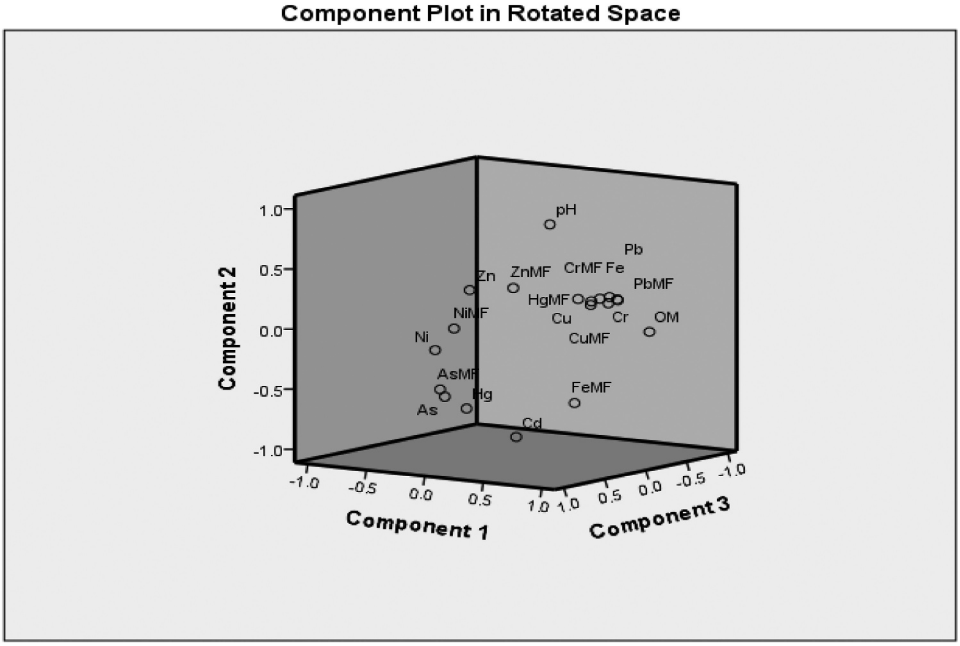

Figure 3. Loading plot of the first three principal components.

Risk assessment

The Risk Assessment Code (RAC) was used to evaluate the risk associated with the contamination of heavy metals in the sediments of the Korle lagoon. The RAC system considers the percentage of heavy metals present in F1 (the exchangeable and carbonate-bound forms). Figure 4 shows the risk analysis calculated with the concentration of metals in F1. Cd presented no risk in the sediments for all sample sites. Similarly, Hg presented no risk for all sampling sites except site 1 which was low risk ($1 < \text{RAC} \leq 10$). Cu showed medium risk ($10 < \text{RAC} \leq 30$) for sample site 1 and high risk ($30 < \text{RAC} \leq 50$) for Site 2, 3, 4. Cr showed low risk for site 1 ($\text{RAC} = 10$) and medium risk ($10 < \text{RAC} \leq 30$) for site 2, 3, 4. Similarly, Ni showed medium risk ($10 < \text{RAC} \leq 30$). As shown, high risk ($30 < \text{RAC} \leq 50$) for sampling site 1 and very high risk ($\text{RAC} > 50$) for Site 2, 3, and 4. Similarly, Zn showed high risk ($30 < \text{RAC} \leq 50$) for sampling site 1 and 2 and very high risk ($10 < \text{RAC} \leq 30$) for sampling site 3 and 4. As, Cu, Fe, Pb, and Zn fall under high risk to very high-risk category and can easily enter the food chain causing serious problems in the ecosystem.

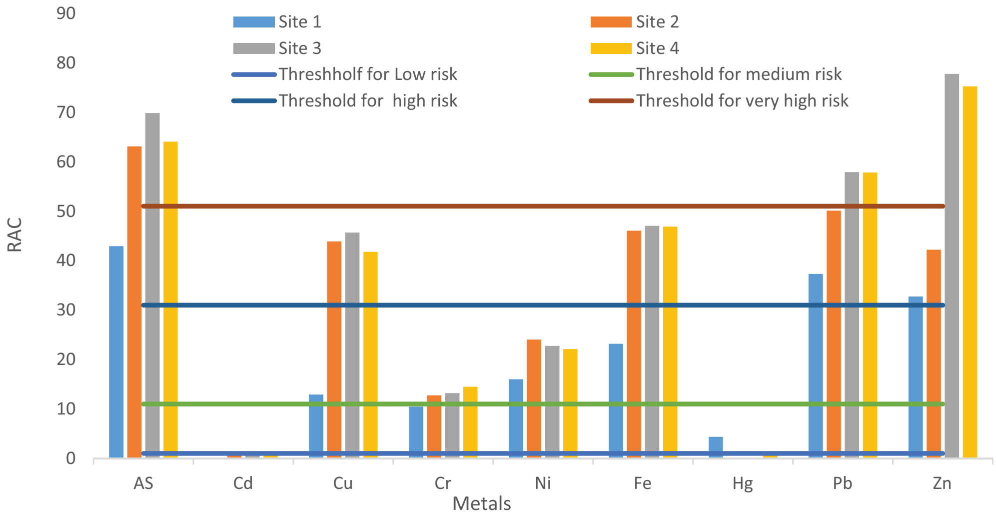

Figure 4. Risk assessment code for metals in sediments of the Korle Lagoon.

Discussion

The results revealed that the HM in the sediments of Korle Lagoon are distributed between different geochemical fractions. The sequential extraction procedure adopted in this work allowed us to recognise that As, Cd, Cr, Pb, Ni, Cu, Fe, and Zn are significantly associated with forms such as carbonates, oxides of Fe and Mn and organic matter.

Many studies have shown that organic matter plays a major role in the ability of bottom sediments to accumulate metals [10,21–23]. Sediments from the Korle Lagoon showed high concentrations of organic matter (6.5–7.6%). Because of the presence of negatively charged groups, organic matter has a high capacity to complex and adsorb to cations [10]. As a result, enrichment of trace metals in organic-rich sediments has been reported [21,24]. The rich organic matter in the study area can result in the formation of heavy metal-organic matter complexes reducing the bioavailability of metals [25,26]. The highest amount of metal for Cu (51%), Cd (95%), Cr (61%), Ni (63%) in the studied location was associated with F3. Similarly, As (35%), Fe (21%), Hg (30%), Pb (19%), and Zn (11%) also showed significant concentration in F3. Therefore, the mobility and bioavailability of HM in the Korle lagoon are highly influenced by organic matter.

It has also been shown that metal-bound organic substances are highly influenced by the pH of the medium [27]. At low pH, trace metals are highly soluble and more bioavailable because of increased desorption and low adsorption. At medium pH, the pH-adsorption edge occurs resulting in increased adsorption of trace metals to organic substances [27]. At high pH, elements become completely adsorbed resulting in low bioavailability [27]. According to Kabata-Pandias [28], the solubility of most trace metals decreases with increasing pH. As such, pH values (8.1–8.3) will suggest that most of the metals tested in our work will be less available because of the alkaline pH of the sediments. Krol *et al* [29] have, however, shown that a significant amount of Pb and Cu can be released at alkaline pH (10.5). This agrees with our findings that showed that even at high pH, some HM can have high mobility. High correlation was found between Cu and pH and Pb and pH (0.715 and 0.683 respectively). Similarly, Fe, Zn, and Cr also showed high correlation with pH (0.722, 0.629, 0.686 respectively). This suggests that the mobility of Pb, Cu, Fe, Zn, and Cr is highly influenced by pH. Arsenic (As), Cd, and Hg, however, had a negative correlation with pH (−0.940, −0.945, −0.980 respectively) which means that a substantial amount of Cd, As, and Hg would be released and become bioavailable following a reduction in the pH.

Arsenic (As), Zn, Pb, and Fe have the highest possibility of being released from the sediment by a simple ion-exchange mechanism. Zn has the highest mobility since it presented the highest concentration in F1. Similar observations about Zn have been made by many authors [10,25]. High levels of Zinc in water occur as a by-product of steel production and from coal-fired power stations and burning of waste materials. The burning of electronic waste that occurs within the fringes of the Korle lagoon could be the source of Zinc in its waters. A significant correlation between Zn and pH has been reported [25,30] which agrees with our findings. Baran and Tarnawski [10],, however, did not observe any positive correlation between Zn and pH. Under reduced conditions, the release of Pb, Zn, and Hg is expected to be high because they were more associated with the reducible fraction F2.

Principal component analysis (PCA) was applied to the present data obtained from the total HM and mobile fraction in sediments to identify the sources of pollution of the Korle lagoon. The first PC which accounts for 72.6% of the total variance is highly correlated with organic matter, total HM of Cu, Fe, Cr, Pb and the mobile fractions (CuMF, FeMF, CrMF, PbMF) of those elements with loadings of 0.905, 0.922,0.948, 0.956, 0.888, 0.904, 0.924, 0.944 respectively. PC1 also correlated with Hg (−0.567), AsMF (−0.748) and HgMF (0.833). The correlation of total HM, non-residual fraction, and organic matter indicates anthropogenic inputs [31,32]. Treated and untreated industrial sewage, municipal sewage, household waste, and waste from agricultural fields are the main sources of pollutants in the Korle Lagoon [4]. The different concentration of metals in the fractions indicates the different sources of pollution. To identify the sources and transport of heavy metals, Pearson's correlation was carried out [33]. A significant positive correlation between Cu, Pb, Fe and Cr ($0.683 < r < 0.997$) implies that these elements have a common origin and are associated with increasing organic matter. The high correlation of Pb and Cu agrees with the findings of Zhang *et al.* [11], according to whom the sources of contamination are likely related to the input of pesticides and fertilisers. The negative or less correlation of the other metals indicates the different sources of contamination.

Mostly, because of the weak association between the ion-exchangeable fraction and sediments, the high concentration of metals in this fraction is assumed to result from a more recent pollution. Similarly, those bound to reducible and oxidisable fraction indicate that pollution is less recent [3]. This means that, although the Korle Lagoon may have received recent pollution from As (F1 = 60%), Fe (F1 = 40%), Pb (F1 = 50%), and Zn (F1 = 57%), pollution from Cd, Cu, Cr, Ni, and Hg may be less recent as they are more associated with F2 and F3. Mitigation strategies to reduce pollution of the Korle Lagoon may have been unsuccessful as Korle still receives a significant amount of metals. This is corroborated by the significant concentrations of As, Cd, Cu, Cr, Ni, Pb, and Zn observed in F1 (recent) and F2+ F3 (less recent). There is continuous pollution from anthropogenic sources over time.

The risk assessment code (RAC) was used to demonstrate that there was a very high risk of metal mobilisation from the sediments of the Korle lagoon. This implies that aquatic organisms and plants around the Korle Lagoon are at risk of HM accumulation. Lands and agricultural fields around the Korle lagoon has been shown to have high levels of heavy metals [9]. High concentration of metals in aquatic organisms obtained from the estuary of the Korle lagoon has also been reported [8]. This agrees with our finding that showed that metals stored in the sediments have high mobility and hence are highly available to be absorbed into the tissues of aquatic organisms and plants within the catchment area of the lagoon. Human exposure to heavy metals occurs through the consumption of contaminated water and food [34]. Consumption of food with a high concentration of heavy metals can cause adverse effects such as infertility, cardiovascular diseases, hormonal imbalance, neurological disorders, digestive tract disorders, and cancer [35].

Conclusion

The analysis of the concentrations of heavy metals and their chemical forms showed that sediments of the Korle lagoon are contaminated with heavy metals, from anthropogenic sources. This research revealed that all studied metals were in the highly mobile phases of the sediments. Organic matter and pH are the most important factors controlling heavy metal distribution and mobility in the sediment. Cu, Cr, Fe, Pb, and Cd were found to be dominant in sediments of the Korle Lagoon. Further, As, Zn, Pb, Cu, and Fe have the highest possibility of being released as they were more associated with the exchangeable and carbonate-bound fraction. Hg is less mobile, but mobility may increase following a reduction in pH. The risk analysis with the RAC indicated that As, Cu, Fe, Pb, and Zn fall under the high-risk to the very high-risk category and can easily enter the food chain.

It is advisable to monitor the heavy metal concentration in aquatic biota and plants around the Korle Lagoon to assess the risk of consumption of such foods. The local residents should be educated about the dangers identified in this study. Disposal of waste should be conducted to appropriate standards, and not be haphazard. Sanitation should be according to modern hygienic requirements. Pollution control should be carried out according to law. There should be adequate treatment of waste before discharge. Remediation of the lagoon as well as the sediments and soils around the lagoon should take place in conjunction with these other measures. There should be epidemiological research into the health status and mortality of local residents in regard to the diseases found to be linked to exposure to heavy metals. Otherwise, the quality of the environment and public health in the Korle Lagoon area cannot be guaranteed.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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