

Heavy Metals Contamination and Speciation in Sediments of the Owabi Reservoir

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Abstract: Heavy metals are potentially toxic to humans and the environment. Metal toxicity depends on the chemical forms in which they exist. In this research, an investigation was conducted to study the contamination and speciation of some heavy metals (Cu, Zn, Pb and Cu) in sediments from the Owabi reservoir in Kumasi, Ghana. The mean concentrations of Pb and Zn were higher than the Continental Average Shale (CAS) and were beyond the Threshold Effect Level (TEL), implying contamination of these metals in the sediments. This observation was also confirmed by geoaccumulation index calculations. Canonical correlation analysis revealed that leaching of Zn is associated with pH while co-precipitation of Fe and Pb is also associated with EC. Speciation analysis showed significant amount of Zn Cu and Pb were available in the Fe-Mn fractions. But major amount of Fe was found in the residual fraction. The amount of Zn and Pb present in the bioavailable from have the potential to induce ecological risk. The results stresses that discharge of untreated waste into streams serving the reservoir should be avoided to reduce contamination since the contaminants found in this research are mainly release into the environment through human activities. Factor analysis showed that site S₁ and S₃ are the most polluted sites.

Key words: Ecological risk, factor analysis, metal speciation, heavy metals, Owabi, sediments

INTRODUCTION

The aquatic ecosystems are strongly influenced by long term discharge of untreated domestic and industrial wastewaters, storm water runoff, accidental spills and direct solid waste dumping. All these release pollutants including heavy metals that have a great negative ecological impact on the water quality and its surrounding food web (Hejabi and Belagali, 2009; Jumbe and Nandini, 2009). Heavy metals are among the most serious pollutants of great environmental concern because they are non-degradable, toxic and persistent with serious ecological consequences especially on aquatic ecosystem (Ahmad *et al.*, 2010; Brunner *et al.*, 2008; Idris *et al.*, 2007). Humans have always depended on aquatic resources for food and medicines as well as recreational and commercial purposes such as fishing and tourism. In addition, aquatic ecosystems have significant impact on migratory bird species that use the water bodies and surroundings as sanctuary, stop-over for food, breeding and nesting (Jumbe and Nandini, 2009; Phuong *et al.*, 2001).

Through the processes of precipitation and sedimentation, heavy metals that are introduced into the aquatic system are deposited in sediments. Heavy metals accumulation in sediments can therefore increase to toxic levels and pose a serious threat to native plants and animals. Due to the large amount of organic matter in reservoir sediments and its strong binding capacity for metal cations, sediments are capable of adsorbing and retaining a significant amount of anthropogenically deposited heavy metals (Perkins *et al.*, 2000) as well as sequestering large quantities of contaminants (Avila-Perez *et al.*, 1999; Gray *et al.*, 2000). The concentration of metals in sediments is often treated as an indicator of anthropogenic contamination of rivers and lakes. Sediments are integral and inseparable parts of the aquatic environments because they help to determine the overall assessment of heavy metals in water vis a vis aquatic life and its survivability (Jumbe and Nandini, 2009).

Various studies have demonstrated that aquatic sediments are contaminated by heavy metals from anthropogenic activities (Wang *et al.*, 2011; Jumbe and

Nandini, 2009; Meybeck *et al.* 2007; Osan *et al.*, 2007; Feng *et al.*, 2004). Quantification of heavy metal concentrations conducted in these studies have provide a general estimation of the overall intensity of heavy metal contamination in sediments but cannot provide useful information about the chemical nature, mobility and bioavailability and toxicity of these contaminants. Thus, the analysis of heavy metal speciation which offers a more objective assessment of the element's actual environment impact is critically important (Cuong and Obbard, 2006; Relic *et al.*, 2005). As a sink and source of metal ions, sediments constitute most of the bioavailable metals in aquatic environment and also play an important role in the biogeochemical cycle of these metals. The mobility and bioavailability of metals in sediments strongly depend on the chemical forms in which they occur (Baeyens *et al.*, 2003). The purpose of this research was to determine heavy metal concentrations and speciation in sediments from the Owabi reservoir. Again use factor analysis and geo-accumulation index calculations to examine the extent of heavy metal pollution in the sediments. The results obtained would highlight the possible potential treats that the pollution of the reservoir will have on the health of humans and other organisms that depend on the reservoir. Finally, baseline information that would allow for specific management plan to be implemented for conservation will be available.

MATERIALS AND METHODS

In carrying out this study, 10 sampling sites were selected within the reservoir using global positioning system (Fig. 1).

Sampling and sample analysis: Sediments were sampled from ten different sampling points within the Owabi reservoir as presented in Fig. 1. The samples were packed into plastic bags and transported to the laboratory in low-temperature containers and frozen immediately.

At the laboratory, the samples were air dried, ground and sieved through a 1 mm mesh to remove roots and other debris then stored in closed plastic containers. Afterwards about 1.0 g of the sample was weighed into a digestion tube and digested with 20 mL of aqua regia (HCl and HNO₃ solution in a ratio of 1:3) on a hot plate for about 2 h. The tubes were then removed and allowed to cool to room temperature. The contents were filtered into 50 mL volumetric flasks through 0.45 μm what man filter paper and topped to the mark with distilled water and stored in plastic containers ready for analysis. This digest was used to measure total metals concentrations in the sample.

To establish the distribution of metals in the sediments, four selective sequential extraction procedure based on the modified Tessier's Method was employed

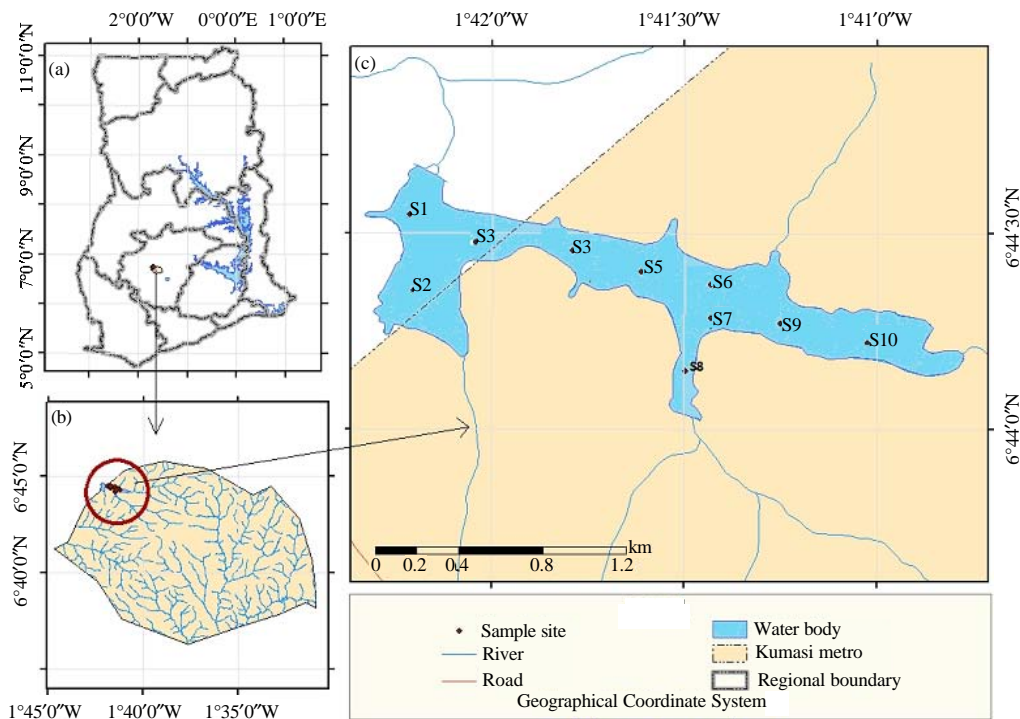


Fig. 1: a-c) The map showing the sampling points within the Owabi reservoir

(Blanchard, 2000). According to this method, the species of the metals in the sediments exist as acid soluble fraction or carbonates (F_1), reducible fraction or Fe-Mn oxides (F_2), oxidizable fraction or organic bound (F_3) and the residual fraction (F_4). The sequential extractions were carried out with 1 g of the sieved sediments samples. For fraction F_1 , the sample was digested with 40 mL of 0.11 M CH_3COOH for 16 h. The residue from (F_1) was extracted with 40 mL of 0.1 M $\text{NH}_2\text{OH.HCl}$ at pH 2 for 16 h to obtain F_2 . The extraction of F_3 was done by adding to the residue from (F_2), 10 mL of 8.8 M H_2O_2 (pH = 2). After 1 h, the mixture was heated at 90°C for another 1 h. Another amount of 10 mL of 8.8 M H_2O_2 was added and heated again at 90°C for 1 h. The mixture was then cooled to room temperature and to the cooled residue, 50 mL of 1M $\text{CH}_3\text{COONH}_4$ were added and agitated for 16 h. Heavy metals concentrations in the digested samples were measured using atomic absorption spectroscopy (UNICAM 929 Model). F_4 was obtained by subtracting sum of the three previous fractions from the total contents. After each extraction, the mixture was centrifuged and then the supernatant was filtered through a 0.45 μm membrane filter (Kashem *et al.*, 2007).

Soil texture was investigated by using the pipette method. Organic Matter (OM) contents were determined by soil ignition at a temperature of 450°C. Electrical Conductivity (EC) and pH were measured in a soil deionized water suspension (soil:water, 1:2.5 by volume) by a calibrated pH meter and EC meter, respectively. Soil samples were analyzed for Cation Exchange Capacity (CEC) using the ammonium acetate method at pH 7 (Yobouet *et al.*, 2010).

RESULTS AND DISCUSSION

The pH values of the sediments ranged from a minimum of 4.29 recorded at site S_8 to a maximum of 6.61 at site S_1 with an average of 5.32 ± 0.82 (Table 1). All the selected sites presented acidic pH, partially due to active microbial decomposition of drowned vegetation and other organic matter which is accompanied by the release of methane and H_2S gas in the hypolimnion.

Table 1: Ranges, means and standard deviations of physico-chemical characteristics and metal concentrations of sediments from the Owabi reservoir

Parameters	Range	Mean±SD
OM (%)	13.84-19.53	16.35±2.05
pH	4.29-6.61	5.32±0.82
EC ($\mu\text{S cm}^{-1}$)	474.11-1728.02	1249.70±394.11
CEC (cmol kg^{-1})	16.21-22.42	19.83±2.01
Fe (g kg^{-1})	3.52-5.43	4.03±0.56
Pb (g kg^{-1})	0.08-0.12	0.098±0.01
Zn (g kg^{-1})	0.14-0.67	0.40±0.16
Cu (g kg^{-1})	0.02-0.05	0.03±0.01

The OM content in sediments of the Owabi reservoir ranged from a minimum of 13.84% recorded at site S_8 to a maximum of 19.53% recorded at site S_{10} . The relative high content of OM in the sediments is mainly related to the high organic content of waste water and runoffs from agricultural and commercial activities that are discharged into the rivers that serve the reservoir. EC and CEC recorded mean values of $1249.70 \pm 394.11 \mu\text{S cm}^{-1}$ and $19.83 \pm 2.01 \text{ cmol kg}^{-1}$, respectively.

Concentrations of metals in the sediments are represented in Table 1. Iron concentrations ranged from a minimum of 3.52 g kg^{-1} to a maximum of 5.43 g kg^{-1} with an average of $4.03 \pm 0.57 \text{ g kg}^{-1}$.

Zinc concentrations ranged from 0.67 g kg^{-1} at site S_3 to a minimum of 0.14 g kg^{-1} site S_9 with an average of $0.40 \pm 0.16 \text{ g kg}^{-1}$. Lead concentrations in the sediment samples had an average value of $0.098 \pm 0.01 \text{ g kg}^{-1}$ while copper ranged from 0.02 g kg^{-1} at site S_{10} to 0.05 g kg^{-1} at site S_1 .

An assessment of metal pollution of the sediments was made by comparing mean concentrations of the selected metals with values of the Continental Average Shale (CAS) which gives an indication of possible anthropogenic impact and USEPA Threshold Effect Concentrations (TEC). The TEC provides values for the metals above which toxic effect can be observed (Turekian and Wedepohl, 1961).

The observed values for Fe were after the TEC and CAS (Turekian and Wedepohl, 1961). This gives an indication that there is no form of anthropogenic impact with respect to Fe concentration throughout the reservoir. The variations of Fe in the sediment among the sampling sites were statistically insignificant ($p < 0.05$). Cu concentrations at sites S_1 , S_2 , S_3 and S_7 were above the TEL of 0.036 g kg^{-1} (Buchman, 2008) while that of sites S_2 and S_3 were earlier CAS value of 0.045 g kg^{-1} (Turekian and Wedepohl, 1961). This indicates that the reservoir sediment is generally not polluted with Cu but there are few spots within the reservoir where Cu pollution is possible. The variations of copper in the sediment among the sampling sites were statistically insignificant ($p < 0.05$).

Zinc and Pb concentrations in the sediments were above the CAS and TEL values (Buchman, 2008; Turekian and Wedepohl, 1961). This indicates that the sediments are polluted with Zn and Pb to an extent that can produce toxic effects associated with Zn and Pb pollution in organisms that live in the sediments of this reservoir.

The geoaccumulation index (I_{geo}), a quantitative measure of the degree of pollution of metals proposed by Muller in late 1970s which has been widely used in heavy

metal studies in aquatic sediments (Frostner *et al.*, 1990) was used to quantify the degree of contamination in the reservoir sediments. The I_{geo} was calculated by using the expression:

$$I_{geo} = \text{Log}_2 \left(\frac{C_n}{1.5B_n} \right)$$

Where:

C_n = The concentration of a given metal in the soil tested

B_n = The background value (average shale) of metal n

The constant 1.5 is a background matrix correction factor due to possible variations in baseline data attributable to lithogenic effects. Descriptive classification for the index of geoaccumulation given by Frostner *et al.* (1990) is used: $I_{geo} < 0$ = practically unpolluted; 0-1 = unpolluted to moderately polluted; 1-2 = moderately polluted; 2-3 = moderate to highly polluted; 3-4 = highly polluted; 4-5 = highly to very highly polluted and > 5 = very highly polluted.

The results showed that the I_{geo} of Fe (-4.13) and Cu (-1.16) were below grade zero indicating no anthropogenic contaminants in the sediments. Based on this estimate, it can be said that the regional parent bedrock properties and natural accumulation process within the catchment are the primary factors controlling Fe and Cu concentrations in the sediments (Zhang *et al.*, 2011). However, Pb with an average I_{geo} of 1.71 and Zn with an average of 1.48 suggest the sediments are moderately polluted with these two metals.

Metal release from sediments at the sediment-water interface is largely controlled by EC and pH of a sediment system. Metals such as Cu, Cd, Pb and Zn can be mobilized during oxidation of low pH sediments through oxidation of sulphide phases and oxidation of organic matter (Kerner and Wallmann, 1992). So, apart from elemental concentrations, other factors such as OM and pH can influence the release of metals from the sediment to solution and vice versa.

Considering the aforesaid discussion, canonical correlation was carried out in an attempt to investigate the importance of pH and OM on the behavior of metals in the Owabi reservoir sediment. For this purpose, OM and pH were considered as criterion variables while the heavy metals were reserved for the predictor variables to document the importance of OM and acidity in displacement of the metals between solid and dissolve phases in the water-sediment system.

The standardized canonical coefficients of first canonical variate for the predictor variables suggested that Zn is more influential in forming the first canonical variate whereas that of the dependent variables implying that pH is more important (Table 2). Therefore, it can

Table 2: Standardized canonical coefficients for heavy metals related to pH and OM of the Owabi sediments

Covariates	V_1	Dependent variables	W_1
Fe	-1.0437	pH	0.8599
Pb	-1.5259	-	-
Zn	1.6378	OMC	0.2813
Cu	1.1273	-	-

Table 3: Standardized canonical coefficients for heavy metals related to CEC and EC measured in the sediments of the Owabi reservoir

Covariates	V_1	Dependent variables	W_1
Fe	1.4894	CEC	0.0245
Pb	1.1952	-	-
Zn	-1.2207	EC	1.0097
Cu	-1.2471	-	-

Table 4: Factor loadings for selected heavy metals in the Owabi reservoir sediment

Variables	Factor 1	Factor 2	Factor 3	Communality
Fe	0.481	0.632	0.2330	0.685
Pb	0.889	-0.403	-0.1930	0.989
Zn	0.698	0.537	-0.2140	0.822
Cu	0.781	-0.411	0.2683	0.851
Variance	2.249	1.220	0.4060	3.875
Total variance (%)	56.232	30.511	10.1490	96.892

be mentioned that pH is of great importance in co-precipitation of the soluble Zn. Thus, leaching of zinc is associated with pH.

In the second study, CEC and EC were considered as the dependent variables and the heavy metals as covariates to examine the importance of these two parameters in co-precipitation reactions. The results in Table 3 showed that Fe and Pb had high positive standardized coefficient whereas Cu and Zn had negative coefficients among covariates. On the other hand, EC was more important in the dependent variables. In this regard, it could be mentioned that the co-precipitation of Fe and Pb will more likely be associated with EC whereas Zn and Cu will more likely be associated with CEC as they had a low coefficient in the first variate.

Due to the negative effects of metals pollution in aquatic environment their sources in sediments is very important. For this reason factor analysis was used to identify sites that are significantly polluted by heavy metals. Three major factors were extracted and accounted for 96.905% of total variance as shown in Table 4. With the extraction of the first factor, which accounted for 56.24% of total variance, Pb, Zn and Cu had high loadings of 0.889, 0.699 and 0.781, respectively. In this regard site S_1 which recorded the highest factor score of 2.04 (Table 5) in factor one implies that the amount of these metals at this site were higher than the other stations. The second factor which accounted for 30.50% of total variance yielded high loadings for Fe and Zn with values

Table 5: Factor scores of selected heavy metals in the Owabi reservoir sediment

Locations	Factor 1	Factor 2	Factor 3
Site 1	2.04382	-0.76408	-0.91956
Site 2	0.18896	0.14433	1.23114
Site 3	0.67048	2.16514	0.45853
Site 4	-0.38766	-0.11981	-0.37022
Site 5	0.05253	-0.48072	-0.22198
Site 6	0.26517	-0.08820	0.45581
Site 7	-0.12060	-0.84605	0.10278
Site 8	-0.04190	-0.64497	0.07862
Site 9	-1.59599	-0.34657	0.64875
Site 10	-1.07482	0.98091	-1.46389

Table 6: Mean concentrations of selected heavy metals in the different phases of sediments from the Owabi reservoir after sequential extraction

Leachates	Metal concentration (g kg ⁻¹)			
	Fe	Pb	Cu	Zn
Carbonate	<0.005	0.005	<0.005	0.089
Fe-Mn oxide	0.958	0.035	0.017	0.250
Organic bound	0.056	0.024	0.005	0.089
Residual	3.404	0.032	0.011	0.135

of 0.632 and 0.537, respectively. Site S₃ which had the highest factor score of 2.16 in the second factor can be said to be the next polluted site after site S₁. The third factor which accounted for 10.17% of total variance yielded high loadings for Fe and Cu. Site S₂ had the highest factor score of 1.2311. This makes site S₂ the next polluted site after sites S₁ and S₃.

Metal speciation has helped in assessing the mobility, bioavailability and toxicity of metals and hence gives a better insight into the ultimate fate of metal which are introduced into the reservoir sediments. The result of the heavy metal speciation is presented in Table 6.

Major amount of Fe was found to be present in the residual fraction with the least present in the carbonate fractions at mean concentrations of less than 0.005 g kg⁻¹. This amount represents less the 1% of the total amount of Fe in the Owabi sediments. Only minor amounts of Fe were detected in the oxides and organic bound fractions (Table 6). Analysis of the data obtained shows that bioavailable fraction (which is the sum of carbonate and oxide bound fractions) of Fe recorded an average value of 0.97 g kg⁻¹ which represent about 22.04% of the total Fe detected in the sediments. At this concentration Fe is believed to have no tendency towards remobilization from the sediments phase to the more bioavailable pore water phase and consequently pose no induced ecological risk (Wang *et al.*, 2011).

Copper in the sediments from the Owabi reservoir was found mainly in the form bound mainly to oxides of Fe and Mn (57%) than in the residual fraction (37%). Lesser amount were determined in the carbonate fractions.

The bioavailable fraction recorded an average value of 0.027 g kg⁻¹ which was below the TEL of 0.038 g kg⁻¹ (Buchman, 2008). This outcome therefore suggests that copper is not present in any form that can be considered toxic in the sediments.

Significant amounts of Pb were bound to the Mn-Fe, organic and the residual phases. An average of 0.035 g kg⁻¹ was found to be bound to the Mn-Fe phase constituting 34.44% of total mass while organic bound and residual fractions recorded mean mass percentages of 23.86 and 32.65%, respectively. Significant amount of Pb was found to be present in the bioavailable fractions with an average concentration of 0.045 g kg⁻¹ which was above the TEL which is 0.035 g kg⁻¹ indicating potential bioavailability of this element but the value was below the PEL of 0.091 g kg⁻¹ (Buchman, 2008) which suggests that toxic effects would not be observed on the organisms within the reservoir sediments.

Like Pb and Cu, significant amount of Zn was also available in the Mn-Fe fraction which recorded an average concentration of 0.25 g kg⁻¹. This constitutes about 44.08% of total mass of Zn in the sediments. This observation may be attributed to the fact that Pb, Zn and Cu have similar valency and therefore have the affinity to bind to the same site. The residual fraction phase recorded an average mass percentage of 23.672% of total mass. The amount of zinc present that can induced ecological risk (0.35 g kg⁻¹) was above the TEL of 0.123 g kg⁻¹ indicating potential bioavailability of this element and also higher than the PEL value of 0.315 g kg⁻¹ (Buchman, 2008) which suggests that toxic effects would be observed in the organisms within the reservoir. This observation confirms the results of the I_{geo} which suggested that Zn is considered as a pollutant in the reservoir's sediments.

CONCLUSION

The sediment samples are generally acidic and have relatively high OM content. Sediments pollution loads which was assessed using geo-accumulation index revealed that the sediments in the Owabi reservoir are moderately polluted with Pb and Zn. Different geochemical fractions were operationally defined by an extraction sequence that followed the order of decreasing solubility. The Mn-Fe fraction was the most abundant pull for all of the metals except Fe. The results of the sequential extraction and risk assessment code were used to evaluate the potential mobility and environmental significant of Zn and Pb present in the sediments. The data showed that Pb poses a low environmental risk while Zn poses a high environmental risk.

Factor analysis performed on the metals identifies three major factors which showed high loading for Pb, Zn and Cu in factor 1, Fe and Zn in factor 2 and Fe and Cu in factor 3. Site S₁, S₃ and S₂ recorded the highest factor score for factors 1, 2 and 3, respectively indicating that these sites are the have high concentrations of these metal and therefore have a high probability of being polluted with these metals.

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