



Speciation of selected heavy metals in some abandoned mining pond sediments of Barkin-ladi Lga, plateau state Nigeria

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Abstract

Industrial and anthropogenic activities have resulted in high levels of heavy metal contents in some environmental aquifers such as mining abandoned ponds in like that in Barkin-ladi, thus creating imbalance in the biotic and abiotic regimes of the ecosystem. This study reveals the level and concentration of some selected heavy metals in the mining ponds which includes Cadmium (Cd), Chromium (Cr), Nickel (Ni) and lead (Pb). Sediment samples from these selected ponds were obtained and various fractions of the elements were produced by sequential extraction of the sediment samples using the modified Tessier *et al.* (1979) procedures. Concentrations of these heavy metals were determined using Microwave Plasma Atomic Emission Spectrophotometer (MP-AES), Agilent 4210. The results obtained showed that Lead and Cadmium were present in all the sites and fractions except for Cd were it was very low in all sites. Mean value were in the order of Pb > Cd > Ni > Cr with mean concentrations (mg/kg) of Cd = 0.023±0.003, Cr = 0.004±0.002, Ni = 0.008±0.002, Pb = 0.136±0.007. Results also indicated that Cd and Cr are predominantly available in all fractions 1 – 9 and 3 respectively. Cd and Pb shows significant positive correlation, indicating likely existence either as similar specie or same point source. The presence of Lead in all sample sites shows that Lead is possibly associated with Tin, since study areas were all abandoned tin mining site. The research generally reveals that the heavy metals determined were in potentially available forms that could pose serious health problems to the agricultural and aquatic systems, especially Pb, Cd and Cr.

Keywords: Barkin-ladi, heavy metals, speciation, sediment

1. Introduction

Plateau state is one of the oldest mining areas in Nigeria (Jordao *et al.*, 2006.)^[1]. Minerals from the state and some others had been some of the main financial resources of Nigeria up to early 1960's. When petroleum was discovered, attention was then diverted. Today, these mining sites still remain, either as unclaimed alluvial deposits or large pools of water, which has opened up opportunities for dry season farming and other agricultural uses. The extraction and processing of mining ore deposits involves large amount of mineral waste. These mining wastes contain heavy metals which are potentially toxic to human life and environment. Mining industries throughout history has seriously caused immense environmental pollution in industrialized and developing countries (Aucamp, 2003).

Heavy metal pollution is one of the major environmental problems in the world, and present everywhere in the modern industrial environment (Mohammed, 2008). Some of these metals are natural components of the soil and present mainly in the form that are available for organisms (Ross, 1994). Anthropogenic activities such as industrial, agricultural, mining, domestic, construction and population growth have resulted in high levels of contaminants in the environment, thus creating imbalance in the biotic and abiotic regimes of the ecosystem (Nangbes *et al.*, 2015; Ping *et al.*, 2013; Ashraf *et al.*, 2012)^[3]. This has remained as a stabbing problem in the minds of environmental and agricultural scientists, since these heavy metals, which are unlike biodegradable contaminants are persistent in affecting the biophysical population of our

environment. Metals occur naturally in the earth's crust, and their contents in the environment can vary between different regions resulting in spatial variations of background concentrations. According to the environmental Data report of the United Nations Environmental Program (UNEP 1993), there is an increasing awareness that the health of population is at risk from pollution hazard, an amount which far exceed the world's total accumulated mineral garbage.

In order to protect the aquatic life community, comprehensive methods for identifying and assessing the severity of sediments contamination have been introduced, since the determination of total concentration of heavy metals are not the best indicator of their mobility, bioavailability and toxicity (Lim and Kiu, 1994; Bunzl *et al.*, 1999; Korfali and Jurdi, 2010). The nutritional value of a food containing a given mineral depends not only on its content, but also on its bioavailability (Luana *et al.*, 2015)^[15]. Analytical measurements expressed as total content of specific metal in an environmental and biological material are insufficient. Therefore, one of the most important significance of speciation analysis is the qualitative and quantitative signature it has given to specific metal species, which could be employed in the assessment of the index of toxicity impacts of elements. Speciation analysis is an important present-day analytical tool particularly used for the elucidation of the chemical form(s) as well as the quantitative estimation of a specific element when conducting toxicological and biochemical investigations (Nsikak *et al.*, 2013)^[25].

Sediments are vital components of aquatic ecosystems in which toxic metals accumulate through complex physical and chemical adsorption mechanism which depend on the nature of the sediment matrix and the properties of adsorbed compounds (Abul *et al.*, 2007). The Sediments are normally mixtures of several components, including different mineral species as well as organic debris (Ghrefat and Yusuf, 2006). Sediment can act as both a sink and a source for contaminants. It reflects the quality of surface water as well as provides information on the transportation and fate of pollutant (Santchi, 1984; Finney and Huh, 1989).

The food plants whose examination system is based on exhaustive and continuous cultivation have great capacity of extracting elements from the soil. The cultivation of such plants in contaminated soil represents a potential risk since the vegetal tissues can accumulate heavy metals (Jordao *et al.*, 2016).

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues (Guala *et al.*, 2007). Chronic level ingestion of toxic metals has undesirable impacts on human and the associated harmful impacts become perceptible only after several years of exposure (Khan *et al.*, 2010).

The elements of great concern to this project include Cadmium (Cd), lead (Pb), Chromium (Cr) and Nickel (Ni). These elements have no beneficial effects in humans, and there is no known homeostasis mechanism for them (Vieira *et al.*, 2011; Draghici *et al.*, 2010). They are generally considered the most toxic to humans and animals; the adverse human health effects associated with exposure to them, even at low concentrations, are diverse and include, but are not limited to, neurotoxic and carcinogenic actions (Templeton *et al.*, 2000) [31] (Jomova & Valko, 2011; Tokar *et al.*, 2011; Castro-González & Méndez-Armenta, 2008; ATSDR, 2008, 2007, 2003a, 2003b).

Several sequential extraction have been developed by many researchers which are variant on the Tessier *et al.* (1979) [32] procedure in which the exchangeable metals and those nominally associated with carbonate, Fe-Mn oxides, organic material and silicate residues were extracted with different reagents in order to address this issue to estimate the amounts and proportion of metals present in different forms in sediment samples (Tessier *et al.*, 1979; Sobczynski and Siepak, 2001) [32]. Sequential extraction consists in the use of a number of extractors with different chemical properties that are progressively applied in a sample (Luana, *et al.*, 2015) [15].

Speciation study of heavy metals in bottom sediments of surface water reservoir are usually conducted in the areas subjected to anthropogenic factors or activities since an increased level of heavy metal presence is a consequence of man's activity (Sobczynski and Siepak, 2001). Speciation analysis is an important methodology in elemental analysis, which must be

considered in environmental and biophysicochemical systems for reliable and efficient assessment and monitoring of trace metals (Nsikak *et al.* 2013) [25]. Therefore, it is of importance to establish the degree of trace metal contamination and to discuss the origin of these contaminants in the sediments of the mining ponds. An analytical procedure involving Sequential chemical extractions has been developed for the partitioning of Particulate trace metals (Cd, Co, Cu, Ni, Pb, Zn, Fe, and Mn) into five fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual (Tessier *et al.*, 1979) [32].

Anthropogenic activities such as industrial and mining activities etc are source of heavy metals into the environment with potential health hazard to plants, animals and human. The use of mining ponds for irrigation pose great danger as the bioaccumulation of the heavy metals by vegetables and other edible aquatic lives introduce the metals into the food chain. Therefore, it is of important to establish the degree of trace metal contaminations in these bioata.

The objective of this study is to investigate the abundance of some heavy metals in bottom sediment within each chemical fraction and potential risk of sediment-bound metals to the aquatic and biotic systems.

2. Materials and Method

2.1 Pre-treatment and Sterilization of Apparatus

All glass wares used were washed with liquid detergent and rinsed thrice with distilled water followed by oven drying. Polyethylene sample bottles and Teflon beakers were washed with liquid detergent and rinsed with distilled water prior to sample collection (Ogunfowokan *et al.*, 1998, 2008) [26]

2.2 Description of sample sites

Barkin-ladi is a local government in Plateau state of Nigeria at latitude 9°32 north and 8°54 east. It has an area of 1,032km³. The speciation study covered seven mining ponds. They are one of the notable areas because of their large industrialization that potentially contribute to soil pollution. The locations of the sample sites are shown below

Table 1

S/No.	Site	Latitude	Longitude	Altitude (M)
1.	Lokojoro (Kassa)	09°33.907'	008°54.030'	1299
2.	Gonan Yashi	09°31.748'	008°54.091'	1295
3.	Marit	09°32.966'	008°53.173'	1287
4.	Mararaban Kantoma	09°30.869'	008°59.997'	1297
5.	Rakung	09°32.877'	008°53.115'	1289
6.	Ngwetti	09°33.009'	008°53.270'	1291
7.	Boyi	09°33.097'	008°54.230'	1294

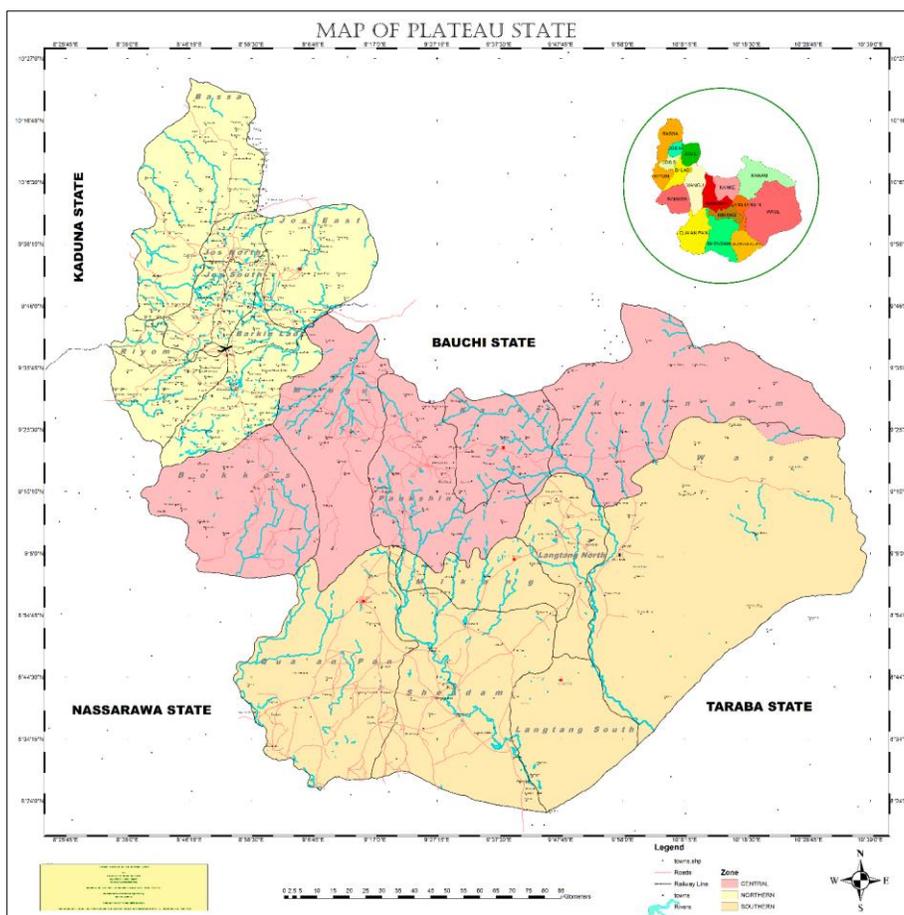


Fig 1: Map of Plateau State

2.3 Sample Collection/Preparation

The samples were collected at seven mining ponds spot at the depth of 15cm using stainless steel shovel. The collected dried samples were pounded with piston and mortar and kept in polythene bags in an oven. The oven dried samples were further exposed to air and dried to constant weight. The samples were the coning and quartering sampling technique until the desired amounts of laboratory samples were obtained. The samples were again oven dried at 105 °C and then pulverized using the Fritsch pulverizer, Pulverisette 7 machine. Finally, the pulverized samples were stored in clean labeled plastic bags and kept at room temperature until digestion was carried out.

2.4 Experiment Procedure

The procedure of Tessier *et al.*, (1985, 1979)^[32] was used for the speciation study except that water soluble and plant available fractions were included. Thus, the sediment samples were subjected to a nine-stage sequential procedure to extract and partition Cd, Pb, Cr and Ni, into water soluble, exchangeable, bound to carbonate, plant available, bound to Mn oxides, bond to amorphous Fe-oxide, bound to crystalline Fe-oxide, bound to organic matter and residual fractions. One gram of each soil sample was weighed and extractions were made through steps (F1- F9) by centrifugation and filtration at 10,000rpm placing the sample in polyethylene centrifuge tubes. Distilled water was used

to wash the residues following subsequent extraction in order to ensure selective dissolutions and to prevent possible interphase mixing between the extracts. All samples were run in duplicates.

F₁: Water soluble fraction. Water soluble metals were extracted with a solution of 50mL distilled at 28°C water for 2 hours. This forms the F_1

F₂: Exchangeable Fraction. The residue from F_1 was extracted with 25mL of 1.0M $\text{CH}_3\text{COONH}_4$ (pH=7.0). The suspension was shaken for 30 minutes at 28°C. Soil and extraction solution were thoroughly agitated throughout the extraction. The extracted metals were then decanted from the residual soil.

F₃: Carbonate Bound fraction. The metals bound to carbonate phase are affected by ion exchange and changes of pH. The residue of F_2 was extracted with 16mL of 1M sodium acetate/acetic acid ($\text{CH}_3\text{COONa}^+$) buffer with acetic acid (CH_3COOH) at pH 5 shaken for 5 hours at room temperature. The extracted metal solution was decanted from the residual soil. The residual soil was used for the next extraction.

F₄: Plant Bound fraction. The residue form F_3 was extracted by shaking with a solution mixture of 50mL of 0.025M HCl + 0.05M H_2SO_4 for 30 minutes at 28°C.

F₅: Mn Oxides Bound fraction. The residue from *F₄* was shaken for 30 minutes at 28°C with a solution of 25mL 0.1MNH₂OH·HCl in 25% CH₃COOH.

F₆: Amorphous Fe-Oxide Bond. The residue from *F₅* was extracted with 25mLof 0.2M (NH₄)₂C₂O₄ for 30 minutesat50°C using a water bath with occasional stirring.

F₇: Crystalline Fe-oxide Bond fraction. The residue form *F₆* was extracted using 25mLof 0.04M NH₂OH·HCl in 25% acetic acid and heated in a water bath with occasional stirring at 100°C for 6hours.

F₈: Organic matter Bond fraction. The residue from *F₇* was extracted with 1mL of 0.02M HNO₃ and 15mL of 30% H₂O₂. The mixture is then heated to 85°C for 5hourswith occasional agitation. A second 15mLof 30% aliquot was added and the mixture heated again to 85°C for 3hourswith intermittent agitation. After cooling, 5mLof 3.2M CH₃COONH₄ in 20%HNO₃was added and the samples diluted to 20mL and agitated continuously for 30minutes.

F₉: Residual fraction. The residue from *F₈* was digested with a mixture of concentrated HNO₃ and HClO₄ for 8hours. The levels of Cd, Pb, Cr and Ni in the worked-up samples were profiled using Microwave Plasma Atomic Emission Spectrophotometer (MP-AES), Agilent 4210 at thee Nation Metallurgical Development Center, Jos, Plateau State. Each determination was done in triplicate.

3. Results and Discussion

3.1 Results

Average results obtained were as displayed in Table 1 below. The

table indicates the average concentration of each metal in fraction of the various sample sites.

Table 1: Average concentration of elements in each Sample Site

Sample Sites	Element Concentration mg/kg			
	Cd	Cr	Ni	Pb
1	0.022±0.001	0.001±0.003	0.006±0.002	0.117±0.004
2	0.022±0.001	0.002±0.002	0.005±0.002	0.180±0.005
3	0.019±0.001	0.005±0.003	0.009±0.002	0.176±0.008
4	0.022±0.001	0.009±0.002	0.008±0.002	0.194±0.008
5	0.023±0.001	0.012±0.003	0.010±0.003	0.188±0.011
6	0.027±0.001	0.002±0.002	0.008±0.003	0.185±0.008
7	0.023±0.001	0.003±0.001	0.012±0.003	0.125±0.010
Mean	0.023±0.001	0.005±0.002	0.008±0.002	0.166±0.008

Table 2: Average concentration of elements in each fraction

Fractions	Element Concentration mg/kg			
	Cd	Cr	Ni	Pb
F1	0.023±0.000	0.006±0.001	0.003±0.002	0.228±0.006
F2	0.036±0.001	0.005±0.003	0.005±0.002	0.183±0.013
F3	0.033±0.001	0.011±0.003	0.011±0.002	0.237±0.006
F4	0.017±0.001	0.008±0.000	0.003±0.000	0.192±0.013
5	0.009±0.000	0.005±0.001	0.001±0.000	0.092±0.008
F6	0.011±0.000	0.002±0.001	0.002±0.000	0.107±0.005
F7	0.013±0.000	0.005±0.002	0.003±0.001	0.144±0.006
F8	0.018±0.001	0.001±0.000	0.003±0.001	0.185±0.006
F9	0.075±0.002	0.003±0.001	0.006±0.002	0.181±0.005
Mean	0.023±0.001	0.005±0.001	0.004±0.001	0.172±0.008

Table 3: Pearson Correlation Table

		Correlations									
		ST	Cd	Cr	Ni	Pb	FR	FCr	FNi	FCd	FPb
ST	Pearson Correlation	1	.553	.242	.817*	.112	1.000**	-.409	-.372	-.746	-.748
	Sig. (2-tailed)		.198	.601	.025	.811	.000	.362	.411	.054	.053
	N	7	7	7	7	7	7	7	7	7	7
Cd	Pearson Correlation	.553	1	-.160	.055	.098	.553	-.920**	-.742	-.675	-.765*
	Sig. (2-tailed)	.198		.732	.906	.834	.198	.003	.056	.096	.045
	N	7	7	7	7	7	7	7	7	7	7
Cr	Pearson Correlation	.242	-.160	1	.397	.567	.242	.256	-.194	-.403	-.348
	Sig. (2-tailed)	.601	.732		.378	.185	.601	.579	.677	.370	.445
	N	7	7	7	7	7	7	7	7	7	7
Ni	Pearson Correlation	.817*	.055	.397	1	-.122	.817*	.050	-.085	-.601	-.432
	Sig. (2-tailed)	.025	.906	.378		.794	.025	.915	.856	.153	.334
	N	7	7	7	7	7	7	7	7	7	7
Pb	Pearson Correlation	.112	.098	.567	-.122	1	.112	.065	.067	-.002	-.299
	Sig. (2-tailed)	.811	.834	.185	.794		.811	.890	.887	.997	.514
	N	7	7	7	7	7	7	7	7	7	7
FR	Pearson Correlation	1.000**	.553	.242	.817*	.112	1	-.627	-.169	.240	-.418
	Sig. (2-tailed)	.000	.198	.601	.025	.811		.071	.664	.535	.262
	N	7	7	7	7	7	9	9	9	9	9
FCr	Pearson Correlation	-.409	-.920**	.256	.050	.065	-.627	1	.602	-.018	.522
	Sig. (2-tailed)	.362	.003	.579	.915	.890	.071		.086	.963	.150
	N	7	7	7	7	7	9	9	9	9	9
FNi	Pearson Correlation	-.372	-.742	-.194	-.085	.067	-.169	.602	1	.553	.674*
	Sig. (2-tailed)	.411	.056	.677	.856	.887	.664	.086		.123	.047
	N	7	7	7	7	7	9	9	9	9	9

FCd	Pearson Correlation	-.746	-.675	-.403	-.601	-.002	.240	-.018	.553	1	.400
	Sig. (2-tailed)	.054	.096	.370	.153	.997	.535	.963	.123		.286
	N	7	7	7	7	7	9	9	9	9	9
FPb	Pearson Correlation	-.748	-.765*	-.348	-.432	-.299	-.418	.522	.674*	.400	1
	Sig. (2-tailed)	.053	.045	.445	.334	.514	.262	.150	.047	.286	
	N	7	7	7	7	7	9	9	9	9	9

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

** . Correlation is significant at the 0.01 level (2-tailed).

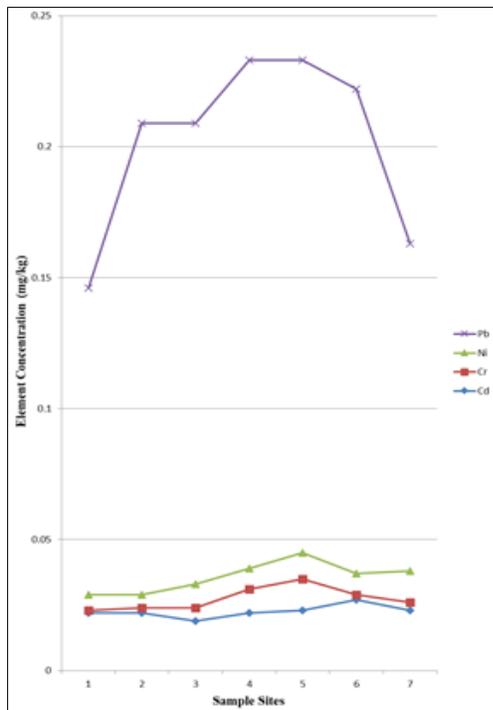


Fig 2: Mean Concentration Plot of elements in each Sample Site

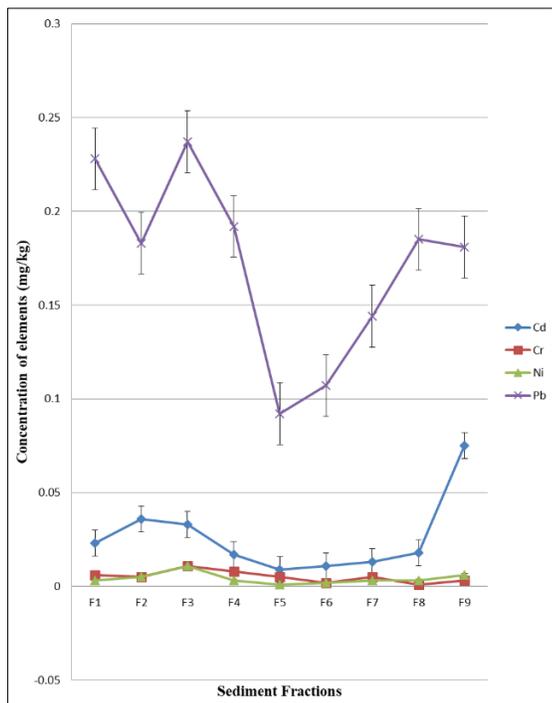


Fig 3: Mean Concentration Plot of elements in each fraction

Discussion

The speciation patterns of heavy metals in the bottom sediment at Barkin-Ladi mining ponds were based on the different sampling sites as shown in table 1 as well as the different speciation fractions generated as shown in table 2. These charts (Figures 2 and 3) represent the concentration of the metal species among the different sampling locations and fractions respectively. In all the fractions, Lead is predominantly high followed by Cadmium, then Nickel, while Chromium is the lowest. The concentrations of Chromium in all the fractions were almost similar. With respect to water soluble fraction, Cadmium and Nickel are conspicuously high in site 2, 3 and 5, while Lead is high, just as observed by other researchers (Kai *et al.*, 2018; Sharma *et al.*, 2015) [13, 29] in all the sites but is higher in site 7 was mostly in the forms bound to hydrated iron and manganese while the least amount of lead was in the fraction bound to organic matter and it practically did not occur in the exchangeable fraction (Welte *et al.*, 1983). Sherene *et al.* (2011) and Templeton *et al.*, (2000) [31] Korfali and Jurdi reported high percentage speciation of lead in the organic and sulphide fraction. The concentration of Ni and Cr are almost similar in all locations. The exchangeable fraction showed the highest concentration of Cr in site 5. Metal bound to carbonate showed that sample site 7 has the highest concentrations of Nickel, followed by site 5, 4 then 1, while the concentrations of Cr were almost similar for all the sites. Plant available fraction showed the highest concentration of Chromium in site 7 followed by site 5. The highest concentration of Cadmium was recorded in site 5. The trend in manganese-oxide fraction showed that the highest concentration of Cd and Ni occurred in site 1. The fractionation and bioaccessibility of heavy metals may have also been influenced by pH, cation exchange capacity, and organic matter (Kai *et al.*, 2018) [13] Cr was below detection limit at site 1, 2 and 7 respectively, while the concentration of lead was almost the same in all the sites.

The concentrations of Cd and Ni were high in site 1 followed by those in sites 1 and 3 respectively for amorphous iron-oxide fraction. The concentrations of Chromium were almost similar in the entire locations crystalline iron-oxide site 1 and 4 respectively. The organic matter fraction showed that concentration of Cd was high at site 4 whereas Ni had the same concentration at site 6 and 7. Cr was below detected at almost all the sites. On a contrary, lead was extremely high in site 4 compared to the others. In nearly all the metals, site 5 recorded the largest concentration carbonates fraction; fraction iron is exceptionally high in site 5 and 6. The residual fraction showed that Cadmium was very high in locations 2, 1 and 6, while Chromium was very high in site 4. Nickel was high in site 4 but low in site 1 and also below detection at site 2 and 7. Researchers (Nouri *et al.* 2008, 2011; Lim and Kiu, 1994) [22, 23] concluded that irrespective of the sampling sites, the speciation pattern of Lead indicates that more than 50% of the metal was associated with the

moderately reducible and easily reducible fractions. The co-precipitation with carbonate minerals is of importance for a number of metals such as cadmium and zinc (Frostner and Wittmann, 1983; Alloway, 1995).

The chart below shows that Lead has high concentrations in all the sample sites and highest in site four and this could mean or possibly be that the metal Lead is in association with Tin being an abandoned tin mining site.

The concentrations of the elements displayed a similar pattern for Ni, Cr and Cd, indicating same point source for the elements which is further confirmed by their positive correlation. Site 5 showed highest concentrations in all the elements except for Pb where the concentration of Pb is same in sites 4 and 5. The speciation result revealed that high levels of these metals studied (Mn, Fe, Cu, Zn, and Pb) were associated with exchangeable and carbonate bound fractions, pointing out that they are in potentially available forms and may pose serious problems to the reservoir ecosystem (Olutona *et al.*, 2012)^[28].

For the various fractions, the concentrations of Cd, Cr and Ni showed similar characteristic pattern; with Cr showing highest concentration in fractions 9, indicating that most of the element existed in the residual forms; followed by those in fractions 2 and 3. Cr and Ni gave similar regular and characteristic display of concentration pattern where the maximum is recorded in fraction 4 and the least in fraction 6. This similar characteristic behavior in the concentration patterns were further buttressed by their positive correlation. This indicated that Ni, Cr and Cd were either having same point source for the fraction of species. The concentration of Pb is distributed in all the sample fractions with the highest in fraction 5. Also, Cd and Pb were found to be highly associated with the labile fraction in all the sampling sites and thus posed a high risk of remobilization in the water system, concurring with the recent work of Sharma *et al.* (2015; Ogunfowokan *et al.*, 2013)^[29, 27]. This discrete and characteristic distribution in all fractions indicated that Pb concentration is varied in all the sediment samples.

The environmental impact of the nine speciation phases depends upon the ease of remobilization. The exchangeable and adsorptive, bound to carbonate and reducible phases are the most dangerous (Horsfall *et al.*, 1999). Table 3 revealed that the metals considered in this study sites and fractions have different entry route. Lead and Cadmium might be vulnerable, since both appear most in the residual. Further, the association of these metals being distributed in the iron/manganese-oxide, residual and oxidizable phase are in excellent agreement with metal speciation studies of sediments from other rivers and reservoirs (Calmano and Forstner, 1983). Metals bound in these different fractions will behave differently in the sedimentary and dia-magnetic environment, and therefore have different potential for remobilization and for uptake by biota (Fytianos and Lonrantonou, 2003).

The correlation value between Cr and Pb showed positive correlation of 0.567 which indicates strong correlation while Cr/Ni shows weak correlation of 0.397, with a 2-Tailed positive significance of 0.698 while a positive significant correlation of 0.870 is observed for Cr/Cd. This indicates that either Cr or Pb is either of the species of the same source with Sn. Whereas Ni/Cd has 2-Tailed weak correlation of 0.745 positive significance, which could be due to run-off.

Lead is negatively correlated with Nickel; this shows that both were not of the same source. The positive correlation between these metals shows that there was an association or interaction of these metals in the study area, and on the other hand, that these metals might have similar sources of input into the ponds, according to Miller and Miller (2000), a strong correlation between two variables or metals may be an occurrence of strong dependence of both variables on the same causal factor. This suggested that sources of the trace metals are essentially anthropogenic.

4. Conclusion/ Recommendation

4.1 Conclusion

This research revealed that the metals considered in this study exist in different form that could pose serious health problems to the agricultural and aquatic system within the sample sites having a prolonged operation within the vicinity of the aquatic system. Although, part of the metals was probably a contribution through anthropogenic means or possibly as associated with Tin, being an abandoned tin mining site.

4.2 Recommendation

The study reveals that the ponds are polluted with heavy metals which pose potential health hazards to the biota, thus the need for bioremediation strategy. Further studies should focus on application of novel technologies to recovery of studied heavy metals from contaminated pond sediments.

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