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The Impact of a River on the Water Quality of Nearby Wells: A Case Study of Aluko River, Ilorin, Nigeria

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ABSTRACT

Hand dug wells were sampled in 5 selected areas in the vicinity of River Aluko course, Ilorin. The ranges of the average value of the parameters studied are: 6.8-8.3 for pH; 325-524 mg/l for total hardness (TH); 0.039-0.69 for organic carbon content; 29-30 °C for temperature; 0.683-0.863 mg/l for total dissolved solids (TDS); 0.014-0.068 mg/l for total suspended solids (TSS); 0.701-0.914 mg/l for total solids (TS); 6.60-21.50 mg/l for total alkalinity; 0.73-1.90 mg/l for chloride; 0.129-0.273 mg/l for nitrate; and 0.008-0.243 mg/l for sulphate. All the trace metals except Fe and K were within the WHO standard for drinking water. The % bioavailable metals (F1 + F2 + F3) for Fe, Mn, Ni, Zn, Co, Cd and Cu ranges between 87.1 and 95.4, 20.7 and 78.4, 39.3 and 68.7, 42.5 and 65.8, 64.0 and 86.6 and 92.9, 88.2 and 92.9, 40.00 and 60.10 respectively. The proportion of the mean metals concentrations of the bioavailable metals follows the order Fe > Cd > Co > Ni > Zn > Cu > Mn and the % bioavailable metal for the five locations is in the order: Ikokoro > Baboko > Ita-Amodu > Opomolu > Edun. The assessment of the well sediment using enrichment factor, EF, and geoaccumulation index revealed that Co and Cd from all the sampling points were evidenced as having more enrichment and mostly due to anthropogenic sources; whereas, Mn, Ni, and Zn were enriched from natural sources.

Keywords: Bioavailability, Geochemical indices, Sequential extraction, Well-water

Introduction

Water is that chemical substance which is essential for every living organism to survive on this planet. It is needed by every cell of the organism's body to perform normal function. It covers 71% of the Earth's surface, mostly in oceans and other large water bodies, with 1.6% of water below ground in aquifers and 0.001% in the air as vapor, clouds and precipitation (Dunk *et al.*, 2005). Clean, fresh drinking water is essential to human and other life. It has been predicted that by 2025 more than half of the world population will be facing water-based vulnerability, a situation that has been called 'water crisis' by the United Nations (Kulshre-Shtha 1998). A report suggests that by 2030, water demand will exceed supply by 50% in some developing regions of the world (Long *et al.*, 1998). Pure uncontaminated water does not occur in nature. Water pollution is the second most important environmental issue next to air pollution and it is any change in the physical, chemical and biological properties of water that has a harmful effect on living things. A more serious aspect of water pollution is that which is caused by human activity and industrialization (Zufiaurre *et al.*, 1998, Salami and Adekola, 2002). There are also various micro-biological agents that include bacteria, viruses and protozoa which can also cause

water pollution and may cause various water-borne diseases.

The physicochemical characteristics that are commonly measured in water quality assurance are the temperature, transparency, colour, turbidity, total dissolved solid, dissolved oxygen, pH, chemical oxygen demand, nitrates, cations and anions. These parameters, usually, provide valuable information on the quality of the water, the source(s) of variations and their impact on the functions and biodiversity of the water body (Djukic *et al.*, 1994).

Heavy metals are toxic to biota even at relatively low concentrations. These metals can be bioaccumulated and hence, biomagnified in living organisms that ingest it. Some of these metals can impart distinctive odour and taste on the well water while some others may alter the physiological functions of the cells. Cadmium is accumulated in mineralizing tissues (Salami and Adekola, 2002) destroying erythrocytes and causing nausea, salivation, skeletal deformation, diarrhea and muscular cramps (Mohan and Singh, 2002). The maximum permissible standard for metals concentrations in drinking water varies depending on the metal toxicity to life. The lower the permissible limit value, the higher the toxicity of the metal species to life. The WHO recommended the maximum acceptable concentrations of zinc in

drinking water as 5.0 mg/l, 0.5 mg/l for manganese, 0.2 mg/l for nickel, 0.003 mg/l for cadmium and 2.0 mg/l for copper (WHO, 1996). Many of the sediments in our rivers, lakes, and oceans have been contaminated by heavy metal pollutants. Many of the contaminants were released years ago while other contaminants enter our water every day mainly through industrial and municipal discharges (Zufiaurre, *et al.*, 1998). Poorly constructed wells including hand-dug wells and some older wells without sanitary seals may allow contaminants to seep into the well.

The behavior of metals in water is a function of sediment composition and the chemistry of water. The rate of metals adsorption and desorption is, however, controlled by the chemistry of the water system (Adekola *et al.*, 2010). The phase-specific binding forms of trace metals in sediments determine its mobility and bioavailability (Szarek-Gwiazda, 2005). The partitioning of these metals in water and sediments is an important factor in the understanding of their behavior and environmental fate. Over the years, chemical extraction methods are relied upon as operational tools for the establishment of metal forms in soils and sediments.

The sequential extraction protocols provide information about the origin, mode of occurrence, biological and physicochemical availability, mobility and transportation of trace metals (Tokalioglu *et al.*, 2000, Dundar and Altundag, 2007, Dundar *et al.*, 2012). The Tessier scheme (Tessier *et al.*, 1979) or its modified forms (Polyak and Hlavay, 1999) and the three-step sequential extraction protocol of the Community Bureau of Reference, BCR (Tokalioglu *et al.*, 2003, Dundar *et al.*, 2012) are the common extraction scheme for metal speciation studies. In developing nations, both solid and liquid wastes are poorly managed. Banks of streams and rivers are often used as dumpsites, thinking that when it rains, it will be washed away. This study was, therefore, conducted on the wells in the vicinity of Aluko river that runs through Ilorin Township and which was often loaded with domestic waste discharges with the view to knowing the impact on the nearby wells. The wells provide the community around it with about 50 % of the domestic water need of the people.

Materials and Methods

Sampling

Representative sample of water were collected from five hand-dug wells that are within 50m range to river Aluko that transverse the area (Table 1). Samples were collected in polyethylene bottles which were pre-washed with hot detergent, rinsed in de-ionized water, then soaked in 10% HNO₃ over night and finally rinsed with de-ionized water three times. The samples for metals determination were stored in one litre polyethylene

bottles and acidified with 3 ml of 1:1 HNO₃ and HCl. These samples were subsequently stored at 4°C prior to analysis to minimize physico-chemical changes (Ademoroti, 1996).

Analysis

The water pH, conductivity and total dissolved solids (TDS) were measured *in-situ* prior to acidification with the aid of multi-functional water quality parameter field instrument, HANA portable pH/EC/TDS/temperature proof tester model HI 98129. The instrument was calibrated against standard solution before use. The TSS was determined gravimetrically while TS was determined by summing TDS and TSS together. The Temperature was measured with the aid of a mercury bulb field thermometer, total hardness by complexometric titration with EDTA, alkalinity by titrimetric method (Ademoroti, 1996). The phosphate, sulphate, nitrate, chloride and residual chlorine were all determined spectrophotometrically using standard methods (Ademoroti, 1996).

The wells sediments were collected from five different locations (Table I) with the aid of a stainless bottom grab. The content of the grab was emptied into a black polythene bag at each location. Plants, metals or plastics debris in the sediments were removed manually prior to chemical treatment. The sediment samples were air-dried, grounded with the aid of pestle and mortar, sieved and thoroughly homogenized. The homogenized sample was used for sequential extraction (Adekola *et al.*, 2010). The filtrates from each step of extraction were analyzed for heavy metal contents using Alpha-4 model of AAS.

Quality Assurance

Analyses were carried out in triplicates and the average of the data was used for data analysis. Results were compared with blank and at intervals; the standard and the blank were re-ran to validate the working conditions of the instrument. Quantification of metals was based on calibration curves of standard solutions of the metals. The minimum detection limit of the AAS used for the metals Fe, Zn, Mn, Cu, Pb, Ni, Cd and Co are 12.4, 0.8, 0.17, 0.05, 0.06, 0.10, 0.02 and 0.001mg/L respectively.

Pollution Index

Enrichment factor (EF) is commonly used for pollution assessment of water and sediment (Adekola *et al.*, 2010, Zhang *et al.*, 2009, Yap and Pang, 2011). The EF approach can discriminate trace metal source to natural weathering processes of bedrock or anthropogenic. The analysis of EF data could provide information on the status of environmental contamination. In the calculation of EF, Al or Fe are often used as normalizers. In this study Fe was used since Al was not analysed. The

EF approach used in this study was based on the reported (Muller, 1979, Zhang *et al.*, 2009, Yap and Pang, 2011) mathematical expression given as

$$EF = \frac{\left(\frac{Me}{Fe}\right) Sample}{\left(\frac{Me}{Fe}\right) Background} \quad (1)$$

Where $\left(\frac{Me}{Fe}\right) Sample$ is the metal Me to Fe ratio in the sample of interest and

$\left(\frac{Me}{Fe}\right) Background$ is the metal Me to Fe ratio in the natural background

Geoaccumulation index, I_{geo} , (Muller, 1979, Raju *et al.*, 2012) is another means of assessing anthropogenic influence on trace metal contamination of sediments. The Igeo compares the extent of metal contamination with respect to global standard and is often used as the basis of classification of sediment to different degrees of

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \quad (2)$$

Where C_n is the mean measured total concentration of the examined metal 'n' in the sediment; B_n is the average (crustal) geochemical background value for concentration of metal 'n' in fossil argillaceous sediment and sometimes referred to as 'average shale'; 1.5 is the background matrix correction factor due to lithogenic effect (Taylor, 1964). Because we did not have the background values of metals of interest in the studied area, we adopted the average crustal values for the metals [Fe, 46,700 µg/g; Pb, 20 µg/g; Zn, 95 µg/g; Ni, 68 µg/g; Cr, 90 µg/g; Mn, 850 µg/g; Cu, 45 µg/g; Co, 29 µg/g; and Cd, 29 µg/g] for the calculations of EF and Igeo as commonly used (Yap and Pang, 2011; Raju *et al.*, 2012).

Results and Discussion

All the well water sampled exhibited pH and temperatures within the WHO limits of natural water for domestic uses. The Ita-Amodu and Edun wells gave the highest values of pH while Opomalu sample had the least value, although, all the values are within the WHO standard. The average pH ranged between 6.8 and 8.3 while there was no marked difference in temperatures which ranged between 29 and 30 (Table 2). The organic carbon content of the sediment ranged between 0.039 to 0.69% which is expected of water with low load of organic matter. The pH and organic matter load are important variables in the determination of dissolution, adsorption and desorption of trace metals from or onto sediment and change of concentration of the same between water and sediment. The average TDS, TSS and TS values were very low and within the WHO limits, hence it poses no problem to human health (WHO, 1996). The TH ranged between 325 to 524mg/l. Generally, water having 0-75mg/l $CaCO_3$ is soft, 75-150mg/l $CaCO_3$ moderate and greater than 300mg/l $CaCO_3$

pollution (Förstner *et al.*, 1990). There are 7 classified grades (0 - 6), the lowest grade 0 reflects the background concentration while highest grade 6 reflects 100-fold enrichment of the sediment (Table 3). The Igeo is calculated from the mathematical expression

as hard. Based on this, the water samples in this study are classified as hard water. Eczema is a risk factor associated with exposure to hard water which is attributable to deposition of metal or soap salt residues on the skin that are not easily rinsed off and which can cause contact irritation (Thomas and Sach, 2000).

The average values (Table 2) for the concentrations of NO_3^- , Cl^- , and SO_4^{2-} in well water were within the WHO standard. These ions have no health implication on the users. The WHO has no standard for phosphate, however, a safe limit of phosphate concentration in uncontaminated water in the range of 0.01 - 0.03mg/L had been established (Izonfuo and Bariweni, 2001). Therefore, the phosphate concentrations (Table 2) in the wells sampled exceeded this limit.

The Environmental Protection Agency (EPA) standards for drinking water classified iron and manganese presence under the Secondary Maximum Contaminant Level (SMCL) standards. The Secondary Standards are based on taste, odour, colour, corrosives, foaming and staining properties of water (WHO, 1996). The SMCL for Fe and Mn in drinking water are 0.3mg/L and 0.5mg/L respectively. Water with less than these concentrations should not have an unpleasant taste, odour, appearance or side effect caused by a secondary contaminant (WHO, 1996). The average value for Fe concentrations in all locations exceeded the SMCL limit for drinking water while the average value for Mn concentrations in all locations, except Baboko sampling point, were within the SMCL limit for drinking water. The average values for the concentrations of Zn, Cu and Na were within the WHO limits for drinking water while Ni, K and Cd, except in Edun where it was below detection level, exceeded the WHO limits for drinking water

(WHO, 1996). All the samples were high in Ni and its mean values exceed the WHO standard of 0.05mg/L. Virtually all the samples were within the WHO standard of 30mg/L, 0.05mg/L and 2.0mg/L for Zn, Pb and Cu respectively. The measurable amount of Na in all the samples (Table 4) ranges from 7.02 to 15.60mg/L which is more than the value of about 0.20mg/L in rain and snow but is within WHO (1996) standard for drinking water.

The determination of the trace metal concentrations in the sequential fractions allows for the prediction of the mobility order, bioavailability and toxicity of the trace metals considered in river Aluko. The concentrations of Fe, Mn, Ni, Zn, Co, Cd and Cu in the bottom sediments of the wells samples were fractionated to understand their relative mobility. The mean metal concentrations (mg/L) for the extraction stages: exchangeable metals, carbonate-bound metals, Fe-Mn oxide metals, organic and sulphide metals and residual fraction are reported in Table 5. These fractions represent the ease of leachability of bound metals into well water when the conditions changes. These metals were further grouped into bioavailability (exchangeable, bound to carbonates, bound to Fe-Mn oxide fractions) and non-bioavailable (organic and sulphide bound and residual fractions) based on relative mobility and toxicity to aquatic environment and are reported in Table 6. Under the anoxic conditions for the bottom river sediment, metals bound to oxides of Mn and Fe are more thermodynamically unstable and are more easily leached than the metals bound to organics and sulphide. The combined conditions of pH and of the redox potential required for the release of metals bound to organics and sulphide fraction are not easily attainable (Adekola *et al.*, 2010).

When metal fractions in the various phases are considered (Table 6), the proportion of the mean metal concentrations to bioavailable metals follows the order Fe > Cd > Co > Ni > Zn > Cu > Mn. The bioavailable fraction represents the fraction that when the right pH and redox conditions are favourable, the trace metal will become soluble and can be taken up by aquatic plants or ingested by animals. Although, the contribution of Cd to the bioavailable fraction is low (Table 5), the non availability of it in the residual fractions except at Ita-Amoudu sediment sample makes it a serious source of environmental concern. This observation suggests that Cd is highly mobile and it is a cumulative toxic metal in mammals when its presence is above threshold (Tokalioglu *et al.*, 2003). In an uncontaminated setting, the residual fraction is a significant geochemical phase for trace metal retention. The relative content of a metal in the residual phase can be used as a measure of the contribution of natural sources and also of the degree of contamination of the fluvial system, with a lower percentage indicative of higher levels of

pollution (Singh *et al.*, 2005). In the present study, the amount of metals associated with this phase was significantly low or absent which suggest high degree of pollution from sources other than natural. The differences in human activities around the sampling locations are the major contributor to the differences in the mean concentrations of the trace metals. The mean bioavailable metal (%) relative to total metal contents for the five locations is in the order: Ikokoro > Baboko > Ita-Amodu > Opomolu > Edun.

The relative percentage contributions of each metal to the bioavailable fraction are represented by Figs. 1a-1e. The contributions of Fe and Cd were higher while Cu and Mn were the least to bioavailable fraction in all the sites. Comparing the results of the water and the sediments, it is obvious that concentration of the bottom sediments were much higher than that of the water samples, which exceed the tolerable range set by WHO (1996). This may be due to the effect of flowing river in the vicinity of the wells carrying domestic and commercial solid wastes, which are rich in heavy metal or may also, be due to geological properties of the sediments. The presence of these metals in the soil will dissolve gradually into the water medium.

The application of the established pollution indices to our data gave an insight to the degrees and various sources of the trace metals input into the wells. The EF values for the trace metals are presented in Table 5. The degrees of enrichment based on the classification of Acevedo-Figueroa *et al.* (2006) were used. The trace metals, Mn, Ni, Zn and Cu can be classified as no enrichment from anthropogenic source as $0.5 \leq EF \leq 1.5$ and the metal fractions originate essentially from crustal materials or natural weathering processes. Both Cd and Co belong to the minor enrichment class of $2.0 \leq EF \leq 3$. There was minor contribution from non crustal materials or weathering processes into pollution. The EF values in this site are in the decreasing order Co > Cd > Ni > Cu > Zn > Mn.

The EF values (Table 3) for Mn, Ni and Zn in the Ita- Amodu well indicated that there was no anthropogenic enrichment. Therefore, the presence of these trace metals were entirely from crustal materials or natural weathering processes; whereas, there was minor anthropogenic enrichment to Co and Cd (Zhang and Liu, 2002 and Acevedo-Figueroa *et al.*, 2006). The trace metals in Baboko well could be classified into 3. Although, Co is moderately enriched, a significant of it could have been delivered from non-crustal materials or non-weathering processes; Cd and Cu have minor enrichment from anthropogenic source; while Mn, Zn and Ni entirely from crustal material on natural weathering processes.

The Opomolu well gave a similar pattern of enrichment of Mn, Zn and Ni with that of Ita-

Amodu well in which the EF values were within the contributions that were entirely from crustal materials or natural weathering processes ($0.5 \leq EF \leq 1.5$) (Zhang and Liu, 2002). The $EF_{Cu} < 3$ is an indication of minor enrichment from anthropogenic source while EF_{Co} and EF_{Cd} ($EF = 5-10$) is an indication that there were moderately severe enrichment from non-crustal materials or non-natural weathering processes (Acevedo-Figueroa *et al.*, 2006). Most of the trace metals (Mn, Zn, Ni and Cu) in Edun well originated from crustal materials or natural weathering processes. The $EF_{Cd} < 3$ indicating that these trace metals have minor enrichment while that of $EF_{Co} > 3$ had moderate enrichment from non-crustal material or non-weathering processes.

On the basis of Igeo classification in Table 3, all the trace metals studied from all the well sites as reported in Table 5 had the $I_{geo} < 0$ which is an indication of an unpolluted to moderately polluted sites (Muller, 1981; Yap and Pang, 2011).

Conclusion

Sediments in wells within 50m vicinity of River Aluko actively accumulate trace metals from both natural and anthropogenic origin. The % bioavailable metals ($F1 + F2 + F3$) for Fe, Mn, Ni, Zn, Co, Cd and Cu ranges between 87.1 and 95.4, 20.7 and 78.4, 39.3 and 68.7, 42.5 and 65.8, 64.0 and 86.6 and 92.9, 88.2 and 92.9, 40.00 and 60.10 respectively. The mean bioavailable metal (%) relative to total metal contents for the five locations is in the order: Ikokoro > Baboko > Ita-Amodu > Opomolu > Edun. The contribution of metals bound to organic and residue were high in non-bioavailable metal content. The combination of geochemical indices gave a better interpretation of the sequential fractions. Thus, classification based on the degree of bioavailability is only useful for metal pollution load, while geochemical indices provide an insight into the source of pollution. The seven wells are moderately polluted with Co and Cd significantly delivered from non-crustal or non weathering processes. Generally, the wells pollution due to Mn, Ni, and Zn were entirely from crustal or natural weathering processes. Therefore, it is concluded that the indiscriminate dumping of municipal solid wastes into a nearby river course had impacted negatively on the quality of the wells. It is recommended that wells within 50 meters from pollution source should be abandoned and future wells should be constructed beyond 250 meters from pollution source. Adequate solid wastes disposal method should be adopted, phasing out open dumpsites to safeguard public health from water borne diseases. Based on these results, citing of wells within the study range to this river for the purpose of drinking and domestic uses is undesirable.

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Table 1: Description of sampling points referenced with global positioning system (GPS)

S/ No	Locations	Description	GPS Locations
1	Opomolu	Near the bridge	N08° 29.470' and E004° 33.548'
2	Edun	Along Edun road	N08° 29.375' and E004° 33.401'
3	Ikokoro	Just beside Ikokoro bridge	N08° 29.353' and E004° 33.272'
4	Ita-Amodu	Ita-Amodu, under the bridge	N08 29.286' and E004° 33.033'
5	Baboko	Baboko bridge along Abdul-Azeez Atta road	N08° 29.153' and E004° 32.343'

Table 2: Mean of some Physico-chemical Parameters of Well Water from Different Locations

Parameter	Ikokoro	Ita-Amodu	Baboko	Opomalu	Edun	WHO 1993
pH of soil sample	7.6	8.3	6.8	7.1	8.0	6.5-9.2
Temperature (°C)	29	30	30	29	30	28-30
% Organic Carbon	0.27	0.52	0.67	0.039	0.16	
CEC meq/100g	388.85	236.92	217.56	95.11	218.21	
TSS (mg/l)	0.014	0.043	0.068	0.057	0.051	
TDS (mg/l)	0.687	0.783	0.787	0.684	0.863	
TS (mg/l)	0.701	0.826	0.855	0.741	0.914	500
Total Alkalinity (mg/l)	11.6	13.2	21.5	10.1	6.6	250
Chloride (mg/l)	1.1	1.5	0.73	1.9	1.3	200
Acidity (mg/l)	3.8	3.5	2.8	1.9	3.0	
Hardness (mg/l)	387.5	524	464	325	422	300-500
Phosphate (mg/l)	0.20	0.34	0.41	0.51	0.70	
Nitrate (mg/l)	0.157	0.210	0.273	0.129	0.136	10
Sulphate (mg/l)	0.012	0.017	0.0082	0.243	0.0082	200

Table 3: Geoaccumulation Index (I_{geo}) and pollution Intensity (Muller, 1981, Yap and Pang, 2011)

I_{geo} Value	I_{geo} Class	Pollution Intensity
0	0	Unpolluted
0-1	1	Unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	Moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	Strongly to very strongly polluted
>5	6	Very strongly polluted

Table 4: Metal concentrations in well water samples (mg/L)

Parameter	Ikokoro	Ita-Amodu	Baboko	Opomalu	Edun	WHO 1993
Fe	3.96	1.57	5.85	3.83	29.62	0.30
Mn	0.11	0.14	1.10	0.06	0.27	0.50
Ni	1.12	0.60	0.91	0.67	0.52	0.07
Zn	0.19	0.15	0.71	0.10	0.18	5.0
Co	0.04	0.03	0.01	0.02	0.02	
Cd	0.01	Nd	0.01	0.02	0.02	0.005
Cu	0.03	0.03	0.04	0.02	0.07	2.0
Pb	Nd	Nd	Nd	Nd	0.02	0.05
Na	15.60	12.48	7.02	14.04	15.60	200
K	10.40	6.00	2.40	6.00	4.00	10.00

Table 5: Mean metal content (mg/L) for five step sequential extraction in the five locations and pollution indices

Location	Fraction	Fe	Mn	Ni	Zn	Co	Cd	Cu	Total Metal
Ikokoro	Exchangeable metal	462.4	1.50	0.73	0.38	1.43	0.16	0.26	466.86
	Carbonate-bound metal	965.1	5.26	0.30	0.41	1.22	1.79	0.28	956.36
	Fe-Mn oxide metal	38.83	0.28	0.44	0.30	0.31	0.12	0.12	36.49
	Organic & sulphide metal	11.74	1.42	0.16	0.11	0.07	0.06	0.06	13.61
	Residual metal	22.69	0.16	0.99	nd	0.03	0.23	0.23	24.10
	Total metal	1496.76	8.62	2.62	1.21	3.06	2.21	0.95	
	EF		0.32	1.20	0.40	3.29	2.38	0.66	
	Igeo	0.01	0.01	0.01	0.01	0.03	0.02	0.01	
Ita-Amodu	Exchangeable metal	1123.6	2.68	1.08	0.82	1.10	0.14	0.55	1129.97
	Carbonate-bound metal	454.6	2.95	0.37	0.41	1.04	1.71	0.32	461.4
	Fe-Mn oxide metal	65.84	0.36	0.41	0.32	0.34	0.14	0.13	67.54
	Organic & sulphide metal	21.70	7.16	0.12	0.24	0.11	0.04	0.14	29.51
	Residual metal	25.05	0.51	0.11	0.38	0.04	Nd	0.47	26.56
	Total metal	1690.79	13.66	2.09	2.17	2.63	2.03	1.61	
	EF		0.45	0.85	0.63	2.51	1.93	0.99	
	Igeo	0.01	0.01	0.01	0.01	0.03	0.02	0.01	
Baboko	Exchangeable metal	949.3	3.32	1.12	1.31	1.08	0.17	1.08	957.38
	Carbonate-bound metal	265.4	1.91	0.44	0.49	1.00	1.69	0.44	271.37
	Fe-Mn oxide metal	27.21	0.65	0.46	0.62	0.52	0.15	0.21	29.82
	Organic & sulphide metal	21.96	8.05	0.13	0.17	0.21	0.05	0.17	30.74
	Residual metal	50.01	0.99	0.12	0.49	0.04	Nd	0.63	52.28
	Total metal	1313.88	14.92	2.27	3.08	3.37	2.06	2.53	
	EF		0.49	0.62	1.15	4.13	2.53	2.00	
	Igeo	0.01	0.01	0.01	0.01	0.04	0.02	0.02	
Opomalu	Exchangeable metal	325.6	0.28	0.34	0.15	0.40	0.03	0.20	32.70
	Carbonate-bound metal	46.64	0.60	0.43	0.30	0.96	1.60	0.22	50.75
	Fe-Mn oxide metal	18.83	0.22	0.31	0.33	0.31	0.14	0.09	20.23
	Organic & sulphide metal	19.10	2.82	0.10	0.17	0.15	0.02	0.15	22.23
	Residual metal	17.02	0.34	0.21	0.11	0.44	Nd	0.39	18.11
	Total metal	427.19	4.26	1.39	1.06	1.86	1.79	1.05	
	EF		0.55	1.19	1.22	7.01	6.75	2.55	
	Igeo	0.00	0.00	0.01	0.00	0.02	0.02	0.01	
Edun	Exchangeable metal	971.80	2.45	0.67	0.43	1.59	0.13	0.37	977.44
	Carbonate-bound metal	244.20	0.31	0.49	0.34	1.00	1.97	0.22	248.53
	Fe-Mn oxide metal	11.94	0.05	0.31	0.34	0.26	0.13	0.06	13.09
	Organic & sulphide metal	20.58	5.68	0.07	0.13	0.16	0.03	0.20	26.85
	Residual metal	33.32	0.43	0.17	0.07	0.97	Nd	0.22	35.18
	Total metal	1288.40	8.92	1.71	1.31	3.98	2.26	1.07	
	EF		0.38	0.91	0.50	4.98	2.83	0.86	
	Igeo	0.01	0.00	0.01	0.01	0.04	0.02	0.01	

Key:

F1 – Exchangeable metal fraction; F2 - Carbonate-bound metal fraction

F3 – Fe-Mn oxide metal fraction; F4 – Organic and sulphide metal

F5 - Residual metal fraction; Nd – Not detected.

EF- Enrichment factor

Igeo- Geoaccumulation index

Table 6: The % Bioavailable and % Non-bioavailable fractions

Location	Fraction	% Fe	% Mn	% Ni	% Zn	% Co	% Cd	% Cu	% Total Metal
Ikokoro	Bioavailable	95.4	78.4	39.3	65.8	86.6	88.2	51.9	95.10
	Non-bioavailable	4.63	21.6	60.7	34.2	13.4	11.8	48.1	4.90
Ita-Amodu	Bioavailable	93.4	41.2	66.5	56.7	81.4	91.1	54.0	92.79
	Non-bioavailable	66.65	58.8	33.4	43.3	18.6	8.89	45.9	7.21
Opomolu	Bioavailable	92.5	35.1	68.7	58.5	64.0	90.3	60.1	91.56
	Non-bioavailable	7.55	64.9	31.3	41.6	36.0	9.71	39.9	8.44
Edun	Bioavailable	87.1	20.7	55.4	42.5	73.1	91.1	40.0	84.74
	Non-bioavailable	12.9	79.4	44.6	57.6	26.9	9.10	60.0	15.26
Baboko	Bioavailable	94.9	30.9	67.8	58.8	65.1	92.9	55.2	94.22
	Non-bioavailable	5.14	69.1	32.2	41.2	34.9	7.08	44.9	5.78

KEY: Bioavailable = F1 + F2 + F3

Non-bioavailable = F4 + F5

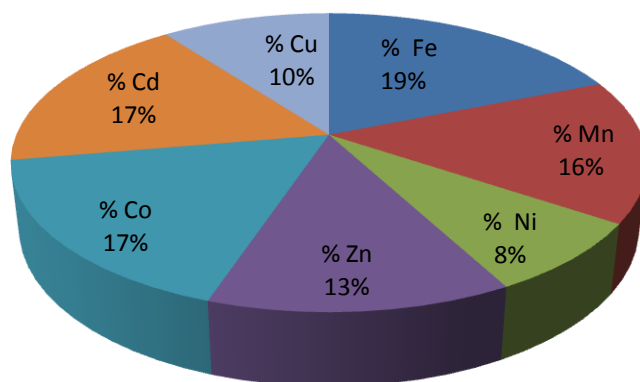


Fig. 1a: Bioavailable fractions in Ikokoro

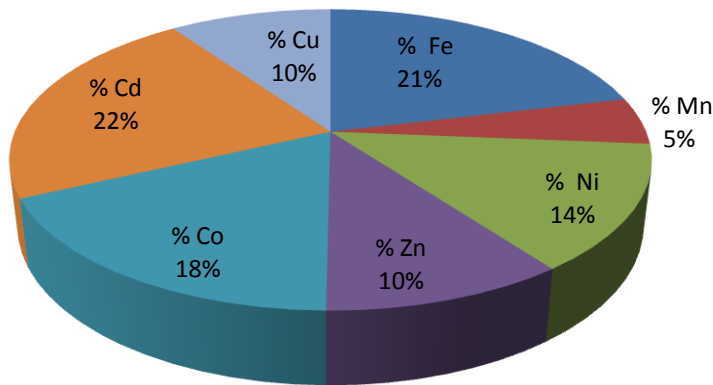


Fig. 1b: Bioavailable fractions in Ita-Amodu

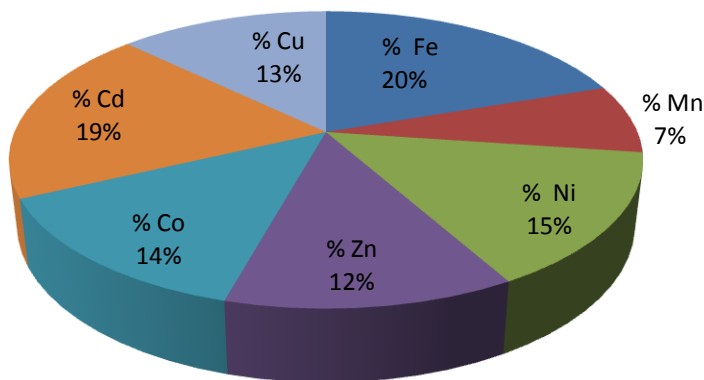


Fig. 1c: Bioavailable fractions in Opomolu

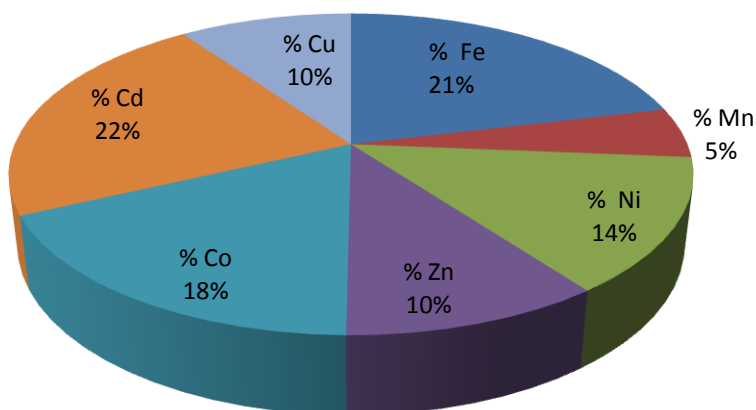


Fig. 1d: Bioavailable fractions in Edun

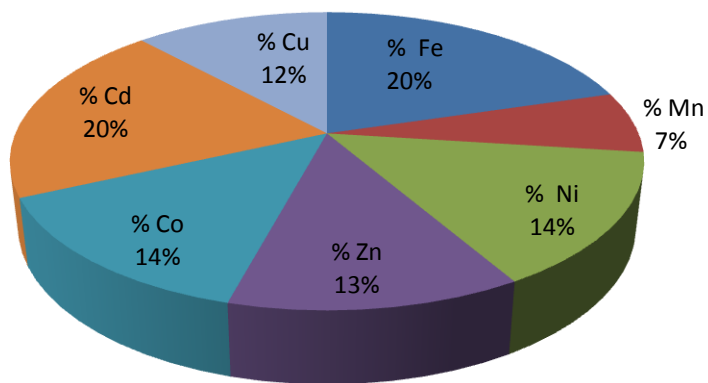


Fig 1e: Bioavailable fractions in Baboko