



Asian Journal of **Biochemistry**

ISSN 1815-9923



Academic
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Research Article

Influence of Soil Properties on Metal Availability: A Case Study of Arufu and Akwana Mine, Taraba State, Nigeria

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Abstract

Background and Objectives: To assess the level of interactions between soil pH, organic matter, carbonate cation exchange capacity and trace metals present in mine soil. Hence determine the release and concentrations of these metals in the soil as may pose serious health challenges to both man and animals. This study aimed at the influence of soil properties on trace metals availability. **Material and Method:** Soil digests were determined by using Varian AA240 Atomic absorption spectrophotometer equipped with Zeeman's background correction (Varian, New Jersey, USA). **Results:** The study reveals that soil pH in Arufu and Akwana are within the range of 6.42-7.54 and 6.42-7.53, respectively while organic matter content ranged from 0.278-0.493 in Arufu soils, 0.212-0.483 in Akwana soils. The average availability of metals in soils are in the order: Mn>Pb>Zn>Cu>Co>Cr. Arufu and Akwana soils displayed similar inter-element Pearson correlation which revealed a very high positive correlation with high significant probability ($p<0.01$) between Zn/Cu. and a weak positive correlation with high significant probability ($p<0.05$) between Zn/Cr. **Conclusion:** The positive relationship observed is an indication of possible geochemical and probable mineralogical association between these metals.

Key words: Soil, availability, trace metals, concentration, mine, acidic, alkaline

Citation: G.G. Yebpella, B. N. Hikon, A.M. Magomya, Y. Joshua and M. Paninga, 2020. Influence of soil properties on metal availability: A case study of Arufu and Akwana mine, Taraba State, Nigeria. Asian J. Biochem., 15: 28-35.

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Environmental pollution with toxic trace metals is now a global phenomenon. As a result of the increasing concern on the potential effects of the metallic contaminants on the environment and human health, the research on fundamental, applied and health aspects of trace metals in the environment is also increasing¹. Industrial processes that release a variety of trace metals into waterways include mining, smelting and refining². The tailings, sands and waste rocks deposited close to the mining area are the main sources of heavy metals in the environment^{3,4}. Large amounts of these heavy metals are released into soil as a result of increased anthropogenic activities such as agricultural practices, waste disposal and energy consumption leading to the contamination of the soil⁵. Soil is a natural reservoir of metals whose concentrations are associated with several factors such as biological and biogeochemical cycling, parent material and mineralogy, soil age, organic matter, soil pH, redox concentrations and microbial activities⁶. Different mechanisms are responsible for the adsorption and retention of heavy metals in polluted soils: specific adsorption, cation exchange, organic complexation and co-precipitation⁷. The distribution coefficient of trace metals varies due to pH, redox conditions, ionic strength and dissolved organic matter concentrations. Factors affecting the speciation and fate of cobalt in water, sediments and soil include organic ligands such as humic acids, anions, pH and redox potential. Single and sequential extraction methods are applied for assessment of currently available and potentially available metal fractions in soil. There are several kinds of extraction solutions, the most commonly used being 0.001 to 1 M salt solutions (CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, NaNO_3), weak acids (acetic acid, citric acid) and strong complexes: Ethylene Diamine Tetra Acetic acid (EDTA) and Diethylene Triamine Pentaacetic acid (DTPA). Extraction methods are based on complexometric reactions between extractants and metals^{8,9}. The physico-chemical parameters of soil have been reported to have a profound influence on the mobility and availability of heavy metals¹⁰. In view of the above, the study was therefore aimed at the influence of soil physical and chemical properties on metal availability.

MATERIALS AND METHODS

Description of study area: The study areas, Arufu and Akwana are district in Wukari Local Government area of Taraba state, north eastern Nigeria. These areas are 10 km from each other. The areas have been a mining fields for galena and table salts

till date. Wukari is located between latitude $7^\circ 51' 0''$ North and $9^\circ 47' 0''$ of the Greenwich meridian and is about 200 km away from Jalingo the state capital and is bounded by Plateau state in the North, Benue state in the Southwest.

Collection and preparation of soil samples: The samples for this study were collected on 16th February, 2018. Stratified sampling technique was applied for soil sample collection¹¹ with little modification. Under this sampling technique, sample areas around Arufu mining fields were broken into subgroups that are 100 meters apart and are designated as ARA, ARB, ARC, ARD, ARE while those around Akwana mining fields were labelled AKA, AKB, AKC, AKD and AKE, respectively. Three sample areas were mapped out and samples were collected randomly from each subgroups. A 50 g each of soil samples were collected at the depth of 0-15 cm. The sample of approximately equal size were pooled together to form composite samples for the area. Samples were thoroughly mixed to obtain representative samples which was dried at room temperature for 3 days. This was followed by grinding and sieving through a nonmetallic sieve with mesh size of 2 mm diameter. The air dried soil formed the sample for extraction and analysis which were stored in glass bottle at room temperature. The same method was used for other subgroups and study area.

Determination of Soil pH: Hydrogen ion concentration was determined by using the method described by McLean¹². In this method, 20 g of fine sieved soil into a glass beaker followed by addition of 20 mL of deionized distilled water then stirred gently to enhance H^+ (Hydrogen ions) release from soil and allowed to stand for 30 min. A pH meter, HANNA Instrument, (model HI 8014), Limena, Northern Italy was used to determine the pH.

Organic carbon: Soil organic carbon was determined by using the Walkley-Black method¹³. A portion of 5.0 g soil sample each was weighed into 250 mL Teflon beakers. Each of the sample beakers was subjected to rapid dichromate oxidation by addition of 50 mL potassium dichromate (0.5 M $\text{K}_2\text{Cr}_2\text{O}_7$) and 2.5 mL concentrated sulphuric acid in 5% FeSO_4 . The resulting solution was swirled and allowed to stand for a while to reduce the heat generated by exothermic reaction. The sample was boiled gently for 30 m at 150°C followed by addition of water to the digestive mixture to halt the reaction. Phosphoric acid (H_3PO_4) was added to the digestive mixture when cooled to eliminate interference from Fe^{3+} that may be present. Excess $\text{Cr}_2\text{O}_7^{2-}$ was titrated with 0.25 M Ferrous

ammonium sulphate by using barium diphenylamine sulphonate as indicator. Considering that the average content of carbon in soil organic matter is equal to 58%. The conversion factor 1.724 was used to calculate the percentage of organic matter from the content of organic carbon.

Determination of Cation Exchange Capacity (CEC) and extraction of exchangeable cations: Cation exchange capacity was determined by weighing 5.0 g of the dried soil into a previously cleaned 50 mL beaker followed by addition of 25 mL of 1 M KCl solution. The soil suspension in the beaker was thoroughly stirred and filtered into a 100 mL collecting bottle using a Whatman filter paper. After complete draining of the liquid portion, the residue was further leached thrice with 25 mL KCl in turns until 100 mL of the leachate was collected. By means of a measuring cylinder, 25 mL of the leachate was transferred into cleaned 50 mL beaker and a solution of 1 mL Sr (NO₃)₂ was added to it. The leachate was then used for atomic absorption spectrophotometric determination of Ca and Mg while flame photometer was used for the determination of Na and K¹⁴.

Determination of carbonate content in soil: A portion of 10.0 g air dried soil sample was weighed into a 250 mL plastic conical flask followed by careful addition of 25 mL of 1 M HCl. The flask was covered with a watch glass and allowed to stand for 1 h with occasional swirling to mix the contents. The mixture was quantitatively transferred to a 100 mL volumetric flask, made-up to volume with distilled water and filtered into a clean dried flask using filter paper. Then, 20 mL of the clear liquid was transferred to a 150 mL Erlenmeyer flask, small portion of distilled water was added to it, allowed to boil for a while and cool for some minutes. About 6-10 drops of bromothymol blue was added and the solution was titrated hot with 0.2 M NaOH until the blue colour persists for 30 sec. Blank solution 20 mL was titrated simultaneously (blank was made by taking 25 mL 1 M HCl in 100 mL volumetric flask, diluted with distilled water and made up to mark) with 0.2 M NaOH¹⁵:

$$\text{Percentage carbonate in soil} = \frac{0.04(\text{blank} - T)}{W} \times 100$$

W = Weight of sample in gram

Blank = A solution without analyte

T = Average volume of acid in mL

0.04 = A factor for the carbonate determination

Investigation of trace metals availability: Trace metal availability were determined by using an extraction procedure for the determination of metals in environmental samples¹⁶. A portion of each sample in this study was extracted using 1 M hydrochloric acid. One gram of soil sample was mixed with 25 mL of 1 M HCl. The samples were placed on a shaker for 30 m and then heated to 60°C for 30 min with periodical mixing of acids and residue during the heating process. Vigorous boiling was avoided. After cooling, the samples were centrifuged for 30 min at 3000 rpm. The supernatants were analyzed for available trace metals (Co, Cr, Cu, Mn, Pb and Zn) by using the method above.

Statistical analysis: Data was subjected to statistical tests of significance by using the one way analysis of variance (ANOVA) to assess significant variation in the concentration of the trace metals in the soils sample across the sampling sites and fields. Probability less than 0.05 (p<0.05) was considered statistically significant. Correlation coefficient was used to determine the association between trace metals in the samples at α≤0.05. The statistical analysis was done by SPSS 20.0 for windows.

RESULTS AND DISCUSSION

The investigated physicochemical parameters in soils around the study areas (Arufu and Akwana) were represented in Table 1 below. Soil pH in Arufu ranges from 6.42-7.51, Akwana ranges from 6.25-7.53. The potentials of soil trace metals to form complexes with organic matter, mineral colloids and inorganic complexes depend on the soil solution reaction which determines their bioavailability for plant uptake¹⁷. The solubility of the trace metals that can occur as free hydrated cations generally increases with decreasing pH. Soil pH value ranged were interpreted as follows; <5.5 = Strongly acidic, 5.5-5.9 = Medium acidic, 6.0-6.4 = Slightly acidic, 6.5-6.9 = Very slightly acidic, 7.0 = Neutral, 7.1-7.5 = Very slightly alkaline, 7.6-8.0 = Slightly

Table 1: Physical and chemical properties of soils in the study and control areas

Mine field	pH	CaCO ₃ (%)	OM (%)	CEC (cmol kg ⁻¹)
ARA	6.42	1.44	5.49	101
ARB	6.43	1.64	3.45	110
ARC	6.73	2.12	2.46	120
ARD	7.54	1.68	2.28	140
ARE	7.51	2.48	1.44	145
AKA	6.25	1.56	2.21	107
AKB	6.42	1.88	5.40	120
AKC	7.46	2.08	3.44	110
AKD	6.95	1.72	3.48	140
AKE	7.53	2.28	6.49	142

CEC: Cation exchange capacity, OM: Organic matter, CaCO₃: Percentage calcium carbonate

Table 2: Concentrations ($\mu\text{g g}^{-1}$) of available trace metals in Arufu and Akwana soils

Samples	Co	Cr	Cu	Mn	Pb	Zn
ARA	0.560±0.022	ND	1.200±0.090	70.120±1.3200	39.300±0.9000	13.350±0.7800
ARB	0.260±0.090	ND	1.860±0.030	12.660±1.0000	37.910±1.0150	20.820±1.0450
ARC	0.620±0.080	ND	2.880±0.070	26.400±2.3130	38.250±1.0140	32.870±1.0750
ARD	0.530±0.420	ND	1.400±0.021	26.020±1.1160	11.340±2.0150	10.560±0.0350
ARE	0.520±0.084	ND	1.740±0.180	35.140±2.0130	25.320±0.0460	11.840±0.0900
AKA	0.890±0.100	ND	3.430±0.900	46.850±1.0120	46.290±1.7500	31.620±1.0190
AKB	1.290±0.090	ND	3.600±1.300	45.110±1.0340	35.330±0.0150	35.170±1.0850
AKC	0.780±0.120	ND	4.130±0.910	48.950±1.0320	14.260±1.3000	33.190±1.0680
AKD	1.090±0.015	0.350±0.012	1.830±0.035	16.490±1.0960	60.830±0.2180	90.010±0.9850
AKE	1.040±0.035	0.080±0.018	1.930±0.015	16.260±1.0260	60.570±0.1150	90.230±0.9500

ND: Not detected, ARA: Arufu mining field, AKA: Akwana mining field

alkaline, 8.1-8.5 = Medium alkaline, >8.5 = Strongly alkaline¹⁸. It is clear from these pH ranges, that soils from these study areas varied from very slightly acidic to very slightly alkaline. In acidic soils, the mobility and availability of trace metals is much higher than in soils with neutral and alkaline reaction. This is evident in soil samples ARA, ARB, ARC and AKA, AKB and AKD with very slightly acidic pH value in the range of 6.25-6.95 showing relatively high level of available metal content than soil samples ARD, ARE, AKD and AKE that are very slightly alkaline with pH value between 7.51 and 7.54 showing low value of available elements Pb, Zn, Mn, Cu (Table 2). The effect of pH on the availability of trace metals in the soil has been observed to vary with the content and type of organic matter and pH affects the sorption of metals cations on variable charge minerals^{19,20}.

Percentage calcium carbonate (CaCO_3) in soils varied from 1.44-2.48-1.56-2.28% in Arufu soil and Akwana soil. There is no significant difference between the carbonate content of the studied areas. The presence of free CaCO_3 generally reduces the solubility of trace elements, as CaCO_3 raises the soil pH²¹. Generally, percentage carbonate contents of soils in the studied areas increases with decrease cation exchange capacity. This is supported by Dohrmann²² that it may be due to the limitations of the measurement for soils containing minerals that are partly dissolved during the procedure of CEC measurement as calcareous particles.

Organic matter content were within the range of 2.28-5.49 in soils around Arufu study area, 2.21-6.49 in soils around Akwana study area. The relevance of organic matter to this study is therefore, its influence on availability and flux of trace metals in the soils. The results showed slightly higher organic matter content in Arufu soil than soil from Akwana. The percentage of organic matter determined in this work falls within the typical amount of organic matter in soil which varies from <1% in ordinary soils to 90% in mineral soils²³. The normal range of organic matter found signified that the trace metals in the soils would be available since trace metals are known to form complexes with organic matter which

influence their availability²¹. The concentrations of organic matter obtained in this work were higher than 1.13-2.5 1% reported by Fosu-Mensah *et al.*²⁴ in their findings. Organic complexes of Cu and Pb remain stable until pH 4 while complexes of Cd and Zn are less stable and dissociate when the pH is below 6. Soils high in organic matter therefore can bind metals efficiently even in acidic soil conditions. At pH>6 or 7, the concentration of metals in solution can increase due to the formation of soluble metal-organic complexes²⁵. Soils Cation Exchange Capacity was: 101-145 cmol kg^{-1} in Arufu study area, 107-142 cmol kg^{-1} in Akwana study area. The result revealed that soil from Arufu to have higher capacity of neutralizing the negative ions in soil colloids than soils from Akwana. The CEC range in the soils fell below the 100-300 cmol kg^{-1} range reported in the literature²⁶, although it depend on nature and composition of the soil. The presence of the organic matter may result from deposition of carbon containing compounds in the soil and or decay of organic materials. This acts as a reservoir for both essential and non-essential mineral elements for plant growth and development. Organic matter is a rich source of negative charges and therefore can make a significant contribution to the cation exchange capacity of soil²⁷.

The result of available trace metals determined in soil samples from the vicinity of Arufu and Akwana study areas were presented in Table 2 below.

The mean concentration of available trace metals in Arufu soil were in the range, Co: 0.26-0.58 $\mu\text{g g}^{-1}$, Cu: 1.20-2.88 $\mu\text{g g}^{-1}$, Mn: 7.12-35.14 $\mu\text{g g}^{-1}$, Pb: 11.34-39.30 $\mu\text{g g}^{-1}$, Zn: 10.56-32.87 $\mu\text{g g}^{-1}$ and the corresponding Akwana soil ranged from Co: 0.78-1.290 $\mu\text{g g}^{-1}$, Cr: 0.080-0.350, Cu: 1.830-4.130 $\mu\text{g g}^{-1}$, Mn: 16.26-48.95 $\mu\text{g g}^{-1}$, Pb: 6.570-46.29 $\mu\text{g g}^{-1}$, Zn: 9.010-35.87 $\mu\text{g g}^{-1}$, Sample AKB has highest concentration of available Zn (35.17 $\mu\text{g g}^{-1}$) and Co (1.29 $\mu\text{g g}^{-1}$). Concentrations of available Cu (4.13 $\mu\text{g g}^{-1}$) and Mn (48.95 $\mu\text{g g}^{-1}$) were high in sample AKC than there corresponding AKB and AKC, respectively. Pb and Zn showed the least concentrations in sample AKD and AKE compared to

ARD and ARE. Maximum level of available Pb ($46.29 \mu\text{g g}^{-1}$) is observed in sample AKA. The concentration of available Co was high in sample ADB, followed by AKD and AKE. The highest concentration of Co in Arufu was recorded in sample ARC with value $0.620 \mu\text{g g}^{-1}$. Cr concentration was below the detection limit of the machine, hence no available Cr in Arufu (sample ARA-ARE) and Akwana sample AKA-AKC, respectively. Generally, the concentrations of all studied elements were higher in Akwana samples (AKA-AKE) compared to Arufu sample (ARA-ARE). The high concentrations of these elements could be attributed to the excessive mining, agricultural and automobiles repairs activities in Akwana which than Arufu.

Results of the study of available trace metals in the soils showed in Table 2 above, revealed very high levels of available Pb, Zn and Mn in soils from the studied areas. This indicates good potentials of the dilute acid to extract available and potentially bioavailable trace elements in soil. Cu and Co were detected at lower concentration suggesting low presence of the available form of these metals. The low concentrations of Cr in AKD and AKE is due to their high pH level. This is supported by previous research of Avudainayagam *et al.*²⁸, that low solubility of Cr and strong retention on soil particle surfaces limits its bioavailability in soils with $\text{pH} > 5$. The results of available metals obtained in this work agreed with the findings of Rieuwerts²⁹, that the relatively low organic matter content of tropical soils suggests that it cannot be relied upon to retard the downward movement, or enhanced availability, also organic matter appears to be important in the retention of Cu and Pb and possibly Zn, as observed in temperate soils. It has been reported by Mesquita and Carranca³⁰ that the presence of dissolved organic matter in soil decrease Cu adsorption. The low values of Cu could due to the fact that it

is adsorbed stronger in polluted soils than in the spiked soils, as reported by Ottosen *et al.*³¹. The high concentration of Pb is attributed to the high carbonate content which generally released higher amount of Pb³². Accumulations of Pb tend to be associated with organic-rich layers; hence organic matter can be considered an important sink for Pb and other heavy metals in soils³³. This findings are in agreement with the results obtained in this work. Sample ARA, ARB from (Arufu) and AKA, AKB from Akwana showed high organic matter content which correspond to high availability of Pb as evident in Table 1 and 2. The low concentration of bioavailable cobalt is evident by Underwood³⁴ that cobalt deficiency is frequent on sandy podzols and also occurs on very acidic leached ferritic and peaty soils which may not provide sufficient amounts of Co to grazing ruminants depending on this source. As a consequence, Co deficiency is a potential problem primarily for grazing livestock in areas with soils of low plant-available Co concentrations³⁵. The average availability of trace metals in soils are in the order: $\text{Mn} > \text{Pb} > \text{Zn} > \text{Cu} > \text{Co} > \text{Cr}$.

Available metal concentrations obtained in this work displayed an inter-element Pearson correlation matrix in soil from the study areas (Table 3 and 4).

Trace metals displayed an inter-element Pearson correlation matrix in the soil from Arufu (Table 3). A very high positive correlation with high significant probability ($p < 0.01$) was observed between Zn/Cu and a weak positive correlation with high significant probability ($p < 0.05$) between Zn/Cr. A strong negative correlation was also observed between Zn/Co ($p < 0.01$). A high positive correlation ($p < 0.01$) was observed between Cu/Cr while between Cu/Mn, was observed at $p < 0.05$ level of confidence. The above observations reflected common association of Pb-Zn ores with other minerals. Under

Table 3: Inter-element Pearson's correlation matrix for Arufu soils

Arufu	Zn	Cu	Co	Cr	Mn	Pb
Zn	1					
Cu	0.614**	1				
Co	-0.377	0.016	1			
Cr	0.471*	0.514*	-0.020	1		
Mn	0.123	0.119	0.465*	0.340	1	
Pb	-0.213	0.059	0.445*	0.179	0.042	1

*Pearson's correlation significant at $p < 0.05$, **Pearson's correlation significant at $p < 0.01$

Table 4: Inter-element Pearson's correlation matrix for Akwana soils

Akwana	Zn	Cu	Co	Cr	Mn	Pb
Zn	1					
Cu	0.762**	1				
Co	0.488**	0.708**	1			
Cr	0.745**	-0.409	0.221	1		
Mn	0.311	0.582**	0.300	0.060	1	
Pb	0.064	0.028	0.426	0.390	0.081	1

*Pearson's correlation significant at $p < 0.05$, **Pearson's correlation significant at $p < 0.01$

acidic conditions Copper (II) ion (Cu^{2+}) is more soluble, but could be redeposited at a redox interface as covellite, chalcocite, native Cu and or copper oxide phases³⁶. Pb showed a particular behavior in soil from this study area. Negative correlation ($p < 0.05$) was observed between Pb/Co.

The inter-element Pearson correlation matrix in Akwana soil (Table 4) displayed by the heavy metals reveals a very high positive correlation with high significant probability ($p < 0.01$) between Zn/Cu and between Zn/Cr ($p < 0.05$) while a weak positive correlation with significant probability ($p < 0.05$) was observed between Zn/Co. The positive relationship is an evidence of chemical and mineral association among the metals involved. Similar trend in relationship was observed between Zn/Cu in Akwana and Arufu soils except for positive correlation that was found between Zn/Co in Akwana soil against the strong negative correlation observed in Arufu soil. The positive relationship observed is a pointer to possible geochemical and probable mineralogical association among these metals. The results of correlation study also revealed a weak positive relationship between Mn/Co ($p < 0.05$) which may suggest similar source of Mn and Co in the analyzed soils. A strong positive correlation was observed between Cu/Cr ($p < 0.05$) ($p < 0.01$). Pb only show a positive correlation with Co ($p < 0.05$) suggesting galena occurrence in the area may contain cobalt bearing ore or as one of its associated metals. A positive relationship was found to exist between Cr/Zn and Cr/Cu ($p < 0.05$). Pb have been implicated in many studies as a threat to vegetation and animals and ultimately affecting the quality of human life through food chain. The elevated levels of Pb, Cr, Zn and Mn in soils from Arufu and Akwana study areas are largely derived from the mineralogical soil background and mining activity³⁷.

CONCLUSION

Based on the results obtained, it is clear that soils from the study areas have similar pH ranges despite their distance apart. The pH varied from slightly acidic to very slightly alkaline. Generally, the concentrations of trace metals were higher in Akwana samples (AKA-AKE) compared to Arufu samples (ARA-ARE). The high concentrations of these elements in Akwana could be attributed to the excessive mining, agricultural activities and automobiles repairs in Akwana than Arufu. Hence the highly available metals may accumulate plant tissues and pose great health challenges to the inhabitants.

SIGNIFICANT STATEMENT

This study revealed that the high concentrations of Pb is attributed to the high carbonate content which generally released higher amount of Pb and its accumulations tend to be associated with organic-rich layers, hence organic matter can be considered an important sink for Pb and this can be beneficial for lead mining and relevant agricultural activities. This study will help researcher to uncover the critical areas of soil-metal complexity that may be of help to many researchers to explore. Hence, the mineralogy study of the area may be established.

ACKNOWLEDGMENT

The authors thank Mr. Godfrey G. S for his laboratory assistance.

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