ASSESSMENT OF SELECTED METAL LEVELS IN ISHIAGU Pb-Zn MINE DISTRICT SOILS AND *Oryza sativa*, SOUTHEAST, NIGERIA.

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ABSTRACT

Pollutants have a tendency to sequestrate into remote sites in different environmental matrices thereby reducing the level of available fraction for uptake in living organisms. We examined availability of metals by subjecting soil and rice plant samples from Ishiagu mining district to a sequential extraction procedure and subsequently analyzed the extracts using Atomic Absorption Spectrophotometer (AAS). Our results revealed that metals were moderately available in samples in the following decreasing order: Zn>Pb>As>Cd>Se>Cu. Though metal levels differed in rice plant samples compared to soil, we noted also that availability of these pollutants varied spatially among various study locations. Based on available acceptable range, copper and zinc were within tolerable limits while cadmium was in excess in some study locations. On the other hand, levels of lead in rice plant samples exceeded acceptable limits. Considering the levels reported from different locations, it is possible that metals were immobilized in soil organic matter or trapped in other forms. Though in general metal levels were within acceptable limits in our study locations, we recommend that deliberate steps be taken by authorities to curtail indiscriminate mining activities capable of polluting soils and farm lands. For this reason, farmers should be encouraged to plant safe cultivars since this rice variety is a known poor metal accumulator.

KEYWORDS: Heavy Metals, Soil, Rice Plants, Ishiagu, Mining District.

INTRODUCTION

Adverse effects of heavy metals and metalloids including Cd, Pb, Hg, As and Se in natural environment are of great concern (Adriano, 1986; 1992). In particular, heavy metals abound near former mine sites, dumps, tailing piles, and impoundments. Elevated levels of these pollutants have been reported in different environmental matrices including soil, sediment, water sources, and organic matter present in urban and industrial areas (Adriano, 1992).

In order to estimate potential effects due to exposure to elevated metal concentrations from natural weathering of mineral deposits or mining activities, a relevant fraction of the total elemental abundance in water, sediment, or soil is normally required. Briefly, bioavailability is a prediction of the contaminant fraction that is available for uptake in biological organisms, thereby exerting undesirable consequences. Typically, total concentration of a metal does not necessarily correspond with its bioavailability. For example, a sulfide mineral may be encapsulated in quartz or other chemically inert minerals, and despite highly total concentrations of such metal in sediment and soil (containing its minerals), it is not readily available to exert toxicity in biota. As a result, their associated environmental effects may be low (Davis *et al*, 1994).

Metals of major concern in bioavailability studies as listed by the United States Environmental Protection Agency (US EPA, 1988) are Al, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, and Sb (McKinney and Rogers, 1992). Other metals that are less emphasized because of reduced potential for human exposure and health associated consequences include Ag, Ba, Co, Mn, Mo, Na, Ti, V, and Zn. Apart from direct human exposures, metal contaminants can also accumulate in aquatic organisms as well as in terrestrial plants and animals, where they can adversely affect humans. Overall, the tendency of these metal contaminants to exert toxicity in biota is a complex function of total concentration, speciation and physico-chemical affinity, mineralogy, redox potential, temperature, total organic content (both particulate and dissolved fractions), and suspended particulate contents. Also, this includes other factors including volume of water, water velocity and duration of water availability particularly in arid and semi-arid

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environments (Luoma, 1989). In addition, poorly understood biological factors appear to strongly influence bioaccumulation of metals and hence tend to hamper the prediction of their bioavailability (Luoma,1989).

STATEMENT OF THE PROBLEM.

Soil constitutes a vital part of environmental, ecological and agricultural resources that requires adequate protection (Alloway, 1990). For this reason, determination of elemental status of cultivated lands is necessary to identify yield limiting deficiencies of essential micro-nutrients and polluted soils (Alloway, 1990). This is particularly necessary in Ishiagu area of South-Eastern Nigeria as the inhabitants are mostly farmers and large quantities of rice, yams and okro are produced, not only for local consumption but also for supplies to other parts of Nigeria (Ezeh and Chukwu, 2011). In addition, large proportion of the population is engaged in mining because of the presence of Pb-Zn lodes in the area.

In the past, several studies have investigated aspects of mineralization in Ishiagu area. These include notable works by Farrington (1952), Reyment (1965), Offodile (1976), Olade (1976), Ezepue (1984), and Kogbe (1989), which evaluated the nature and origin of ore-forming fluids including the underlying mechanisms of Pb-Zn mineralization. Even more recently, Ezeh and Chukwu (2011) investigated the consequences of pollution resulting from small-scale mining activities on surrounding agricultural soils. Considering the length of time and several physic-chemical processes that may influence contaminant speciation, partitioning and distribution, it is crucial to investigate how these factors can influence availability of Cu, Zn, Cd, Pb, Se and As in Ishiagu. This is particularly because these metals are perceived to originate from Pb-Zn ores in the veins and lodes available in the area.

OBJECTIVES OF THIS STUDY.

The objectives of this research are:
1.   To determine availability of Cu, Zn, Cd, Pb, Se and As in soil and rice plants from Ishiagu area, South-Eastern   Nigeria and compare values with acceptable limits;

2.   To determine the concentrations of the selected heavy metals in samples;
3.   To assess the extent of interaction between soil and rice from Ishiagu in order to compare measured physico-chemical parameters with acceptable standards.

DESCRIPTION OF STUDY AREA.

Ishiagu is located between latitude 5º55' and 6º00'N and longitude 7º30' and 7º35'E (Fig.1). This corresponds to the Universal Transverse Mercator (UTM) readings of Nothings between 654192 – 663431 and Eastings between 333977 – 343178, respectively. The entire mapped area covers Ishiagu, including Amagu, Ugwutangele, Ihietutu, Ngwogwo, Amokwe, Okwe, Ogwor, Amagu/Ihie, Amaeze, EguAmaeze, Amaeze/Eziator and Eziator areas. The total area is about 81km^2. The geology of the area comprises sequences of sandy shales with fine grained micaceous sandstones and mudstones that is Albian in age and constitutes the Asu River Group. The Shales are often calcareous and pyritic. There are also lenses of sandstone and limestone. The rocks are extensively fractured, folded and faulted. There are several isolated minor basic and intermediate intrusives, which are viewed as sills (Ezepue, 1984). Also, there are several Pb-Zn veins which are hosted by the gently dipping Azu River shales. The shale is often dark-grey and finely laminated with clay and siltstone interlayers. The fault zones are the main zones of mineralization. The mineralization is generally in open space fillings of series of steeply dipping fractures, which cut the regional fold axis of the Abakaliki Anticlinorium (Ezepue, 1984). The sulphide rich veins are confined to NE-SW trending fault zones, 10-30cm wide. The dominant constituents of the veins are galena and sphalerite in a gangue of siderite (Farrington, 1952). Soils in the area comprise reddish brown gravely and pale clayey soils derived from sandy shales. All the soils are residual. The red-yellow soils are derived from red and reddish-yellow earth formed by weathering and subsequent ferruginisation of the underlying sandstone units, the shales and the igneous rocks, which form the bedrock (Ezeh and Chukwu, 2011).
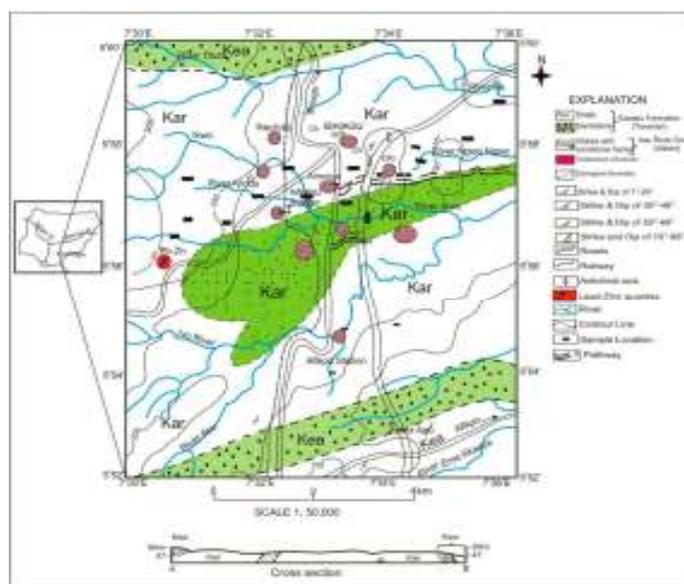
Fig 1.: Geology Map of Ishiagu area showing sampled points (Modified from Ezepue, 1984).

MATERIALS AND METHODS:
COLLECTION OF SOIL AND RICE PLANT SAMPLES.
Sampling was performed on a grid of approximately 100m. Soil samples were taken from the bottom of holes about 15cm deep, cut with a pick and cutlass. The depth is sufficient to characterize cultivatable top soil (Ezeh and Chukwu, 2011). About 100g of soil samples were collected in clean polythene bags and labeled adequately. In total, eighteen samples of soil were collected at locations $Soil_{1-18}$ that correspond with the sample locations, Rice $plant_{1-18}$, where rice plants were collected. All samples were transported back to the laboratory and adequately stored until analysis. Only *in situ* soil samples were collected and processed in the field. The sampling stations are shown in the geology map of Ishiagu area (Fig. 1). The exact positions with their respective names are shown in Tables 1 and 2.

Prior to collection of soil and rice plant samples, the sampling locations were established using a global positioning system (GPS) device. As a precaution against contamination of samples, clean hand gloves were used during sample collection. Also, the characteristics of each soil sample in terms of colour, friability and texture were determined.

PREPARATION AND ANALYSIS OF SOIL SAMPLES.
Leaves, roots and stones were manually removed from each soil sample and air-dried at room temperature for a week. Residual moisture was removed by heating at $105\pm5°C$ for 3 hrs. Subsequently, the soil samples were ground to fine powder in a tungsten-carbide swing mill for three (3) minutes and sieved through a 63 micron sieve. Each of the samples was extracted in 20ml of

$MgCl_2$ solution/CH_3COONa and shaken mechanically for 1hr at 20°C. The mixtures were filtered separately through Whatman filters and filtrates analyzed for Cu, Zn, Cd, Pb, Se, and As by Atomic Absorption Spectroscopy (VPG Bulk Scientific, Model 210) in the Department of Earth Sciences, Kogi State University, Anyimgba, Nigeria.

PREPARATION AND ANALYSIS OF RICE PLANT SAMPLES.
Plant samples analysis were based on a previous protocol by Allen (1989). Briefly, 1.0 g each of dry ground plant stem samples was weighed into a 100 ml Berzelius beaker and subsequently, 5ml of HNO_3 and 2ml of $HClO_4$ were added together and allowed to stand in a fume cupboard. The mixture was digested for 15mins after the appearance of white fume. The solution was allowed to cool and then filtered through a Whatman filter paper into a 50 ml volumetric flask. Each filtrate was then diluted to volume and analyzed by Atomic Absorption Spectroscopy (VPG Bulk Scientific, Model 210) in the Department of Earth Sciences, Kogi State University, Anyimgba, Nigeria.

RESULTS AND DISCUSSION

SOIL AND RICE PLANT SAMPLE ANALYSES.
Results from the analyses of soil and rice stem samples for Cu, Zn, Cd, Pb, Se, and As are shown in tables 1 and 2, respectively.

Table 1: Metal analysis of soil samples from Ishiagu

Sample no.	Location	Concentration (mgkg⁻¹)					
		Cu	Zn	Cd	Pb	Se	As
L1	Ugwutangele	1.34	8.24	1.70	5.21	1.08	1.58
L2	Ihietutu I	0.93	7.32	1.51	4.91	0.20	0.87
L3	Ihietutu II	1.20	7.91	1.62	4.96	0.22	1.01
L4	Ngwogwo	BDL	5.22	0.69	2.31	BDL	0.04
L5	Amokwe I	BDL	4.61	0.24	2.88	BDL	0.05
L6	Amokwe II	0.04	5.03	0.03	3.33	0.02	0.18
L7	Okwe I	0.03	1.12	BDL	3.40	0.02	1.19
L8	Okwe II	0.12	4.92	0.50	2.92	0.15	1.38
L9	Amagu I	0.11	4.96	1.20	3.11	0.13	2.45
L10	Ogwor	0.09	2.21	0.83	1.98	0.64	0.23
L11	Amagu II (Near Schl of Agric)	0.10	3.53	0.92	2.04	0.64	0.35
L12	Amagu/Ihie	0.04	4.22	0.42	0.92	0.61	1.18
L13	Amaeze	0.07	5.34	0.66	2.70	0.63	0.48
L14	EguAmaeze I	0.08	2.81	0.82	2.98	0.04	0.83
L15	EguAmaeze II	BDL	3.72	1.01	3.49	BDL	BDL
L16	Amaeze/Eziator	1.03	3.09	0.90	3.82	0.24	0.78
L17	Eziator I	0.01	2.01	1.20	2.18	BDL	BDL
L18	Eziator II	0.08	3.33	1.10	2.61	BDL	0.01

Standard tolerable limits   **60**   **70**   **5**   **10**   **30**   **25**

BDL = Below detection limit

Table 2: Metal analysis of rice plant samples from Ishiagu.

	Location	Concentration (mgkg⁻¹)					
Sample no.		Cu	Zn	Cd	Pb	Se	As
L1	Ugwutangele	BDL	5.22	BDL	0.22	0.38	0.23
L2	Ihietutu I	BDL	5.05	0.01	0.74	BDL	0.04
L3	Ihietutu II	BDL	5.21	0.02	0.78	BDL	0.03
L4	Ngwogwo	BDL	2.06	0.01	0.80	BDL	BDL
L5	Amokwe I	BDL	1.98	BDL	0.94	BDL	0.01
L6	Amokwe II	0.01	4.32	0.08	0.24	BDL	0.24
L7	Okwe I	0.02	1.60	BDL	0.38	BDL	0.38
L8	Okwe II	0.03	2.35	BDL	0.41	0.05	0.50
L9	Amagu I	0.04	3.21	0.02	0.27	0.04	0.22
L10	Ogwor	0.03	1.57	BDL	BDL	0.13	0.11
L11	Amagu II (Near Schl of Agric)	0.04	1.31	0.01	0.43	0.11	0.13
L12	Amagu/Ihie	0.03	3.09	0.02	1.04	0.09	0.03
L13	Amaeze	0.03	2.04	BDL	0.82	0.08	0.01
L14	EguAmaeze I	0.03	3.12	0.02	0.80	0.02	0.06
L15	EguAmaeze II	BDL	4.10	0.03	0.23	BDL	BDL
L16	Amaeze/Eziator	0.53	2.09	0.35	0.28	0.02	0.02
L17	Eziator I	BDL	1.24	0.43	0.10	BDL	BDL
L18	Eziator II	0.04	2.00	0.38	0.09	BDL	BDL
	Mean values	**0.07**	**2.86**	**0.12**	**0.5**	**0.10**	**0.14**

Recommended limits (FAO/WHO, 2002)   **20**   **50**   **0.2**   **0.2**   **-**   **-**

BDL = Below detection limit

Upon soil sample analysis, Zn levels were observed to be the most dominant followed by Pb, while Cu and Se were among the least (Table 1). We noted similar dominance of Zn after plant samples were analyzed. However, Pb did not seem to accumulate proportionately in plants and hence was detected in low levels as the remaining metals including As, Cu, Se, and Cd (Table 2). In the same way, Cu and Se levels were similarly low and reportedly below detection limits in seven and nine similar sampling locations, respectively (Table 2). Rice plant analysis revealed that Cd levels were the least ($0.01mgkg^{-1}$) in Ihietutu I, Ngwogwo and Amagu II; nonetheless, concentrations peaked at $0.43mgkg^{-1}$ in Eziator I, which has active as well as abandoned mines. We observed that Se was below detection limit in half of the sampled locations (Table 2). It is therefore not surprising that certain metals occurred in relatively high levels given the close proximity of sampling locations to existing mines. When one considers the level of a particular metal in soil compared to the amount eventually taken up and detected in rice plant samples, it is interesting to note that the elevated Zn levels detected in soil were available for uptake in rice plants in corresponding proportions (Tables 1 and 2). This may imply that total concentrations of certain metal contaminants may actually constitute close prediction of bioavailable fractions readily taken up in plants. For some metals, however, environmental processes including active sorption and partitioning into remote sites, solubility and speciation, biological activity and protein-specific affinity for certain metals can influence bioavailable fractions taken up in living organisms. In essence, it is the dissolved fraction that is perceived to exert deleterious effects in biota especially when these contaminants are present in ground or surface water, plant and vegetable tissues for livestock but also in invertebrate populations with a risk of trophic transfer across the food chain.

However, when one considers the tolerable limits set by various established standard organizations for Cu, Zn, Cd, Pb, Se and As in tropical soils and rice plants (Table 3), it is apparent that levels detected in the sampling sites were substantially below the thresholds. Similarly, Ezeh and Chukwu (2011) noted that other tolerable limits for these contaminants in rice and soil are generally lower than the levels proposed by Kabata-Pendias and Pendias (1984).

Table 3: Tolerable limits ($mgkg^{-1}$) for metals in soils.

Metal	WHO (1996)	Bowen (1979)	European Community (1982)	Kabata-Pendias and Pendias (1984)
Cu	36	30	50 – 140	60
Zn	50	90	150 – 300	70
Cd	0.8	3	1 – 3	5
Pb	85	35	50 – 300	100
Se	-	25	5 – 65	30
As	-	20	20 - 50	25

In some of the studied areas that include Ugwutangele, Ihietutu, Ngwogwo, Amokwe 1, Egu Amaeze and Eziator 1, soils and rice plants could be assumed to be deficient in Cu and Se considering the maximum concentration recorded coupled with measurements below detection limits in several sampling locations (Table 2). Though required in very small amounts, trace elements including Cu and Se are vital micro minerals and co-enzyme factors required to maintain cellular health and vitality. Occurrence of these metals in such trace quantities may be due to their characteristic potential to become highly mobile in a weathering environment such as the study site for this present work. Due to this phenomenon, therefore, it was challenging to detect Cu and Se in appreciable quantities (Mason, 1966). On the other hand, Zn was detected in substantial amount in both soil and rice samples in all study locations, though in levels below tolerability limits (FAO/WHO, 2002). This might be an indication that Zn has moderate availability and distribution. For a less physiologically relevant contaminant, it is possible that Cd adsorbed to surfaces of clay materials and organic matter, which reduced its mobility and potential bioavailability in soil (Kabata-Pendias and Pendias, 1984). According to the National Environmental Policy Institute report (2000), Pb tends to sorb strongly to soil particles under neutral to basic conditions. The implication is that under acidic conditions, Pb tends to exhibit biophilic characteristics, which might explain our observations in Amagu/Ihie. Though total concentrations of contaminants were determined in soil and rice plants in this study, the values do not necessarily translate to bioavailability and uptake in biological organisms including plants. This is because certain metals tend to become more or less available following variations in prevailing environmental conditions including pH and speciation, ageing and complexation, nature of biological membrane, and water chemistry. The fact that certain metals under study were not detected in measurable quantities in rice plants conforms to the observations of Chaney (1988), that a limit exists for entry of metallic substances into the food chain, especially in exchanges between soil and roots of plants. A complementary study opined that such interactions depend on the exchange dynamics between plants and soil pore water (Salomons, 1995). However, this phenomenon is believed to be controlled by soil physico-chemical characteristics including moisture contents, pH, E^h, temperature, total organic content and suspended particulates. Considering the influence of climate variations and soil types, one can infer that these factors control mobility and availability of environmental contaminants including heavy metals (David and Joel, 2002). Chaney (1988) argued that apart from the relative abundance of metal contaminants, their availability for uptake in plants is very crucial when considering their potential threat to

health. In fact, essential nutrients in bioavailable forms can influence and ultimately decrease plant uptake of non-essential but chemically similar elements such as As and Cd. Similarly, Chaney (1988) opined that Cu toxicity is related to low abundance of Zinc and Iron. On this basis, one may argue that the position of Cu as one of the least available metals studied is related to the high amount of available Zn.

In recent organic carbon-rich sediments, trapped interstitial fluids can commonly form a strongly reducing (anoxic) environment. Low redox potential in this environment can promote sulphate reduction and deposition of sulphide mineral (David and Joel, 2002). During diagenesis, much of the non-silicate-bound fraction of potentially toxic metals such as As, Cd, Cu, Hg, Pb, and Zn, can be co-precipitated with pyrite, form insoluble sulphides and become unavailable to biota (Morse, 1994). This is the likely fate of Cu, Cd, Pb, Se and As bioavailability which are in amounts below detection limits in the present study.

CONCLUSIONS

This study has shown that composition and physico-chemical characteristics of soils can influence partitioning of metals. Cu and Zn were detected in appreciable levels below their tolerable limits, whereas Cd and Pb occurred within toxic limits in certain parts of the study area but exceeded available limits in other locations.

Availability of metal contaminants is a function of their mobility and interactions with adsorption surfaces including clay and binding to organic matter. Therefore, environmental factors include pH, ageing and remote partitioning processes can influence release and availability of even strongly bound species for uptake and accumulation in living organisms. Considering that active or abandoned mining sites is often associated with high levels of contaminating metals, it is imperative to conduct assessment studies to determine the extent of pollution and associated risks to human and the environment. Ultimately, this study enabled us therefore to establish that in many cases, metal levels were within tolerable limits to reassure local residents and indigenous people of Ishiagu that speculated threat to community is minimal.

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