Research Paper

Comparative Techniques for Extraction of Ni, Cu, Zn and Pb in Guinea Corn Fields of Kaduna Metropolis, Nigeria

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Abstract-The potential migration of metals in soil systems is dependent on the chemical form of the metal which is necessary for estimating its biological availability, physico-chemical reactivity and transport in the environment and into the food chain. Chemical extraction procedures are able to predict the changes in the heavy metal mobility or bioavailability in soils. In this study, the Ni, Cu, Zn and Pb concentrations of soil samples from guinea corn fields in Kaduna Metropolis were determined using Flame Atomic Absorption Spectrometry (FAAS). Hot and cold extraction techniques were employed for the digestion and extraction of the soil samples using 0.05mol/L EDTA, 1.0mol/L oxalic acid and 1.0mol/L acetic acid. The results indicated that there is no significant difference between hot and cold extraction techniques for these metals in these reagents except for Zn in 1.0mol/L Oxalic acid where there is a significant difference between hot and cold extraction and that the hot extraction is superior to the cold extraction with a mean of 6.37 against 1.41.

Key words: *Guinea corn fields, Kaduna Metropolis, Chemical extraction, Flame atomic absorption spectrometry, heavy metals* etc.

Introduction

In many developing countries like Nigeria, soils are affected by mine waste disposal acid deposition, sewage sludge and other anthropogenic and agricultural activities.
Heavy metal contamination of arable soils through industrial and anthropogenic activities is a serious problem in Nigeria. The impact of contamination on the environment should be of scientific concern, in order to minimize the threat of soil and groundwater contamination [6].

Much research has been conducted on heavy metals contamination in soils from various anthropogenic sources such as industrial wastes [10] [1], automobile emissions [2], mining activity [4] and agricultural practice [5], [3].

The total heavy metal content in soils provide a convenient means of expressing a measure of pollution, numerous reports have highlighted that such measures are deficient in predicting toxicity of metal pollutants [10]. Heavy metals may be distributed among many components of the soil or sediment and may be associated with them in different ways [4]. The nature of the association is referred to as speciation. The general approach for the soil speciation studies has been to separate the soil using different chemical reagents or solvents fractions and, by analyzing each fraction, to determine the amount of element combined or associated with each soil fraction or phase [9].

A large number of extracting solutions have been used to assess plant available trace elements [7]. Single extractants may be divided into three main classes: (i) weak replacement of ion salts ($MgCl_2$; $CaCl_2$; NH_4NO_3), (ii) dilute solutions of either weak acids (acetic acid) or strong acids (HCl, HNO_3) and (iii) chelating agents (DTPA, EDTA). The first type of extractants is able to release into solution metals which are associated with the exchange sites on the soil solid-phase and hence can be considered as bioavailable [7]. The chelating agents, such as DTPA and EDTA, form complexes with free metal ions in solution and this reduce the activities of the free metal ions in solution.
In this research, the extractable Ni, Cu, Zn and Pb in soil samples were determined by Flame Atomic Absorption Spectrometry (FAAS). The soil samples were dissolved using the chemical reagents, EDTA, acetic and oxalic acids. The two extraction techniques employed were compared.

Material and Methods

A flame atomic absorption spectrophotometer model 8010 Youg Lin was used for the Ni, Cu, Zn and Pb determinations. In the extraction procedures, 1.0 M oxalic acid, 0.05M Na, EDTA and 1.0 M acetic acid were used.

Stock solutions of the metals were prepared as follows: Ni (1000mg/L) was prepared by dissolving 4.929g of $Ni(NO_3)_2.6H_2O$ in $10cm^3$ of 10% HNO_3, Cu (1000mg/L) was prepared by dissolving 3.7980g of $Cu(NO_3)_2.3H_2O$ in water, Zn (1000mg/L) was prepared by dissolving 4.569g of $Zn(NO_3)_2.6H_2O$ in $10cm^3$ of 10% HNO_3 and Pb (1000mg/L) was prepared by dissolving 1.599g of $Pb(NO_3)_2$ in $10cm^3$ HNO_3.

Preparation of Samples

The research covered seven agricultural sites in Kaduna, Nigeria. The sites are: Nasarawa (NS), Sabon Tasha (ST), Unguwan Mu'azu (UM), Tudun Wada (TW), Kakuri (KK), Mando (MD), Kabala West (KB) and Kachia (KC).

To evaluate the variability between the different agricultural soils, 63 soil samples were collected between October – November, 2008, 2009 and 2010 from the different agricultural locations. The soil samples were collected from the different areas enumerated at a depth of about 10cm below the surface [8]. Kachia, a town situated about 130 km away from Kaduna was taken as a control, Fig. 1(A, B).

The soil samples were crushed sieved and dried at 85^0C. All the analyses were carried out in the analytical laboratory of the department of Applied Science, College of Science and Technology, Kaduna Polytechnic, Kaduna – Nigeria.

Extraction of Soil

A modified extraction method developed by Yaman et al. (2005) was used. Soil extracts were obtained by shaking separately 5g of soil samples with $10cm^3$ of 0.05 mol/L NA_2EDTA (for carbonate and organically bound phases), 1.0 mol/L, oxalic acid (for oxide phases) and 1.0 mol/L acetic acid (for carbonate phases). The mixture was evaporated with occasional shaking on a hot plate. $4cm^3$ of 1.5 mol/L nitric acid was added to the remainder and centrifuged. This is referred to as hot extraction. The digest was diluted to $60cm^3$ and analyzed for Ni, Cu, Zn and Pb using FAAS model 8010 Young Lin. A blank digest was carried in the same way. $10cm^3$ of 0.05 mol/L Na_2EDTA, 1.0 mol/L Oxalic acid and 1.0mol/L acetic acid were added to 5g of separate soil samples at room temperature and centrifuged after stirring for 5 min. This procedure is referred to as cold extraction [8]. The digest was diluted to $60cm^3$ with water analyzed for Ni, Cu, Zn and Pb using FAAS model 8010 Young Lin. A blank digest was carried out in the same way.

Results and Discussion

The concentration of the metals in soils varies from one agricultural location to another, thus large number of samples was analyzed and the results treated statistically for meaningful correlation. The trace metal concentrations in soils were determined using atomic absorption spectroscopic method. The mean concentrations of the elements in soils and coefficient of variations were employed in assessing their levels. The independent sample t-test was employed to compare the hot and cold extraction techniques for each of the

trace metals; Ni, Cu, Zn and Pb for 0.05mol/L EDTA, 1.0mol/L Oxalic acid and 1.0mol/L Acetic acid in the guinea corn fields. This is represented in Tables 1 – 6.

For 0.05mol/L EDTA, $p = 0.282 > 0.05$, $p = 0.592 > 0.05$ and $p = 0.996 > 0.05$ for Ni, Cu, Zn and Pb respectively. Hence it was concluded that there is no significant difference between hot and cold extractions in the guinea corn fields studied.

Similarly, for 1.0 mol/L Oxalic acid, $p = 0.118 > 0.05$, $p = 0.906 > 0.05$ and $p = 0.433 > 0.05$ for Ni, Cu and Pb respectively and hence concluded that there is no significant difference between hot and cold extraction techniques for these metals in the guinea corn fields considered. On the other hand, $p = 0.000 < 0.05$ for Zn therefore, it was concluded that there is significant difference between hot and cold extraction techniques for this metal in the guinea corn fields studied. From the group statistics in Table 2, it is evident that the hot extraction is superior to the cold extraction with a mean of 6.37 against 1.41.

Finally, for 1.0mol/L Acetic acid, $p = 0.534 > 0.05$, $p = 0.144 > 0.05$, $p = 0.175 > 0.05$ and $p = 0.067 > 0.05$ for Ni, Cu, Zn and Pb respectively and hence concluded that there is no significant difference between hot and cold extraction techniques for these metals in the guinea corn fields studied.

Conclusion

Total trace metal composition of soil is of little importance in determining its uptake by plants and consequently, in contaminating the food chain since the different forms have different mobilities, bioavailabilities and potential environmental contamination potential. The results on heavy metal speciation in the study indicated that the soil samples collected from various areas contain varying amounts of the metal. The metal was distributed between residual, oxide and carbonate fractions. An increase of the metal concentration in some areas suggests that heavy use of agrochemical materials for planting activities could cause increase in the content of heavy metals in the soil.

Acknowledgement

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Table 1: Group Statistics for 0.05mol/L EDTA Extraction Techniques in Guinea Corn Fields

Metal	Method of extraction	N	Mean (mg/L)	Std. Deviation	Std. Error Mean
Nickel (Ni)	Hot extraction	63	3.06	3.38	0.43
	Cold extraction	63	2.45	3.01	0.38
Copper (Cu)	Hot extraction	63	44.52	58.51	7.37
	Cold extraction	63	38.72	62.79	7.91
Zinc (Zn)	Hot extraction	63	4.20	6.53	0.82
	Cold extraction	63	7.38	28.25	3.56
Lead (Pb)	Hot extraction	63	3.20	8.14	1.03
	Cold extraction	63	3.19	8.70	1.10

Table 2: Group Statistics for 1.0mol/L Oxalic Acid Extraction Techniques in Guinea Corn Fields

Metal	Method of extraction	N	Mean (mg/L)	Std. Deviation	Std. Error Mean
Nickel (Ni)	Hot extraction	63	7.29	22.51	2.84
	Cold extraction	63	2.76	3.78	0.48
Copper (Cu)	Hot extraction	63	38.04	77.04	9.71
	Cold extraction	63	39.41	48.17	6.07
Zinc (Zn)	Hot extraction	63	6.37	9.75	1.23
	Cold extraction	63	1.41	1.96	0.25
Lead (Pb)	Hot extraction	63	2.54	8.13	1.02
	Cold extraction	63	3.78	9.89	1.25

Table 3: Group Statistics for 1.0mol/L Acetic Acid Extraction Techniques in Guinea Corn Fields

Metal	Method of extraction	N	Mean (mg/L)	Std. Deviation	Std. Error Mean
Nickel (Ni)	Hot extraction	63	3.07	3.28	0.41
	Cold extraction	63	2.71	3.24	0.41
Copper (Cu)	Hot extraction	63	53.03	88.44	11.14
	Cold extraction	63	34.41	48.00	6.05
Zinc (Zn)	Hot extraction	63	4.75	7.80	0.98
	Cold extraction	63	2.33	11.74	1.48
Lead (Pb)	Hot extraction	63	2.60	3.56	0.45
	Cold extraction	63	1.57	2.67	0.34

Table 4: Independent Sample t-Test for 0.05mol/L EDTA Extraction Techniques in Guinea Corn Fields

Metal	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference
Nickel (Ni)	1.080	124	0.282	0.616	0.570
Copper (Cu)	0.537	124	0.592	5.806	10.813
Zinc (Zn)	0.872	124	0.385	3.187	3.653
Lead (Pb)	0.005	124	0.996	0.008	1.501

Table 5: Independent Sample t-Test for 1.0mol/L Oxalic Acid Extraction Techniques in Guinea Corn Fields

Metal	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference
Nickel (Ni)	1.576	124	0.118	4.530	2.875
Copper (Cu)	0.119	124	0.906	1.361	11.448
Zinc (Zn)	3.958	124	0.000	4.962	1.273
Lead (Pb)	0.769	124	0.443	1.240	1.613

Table 6: Independent Sample t-Test for 1.0mol/L Acetic Acid Extraction Techniques in Guinea Corn Fields

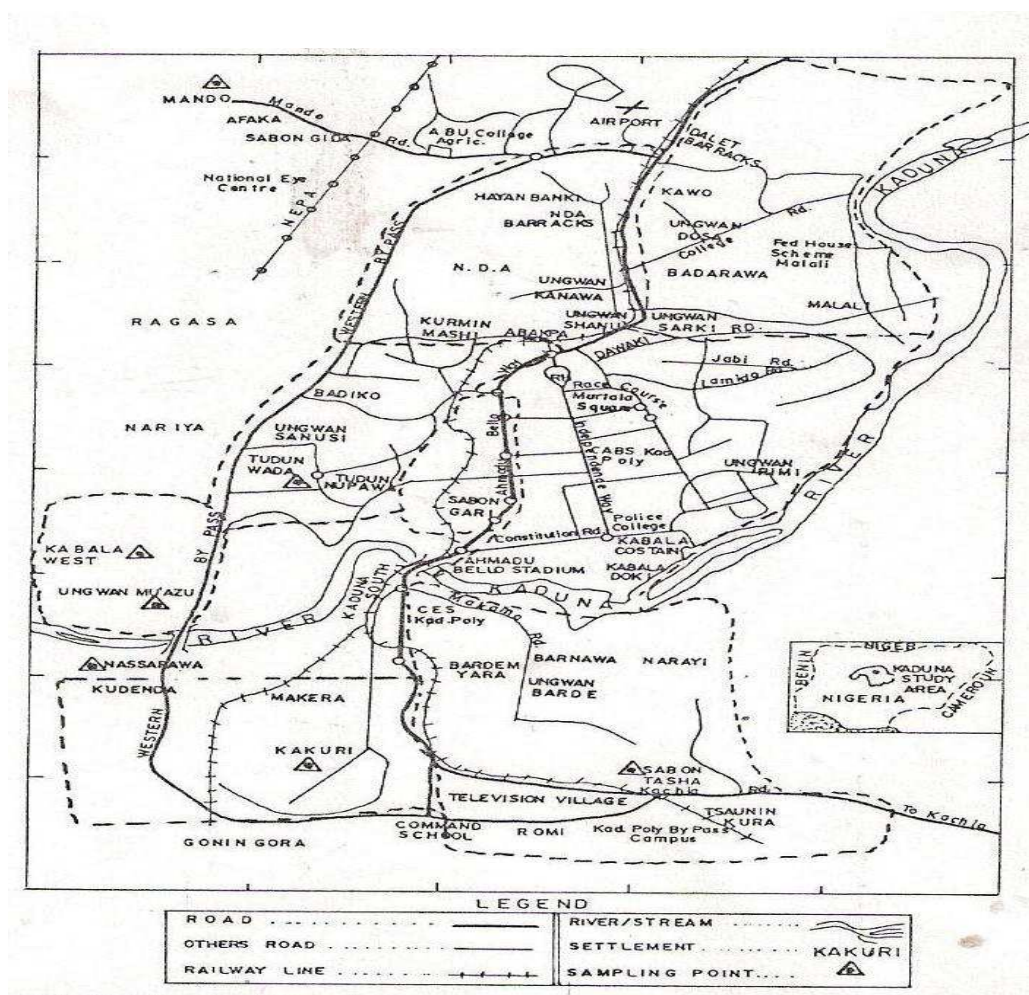| Metal	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference
Nickel (Ni)	0.623	124	0.535	0.361	0.580
Copper (Cu)	1.469	124	0.144	18.628	12.677
Zinc (Zn)	1.365	124	0.175	2.424	1.776
Lead (Pb)	1.847	124	0.067	1.036	0.561

Figure 1: Map of Kaduna State showing Kaduna Metropolis

Figure 2: Map of Kaduna Metropolis