

Comparison of Extraction Techniques for the Determination of Ni, Cu, Zn and Pb in Maize grown soils of Kaduna Metropolis, Nigeria

¹S.S. Mohammed and ²J.T. Ayodele

¹Department of Applied Science, College of Science and Technology,
Kaduna Polytechnic, Kaduna, Nigeria

²Department of Pure and Industrial Chemistry, Bayero University, Kano, Nigeria

Abstract: To assess the availability of metals in soil for absorption, the chemical forms must be determined. Sequential extraction procedures are useful to determine the geochemical partitioning of heavy metals in the soil. In this study, the Ni, Cu, Zn and Pb concentrations of soil samples from maize grown soils 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 0.05 mol/L EDTA, 1.0 mol/L oxalic acid and 1.0 mol/L acetic acid. The results indicated that there is no significant difference between hot and cold techniques for these metals in the reagents except for Zn in 0.05 mol/L EDTA and 1.0 mol/L oxalic acid where there is significant difference between hot and cold extraction and that the hot extraction is superior to the cold extraction with mean values of 25.63 for 0.05 mol/L EDTA and 26.37 for 1.0 mol/L oxalic acid.

Key words: Chemical extraction, flame absorption spectrometry, heavy metals, kaduna metropolis, maize grown soils

INTRODUCTION

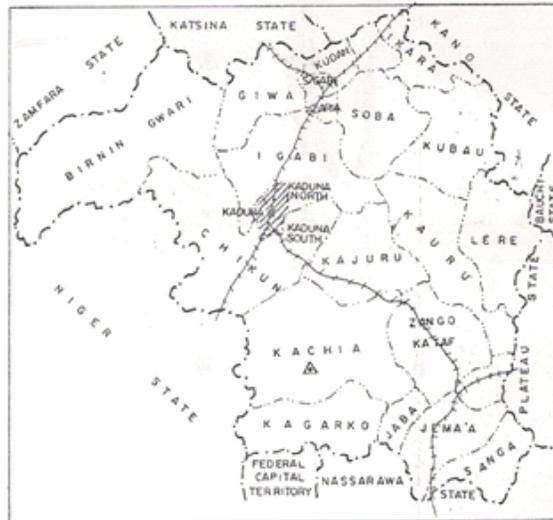
Soils are receptacles for heavy metals released from industrial activities, municipal wastes, water sludge, urban composts, road traffic, atmospheric deposits and chemicals used in agriculture (phosphate fertilizers, pesticides) and spread out into the environment (Adriano, 1986). Heavy metals are persistent in the environment; they are non-thermo degradable and thus readily accumulate to toxic levels (Sharma *et al.*, 2007). Many soils especially those in hazardous waste sites are contaminated heavy metals Ni, Cu, Zn, Pb etc. Heavy metal contamination as arable soils through industrial and anthropogenic activities is a serious problem in Nigeria. Metals uptake by plants may pose risks to human health when such plants are grown on or near contaminated areas. Metals accumulation in plant depends on plant species, growth stages, types of soil and metals, soil conditions, weather and environment (Chang *et al.*, 1984; Petruzzelli, 1989). Determination of metals in soil can be accomplished via single reagent leaching, ion-exchange resins and sequential extraction procedures. The number of available extraction techniques developed over the last three decades begs inquiry as to which technique is preferable over another. A large number of extracting solutions have been used to assess plant available trace elements (Gupta and Aten, 1993; He and Singh, 1993; Ayodele and Mohammed, 2011). 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 extracted using the chemical reagents, 0.05 M EDTA, 1.0 M acetic acid and 1.0 M oxalic acid. The two extraction techniques employed were compared.

MATERIALS AND METHODS

A flame atomic absorption spectrophotometer model 8010 Young Lin was used for the Ni, Cu, Zn and Pb determinations. In the extraction procedures, 1.0 M oxalic acid, 0.05 M Na₂EDTA and 1.0 M acetic acid were used.

Preparation of samples: The research covered seven agricultural sites in Kaduna, Nigeria. The sites are: Nasarawa, Sabon Tasha, Ungwan Mu'azu, Tudun Wada, Kakuri, Mado, Kabala West and Kachia. To evaluate the variability between the different agricultural soils, 63 soil samples were collected between October - November, 2008, 2009 and 2010 from the following agricultural locations; Nasarawa, Sabon Tasha, Ungwan Mu'azu, Tudun Wada, Kakuri, Mado, Kabala West within Kaduna Metropolis, and Kachia as control. The soil samples were collected from the different areas enumerated at a depth of about 10 cm below the surface (Yaman *et al.*, 2005). Kachia, a town situated about 130 km away from Kaduna was taken as control, Fig. 1 (A, B).



(A)



(B)

Fig..1: (A) Map of Kaduna State showing Kaduna Metropolis, (B) Map of Kaduna Metropolis

The soil samples were crushed, sieved and dried at 85°C. 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 Tessier *et al.* (1979) extraction method developed by Yaman *et al.* (2005) was used. Soil extracts were obtained by shaking separately 5g of soil samples with 10 cm³ of 0.05 mol/L Na₂EDTA (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. 4 cm³ 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 60 cm³ water and filtered. The clear digest was carried out in the same way. 10 cm³ of 0.05 mol/L Na₂EDTA, 1.0 mol/L oxalic acid and 1.0 mol/L acetic acid were added to 5 g of separate soil samples at room temperature and centrifuged after stirring for 5 min. This procedure is referred to as cold extraction (Yaman *et al.*, 2005). The digest was diluted to 60 cm³ with water and filtered. The clear digest was analyzed for Ni, Cu, Zn and Pb using FAAS model Young Lin. A blank digest was carried 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 method. The mean concentrations of the elements in soils and coefficient of variations were employed in assessing their levels. The independent sample-test was employed to compare the hot and cold extraction techniques for each of the trace metals; Ni, Cu, Zn and Pb for 0.05 mol/L EDTA, 1.0 mol/L oxalic acid and 1.0 mol/L acetic acid in the maize grown soils. This is represented in Table 1-6.

For 0.05 mol/L EDTA, $p = 0.586 > 0.05$ and $p = 0.580 > 0.05$ for Ni, Cu and Pb respectively. Hence it was concluded that there is no significant difference between hot and cold extraction techniques for these metals in maize grown soils considered. On the other hand, $p = 0.001 < 0.05$ for Zn and therefore, it was concluded that there is significant difference between hot and cold extraction techniques for this metal in the maize grown soils studied in 0.05 mol/L EDTA. From the group statistics in Table 1, it is evident that the hot extraction is superior to cold extraction with a mean of 25.63. 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 thus concluded that there is no significant difference between hot and cold extraction

Table 1: Group statistics for EDTA 0.05 m extraction techniques in Maize grown soils

Metal	Method of extraction	N	Mean±SD	SEM
Nickel (Ni)	Hot extraction	63	38.05±36.6	34.61
	Cold extraction	63	41.51±34.49	4.35
Copper (Cu)	Hot extraction	63	9.72±10.26	1.29
	Cold extraction	63	16.58±30.00	3.78
Zinc (Zn)	Hot extraction	63	25.63±14.40	1.81
	Cold extraction	63	18.41±9.44	1.19
Lead (Pb)	Hot extraction	63	28.29±26.17	3.30
	Cold extraction	63	25.85±23.06	2.90

SEM: Standard Error Mean

Table 2: Group statistics for oxalic acid 1.0 m extraction techniques in Maize grown soils

Metal	Method of extraction	N	Mean±SD	SEM
Nickel (Ni)	Hot extraction	63	45.79±33.02	4.16
	Cold extraction	63	57.93±37.92	4.78
Copper (Cu)	Hot extraction	63	19.37±32.33	4.07
	Cold extraction	63	20.53±34.16	4.30
Zinc (Zn)	Hot extraction	63	26.37±15.62	1.97
	Cold extraction	63	21.26±9.07	1.14
Lead (Pb)	Hot extraction	63	31.53±26.69	3.36
	Cold extraction	63	28.25±21.08	2.66

SEM: Standard Error Mean

Table 3: Group statistics for Acetic Acid 1.0 m extraction techniques in Maize grown soils

Metal	Method of extraction	N	Mean±SD	SEM
Nickel (Ni)	Hot extraction	63	43.24±30.07	3.79
	Cold extraction	63	44.27±34.00	4.28
Copper (Cu)	Hot extraction	63	20.76±36.73	4.63
	Cold extraction	63	20.43±36.86	4.64
Zinc (Zn)	Hot extraction	63	21.74±10.19	1.28
	Cold extraction	63	19.42±10.07	1.27
Lead (Pb)	Hot extraction	63	26.12±19.46	2.45
	Cold extraction	63	22.31±21.13	2.66

Table 4: Independent sample t-test for EDTA 0.05 m extraction techniques in Maize grown soils

Metal	T	df	Sig. (2-Tailed)	Mean difference	SE difference
Nickel (Ni)	0.547	124	0.586	3.464	6.338
Copper (Cu)	1.718	124	0.088	6.860	3.994
Zinc (Zn)	3.327	124	0.001	7.218	2.169
Lead (Pb)	0.554	124	0.580	2.435	4.394

Table 5: Independent Sample t-Test for Oxalic Acid 1.0m Extraction Techniques in Maize grown soils

Metal	T	df	Sig. (2-Tailed)	Mean difference	SE difference
Nickel (Ni)	1.917	124	0.058	12.141	6.334
Copper (Cu)	0.195	124	0.846	1.153	5.926
Zinc (Zn)	2.244	124	0.027	5.105	2.275
Lead (Pb)	0.767	124	0.445	3.285	4.285

Table 6: Independent sample t-test for Acetic Acid 1.0 m extraction techniques in Maize grown soils

Metal	T	df	Sig. (2-Tailed)	Mean difference	SE difference
Nickel (Ni)	0.179	124	0.858	1.024	5.719
Copper (Cu)	0.050	124	0.960	0.330	6.555
Zinc (Zn)	1.284	124	0.201	2.318	1.805
Lead (Pb)	1.052	124	0.295	3.807	3.619

techniques for the metals in the maize grown soils studied. On the other hand, $p = 0.027 < 0.05$ for Zn, and hence concluded that there is significant difference between hot and cold extraction techniques for the metal in the maize grown soils in 1.0 mol/L oxalic acid. From the group statistics in Table 2, it can be deduced that the hot extraction is superior to the cold extraction with a mean of 26.37. Lastly, for 1.0 mol/L acetic acid, $p = 0.858 > 0.05$, $p = 0.906 > 0.05$, $p = 0.201 > 0.05$ and $p = 0.295 > 0.05$ for Ni, Cu, Zn and Pb respectively and thus concluded that there no significant difference between hot and cold extraction techniques in maize grown soils for these metals in 0.1 mol/L acetic acid.

CONCLUSION

The comparison of single and sequential extractions techniques provided an interesting insight in extracting mobile/bioavailable fraction of heavy metals in the maize grown soils in this study.

ACKNOWLEDGMENT

The authors show great appreciation to Kaduna Polytechnic, Nigeria for providing facilities to analyze the samples and to Nasiru Musa and Yusuf Abdul-raheem for the help in sample collection and analysis.

REFERENCES

Adriano, D.C., 1986. Trace Elements in the Terrestrial Environment. Springer-Verlag, New York, pp: 533.

- Ayodele, J.T. and S.S. Mohammed, 2011. Speciation of nickel in soils and cereal. *Res. J. Appl. Sci. Engine. Technol.*, 3(3): 202-209.
- Chang, A.C., A.L. Page, J.E. Warneke and E. Grgurevic, 1984. Sequential extraction of soil heavy metals following a sludge application. *J. Environ. Qual.*, 1: 33-38.
- Gupta, S.K. and C. Aten, 1993. Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments. *Int. J. Environ. Anal. Chem.*, 51: 25-46.
- He, Q.B. and B.R. Singh, 1993. Plant availability of cadmium in soils. I. extractable cadmium in newly and long term cultivated soils. *Acta Agric. Scand. Sect. B. Soil Plant Sci.*, 43: 134-141.
- Petruzzelli, G., 1989. Recycling wastes in agriculture. Heavy metal bioavailability. *Agric. Ecosyst. Environ.*, 27: 493-503.
- Sharma, R.K., M. Agrawal and F. Marshall, 2007. Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India. *Ecotoxicol Environ. Safety*, 66: 258 -266.
- Tessier, A., P.G.C. Campbell and M. Bisson, 1979. Sequential extraction procedures for the speciation of particulate trace metals. *Anal. Chem.*, 51: 844-850.
- Yaman, M., N. Okumus, S. Bakirdere and I. Akdeniz, 2005. Zinc speciation in soils and relation with its concentration in fruits. *Asian J. Chem.*, 17 (1): 66-72.