Sequential Extraction of Nickel in Soil and Fruits

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Abstract: The identification of chemical forms of Ni in agricultural samples is of interest for the evaluation of its mobility, bioavailability and ecotoxicity. In this study, the Ni concentration of the fruit and soil samples were determined using Flame Atomic Absorption Spectrometry (FAAS). The soil samples related to the fruits were digested and extracted using different digestion and extraction reagents. The result revealed that the soil samples obtained from various locations contain varying amount of Ni and was distributed between residual, oxide, carbonate and exchangeable fractions. The result also showed that the concentration of Ni in the soil samples recorded was within the allowable limits of 40mg/kg and the ANOVA (p=0.017<0.05), showed that there is significant difference in the concentration of Ni in mango, orange, cashew and pawpaw fruits. Similarly, from the Duncan post hoc test, in the third homogenous subset, mango and orange have the highest Ni concentration followed by pawpaw in the second homogenous subset. In the first homogenous subset, cashew has the least Ni concentration.

Keywords: Chemical forms, flame atomic absorption spectrometry, fruits, nickel, soil

1. 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^[1]. Heavy metals are persistent in the environment; they are non-thermo degradable and thus readily accumulate to toxic levels ^[2]. Many soils especially those in hazardous wastes sites are contaminated by heavy metals such as Ni, Cu, Zn, Cu, etc. Heavy metal contamination in 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 condition, weather and environment [3,4]. Nickel is an element that occurs in the environment only at very low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer on different sites within the bodies of animals, mainly of those that live near refineries. The most common application of Ni is an ingredient of steel and other metal products. The major sources of nickel contamination in the soil are metal plating industries, combustion of fossil fuels, and nickel mining and electroplating [4]. It is released into the air by power plants and trash incinerators and settles to the ground after undergoing precipitation reactions. It usually takes a long time for nickel to be removed from air. Nickel can also end up in surface water when it is a part of wastewater streams. The larger part of all Ni compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result. In acidic soils, however, Ni becomes more mobile and often leaches down to the adjacent groundwater. Microorganisms can also suffer from growth decline due to the presence of Ni, but they usually develop resistance to Ni after a while. Nickel is not known to accumulate in plants or animals and as a result Ni has not been found to biomagnify up the food chain. For animals Ni is an essential foodstuff in small amounts. Nickel is generally distributed uniformly through the soil profile but typically accumulates the surface from disposition by industrial and agricultural activities. Nickel may present a major problem in land near towns, in industrial areas or even in agricultural land receiving waste such as sewage sludge. Nickel can exist in soils

in several forms such as inorganic crystalline minerals or precipitates, complexes and absorbed on organic cations surface or on inorganic cations exchange surfaces, water-soluble, and free-ion or chelated metal complexes in soil solution [5]. 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 [5]. Heavy metals may be distributed among many components of the soil or sediment and may be associated with them in different ways [6,7,8, 9]. 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 ^[10]. Therefore, the identification of the chemical form or phases of Nickel in soil is necessary for estimating its biological availability, physico-chemical reactivity and transport in the environment and into the food chain [11]. This research is aimed at investigating the levels of Ni and relation to its concentrations in fruits.

2. MATERIALS AND METHODS

2.1 Study Area

The study area is located at Yelwa in Keffi town which is in the northern part of Nigeria. Yelwa is about 50km from Abuja, the Federal Capital Territory (FCT) and about 118km from Lafia, the Nasarawa State Capital, Nigeria. Yelwa is situated on latitude 10° 5', north of the equator and longitude 10° 35' west. This location is close to a major road, a mechanic workshop and some meters away surrounded by houses.

2.2 Instrumentation, Apparatus and Reagents

A flame atomic absorption spectrometer (model 8010: Young Lin) was used for Ni determination in the fruit and soil samples. An electro thermal oven (model: DHG) was used for drying the fruits samples, a 90 mics (0.09 mm) Standard Test Sieve was used for sieving the soil samples.

All of the reagents used to digest samples and for sequential extraction were of analytical reagent grade. 10 cm^3 of a mixture of nitric acid and hydrogen peroxide (2+1) was used for the digestion of fruit and soil samples. In the extraction procedures,

1.5 mol L^{-1} niric acid, 1.0 mol L^{-1} oxalic acid, 0.05 mol L^{-1} EDTA, and 1.0 mol L^{-1} magnesium chloride were used.

2.3 Sample Collection

Random sampling was used in the collection of both the fruits and soil samples. The samples were collected in October, 2015. The soil samples were obtained at 10cm depth and 100cm away from the trees where the fruits were obtained ^[12] and were put into separate polythene bags and labeled accordingly.

2.4 Sample Preparation

The fruit samples collected were washed thoroughly, rinsed with tap water, and allowed to drain. The fruits were peeled and then sliced into smaller pieces and the seeds removed. The peels were dried at 85°C; using an electro thermal oven, model DHG. The oven dried fruits samples were stored in sample containers respectively and ready for ashing.

The soil samples were also oven dried at 85°C; size reduced by the use of mortar and pestle; sieved using a Standard Test Sieve of 90 mics (0.09 mm) and then stored in samples containers respectively and ready for digestion and extraction.

2.5 Samples Digestion

Wet Ashing

Five grams (5g) each of oven dried fruit samples were accurately weighed using analytical balance into an evaporating dish and heat at 480°C in an ashing furnace for 4 hours (4hrs). 10 cm³ of a mixture of nitric acid-hydrogen peroxide (2+1) was added to each of the ashed samples and dried with occasional shaking on a hot plate and cooled, 4 cm³ of 1.5 mol L⁻¹ nitric acid was then added, and centrifuged and 6 cm³ distilled water was added to the clear digest ashed samples and were filtered [13]. These samples were analyzed for Ni, using FAAS model 8010 young Lin. Blank digests were also carried out in the same ways.

2.6 Digestion and Extraction of Soil samples

A modified sequential extraction method [11] developed by Yaman was used ^[13]. 10 cm³ of a mixture of nitric acid-hydrogen peroxide (2+1) was added to 5 g of the soil samples and dried with occasional shaking on a hot plate and cooled. 4 cm³ of 1.5 mol L-1 nitric acid was added to the reminders, centrifuged and diluted to 60 cm³ with water and were filtered. The clear digests were analyzed for Ni using FAAS model 8010 Young Lin. Blank digests were carried out in the same way. Soil extracts were obtained by shaking separately, 5 g of soil samples with 10 cm³ of 0.05 mol L⁻¹ EDTA (for carbonate and organically bound phases), 1.0 mol L⁻¹ oxalic acid (for oxide phases) and 1.0 mol L⁻¹ MgCl₂ (for exchangeable phases). The mixtures were evaporated with occasional shaking on a hot plate. 4 cm³ of 1.5 mol L-1 nitric acid was added to the reminders, centrifuged and diluted to 60 cm³ with water and were filtered. The clear digests were analyzed for Ni using FAAS model 8010 Young Lin. Blank digests were carried out in the same way.

3. RESULTS AND DISCUSSION

3.1 Content of Nickel (Ni) in Soils and Fruits

The results of Ni concentration in fruit and soil samples are shown in Table 1.

The results showed that mango, orange, pawpaw and cashew have lower concentrations of Ni as compared to their corresponding soils. This could be due to agricultural practices and other anthropogenic activities such as dumping of used alloy and batteries in these locations ^[14]. The concentration of Ni in the soils was recorded below the average concentration in the World soil of 40 mg/kg ^[9]. The concentration of Ni in fruits ranged from 0.040 mg/kg to 0.640 mg/kg. The concentration of Ni in mango, Orange and pawpaw was higher than in cashew.

Other values reported by ^[15] are 0.08 mg/kg, 0.26 mg/kg and 0.72 mg/kg for orange, pawpaw and mango respectively.

3.2 Nickel (Ni) Speciation

The distribution of Ni in the soil samples showed that Ni exists in the forms; residual, oxide, carbonate and exchangeable phases. The concentration of Ni bound to the residual fraction is higher in mango and pawpaw soils as compared to its concentrations in the other extraction media. Hence, Ni is bioavailable, mobile in the soil and available for plant uptake ^[13].

The concentration of Ni bound to the exchangeable fraction is higher in cashew soil than in other extraction media; $Ni^{2+} + Cl^{2-} \rightarrow NiCl_2$

Thus, Ni is said to be available in an exchangeable species. The concentration of Ni bound to carbonate fraction is higher in orange soil as compared to its concentration in the other extraction media;

 Ni^{2*} + $CO_3{}^{2*} \rightarrow NiCO_3$ Hence, it is said to be a carbonate species $^{[15]}$

The HNO₃/H₂O₂, EDTA, $H_2C_2O_4$, and $MgCl_2$ extractables are considered available in the locations.

3.3 Comparing the Concentration of Nickel in Different Fruits

Here we need to compare the concentration of Nickel in mango, orange, cashew and pawpaw fruits. The one-way analysis of variance (ANOVA) is hereby applied for the test.

Table 1: Shows Results of Ni Concentrations in Fruit and Soil Samples

Results of mean value (mg/kg) ± STD DEV (n=3)

Sample	HNO ₃ /H ₂ O ₂ (2+1)	HNO ₃ / H ₂ O ₂ (2+1)	Oxalic Acid 1.0M	EDTA 0.05M	MgCl ₂ 1.0M
Mango	0.630 ± 0.101	13.413±2.300	4.813±0.800	5.120 ± 0.100	1.770 ± 0.064
Orange	0.640 ± 0.314	4.330 ± 0.200	0.530 ± 0.050	6.400 ± 2.500	3.100 ± 0.200
Cashew	0.040 ± 0.020	0.134 ± 0.020	0.023 ± 0.004	0.020 ± 0.010	1.041 ± 0.100
Pawpaw	0.460 ± 0.203	13.413±2.300	4.800 ± 0.800	$5.120{\pm}0.110$	1.810 ± 0.012

Table 2: Nickel Concentration in Fruits (mg/kg)					
Fruits	N	Mean	SD		
Mango	3	0.63	0.10		
Orange	3	0.64	0.31		
Paw-paw	3	0.46	0.20		
Cashew	3	0.04	0.02		

Table 3: ANOVA of Nickel Concentration in Fruits

Source of Variation	Sum of Squares	Mean df Square F		Sig.	
Between Groups	0.706	3	0.235	6.251	0.017
Within Groups	0.301	8	0.038		
Total	1.007	11			

From Table 3 above, since p=0.017<0.05, we conclude there is significant difference in the concentration of Nickel in mango, orange, cashew and pawpaw fruits. The real difference is further investigated by the following Duncan multiple range post hoc test.

		Subset			
Type of fruit	Ν	1	2	3	
Cashew	3	0.04			
Pawpaw	3		0.46		
Mango	3			0.63	
Orange	3			0.64	
Means for groups in homogeneous subsets are displayed.					

 Table 4: Duncan test for Nickel Concentration in Fruits

From the Table 4 above, Duncan post hoc test showed that, in the third homogenous subset, mango and orange have the highest Nickel concentration followed by pawpaw in the second homogenous subset. In the first homogenous subset, cashew has the least Nickel concentration. This is shown in Fig. 1 below.



Figure 1: The mean concentration of nickel against the type of fruit.

4. 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 environment 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, exchangeable and carbonate fractions. An increase of the metal concentration in some areas suggests that heavy use of agrochemicals for planting and other agricultural practice could cause increase in the content of heavy metals in the soil.

5. **REFERENCES**

- [1] Adriano, D.C., 1986. Trace Element in the Terrestrial Environment. Springer-Verlag. New York, Pp. 533.
- [2] Sharma, R. K., Agrawal, M. and Marshall, F. 2007. Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India. Ecotoxicol. Emviron. Safety., 66:258-266.
- [3] Chang, A.C., Page, A.L., Warneke J. E. and Grgurevic, E. 1984. Sequential extraction of soil heavy metals following a sludge application. *J. Environ. Qual.*, 1:33-38.
- [4] Petruzzelli, G., 1989. Recycling wastes in agriculture: Heavy metal bioavailability. Agric. Ecosyst. Environ., 27:493-503.

- [5] Yusuf, K. A., 2006. Evaluation of the three-stage BCR (European Community Bureau of Reference) sequential extraction procedures to assess the potential mobility and toxicity of heavy metals in roadside soils.*Pak. J. Sci. Ind. Res.*, 49:181-188.
- [6] Harrison, R. M., Laxen, D. P. H. and Wilson, S. J. 1981. Chemical association of Pb, Cd, Cu and Zn in in street dusts and roadside soils.*Environ. Sci. Technol.*, 15:1378-1383.
- [7] Chlopecka, A., Bacon, J. R., Wilson, M. J. and Kay, J. 1996. Forms of Cadmium, Lead and Zinc in soils from Southwest Poland. *Sci. Total Environ. Qual.*, 25:69-79.
- [8] Kabala, C. and Singh, B. R. 2001. Fractionation and mobility of Copper, Lead and Zinc in soil profiles in the vicinity of a Copper Smelter. J. Environ. Qual., 30:485-492.
- [9] Khairah, J., Habibah, H. J., Anizan, I., Maimon, A., Aminah, A. and Ismail, B. S. 2009. Content of Heavy metals in soil collected from selected paddy cultivation areas in Kedah and Perlis, Malaysia. J. Appl. Sci. Res., 5(12):2179-2188.
- [10] Yaman, M. Y., Dilgin and Gucer, S. 2000. Speciation of lead in soil and relation with its concentration in fruits. *Anal.ChimicaActa*, 410:119-125.
- [11] Yaman, M., Okumus, N., Bakirdere, S. and Akdeniz, I., 2005. Zinc speciation in soils and relation with its concentration in fruits. *Asian Journal of Chemistry*. 17(1): 66-72.
- [12] 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.
- [13] Ayodele, T.J. and Mohammed, S.S., 2011. Speciation of Nickel in Soils and Cereals. Res. J. Appl. Sci. Engineering Tecnol., 3(3):202-209
- [14] Orisakwe, O.E., Nduka, J.K., Amadi, C.N., Dike., D.O. and Bede, O., 2012. Heavy metals risk assessment for population via consumption of food crops and fruits in Owerri, South Eastern, Nigeria. *Chem. Centr. J.* 6: 77–83.
- [15] Hickey, M.G. and Kittrick, J.A. 2004. Chemical partitioning of Cd, Cu, Ni and Zn in soils and sediments containing high levels of heavy metals. *J. Environ. Qual.*, 13: 372-376.