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The Uptake of Cadmium by Fruits Grown on Selected Agricultural Areas

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Abstract: *Consumption of fruits grown in a contaminated area with heavy metals is a major health problem for both humans and animals. The study involved determination of Cd in Mango, Orange, Pawpaw and Cashew and their corresponding soils from Yelwa in Keffi Local Government Area of Nasarawa State, Nigeria. The objective of the study was to determine bioavailable Cd in these fruits and soil samples by flame atomic absorption spectrometry (FAAS) using sequential extraction technique. The concentrations of the metal in the fruit and soils vary from one sampling site to another. The soil samples related to the fruits where digested and extracted using different digestion and extraction reagents. The result revealed that the soil samples obtained from various locations contain varying amount of cadmium and was distributed between residual, oxide, carbonate and exchangeable fractions. The result also showed that the concentration of Cd in the soil samples recorded was within the allowable limits of 100mg/kg and the ANOVA ($p=0.017<0.05$), showed that there is significant difference in the concentration of Cadmium 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 Cadmium concentration followed by pawpaw in the second homogenous subset. In the first homogenous subset, cashew has the least Cadmium concentration.*

Keywords: *Chemical forms, sequential extraction, FAAS, fruit, soil, Cd*

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I. Introduction

Heavy metals occur in soils of the world and are essential to plants and animals. We ingest them through food, water and air. Their concentrations are usually low and hazardous with little or no environmental disturbance[1].Most heavy metals remain in the soil nearly indefinitely as soils have long memories and do not degrade them. Ruinoffs as well as dust falls can result in accumulation in the roadside dusts/soils at levels that are toxic to organisms in the surrounding environments. These heavy metals remains bound to organism matter unless they are remobilized as windblown dust[2]. Living organisms require trace amounts of some metals like, cobalt, copper and zinc but their excess levels can be detrimental[3]. Other heavy metals such as mercury, lead and cadmium have no known or beneficial effects on organisms and their accumulation overtime in the bodies of mammals can cause illness[3]. Cadmium is directly below Zn in the periodic table and has a chemical similarity to that of Zn, an essential micronutrient for plants and animals. This may account in part for Cd's toxicity; because Zn being an essential trace element, its substitution by Cd may cause the malfunctioning of metabolic processes [4]. The most significant use of Cd is in Ni/Cd batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance, and high tolerance to physical and electrical stress. Cadmium coatings provide good corrosion resistance coating to vessels and other vehicles, particularly in high-stress environments such as marine and aerospace. In addition, acid rain and the resulting acidification of soils and surface waters have increased the geochemical mobility of Cd, and as a result its surface-water concentrations tend to increase as lake water pH decreases[4]. Cadmium is produced as an inevitable byproduct of Zn and occasionally lead refining. The application of agricultural inputs such as fertilizers, pesticides, and biosolids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils, and the bioavailability of this metal determines whether plant Cd uptake occurs to a significant degree [5]. Cadmium is very bio persistent but has few toxicological properties and, once absorbed by an organism, remains resident for many years. Cadmium in the body is known to affect several enzymes. It is believed that the renal damage that results in proteinuria is the result of Cd adversely affecting enzymes responsible for reabsorption of proteins in kidney tubules. Cadmium also reduces the activity of delta-aminolevulinic acid synthetase, arylsulfatase, alcohol dehydrogenase, and lipoamide dehydrogenase, whereas it enhances the activity of delta aminolevulinic acid dehydratase, pyruvate dehydrogenase, and pyruvate decarboxylase [4]. The major threat to human health is chronic accumulation in the kidneys leading to kidney dysfunction. Food intake and tobacco smoking are the main routes by which Cd enters the body[4].Acute exposure to cadmium generally occurs in the workplace, particularly in the manufacturing processes of batteries and color pigments used in paint and plastics, as well as in electroplating and galvanizing processes. Symptoms of acute cadmium exposure are nausea, vomiting, abdominal pain, and breathing difficulty.This research is aimed at investigating the levels of Cd and relation to its concentrations in fruits.

II. Materials And Methods

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.

Instrumentation, Apparatus and Reagents

A flame atomic absorption spectrometer (model 8010: Young Lin) was used for Cd determinations.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, funnel, filter paper, measuring cylinder, analytical balance, conical flask (pyrex), mortar and pestle, evaporating dish and centrifuge.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.

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 [6] and were put into separate polythene bags and labeled accordingly.

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.Most samples require digestion before analysis so as to reduce organic interference by destroying all or most of the organic matter present in the sample into such a form that they can be analyzed with minimal interference.

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 cm^3 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 cm^3 of 1.5 mol L^{-1} nitric acid was then added, and centrifuged and 6 cm^3 distilled water was added to the clear digest ashed samples and were filtered [6]. These samples were analyzed for Cd using FAAS model 8010 young Lin. Blank digests were also carried out in the same ways.

Digestion and Extraction of Soil samples

A modified sequential extraction method [4]developed by Yaman was used (Tessieret al., 1979). 10 cm^3 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 cm^3 of 1.5 mol L^{-1} nitric acid was added to the reminders, centrifuged and diluted to 60 cm^3 with water and were filtered. The clear digests were analyzed forCd 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 cm^3 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} $MgCl_2$ (for exchangeable phases). The mixtures were evaporated with occasional shaking on a hot plate. 4 cm^3 of 1.5 mol L^{-1} nitric acid was added to the reminders, centrifuged and diluted to 60 cm^3 with water and were filtered. The clear digests were analyzed for Cd using FAAS model 8010 Young Lin. Blank digests were carried out in the same ways.

III. Results And Discussion

Content of Cadmium (Cd) in Soils and Fruits

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

The results showed that mango, orange, and pawpaw have lower concentrations of Cd as compared to their corresponding soils. This could be due to agricultural practices such as application of fertilizer, pesticides and heavy traffic and other human activities [7]and disposal of industrial wastes and deposition of atmospheric contaminants increases concentration of Cd in soils and bioavailability of this metal[8]. The concentration of Cd in the cashew was recorded below detection limit. This observation may be due to the lower concentration of Cd in the cashew soil and the nature of the rate of uptake of the metal[9]. The concentration of Cd in the soil samples recorded was within the allowable limits of 100mg/kg [10].

Cadmium (Cd) Speciation

Cadmium exists in the forms; residual, oxide, carbonate and exchangeable phases. The concentration of Cd bound to the residual fraction is higher in orange and cashew when compared to its concentration in the other extraction media. This probably caused a release of Cd in the soil solution, and hence available for plant uptake [11]. The concentration of Cd bound to the carbonate fraction is higher in mango and pawpaw soils as compared to its concentration in the other extraction media. Thus, Cd in the soil was organically bound (carbonate species); $\mathbf{Cd^{2+} + CO_3^{2-} \rightarrow CdCO_3}$.Therefore, it is bioavailable and mobile for plant uptake, [13]. The HNO_3/H_2O_2, EDTA, $H_2C_2O_4$, and $MgCl_2$ extractables are considered available in the location.

Comparing the Concentration of Cadmium in Different Fruits

Here we need to compare the concentration of Cadmium 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 Cd Concentrations in Fruit and Soil Samples
Results of mean value (mg/kg) ± STD DEV (n=3)

Sample	Cd Conc. in fruit sample (mg/kg) $HNO_3/H_2O_2(2+1)$	Cd Conc. in soil sample (mg/kg) $HNO_3/H_2O_2(2+1)$	Oxalic acid	EDTA	$MgCl_2$
Mango	0.240±0.120	0.895±0.200	0.420±0.200	1.335±0.500	0.113±0.060
Orange	0.280±0.069	12.160±1.322	0.260±0.040	1.413±1.30	0.730±0.121
Cashew	ND	1.973±0.210	0.103±0.010	1.960±0.140	1.480±0.370
Pawpaw	0.200±0.100	0.895±0.200	0.433±0.200	1.335±0.510	0.110±0.064

Table 2: Cadmium Concentration in Fruits (mg/kg)

Fruits	N	Mean	SD
Mango	3	0.24	0.11
Orange	3	0.28	0.07
Pawpaw	3	0.12	0.12
Cashew	3	0.00	0.00

Table 3: ANOVA of Cadmium Concentration in Fruits

Source of Variation	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	0.144	3	0.048	6.316	0.017
Within Groups	0.061	8	0.008		
Total	0.205	11			

From Table 3 above, since $p=0.017<0.05$, we conclude there is significant difference in the concentration of Cadmium in mango, orange, cashew and pawpaw fruits. The real difference is further investigated by the following Duncan multiple range post hoc test, as shown in Table 4 below:

Table 4: Duncan test for Cadmium Concentration in Fruits

		Subset		
Type of fruit	N	1	2	3
Cashew	3	0.000		
Pawpaw	3		0.120	
Mango	3			0.240
Orange	3			0.280
Means for groups in homogeneous subsets are displayed.				

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

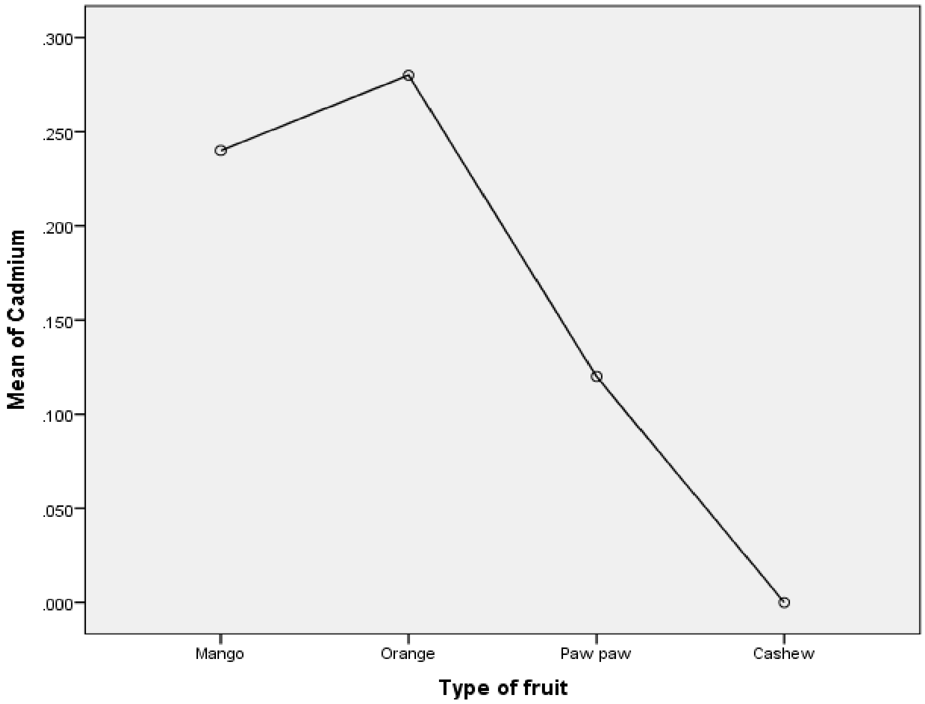

Fig. 1: Themean concentration of Cadmium against the type of fruit

IV. 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 could be attributed to various agricultural practices in those areas.

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