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Analysis of Heavy Metals Mercury, Arsenic, Cadmium, Lead, Chromium, and Nickel in Waste Currency Dumpsite and its Environmental Implications

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Abstract
Analysis of mercury, arsenic, cadmium, lead, chromium and nickel in soils and food crops (Cassava tuber and plantain fruits) within and around Nigeria waste currency dumpsite have been carried out using Atomic Absorption Spectrometry (AAS) Unicam Modern 969 Series with air acetylene flame with aim to determine the level of concentration, source(s) and level of pollution by comparing with established standards. The study area is located within Oluku on 6^0 27' 4.4'' N and $005^0$35' 53.5'' E in Ovia North East Local Government Area in Edo State, Niger Delta, Nigeria. A total of 24 samples were collected from field; 12 soil samples, 11 from within and around the currency waste dumpsite at a depth of 0-15cm topsoil (TS) and 15-30cm subsoil (SS) with the aid of a hand auger while, 1 soil sample was taken from Iguosa at a distance of 1000m (1km) away from the dumpsite as a control. The food crops (Cassava tuber and Plantain fruits) 5 each were taken from the farms around the dumpsite 20 m away from the center of the dumpsite while, 1 each of the food crops were taken at a distance of 1000 m away. The analytical results were further subjected to statistical treatment at $P < 0.05$ percentage confidence level using SPSS. The results obtained were presented in a table as Mean ± SD, this shows that there was a significant decrease from topsoil (TS) to subsoil (SS) within and away from the dumpsite, while, the results obtained from the food crops show a similar trend. Cadmium was found to be higher than the permissible limit of 3 mg kg^{-1} soil while, other heavy metal were below the require limits. The concentration of the heavy metal in food crops were higher compared to the require standard for food crops. The ultimate results show that the concentration of the heavy metals analyzed in soil and food crops were from anthropogenic source which could be attributed to the dumping and burning of Nigeria currency note in the area. The high concentration of food crops could expose human to health risk through direct or indirect consumption of the food crops from the site. Consequently, the dumping and burning of waste currency by the apex bank in Nigeria should be discontinued while alternative method for burning of waste currency should be adopted.

Key words: Concentration, Food Crops, Currency, Heavy Metal and Standard.

Introduction

Recently, researchers are focusing at evaluating the levels of heavy metals around waste dumpsite due to the growing concerns expressed by the government, regulatory agencies and the public [1-3] over the large acres of land covered by these dumpsites and its relationship to environmental and health implications. Heavy metals contamination has been identified as a silent killer of man-kind and causes environmental degradation. Human activities enhance the concentrations of these metals in the environment [4].

Some of the metals found as contaminant in crops include As, Cd, Pb, Hg etc. These metals can pose a significant health risk to humans, particularly in elevated concentrations [5]. For example, the quality of soil intended for agricultural use depends on the concentration of heavy metals in it. Solid waste dump at different site include food waste, chemical waste, hazardous waste, electronics waste etc. Certainly, all solid waste occupy space and, for many countries, the disposal and management of these wastes are persistent problems. Increase in population and development have led to gradual change in the practice of disposal of solid waste indiscriminately at dumpsites to

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sanitary landfills and incinerators in developed countries [6]. One can not overlook the possible hazards that can be created as a result of long time dumping of refuse in the soil. For example, a residence time of about 1000 to 3000 years has been estimated for heavy metals like Cu, Ni, Pb and Zn in temperate zones [7]. Heavy metals have great ecological significance due to their toxicity and accumulative behaviour [8]. Assessment of heavy metals is an important tool in environmental monitoring [9].

Soil is very important in ecosystem research as it is the place where many kinds of interaction take place between minerals, air, water and biota. In the recent past, the soil system has been subjected to physical stress by input of foreign substances such as heavy metals [10]. Generally, soil react much more slowly to external influences than water and air as it is able to bind substances into complexes. This is carried out mainly with the help of clay minerals and humic acids which are capable of binding ion superficially. In this process, soil accumulates both organic and inorganic substances and act as a nutrient reservoir for plants and microorganisms [11]. The cultivated plants take up the metals either as mobile ions present in the soil solution through the roots [12] or through folia absorption [13]. The uptake of the metals by crops results in bioaccumulation of the elements in plant tissues. This is known to be influenced by the metal species, plant species and plant parts [14]. Subsequently when these plants are eaten by man, the elements are transferred to the body tissue consequently causing health hazards due to its bioaccumulation and biomagnifications.

Rahlenbeck et al. [15] defined heavy metals as those having a density greater than $5 g/cm^3$ but most often denotes metals that are toxic. These metals include Al, As, Hg, Ni, Se and Zn. Since these heavy metals can become a threat to vegetation and animals and ultimately affect the quality of human life [16] through food chain, it is important to continuously monitor the level of such pollutants in the environment.

Recently, the United Nation on Environmental Protection (UNEP) mapped out strategies and guidelines for the regulation of Mercury (Hg) waste disposal because of its harmful effect on the environment. Some of the common diseases of mankind today such as cardiovascular diseases e.g. heart failure; kidney and liver problems have been traced to heavy metal concentration in the body system. Other diseases caused by heavy metal pollution include but not limited to chromosome breakage, birth defect, paralysis, blindness, insanity, severe dysfunction in the kidneys, reproductive system and central nervous system (CNS) [17].

Several researchers have worked on different dumpsites, but no mention of waste currency dumpsite exist in the literatures and little or nothing have been done or said about the health consequences of the heavy metals present in food crops grown in farm around this site. This present research was carried out to determine the concentrations of the following heavy metals; Mercury, Lead, Cadmium, Chromium, Arsenic and Nickel within and around the waste currency dumpsite in the soil and two food crops namely cassava and plantain grown around the study area, and its environmental and health implications.

Materials and Methods

The study was conducted within and around a waste currency dumpsite at Oluku. Oluku is the gate way town to Benin City when coming in through the western route [4]. Geologically, the area belongs to the Benin Formation (BF) which is made up of yellow to white (sometimes cross bedded) sand, largely unconsolidated with pebbles, clays and sandy clays occurring in lenses [18-20]. Oluku which is located on N06^{o} 27’ 4.8” and E005^{o} 35’ 53.5” is experiencing influx of migrants within and around Benin City

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because of its strategic position as a satellite/ commercial town with natural vegetation.

Twenty four samples were collected in all; eleven soil samples within and around the waste currency dumpsite and one from a distance of one thousand (1000) meters as control. Twelve food crop samples; five Cassava tubers taken from twenty meter from the center of the dumpsite and one from a distance of one thousand meters as control. The same method of sample collection was applied to the plantain fruits. The soil samples were collected with the aid of soil auger and a trowel and were stored in a polythene bag which was then carefully labelled and transported to laboratory for digestion analysis.

The soil samples collected were air dried for 3 days within the laboratory. The soil was then ground in an agate mortar and sieved through 2 mm sieve. 0.5 g of the processed sample was weighed in conical flask. 5 ml of $HClO_4$ and 10 ml of HNO_3 plus 5 ml of HF (1:2:1) was then added to the sample in the conical flask and heated for an hour in a fume cupboard to observe colour change from dirty brown to white. The content was then allowed to cool for 30 minutes after which 20% HCl was added, mixed thoroughly and filtered into one hundred and twenty ml rubber bottle while distilled water was added to make up [21]. The content was properly mixed by shaking; the concentrations of Chromium, Cadmium, Nickel, Lead, Arsenic and Mercury were determined using Atomic Absorption Spectrophotometer (AAS) model Solaar 969 Unicam Series with Air Acetylene flame; this is in conformity with [22].

Plant Analysis

The plants (cassava tuber and plantain fruits) were sampled at 20 m away from the dumpsite and carefully labelled. The cassava tubers were gently washed with distilled water and then cut into sizes and wrapped in a foil paper and kept in the oven for 72 hours, at a steady temperature of 60^oC. The dried samples were mechanically ground with the aid of an agate mortar. 1 g of the processed sample was then weighed into a crucible and kept in the desiccators for 3 hours. The content was allowed to cool for at least 2 hours before adding 20% HCl and filtered. The extract was analysed for elemental concentration of the heavy metals Chromium, Cadmium, Nickel, Lead, Arsenic and Mercury using the same method above.

Statistical Analysis

Statistical analysis was carried out on the results obtained from both soil and food crops using SPSS software at $p < 0.05$ (95%) confidence level.

Results and Discussion

Table 1 shows the various concentrations of heavy metals within and around the dumpsite. The alphabet a, b, c and d on the same vertical (column) are used to define the degree of significant differences between the metals, those with dissimilar case shows a significant difference. Concentration of Cr, (44.51 ± 0.01 mg kg^{-1}) was the highest followed by Cd, (35.81 ± 0.01 mg kg^{-1}), Pb, (30.58 ± 0.01 mg kg^{-1}), As, (24.60 ± 0.01 mg kg^{-1}), Ni, (18.23 ± 0.07 mg kg^{-1}) and Hg, (8.51 ± 0.03 µg kg^{-1}) in the topsoil (TS) at the dumpsite. In the subsoil (SS) at a depth of (15-30cm), Pb has the highest concentration of (20.42 ± 0.01 mg kg^{-1}) followed by As, (17.52 ± 0.99 mg kg^{-1}), Cd, (17.31 ± 0.01 mg kg^{-1}), Cr, (15.00 ± 0.06 mg kg^{-1}) and Hg, (6.11 ± 0.00 µg kg^{-1}).

The result obtained at 1000 m (1km) away from the site shows a significant difference both at the TS and in the SS (the concentrations of the metals decrease from topsoil to subsoil as well as away at a distance of one thousand meters). There were significant differences in the food crops within and around the dumpsite as well as away from the dumpsite as shown in (Table 1). The concentrations in the heavy metals in food crops near the dumpsite were higher in values than those from the control site. The decrease in concentrations from top to subsoil

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and food crops obtained within and away from the dumpsite coupled with a strong positive correlation at P < 0.001 (two tailed) with a correlation density r^2= 0.99 – 0.82 in soil and r^2= 0.96-0.44 in food crops indicated that the metals assessed were from anthropogenic activities from a similar source (Tables 2, 3, 4 & 5).

Table 1: Concentration of Heavy Metals in Soils within and around the Dumpsite

		Heavy Metals Concentration (mg/kg)					
Distance from dumpsite (m)	**Soil Depth (cm)**	**Cr**	**Cd**	**Ni**	**Pb**	**As**	**Hg**
0	0-15 (TS)	44.51 ± 0.01^{d}	35.81 ± 0.01^{d}	18.23 ± 0.07^{c}	30.58 ± 0.01^{d}	24.60 ± 0.01^{c}	8.15 ± 0.03^{c}
1000	0-15 (TS)	10.13 ± 0.03^{b}	12.27 ± 0.03^{c}	10.10 ± 0.00^{a}	11.62 ± 0.02^{b}	5.46 ± 0.07^{a}	0.30 ± 0.00^{a}
0	15-30 (SS)	15.00 ± 0.06^{c}	20.27 ± 0.03^{c}	14.19 ± 0.01^{b}	20.42 ± 0.01^{c}	17.52 ± 0.99^{b}	6.11 ± 0.00^{b}
1000	15-30 (SS)	9.92 ± 0.02^{a}	12.12 ± 0.02^{a}	10.03 ± 0.03^{a}	11.35 ± 0.13^{a}	5.35 ± 0.30^{a}	0.30 ± 0.00^{a}`

Mean values ± SEM along the same column with different super script alphabet are significantly different from each other (P < 0.05)

Table 2: Correlation of the Heavy Metals in Soil

	Cr	Cd	Ni	Pb	As	Hg
Cr	1					
Cd	0.978643	1				
Ni	0.929321	0.985383	1			
Pb	0.942833	0.991192	0.999247	1		
As	0.875719	0.956268	0.992113	0.986528	1	
Hg	0.822349	0.921744	0.974315	0.96488	0.994855	1

Table 3: Composite Correlation of Heavy Metals in Soil

	Cr	**Cd**	**Ni**	**Pb**	**As**	**Hg**
Cr	**1**	**0.978643**	**0.929321**	**0.942833**	**0.875719**	**0.822349**
Cd	0.978643	**1**	**0.985383**	**0.991192**	**0.956268**	**0.921744**
Ni	0.929321	0.985383	**1**	**0.999247**	**0.992113**	**0.974315**
Pb	0.942833	0.991192	0.999247	**1**	**0.986528**	**0.96488**
As	0.875719	0.956268	0.992113	0.986528	**1**	**0.994855**
Hg	0.822349	0.921744	0.974315	0.96488	0.994855	**1**

Table 4: Concentration of Heavy Metals in Food Crop (Cassava and Plantain) within and around the Dumpsite

Distance from dumpsite (m)	Food crop	Heavy Metal Concentration (mg/kg)					
		Cr	**Cd**	**Ni**	**Pb**	**As**	**Hg**
20	Cassava	12.13 ± 0.01[d]	10.21 ± 0.00[d]	19.60 ± 0.01[d]	6.42 ± 0.01[c]	2.44 ± 0.00[c]	3.00 ± 0.00[a]
1000	Cassava	3.75 ± 0.09[b]	4.41 ± 0.01[b]	2.66 ± 0.00[b]	5.41 ± 0.01[b]	0.60 ± 0.01[a]	0.99 ± 0.09[c]
20	Plantain	9.35 ± 0.01[c]	5.21 ± 0.00[c]	9.18 ± 0.01[c]	8.34 ± 0.01[d]	4.03 ± 0.04[d]	2.07 ± 0.03[b]
1000	Plantain	1.67 ± 0.01[a]	2.03 ± 0.03[a]	1.35 ± 0.01[a]	1.50 ± 0.01[a]	0.71 ± 0.00[b]	0.06 ± 0.00[a`]

Mean values ± SEM along the same column with different superscript alphabet are significantly different from each other ($P < 0.05$)

Table 5: Correlation of Heavy Metals in Food Crops

	Cr	**Cd**	**Ni**	**Pb**	**As**	**Hg**
Cr	1					
Cd	0.909143	1				
Ni	0.950849	0.967295	1			
Pb	0.785671	0.587951	0.571404	1		
As	0.778017	0.445856	0.580408	0.814266	1	
Hg	0.989425	0.944089	0.948912	0.797711	0.704901	1

Of the metals assessed in the soil, only Cadmium exceeds the 3 mg kg^{-1} threshold value (Table 6), while others were below the permissible threshold value (Table 6). The land could still be used for residential and commercial purposes but thorough remediation should be administered to the soils if desired for agricultural purpose with regard to Cadmium. Table 7 shows the permissible values of the metals assessed in food crops; the results obtained from the study prove that the heavy metals are above permissible limits except Mercury. The high concentration could be as a result of affinity and absorption of the food crop. When these food crops are consumed by animal including man, the metals gain access to the human system. Heavy metals constitute nuisance on the environment because of its ability to undergo bioaccumulation and biomagnifications, and once introduced to the environment, it becomes very difficult to remove [23]. The health hazards that these heavy metals can cause in humans are so enormous [29]. The health implications of heavy metals are grievous, for example, Arsenic is well-known as a poison and a carcinogen. Its' amount in the soil is related to rock type and industrial activity. High exposure to arsenic can cause vomiting, anorexia, muscle cramps, burning of throat and mouth, and diarrhoea. High level of arsenic in the body is also linked to cancers of the liver, the gastrointestinal tract, the respiratory tract and the skin [29]. Arsenic has no positive effect in human system.

Cadmium toxicity is linked with reproduction problem because it affects sperm and reduces birth weight. It is a potential carcinogen and seems to be a causal factor in cardiovascular diseases and hypertension. Large concentrations of Cd in the soil are associated with parent material (black slates) and most often are man-made (burning of fossil fuels, application of fertilizers, sewage sludge, and plastic waste). Cadmium is also reported to have caused pains in the bones, a popular disease called Itai-Itai – a Japanese word meaning pains [17].

Chromium is required for carbohydrate and lipid metabolism and the utilization of amino acids. Its biological function is also closely associated with that of insulin and most Cr-stimulated reactions depend on insulin. However, excessive amount could be toxic. Toxic levels are common in soils applied with sewage sludge [30].

Lead poisoning is one of the most prevalent public health problems in many parts of the world [31]. It was the first metal to be linked with failures in reproduction. It can cross the placenta easily. It also affects the brain, causing hyperactivity and deficiency in the fine motor functions, thus, it results in damage to the brain. The nervous systems of children are especially sensitive to Lead, leading to retardation. It is also cardiotoxic and contributes to Cardio-myopathy (disease of the heart muscle leading to the enlargement of the heart). Recently in Nigeria, the Federal Ministry of Health reported between March and June 2010 cases of 163 deaths as a result of Zamfara lead poisoning.

Mercury is a toxic heavy metal even at low concentrations to a wide range of organisms including humans. The organic form of mercury can be particularly toxic, and the methyl-and ethyl-forms have been the cause of several major epidemics of poisoning in humans resulting from the ingestion of contaminated food, e.g. fish. Two major epidemics in Japan were caused by the release of methyl and other mercury compounds [32].

Nickel occurs in the environment only at very low levels. Foodstuffs have low natural content of nickel but high amounts can occur in food crops growing in polluted soils. Uptake of high quantities of nickel can cause cancer, respiratory failure, birth defects, allergies, and heart failure [33]. Soils contaminated with heavy metals can be prevented or reduced to the barest minimum in the environment if proper monitoring is put in place. Some of the ways in which heavy metals can be removed from the soil is by phytotechnology [34].

Table 6: Permissible Limit of Heavy Metals as adopted by Three Countries

Country	Soil Use	As (mg/kg)	Cd (mg/kg)	Cr (mg/ kg)	Pb (mg/kg)	Ni (mg/ kg)	Hg (mg/kg)
Germany	Agriculture	50	5	500	1000	200	20
***Canada**	Agriculture	30	3	750	200	150	0.8
Taiwan	Agriculture	60	5	250	500	200	2

* Limit used for this work

Culled from Regulatory standard of heavy metal pollutants in soil and ground water in Taiwan by [24]

Table 7: Permissible Limit of Heavy Metals in Plants

Heavy Metals Concentration in plants (mg/kg)					
Cr	**Cd**	**Ni**	**Pb**	**As**	**Hg**
0.2	0.6	0.23	2.7	3	0.015

Culled from chemical element contents of the Lithosphere, soils and plants (mg/kg) from [25-28].

Conclusion

Literatures have proved beyond reasonable doubt that increases in population and human activities have contributed immensely to heavy metal concentration in soils, air, sediments, water and plants. In the study area, the results obtained show that the concentration of heavy metals was as a result of the indiscriminate dumping and burning of waste currency occasion by the apex bank of Nigeria. This was strongly supported by the positive correlation range of ($r^2 = 0.82 – 0.99$) in soil and ($r^2 = 0.44 – 096$) in food crops. Ukpebor et al. [6] and Harrison [16] reported that soil contaminated with heavy metals is not only a problem with respect to plant nutrition but also constitute a direct health hazard. Some of the heavy metals assessed in the soil and plants (food crops) were below the threshold value while others were above (Tables 1 and 4) when compared to standards (Tables 6 and 7). The highest concentration of the metals assessed were found in soil with Cr > Cd > Pb >Ni >As > Hg at the top soil while Pb > Cd > As > Cr > Ni > Hg at the subsoil; however, there was a significant decrease from top soil to subsoil and at a distance of 1000 m away. The results obtained from food crops analysed show that the food crops grown close to the dumpsite have higher values compared to those obtained from the control site. The overall results show that the dumping and burning of waste currency note is the main source of the metals assessed, and the continuity will amount to environmental and health risk in the area of study [16, 23, 29]. It is therefore strongly recommended that the dumping and burning of currency notes in the site should be discontinued while thorough remediation should be administered to the soil and health survey carried out on the receiving communities to ascertain the level of health impact. We further suggest that speciation studies should also be carried out on the area of study using ICP-MS.

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