ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25mar1633

Heavy Metal Concentrations in *Amaranthus dubius* (Thellung 19123) Grown on Soil Mixed with Compost Manure in Makurdi, Benue State, Nigeria

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Publication Date: 2025/04/10

Abstract: This study investigated the heavy metal concentration in Amaranthus dubius grown on soil mixed with compost manure in Makurdi, Benue State. Two different composts used in this study were produced from rice husk and orange peel, while cow and goat dung were used as soil modifier. Top soil collected from study area was sieved through an array of sieves with different pore sizes which were arranged in descending order. Sand fraction was found to be 90 %, 7 % silt and 3 % clay. The compost, drained water and Amaranthus dubius plant were analyzed for the presence and concentration of heavy metal content using Atomic Absorption Spectrophotometer. The data obtained were subjected to statistical analysis ANOVA. The mean concentrations of heavy metals in Rice husk and Orange peel compost showed that Cadmium (0.017), Iron (9.867), Lead (0.228) mg/l were significantly different at 5% level of probability. The analysis of variance from the mean concentration of heavy metals in Amaranthus dubius and water drained showed that Cadmium, Iron, Lead and Zinc were statistically significant at 1% level of probability. The heavy metal concentration: Cadmium (0.042), Iron (3.25), Lead 0.449(), Zinc (0.811) mg/l in Amaranthus dubius treated with orange peels and rice husk compost are higher than the permissive limit which portend public health challenge.

Keywords: *Heavy Metals, Rice Husk, Orange Peel, Compost, Permissive Limit, Amaranthus Dubius.*

How to Cite: Mercy Omeche Ogabiela; Hyacinth O. A. Oluma; Innocent Okonkwo Ogbonna. (2025). Heavy Metal Concentrations in Amaranthus Dubius (Thellung 19123) Grown on Soil Mixed with Compost Manure in Makurdi, Benue State, Nigeria *International Journal of Innovative Science and Research Technology*, 10(3), 2555-2560. https://doi.org/10.38124/ijisrt/25mar1633.

I. INTRODUCTION

Amaranthus dubius is an annual vegetable herb, particularly grown in African but is grown in most tropical and subtropical regions. This species has been widely introduced as a green vegetable for human consumption and as a medicinal herb. USDA- ARS, 2015).

In Africa, vegetables are important components of daily diets and important sources of income especially in urban and pre-urban areas (Ogwu *et al*., 2016). These crops provide a cheap source of proteins, vitamins and other elements essential for human health and wellbeing (USDA-ARS, 2015).

The contaminations of soil and vegetables by heavy metals is a global environmental issue (Oluwele *et al.*, 2020). Soil is the primary reservoir of heavy metals and thus plays a fundamental role in the overall metal cycle in nature (Shuaibu *et al*., 2013).

Heavy metals are generally referred to as those metals that possess a specific density of more than 5g/cm^3 and adversely affect the environment and living organisms (Adebawo *et al*., 2016). These metals can be leached by rain water, they might be transported from soil to ground waters or may be taken up by plants including agricultural crops, (Adebawo *et al.*, 2016).

Excessive amount of heavy metals in food cause a number of diseases, especially cardiovascular, renal, neurological and bone diseases (Shuaibu *et al*., 2020). These metals could reach food chain through various biochemical processes and ultimately biomagnified in various tropic levels and eventually threaten the health of human (Oluwole *et al*., 2020).

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25mar1633

Once heavy metals are deposited in the soil, they are not degraded and persist in the environment for a long time causing serious environmental pollution (Oluwole *et al*., 2020).

Compost is a combination of decomposed plant and animal materials and other organic materials that are broken down largely through aerobic decomposition into a rich black soil (Goldstein, 2014). Since compost is produce from waste material which contain pathogens, the use of compost may pose health hazards to workers and inhabitants (El-sayed, 2015).

II. MATERIALS AND METHODS

➢ *Study Area*

The study was conducted at the Teaching and Research Farm at Joseph Sarwruan Tarka University, Makurdi, Benue State, Nigeria. (The defunct Federal University of Agriculture). Makurdi (latitude 7°38°N – 7°5°N and longitude 8°24^{O}E 8°38°E (Aboh, 2013).

A. *Experimental Design*

Completely Randomized Experimental Design was used for this study. Randomization ensures that the treatment groups are comparable and that any observed differences in the response variable can be attributed to the treatments rather than other factors. This allows for proper statistical analysis, hypothesis testing and estimation of treatment effects with confidence intervals (Smith *et al*., 2020).

➢ *Soil Sample Collection (Pre - Experiment)*

Top soil (0-5cm) was collected from study area for per soil analysis which was taken to the laboratory for per experiment of soil.

B. *Compost Production*

Two different composts were prepared using orange peels and rice husks, while cow and goat dung were used as soil modifier. Forty kilograms (40kg) each of orange peels and rice husks were separately pour on the bar floor. Twenty kilograms of cow and twenty kilogram of goat dung were then added to the rice husk and same quantity of cow and goat dung was also added to the orange peel. These was mixed properly using shovel and it was watered daily and mixed while it digested (decompose). Ten grams (10g) each of the compost sample was taken in sterilized polythene bag and taken to the laboratory for analysis for the presence and concentration of heavy metals. Data obtained were similarly subjected to statistical analysis ANOVA.

➢ *Experimental Set up*

The experiment had a 4×5 factorial design with treatments consisting of rice husk compost, orange peel compost, urea fertilizer which is applied twenty grams (20g) per twenty kilogram (20kg) of soil and a control which had no treatment application. Each of the treatment was replicated five times making a total of twenty five experimental units and were arranged in completely randomize design. The four volume plastic pot used for the experiment contain five kilogram each of the three soil type and was mixed with five kilogram of the compost before the planting of the seed *Amaranthus dubius*, which was watered twice daily morning and evening and the *Amaranthus dubius* was harvested at six weeks after planting. The *Amaranthus dubius* was washed with clean water, sun dried and packed in sterilized polythene bag and taken to the laboratory for analysis for the presence and concentration of heavy metal using Atomic Absorption Spectrophotometer (AAS).

C. *Water Drained from Vegetable Plant*

Collecting pots were placed underneath the pot used to plant the *Amaranthus dubius* seeds so as to collect drained water. Water drained from each of the pots were collected in clean plastic bottles and labeled to reflect treatment used. The water samples were taken to the laboratory for analysis of the concentration of heavy metals. Data obtained were similarly subjected to statistical analysis ANOVA.

D. *Laboratory Analysis of Soil Samples*

One hundred kilograms (100kg) of top soil (0-5cm) collected from the study area was oven dried at one hundred degree cientigreat (100°C) for twenty four hours (24h). The procedure involve an array of sieves with various diameter sizes with the bigger mesh diameters on top and the smaller at the bottom. The sets of sieves were shaken mechanically for fifteen minutes in other to separate the soil partials into their various sizes. After shaking, the contents of each sieve were weighed using a weighing balance and the weight recorded for that mesh diameter.

III. DETERMINATION OF THE PH OF COMPOST SAMPLE

The pH of the orange peel and rice husk compost were determined in 1:1 compost, water ratio using Jenway 3015 pH meter. Twenty grams (20g) of compost sample was weighed into a fifty (50ml) beaker and twenty gram of the compost sample and allowed to stand for thirty minutes with intermittent stirring using a glass rod. The electrode of the pH meter was instead into partly settled suspension and the pH of each suspension was determined (Buol *et al*., 1973).

A. *Compost Sample Digested and Analyze for Phosphorus*

The Bray one method as described by IITA, (1979) was use in the determination of extractable Phosphorus content in the compost sample.

- **Digestion**: Forty gram (40g) of each of the compost samples were air dried and crushed to a very fine powder. The temperature of the samples digested were checked to ensure that it was between 20° – 25°C (68°-77°F). One gram (1g) each of the compost sample was weighed into a clean crucible, and ashed at 550° for two hours and there after transferred into two hundred and fifty mill (250ml) beaker, fifteen mill (15ml) of concentrated hydrochloric acid and 15ml of concentrated nitric acid were added and the beaker was placed on hot plate and heated to dryness at 100°C and 10ml of distil water was added and filter worm into 100° volumetric flask which was made up to the volume. After the digestion of the rice husk and orange peel compost, they were analyzed for Phosphorus,

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25mar1633

using Molybdanadate method (0.3 to 45.0mg/PO_4) in which the reagent was added to the digest. When it added to the digest, a yellow colour will formed which showed the presence of Phosphorus. A graduated cylinder was used and a round sample cell was filled with 25ml of deionize water. Another graduated cylinder was used and 25ml of the prepared sample was measured and poured into one mil Molybdovanadate reagent was added and swirled to mix properly. The reaction was allow to take place for three minute using a timer beeped, the blank was placed into the cell holder. When zero was touch, the display shows 0.0mg/l PO_4, the prepared sample was wiped and placed into the cell holder and the timer was touch to read and the result was recorded.

B. Proximate Analysis for Rice Husk and Orange Peel Compos

Orange peel and Rice husk compost were first digested. 1.5g of each sample was measured into an ash less filter paper which was dropped into 300ml kdjedal flask. 25mls of concentrated HSO and three gram of digesting mixed catalyst were also dropped into the kdjedahi flask. The flask was then transferred to the kdjedahl digestion apparatus. The sample were digested until a clear green colour was obtained. The digest was allowed to cool and was diluted with 100ml of distilled water. This water went through the process of distillation. 20ml of the diluted digest was measure into 500ml kdiedal flask containing anti bumping chips and40ml of 40% NaOH was slowly added by ensuring that it entered by the side of the flask. Using a 250ml concial flask in which a mixture of 50ml of 2% boric acid and 4 drops of mixed indicator were used to trap Ammonia being liberated. The conical flask and the kdjedahl flask were placed on a distillation apparatus and then heated to distil out Ammonia that evolved. The distillate was collected into the boric acid solution. From the point where boric acid turns green, the distillates was allowed ten minutes for complete distillation. The distillate was then filtered with 0.1ml HCL and fixed Nitrogen was calculated as follows:

$\%N = 14 \times MVt \times Tv \times 100$
Weight of sample (Mg) $\times$ Va
%Crude protein = $\%N \times 6.25$

Where
M = actural morality of acid
Tv = Titre volume of HCL used
Vt = Total volume of diluted digest
Va = Aliquot volume distilled

IV. DETERMINATION OF FIXED CARBON

Fixed carbon was determined indirectly by deducting the sum total of moisture, volatile matter and percentage (%) ash from hundred.

Percentage Fixed Carbon = 100 – Percentage Moisture + Percentage Ash + Percentage volatile matter

A. Analysis of Rice Husk and Orange Peel Compost for Heavy Metals

Digestion of the compost sample was made with $HNO_3/HCLO_4$, thereafter, Zinc, Iron, Potassium, Magnesium, Selenium, Lead and Cadmium was determined using Atomic Absorption Spectrophotometer (AAS).

B. Analysis of Amaranthus dubius for Heavy Metals

Plant samples were first air dried and crushed to a very fine powder. One gram of the sample was weighed into a clean crucible which was ashed at 55^0C for two hours and transferred into 250ml beaker. 15ml of concentrated hydrochloric and 5ml of concentrated nitric acid were added and the beaker was transferred to a hot plat heat at 100^oC for dryness. 10ml of distilled water was added and filter worm into 100^OC volumetric flask and was made up to the volume, thereafter, AAS principle was applied to analyze for heavy metals

C. Analysis of Drained Water for Heavy Metals

Two point five mill (2.5ml) concentrated HNO_3 was added to 50ml of the compost sample and digested until a colourless solution was obtained. The digested sample was filtered to remove insoluble materials and the volume of the digested sample made to 50ml with distilled water. The sample was stored at 40^oC until analysis was done. The heavy metals in the filtered and digestive samples are determined by using Atomic Absorption Spectrophotometer Analysis was carried out in triplicate and average value of Cadmium, Iron, Zinc, Magnesium and Potassium are reported.

V. RESULTS

Analysis of the physical properties of the soil used for this experiment showed that the soil texture varied from sand to sandy loam on the surface and the subsurface respectively. The sand fraction was found to be 90%, 7% silt and 3% clay an indication that the soil type is medium grained see table 1.

The heavy metal concentrations of Phosphorus, Nitrogen, Fixed Carbon, and pH of the both Compost Samples were significantly different at 5% level of probability which were higher than the permissive limit see Table2.

The heavy metals concentrations in orange peel and rice husk compost showed that Cadmium, Iron, Magnesium, Selenium, Zinc and Potassium concentrations were significantly different at 5% level of probability. There was no significantly different in Lead concentration between rice husk and orange peel compost at 5% level of probability (Table 3). Lead, Cadmium, Selenium, Iron concentration in the both compost were all higher than the permissive limit.

The heavy metals concentration in *Amaranthus dubius* showed that the result of analysis of variance indicating the treatment effect from vegetable plant showed that the concentration of Cadmium, Iron, Magnesium, Lead were all statistically significant at 1% level of probability and were all higher than the permissive limit (Table 4).

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25mar1633

Analysis of variance of the heavy metals concentration in water sample Indicated that the concentration of Cadmium, Iron Potassium, Magnesium, Lead and Zinc were statistically significant at 1% level of probability. Cadmium and lead concentration were above permissive limits (Table 5).

VI. DISCUSSION

The results of the physical analyses of soil used for this work as shown in Table 1, showed that the soil had a high proportion of sand. The high proportion of sand could be attributed to the parent materials. Soils of Makurdi area which are believed to have been derived from the cretaceous sandstone and therefore have high proportions of sand (Idoga, 2005).

Phosphorus is one of the major plant nutrients in the soil. It is a constituent of plant cells, essential for cell division and development of the growing tip of plant. For this reason, it is vital for seedlings and young plants. At high concentration, Phosphorus (P) causes nutrient imbalance in plants as it encourages a deficiency of Zinc, Iron, or Copper (Brady, 1978). If on the other hand the Phosphorus is laterally translocated to water bodies, it encourages algal growth. Algal production has being linked with reduction in oxygen supply, which adversely affect other aquatic organisms, including fish. This is a very important environmental effect of phosphorus loading, as a result of hydrocarbon pollution.

The high content of fixed carbon in both compost is probably because of the abundance of organic materials and their decomposition at the soil surface (Okusami, 1986). Fixed carbon itself contain coal and coal is normally use for water treatment to remove smell and odor to make water potable for drinking.

The analysis of the heavy metals concentration in the both compost sample, *Amaranthus dubius* and water samples all showed traces of pollution with heavy metals. Which could be as a result of the bar flow were the compost was produced. The laterite outcrop undernet the soil of Makurdi area (Ofodile, 1989).

The high concentration levels of Cadmium, Lead, Iron, Zinc and Selenium could also be associated with the lead, Zinc mineralization in the Benue valley (Ofodile, 1989).

VII. CONCLUSION AND RECOMMENDATION

Investigations in this study of heavy metals concentration in *Amaranthus dubius* grown on soils mixed with compost manure indicated that compost produced on the bar floor of Makurdi, Benue State are polluted with heavy metals.

All the indices considered reveal some levels of concentrations. This contamination levels can be trace to geographical origins of Makurdi which is associated with the Lead, Zinc, and Cadmium mineralization in the Benue valley. The presence of heavy metals in the soils may change the physical, chemical and biological properties of the soil. Soil runoffs containing heavy metals seep into aquatic environments, and harmful to aquatic plants and animals as well as humans who consume them. These metals are in turn taken up by terrestrial plants from the soil and ground water. In the plants, it reduces productivity by inhibiting its physiological metabolism. Heavy metals uptake by plants and successive accumulation in human tissues as well as its bio magnifications through the food chain causes both human, environmental health concerns.

To reduce the absorption of these heavy metals, the soil should be treated with a basic medium such as potassium hydroxide before the applying of compost treatment. Also basic medium should be introduced in the soil so that transition metals like lead will be in solid form and not in soluble form so that vegetable crops will not absorb it. The heavy metal concentration in the plant is also as a result of the laterite Undernet the soil where the compost was produced since it was produce on the bar floor. Basic medium should also be introduced in the soil which will also have a positive impact on the health of the surrounding environment which may include residential areas and farm lands.

➢ *Recommendations*

- Laterite outcrops areas should be avoided for vegetable production.
- Because of the Lead, Zinc and Cadmium mineralization in the Benue valley, the laterite outcrop Undernet the soil of Makurdi, Compost should not be produced on the bar floor of Makurdi. Also, vegetable farmers in Makurdi should always apply a basic medium to the soil such as Potassium hydroxide before the planting of vegetables.
- Measures should be taken by the relevant health and environmental safety institution of government/non-governmental organizations to promote and implement international best practices in occupational health for vegetable farmers in Makurdi, Benue State, Nigeria.

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Table 1: Physical Properties of the Soil Sample used for the Growth of Vegetable (*Amaranthus dubius*)

Sieve size	**3.35**	**2.36**	**1.7**	**1.18**	**.850**	**.600**	**.425**	**.300**	**.150**	**.075**	**Pan**
Weight	-	50.0	35	66	24	46	101	55	75	29	19
Weight%	-	10.0	7.0	13.2	4.8	9.2	20.2	11.0	15.0	5.8	3.8
Cumulative weight%	-	100	90	83	69.8	65	55.8	35.0	24.6	9.6	3.8

➢ *Note:*

- Clay = 3%
- Silt = 7%
- Sand = 90%
- Soil type is Medium grained sand

Table 2: Heavy Metal Concentration in Phosphorus, Nitrogen, Fixed Carbon and pH Levels in Rice Husk and Orange Compost (mg/l)

Element	**Rice husk compost**	**Orange peel compost**	**t-statistics**	**P-value**	**NMC**	**WHO**
P	5.15	2.40	7.21	0.001	0.1-1.7	-
N	0.29	0.76	23.44	0.001	0.1-1.8	-
C	77.78	84.50	3.74	0.010	10-30	-
pH	6.19	6.75	-	-	6-9	7.0-8.5

➢ *Note:*

- P>0.05 = No significant difference between samples
- P<0.05 =There is significant difference between samples
- NMC = Normal concentration levels of the finished mineral in the compost according to El-sayed, (2011).
- WHO = World Health Organization Standard

Table 3: Heavy Metals Concentrations in Rice Husk and Orange Peel Composts

Element	**Orange peel compost**	**Rice husk compost**	**t-statistic**	**P-value**	**WHO**
Cd	0.017	0.053	62.54	0.001	0.003
Fe	8.360	9.867	17.49	0.001	0.300
Mg	1,899	2.544	17.53	0.001	50.0
Pb	0.228	0.218	0.53	0.630	0.10
Se	2816	3150	94.67	0.001	0.05

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25mar1633

Zn	0.473	4.270	25.20	0.001	5.00
K	0.438	1.1492	30.27	0.001	5.20

➢ *Note:*

- $P>0.05$ = No significant difference between sample mean
- $P<0.05$ = There is significant difference between sample means Cadmium (Cd), Iron (Fe), Lead (Pb), Selenium (Se), Zinc (Zn), Potassium (K)
- WHO = World Health Organization (2011) (International Standard for drinking water after world health organization 4Th edition)

Table 4: Heavy Metals Concentration in *Amaranthus dubius* (mg/l)

Sample	**Cd**	**Fe**	**K**	**Mg**	**Pb**	**Zn**
Control plant	0.032b	3.271b	6.105c	0.819a	0.449c	0.612b
Plant +orange peel compost	0.032b	2.466c	5.388d	0.839a	1.237a	0.633b
Plant + urea fertilizer	0.053a	4.394a	9.221a	0.775a	0.916b	0.526c
Plant + rice husk compost	0.092a	3.259b	7.082b	0.794a	0.174d	0.811a
F-LSD (P>0)	0.01	0.54	0.55	0.04	0.16	0.03
CV	5.70	10.50	5.10	3.20	18.20	3.30
SD	0.03	0.78	1.52	0.03	0.43	0.11
WHO	0.03	0.30	5.20	50.0	0.10	5.00

➢ *Note:*

- LSD =Least significant difference
- CV = Co-efficient of variance
- SD = Standard deviation
- Cadmium (Cd), Iron (Fe), Potassium (K), Magnesium (Mg), Lead (Pd), Zinc (Zn)
- WHO = World Health Organization (International standard for drinking water 4Th edition, 2011)

Table 5: Heavy metals concentration of water drained from the *Amaranthus dubius* (mg/l)

Sample	**Cd**	**Fe**	**K**	**Mg**	**Pb**	**Zn**
Water from control plant	0.0023d	0.2123a	0.0083d	0.0071c	0.2188c	0.0079a
Water from orange peel compost plant	0.1206a	0.0732b	0.0538a	0.0445b	0.4139a	0.0185a
Water from Urea plant	0.0235c	0.2330a	0,0239c	0.0115c	0.1167d	0.0030b
Water from rice husk compost plant	0.0394b	0.0407c	0.0450b	0.0811a	0.3951b	0.0124a
F-LSD (P<0.05)	0.0122	0.0132	0.0063	0.0031	0.0176	0.0019
CV (%)	10.1	4.10	4.80	4.90	4.40	4.80
SD	0.05	0.09	0.02	0.03	0.01	0.01
WHO	0.003	0.3	5.2	50.0	0.1	5.00

➢ *Note:*

- CV = Co-efficient of variation
- SD =Standard deviation
- LSD = Least significant difference
- WHO = World Health Organization Standard 4Th edition, (2011)
- Cadmium (Cd), Iron (Fe), Potassium (K), Magnesium (Mg), Lead (Pb) and Zn (Zn)