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Sawdust as an Organic Amendment on Uptake of Herbicide Residues by *Amaranthus dubius* in Contaminated Soil

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ABSTRACT

Herbicide use and varieties have greatly risen during the past few years. As a result of this, concern over potential health effects such cancer, birth deformities, reproductive issues, tumours, and harm to the liver, kidneys, and nervous system is on the rise. This has an impact on the environment because the misuse of herbicides contaminates the soil, water, and air; harming the local ecology and other living things vital to preserving ecological balance. This study investigated the effect of sawdust as an organic amendment on mobility of herbicides residues in contaminated soil, in which Chinese Spinach (*Amaranthus dubius*) was grown. Sawdust of Doka (*Isoberlinia doka*), African Mahogany (*Khaya senegalensis*) and Beach Wood (*Gmelina arborea*), were used in a randomized complete block design. A composite sample of topsoil (110 kg) and sawdust compost (10kg) was used. 120kg of topsoil without sawdust compost was also used as control. *Amaranthus dubius* was planted in the potted mixtures and 120ml of herbicide (Glyphosate 41% SL) was diluted with 5 litres of water and was applied to all treatment at an equal rate after sowing. Gas Chromatography Mass Spectroscopy (GCMS) analysis of the active ingredient in the glyphosate 41% SL indicated that the quantity of Isopropylamine was 34.093ppm. The highest mean of Isopropylamine (32.75ppm) was found in the control treatment without sawdust amendment, as compared with other samples. The chemical herbicide was detected, at negligible rates, in *Amaranthus dubius* grown in the soil amended with *Gmelina arborea* (10.49ppm) and *Khaya Senegalensis* (8.93ppm). The concentrations in *Amaranthus dubius* from the two amended soils were significantly lower than that of the control (22.56ppm) without compost treatment. However, no herbicide was detected in the vegetable raised on soils amended with compost made from *Isoberlina doka* specie.

1. Introduction

According to research, majority of farmers use synthetic pesticides to manage weeds in an effort to minimize, or completely eliminate yield losses and maintain excellent product quality [1]. For more than 50 years, chemical herbicides have aided in the preservation of crop, human, and animal health. However, due to a lack of resources, herbicide management in underdeveloped nations is frequently insufficient. This is especially true in nations where laws are not properly followed, and farmers frequently lack appropriate knowledge about safe handling practices [2]. Many African nations, including Nigeria, struggle with lax import regulations, inadequate instruction on the proper use of herbicides, inappropriate donations and pushy sales tactics, subpar storage and stock management, pressure to build emergency supplies, and a lack of safe preservation technology [3]. Despite the fact that most farmers are inclined to use herbicides, many are ignorant

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of the different types of herbicides existing, the degree of poisoning they can cause, safety procedures, and the risks of these herbicides to their health and the environment [4].

Additionally, it was found that both small- and large-scale farmers lacked a thorough understanding of the application and effects of these herbicides, which led to their misuse and eventual buildup in the soil. Additionally, it was revealed that 84.2% of farmers are aware that nausea, headaches, and vomiting are symptoms of herbicide poisoning and that 75.8% of farmers are aware that herbicides may affect the ecosystem [5].

The quantity and variety of herbicides have considerably expanded during the previous ten years. The potential negative effects on human health, including cancer, birth defects, reproductive issues, tumours, and harm to the liver, kidney, and neurological systems, have given rise to increased worry [6]. The environment is also impacted since misuse of herbicides may contaminate the soil, water, and air; harming the local ecosystem and other living things essential to maintaining ecological balance like insects, birds, worms, fish, and other creatures [7-10]

There have been numerous studies that determined the effectiveness of sawdust in amending soils with pesticide residues when growing vegetables, but none has been conducted on sawdust from the tree species used in this study, when growing *Amaranthus dubius* To this effect, this study was carried out to ascertain the effect of sawdust as an organic amendment on mobility of herbicides residues in contaminated, soil in which *Amaranthus dubius* (Chinese Spinach) was grown. This was done using sawdust of the following tree species: *Isoberlinia doka*, *Khaya senegalensis*, and *Gmelina arborea.*

This study indicates the level of herbicide contamination in the soil and the effect of sawdust in reducing transfer of herbicides into vegetables. Sawdust, which is a waste material in the environment, is put to use, thereby controlling pollution, which results from sawdust. This research gives an insight on the protection of soil from herbicides residue and this will help farmers in producing high quality farm produce free from contamination from herbicide residues.

2. Experimental

2.1 Description of Experimental Site

The experiment was conducted at the Federal College of Forest Resources Management, Gongolong, Jere Local Government Area of Borno State, Nigeria; in the year 2021, under screen house condition. The area lies between latitude 11049’59.99’’ North and latitude 13008’60.00’’ East, with annual rainfall of about 300 – 500mm and the average daily temperature ranging from 22 – 35^{0}C with mean of daily maximum temperature exceeding 400^{0}C between March and June before the onset of the rain in July to September.

2.2 Treatment of Wood Samples (Composting)

Composting process needs four main ingredients, which are: air, carbon materials (sawdust in this case), green grass (nitrogen source), and moisture which will be mixed and packaged into bags, with small holes to allow air passage and regular mixing [11]. The sample sawdust were mixed in this manner for a period of six weeks before its application on the soil samples.

2.3 Collection of Soil and Potting Mixture

Topsoil (0 – 15cm) was collected from the farm site at Gongolong. The soil was sieved to remove plant roots, as adapted from Beesley *et al.* [12]. According to the adaptation of the method prescribed by Grey *et al.* [13], 110 kg of topsoil and 10kg of sawdust compost of 3 different tree species were separately mixed using shovel and hoe for each treatment. A control sample, without sawdust compost was also prepared. They altogether make 4 treatments.

The treatments are:

A- 10 kg of sawdust compost of *Khaya senegalensis* tree and 110kg of topsoil were mixed.

B- 10kg of sawdust compost of *Gmelina arborea* tree and 110kg of topsoil were mixed.

C- 10kg of sawdust compost of *Isoberlina doka* tree and 110kg of topsoil also mixed.

D- 120kg of topsoil without sawdust compost as control.

Bucket size polypot was used for the potting mixture, where each sample in the treatment was filled with 20kg of the mixture, making 6 samples in each treatment.

2.4 Experimental Design

The experimental design used for this research was randomized complete block design. It is a design in which experimental materials are divided into blocks of homogenous experimental units. Experimental unit has same characteristics and each block contained a complete set of treatment which is assigned at random to the experimental unit. Labelling of pot samples was done by using small flat wood tack on each sample to indicate treatment.

2.5 Sowing, Herbicide Application and Harvesting

The seed of *Amaranthus dubius* was purchased from the local market at Gongolong, and used for the experiment. The seed was placed on the filled pot and covered with soil at shallow depth, and it was watered immediately after planting. The sowing was done on 03-09-2021 and germinated 07-09-2021, and watering were ongoing at the interval of 2 days for 6 weeks.

Mixture of Glyphosate, water and soil was modified from many kinds of methods reported by Grey *et al*. [13] and Ouyang *et al*. [14]. 120ml of (Glyphosate 41% SL) herbicide was diluted with 5 litres of water and was applied to all treatment at equal rates after sowing.

Two plant stands of grown *Amaranthus dubius* from each sample was harvested six weeks. They were washed, shade dried and grounded to powder before taken for gas chromatography analysis at the Multi-User Science Research Laboratory ABU Zaria, Nigeria.

2.6 Analysis of Topsoil and Sawdust Compost before Amendment

Samples of topsoil and sawdust compost of three different tree species were subjected to laboratory analysis to determine the following: PH, total nitrogen, organic carbon, organic matter, total phosphorus and total potassium in them. The samples were analysed at the Soil and Water Management Laboratory, Institute for Agricultural Research, ABU Zaria, Nigeria.

2.7 Determination of Herbicides Residue in the Amaranthus dubius through Gas Chromatography

Gas chromatographic (GC) methods are suitable for the separation and quantitative determination of compounds which are volatile or semi-volatile and thermally stable at the temperature of the measurement. It is thus used to separate and detect small molecular weight compounds in the gas phase. The sample is either a gas or a liquid.

Gas chromatography was employed for the determination of the herbicides residues in the *Amaranthus dubius*.

2.8 Analytical Procedure

Soil extracts were analysed by a Hewlett Packard Shimadzu model HPLC equipped with degasser and Spectrophotometric UV detector. A reverse-phase column with isocratic 4:1 methanol/H2O mobile phase was used. The Rt of the main peak was about 5.1 min. The pH of the mobile phase was 2.52. Buffer:methanol (ratio 60:40) was the mixture for the mobile phase [15]. A 25 cm × 4.6 mm i.d. Adsorbosphere C18 column, a flow rate of 0.5 ml/min, and a detector wavelength of 290 nm were determined to be optimum for the analysis. A 20 µL injection volume was used. The mobile phase and the standard solutions were prepared from filtered HPLC grade solvents. Glyphosate dissipation curves in soil samples were fitted to first-order kinetics (C = Ci e-kt) and half-lives (t1/2) calculated.

3.0 Results and Discussion

3.1 Analysis of topsoil and sawdust compost before amendment

Samples of topsoil and sawdust compost of 3 different tree species were subjected to laboratory analysis to determine the following chemical composition: pH, total nitrogen, organic carbon, organic matter, total phosphorus, and total potassium in them. The samples were analysed at the Soil and Water Management Laboratory Institute for Agricultural Research (A.B.U. Zaria). The results obtained are shown in Table 1 below. Top soil without sawdust compost (control) was found to have a pH of 7.8, total nitrogen (0.06), organic carbon (6.50g.kg^{-1}), organic matter (11.28g.kg^{-1}), total phosphorus (0.19%) and total potassium (0.06%).

Table 1 Analysis of Topsoil

	P.H	**Total Nitrogen**	**Organic Carbon**		**Organic Matter**		**Total Phosphorus**		**Total Potassium**	
			(%)	(g.kg^{-1})	(%)	(g.kg^{-1})	(%)P	(P_2O_5%)	(%)k	%$k_2$0
Topsoil	7.8	0.06	0.65	6.50	11.28	112.8	0.19	0.43	0.06	0.07

(Source: Survey Experiment, 2021).

Khaya senegalensis was found to have a pH (8.1), total nitrogen (0.53), organic carbon (58.30g.kg^{-1}), organic matter (100.40g.kg^{-1}), total phosphorus (0.27%) and total potassium (0.21%). *Gmelina aborea* is found to have a pH (7.8), total nitrogen (0.55g.kg^{-1}), organic carbon (60.60g.kg^{-1}), organic matter (104.60g.kg^{-1}), total phosphorus (0.32%) and total potassium (0.30%). *Isoberlina doka* is found to have a pH of 7.8, total nitrogen (1.57), organic carbon (172.40g.kg^{-1}), organic matter (297.20g.kg^{-1}), total phosphorus (0.22%) and total potassium (0.21%). A research close to this was carried out by Horisawa *et al*. [16], who studied the physical and chemical properties of three sawdust species (*Abiessachaliensis masters, Larix kaempferi and Picea ezonensis*) and soil. The total nitrogen, organic and carbon content results are similar to the result of this study, other parameters from this study are not understudied by Horisawa et al. [16]. The mixing procedure was however, done as adapted from Beesley *et al*. [12].

Table 2 Analysis of sawdust compost before amendment

Tree Species	P.H	Total Nitrogen	Organic Carbon		Organic Matter		Total Phosphorus		Total Potassium	
			(%)	(g.kg^{-1})	(%)	(g.kg^{-1})	(%)P	(P_2O_5%)	(%)k	%k_2O
Khaya senegalensis	8.1	0.53	5.88	58.30	10.04	100.40	0.27	0.62	0.21	0.252
Gmelina arborea	7.8	0.55	6.06	60.60	10.46	104.60	0.32	0.74	0.30	0.360
Isoberlina doka	7.8	1.57	17.24	172.40	29.72	297.20	0.22	0.49	0.21	0.25

(Source: Survey Experiment, 2021).

3.2 GC-MS analysis of the active ingredient in glyphosate 41% SL

GC-MS was carried out on glyphosate 41% SL to estimate the quantity of its active ingredient in part per million (PPM). The active ingredient in the glyphosate 41% SL was found to be Isopropylamine salt and it is soluble in water. The GC-MS analysis of the active ingredient in the glyphosate 41% SL indicated that the quantity of Isopropylamine was 34.093 PPM, this is in conformity to what was obtained by Satchivi *et al.* [17], who understudied the glyphosate isopropylamine salt content of glyphosate.

3.3 GC-MS of amended soil in which Amaranthus samples were planted

Gas Chromatography and Mass Spectroscopy (GC-MS) of Glyphosate 41% SL herbicide solution was carried out at the MULTI-USER Science Research Laboratory, Ahmadu Bello University, Zaria, in order to determine the uptake and the rate of immobilization of the active ingredient (Isopropylamine salt) in both the amended soil and *Amaranthus* samples (A-E) respectively. The control sample for the contaminated soil was also analyzed. The mean concentrations of Isopropylamine salt contained in soil samples amended with saw dust compost derived from various tree species is shown in Figure 1.

It can be seen from Figure 1 that the highest mean of Isopropylamine (32.75ppm) was found in the control treatment which was not amended with sawdust compost. For the other samples with sawdust amendment, the Isopropylamine salt mean concentrations are as thus: *Khaya senegalensis* sample (10.30ppm), *Gmelina arborea* sample (11.10ppm) and *Isoberlina doka* (11.48ppm). The mean concentrations of Isopropylamine salt in the amended soil are observably significantly low, relatively to the concentration of the control sample. This indicates the efficacy of the sawdust compost of varying species in contaminated soil amendment. Mendes *et al.* [18] also observed a significant reduction in the soil herbicide content, which involved the use of biochar as amendment on herbicide-contaminated soil.

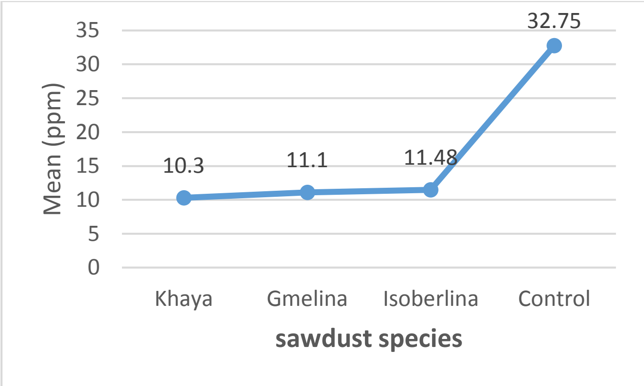

Fig 1 Concentration of Isopropylamine salt in contained soil samples (Source: Survey Experiment, 2021).

3.4 Concentration of Glyphosate in Amaranthus spp grown in soil amended with various sawdust compost

The mean values of Isopropylamine salt in *Amaranthus dubius* raised in soils amended with compost derived from various tree species is shown in Figure 2. Isopropylamine salt was detected in *Amaranthus dubius* raised in the soil amended with *Gmelina arborea* (10.49ppm) and *Khaya senegalensis* (8.93ppm).

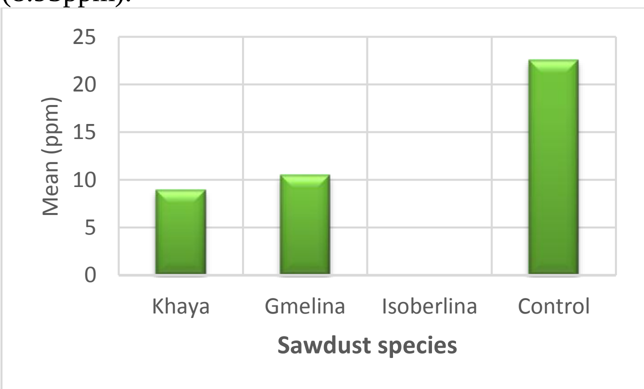

Figure 2 Mean concentration of Glyphosate in Amaranthus dubius in soil amended with various sawdust compost (Source: Survey Experiment, 2021).

The concentrations of Isopropylamine salt in the *Amaranthus dubius* grown in the two amended soils were significantly lower than that of the control (22.56ppm) without compost treatment. However, no herbicide was detected in the vegetable raised on soils amended with compost made from *Isoberlina doka*. This is in conformity with the study of Mendes *et al*., 2018. As permitted for human food consumption, isopropylamine concentration of 250 parts per million and below is safe for consumption [19]. Therefore, it can be inferred that the grown *Amaranthus dubius* in the treated samples are safe for consumption.

3.5 Enrichment factor (EF) of Herbicides in Soils and Vegetable

Figure 3 below shows the enrichment factors of *Khaya senegalensis*, *Gmelina aborea* and their corresponding vegetables, being the ones with uptaken herbicide content. *Khaya Senegalensis* has an enrichment factor of 1.21ppm, while *Gmelina arborea* has an enrichment factor of 1.14ppm. No trace of herbicide was detected in *Isobelinia doka*, which means the herbicide content in the soil was completely intercepted from being uptaken by the plants, through the interceptive action of the sawdust compost in the contaminated soil. As similarly observed by Erban *et al*. [20], the amounts of glyphosate amended in the soil is dependent on the sampling depth and compost dose. Also, Bryndina & Baklanova [21] observed that sawdust stimulates the vital activity of soil microorganisms, increasing their population, and also increasing the biodegradation of the herbicide in the soil by 5 times, in comparison with the soil without sawdust treatment.

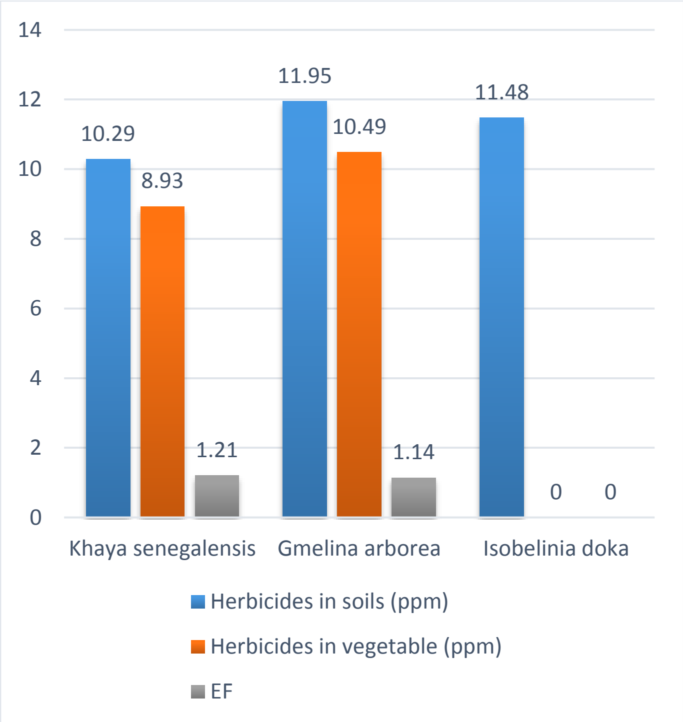

Figure 3 Enrichment Factor (EF) of Herbicides in Soils and Vegetables (Source: Survey Experiment, 2021).

3.6 Chemical Interplay between Sawdust and Isopropylamine

During the incubation period, the uncontaminated control soil without sawdust exhibited normal agricultural soil behaviour, including high initial nitrogen mineralization and a subsequent trend toward stability. By the conclusion of the incubation time, the ammoniacal nitrogen (N) had almost completely gone due to the predominance of nitrate N [22].

The nitrogen mineralization kinetics were significantly changed by the addition of isopropylamine to the soil samples. First off, in direct proportion to the incubation time, the total amount of N extracted increased significantly compared to the sample. Secondly, over the course of the incubation period, the nitrate output tended to decline. The rise in inorganic N must be due to the isopropylamine-induced death of a portion of the edaphic microbiota [23]. The dead microorganisms' cellular material would have gotten into the soil solution, where the microbes that survived could have used it as a source of nutrition. Additionally, the reduced relative concentration of nitrate N indicates that the nitrifying organisms were severely impacted. This is not surprising, given that nitrifying bacterial populations have been shown to be extremely sensitive to soil contaminant levels by a number of writers [24]. The nitrogen cycle in the soil was undoubtedly impacted by the presence of isopropylamine, and any remediation efforts should eliminate this impact.

3. Conclusion

Gas Chromatography and Mass Spectroscopy (GC-MS) was employed to gather useful information on the chemical composition of Glyphosate herbicide solution and this was found to be Isopropylamine. GC-MS was also used to analyse the isopropylamine content of the compost-amended soil samples, as well as the *Amaranthus dubius* grown in them. In addition, it was observed that Isopropylamine was present, at negligible rates, only in two of the *Amaranthus dubius* raised in samples of soil amended with compost. These are samples of *Khaya senegalensis* and *Gmelina arborea*. No content of Isopropylamine was found in *Isoberlina doka*, which means the chemical has been totally immobilized by the sawdust compost in the soil. It was found that the sawdust compost in the soil samples plays significant roles in substantially reducing the content of herbicide in the grown *Amaranthus dubius*. Lastly, as permitted by the Food and Drug Administration [19] for human food consumption, isopropylamine concentration of 250 parts per million and below is safe for consumption. Therefore, it can be inferred that the grown *Amaranthus dubius* are safe for consumption.

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