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Effect of Herbicide Application on Residue Content and Nutritional Composition of Maize from a Pilot Maize Farm

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Abstract
Herbicides, also commonly known as weed killers, are pesticides used to kill unwanted plants. Glyphosate, applied pre-plant, Atrazine applied pre-emergence and 2,4-dichlorophenoxyacetic acid, applied post-emergence, residues were analysed in harvested grains and stems using standard methods, the effects on nutritional composition of the maize grains were studied. The herbicide residues were found in amount below tolerate daily intake but the long-time effect of such cannot be undermined. Herbicide application has minimal effects on nutritional status of the harvested grains. The long term effects of the pesticide residues in food commodity cannot be undermined, therefore closer look and attention to reduce intake as much as possible could safe guide the health of consumers of agricultural products. Total estimation of residues in diet contributed from various ingredients could give actual amount of the residues consumed per meal.

1. Introduction

Herbicides, also commonly known as weed killers, are pesticides used to kill unwanted plants (EPA, 2011). Selective herbicides kill specific targets, while leaving the desired crop relatively unharmed. Some of these act by interfering with the growth of the weed and are often synthetic mimics of natural plant hormones. Herbicides used to clear waste ground, industrial sites, railways and railway embankments are not selective and kill all plant material with which they come into contact. Smaller quantities are used in forestry, pasture systems, and management of areas set aside as wildlife habitat. Some plants produce natural herbicides, such as the genus *Juglans* (walnuts), or the tree of heaven; such action of natural herbicides, and other related chemical interactions, is called allelopathy. Herbicides have widely variable toxicity in addition to acute toxicity from occupational exposure levels. Some herbicides cause a range of health effects ranging from skin rashes to death. The pathway of attack can arise from intentional or unintentional direct consumption, improper application resulting in the herbicide coming into direct contact with people or wildlife, inhalation of aerial sprays, or food consumption prior to the labeled pre-harvest interval. Under some conditions, certain herbicides can be transported via leaching or surface runoff to contaminate groundwater or distant surface water sources. Generally, the conditions that promote herbicide transport include intense storm events (particularly shortly after application) and soils with limited capacity to adsorb or retain the herbicides. Herbicide properties that increase likelihood of transport include persistence (resistance to degradation) and high water solubility (Havens *et al.,* 1995). The health and environmental effects of many herbicides are unknown, and even the scientific community often disagrees on the risk. For example, a panel of 13 scientists reviewing studies on the carcinogenicity of 2,4 D had divided opinions on the likelihood 2,4 D causes cancer in humans (Ibrahim *et al.,* 1991). As of 1992, studies on phenoxy herbicides were few to accurately assess the risk of many types of cancer from these herbicides, even though evidence was stronger that exposure to these herbicides was associated with increased risk of soft tissue sarcoma and non-Hodgkin lymphoma (Howard *et al.,* 1992). Furthermore, there were suggestions that herbicides can play a role in sex reversal of certain organisms that experience temperature-dependent sex determination, which could theoretically alter sex ratios (Gilbert, 2010). Herbicide breakdown requires sufficient time under adequate moisture and soil temperature to support the growth of microbes that degrade herbicide molecules. Some herbicides are broken down quickly or are bound tightly to soil, preventing them from causing problems for crops that are planted the following season. Other herbicides take longer time to decay, and as a result, persist into seasons following the year they were applied. These residues can injure sensitive crops that are seeded in following seasons. Herbicides that have restricted re-cropping options are considered residual herbicides. These re-cropping recommendations are developed to cover a range of conditions that might be considered normal for the Canadian Prairies. Occasionally, weather conditions can result in greater than expected herbicide residue remaining in the soil and may call the "normal" re-cropping recommendations into doubt. Many companies with residual herbicides have modified their labels to take unusually dry events into consideration, and further restrict the crops considered safe to seed following their residual herbicide. Problems with greater than expected herbicide carryover can occur in seasons following exceptionally dry seasons, such as those of 2001, 2002 and 2003. A drought condition, where the soil surface dries to less than the permanent wilting-point, causes microbial activity and the resulting herbicide breakdown to stop for large portions of the season. This results in a greater than expected risk of injury and yield loss from herbicide residue. Very wet conditions or cool conditions can also result in the slowing of herbicide breakdown. Oxygen, required by the aerobic microbes that break down most herbicides, is not available in saturated soils, resulting in the stopping or slowing of breakdown of many herbicides in soil. Some herbicides are broken down at an accelerated rate under oxygen limiting conditions and can result in a loss of weed control activity in saturated areas.

It is unknown whether moist but cool conditions will provide as much breakdown potential as "normal" summer conditions with warm temperatures interspersed with periodic rainfall. This paper presents the effect of herbicide application on residue content and nutritional composition of maize from a pilot maize farm.

2. Materials and Methods

2.1. The Study Site

This study was conducted at the pilot farmland situated behind Food Science and Technology Complex, Osun State Polytechnic, Iree (7°55′N, 4°43′E), Osun State, Nigeria. The location is characterised by a bimodial pattern of rainfall with an annual mean of about 300mm. the soil at the experimental site was sandy clay loam.

2.2. Land Preparation and Planting

The experimental site was manually prepared using cutlass and hoe, but no fertilizer application was employed. The planting was carried out on plots measuring 5×2 m at a spacing of 60×30 cm with 1 m alley-way between plots. Three seeds of Downy Mildew Resistant (DMR) variety of maize were sown per stand but subsequently thinned to one seeding per stand at two weeks after planting (WAP).

2.3. Treatment Application and Experimental Design

The experiment consisted of four treatments:

Glyphosate applied preplant the the rate of 1.41 kg *a. e* ha^{-1}

Atrazine applied preemergence at the rate of 3.0 kg *a. i.* ha^{-1}

2,4 D applied postemergence at the rate of 1.0 kg *a. i* ha^{-1} and

Handweeding at 3 and 7 weeks after planting. All the treatments were assigned to plots arranged in a randomized complete block design involving three replications per treatment.

2.4. Maize Plant Materials Harvesting

The maize corn were harvested after the 12 WAT, the samples were homogenised and stored temperature < 4°C prior to analysis.

2.5. Chromatography Quantification of the Herbicide Residue

The gas chromatography with Pulsed Flame Photometric

Detector (PFPD) was employed. 2 ml of the extract was injected through the sample port, the equipment was made to run at standard conditions and the chromatograms obtained. The standards were run first and integrated into the equipment for subsequent quantification of the samples. Experimental conditions for capillary GC analysis were developed under the following conditions. Capillary column (Crosslinked 5% phenylmethylsiloxane, 30 m x 0.25 mmx 0.25mm (i.d.), with 0.17 µm film thickness, model no HP6890 powered with HP ChemStation Rev. A 09.01 [1206] software), injector temperature 250°C, carrier gas hydrogen (1 mL/min), split ratio 1/20, injection volume 0.2 µl. GC initial oven temperature was kept at 60°C, first ramping was at 10 °C/min for 20 min, second ramping was at 15°C/min for 4 min.

2.6. Proximate and Mineral Composition Determination

Analyses were carried out according to the analytical methods described by Association of Official Analytical Chemists (A. O. A. C., 2010). Air-dried sample (5 g) was sieved with 2 mm sieve size and weighed into the extraction bottle while 25 ml of 1 N ammonium acetate containing 0.01 N EDTA pH 7 was added. The bottle was covered and shaken for 30 minutes on the mechanical shake. Filtered through Whitman filter paper No1, the elements were determined on the Atomic Absorption Spectrophotometer (AAS).

3. Results and Discussion

Table 1 represents Herbicides residues in the maize and stem harvested from the pilot maize farm. The residues are present in ultra minute quantities, that is, in part per trillion. This small residue quantity would have resulted because of the interval between the periods the maize plant produces the grains (12 wks) compared to the time of pesticide application. The residue in the grains is a direct function of the residues in the soil and the maize plant bodies. Pesticides find its way into food commodities by direct application and through residues. Many herbicides exhibit bioaccumulation which could build up to harmful levels in the body as well as in the environment (Walter, 2009). Persistent herbicides are magnified through food chain and could lead to products like meat, poultry, fish, vegetable oil, nuts and fruits commodities having substantial amount of the herbicide residual in them. Plant produce such as grains, vegetable and fruits could be the primary source of these herbicides with bioaccumulation properties (Chung and Chen, 2011). US EPA (2007) gives the Non-carcinogen Tolerable Daily Intake Values for Atrazine to be 0.035mg/kg/day, 2, 4 D to be 0.01mg/kg/day and glyphosate to be 0.1mg/kg/day; Also, Department of Health, Australian Government in 2013 (http://www.ag.gov.au/cca) review the Acceptable Daily Intake (ADI) and No Observable Effect Level (NOEL) for agricultural and veterinary chemicals; The NOEL is the highest administered dose which does not cause any detectable (usually adverse) effect in the study. The overall NOEL for chemical, determined in the most sensitive species is then used to estimate the Acceptable Daily Intake (ADI). The ADI for humans is considered to be a level of intake of a chemical that can be ingested over an entire lifetime without any appreciable risk to health. It is calculated by dividing the overall NOEL from the animal study by a safety factor. The magnitude of the safety factor is selected to account for uncertainties in extrapolation of animal data to humans, variation between humans, the completeness of the toxicological data base and the nature of the potential adverse effects the most safety factor is 100 which takes account that humans may be 10 times more sensitive to the chemical than experimental animals and that a proportion of humans may be 10 times more sensitive than the average person. The ADI and NOEL for atrazine is 0.005mg/kg body weight/day and 0.5mg/kg body weight/day, 2, 4 D is 0.01mg/kg body weight/day and 1mg/kg body weight/day and glyphosate is0.3mg/kg body weight/day and 30mg/kg body weight/day respectively. All the herbicide residues concentration in the maize grains is far lower (part per trillion to part per million) compare to Acceptable Daily Intake or the Tolerable Daily Intake (TDI) values as the case may imply; but there are three important contributions of these residues to human health; first, the total herbicide consumption per meal of an individual is dependent on the various component of the meal; to determine how much pesticide an individual is consuming per meal, it will have to be the sum total of all pesticide components of each of the meal composition. The estimation of this could help to know the actual consumption of the herbicide an individual is taking per meal. That herbicide residues are found in the maize shows that it is a contributing agent of herbicide residues to meal. Secondly, maize is not only consumed by humans, other animals that consume it stand the risk of herbicides bioaccumulation which overtime could pose threat not only to the animals but also the consumers of the animals and therefore increase herbicide component of food chain. Other products of maize grain, such as maize oil, gel and the like could also have some residue in them. It is not the magnitude but the bioaccumulation effect over time that is of health concern. Thirdly, maize is the second most important grain in Nigeria, behind sorghum (CBN, 1992) its consumption level is high; therefore, with the level of its consumption, it is reasonable to be a concern for its consumer of the possible long term effect of its herbicide residues. A 2 – year dietary study by the Department of Health, Australia Government in 2005, on rat when fed with No Observable Effect Level (NOEL) of 10ppm of atrazine concentration (0.5mg/kg body weight/day) revealed mammary tumours in female rats, A similar two year study in which 2, 4 D is administered at NOEL also reveal abnormal renal morphology, similar outcomes were observed on 2-year mouse and 1 year dog studies. 2, 4 D has the highest concentration in its applied produced grain (in the region of 100times); this could be a result of the time of application of the pesticide to the plant (5 weeks after planting). This could explain the reason so much residue is detected in its grains. This is a dangerous signal for farmers applying 2, 4 D to farms which is usually used alternative to hand weeding in the planting of monocots crops to destroy broadleaved weeds (dicots) in the farm, the health effect of the produced grain on the consumer could outweigh benefits of its usage. The least concentrations of the residues were found in the grains produced from the farmland hand weeded. It implies that the grains produced from hand weeding are safer in terms of pesticide residues in them but the labour involved and the output benefits needs be considered to the extent of its health benefit. The concentrations of the herbicide detected in the maize stem are higher than that of the grains. This implies those herbicide residues are more concentrated in the stem and leaves than the grain. Possibilities exist that in herbicide application to farm, more residues could be in the leaves and stems of plants than its produce; that means, for plants that their leaves and stem are consumed, such as vegetables, there is a tendency of higher concentration of pesticide residues in their stems and leaves and poses higher health risk to the consumers. As expected, glyphosate residues were highest in stems of maize plant of the farmland in which glyphosate was applied, atrazine residues were highest in the stems of maize plant in which atrazine was applied and 2, 4 D was highest in the stem of the maize plant of the farmland in which 2, 4 D was applied. The concentration of atrazine detected in its farmland grain was higher than that detected in the grain produced by glyphosate applied farmland; whereas the amount of the residue found in the grain of the 2,4, D is the highest. This could have been a resultant effect of the time of application of the various herbicides.

Table 2 represents the proximate composition of the harvested maize grains in percentage composition. The result obtained is in comparison with the nutrients of major staple foods by the United States Department of Agriculture (2014), it published water to be 10%, protein 9.4%, fat 4.74%, carbohydrate 74% and fibre 7.3%, slight differences could be due to species, place of planting and different environmental effect of the maize plants and subsequent effects on its grain and also method of analysis. The results of the proximate composition of the harvested maize grains shows no pronounce significant difference in the nutritional composition of the maize grains. This implies that application of pesticide to cultivate maize plant does not have anything to do with the nutritional composition of the maize. The crude fat of the grains ranges between 3.21 ± 0.11% to 3.43 ± 0.09%, crude protein ranges between 9.24 ± 0.13% to 11.58 ± 0.13%, Ash content ranges between 3.76 ± 0.12% to 4.39%, carbohydrate ranges between 64.02 ± 0.39 to 67.68 ± 0.14% and Crude fibre ranges between 6.18 ± 0.06 to 7.68 ± 0.14. No specific effect pattern could be seen in the result outcome, differentiation could be linked to fluctuations in natural produce and analytical methods.

Table 3 represents the result of Elemental analysis of the harvested maize grains as influenced by herbicides used on the farm in mg/100g. The result compares favourable with the nutrients of major staple foods by United States Department of Agriculture (2014) in terms of calcium, magnesium, potassium and iron. Sodium content was was slightly lower and phosphorus and zinc contents were slightly higher. Copper and manganese were not detectable by the analytical methods in the maize grain. Maize grain produced from the farmland that 2, 4 D was applied appear to be slightly higher in calcium, magnesium sodium, zinc and potassium content but slightly lower in Iron and phosphorus content. This statement needs a closer look to prove; it is a possibility if 2, 4 D as a substance has ability to solvate ions and make them available to plant, considering that it is applied to plant five (5) weeks after planting. By that time, the maize crop was in a growing stage, and could have ability to absorb any solvated ion which effect could be the result so seen. Further experiments are needed to substantiate this. Not so much difference exists between elemental contents of maize grain from glyphosate and atrazine applied farms. Potassium content of the hand weeded farmland only stands out. Stating that pesticide application on farmland does not affect the nutritional content of maize grain, it appears that pesticide application affect the elemental content of maize grain resulting from such cultivation.

4. Conclusion

Applied herbicides, pre-plant (glyphosate), pre-emergence (Atrazine) and post-emergence (2,4 D amine) to the pilot maize farm indicated residues in the maize grains and stems at a level lower than the daily tolerable level stipulated for pesticide residues in grains. Residues contents showed dependence on the closeness of time of application to harvest time. The long term effects of the pesticide residues in food commodity cannot be undermined, therefore closer look and attention to reduce intake as much as possible could safe guide the health of consumers of agricultural products. Total estimation of residues in diet contributed from various ingredients could give actual amount of the residues consumed per meal.

Table 1. *Herbicides Residues in Harvested Maize Grains and Stems.*

Maize Samples	Maize grains ($x10^{-7}$mg/kg)	Maize Stems ($x10^{-5}$mg/kg)	Control Grains ($x10^{-7}$mg/kg)	Control Stems ($x10^{-5}$mg/kg)
Glyphosate	456.63±0.0015*	86.43±0.0014	3.85±0.0017	5.96±0.0019
Atrazine	128.43±0.0019	210.13±0.0013	2.80±0.0015	1.96±0.0026
2,4, - D	4585.42±0.0013	407.81±0.0025	16.93±0.0021	2.81±0.0019

*Means followed by the same letter within columns do not differ significantly by DMRT (P = 0.05)

Table 2. *Proximate Composition of Harvested Maize Grains (in %).*

Samples	Dry Matter	Crude protein	Ash content	Moisture content	Carbohydrate	Crude fibre	Crude fat
Glyphosate	89.69±0.05^{c*}	9.78±0.26^{c}	4.09±0.11^{b}	10.31±0.05^{a}	66.18±0.43^{b}	6.26±0.16^{c}	3.38±0.06^{a}
Atrazine	90.13±0.07^{b}	9.24±0.13^{d}	3.96±0.36^{b}	9.87±0.07^{b}	67.46±0.29^{a}	6.18±0.06^{c}	3.29±0.09^{b}
2,4, - D	89.61±0.13^{c}	9.94±0.06^{bc}	3.82±0.12^{c}	10.39±0.12^{a}	66.35±0.10^{b}	6.29±0.24^{c}	3.21±0.05^{b}
Hand weeding	91.88±0.14^{a}	10.25±0.12^{b}	3.76±0.12^{d}	8.12±0.14^{c}	66.80±0.37^{ab}	7.68±0.14^{a}	3.39±0.05^{a}
Control	89.63±0.14^{c}	11.58±0.13^{a}	4.39±0.13^{a}	10.37±0.14^{a}	64.02±0.39^{c}	7.21±0.12^{b}	3.43±0.05^{a}

*Means followed by the same letter within columns do not differ significantly by DMRT (P = 0.05)

Table 3. *Elemental Analysis of Harvested Maize Grain as influenced by Herbicides (mg/100g).*

Samples	Ca	Mg	Na	K	P	Cu	Mn	Zn	Fe
Glyphosate	4.83±0.21^{c}	125.83±2.47^{b}	0.00±5.00^{a}	227.50±1.32^{e}	394.57±0.25^{a}	-	-	5.00±0.50^{c}	2.20±0.22^{b}
Atrazine	6.30±0.44^{b}	124.50±1.32^{b}	20.67±5.13^{a}	273.00±1.32^{d}	340.43±0.40^{d}	-	-	4.87±0.25^{c}	1.50±0.13^{c}
2,4, - D	7.80±0.30^{a}	142.50±0.50^{a}	22.00±2.00^{a}	318.50±1.32^{c}	362.90±1.05^{c}	-	-	7.13±0.32^{a}	1.53±0.08^{c}
Control (Hand weeding)	6.17±0.15^{b}	117.00±0.50^{c}	16.33±1.53^{a}	385.70±0.10^{a}	316.77±0.45^{e}	-	-	6.20±0.26^{b}	2.50±0.13^{ab}
Control (Commercial)	7.20±0.20^{a}	115.00±1.32^{c}	26.00±3.61^{a}	345.00±1.32^{b}	366.20±0.78^{b}	-	-	3.20±0.26^{d}	2.80±0.26^{a}

*Means followed by the same letter within columns do not differ significantly by DMRT (P = 0.05)

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