Assessment of Pesticide Residues in Grains Sold In Major Commercial Markets in Ilorin, Kwara State, Nigeria

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Abstract: **Pesticides provide protect to grains against destructive pests but its residues or metabolites has been linked to various health challenges. Its lipophilic nature and consumption of food with residue results into the accumulation of the residues beyond the level which the body can handle which leads to gradual deterioration of health and eventual emergence of disease state. The aim of this study is to assess nine (9) composite samples of the grains that are mostly consumed in the study area (millet, maize and beans) in order to ascertain presence of pesticide in grans sold I the study area. Samples were randomly collected from three (3) major markets in Ilorin Kwara State, Nigeria. Laboratory Analysis was carried out by extraction method for de-fatting of the samples. Qualitative and quantitative analysis were performed using gas chromatography with electron capture and flame ionization. All the nine (9) samples (100%) contained several pesticide residues which are not conventional with hexadecanoic acid (with mean value of 21.07, 33.06 and 13.38 in millet, maize and beans), hexadecanoic acid, methyl ester (with mean value of 4.43, 7.95 and 5.43 in millet, maize and beans) and 9, 12 octadecanoic acid (with mean value of 9.41, 19.10 and 4.57 in millet, maize and beans) recorded in all the samples collected from the three (3) markets. Hexadecanoic acid, an acaricide pesticide residue that is neither classified by WHO nor approved by EU for use as preservative. No residue of conventional pesticide was detected in any of the samples analysed which is an indication that use of conventional pesticide is phasing out among the traders in the markets surveyed.**

Keywords: **grains, pesticide residues, composite, chromatography, hexadecanoic acid**

I. INTRODUCTION

The world population is projected to be 8.5 billion people by 2030 with an annual growth rate of 1.2% of world population [12,3] and with increasing food demand to feed the growing population, the use of pesticides in meeting this increasing food demand has become imminent [22].

The United Nations (UN) has stated that 95% of this increase will occur in developing countries and regions such as sub-Sahara Africa (24) hence there is need to step-up food production through increase in agricultural productivity to ensure food security.

Nigeria food regime is based essentially hinged on two foods: grains, which provide 46% of calories and 52% of protein consumed, and root crops/tubers, which provide 20% of calories and 8% of proteins consumed. Consumption of grains and root crops/tubers to 150kg and 214kg respectively per person per year (in 2007)

Grains which consist of Cereals and legumes generally constitute the most vital diet component for the majority of people in the world [8,18] by providing the calories and protein consumed majorly by poor people.

Food Security in Africa is largely affected by poor agricultural practices and post-harvest loses due to infestation [1]. However various methods adopted in reducing this post-harvest loss has largely affected the food quality and environment by being largely compromised and adversely affected.

Food safety has for many years been a growing concern in Nigeria with several cases of fatalities as a result of contaminated meals.

Annual sales of about 150,000 metric tons of pesticide related chemicals ship into Nigeria portend danger to human health as a result of high chemical usage [17]. This has led to high rate of contamination of food products which have been reported to occur mostly during storage and processing.

Improper use of agro-chemicals and pesticide to control pests on agricultural products especially on grains is one of the leading causes of raising cases of food poisoning in Nigeria [23]. Among the reported case of food poisoning cases by in Nigeria are: Two children who died and 112 people were hospitalized after eating a meal prepared from cowpea treated with pesticide in Cross rivers state. In 2010, it was reported that twenty (20) fast food outlets were closed in Nigeria because of fatalities traced to pesticide residue in their products [4]. On September 17, 2019, a family of seven at Mofoluku, Lagos, comprising of husband, wife and five children were found dead after eating a meal suspected to containing poisonous substance, in Adamawa three [3] members of a family died after eating a local delicacy prepared from beans suspected to be contaminated in 2018. In November, 2018, another four [4] members of a family in Ilorin, kwara state capital died after eating a meal prepared from yam.

There was also a case of "killer" noodles in Nigeria, some children died and others were hospitalized after eating a

particular brand of noodles in 2004. The incidents were investigated and several laboratory analyses conducted by the National Agency for Food and Administrative Control (NAFDAC) concluded that the deaths were caused by the consumption of contaminated grains used in production of the noodles which contained high levels of pesticides [26].

This study attempts to provide monitoring information on the levels of pesticides' residues in grains commonly consumed in Ilorin, a city where many people depend on grains and there is paucity of information on the pesticide residue in the grains consumed in the city.

The objectives of this work include:

i. To ascertain the presence of pesticide in the grains samples from the sampled areas
ii. To determine the concentrations level of pesticide residues presents in the grains samples collected

Pesticide Residue

Pesticide residues in food refers to the pesticides or its metabolic products that may remain in food. Many of these substances, especially those derivatives of chlorinated pesticides could build up to harmful levels in the body as well as in the environment [20].

The presence of pesticide residue affects human as well as non-target organisms [13].

Persistent pesticide active ingredient is magnified along the food chain [7]. Accumulation and magnification of pesticide residues depends on nature of pesticide molecules as well as properties of the food itself [2].

Food and Agriculture Organization/ World Health Organization [10] and European Union [9], stated that food is safe for eating not only if it is free of extraneous materials, unusual odour and colour but also when the concentration of active substances of pesticides fall within recommended Maximum Residue Limit

Organophosphates, carbamates, synthetic pyrethroids and insect growth regulators which can be broken-down to safe products are used for grains protection both in storage and before exporting [6].

Majority or human's and animal's daily foods are not free of residue of pesticide [5]. Furthermore, food processing such as peeling, washing, frying, boiling fermenting e.t.c does not isolate pesticide residue form the food products [19]

Pesticide Residues in Grains

According to a study [17] organochlorine pesticide residues (aldrin, dichloran, dieldrin, endrin, endosulfan, heptachlor epoxide, dichlorodiphenyltrichloroethane lindane, methoxychlor, and mirex) in cereal grains samples collected in some major markets from different location in the country. For example, significant contamination of cowpea was reported in Nigeria in 2010 which led to closure of twenty (20) fast food outlets as a result of fatality cases traced to pesticide residue in their products [4].

Cases of pesticide contamination of grains is not peculiar to only Nigeria or Africa alone. This is evident with a study conducted in Pakistan on pesticide residue in cereal, which revealed higher level of pesticide residue found in wheat compare to maize and rice while rice was found to have higher concentration of pesticide residues than rice [28]. Also, in another research carried out by [25], a thirty (30) day window was found to be appropriate and adequate for a grain treated with recommended doses of pesticide before it will be ready for consumption.

However, presence of pesticide residues in grains does not necessarily mean that it is hazardous. To be toxic, the residues have to be present in quantities large enough to be considered unsafe [21].

II. DESCRIPTION OF THE STUDY AREA

Ilorin is located in North Central of Nigeria, the most populous town and capital of Kwara State. It is located on latitudes $08^0\ 32^1$ N and $04^0\ 35^1$N East. It has a forest area of about 1000km^2 situated in the transaction zone between the forest woodland of the South and Savanna of the North in South Western of Nigeria

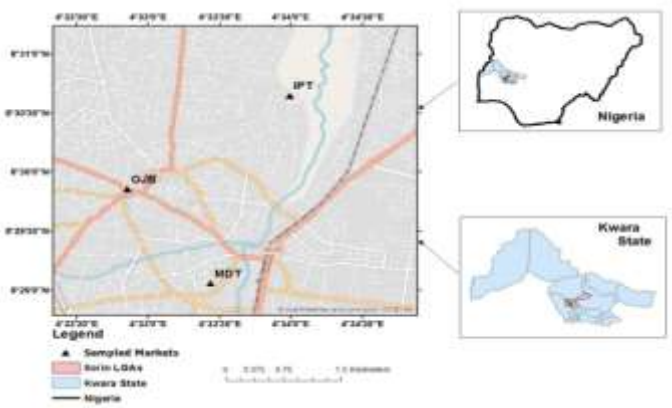

Figure 1: Map of Ilorin West and Ilorin East Showing the three market locations

Grains Samples were maize *(Zea mays L)*, brown beans *(Vigna unguiculata)* and millet *(Panicum miliaceum)*. These grains were purchased from three major food stuff markets in Ilorin, kwara State. The markets are: Ipata market, Mandate market and market Oja Oba market. Traders from whom grains were bought were randomly selected. Seven traders were selected at each market for each of the grains to give a total of sixty-three (63) samples from sixty-three different traders and about 200g of grains was taken from the seven different traders for each of the grain in each market. The seven (7) samples of each of the grains collected from each of the markets were thoroughly

III. MATERIALS AND METHODS

Preparation of samples

Extraneous materials were picked out of the sample selected to reduce interference to minimum. About 200.0g portion of the sample was taken and grounded to about 20 mesh particle size to achieve homogeneity. The milled samples were adequately labelled and stored in a glass bottle in a refrigerator at 4^0C. Back up samples of about (200.0g) were stored as whole grains in labelled glass bottles in the refrigerator.

Extraction of samples

Extraction methods was carried out with some modification The milled sample was properly mixed and 2.0g was weighed into a sample vial of 1.0g sodium sulphate that has been previously heated at 650^0C for one hour in a furnace and stored in a desiccator was added to absorb any moisture present

A gas chromatography from Agilent USA shimadau hydrated to a mass spectrophotometer (5975c) with triple axis detector equipped with an auto injector (10ml syringe) was used with Helium as carrier gas

IV. RESULT AND DISCUSSION

Grain samples collected from all the three main markets from did not contain synthetic pesticide residue as envisaged, however many bioactive substances which have pesticide activity were detected in the grain samples from various market with n-Hexadecanoic acid, Hexadecanoic acid, methyl ester and 9,12-Octadecadienoic acid (Z, Z)-, methyl ester found in all the samples ad are presented as follows

From comparison of the grains from all the markets for the presence of Hexadecaoic acid, it was observed that maize have the maize have the highest mean value of 33.06 as against the least value recorded in beans with mean value of 13.38

Table 1: Abundance of the composite value of pesticide found in the grains from Oja Oba Market

Pesticide Residue	Millet from Oja Oba Area %	Maize from Oja Oba Area %	beans from Oja Oba Area %
Hexadecanoic acid	4.80	3.87	4.61
Hexadecaoic acid, methyl ester	4.80	4.575	5.37
9,12-Octadecadienoic acid (Z ,Z)-, methyl ester	14.64	11.198	4.25
Dichlorvos	ND	ND	ND
Aluminum phosphate	ND	ND	ND
Carbofuran	ND	ND	ND
Mevinfos	ND	ND	ND
Carbaryl	ND	ND	ND
Dimethoate	ND	ND	ND
Diazinon	ND	ND	ND

Table 2: Abundance of the composite value of pesticide found in the grains from Mandate Market

Residue	Millet from mandate Area %	Maize from mandate Area %	beans from mandate Area %
Hexadecanoic acid	4.575	8.24	6.18
Hexadecaoic acid, methyl ester	3.87	8.24	4.73
9,12-Octadecadienoic acid (Z ,Z)-, methyl ester	10.55	21.73	4.73
Dichlorvos	ND	ND	ND
Aluminum phosphate	ND	ND	ND
Carbofuran	ND	ND	ND
Mevinfos	ND	ND	ND
Carbaryl	ND	ND	ND
Dimethoate	ND	ND	ND
Diazinon	ND	ND	ND

Table 3: Abundance of the composite value of pesticide found in the grains from Ipata Market

Residue	Millet from ipata Area %	Maize from ipata Area %	beans from ipata Area %
Hexadecanoic acid	5.37	4.73	6.18
Hexadecaoic acid, methyl ester	4.61	11.04	6.18
9,12-Octadecadienoic acid (Z ,Z)-, methyl ester	13.05	24.38	4.75
Dichlorvos	ND	ND	ND
Aluminum phosphate	ND	ND	ND
Carbofuran	ND	ND	ND
Mevinfos	ND	ND	ND
Carbaryl	ND	ND	ND
Dimethoate	ND	ND	ND
Diazinon	ND	ND	ND

Table 4: Hexadecaoic acid pesticide residue available in the sample analyzed

s/n	millet	Maize	Beans
Oja oba	4.80	13.816	9.69
Mandate	18.87	40.02	1.63
Ipata	39.56	45.35	6.18
Mean	21.07	33.06	13.38

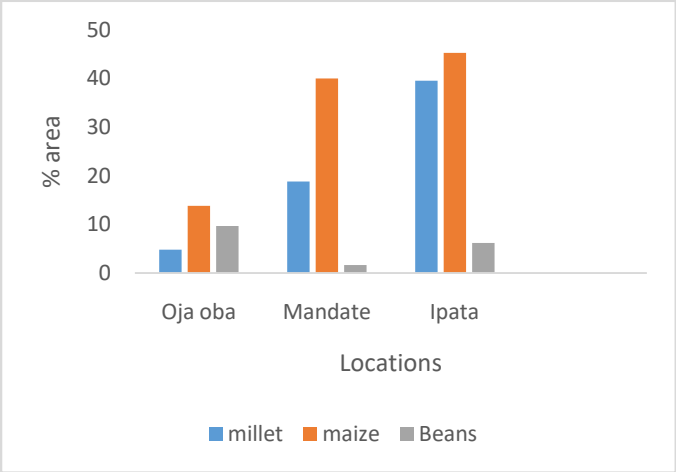

Figure 2: pictorial representations of comparison of Hexadecaoic acid, methyl ester available in samples from different markets

Table 5: Hexadecaoic acid, methyl ester pesticide residue available in the sample analyzed

s/n	Millet	Maize	Beans
Oja oba	4.80	4.575	5.37
Mandate	3.87	8.24	4.73
Ipata	4.61	11.04	6.18
Mean	4.43	7.951	5.43

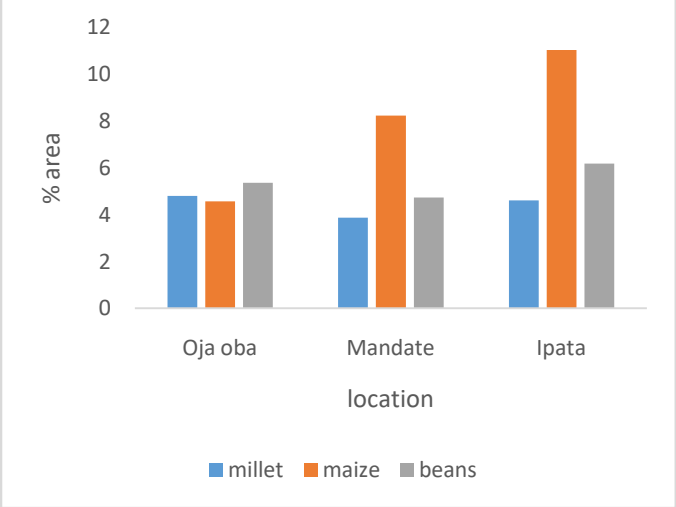

Figure 3: pictorial representations of comparison of Hexadecanoic acid, methyl ester available in samples from different markets

Table 6: 9,12-Octadecadienoic acid (Z, Z)-, methyl ester pesticide residue available in the sample analyzed

s/n	millet	maize	Beans
Oja oba	14.64	11.198	4.25
Mandate	10.55	21.73	4.73
Ipata	13.05	24.38	4.75
Mean	9.41	19.10	4.57

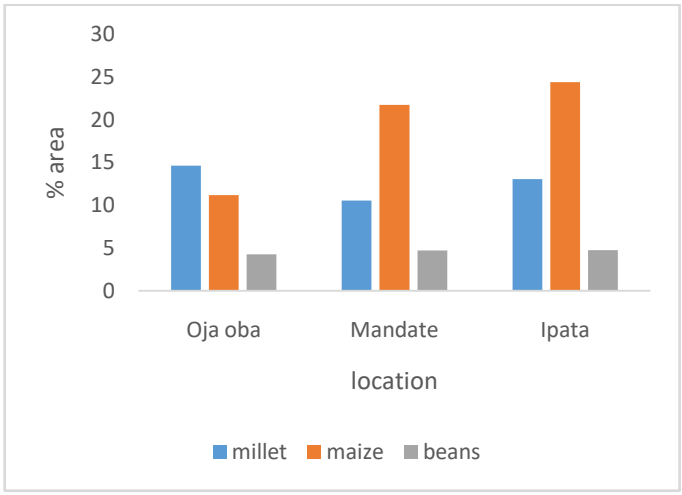

Figure 4: pictorial representations of comparison of 9,12-Octadecadienoic acid (Z, Z)-, methyl ester available in samples from different markets.

V. CONCLOSION AND RECOMMENDATION

The result obtained revealed the presence of active substances which the prominent is Hexadecanoic acid which is also an acaricide, an unclassified a**n**d unapproved compound by WHO ad EU [14]. It presence in all the samples analyzed signal danger ad it is see as a threat to food security for the people of the area and beyond.

The absence of the conventional synthetic pesticide is an indication that the grain sellers in Ilorin have a fair knowledge of the use of conventional pesticides, however the presence of some chemical compound which are bioactive substances among which is hecadecanoic acid, an acaricide which has insecticidal prosperities against soft body pest [15] is a signal that the traders may be involve is sharp practice with the use of unconventional pesticide that are neither registered nor approved by regulatory bodies to be used as pesticide.

In view of the above the, it is recommended that:

- More research should be instituted to find out the effect of some unconventional residues in the samples.
- Traders should be educated more on the danger of using unapproved pesticides.
- Consumers should also be conscious of the toxic effect of pesticide to their health.

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