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Determination of Pesticide Residue in Some Cereals in Wukari, Nigeria

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ABSTRACT

Cereal grains such as rice, sorghum, maize and millet are the staple foods in large parts of the world, supplying most energy and bulk in diets. This research work focused on evaluating and estimating the level of pesticides present in cereals grains consumed in Wukari, Nigeria, and the risk associated with its consumption. Maize, millet, sorghum and rice samples grains were collected randomly at different local markets within Wukari Local Government Area. The samples were cleaned by picking out stones, weevils and other non-essential materials. The different samples were homogenized separately. A gas chromatography hyphenated to a mass spectrophotometer was used to determine the pesticide residue in the cereal grains. Data was analyzed using SPSS. The following pesticide residues were detected in the evaluated cereal grains at the different sampling locations; Delta-Lindane, Alpha-Lindane, Gamma-Lindane, Heptaclor, Aldrin Heptaclor Epoxide, Endosulfan I, P, P-DDE, Endrin, Endosulfan II, P, P-DDD, P, P-DDT, Methoxyclor. Most of the residues occurred at concentrations greater than their respective maximum residue level (MRL). This could be due to high utilization of various pesticides during plant cultivation and storage thereby leading to the bioaccumulation of this substance in the individual cereals. It indicates high levels of non-carcinogenic risk associated with the lifetime consumption of cereals produced and sold within this region. Organochlorine pesticide presence suggests the continuous use of obsolete banned pesticides in the cultivation and storage of cereals.

Keywords: Cereals, pesticides, Wukari, GC-MS

INTRODUCTION

Pesticides are key factors in achieving greater yield in crop production, since, in high-input agricultural production systems, pests, among other crop invaders, including weeds and fungi inevitably need to be managed [1,2]. However, reliance on pesticides is unsustainable due to their harmful effects on the environment and human health. The risk to human health comes from direct or indirect exposure to pesticide residues in primary or derived agricultural products [3]. Pesticide residue refers to the pesticides that may remain on or in food after they are applied to food crops. It is defined by WHO [4] as any substance or mixture of substances in food for man or animals resulting from the use of pesticides and includes any specified derivatives, such as degradation and conversion products, metabolites, reaction products, and impurities that are considered to be of toxicological significance. Infants, children and adults are commonly exposed to pesticides by eating them on and in our food [1].

Pesticides applied to food crops in the field can leave potentially harmful residues [3, 5]. According to Arowora [6], after pesticides are applied to the crops, they may interact with the plant surfaces, be exposed to environmental factors such as wind and sun and may be washed off during rainfall. The pesticide may be absorbed by the plant surface (waxy cuticle and root surfaces) and enter the plant transport system (systemic) or stay on the surface of the plant (contact). The pesticides that get into the plant tissues may be transformed (metabolised) or sequestered in the tissues to form the pesticide residue. Pesticide residues are the deposits of pesticide active ingredient, its metabolites or breakdown products present in some component of the environment after its application, spillage or dumping [7]. The presence of pesticide residues is a concern for consumers because pesticides are known to have potentially harmful effects on other non-targeted organisms than pests and diseases [5].

Previous works by Obida *et al*. [8] and Ogar *et al*. [9] reported organochlorine pesticides such as Aldrin, dieldrin and DDT at concentrations higher than the MRL set by European Union, in bean samples from Maiduguri and Lagos respectively. Odika and Okoye [10] reported average PAH concentrations ranging from 0.04 to 4.68, 0.03 to 5.27, 0.03 to 5.64, 0.02 to 6.55, 0.03 to 4.75, 0.06 to 4.46, 0.03 to 5.91 and 0.02 to 6.31 in rice, maize, wheat, guinea corn, beans, soya beans, pigeon peas and bambara nut, respectively, using gas chromatography coupled with flame ionization detector (GC-FID).

There is limited data on the pesticide levels of cereals consumed within Wukari Local government area of Taraba state and there is a lack of research on the determination of pesticides in the cereals by GC-MS. Therefore, this study aims at assessing the level of pesticide residue deposition in selected cereals in Wukari Local Government Area, Taraba State, Nigeria. The objectives of the study are to determine the presence of pesticides, measure their levels in cereals consumed in Wukari and create awareness of the risks associated with pesticides.

MATERIALS AND METHODS

Study area

This study was conducted in Wukari situated on longitude 9° 47'E and latitude 7° 51'N in Taraba State, Northeastern Nigeria. The vegetation of the area is predominantly characteristic of the savannah zone and with major climatic seasons rainy and dry seasons, which start in March or April, and end in October for the rainy season and the dry season, which starts in November and ends in March or April. Wukari covers an area of 4,308 km^2 and with a population of about 241,546 at the 2006 census Fishing, farming and trading are the major occupations of the people.

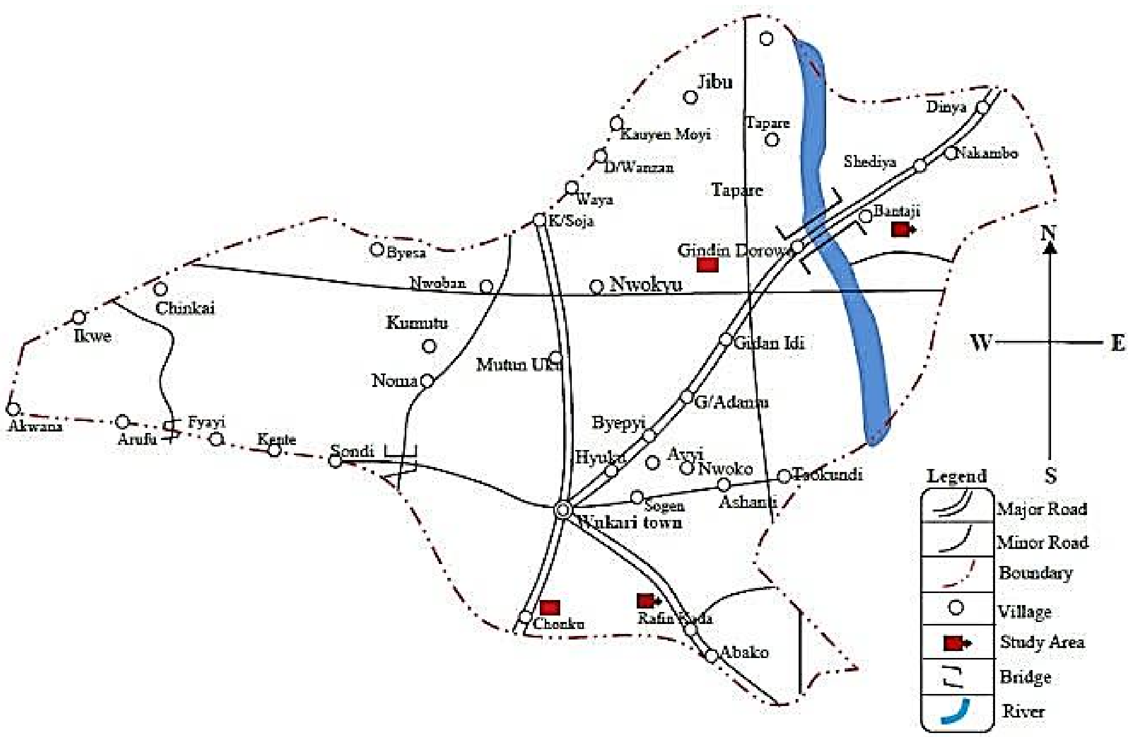

Figure 1: Map of Taraba showing the study area in Wukari

Sampling techniques

Different samples of cereals were collected randomly from different markets within Wukari town which include Rafinkada (7° 43’0’’N, 9° 53’0” E), Bantaje (7° 87’0’’N, 9° 79’0” E), Chonko (7° 88’0” N, 9° 79’0” E), and Gindin Dorowa (7° 88’0’’N, 9° 78’0” E). These are the major markets in Wukari Local Government area where large food items including beans, cereals and other grains are sold. Samples were collected in sterile poly bags to protect them from moisture and contamination. The samples were labelled and stored in a refrigerator at 4 °C until ready for use.

Sample preparation

The cereal grains (maize, millet, sorghum and rice samples) were cleaned by picking out stones, weevils and other non-essential materials. The samples were purchased in dry form and no further drying was required. The different samples were then milled separately, first, using a mortar and pestle and then milled to powder using a hand-grinding machine. Precautionary measures were taken to avoid cross-contamination of the samples during and after milling.

Extraction

Extraction was done using the method of Barron *et al.* [11], with slight modifications. An aliquot of 10 g of each powdered sample was weighed, using an electronic weighing balance, into a 250 ml beaker. The initial weight of the beaker was recorded as Wb and the weight of the beaker with the sample was recorded as Wb+s. About 30 ml of the extraction solvent name it was introduced into 10 g of the powdered sample contained in the beaker. The mixture was properly sealed airtight using foil and tape. This was allowed for 48 h for extraction. The samples after extraction were filtered using filter paper and a funnel and then concentrated by evaporation at room temperature for 24 to 72 h. Heating using a rotary evaporator was avoided to prevent the evaporation of heat-labile pesticide residues. The organic residue was then diluted with 1 ml n-hexane and stored in reagent bottles ready for Gas chromatography-mass spectrometry (GC-MS) analysis.

Recovery

Blank samples were determined by injecting 1 µl of the cleaned-up eluents and solvent into the GC coupled with an electron capture detector. No pesticide residue was detected. Recovery studies followed the method of Ogar *et al*. [9] using blank samples selected for spiking. Six levels of mixed pesticide standard solutions were used for spiking the blank samples. Each standard solution (1 ml) was added to 2 g of ground sample to give fortification levels of different concentrations. Each spiked sample was allowed to stand for five hours and then extracted, cleaned up and analyzed like the test samples. Peak area ratios of pesticides in spiked samples and those of standard were calculated. The percent recovery of each pesticide was then calculated as shown in Equation 1

$$\%\ \text{Recovery} = \frac{\text{Peak area ratio of pesticides in spike sample}}{\text{Peak area ratio of pesticides in standards}} \text{x } 100 \qquad (1)$$

The percent recovery obtained was within the 80-115% range for acceptable recovery values stipulated by the European Union's guidelines for evaluating the accuracy and precision of a method [11].

Detection limits

Running an air-blank sample under the experimental conditions was used to obtain the detector baseline noise. Three times the standard deviation of the blank was recorded as the LOD; this was calculated as the concentration at which baseline noise to signals is three at the expected retention time for the individual target pesticide. LOQ was the concentration leading to a signal-to-noise ratio of 10 [9].

GC/MS analysis and conditions

A gas chromatography, from Agilent USA (7890A) (hyphenated to a mass spectrophotometer (5975C) with a triple axis detector equipped with an auto-injector (10 µl syringe) was used. Helium gas was used as a carrier gas. All chromatographic separation was performed on capillary column having specifications: length; 30 m, internal diameter 0.2 µm, thickness; 250 µm, treated with phenyl methyl silox. Other GC-MS conditions are ion source temperature, 250 °C, internal temperature; 300 °C, pressure; 16.2 psia, out time, 1.8 mm, 1 µl injector in split mode with split ratio 1:50 with injection temperature of 300 °C. 1 µl of the sample was injected. The condition temperature started at 35 °C for 5 min and changed to 150 °C at the rate of 4 °C/min. The temperature was raised to 250 °C at the rate of 20 °C /min and held for 5 min. The total elution was 47.5 min.

RESULTS AND DISCUSSION

Pesticide residues in grains collected from the Bantaje market

The result of pesticide residues in grains from Bantaje is presented in Table 1. Delta-Lindane values from the evaluated grains range between 0.0000 ± 0.00 to 0.0650 ± 0.01 with millet and rice having the lowest and highest values of Delta Lindane respectively. Alpha Lindane values in the evaluated grains range between 0.1950 ± 0.01 to 0.4300 ± 0.00 with sorghum and millet having the lowest and highest values respectively. Gamma-Lindane values in the evaluated grains range from 0.0100 ± 0.00 to 0.2050 ± 0.01 with millet and rice having the lowest value while the highest Gamma-Lindane value was recorded in maize. Heptaclor values in the evaluated grains range between 0.0100 ± 0.00 to 0.2450 ± 0.02 with sorghum and millet having the lowest and highest values respectively. Aldrin values in the evaluated grains range between 0.0000 ± 0.00 to 0.4600 ± 0.01 with rice and maize having the lowest and highest values respectively. Heptaclor Epoxide residual values in the evaluated grains range between 0.0000 ± 0.00 to 0.0300 ± 0.00 with maize and rice having the lowest values while sorghum had the highest value respectively. Endosulfan I values in the evaluated grains range between 0.0000 ± 0.00 to 0.0850 ± 0.01 with maize and millet having the lowest and lowest residues respectively. P, P-DDE residual values in the grains range between 0.0150 ± 0.01 to 0.4500 ± 0.07 with sorghum and millet having the lowest and highest residual values respectively. Endrin residual values range from 0.0000 ± 0.00 to 0.0100 ± 0.00 with maize and sorghum having the lowest and highest values respectively. Endosulfan II values range between 0.0150 ± 0.01 to 0.3600 ± 0.03 with rice and sorghum having the lowest and highest residual values respectively. P, P-DDD residual values range between 0.0000 ± 0.00 to 0.8750 ± 0.02 with millet and sorghum having the lowest and highest residual values. P, P-DDT residual values range from 0.0000 ± 0.00 to 0.0200 ± 0.00 with maize, millet and rice having the lowest values while sorghum had the highest value. Methoxychlor residual concentration ranges between 0.0650 ± 0.01 to 0.8850 ± 0.01 with sorghum and rice having the lowest pesticide residual values respectively.

Table 1: Pesticides residues in grains from Bantaje

Pesticide residues	Maize (PPM)	Millet (PPM)	Sorghum (PPM)	Rice (PPM)	MRL
Delta-Lindane	0.0150 ± 0.01[b]	0.0000 ± 0.00[a]	0.0100 ± 0.00[ab]	0.0650 ± 0.01[c]	0.01
Alpha-Lindane	0.3450 ± 0.01[c]	0.4300 ± 0.00[d]	0.1950 ± 0.01[a]	0.3200 ± 0.01[b]	0.01
Gamma-Lindane	0.2050 ± 0.01[c]	0.0100 ± 0.00[a]	0.0550 ± 0.01[b]	0.0100 ± 0.00[a]	0.01
Heptaclor	0.0300 ± 0.00[ab]	0.2450 ± 0.02[c]	0.0100 ± 0.00[a]	0.0550 ± 0.01[b]	0.02
Aldrin	0.4600 ± 0.01[b]	0.0100 ± 0.00[a]	0.0100 ± 0.00[a]	0.0000 ± 0.00[a]	0.10
Heptaclor Epoxide	0.0000 ± 0.00[a]	0.0200 ± 0.00[b]	0.0300 ± 0.00[c]	0.0000 ± 0.00[a]	0.05
Endosulfan I	0.0000 ± 0.00[a]	0.0850 ± 0.01[d]	0.0200 ± 0.00[b]	0.0300 ± 0.00[c]	0.50
P,P-DDE	0.1200 ± 0.01[b]	0.4500 ± 0.07[c]	0.0150 ± 0.01[a]	0.2100 ± 0.01[b]	0.14
Endrin	0.0000 ± 0.00[a]	0.0100 ± 0.00[a]	0.1000 ± 0.01[b]	0.0000 ± 0.00[a]	0.05
Endosulfan II	0.0200 ± 0.01[a]	0.0250 ± 0.01[a]	0.3600 ± 0.03[b]	0.0150 ± 0.01[a]	1.00
P,P-DDD	0.0550 ± 0.01[b]	0.0000 ± 0.00[a]	0.8750 ± 0.02[c]	0.0100 ± 0.00[a]	0.10
P,P-DDT	0.0000 ± 0.00[a]	0.0000 ± 0.00[a]	0.0200 ± 0.00[b]	0.0000 ± 0.00[a]	0.10
Methoxychlor	0.0800 ± 0.01[a]	0.1600 ± 0.01[b]	0.0650 ± 0.01[a]	0.8850 ± 0.01[c]	0.01

Pesticide residues in grains collected from the Chonku market

The result of pesticide residues in grains from Chonku is presented in Table 2. Delta-Lindane values from the evaluated grains range between 0.0000 ± 0.00 to 0.1050 ± 0.01with maize and millet having the lowest and highest values of Delta Lindane respectively. Alpha Lindane values in the evaluated grains range between 0.2700 ± 0.03 to 0.4800 ± 0.00 with maize and millet having the lowest and highest values respectively.

Gamma-Lindane values in the evaluated grains range from 0.0100 ± 0.00 to 0.1250 ± 0.01 with maize and millet having the lowest value while the highest Gamma-Lindane value was recorded in maize. Heptaclor values in the evaluated grains range between 0.0100 ± 0.00 to 0.1250 ± 0.01 with maize and millet having the lowest and highest values respectively. Aldrin values in the evaluated grains range between 0.0000 ± 0.00 to 0.4400 ± 0.00 with maize and millet having the lowest and highest values respectively. Heptaclor Epoxide residual values in the evaluated grains range between 0.0000 ± 0.00 to 0.0300 ± 0.00 with maize and sorghum having the lowest and highest values respectively. Endosulfan I values in the evaluated grains range between 0.0150 ± 0.01 to 0.0350 ± 0.01 with maize and rice having the lowest and lowest residues respectively. P, P-DDE residual values in the grains range between 0.0100 ± 0.00 to 0.1800 ± 0.01 with rice and sorghum having the lowest and highest residual values respectively. Endrin residual values range from 0.0050 ± 0.01 to 0.0750 ± 0.01 with millet and rice having the lowest and highest values respectively. Endosulfan II values range between 0.0000 ± 0.01 to 0.1150 ± 0.01 with millet and rice having the lowest and highest residual values respectively. P, P-DDD residual values range between 0.0000 ± 0.00 to 0.3550 ± 0.01 with maize and rice having the lowest and highest residual values respectively. P, P-DDT residual values range from 0.0000 ± 0.00 to 0.1000 ± 0.01 with maize and millet having the lowest and highest concentrations respectively. Methoxychlor residual concentration ranges between 0.0100 ± 0.00 to 0.3800 ± 0.00 with maize and millet having the lowest pesticide residual value respectively.

Table 2: Pesticides residues in grains from the Chonku market

Pesticide residues	Maize (PPM)	Millet (PPM)	Sorghum (PPM)	Rice (PPM)	MRL
Delta-Lindane	0.0000 ± 0.00^{a}	0.1050 ± 0.01^{b}	0.0200 ± 0.01^{a}	0.0150 ± 0.01^{a}	0.01
Alpha-Lindane	0.2700 ± 0.03^{b}	0.4800 ± 0.00^{d}	0.4100 ± 0.00^{c}	0.0450 ± 0.01^{b}	0.01
Gamma-Lindane	0.0100 ± 0.00^{a}	0.1250 ± 0.01^{c}	0.1250 ± 0.02^{c}	0.0700 ± 0.00^{b}	0.01

Heptaclor	0.0500 ± 0.00[b]	0.0750 ± 0.01[c]	0.0500 ± 0.01[b]	0.0100 ± 0.00[a]	0.02
Aldrin	0.0100 ± 0.00[a]	0.4400 ± 0.00[d]	0.3750 ± 0.02[c]	0.2150 ± 0.01[b]	0.10
Heptaclor Epoxide	0.0000 ± 0.00[a]	0.0000 ± 0.00[a]	0.0300 ± 0.01[b]	0.0150 ± 0.01[ab]	0.05
Endosulfan I	0.0150 ± 0.01[a]	0.0250 ± 0.01[ab]	0.0200 ± 0.00[ab]	0.0350 ± 0.01[b]	0.50
P,P-DDE	0.1450 ± 0.01[b]	0.1400 ± 0.01[b]	0.1800 ± 0.01[c]	0.0100 ± 0.00[a]	0.14
Endrin	0.0100 ± 0.00[a]	0.0050 ± 0.01[a]	0.0150 ± 0.01[a]	0.0750 ± 0.01[b]	0.05
Endosulfan II	0.0250 ± 0.01[b]	0.0000 ± 0.00[a]	0.0000 ± 0.00[a]	0.1150 ± 0.01[c]	1.00
P,P-DDD	0.0000 ± 0.00[a]	0.0850 ± 0.01[b]	0.1700 ± 0.00[c]	0.3550 ± 0.01[d]	0.10
P,P-DDT	0.0000 ± 0.00[a]	0.1000 ± 0.01[c]	0.0150 ± 0.01[a]	0.0550 ± 0.01[b]	0.10
Methoxyclor	0.0100 ± 0.00[a]	0.3800 ± 0.00[a]	0.2700 ± 0.00[a]	0.2820 ± 0.03[a]	0.01

Pesticides residues in grains from Gindin Dorowa market

The result of pesticide residues in grains from Gindin Dorowa is presented in Table 3. Delta-Lindane values from the evaluated grains range between 0.0300 ± 0.00 to 0.4500 ± 0.00 with millet and sorghum having the lowest and highest values of Delta Lindane respectively. Alpha Lindane values in the evaluated grains range between 0.3400 ± 0.00 to 2.590 ± 0.09 with millet and sorghum having the lowest and highest values respectively. Gamma-Lindane values in the evaluated grains range from 0.0500 ± 0.00 to 0.5050 ± 0.02 with sorghum and rice having the lowest and highest Gamma-Lindane concentrations in the grains. Heptaclor values in the evaluated grains range between 0.0500 ± 0.00 to 0.3600 ± 0.01 with maize and millet having the lowest concentrations while sorghum had the highest concentration respectively. Aldrin values in the evaluated grains range between 0.0100 ± 0.00 to 0.4300 ± 0.01 with rice and millet having the lowest and highest values respectively. Heptaclor Epoxide residual values in the evaluated grains range between 0.0100 ± 0.00 to 0.0350 ± 0.00 with maize and sorghum having the lowest and highest values respectively. Endosulfan I values of the evaluated grains range between

0.0550 ± 0.06 to 0.1500 ± 0.00 with maize and sorghum having the lowest and highest residual concentrations respectively. P, P-DDE residual values in the grains range between 0.1300 ± 0.00 to 0.7950 ± 0.01 with millet and sorghum having the lowest and highest residual values respectively. Endrin residual values range from 0.0000 ± 0.00 to 0.0300 ± 0.01 with millet and sorghum having the lowest and highest values respectively. Endosulfan II values range between 0.0100 ± 0.01 to 0.0300 ± 0.00 with maize and sorghum having the lowest and highest residual values respectively. P, P-DDD residual values range between 0.0000 ± 0.00 to 0.1800 ± 0.01 with millet and Sorghum having the lowest and highest residual values respectively. P, P-DDT residual values range from 0.0000 ± 0.00 to 0.0200 ± 0.00 with millet and sorghum having the lowest values and 0.0200 highest concentrations respectively. Methoxychlor residual concentration ranges between 0.0500 ± 0.00 to 0.3100 ± 0.00 with millet and sorghum having the lowest pesticide residual values respectively.

Table 3: Pesticides residues in grains from Gindin Dorowa market

Pesticide residues	Maize (PPM)	Millet (PPM)	Sorghum (PPM)	Rice (PPM)	MRL
Delta-Lindane	0.0400 ± 0.00^{a}	0.0300 ± 0.00^{a}	0.4500 ± 0.00^{c}	0.0800 ± 0.00^{b}	0.01
Alpha-Lindane	0.4200 ± 0.01^{a}	0.3400 ± 0.00^{a}	2.590 ± 0.09^{c}	0.8500 ± 0.01^{b}	0.01
Gamma-Lindane	0.0900 ± 0.00^{b}	0.4050 ± 0.01^{c}	0.0500 ± 0.00^{a}	0.5050 ± 0.02^{d}	0.01
Heptaclor	0.0500 ± 0.00^{a}	0.0500 ± 0.00^{a}	0.3600 ± 0.01^{c}	0.2400 ± 0.00^{b}	0.02
Aldrin	0.0500 ± 0.01^{a}	0.4300 ± 0.01^{b}	0.0250 ± 0.01^{a}	0.0100 ± 0.00^{a}	0.10
Heptaclor Epoxide	0.0100 ± 0.00^{a}	0.0100 ± 0.00^{a}	0.0350 ± 0.01^{b}	0.0300 ± 0.00^{b}	0.05
Endosulfan I	0.0550 ± 0.06^{a}	0.0700 ± 0.00^{ab}	0.1500 ± 0.00^{b}	0.0600 ± 0.00^{ab}	0.50
P,P-DDE	0.1550 ± 0.01^{b}	0.1300 ± 0.00^{a}	0.7950 ± 0.01^{d}	0.7600 ± 0.01^{c}	0.14
Endrin	0.0200 ± 0.00^{ab}	0.0000 ± 0.00^{a}	0.0300 ± 0.01^{b}	0.0200 ± 0.00^{ab}	0.05

Endosulfan II	0.0100 ± 0.00[a]	0.0150 ± 0.01[ab]	0.0300 ± 0.00[c]	0.0250 ± 0.01[bc]	1.00
P,P-DDD	0.0650 ± 0.01[b]	0.0000 ± 0.00[a]	0.1800 ± 0.01[c]	0.0100 ± 0.00[a]	0.10
P,P-DDT	0.0100 ± 0.00[b]	0.0000 ± 0.00[a]	0.0000 ± 0.00[a]	0.0200 ± 0.00[c]	0.10
Methoxychlor	0.0950 ± 0.01[b]	0.0500 ± 0.00[a]	0.3100 ± 0.01[d]	0.2450 ± 0.01[c]	0.01

Pesticides residues in grains from Rafin Kada market

The result of pesticide residues in grains from Rafin Kada is presented in Table 4. Delta-Lindane values from the evaluated grains range between 0.0000 ± 0.00 to 0.2800 ± 0.00 with maize having the highest concentration. Alpha Lindane values in the evaluated grains range between 0.0100 ± 0.00 to 1.1900 ± 0.00 with Sorghum and rice having the lowest and highest values respectively. Gamma-Lindane values in the evaluated grains range from 0.0200 ± 0.01 to 0.1100 ± 0.01 with sorghum and millet having the lowest and highest Gamma-Lindane concentrations in the grains. Heptaclor values in the evaluated grains range between 0.0000 ± 0.00 to 0.0500 ± 0.01 with millet and sorghum having the lowest concentrations while sorghum had the highest concentration respectively. Aldrin values in the evaluated grains range between 0.0000 ± 0.00 to 2.5100 ± 0.01 with maize and rice having the lowest and highest values respectively. Heptaclor Epoxide residual values in the evaluated grains range between 0.0000 ± 0.00 to 0.0500 ± 0.00 with millet and sorghum having the lowest and highest values respectively. Endosulfan I values in the evaluated grains range between 0.0100 ± 0.00 to 0.2300 ± 0.00 with maize and sorghum having the lowest and highest residual concentrations respectively. P, P-DDE residual values in the grains range between 0.0100 ± 0.00 to 0.3500 ± 0.01 with sorghum and maize having the lowest and highest residual values respectively. Endrin residual values range from 0.0000 ± 0.00 to 0.0350 ± 0.01 with rice and sorghum having the lowest and highest values respectively. Endosulfan II values range between 0.0100 ± 0.00 to 0.0500 ± 0.00 with millet and sorghum having the lowest and highest residual values respectively. P, P-DDD residual values range between 0.0100 ± 0.00 to 0.0750 ± 0.01 with millet and Sorghum having the lowest and highest residual values respectively. P, P-DDT residual values range from 0.0000 ± 0.00 to 0.1400 ± 0.00 with sorghum and millet having the lowest and highest concentrations respectively.

Methoxychlor residual concentration ranges between 0.0400 ± 0.00 to 0.2900 ± 0.00 with sorghum and millet having the lowest pesticide residual values respectively.

Table 4: Pesticides residues in grains from Rafin Kada

Pesticide residues	Maize (ppm)	Millet (ppm)	Sorghum (ppm)	Rice (ppm)	MRL
Delta-Lindane	0.2800 ± 0.01^{c}	0.0000 ± 0.00^{a}	0.0000 ± 0.00^{a}	0.0000 ± 0.00^{a}	0.01
Alpha-Lindane	0.4100 ± 0.00^{c}	0.3450 ± 0.01^{b}	0.0100 ± 0.00^{a}	1.1900 ± 0.00^{d}	0.01
Gamma-Lindane	0.0250 ± 0.01^{a}	0.1100 ± 0.01^{b}	0.0200 ± 0.00^{a}	0.0400 ± 0.00^{a}	0.01
Heptaclor	0.3650 ± 0.01^{d}	0.0600 ± 0.00^{b}	0.0000 ± 0.00^{a}	0.1200 ± 0.00^{c}	0.02
Aldrin	0.0000 ± 0.00^{a}	0.4200 ± 0.00^{c}	0.0200 ± 0.00^{b}	2.5100 ± 0.01^{d}	0.10
Heptaclor Epoxide	0.0200 ± 0.00^{a}	0.0000 ± 0.00^{a}	0.0500 ± 0.01^{a}	0.0200 ± 0.01^{a}	0.05
Endosulfan I	0.2300 ± 0.00^{c}	0.0100 ± 0.00^{a}	0.0150 ± 0.01^{a}	0.0450 ± 0.01^{b}	0.50
P,P-DDE	0.3500 ± 0.01^{d}	0.1800 ± 0.01^{b}	0.0100 ± 0.00^{a}	0.2750 ± 0.01^{c}	0.14
Endrin	0.0350 ± 0.01^{c}	0.0100 ± 0.00^{b}	0.0300 ± 0.00^{c}	0.0000 ± 0.00^{a}	0.05
Endosulfan II	0.0300 ± 0.01^{ab}	0.0100 ± 0.00^{a}	0.0500 ± 0.00^{b}	0.0150 ± 0.01^{a}	1.00
P,P-DDD	0.0100 ± 0.00^{a}	0.0750 ± 0.01^{b}	0.0150 ± 0.01^{a}	0.0100 ± 0.00^{a}	0.10
P,P-DDT	0.1400 ± 0.00^{b}	0.0100 ± 0.00^{b}	0.0000 ± 0.00^{a}	0.0200 ± 0.00^{c}	0.10
Methoxychlor	0.2900 ± 0.00^{d}	0.1100 ± 0.01^{c}	0.0400 ± 0.00^{a}	0.0750 ± 0.01^{b}	0.01

These pesticides are typically very persistent in the environment and are known to accumulate in sediments, plants and animals [12]. The analysis of pesticide residues in grains obtained from Bantaje, Chonku, Gindin Dorowa and Rafin Kada confirmed the presence of various pesticide residues. The detected pesticide residues include Delta-Lindane, Alpha-Lindane, Gamma-

Lindane, Heptaclor, Aldrin Heptaclor Epoxide, Endosulfan I, P, P-DDE, Endrin, Endosulfan II, P, P-DDD, P, P-DDT, Methoxychlor. The different seed grains evaluated include maize, millet, rice and sorghum. Delta Lindane residue values in maize obtained or evaluated from Bantaje, Gindin Dorowa, and Rafin Kada were above WHO-accepted MRL in cereals (0.01) thus implying continuous consumption of maize at these sampling locations will result in a severe health crisis. However, the residual concentration of Delta-Lindane in millet and sorghum was above WHO [4] set MRL in Chonku and Gindin Dorowa implying non-carcinogenic deleterious health implications at these sampling locations through the consumption of millets. The residual concentration of Delta-Lindane in rice was above the WHO [4] recommended MRL in grains in Bantaje, Chonku, and Gindin Dorowa thus continued exposure may result in health anomalies. The presence of Delta-Lindane in the evaluated cereals at the respective sampling locations may be due to its application by farmers either on the farm or as a postharvest treatment to prevent pests. Alpha-lindane and Gamma-Lindane appear to be present in the evaluated grains at the majority of the sampling locations, however, the residual concentration of Alpha-Lindane in the grains in the majority of the sampling locations was above WHO [4] set MRL in grains, thus, continuous exposure through consumption of these pesticide residues via these food grains may result in health complications.

Heptachlor is one of the pesticides that disrupt the endocrine system. Congenital deformities in children, cancer, especially hormonal cancers, delay in sexual development, and delay in the development of the nervous system are possible effects that may be related to the endocrine system in humans due to Heptachlor [13]. The MAC EQS biota of Heptachlor is defined as 6.7×10^{-6} µg/g in 2013/39/EU [13] In this study, the concentration of Heptachlor in the majority of the evaluated grains at the respective sampling locations was above the recommended MRL [4]. The presence of this pesticide residue in the evaluated grains may be due to its applications either on the farm or as a post-harvest chemical to prevent postharvest losses. Consumption of grains of food substances contaminated with Heptachlor residue in levels above the set recommended MRL can be deleterious to health.

DDT and its metabolites DDD and P, P-DDE accumulate in the breasts of women, especially in breast milk, and can cause serious health problems in newborn babies [14]. In a study by Cingi and Dokmeci [15], it was found that DDT, Lindane, and Dieldrin were mostly found in fat tissue and then in the brain and blood. Previous works by Obida *et al*. [8] and Ogar *et al*. [9] have detected the presence of organochlorine pesticides such as Aldrin, dieldrin and DDT at concentrations higher than the MRL, set by European Union, in bean samples from Maiduguri and Lagos respectively.

Many of the older, cheaper (off-patent) pesticides, such as dichlorodiphenyltrichloroethane (DDT) and lindane, can remain for years in soil, water and food products [16]. These chemicals have been banned by countries that signed the 2001 Stockholm Convention – an international treaty that aims to eliminate or restrict the production and use of persistent organic pollutants [4]. Consumption of grains contaminated with DDT and other organochlorine pesticides could cause liver lesions and may also disrupt reproductive functions as well as carcinogenic risks [16, 17]. The MRL is not expected to be exceeded in any foodstuff if the pesticide is applied in accordance with directions for its safe use [9]. If, however, a residue in a food sample exceeds the MRL, the food commodity is unsafe for consumption because it contains an unsafe or illegal amount of the residue.

The present study reveals that most of the evaluated grains from the respective sampling locations have a residual concentration above WHO [4] set MRL. Findings from this study are not in consonance with a report of Emmanuel *et al*. [18] who reported DDT and DDD below WHO-set maximum residue limits. Findings from this study are in consonance with Adeyemi *et al*. [19], who in their studies reported 0.037 ppb for Heptachlor. Endosulfan sulfate is a type of pesticide commonly found. It was defined that endosulfan is the most common species of pesticides in nutrients, solids, and water in Europe. The present study reveals Endosulfan residual concentration in the majority of the sampling locations was above WHO [4] recommended MRL. Findings from the present study are in consonance with the findings of Iliya *et al*. [20] also reported the presence of endosulphan at high concentrations in grains samples evaluated in Adamawa.

Aldrin is widely used in agricultural areas throughout the world. Both chemicals are highly persistent in the environment, toxic and bio-accumulative. Because the toxicity of this persistent pesticide posed an imminent danger to human health, NAFDAC banned the most major uses of dieldrin and Aldrin in 2018, but the product is still in use because of the low cost and affordability. Aldrin is not easily metabolized in water and has a limited capacity to be digested and excreted from the body. It is, however, easily absorbed and transported throughout the blood of vertebrates and hemolymph of invertebrates [21].

Real-life chronic exposure to a mixture of pesticides with possible additive or synergistic effects requires in-depth research. The underlying scientific uncertainty, the exposure of vulnerable groups and the fact that there are numerous possible mixtures reveal the real complex character of the problem [3]. The combination of substances with probably carcinogenic or endocrine-disrupting effects may produce unknown adverse health effects. Therefore, the determination of safe levels of exposure to single pesticides may underestimate the real health effects, ignoring also the chronic exposure to multiple chemical substances. Taking into consideration the health and environmental effects of chemical pesticides, it is clear that the need for a new concept in agriculture is urgent.

The MRL is not expected to be exceeded in any foodstuff if the pesticide is applied in accordance with directions for its safe use [9]. If, however, a residue in a food sample exceeds the MRL, the food commodity is unsafe for consumption because it contains an unsafe or illegal amount of the residue. This suggests the high use of organochlorine pesticides in the storage and or cultivation of the crop.

The study on pesticide residue in cereals from Wukari, Nigeria, has several limitations, including potential inadequacy in sample size and representation. The sampling method might have introduced foreign materials into the sample, and the reliance on traditional analytical techniques might affect the accuracy of detected pesticide levels. The study may not account for temporal and spatial variability, as residue levels can fluctuate based on seasonal changes and different farming practices. Resource constraints, including funding, equipment, and expertise limited the study's scope and depth, affecting the thoroughness of data collection and analysis.

CONCLUSION

Pesticide residue analysis in cereals from the various sampling locations for this study revealed the following pesticide residue; Delta-Lindane, Alpha-Lindane, Gamma-Lindane, Heptaclor, Aldrin Heptaclor Epoxide, Endosulfan I, P, P-DDE, Endrin, Endosulfan II, P, P-DDD, P, P-DDT and Methoxyclor The pesticide residues were detected in the samples of cereals grains (rice, maize, millet and sorghum) analyzed, with most occurring at concentrations greater than their respective MRL. This could be a result of the high utilization of various pesticides during plant cultivation and storage thus leading to the bioaccumulation of this substance in the individual cereals. It indicates high levels of non-carcinogenic risk associated with the lifetime consumption of cereals produced and sold within this region.

This research on pesticide residues in cereals from Wukari, is important for public health and food safety, as it reveals harmful pesticide levels in maize, millet, rice, and sorghum, exceeding WHO-accepted limits and posing severe health risks. The findings highlight the need for stricter pesticide controls and safer agricultural practices, along with public awareness campaigns about pesticide dangers and safe consumption. Future research should include a larger, more diverse sample area, monitor long-term pesticide residue impacts, employ advanced analytical techniques, and investigate eco-friendly pest control methods to enhance food safety.

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