

Full Length Research Paper

Health risk assessment of pesticide residues in bean samples from Wukari, Taraba State, Nigeria

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Man depends heavily on pesticides to boost his agricultural productions. This study aimed at carrying out a risk assessment of pesticide residues in samples of beans stored and sold in Wukari Town, Nigeria. Different samples of beans were collected randomly from different market points within Wukari, Rafin kada and Idofi. The pesticide residue analysis was carried out using GC/MS after sample extraction, filtration and Concentration. The mean estimated consumption rate of beans within Wukari was obtained. The concentrations of each pesticide were compared with their Maximum Residue Levels (MRLs) and the Estimated Daily Intake (EDI) along with the Health Risk Index (HRI) of each pesticide. The results showed that all bean samples analyzed contained some organochlorine pesticides, organophosphates and pyrethroids. The mean consumption rate of beans was found to be 0.624 ± 0.052 kg/day. The calculated Health Risk Index (HRI) of some organochlorine pesticides occurred at ranges greater than 1. However, most of the pesticide residues occurred below critical HRI. Aldrin was detected in all samples analyzed and p,p'-DDT occurred the least with calculated HRI above 1. The presence of organochlorine pesticide residues in all samples analyzed is suggestive of the continuous use of obsolete banned pesticides in the cultivation and storage of agricultural products. HRI values above 1 indicates that the life time consumption of beans containing the measured level of pesticide could pose a non-carcinogenic health risk for adult consumers. Therefore strict enforcement of regulatory measures by policy makers on how to manage the use of pesticides is well recommended.

Key words: Risk assessment, beans, pesticides, residues, Wukari, health risk.

INTRODUCTION

With the increase in the world's population, there is a proportional increase on the dependence of humans on agriculture and its products. To achieve maximum yield, farmers have resorted to the use of different pesticides to boost production. Recently, however, there are complaints among consumers and farmers on the quality of taste and the ability of these farm products to digest

properly due to suspected accumulation of pesticides and/ or other agro inputs.

Pesticide use has several effects on the environment and this has created concerns regarding its potentially toxic or carcinogenic residues remaining in the food chain (Ikpesu and Ariyo, 2013). Misuse and indiscriminate application of pesticides results in residue that enters into

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the environment and accumulates in the food chain (Borrell and Aguilar, 2006; Turgut, 2007). There is thus, a continuing exposure of the general population to low doses of these chemicals through food, water and soil. These may lead to chronic toxicity due to accumulation in the human body over a long period of time (Borrell and Aguilar, 2006). Also, some pesticides, especially the organochlorine compounds are usually persistent in the environment because of their high chemical stability and lipid solubility (Ogar et al., 2012). Thus, they may remain in soil, water, food and in the tissues of various organisms long after their use (Borrell and Aguilar, 2006).

Preservation of food is unavoidable due to many reasons. Some foods are available in specific seasons and not in others. Hence, the preservation, processing and storage are vital for the continuous supply of foods during seasons and off-seasons and to areas where they are less available (Falaju, 2018). Beans (*Phaseolus vulgaris*) is a food crop that requires much preservation due to its unavailability in most part of Nigeria, and to effectively control weevils and beetles when storing these products (Falaju, 2018; Vincent and Safina, 2017), hence, it is most likely to contain high levels of pesticide residues (Ogar et al., 2012). In the past, cereal farmers and grain merchants have often sought ways to preserve their products, beans inclusive, with the application of red dry peppers rather than pesticides, but today, one means of beans preservation is the use of poisonous chemicals and indiscriminate application not minding the consequences (Vincent and Safina, 2017). As a result, most of the crops, including beans have high pesticide residues (Ogar et al., 2012). To this end, the use of chemicals for beans preservation is alarming with regard to food quality and safety in the country (Falaju, 2018).

Several reports show the presence of pesticide residues in several food samples, in Nigeria: beans in Lagos markets (Ogar et al., 2012), and Northeastern Nigeria (Jos, Maidugari) (Obida et al., 2012; Illiya et al., 2012); beans in Ghana (Augustine et al., 2015); and other food like vegetables in Southwestern Nigeria (Oyeyiola et al., 2017; Adeoluwa et al., 2019), grains in Bangladesh (Hossain et al., 2015) and fruits in Nigeria (Oyeyiola et al., 2017). This extensive use of pesticides for agricultural and nonagricultural purposes has resulted in the presence of their residues in various environmental matrices, especially food stuff (Uygun et al., 2005; Tadeo et al., 2008) proving the high risk of these chemicals to human health and environment. A report by NAFDAC revealed that offensive beans were sourced from Taraba State (Northeast Nigeria) (NAFDAC, 2004). NAFDAC laboratory analysis of these beans and its food products such as moi moi showed the presence of outrageously high organophosphates, carbamates, fenithrothion and chlorpyrifos, which are highly toxic pesticides. These must have resulted from either higher dose than recommended or wrong application (Obida et al., 2012).

There are possible health problems associated with pesticide use, which include cancers, congenital

malformations, neurotoxic disorders, infertility, blood dyscrasias and many others (Hossain et al., 2015; Khan and Law, 2005). Apart from chronic toxicity, there is the risk of acute and sub-acute toxicity to people who are directly involved in the manufacture, formulation, mixing and application of pesticides. They may be exposed to high doses through dermal contact, inhalation and accidental ingestion (Uygun et al., 2005; Tadeo et al., 2008; Ogar et al., 2012).

The Maximum Residue Level (MRL) is the maximum amount of the pesticide residue which if found in food substances will not cause any health hazard (Gerken et al., 2001). MRLs encourage food safety by restricting the concentration of a residue permitted on a commodity, and by limiting the type of commodity in which it is allowed (European Communities, 2005; FDA, 2005). Monitoring programs have therefore been established to control pesticide residues in food of plant origin in order to ensure compliance with national and international law, and to reassure consumers that food crops are healthy (Gerken et al., 2001).

Effective regulatory control would help minimize human exposure to these chemicals and reduce potential health hazards posed by their use. Control measures cannot be effective if pesticide residues are not assessed (Ogar et al., 2012). In spite of the different researches carried out on pesticide residues, there is hardly any documented report on pesticide residues in Wukari area of Taraba State. Also, there is a dearth of information on health risk assessment in the few studies on pesticide residues carried out within Northeast Nigeria. Hence, this study aims to providing documented account of pesticide residues in beans sourced from Wukari Town, Taraba State, Nigeria and to assess the level of risk associated with the consumption of these food crops.

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 characteristics of savannah zone and with major climatic seasons of wet or rainy seasons, which starts in March or April, and ends in October and the dry season, which starts in November and ends in March or April. Wukari covers an area of 4,308 km² and with a population of about 241,546 at the 2006 census, a traditional state rich with various cultures, norms and value. Fishing, farming and trading are the major occupation of the people (Figure 1).

Sampling techniques

Different samples of beans were collected randomly from different market points within Wukari Town which include Rafin kada (7° 43'0"N, 9° 53'0" E), Wukari new market (7° 87'0"N, 9° 79'0" E), Yam market (7° 88'0"N, 9° 79'0"E), Idofi (7° 87'0"N, 9° 75'0" E) and FUWukari (7° 88'0"N, 9° 78'0" E). These are the major markets in Wukari where large food items including beans, cereals and other grains are sold. Random collection of beans was done in each

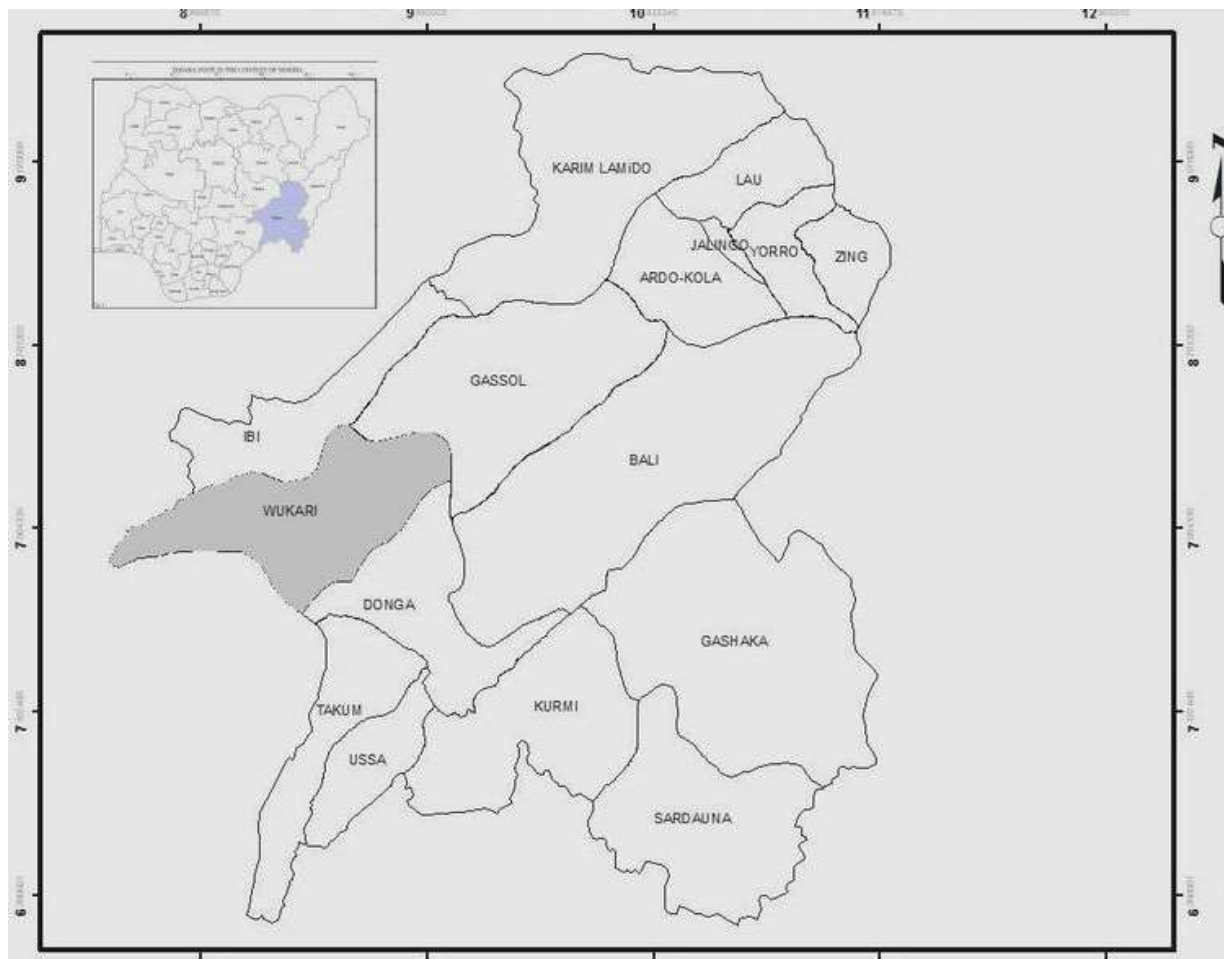


Figure 1. Map of Nigeria and Taraba showing the location of Wukari, study area.

market and divided into 3 groups for each market, making a total of 15 different samples. Samples were collected in sterile poly bags to protect them from moisture and contamination. The samples were then labeled and stored in a refrigerator at 4°C until ready for use.

Sample preparation

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

Reagents and materials

Pesticides standard mix (containing organochlorine, organophosphorus and pyrethroids) in acetonitrile (1 ml for each mix) were obtained from SpexCertiPrep (UK). n-hexane, acetonitrile were bought from Sigma Aldrich, Inc. USA. Solid phase extraction cartridges were bought from Varian Inc., USA; filter paper No. 4 Whatman, from International Ltd England; a gas chromatography, from Agilent USA (7890A) (hyphenated to a mass

spectrophotometer (5975C).

Preparation of extraction solvent

A mixture of acetonitrile and n-hexane in the ratio of 1:20 was prepared with the aid of a measuring cylinder. The extraction solvent was prepared in a 1000 ml beaker. Pesticide standard mixes were serially diluted (0.05, 0.5, 1.0, 2.0, 4.0 and 8.0 µg/ml) for use in the recovery process and as calibration standards.

Extraction

Extraction was done using the method of Oyeyiola et al. (2017), with slight modifications. An aliquot of 10g of each powdered sample was weighed, using an electronic weighing balance, into a 250 ml beaker. Initial weight of the beaker was recorded as W_b and the weight of beaker with sample was recorded as W_{b+s} . 30 ml of the extraction solvent was introduced into 10g 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 funnel and then concentrated by evaporation at room temperature for 24 to 72 h. Heating using 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.

Clean up

Clean up was done using solid phase extraction cartridges, which were conditioned with methanol followed by distilled water and then acetonitrile. The sample extract was loaded on the solid phase extraction column, and eluted with a solvent mixture of n-hexane: acetonitrile (50:50) into a receiving glass tube and rinsed with the eluting solvent. The eluate was evaporated under a gentle stream of nitrogen gas, reconstituted to 1 ml using n-hexane, and taken for GC/MS analysis.

Recovery

Blank samples were determined by injecting 1 µl of the cleaned-up eluents and solvent into the GC coupled with electron capture detector. No pesticide residue was detected. Recovery studies followed the method of Ogar et al. (2012) 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 follows:

Equation 1:

$$\% \text{Recovery} = \frac{\text{Peak area ratio of pesticides in spiked sample}}{\text{Peak area ratio of pesticides in standards}} \times 100$$

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 (EC 2017).

Detection limits

Running an air blank sample under the experimental conditions was used to obtain the detector baseline noise. Three times 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 (Ogar et al., 2012; Oyeyiola et al., 2017). LOQ was the concentration leading to a signal-to noise ratio of 10 (Oyeyiola et al., 2017).

GC/MS analysis and conditions

A gas chromatography, from Agilent USA (7890A) (hyphenated to a mass spectrophotometer (5975C) with 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 specification: 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; 16.2psia, 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 sample was injected. The condition temperature started at 35°C for 5min 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.

Identification and quantification

Pesticide residues were identified by comparison of the retention times, peak area and peak heights of the sample with those of the standards. Pesticide concentrations were within 5% of the standards.

Quality control and assurance

Samples from the different markets were analyzed in triplicates to ensure precision. LOD and LOQ were used to determine sensitivity of the machine. Blank determinations (used to eliminate the interference of reactants) and recovery studies were carried out. Materials used for preparation of samples were well washed and rinsed with ethanol before re-use. Care was taken to avoid cross contamination of the different samples.

Health risk estimates

Probable daily pesticide exposure or estimated daily intake for each pesticide and individual (Adult) consumers was calculated using the following Equation 2 formula:

$$EDI = \frac{\text{Beans consumption} \left(\frac{\text{kg}}{\text{da y}} \right) \times \text{pesticide concentration in the Beans} \left(\frac{\text{m g}}{\text{kg}} \right)}{\text{Body weight}}$$

Estimation of health risk from pesticides

The risk of exposure to a pesticide by an individual (Adults with an average body weight of 60kg) was estimated on the basis of the potential health risk index for non-carcinogenic chemicals, according to Akoto et al. (2015) using the following Equation 3 formula:

$$HRI = \frac{EDI}{ADI}$$

where HRI stands for health risk index, EDI stands for estimated daily intake, acceptable daily intake (ADI) stands for acceptable daily intake. According to Akoto et al. (2015), when HRI is greater than one, lifetime consumption of beans containing the measured level of pesticide could pose health risks

Beans consumption rate

A standard questionnaire (Appendix) with structured questions was used to get information about the rate of beans consumption. A total of 1000 people were interviewed randomly within the study site. The amount of beans consumption rate was converted to kilograms weight and the average estimated beans consumption rate were extracted.

Data analysis

Data generated from the study were presented in tables. Different pesticide concentrations and their health risk index were calculated and tabulated. Normality test was carried out using Shapiro-Wilk prior to ANOVA and a transformation was necessary (Log [x+1]).

Table 1. Concentrations of pesticide residues detected.

Pesticides	Mean concentrations of pesticide residues (mg/kg)				
	New market	Yam market	Rafin Kada	FUWukari	Idofi
Aldrin	0.011±0.0006 ^{a,b}	0.015±0.0041 ^{a,b}	0.054±0.0225 ^b	0.005±0.0017 ^a	0.010±0.0005 ^{a,b}
α – BHC	0.047±0.030 ^{a,b}	0.075±0.020 ^b	0.015±0.002 ^a	0.042±0.028 ^b	0.032±0.020 ^{a,b}
β- BHC	0.015±0.002 ^a	0.016±0.005 ^b	0.053±0.001 ^{a,b}	0.006±0.002 ^b	-
Delta BHC	0.012±0.007 ^a	0.024±0.008 ^a	0.011±0.006 ^b	0.002±0.004 ^{a,b}	-
Aramite	0.017±0.001 ^b	-	-	-	0.042±0.004 ^{a,b}
Dieldrin	0.258±0.013 ^{a,b}	-	-	0.021±0.017 ^a	-
p,p'-DDT	0.171±0.002 ^{a,b}	-	-	-	-
Endosulphan	0.011±0.005 ^{a,b}	-	-	-	-
Chlorthiophos	0.027±0.001 ^{a,b}	-	-	-	-
Iodofenphos	0.023±0.011 ^{a,b}	-	-	-	-
Bromophos-ethyl	0.014±0.003 ^{a,b}	-	0.005±0.010 ^a	0.007±0.001 ^{a,b}	-
Pyriproxyfen	0.026±0.012 ^{a,b}	-	-	-	-
Quinalofop	0.029±0.009 ^{a,b}	-	-	-	-
Phenthoate	0.120±0.01 ^{a,b}	0.059±0.013 ^a	-	-	-
Prothiophos	0.023±0.011 ^{a,b}	-	-	0.009±0.002 ^a	-
Ethion	0.016±0.021 ^a	-	0.015±0.003 ^a	0.003±0.001 ^{a,b}	0.140±0.007 ^b
Esfenalerate	0.043±0.007 ^b	-	-	-	-
Heptachlor	0.015±0.001 ^{a,b}	0.244±0.004 ^{a,b}	0.209±0.09 ^a	0.041±0.001 ^b	0.057±0.001 ^{a,b}
Pyriproxyfen	0.019±0.006 ^a	-	0.064±0.009 ^b	-	0.070±0.003 ^b
Fenitrothion	0.011±0.03 ^{a,b}	0.081±0.03 ^a	0.014±0.012 ^{a,b}	-	0.410±0.03 ^b
4,4-DDE	0.240±0.09 ^a	0.027±0.09 ^{a,b}	0.023±0.09 ^b	-	0.027±0.01 ^a
Fenthionsulphon	0.012±0.002 ^b	0.011±0.002 ^a	-	0.015±0.002 ^b	0.01±0.007 ^a
Oxyfluorfen	0.011±0.019 ^{a,b}	0.01±0.02 ^a	0.011±0.001 ^a	0.007±0.002 ^{a,b}	0.011±0.001 ^b
Chlorpyrifos	-	0.035±0.002 ^a	0.032±0.010 ^a	0.014±0.010 ^b	0.036±0.002 ^{a,b}
Difenconazole	-	-	0.033±0.003 ^a	-	0.024±0.006 ^b
Oxadiazone	-	0.079±0.014 ^a	0.10±0.013 ^a	-	-
Amitraz	-	0.054±0.005 ^a	0.052±0.058 ^a	0.104±0.06 ^{a,b}	0.013±0.05 ^b
Flumioxazin	0.012±0.05 ^{a,b}	0.088±0.05 ^a	0.114±0.012 ^a	0.158±0.05 ^a	0.128±0.066 ^b
Cypermethrin I	-	0.024±0.002 ^a	0.031±0.003 ^b	0.002±0.001 ^{a,b}	0.053±0.006 ^a

Results represent mean ± standard error of group pesticide residues obtained (n=3). Mean in the same row having the same letters of the alphabet are statistically non-significant (p>0.05).

Data generated were subjected to statistical analysis using One-way Analysis of Variance (ANOVA) and statistical package for social sciences (SPSS) version 21. The means were compared for significance at p≤0.05. The values were reported as mean ± standard error.

RESULTS AND DISCUSSION

Pesticide residue levels in bean samples from Wukari

This study shows the presence of 29 different pesticide residues in all samples of beans (Table 1). The result shows that the pesticide residues belong to three major classes, which are Organochlorines, Organophosphates and Pyrethroids as shown in Table 2. Pesticides, percent recoveries as well as LOD and LOQs of residues are presented in Table 3. Figures 2 to 4 show the different concentrations of each class of pesticide residues

detected and their MRLs.

Residues of organochlorine pesticides have the peculiar characteristics of relatively high chemical stability and persist in the environment for long periods (Kaushik and Kaushik, 2007). The organochlorine pesticides detected include Aldrin, Alpha-BHC, Beta – BHC, Delta-BHC, Dieldrin, Endosulphan, p,p' DDT, Aramite and Heptachlor. Aldrin and alpha- BHC were detected in all samples with concentrations ranging from 0.005 ± 0.0017 mg/kg to 0.054 ± 0.0225 mg/kg and 0.015 ± 0.002 mg/kg to 0.075 ± 0.020 mg/kg respectively. These values were below their MRL as indicated in Table 2. Though heptachlor ranged from 0.015 ± 0.001 mg/kg to 0.244 ± 0.004 mg/kg, samples from Yam market and Rafin kada had concentrations above MRL.

Beta-BHC and Delta-BHC were detected in all samples except for samples from Idofi. The residues of this pesticides occurred at concentrations ranging from 0.002

Table 2. Pesticide class, maximum residue levels, and acceptable daily intake.

Pesticides	Class	Type	MRL(mg/kg)	ADI(mg/kg/day)
Aldrin	Organochlorine	Insecticide	0.100	0.0001
α – BHC	Organochlorine	Insecticide	1.000	0.005
β- BHC	Organochlorine	Insecticide	1.000	0.005
Delta BHC	Organochlorine	Insecticide	1.000	0.005
Aramite	Organochlorine	Insecticide	0.020	0.0001
Dieldrin	Organochlorine	Insecticide	0.100	0.0002
P,p'-DDT	Organochlorine	Insecticide	0.010	0.001
Endosulphan	Organochlorine	Insecticide	0.500	0.002
Heptachlor	Organochlorine	Insecticide	0.050	0.0001
Pyriproxyfen	Organochlorine	Insecticide	0.100	0.005
4,4-DDE	Organochlorine	Insecticide	0.140	0.020
Pyriproxyfen	Organophosphate	Insecticide	0.040	0.100
Quizalofop	Organophosphate	Herbicide	0.050	0.013
Phenthoate	Organophosphate	Insecticide	0.100	0.003
Prothiophos	Organophosphate	Herbicide	0.010	0.0001
Ethion	Organophosphate	Insecticide	0.300	0.002
Difenconazole	Organophosphate	Fungicide	0.100	0.010
Chlorthiophos	Organophosphate	Insecticide	0.010	0.043
Iodophenphos	Organophosphate	Insecticide	0.015	0.005
Fenitrothion	Organophosphate	Insecticide	0.140	0.020
Bromophos-ethyl	Organophosphate	Insecticide	0.003	0.050
Fenthionsulphon	Organophosphate	Insecticide	0.020	0.002
Oxadiazone	Organophosphate	Herbicide	0.020	0.0036
Chlorpyrifos	Organophosphate	Insecticide	0.300	0.001
Oxyfluorfen	Pyrethroid	Herbicide	0.025	0.0003
Esfenalerate	Pyrethroid	Insecticide	0.050	0.020
Amitraz	Pyrethroid	Acaricide	0.200	0.003
Flumioxazin	Pyrethroid	Herbicide	0.017	0.009
Cypermethrin I	Pyrethroid	Insecticide	0.200	0.002

Source of MRL and ADI: EU pesticides database, European Commissions (2019).

± 0.004 mg/kg to 0.053 ± 0.001 mg/kg below the MRL (Figure 1). Aramite was only detected in samples from Wukari New market and Idofi with concentrations slightly below the MRL (Figure 1). A study by Lozowicka et al. (2017) also revealed the presence of organochlorine pesticides such as Aldrin, dieldrin, p,p'DDE and p,p'DDD, among others from samples of beans, cucumber, lupine, tomatoes, carrots, celery and parsley collected from Kazakstan and Poland. A report by Sosan and Oyekunle (2017) also shows the presence of similar organochlorine pesticides in cowpeas from markets in Ile-ife, Nigeria.

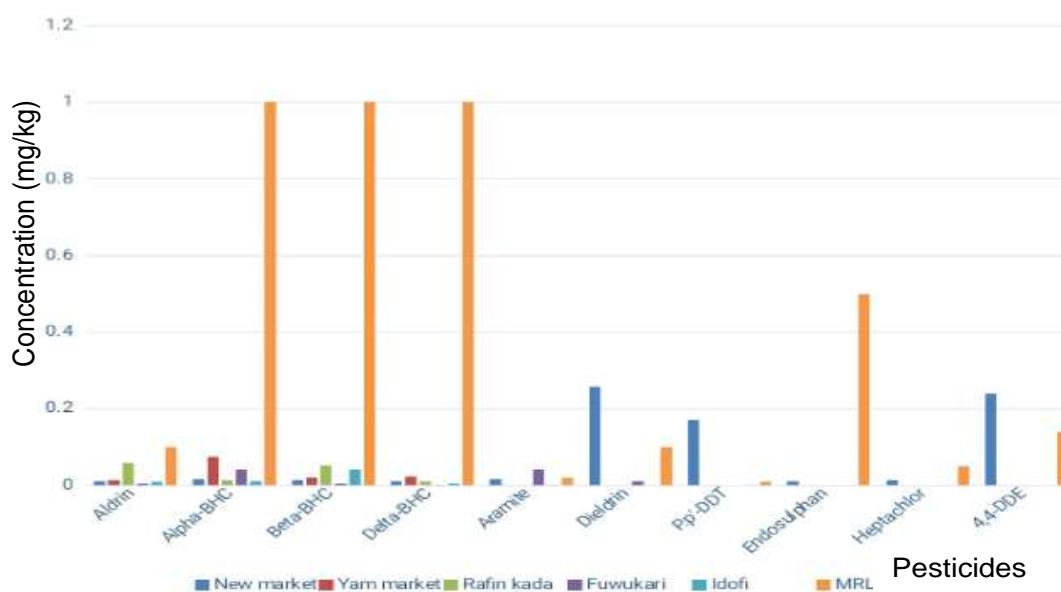
Previous works by Obida et al. (2012) and Ogar et al. (2012) have detected the presence of organochlorine pesticides such as Aldrin, dieldrin and DDT at concentrations higher than the MRL, set by European Union, in bean samples from Maiduguri and Lagos respectively. Many of the older, cheaper (off-patent) pesticides, such as dichlorodiphenyltrichloroethane (DDT) and lindane, can remain for years in soil, water

and food products (Adeoluwa et al., 2019). These chemicals have been banned by countries who signed the 2001 Stockholm Convention – an international treaty that aims to eliminate or restrict the production and use of persistent organic pollutants (World Health Organisation, WHO, 2007). The MRL is not expected to be exceeded in any foodstuff if the pesticide was applied in accordance with directions for its safe use (Ogar et al., 2012). 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.

Both Endosulphan and Dichlorodiphenyltrichloroethane (DDT) were detected at concentrations of 0.011 ± 0.005 mg/kg and 0.171 ± 0.002 mg/kg, respectively, in samples of beans collected from Wukari New Market, but was not detected in other samples. This is alarming due to the fact the residue is at a higher concentration than the MRL. Iliya et al. (2012) also reported the presence of endosulphan at high concentrations in samples of

Table 3. LOD, LOQ (mg/kg) and percent recovery of residues detected.

Pesticides	LOD	LOQ	Recovery (%)
Aldrin	0.2	0.4	108
α - BHC	0.1	0.45	85.5
β - BHC	0.15	0.65	95.2
Delta BHC	0.15	0.005	106
Aramite	0.2	0.005	89
Dieldrin	0.04	0.001	94
P,p'-DDT	0.1	0.003	95.8
Endosulphan	0.04	0.001	97.2
Heptachlor	0.1	0.003	83.3
Pyriproxyfen	0.0007	0.002	113.1
4,4-DDE	0.001	0.003	98.1
Pyriproxyfen	0.001	0.0027	87.4
Quinalofop	0.003	0.0072	93.2
Phenthoate	0.001	0.003	87.9
Prothiophos	0.0013	0.0072	89.1
Ethion	0.001	0.003	94.3
Difenconazole	0.0015	0.004	81.4
Chlorthiophos	0.003	0.009	92.9
Iodophenphos	0.0006	0.002	96.7
Fenitrothion	0.0028	0.0091	89.5
Bromophos-ethyl	0.005	0.01	101
Fenthionsulphon	0.002	0.0048	82.4
Oxadiazone	0.004	0.008	89.5
Chlorpyrifos	0.0012	0.0061	92.1
Oxyfluorfen	0.002	0.007	87.6
Esfenalerate	0.003	0.009	91.2
Amitraz	0.0004	0.001	89.3
Flumioxazin	0.03	0.09	98.1
Cypermethrin I	0.15	0.5	102

**Figure 2.** Comparison of the different concentrations with their MRL and occurrences of organochlorine pesticide residues detected.

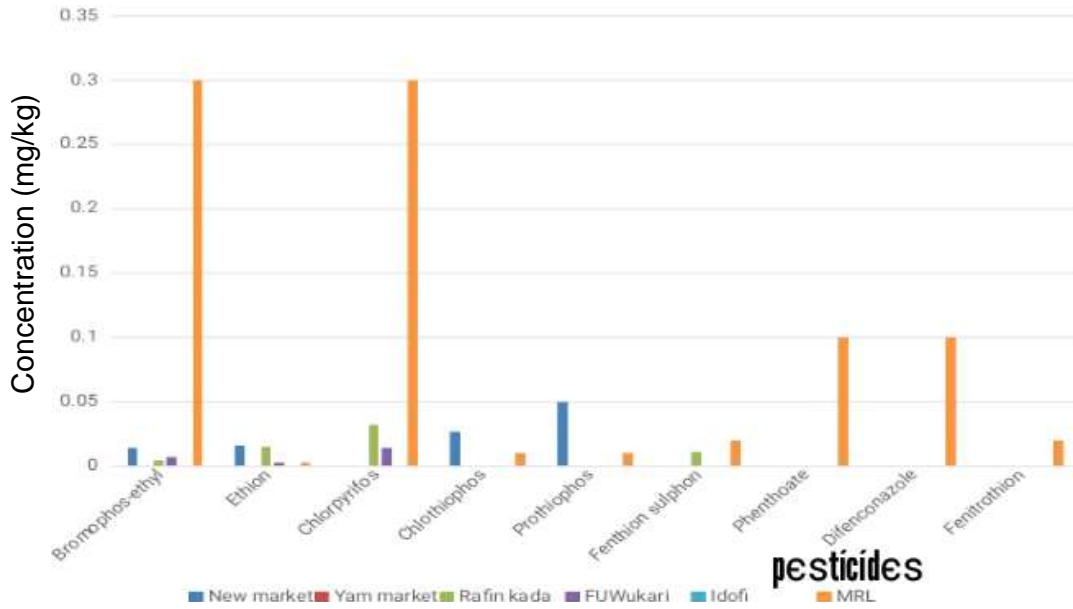


Figure 3. Comparison of the different concentrations with their MRL and occurrences of organophosphate pesticide residues detected.

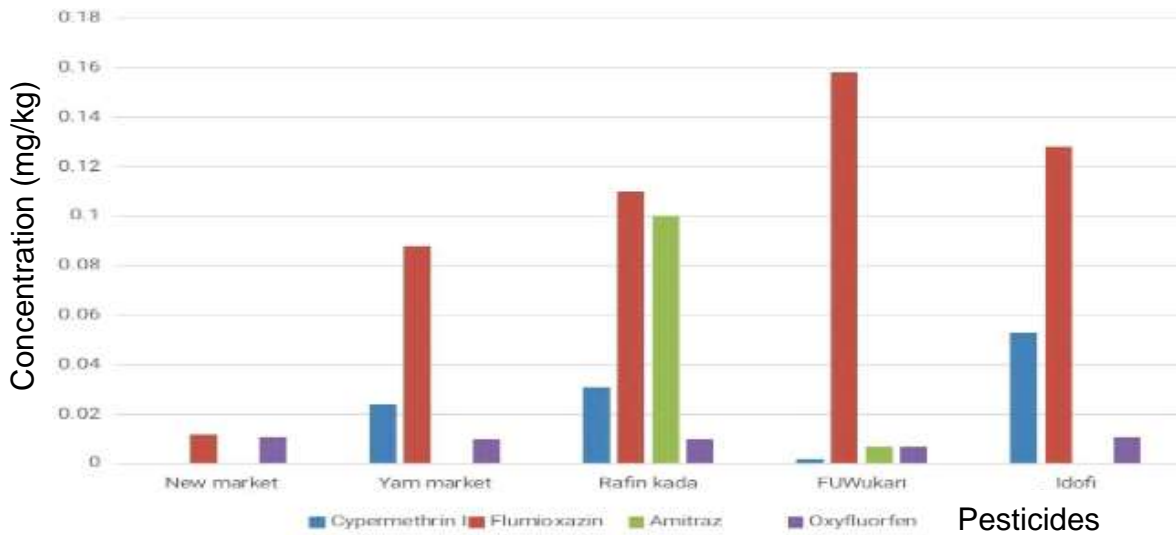


Figure 4. Comparison of the different concentrations and occurrences of pyrethroid pesticide residues detected.

beans within Jos, Nigeria. This suggests the high use of organochlorine pesticides in the storage and or cultivation of the crop. Hence the Health Risk Index (HRI) associated with the consumption of beans containing this pesticide was found to be above 1.00 which poses a significant health risk for consumers within Wukari.

Organophosphates are highly potent compounds used majorly as insecticides in the control of storage insects in food crops. They are very toxic and more often involved in acute poisoning than other classes of pesticides

(Dawson et al., 2010). Results of organophosphate pesticide residues from this study were below acceptable MRL (Figure 2). Organophosphates detected include Chlopyrifos, Bromophos-ethyl, Chlothiophos, Defenconazole, Ethion, Phenthoate, Prothiophos, lodophenphos, Fenthionsulphon. Iliya et al. (2012) have previously detected chlopyrifos in samples of beans within Jos, Nigeria. These residues were also found to be below their respective MRL, which is in tandem with the results of this study.

Pyrethroids has become more popular in the control of pests following outright bans or limitations on the use of cholinesterase-inhibiting insecticides (Luo and Zhang, 2011; Feo et al., 2010). Pyrethroids detected from this study include Cypermethrin I, Flumioxazin, Amitrax, Oxyflourfen and Esfenalaterate. These residues were found to be within concentration levels of 0.002 ± 0.001 mg/kg to 0.158 ± 0.05 mg/kg which is below MRLs for all pesticides (Figure 3). Esfenalaterate was found only in bean samples from Wukari New market. Cypermethrin I, Flumioxazin, Amitrax and Oxyflourfen have 50, 70, 60 and 40% occurrences respectively. Donkora et al. (2015) also reported the presence of cypermethrin in cowpea and Bambara beans found in Accra, Ghana.

Estimated daily intake of each pesticide residue detected

Values in Table 4 indicate the mean \pm standard error of the calculated EDI of each pesticide residue detected across sample sites. The calculated estimated daily intake of Aldrin was found to range from 0.0001 ± 0.00 mg/kg to 0.005 ± 0.007 mg/kg. These values were found to be higher than the acceptable daily intake for Aldrin set at 0.0001 mg/kg by European Union. The calculated EDI for Dieldrin, Aramite and Oxyfluorfen was also found to be above their acceptable daily intake (0.0002 mg/kg, 0.0001 mg/kg and 0.0003 mg/kg respectively). A study by Fredrick et al. (2018) also reported the EDI of Aldrin in fruits from Ghana to be above the ADI, which poses health risk to adult consumers. Previous work by Ogar et al. (2012) also reported that the estimated daily intakes for Aldrin and Dieldrin exceeded their acceptable daily intake in bean samples from Lagos markets, Nigeria. This poses a significant health risk to consumers of beans containing these residues. However, the calculated EDI for all other pesticide residues detected in this study was found to be below their ADI.

Health risk index of each pesticide residue detected

The calculated Health Risk Index (HRI) of 50% of the organochlorine pesticides, such as Aldrin, Aramite, Dieldrin, DDT and Heptachlor occurred at ranges greater than 1. Most of the pesticide residues occurred below critical HRI. This result agrees with previous report by Oyeyiola et al. (2017). However, the HRI for heptachlor ranges between 0.59 and 2.50. It was found in bean samples from Idofi market, Wukari New market, Yam market, Rafin kada market, and Federal University Wukari with pesticide residue concentration ranging from 0.015 ± 0.001 mg/kg to 0.244 ± 0.001 mg/kg; of these, only samples from Wukari New market were below the Maximum Residue Levels (MRL) of 0.05 mg/kg. This contributed to the high calculated HRI values obtained. This high HRI suggests a significant non-carcinogenic

health risk associated with the consumption of bean samples from these sites. Similar studies by Adeoluwa et al. (2019) also indicate a non-carcinogenic health risk associated with organochlorine residues found in vegetables consumed in Southwestern Nigeria.

The HRI calculated for Aldrin indicates values within the range of 1.00 ± 0.00 to 1.53 ± 0.95 across all samples of beans collected from Wukari. This is an indication that banned pesticides such as Aldrin, DDT and Heptachlor are still used in the cultivation of beans and its storage (serving as insecticides) within this region. The Estimated Daily Intake (EDI) of the organophosphates detected in this study gave a calculated Health Risk Index within the range 0.01 to 0.87 which are within safe range to human health when consumed.

Exception, however, is Prothiophos which has HRI very high at 5.25 and 1.00 in samples from Wukari New market and Federal University Wukari, respectively. This very high levels of HRI results from residue concentrations of 0.05 ± 0.011 mg/kg and 0.009 ± 0.002 mg/kg which are above MRL of 0.01 mg/kg and ADI of 0.0001 mg/kg respectively. Hence, although being an organophosphate, this residue level poses a non-carcinogenic health risk to adult consumers within the study site. All pyrethroids detected were below HRI of 1 which are within safe permissible limits, except for Amitrax from Rafin Kada market which has a HRI of 1.20.

The occurrence of some residues detected in this study having a HRI > 1 is indicative of the non-carcinogenic risk associated with long time consumption of beans by adults within the study site.

The residues investigated in the study could pose potential risk to liver and kidney toxicity for adult consumers of beans (Integrated Risk information System, 2019). Consumption of beans contaminated with DDT and other organochlorine pesticides could cause liver lesions and may also disrupt reproductive functions as well as carcinogenic risks (Adeoluwa et al., 2019; Integrated Risk information System, 2019) (Table 5).

Conclusion

The presence of pesticide residues is detected in the samples of beans analyzed, with most occurring at concentrations greater than their respective MRL and ADI; this gives HRI values greater than 1. It indicates certain levels of non-carcinogenic risk associated with the life time consumption of beans sold within this region. Organochlorine pesticides also detected suggest the continuous use of obsolete banned pesticides in the cultivation and storage of beans. Hence, regulatory agencies in Nigeria (such as NAFDAC, SON, NESREA) should step up efforts to ensure compliance with the ban on these chemicals. Farmers and other pesticide users also need to be educated on the dangers of using banned products and on the over application of these pesticides.

Table 4. Mean concentrations of calculated estimated daily intake (EDI) in mg/kg.

Pesticides	New market	Yam market	Rafin Kada	FUWukari	Idofi
Aldrin	0.0001±0.00 ^a	0.0002±0.00 ^a	0.005±0.007 ^b	0.0005±0.004 ^{a,b}	0.0002±0.0001 ^b
α – BHC	0.0002±0.001 ^a	0.0007±0.002 ^b	0.0002±0.002 ^a	0.001±0.0004 ^b	0.0002±0.0001 ^a
β- BHC	0.0002±0.002 ^a	0.0002±0.003 ^a	0.0006±0.002 ^b	0.0005±0.002 ^{a,b}	-
Delta BHC	0.0001±0.002 ^{a,b}	0.0003±0.007 ^b	0.0004±0.008 ^a	0.002±0.001 ^{a,b}	-
Aramite	0.0002±0.011 ^a	-	-	-	0.042±0.004 ^b
Dieldrin	0.003±0.0012 ^a	-	-	0.0003±0.005 ^b	-
P,p'-DDT	0.002±0.0001 ^a	-	-	-	-
Endosulphan	0.0001±0.002 ^a	-	-	-	-
Chlorthiophos	0.0002±0.001 ^a	-	-	-	-
Iodofenphos	0.0002±0.001 ^a	-	-	-	-
Bromophos-ethyl	0.0001±0.005 ^a	-	0.0006±0.005 ^b	0.0011±0.002 ^{a,b}	-
Pyriproxyfen	0.0002±0.002 ^a	-	-	-	-
Quizalofop	0.003±0.0001 ^a	-	-	-	-
Phenthoate	0.001±0.002 ^a	0.0006±0.003 ^b	-	-	-
Prothiophos	0.005±0.001 ^a	-	-	0.0009±0.002 ^b	-
Ethion	0.002±0.001 ^b	-	0.0002±0.002 ^{a,b}	0.0001±0.002 ^b	0.0013±0.001 ^a
Esfenalerate	0.004±0.003 ^b	-	-	-	-
Heptachlor	0.0002±0.001 ^a	0.0003±0.001 ^{a,b}	0.0016±0.008 ^b	0.003±0.001 ^a	0.0006±0.001 ^{a,b}
Pyriproxyfen	0.0001±0.002 ^b	-	0.0008±0.005 ^{a,b}	-	0.001±0.0003 ^a
Fenitrothion	0.003±0.001 ^a	0.0004±0.002 ^b	0.0002±0.008 ^a	-	0.0002±0.001 ^a
4,4-DDE	0.001±0.0001 ^a	0.003±0.0002 ^{a,b}	0.0002±0.01 ^b	-	0.002±0.003 ^b
Fenthionsulphon	0.003±0.002 ^a	0.0004±0.001 ^{a,b}	-	0.006±0.0002 ^a	0.0032±0.002 ^{a,b}
Oxyfluorfen	0.002±0.0001 ^b	0.005±0.0002 ^a	0.001±0.0001 ^{a,b}	0.003±0.0002 ^b	0.002±0.0001 ^a
Chlorpyrifos	-	0.0002±0.002 ^a	0.0007±0.001 ^{a,b}	0.0023±0.001 ^b	0.003±0.002 ^a
Difenconazole	-	-	0.001±0.0012 ^b	-	0.003±0.001 ^a
Oxadiazone	-	0.0001±0.001 ^b	0.005±0.001 ^a	-	-
Amitraz	-	0.002±0.0002 ^a	0.003±0.0001 ^{a,b}	0.0035±0.006 ^b	0.002±0.0005 ^b
Flumioxazin	0.001±0.0002 ^a	0.008±0.0005 ^b	0.007±0.001 ^a	0.002±0.02 ^{a,b}	0.005±0.0004 ^a
Cypermethrin I	-	0.0014±0.002 ^{a,b}	0.001±0.0003 ^b	0.002±0.0001 ^a	0.002±0.0002 ^a

Results represent mean ± standard error of group EDI obtained (n=3). Mean in the same row having the same letters of the alphabet are statistically non-significant (p>0.05).

Table 5. Mean of calculated health risk index.

Pesticides	Mean health risk index				
	New market	Yam market	Rafin Kada	FUWukari	Idofi
Aldrin	1.0	1.53	1.46	1.44	1.00
α – BHC	0.04	0.14	0.32	0.21	0.02
β- BHC	0.03	0.05	0.11	0.25	-
Delta BHC	0.03	0.05	0.06	0.07	-
Aramite	1.79	-	-	-	0.08
Dieldrin	1.27	-	-	0.40	-
P,p'-DDT	1.80	-	-	-	-
Endosulphan	0.05	-	-	-	-
Chlorthiophos	0.01	-	-	-	-
Iodofenphos	0.05	-	-	-	-
Bromophos-ethyl	0.05	-	0.02	0.02	-
Pyriproxyfen	0.03	-	-	-	-
Quizalofop	0.23	-	-	-	-

Table 5. Cont'd

Phenthoate	0.42	0.62	-	0.74	-
Prothiophos	5.20	-	-	1.00	-
Ethion	0.08	-	0.21	0.11	0.09
Esfenalerate	0.20	-	-	-	-
Heptachlor	1.50	2.50	1.70	1.00	0.59
Pyriproxyfen	0.02	-	0.02	-	0.04
Fenitrothion	0.13	0.14	0.30	-	0.40
4,4-DDE	0.03	0.04	0.23	-	0.18
Fenthionsulphon	0.45	0.34	-	0.54	0.28
Oxyfluorfen	0.11	0.34	0.25	0.35	0.25
Chlorpyrifos	-	0.65	0.87	0.76	0.78
Difenconazole	-	-	0.44	-	0.67
Oxadiazone	-	0.66	0.43	-	-
Amitraz	-	0.54	0.81	0.34	0.87
Flumioxazin	0.87	0.67	0.27	0.55	0.61
Cypermethrin I	-	0.43	0.69	0.65	0.55

Mean in the same row having the same letters of the alphabet are statistically non-significant ($p > 0.05$).

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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APPENDIX

Beans consumption rate and storage in Wukari

Questionnaire

We kindly request for your corporation in carrying out a research on the consumption rate of beans and its storage within Wukari, Taraba State. Please kindly fill in the information by ticking the boxes or writing out the information appropriate to you.

Please note that your name or personal details are not required and that the information you give herein will be used solely for research purposes.

Thank you for your corporation.

1. Do you consume beans? Yes No
2. If yes, how often? Always Rarely Atleast once a week
3. What quantity of beans do you normally cook or consume? 1mudu Half mudu Cups (Please specify how many cups _____)
4. Do you experience any adverse effect(s), such as indigestion or running stomach, when you consume beans?
Yes No
5. If yes, how often? Every time Sometimes

QUESTIONS 6 – 8 are for those who engage in beans business

6. When you buy beans, do you sell them immediately or store them for future sale? Sell
immediately Engage in storage
7. Do you use any chemical to store your beans? Yes No beans during storage?
8. What chemical(s) do you use to preserve your beans during storage?
(i) _____ (ii) _____ (iii) _____ (iv) _____
9. What quantity of the chemical do you apply per bag of beans?

10. How long do you store the beans before selling? 1 – 3 months 4 – 6 months
7 – 12 months Above 1 year
11. Where you trained on how to use these chemicals? Yes No