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RESEARCH PAPER

Determination of Pesticide Residues in Selected Cereals Crops Sold in Some Markets in Gbako Local Government, Niger State

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ABSTRACT

This study was conducted to determine the residues of Organophosphorus in composite samples of maize, millet, guinea corn and rice from selected markets in Gbako, Niger State, Nigeria. Modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method was used for the extraction of the pesticide residues from the samples. The pesticide residues; chlorpyrifos and profenofos were determined by gas chromatography-mass spectroscopy (GC-MS) using GC-MS model SHIMADZU, GC 17A). The selected pesticides were extracted from the cereal grain samples using acetonitrile, anhydrous magnesium sulphate, and sodium chloride. Cleanup of the extracts was done with activated charcoal. The concentrations of 0.038 and 0.019 mg/kg were obtained for chlorpyrifos in maize and millet, respectively. The recorded values of the pesticide residues were compared with Codex maximum residue levels and were found to be below the maximum residue limits (MRLs) indicating that the values may not pose any health risk to the consumers at the moment. Although, the consumption of these foodstuffs containing these chemicals, chlorpyrifos, for a long period of time as well as their use on these crops for a long time could pose some health and environmental challenges since they are not biodegradable and their bioaccumulation could ensue. Hence, their use is suggested to be discouraged in favour of their alternatives.

Keywords: Pesticide residues, Bioaccumulation, Chlorpyrifos and Profenofos

INTRODUCTION

Crop production is an important venture especially in Nigeria where it plays an important on her economy. It generates an appreciable percentage of the gross domestic product (GDP) and contributes to the total food needs of the country. It also serves as a source of raw materials for her domestic industries and an easy market for industrial products like pesticides, chemical fertilizers, equipment, and machinery (Raina-Fulton, 2015).

Considering the importance of grain products in the diet of most people living in tropical Africa, lots of countries are involved in these cultivation of the vital crops. Among these countries, Nigeria happens to be one of the countries involved in the cultivation of these crops. However, a major source of concern for farmers in particular and agricultural industries in general is the menace of crop pests. These are living organisms that feed on the leaves, flowers, grains, or fruits of the plants, thereby destroying the plants and making them unavailable for human consumption (FAO/WHO, 2012; Inobeme *et al*., 2020).

During the vegetative growth of grains, chemical plant protection is used to protect them against the harmful impacts of pests, pathogens and weeds (Leong *et al*., 2007; Abimbola et al., 2023). International statistical reports have shown that, in several years, the impacts of pests and diseases on agricultural products on a global scale have reduce the total yield of products by 25%. In many cases, crops are fumigated with pesticides to avoid losses. Some of the chemical substances used to protect the crops from insect attack include organophosphates, carbamates and synthetic pyrethroids (FAO/WHO, 2021).

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Although, the use of chemicals in crop protection brings many benefits, such as increase in efficiency, profitability of production and improved grain quality, the negative effect is the contamination of crops, water, air and soil (EPA, 2021; Adetunji et al., 2022). The term "pesticides" refers to a class of chemicals used to prevent pest infestations and plant diseases in crops.

Contamination of food commodities with trace amounts of these chemicals has become a major source of concern for the general population (EPA, 2021). Continuous use of plant-protecting chemicals may result in their accumulation in agricultural produce. These chemical substances have low biodegradability and, as such, are said to be persistent toxic substances (Raina-Fulton, 2015). The biological stability and higher degree of lipophilicity in food commodities of these substances have significant effects on both human and animal health, with organochlorine pesticides having a wide range of acute and chronic health effects including neurological disruptive and developmental effects, in both humans and animals (Inobeme et al., 2020; FAO/WHO, 2021).

The overuse of pesticides in plant protection on different crops results in its bio-concentrations in both plants and their environment, European Food Safety Authority, (EFSA), 2021. Chemical residue analysis is a means through which the nature and level of any chemical contamination within an environment and its persistence are ascertained. Also, it is based on the residue level in food and food products that a modification of good agricultural practices (GAP) for total quality management (TQM) could be achieved (FAO, 2021). This study is aim to provide information regarding the type, nature and status of the pesticides that are being sold to farmers in the study area as well provide baseline scientific data on the levels of these pesticides in the selected foodstuffs from the study area.

METHODOLOGY

Study area

The study area covered in this study was Gbako Local Government Area, Niger state, Nigeria. Niger State is in the north-central part of Nigeria. The area is divided into three (3) locations of Lemu, Etsu-audu and Edozhigi. The production of cereal crops is supported by the plain alluvial soil in Gbako, which is rich in plant nutrients. The main agricultural activity of the people in this area is the growing of crops for family upkeep and as cash crops. Additional crops are also grown, including vegetables, beans, bananas, sweet potatoes, cassava, and bananas.

Sample Collection

Twelve (12) samples each of guinea corn, maize, millet and rice were collected from the selected farmlands in each of the three districts in Gbako Local Government Area and each were mixed to make a composite sample giving a total of four (4). The samples were code-named and stored in glass bottles with tight covers to protect them from moisture and contamination. They were then stored in the refrigerator until ready for use.

Extraction and Clean up

The extraction of the pesticides was performed according to the method described by Suleiman *et al*. (2022). A solution of acetonitrile was used for the extraction of the pesticide residues from the cereal grains and a clean-up was done. Water was added to 10.0 g of the milled sample in a 50.0 cm^3 extracting tube and allowed to stand for 10-20 minutes and then 15 cm^3 of acetonitrile (ACN) was added, caped and shaken. The cap was then removed and 4.0 g each of Magnesium Sulphate ($MgSO_4$) and Sodium Chloride (NaCl) was added, and the cap was tightened and shaken thoroughly by placing the tube on a shaker (Stuart orbital shaker SSL1 U.K.) for 15 minutes and centrifuged in (Hettick Universal II d-7200 Tuttingen) for 5 minutes at 3000 rpm. About 20 cm^3 of the top acetonitrile layer was then removed and transferred into a 15 cm^3 cleanup tube containing dispersive solid phase (DSP) sorbent. The tube was then caped, vortexed for 30 seconds and then centrifuged for 5 minutes at 3000 rpm. 20 cm^3 of the aliquot of the top layer was transferred into a clean sample bottle for analysis. To this, 1.0 g of anhydrous Sodium Sulphate which was dried at 650^0C for one hour and stored in a desiccator was added and mixed with the sample to absorb any moisture present. The mixtures were vortexed, mixed for 5 minutes and then allowed to stand for 45 minutes; it was mixed again and centrifuged for 5 minutes at 2500 rpm. The supernatant was carefully transferred into a flask. The residue was further extracted twice as described above, using 10.0 cm^3 acetonitrile each time.

The supernatants were combined and reduced to about 5 cm^3 using a rotary evaporator model RE

6000 at 35^0C. The solution was then transferred into a sample tube and reduced to about 1 cm^3 under a gentle stream of nitrogen gas using a nitrogen evaporator at 35^0C. It was then taken for florisil clean up.

The eluent was then evaporated to dryness under a gentle stream of nitrogen gas and the residue was reconstituted for GC-MS analysis (Suleiman *et al*., 2020).

GC/MS Determination of the Pesticide

The SHIMADZU GC/MS (GC-17) equipped with an electron capture detector ECD was used for the chromatographic separation of the pesticides. The injection mode was splitless. Nitrogen gas was used as carrier (1 cm^3min^{-1}) and makeup flow of 60 cm^3 min^{-1}. 1 μdm^3 aliquot of each extract was injected into the gas chromatography through the auto injector. Each sample extract was injected twice.

Identification and Quantification

Pesticide residues were identified if the retention time matched with those of the standards and the relative abundances were within 10% of those of the standards. Identified pesticides were quantified using the external standard methods of comparing sample peak areas with those of the pesticide standards under the same conditions. Each sample was analysed three times and then mean values obtained. The pesticide concentration in each sample was calculated as:

$$\text{Concentration of pesticide} = \frac{A_s \times V_F}{W_t \times C_F}$$

Where A_S = Peak area of sample. V_F = Final volume of clean extract, W_t = Weight of sample extracted and C_F = Calibration factor, The C_F of each pesticide was calculated as the peak area of standard divided by the total amount of the standard injected.

RESULTS AND DISCUSSION

In Table 2, the results for the concentration of organophosphorus pesticides detected in the samples from the selected markets in the Gbako local Government is presented. The least concentration of Chlorpyrifos (0.019 mg/kg) was recorded in the millet from the market, while the highest value of 0.038 mg/kg was obtained in the maize from markets. Though, the levels of the pesticides are low, their presence may be due to their application by the farmers before harvest and for storage to protect it from grain feeders in the field and to improve the shelve life of the produce and quality grains (WHO, 2022). The recorded values of (0.019 mg/kg and 0.038 mg/kg) for maize and millet in this work are in agreement with cereals reported by Adam et al., (2022).

The maximum residue levels (MRLs) of these pesticides in cereals grains for the European Union/CODEX Alimentarus is also presented in table 1. The highest level of chlorpyrifos (0.038 mg/kg) was recorded in maize, while the least was in millet from the region. Organophosphorus pesticides are the common and major classes of pesticides applied to cereals crops in most farms and stores (Obida, 2012). The five pesticides determined in this work include these classes of pesticides. It is not all the pesticides of organophosphates (Chlorpyrifos and Profenofos), that were found in the samples studied. This could be attributed to factors such as non-availability of the chemicals to the farmers, or non-application of them during the period of study or due to their low levels below the detection limits of quantification (Obida, 2012).

Table 2 shows the results from the analysis of guinea corn, maize, sorghum and rice grain samples from the farms for the residues of chlorpyrifos and profenofos using a gas chromatography machine with a limit of quantification of 0.0002 mg/kg. The least concentration of 0.019 mg/kg was found in Millet and the highest value of 0.038 mg/kg was recorded in Maize for Chlorpyrifos. However, these values being low, might pose no immediate threat to humans or animals that feed on the cereal grains since these values low compared to the maximum residue limits (MRLs) for cereal grains. The detection of Chlorpyrifos though, at low concentrations, justifies the statement that some of the chemicals used by the farmers as insecticides are illegal (Elzbieta *et al*., 2015) and banned but due to their availability in the region and farmers' lack of knowledge of the health implications of the use of such substances still use them to improve their crop yields (Lamberth *et al*., 2013). Also, the result of the analysis shows that there was Chlorpyrifos detected in only two of the samples (Maize and Millet), from the Markets. This indicates the level at which the farmers use the pesticide (Chlorpyrifos) for the control of pests of cereal crops. The values of 0.038 and 0.019 mg/kg recorded in this work are lower than 0.4005 and 0.115 mg/kg respectively reported for Chlorpyrifos pesticide residues by Abdelghani and Forthergill (2013) and Lozowicka *et al*. (2014) in cereal grains.

The concentration of the Chlorpyrifos residue found in the maize samples from markets is higher (0.038 mg/kg) than the (0.019 mg/kg) of millet from the same region. The higher amount of pesticides in the market samples of maize could be attributed to the bioaccumulation of the chemicals applied when the edible part of the plant is already formed. More so, the amount of the pesticide recorded in the two samples (maize and millet) from the market could be a result of the post- harvest application of the chemicals on the grains for storage (Abdelghani and Forthergill, 2013).

It is worthy of note that a high number of pest's attack on crops is experienced in the farms than in the stores and as such, there is a need for a reduction in the rate of pesticides application on the stored grain (Seshaiah *et al*., 2013).

This study found various levels of pesticide contamination in maize and millet samples. The levels of Chlorpyrifos in the samples were found to be below their respective European Union MRLs.

The global increase in cereals cultivation particularly maize, rice, g/corn and millet could be due to the use of chemicals such as Chlorpyrifos, atrazine and others. Several published research works have revealed the importance of chemicals herbicides and pesticides in crop production. Scientific reports have been made that the application of herbicides results to 65% - 90% weed control and 100% - 150% more crop yield. In developing countries like Nigeria and Ghana, Atrazine and Chlorpyrifos are discovered to be the most frequently used chemical. However, despite the applications of chemicals to increase crop yield through weed and pest control, the chemicals have been reported to be detrimental to the reproductive system, by inducing estrogen production and inhibiting the production of testosterone thereby causing chemical castration. Many research studies have revealed that, the concentration of pesticides in food in many developing countries including Nigeria is at an alarming rate (Akinneye *et al*., 2018). Earlier studies in some parts of Nigeria indicated the presence of pesticide residues in water, vegetables, legumes, fruits, fish and soil at locations unknown for pesticide usage (Ogbonnaya *et al*., 2017). The high rate of application of these chemical pesticides has resulted in food contaminations; ingestion of which has been linked with negative health conditions. The major source of morbidity, mortality and increased risk of skin cancer, destruction of neurological cellular functions, chronic neurotoxicity, and bladder and lung cancer even at very low concentrations is contaminated foods. The high consumption of cereal grains by Nigerians in both rural and urban has thus necessitated the need to assess the levels of chemical residues to accurately estimate human dietary exposure (Khalatbary and Ghaffari, 2015).

Although residue levels of the Organophosphates (Chlorpyrifos) are below the maximum limits of the codex committee on pesticides residues, as well as EU-MRLs, it does not indicate zero health risk because pesticides might be present in the maize, rice, guinea corn and millet samples but below the detection limit in some cases. Since most chemicals have the properties of being generally persistent, volatile, lipophilic and bio-accumulative both in the environment and at each trophic level of the food chain, there are possibilities of them attaining high concentrations levels through bio-magnification in the tissues of the animals which are high on the food chain including human (Kotila and Yön, 2015). Consequently, this might result in negative environmental and human health challenges and hence devastating problems.

A research publication by Jagadish *et al.* on the pesticide residue in rice, wheat and pulses, reported that chlorpyrifos is the most commonly detected pesticide in cereals and pulses from their studied area (Jagadish *et al*., 2015). The result of this study is in agreement with the above findings and could be a result of the fact that the most commonly available insecticide to the farmers is Dursban or Rocket used for the storage of the grains. While, the low levels of organophosphate residues recorded in this present study might be due to compliance with good agricultural practices (GAP) such as good storage practices and appropriate pesticide application to mitigate insect infestation. When the residual pesticide content in food is found to be above the MRL in any food material, such a food commodity is considered been adulterated and not to be safe for consumption (Sawaya *et al*., 2018) and as such, be banned from been sold at any market (Akinneye *et al*., 2018).

The effects of nitrogen fertilizer rate on total fruit fresh yield (tons) per hectare at Samaru in 2012 and 2013 seasons are also presented in Table 7. The applications of 70 and 140kg N ha^{-1} generally yielded statistically similar and highest total fresh fruit weights (tons) per hectare. These were significantly greater than for those of other N rates and for the unfertilized controls. But further increase in N rate from 140 to 210kg ha^{-1} significantly depressed the total fresh fruit yields in the two seasons. Of the two varieties California Wonder consistently produced significantly higher fresh fruit yield (tons) per hectare than Yolo Wonder. No significant factors interaction was recorded on the fruits produced.

Table 1: Parameters for the Validation of the Pesticide Residues Determined in this Study

	Concentrations in mg/kg		Codex	
Pesticide	LOD	LOQ	MRL(2018)	Retention time (min)
Atrazine	0.001	0.0002	0.05	8.77
Chlorpyrifos	0.001	0.0040	1.00	10.47
Cypermethrin	0.010	0.0100	2.00	13.69
Lambda-Cyhalothrin	0.010	0.0100	0.10	12.47
Profenofos	0.004	0.0130	0.01	9.09

KEY: LOD = Limit of detection, CODEX = , MRL - Maximum Residue Limits

Table 2: Concentrations (mg/kg) of organophosphorus pesticides residues in samples from the markets

	Sample (mg/kg)				CODEX MRL(mg/kg)	
Pesticides	MM	MTM	GM	RM	LOD	2020
Chlorpyrifos	0.038	0.019	ND	ND	0.001	1.000
Profenofos	ND	ND	ND	ND	0.004	0.010

KEY: LOD - Limit of Detection, CODEX MRL - CODEX Maximum Residue Limits and ND - Not Detected, MM - Maize, MTM - Millet, GM - Guinea corn and RM-Rice.

Conclusion

It is apparent from the results of the study that farmers and marketers in the study area in Niger State although, Profenofos and other organophosphates were below detection level in the GF and RF samples from the study area, a detectable level of were found in MF and MTM from the area. Organophospates (chlorpyrifos) were found in maize and millet from the market. The estimated dose for all the organophosphates might not pose a direct danger to human health although present in the maize and millet samples since their values were lower than the toxic thresholds of the reference MRLs doses. Residue levels of these pesticides are below the maximum permissible intake, but there was no zero risk because pesticides were present in maize and millet samples.

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