**QUANTIFICATION OF SOME PESTICIDE RESIDUES IN FRESH PEPPER FROM SELECTED FARMS IN LEMU, GBAKO LOCAL GOVERNMENT, NIGER STATE, NIGERIA**

A. M. Salihu1\*, E.Y. Shaba1, J. T. Mathew3, A. Alheri1, N. K. Gwadabe2, S. Binta2, K.A. Adedokun1, W. Okotubu1.

\* The Corresponding Author’s Email Address: a.salihu@futminna.edu.ng

1Department of Chemistry Federal University of Technology, Minna, Niger State, Nigeria

2Department of Science and Laboratory Technology, Niger State Polytechnic, Zungeru, Nigeria

3Department of Chemistry, Ibrahim Badamasi Babangida University, Lapai, Niger State, Nigeria

ABSTRACT

This study quantifies some pesticide residues (Organochlorine (OCP) and Synthetic pyrethroids (SPP) concentrations in fresh Pepper (*Capsicum annum*) from selected farms in Lemu, Gbako Local Government area of Niger state, Nigeria using a modified QuEChERS method for sample preparation and GC-MS analysis. The results indicate the presence of OCP and SPP residues includes: Heptachlor, Aldrin, Dieldrin, Heptachlor epoxide, Endosulfan II and Endosulfan sulfate; Lambda-cyhalothrin, β-Cypermethrin and zeta-Cypermethrin with concentrations of 1.33 mg/kg, 1.55 mg/kg, 0.33 mg/kg, 0.22 mg/kg,1.31 mg/kg,0.45 mg/kg and 1.00 mg/kg, 1.29 mg/kg and 1.08 mg/kg. All the detected OCPs were above the MRLs. Indeed, these concentrations of both the organochlorine and pyrethroid pesticides detected in the pepper sample analysed were observed to be slightly above the MRLs by the Codex 2022 (WHO and FAO), although the difference may not be too significant and hence, it does not pose a serious danger.

**Key words:** synthetic pyrethroids, Lambda-cyhalothrin, cypermethrin, Heptachlor epoxide, Endosulfan, Aldrin and Dieldrin.

**Introduction**

Vegetables are vital components of nutrition. They are mostly eaten fresh, unpeeled and unprocessed for their high nutritional benefits such as minerals, vitamins, fibers and antioxidants (El-sayed *et al*., 2022).

Pepper is one of the flowering annual vegetables belonging to the piperaceae family and mostly used as condiments. The species Capsicum annum belongs to the family of solanaceae, which represents a group of about twenty seven plants species with only *Capsicum annum*, *C. frutescenens*, *C. genus*, *C. baccatum* and *C. pubescensns* been the only domesticated species and rest undomesticated (Abdelghffar *et al*., 2022). Pepper is one of the highly priced and consumed vegetable across the globe, due to its rich content of vitamins such as ascorbic acid and carotenes. It is also rich in other nutritive compounds such as carotenoids, which have characteristic antioxidant and anticancer potentials and also a promising source of calcium (Azhari *et al*., 2019).

The fruit is a natural source of colour for food and its consumption has proven to be protective against some life-threatening diseases such as cardiovascular diseases. It has also been used as medicine for the management of some health chalenges such as arthritis (Ogunlade *et al*., 2012).

Edozhigi in Gbako Local Government is a strategic and majir cultivators of Pepper and hence contributes greatly in alleviating both poverty and food spicy shortage in Nigeria. Vegetable cultivation is mostly done under irrigation farming system, along river Kaduna. The availability of fertile soil is an asset for vegetable cultivation (Mann *et al*., 2017 ). However, the practice of this farming system in Edozhigi and Nigeria at large is faced with many challenges ranging from pest and disease attack, which account for an estimate of 25 % loss of vegetables. Farmers therefore in an effort to mitigate these losses apply pesticides to increase crop yield (Azhari *et al*., 2019).

The pesticide residues commonly found in Pepper are those purposely applied directly to the crops to prevent them from pest and diseases. Report world wide revealed a rise in the application of the chemicals for crop production which resulted in their enrichment in various food matrices, such as Pepper (Mann *et al*., 2017). However, it is on this reasons that vegetables and fruits cuold be considered an easy route through which humans are exposed to pesticides (El-sayed *et al*., 2022). Also, high concentrations of pesticide residues due to improper and unregulated application and multiple sprays have been reported as major reasons for poisoning and many negative health issues in Nigeria (Mann *et al*., 2017).

In Nigeria, the regulatory agency (NAFDAC) has deem it safe after series of laboratory tests and from the result and findings of their research to declare some the classes of organochlorine pesticides such as dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexanes (HCHs), aldrin, dieldrin, endrin, and heptachlor illegal and banned for use, due to its persistent nature on the biosphere and hence it consequential effects on animal health (Suleiman *et al*., 2020). Sadly, in spite of the status of these pesticides on the NAFDAC list, some countries like Nigeria still found them very much potent to be used for pest control and thus the residual contents of which has become a great challenge to deal with in such countries like Nigeria (Mann *et al*., 2017 and Suleiman *et al*., 2020).

**Maps of the sampling area:**

 



**MATERIALS AND METHOD**

**Reagents**

All reagents and pesticides standard used were of analytical grade and obtained from sigma. The glass wares were cleaned with detergent and water, rinsed with distilled deionized water and then acetone before used. The extraction was carried out using Centrifuge, while Gas chromatograph couple with mass spectrometer detector (GC-MS) was used for the analysis analysis respectively.

**Sample collection**

Pepper samples were collected from three major Peppers farms at Lemu, Gbako Local Government, Niger state. They were mixed to make a composite. The samples were then choped each, grinded and homogenized.

**Samples extraction**

Modified QuEchERS method was used for sample preparation as describe by Suleiman *et al*, 2020. The samples were grinded to homogenized and turn them fine state. 15 g of homogenized sample was weighed into a cleaned 50 Cm3 extraction tube; 15 Cm3 of extraction solvent (acetonitrile) was added to the sample and shake vigorously for 5 minutes. This was done to ensure the organic pesticides residues were dissolved in the solvent and separated from water. 6 g of MgSO4 and 1.5 g NaCl each were added to remove the water and maintained the polarity of the sample respectively, before centrifuge for at least 10 minutes at 600 rpm. The supernatants was then transferred into another cleaned extraction tube followed by the addition of 150 mg of MgSO4 and shake for 30 seconds and centrifuge for 1minute at 1500 rpm, the cleared extract was then used for GC-MS analysis (Mann *et al*., 2017).

**SAMPLE ANALYSIS**

The analysis was carryout at Nigeria institute of Oceanography and Marine Research (NIOMR), Lagos State Using GC-MS model 7890 Agilent technologies, equipped with auto sampler, capillary column length HP 5 ms of length 30 m and internal diameter of 0.320 mm and 0.25 micrometer. The temperature was program at 600 C held for 5 minutes at 8OC per minute to the final temperature of 3000 C held for 30 seconds and the MSD transfer line was held at 3000 C. Split injection of one microliter was carried out at 3000 C injector temperature with a purge flow of 3 Cm3/minute, the carrier gas used was helium, with flow rate of 2.17 Cm3/minute and the pressure was 150 kpa. The interface temperature was 3000 C. The mass spectrometer model 5975 agilent technologies ionization mode was electron impact with ion sources temperature of 2300 C and in full scan mode ranges from 45-500 M/Z. Internal standard technique was employed to analyze the extracts. The standards were prepared in different concentrations from 0.100 ppm to 2.00 ppm and used to generate calibration curves for each compound.

**RESULTS AND DISCUSION**

There was a very high match factor in the spectral due to the reason that the retention times of the pesticides detected in the samples were the same as those of standards.

Tables 1 and 2: Show the concentration of some organochlorine and Synthetic pyrethroids pesticide residues in the fresh pepper sample. Most of the OCPs detected in the samples are declared unsafe for Agriculture and domestic purposes in Nigeria and other developing countries according to (Suleiman *et al*., 2020), from the data sheet of FAO/WHO on banned and restriction of OCPs. Also all the detected pesticides are have the concentrations above maximum Residue limit (MRL) FAO/WHO (2018).

However the concentrations of α-HCH, HCB, β-HCH, Lindane, delta-HCH, Chlorothanil, Endosulfan (I), Endrin, P,P,DDT and Methoxychlor could not be detected in the pepper samples.

Lambda-cyhalothrin, β-cypermethrin and zeta-cypermethrin (SPPs) standards were employed in the analysis as shown in table 2, and these were recorded in pepper samples. Atrazine and cypermethrin which are a common synthetic pyrethroid were not detected, hence it could be said to be below the limit of detection in the extracts, and this may be attributed to the volatile nature of the pesticides (Suleiman *et al*., 2020). The concentration of the Heptachlor pesticide residues obtained in this work is in agreement with the (0.051 mg/Kg and 0.057 mg/Kg) values reported by Azhari *et al*., (2019).

The detection of these pesticides in the sample indicates that most of the farmers in the study area lack adequate information about the dangers associated with OCPs residues in the food product and to the environments. Also, unrestricted and continues applications of this class of chemicals may be due to its availability and its low cost as reported by (Suleiman *et al*., 2020).

Washing with water remove completely some water soluble pesticides residues liker dimethoate, reduces the concentrations of some like heptachlor residues by about 44 - 54%.

**Table 1: Detected OCPs Residues in fresh pepper from selected farms in Edozhigi**

|  |  |  |  |
| --- | --- | --- | --- |
| **OCPs** | **(mg/kg)** | **USDA MRL** | **WHO/NAFDAC** |
| Alpha-HCH | ND | - | Banned |
| HCB | ND | - | Banned |
| Beta-HCH | ND | - | Banned |
| Lindane | ND | 0.05 | Banned |
| Delta-HCH | ND | - | Banned |
| Chlorothalonil | ND | 0.03 | Banned |
| Heptachlor | 1.33 | 0.01 | -N/A |
| Aldrin | 1.55 | 0.05 | Banned |
| Heptachlor Epoxide (B) | 0.33 | - | Banned |
| Endosulfan I | ND | 0.05 | Banned |
| Dieldrin | 0.22 | - | Banned |
| Endrin | ND | 0.01 | -N/A |
| Endosulfan II | 1.31 | 0.05 | Banned |
| Endosulfan sulfate | 0.45 | 0.05 | Banned |
| P, P- DDT | ND | 0.03 | Banned |
| Methoxychlor | ND | - | -N/A  CODEX, 2020 |

**Keys:** ND=not detected; N/A = not available, WHO= World Health Organization**,** NAFDAC= National Agency for Food and Drug Administration and Control, USDA MRL= United States Department of Agriculture Maximum Residue Limits.

Table 1: Indicates the concentration of organochlorine pesticide residues recorded in pepper samples from farms at Edozhigi, Nigeria. These include: Endosulfan (1.31 mg/kg), Endosulfan sulfate (0.45 mg/kg), Dieldrin (0.22 mg/kg), Heptachlor epoxide (0.33 mg/kg), Aldrin (1.55 mg/kg) and Heptachlor (1.33 mg/kg) respectively. In this study, Heptachlor had a GC-MS retention time of (12.602 minutes), while Aldrin (13.713 minutes), Endosulfan II (16.342 minutes), Endosulfan sulfate (16.811 minutes), Dieldrin (15.333 minutes) and Heptachlor epoxide (B) (14.685 minutes). Endosulfan sulfate had the highest retention time while heptachlor had the lowest retention time. These variations in the retention time for the various pesticides could be as a result of their differences in molecular weight.

**Table 2: Detected synthetic pyrethroids fresh pepper from selected farm lands in Edozhigi**

|  |  |  |  |
| --- | --- | --- | --- |
| **OCPs** | **(mg/kg)** | **USDA MRL** | **WHO/NAFDAC** |
| Lambda-cyhalothrin | 1.00 | - | Banned |
| b-cypermethrin | 1.29 | - | Banned |
| Zeta-cypermethrin | 1.08 | - | Banned |
|  |  |  |  |
|  |  |  |  |

Table 2: indicates the concentration of the synthetic pyrethroids detected in the fresh pepper samples from the farms at Edozhigi. These include Lambda-cyhalothrin (1.00 mg/kg), β-Cypermethrin (1.29 mg/kg) and z-Cypermethrin (1.08 mg/kg) respectively. β-Cypermethrin showed the highest concentration values in the samples while lambda-cyhalothrin has the lowest value. Although all the concentrations recorded for the pesticides indicate values within WHO maximum residue limits (MRLs) for spices, a reflection that they are not harmful, but it is necessary to have a continues seasonal monitoring (Onuwa, *et al*., 2017).

From table1 above, the concentrations of the pesticide residues exceeded the maximum residue limit (MRL), which implies that there is a great concern about OCPs pesticides and their carcinogenicity. This is because, Dieldrin and Heptachlor epoxide (B) detected in the sample is capable of inducing cancer in human. Research findings have revealed that these pesticides cause cancer in several organ systems but with other contributing factors such as diet, age and family history. According to the Environmental Protection Agency (EPA), human exposure to dieldrin and other pesticides are carcinogenic (Mann *et al*., 2017). According to FAO/WHO, (2018) approximately not less than 3 million people are poisoned and 220,000 die every year in the world from pesticide poisoning and majority of which occurs in developing countries, though far higher amount of such chemicals are consumed in developed countries (Banke, 2019 ).

Furthermore, the reported organochlorine pesticide residues values in pepper from Sudan is lower compare to the values obtained in this work for the pepper sample from Edozhigi with heptachlor having (0.01 mg/kg) (Azhari O. A. *et al*.,2019). Also, similar research findings on pepper from Otta in Nigeria reported lower values having HCB with (0.54 mg/kg), beta HCH (2.34 mg/kg)) and dieldrin (0.037 mg/kg) respectively (Nsikak *et al*., 2011). Also, the value (0.33 mg/kg) obtained for Heptachlor epoxide in this work for pepper is far below the reported values (2.303 and 3.011 mg/kg) by Nuhu, et al.,(2020), for Onions and spinach. Also, Endosulfan II (1.31 mg/kg) in pepper samples for this work was low compare to (1.433 mg/kg) reported for Lettuce.the same trend was observed for the concentrations of the Heptachlor in carrot, cabbage and tomatoes.

Although, the concentrations of the classes of organochlorines recorded in this work are above the USDAs (MRLs) values, it does not pose a risk to the consumers because of some processes involved in pepper processing (washing, grinding, boiling, frying, drying and others) before consumption, which have been reported to reduce pesticide residues contents in food matrix. Yet, there is need for regulation on pesticide applications on the fruits and periodic monitoring of the pesticide residues concentration in plants (Mann *et al*., 2017).

**Conclusion**

None of the organochlorines and synthetic pyrethroids residues detected collectively posed a great danger; despite they are above the MRLs for the individual pesticides residues. The study showed that organochlorine and pyrethroids pesticide residues still exist in food cultivated in Nigeria. The selected vegetables (pepper) from the farm in Lemu are safe for consumption since the concentration of these pesticide residues show no wide significant difference with the MRLs set by WHO/FAO. However, continuous and regular monitoring, as well as the adoption of good Agricultural practices (GAP) in order to control pesticide residues in food commodities should be enforced to sustain the level of compliance.

**References**

Abdelghffar, E. A.R., Mostafa, N. M., El-Nashar, H. A.S., Eldahshan, O. A. and Abdel Nasser B. S. (2022). Chilean pepper (*Schinus polygamus*) ameliorates the adverse effects of hyperglycaemia/dyslipidaemia in high fat diet/streptozotocin-induced type 2 diabetic rat model. Elsevier Journal of Industrial crops and Products:181(11)49-53

Azhari Omer Abdelbagi., *et al*.(2019). “Pesticides Residues in Samples of Sweet Peppers (*Capsicum annum*) from Khartoum State, Sudan”. *EC Pharmacology and Toxicology* 7.7 (2019): 568-576.

Ajmer Singh Grewal, Ashish Singla, Pradeep Kamboj, Jagdeep Singh Dua (2017). Pesticides residues in food grains, vegetables and fruits: A hazard to human health.

Aman Dekeebo (2022). Major pest and pest management strategies in the sweet pepper (capsicum annum).

Anderson, H.R, Vinggard, A.M, Rasmussen T.H, Gjemadsen I.M and Bonefeld-Jorrgensen, E.C. (2017). Effects of currently used pesticides in Assays for estrohenicity and rogenity and aromatase activity in-vitro toxicol application pharmacol 179, 1-12.

Banke Idayat Yusuf ( 2019) concentration of pesticide residue in beans and maize grains in bodija market, Ibadan, Nigeria

Brhan Khair Saleh, Abdella Omer, Belay Teweldemedhin (2018). Medicinal uses and health benefits of chili pepper (capsicum spp); a review.

Codex Alimentarius Commission, (2009). Pesticide residues in food: Maximum Residue Limits. Maximum Residue Limits.

El-Sayed, A.A., El-Saber, M., Ramadan, M., and Ahmad, A.E. (2022). Effect of nano-chitosan encapsulated spermine on growth, productivity and bioactive compounds of chili pepper (Capsicum annuum L.) under salinity stress. Egyptian Journal of Chemistry, 65(8):187-198

Fabiane Ferraz Wishiewsky and Elisandra Carolina Martins (2022). An integrative review on the analysis of pesticide multiresidues in sweet pepper samples using the QuEchERS method and chromatography techniques.

Gullino ML, Albajes R, Nicot PC. Integrated Pest and Disease Management in Greenhouse Crops. Vol. 9. Swizerland: Springer; (2020)

Maksymiv, I. Pesticides: benefits and hazards. (2015) J VasylStefanykPrecarpathianNatl 2(1):

Mann, A., Ogbonnaya, I, C., Yisa, J. and Bala, A.. (2017). Assessement of organiichlorinepesticle Residue in soil and water from fadama farming communities in Minna, North Central Nigeria. (AASCIT Journal of Environment. 2(5):48-55.

Muinat Ogunbo (2015). Resource-use efficiency and optimal farm plan in pepper (capsicum spp). Production in ogun state, Nigeria.

Nicolopoulou-Stamati P, Maipas S,Kotampasi C, Stamatis P, Hens L.Chemical pesticides and human health:The urgent need for a new concept inagriculture. Frontiers in Public Health (2016);4:148.

Nuhu, A. A., Suleiman, F., Omoniyi, K. I., and Yashim, Z. I. (2020). Determination Of Organochlorine Pesticide Residues In Some Vegetables And Fruit By QuEChERS Techniques And Gas Chromatography /Mass Spectrometry. *Fudma Journal Of Sciences*, *4*(2), 365 - 370.

Ogah C.O, Coker, H.B, Adepoju-Bello A.A, (2011). Organophosphate and carbamate pesticide residues in beans from markets in Lagos State, Nigeria. Journal In Res Eng Sciences 2(1): 50-59.

Onuwa, P.O., Eneji, I,S., Iyodo, A.U. and Sha’Ato R. (2017). Determination of Pesticide Residues in Edible Crops and Soil from University of Agriculture Makurdi Farm Nigeria. Asian Journal Of Physical Aand Chemical Sciences, 3(3): 1-17,

Palma J M., *et al*. “Role of ascorbate on the fruit physiology of pepper (Capsicum annuum L.)”. *Function Plant Science and Biotechnology*

Rathore H.S. and Nollet L.M.L (2012). Pesticides: Evaluation of Environmental Pollution. Taylor and Francis Group, LLC. USA. Pp 544- 545.

Suleiman, M.A.T., Shaibu, M., Lafia-Araga R.A and Salihu, S.O. (2020). Study Of Organochlorine Pesticide Residues Level In Fresh And Dried Tomatoe From Selected Farmlands In Zamfara State, Nigeria. *International Journal of Engineering Applied Sciences and Technology:*5(8), 91-96

World Health Organisation (WHO) (2020). Guidelines for dietary intake of pesticide residues. programme of food safety and food aid