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Organophosphorous Pesticides Residue Contamination Levels of some Selected Vegetables Cultivated in Mubi-north and Mubi-south LGA of Adamawa state, Nigeria.

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ABSTRACT

The objective of the study was to determine the contamination levels of some selected vegetables cultivated in Mubi-North and Mubi-South LGA of Adamawa state with hazardous organophosphorous pesticide residues using QuEChERS method of extraction and GC-MS analyzer. A total of 72 samples (12 of each of the selected vegetables) were analyzed for 9 organophosphorous pesticide compounds. The result obtained showed that organophosphorous pesticide residue levels on the majority of the vegetable samples analyzed were in compliance with the maximum residue limits (MRL) stipulated by the Codex Alimentarius Commission 2004. However, levels higher than the MRLs were also detected. Levels of Organophosphorous pesticide residues higher than the MRLs were recorded most in spinach 16.7% followed by lettuce 13.9% and then tomato 11.1% Despite the fact that majority of the vegetables showed pesticide residue levels below the detectable limits, detection of contamination levels higher than the MRls are strongly indicative of potential health risk to consumers. It is therefore recommended that public awareness programs on pesticide residue should be organized by the authorities in agricultural production communities to protect the consumer from indiscriminate exposure to pesticides.

Keywords: Organophosphorous, contamination levels, Maximum Residue Limits, Vegetables

INTRODUCTION

Organophosphorus pesticides are widely used by farmers throughout the world against the possibility of a devastating crop loss from pests and diseases, as well as to increase agricultural productivity to provide adequate food supply for the increasing world population. Many of these chemicals proved beneficial in pest and disease control, crop production, and industry [1]. These same chemicals, however, have had unforeseen effects on human health and the environment [2]. Such pesticides may remain on or in food after they are applied to food crops as pesticide residues, Food and Agriculture Organization/World Health Organization [3].

Very common effects of organophosphorous pesticide residues in human body include nausea, vomiting,blurred vision, coma, difficulty in breathing, deficit hyperactivity disorder, disorder infetuses and children, *etc.* [4 and 5]. A number of these compounds can cause moderate to severe respiratory and neurological damage oractas genotoxic, carcinogenic and mutagenic agents, endocrine disruption, *etc.*, through routes that include consumption of dietary residues [6]. Pesticides and their residues are also known to be contributory factors in several diseases such as heart diseases, and Parkinsonism [7].

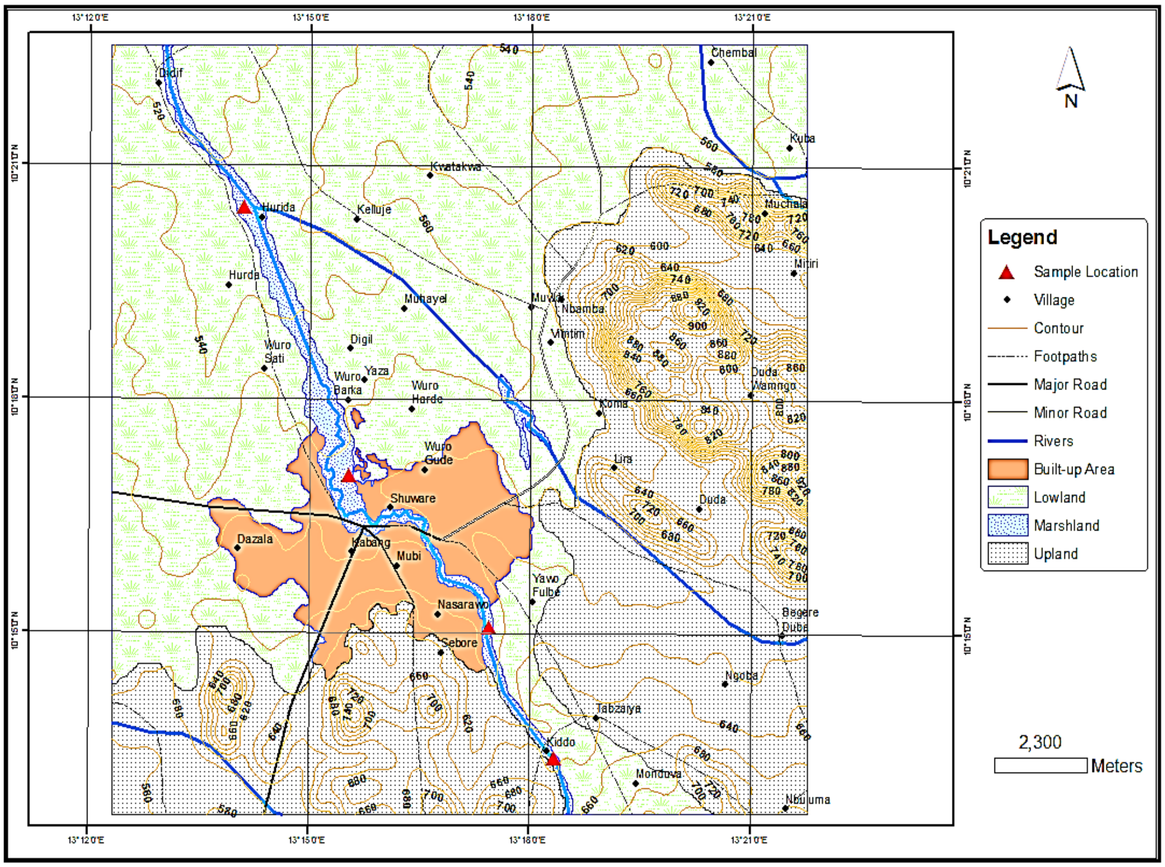
The studied area comprises of four selected vegetable farms in Mubi north and Mubi south local government areas of Adamawa state, these farms accumulates varying amount of pollution load from atmospheric deposits, anthropogenic inputs and agrochemical practices. The pollution load may contain different organophosphorous pesticide chemicals which are gradually taken up by vegetables and finally passed to man via the food chain.With time, the levels of these pesticide chemicals become higher than the acceptable limits which may be responsible for some of the chronic diseases afflicting the human population.A critical perusal of available literature revealed a growing interest in the investigation of pesticide residues in both human and environmental samples [8 and 9]. Nevertheless, to the best of our knowledge, no investigations of regular surveys, monitoring and assessment have been reported on the concentration of pesticides residues levels of vegetables cultivated in Mubi north and Mubi South local government areas.

This work is therefore aimed at assessing the contamination level of some selected vegetables cultivated in the studied area with respect to organophosphorous pesticide chemicals, this will in no doubt provide us with the opportunity to proffer rational advice to the community on the issues of pesticide residues in food crops.

MATERIALS AND METHODS

Study area

The study area comprised of some selected marshlands in Mubi North and Mubi South Local Government Areas of Adamawa State where vegetables are cultivated in commercial quantity



Map of the Study Area

Sampling of Vegetables

Sampling was performed by random collection of the vegetable samples from various sampling points identified in the study areas according to the FAO/WHO recommendation [10]. Three replicate samples about 1kg of the vegetable was collected from each sampling point. All the samples were packed in a well labeled plastic bag and transport to the laboratory in an ice box immediately after collection. Samples were stored between 0°C to 4°C in the laboratory for analysis within 24hrs.

Samples were taken among commodities considered of high consumption rate and commonly cultivated at the study areas. E.g, Lettuce *(Lectuca sativa L.)*, Spinach *(Spinacia oleracea L.)*, Moringa *(Moringa Oleifera L.)*, Okra *(Abelmoschus esculentus L.)*, Pepper *(Capsicum L.)*, and Tomato*(Lycopersicon esculentus L)*.

Extraction and Clean-up from Vegetable Samples

QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) extraction AOAC method [11] with slight modification was used for the extraction of pesticide residues from vegetable samples. Fresh vegetable sample was thoroughly shredded and homogenized. 15g of the homogenized sample was macerated with 15ml acetonitrile (1.0% acetic acid) in 50ml centrifuge tube the screw cap was closed and the tube was then vigorously shaken for 1 min using a vortex mixer at a maximum speed, afterwards, 6 g of anhydrous magnesium sulphate and 1.5 g of sodium chloride was added then extraction was performed by shaking vigorously by hand up to down for 10 min and centrifuged for 10 min at 6000 rpm and 4°C.

An aliquot of 4 ml was transferred from the supernatant to a new clean 15 ml centrifuge tube and cleaned by dispersive solid-phase extraction (SPE) with 100 mg primary-secondary amine (PSA), 20 mg graphitized carbon black and 600 mg of magnesium sulphate ($MgSO_4$). Afterwards, centrifugation was carried out as mentioned above. Then, aliquot of 3 ml of the supernatant was taken and evaporated to dryness using rotary test tube evaporator. The residue was then reconstituted in 2 ml of acetonitrile (i.e. 1.5 g matrix per ml extract). The sample was then analyzed in GC system.

Analysis

Gas chromatography–mass spectrometer (GC-MS) model GCMS-7890A Agilent technologist inert MSD 5975CM Equipped with ^{63}Ni electron capture detector was used for the analysis.

Pure nitrogen was used as the carrier gas and a low polar Hp-5MS was used as the separation column the column dimension was 30cm x 0.34mm, 0.25αm and The operating conditions were: column oven temperature: 60^{0}C, detector temperature: 300^{0}C, injection temperature 250^{0}C, flow rate of the carrier gas was 1.61ml/min, pressure of 100.2kpa and a linear velocity of 46.3cm/sec. Splint injection mode was used; a volume of 1.0μl of the sample extract was injected and 0.1 μl pure reference standard solution was analyzed in a similar manner. Peak identification was done by comparing the retention times of the pure reference standard and those obtained from the extract. Concentration of the pesticide residues was calculated using a five pointer calibration curve. The analysis was carried out at American University of Nigeria (AUN), Adamawa state Nigeria.

Quality control and quality assurance

Quality control and quality assurance were included in the analytical scheme [9]. The recovery, precision and linearity of studied pesticides were evaluated by adding a working mixture to 20g of shredded untreated samples; the spiked samples were made to stand for at least 1hour before the extraction. Three replicate samples were extracted and analyzed according to [11]. Precision was calculated based on daily repeatability of 3 samples, whereas reproducibility was carried out on 3 different days.

Recoveries were calculated for three replicate samples. Percent recoveries in spiked samples ranged between 120% and 180%. Accordingly, the sample analysis data were corrected for these recoveries. Detection limit(s) of the method were also assessed based on the lowest concentrations of the residues in each of the matrices that could be reproducibly measured at the operating conditions of the GC; which were

0.001mg/kg. A blank analysis was also carried out in order to check any interfering species in the reagents.

RESULTS AND DISCUSSION

Levels of Organophosphorous Pesticides Residues in Vegetables Cultivated from Hurida

Table1 showed the prevalence and levels of Organophosphorous pesticide residues found in the vegetable samples collected from Hurida. Among the compounds studied in the samples, dichlovos is the predominant compound detected in the vegetables. Maximum levels of it was detected in tomato 0.052 mg/kg and the lowest level was detected in pepper 0.034 mg/kg followed by chlorpyrifos with highest level of 0.061 mg/kg in lettuce and lowest level of 0.021 mg/kg in moringa. Primifosmethyl was detected in three samples; pepper, spinach and tomatoes, maximum level 0.051 mg/kg was found in tomato and the minimum level 0.027 mg/kg was detected in pepper. Dimethoate, ethion, profenfos and parathion were detected in one sample each (ie spinach, lettuce, tomatoes and okra respectively). While, malathion and diazinone were not detected in all the samples analyzed from this area.

Table 1 Mean Concentration (mg/kg) Op Pesticide Residues on Vegetable Cultivated from Hurida, (Mubi north LGA)

Pesticide type	Lettuce	Moringa	Okra	Pepper	Spinach	Tomato
Diclovos	0.035±0.001	<0.001	0.049±0.001	0.034±0.001	0.048±0.001	0.052*±0.001
Dimethoate	<0.001	<0.001	<0.001	<0.001	0.008±0.001	<0.001
Ethion	0.022±0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Primifos-methyl	<0.001	<0.001	<0.001	0.027±0.001	0.041±0.001	0.051*±0.001
Chlopyrifos	0.061*±0.001	0.021±0.001	<0.001	<0.001	0.052*±0.001	0.023±0.001
Malathiom	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Diazinon	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Profenfos	<0.001	<0.001	<0.001	<0.001	<0.001	0.026±0.001
Parathion	<0.001	<0.001	0.002±0.001	<0.001	<0.001	<0.001

Op= Organophosphorous, Detection Limit (0.001), *Indicates values greater than MRLs

Levels of Organophosphorous Pesticides Residues in Vegetables Cultivated from Wurogude

Table 2 showed the distribution and levels of Organophosphorous pesticide residues found in the vegetable samples analyzed. Among the compounds studied in the samples, premifosmethyl is the prevalent compounds in the vegetables. Maximum levels of it was detected in tomato

0.054 mg/kg and the lowest level was detected in spinach 0.025 mg/kg followed by dichlorvos and chlorpyrifos being detected in three samples each with highest levels of 0.058 mg/kg and 0.055 mg/kg in spinach and lettuce and lowest levels of 0.036 mg/kg and 0.025 mg/kg in tomato and spinach respectively.

Ethion was detected in moringa and spinach, while profenfos was detected in spinach only. Dimethoate, malathion, diazinon and parathion were not detected in all the samples analyzed from Wurogude.

Table 2 Mean Concentration (mg/kg) Op Pesticide Residues on Vegetable Cultivated from Wurogude, (Mubi north LGA)

Pesticide type	Lettuce	Moringa	Okra	Pepper	Spinach	Tomato
Diclovos	0.051*±0.001	<0.001	<0.001	<0.001	0.058*±0.001	0.036±0.001
Dimethoate	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ethion	<0.001	0.007±0.001	<0.001	<0.001	0.004±0.001	<0.001
Primifos-methyl	0.038±0.001	<0.001	<0.001	0.033±0.001	0.025±0.001	0.054*±0.001
Chlopyrifos	0.055*±0.001	<0.001	0.036±0.001	<0.001	<0.001	0.022±0.001
Malathion	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Diazinon	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Profenfos	<0.001	<0.001	<0.001	<0.001	0.011±0.001	<0.001
Parathion	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Op= Organophosphorous, Detection Limit (0.001), *Indicates values greater than MRLs

Levels of Organophosphorous Pesticides Residues in Vegetables Cultivated from Sebore

Table 3 showed the distribution and levels of Organophosphorous pesticide residues found in the vegetable samples analyzed from Sebore. Among the compounds studied in the samples, diclovos and primifosmethyl are the prevalent residues in the vegetables. Maximum level of diclovos was detected in spinach 0.051 mg/kg and that of primifosmethyl0.043mg/kg was detected in lettuce, minimum level of diclovos was detected in lettuce 0.024mg/kg and that of primifosmethyl was detected in tomato 0.043 mg/kg.

Clopyrifos was detected in three samples namely lettuce spinach and tomatoes, maximum level of it was detected in lettuce 0.061 mg/kg and the minimum level was detected in tomato 0.014 mg/kg. parathion was detected in okra 0.022 mg/kg. Dimethoate, ethion malathion and diazinon were not detected in all the samples analyzed from Sebore.

Table 3 Mean Concentration (mg/kg) Op Pesticide Residues on Vegetable Cultivated from Sebore, (Mubi south LGA)

Pesticide type	Lettuce	Moringa	Okra	Pepper	Spinach	Tomato
Diclovos	0.024±0.001	<0.001	0.032±0.001	<0.001	0.051*±0.001	0.033±0.001
Dimethoate	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ethion	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Primifos-methyl	0.043±0.001	<0.001	<0.001	0.021±0.001	0.041±0.001	0.014±0.001
Chlopyrifos	0.061*±0.001	<0.001	<0.001	<0.001	0.052*±0.001	0.024±0.001
Malathion	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Diazinon	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Profenfos	<0.001	0.022±0.001	<0.001	<0.001	0.001±0.001	<0.001
Parathion	<0.001	<0.001	0.022±0.001	<0.001	<0.001	<0.001

Op= Organophosphorous, Detection Limit (0.001), *Indicates values greater than MRLs

Levels of Organophosphorous Pesticides Residues in Vegetables Cultivated from Tantila

Table 4 showed the distribution and levels of Organophosphorous pesticide residues found in the vegetable samples analyzed from Tantila. Among the compounds studied in the samples, diclovos and primifosmethyl are the predominant compounds in the vegetables. Higher levels of diclovos was detected in spinach 0.054 mg/kg while the highest level of primifosmethyl was detected in tomato 0.051 mg/kg, minimum level of diclovos was detected in lettuce 0.022 mg/kg and that of primifosmethyl was detected in pepper 0.043 mg/kg, followed by clopyrifos with highest level of 0.073 mg/kg detected in lettuce and Profenfos and parathion were detected on one sample each (moringa and pepper respectively), while dimethoate, ethion malathion and diazinon were not detected in all the samples analyzed from Tantila.

Table 4 Mean Concentration (mg/kg) Op Pesticide Residues on Vegetable Cultivated from Tantila, (Mubi south LGA)

Pesticide type	Lettuce	Moringa	Okra	Pepper	Spinach	Tomato
Diclovos	0.022±0.001	<0.001	0.036±0.001	<0.001	0.054*±0.001	0.039±0.001
Dimethoate	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ethion	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Primifos-methyl	0.043±0.001	<0.001	<0.001	0.021±0.001	0.043±0.001	0.051*±0.001
Chlopyrifos	0.073*±0.001	<0.001	<0.001	<0.001	0.059*±0.001	0.023±0.001
Malathion	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Diazinon	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Profenfos	<0.001	0.021±0.001	<0.001	<0.001	<0.001	<0.001
Parathion	<0.001	<0.001	<0.001	0.031±0.001	<0.001	<0.001

Op= Organophosphorous, Detection Limit (0.001), *Indicates values greater than MRLs

Table5:Maximum Residue Levels (MRL) of Organophosphorus Pesticides for the Selected Vegetables (mg/kg).

Vegetables	Diazinon	Dimethoate	P-methyl	Chlorpyrifos	Profenfos	Malathion	Parathion	Ethion	Dichlovos
Pepper.	0.02	0.02	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Tomato	0.50	0.02	0.05	0.05	3.00	0.05	0.05	0.05	0.05
Okra.	0.02	0.02	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Lettuce.	0.02	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Spinach.	0.02	0.02	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Moringa	0.02	0.02	0.05	0.05	0.05	0.05	0.05	0.05	0.05

Tables 1 to 4 showed the result obtained from the analysis of organophosphorous pesticide residues on vegetables cultivated from the study areas. The result showed that pesticide residue levels on the majority of the vegetables analysed from the study areas were in conformity with the MRLs recommended by Codex Alimentarius Commission (FAO/WHO, 2004). However, levels higher than the MRLs were also recorded.

Levels of organophosphorous pesticide residues higher than the MRLs were recorded in lettuce and spinach 0.059 mg/kg and 0.052 mg/kg chlopyrifos, tomato 0.052 mg/kg diclovous, 0.051 mg/kg primifos methyl from Hurida. Concentration of diclovous higher than the MRL was also detected in lettuce and spinach 0.051 mg/kg and 0.058 mg/kg, tomato have shown higher level of premifosmethyl 0.054 mg/kg while 0.055 mg/kg chlorpyrifos was recorded in lettuce from Wurogude in Mubi north LGA.

Higher levels of Op pesticide residues were also recorded in spinach 0.051 mg/kg diclovous. chlopyrifos level was found to be higher in lettuce and spinach 0.061 mg/kg, 0.052 mg/kg respectively from Sebore. Meanwhile, in Tantila, lettuce 0.073mg/kg chlopyrifos: spinach, 0.054 mg/kg and 0.059 mg/kg diclorvous and chlopyrifos respectively and tomato 0.051 mg/kg primifosmethyl in Mubi south LGA.

The use of organophosphorus pesticides inagricultureandanimalproductionforthecontrol ofvariousinsects gain acceptance since the middle of the last century for their various benefits. These compounds have higher acutetoxicitythan organochlorinepesticidesand they havetheadvantageofbeingmorerapidlydegraded intheenvironment. Indiscriminate use of organophosphorus pesticides in agriculture is attributed to the demand of more quality and cosmetic quality of farm products which create over reliance on pesticides [12].

Studies' regarding pesticide residue contamination of vegetable in Nigeria is scanty most of the studies on this subject matter centred on dairy product, water and aquatic life (mostly fish). In Ghana, it is estimated that 87% of farmers use pesticides on vegetables; insecticides are the most widely used among the different classes of pesticides [13], this trend also correlates with the findings from the result of this studies as seen from the table of results.

Several research reports on pesticideresidues contamination on vegetables and fruitsindicatedthat different types of pesticidesespecially chlorpyrifos,are widelyusedby vegetableproducersindifferent parts of the world.The results of this research work also corroborate the result ofother studies [14]. Nakata *et al.,* (2002), [15], also found elevated levels of organochlorine/organophosphorous pesticides residues in fruits and vegetables collected from shanghai and yinxing, China. Similarly, Hura (1999), [16], reported that organochlorine pesticide residues were found present on all samples of fruits and vegetables analyzed from Eastern Romania. High levels of organochlorine pesticide residues were also reported by [17], in West Bengal, India.

Conclusion

The result of this work showed the contamination levels of some vegetables with organophosphorous pesticide residues higher than the MRLs, this is as a result of indiscriminate use of the organophosphorous pesticides for the cultivation of vegetable crops in the studied area therefore; consumption of these vegetables poses a significant health risk to the public. The potential harmful effects could be minimized through enforcement of legislation on harmful pesticides. This study has provided more information on the pesticide residue contaminations in food stuffs in Nigeria, which may be added to the information available on pesticide residues found in the food commodities in Nigeria.

Recommendations

On the basis of the above findings, it is recommended that, public awareness programs should be organized by the relevant authorities in agricultural communities to educate famers and the general public on the health hazard and the risk of consumption of pesticide residue laden food commodities. We also recommend for pesticide residue control programs in all food commodities to protect the consumer from indiscriminate exposure to pesticides.

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