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Determination of Organochlorine Pesticide Residues in Pumpkin, Spinach and Sorrel Leaves Grown in Akwanga, Nasarawa State, Nigeria

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Abstract

Three green leafy vegetable samples of pumpkin leaves, spinach leaves, and sorrel leaves were collected from a farm in Akwanga and were tested for the presence of residues of organochlorine pesticides. The concentrations of all the pesticide residues in the vegetable samples were determined using GC/MS. Among the organochlorine pesticide p,p'-DDT was detected in pumpkin (0.75 mg/kg), spinach (0.319 mg/kg) and sorrel (0.219 mg/kg). ∂-BHC and γ-BHC were detected only in pumpkin leaves (0.359 mg/kg and 0.647 mg/kg respectively). Dieldrin was detected in spinach and sorrel (0.124 mg/kg and 0.053 mg/kg respectively). Endrin was detected in pumpkin (0.732 mg/kg) and Aldrin in sorrel (0.095 mg/kg). All these values were above the maximum residue limit (MRL) value of the pesticides. Endosulfan II was detected in sorrel (0.306 mg/kg) below the MRL. The levels of most of the pesticide residues found in vegetables were above the maximum residue limits (MRLs) that call for laws to regulate the use and circulation of such chemicals. Routine monitoring of pesticide residues in this study area is necessary for the prevention, control and reduction of environmental pollution, to minimize health risks.

Keywords

Akwanga, Organochlorine, Pesticide Residues, Maximum Residue Limit, Vegetables

1. Introduction

Pesticides are an extremely diverse group of substances with a wide potential for a variety of toxic effects. They can be acute toxicity at low doses, such as strychnine, to the relatively large quantities, such as sodium chloride, which is also edible in measured quantities. Pesticides have helped to increase crop production by controlling the pests that destroy the crops. However, some of the pesticides have adversely affected the non-target species by inducing carcinogenic, teratogenic, mutagenic, neuro-toxic effects as well as alterations of re-productive processes or functions in experimental animals and in man [1].

Organophosporous (OP) and organochlorine (OC) pesticides are widely used in agriculture as insecticides and leave residues to varying extents in agriculture produce such as vegetable and fruits. Due to their toxic properties and potential risk to consumers, their residues in food commodities are an issue of public concern and controlled by legislation [2].

Farmers around the world including Nigeria use pesticides as a preventive policy against the possibility of a devastating crop loss from pests and diseases. Accordingly in Nigeria, for several decades now, pesticides have been employed in agriculture not only to control and eradicate crop pests but also in the public health sector for disease vector control. Nevertheless, there has been a rapid increase in the use of pesticides in agriculture over the past ten years [3].

Pesticides are widely used in fruit and vegetables because of their susceptibility to insect and disease attack. Consequently, food safety is a major public concern worldwide. During the last decades, the increasing demand of food safety has stimulated research regarding the risk associated with consumption of fruits and vegetables, as they constitute major part of human diet contributing nutrients and vitamins. Therefore, pesticide residues that remain on agricultural commodities are known as carcinogens/or toxins and therefore, it is desirable to reduce their residues [4].

2. Methodology

2.1. The Study Area

Akwanga is one of 13 local Government Area in Nasarawa State, Nigeria and the major occupation here is farming with a total population of 113,430 [5]. It has a land area of 996 km^2 and it lies at latitude 8.9060N and longitude 8.4080E.

2.2. Collection of Vegetable Samples

At each sampling site, 20 g each of the three vegetables: pumpkin, spinach and sorrel were collected from three different locations in one farm to provide replicate samples of each crop. The vegetables samples were collected in to a clean polyethylene bag label and put in a cool box and transported to the laboratory stored in a refrigerator at 4˚C pending extraction.

2.3. Extraction of Vegetable Samples

The samples were chopped to pieces with a stainless steel knife on a clean chopping glass board, before they were macerated to formed paste with Philips mixer. A 15 g portion of the homogenized sample was weighed into a 50 ml polytetrafluoroethylene (PTFE) tube, and then 15 ml of acetonitrile containing 1% acetic acid (v/v) was added followed by 6 g $MgSO_4$ and 1.5 g anhydrous sodium acetate. The sample was shaken vigorously for 3 minutes and then centrifuged at 1500 rpm for 5 minutes.

2.4. Clean up of Vegetable Extracts

After centrifugation, the samples were cleaned up using dispersive solid-phase extraction (dSPE). One milliliter of the supernatant was transferred to a 15 ml PTFE tube to which 50 mg each of C_{18} and PSA (primary and secondary amine sorbents) with 150 mg $MgSO_4$ was added and vortexed for 30 seconds and then centrifuged for 1minute at 1500 rpm. The clear extract was then transferred to an auto sampler vial for GC-MS analysis.

2.5. Determination of Pesticide Residues

The Shimadzu GCMS (GC - 17A) QP 2010 installed with a 35% diphenyl, 65% dimethylpolysiloxane column was used for the chromatographic separation. The oven was programmed as follows: initial temperature 40˚C, 1.5 minutes, to 150˚C, 15 minutes, 5˚C/minute to 200˚C, 7.5minutes. 25˚C/minute to 290˚C with a final hold time of 12 minutes and a constant column flow rate of 1 ml/minute. The detection of the organophosphorus pesticides was performed using the GC-MS. Detection of pesticides was performed using the GC-ion trap MS with optional MSn mode. The scanning mode offer enhances selectivity over either full scan or selected ion monitoring (SIM). At the elution time of each pesticide using selected ion monitoring, the ratio of the intensity of matrix ions increase exponentially versus that of the pesticide ions as the concentration of the pesticide approach the detection limit, decrease the accuracy at lower levels. The GC–ion trap MS was operated in MSn mode and perform tandem MS function by injecting ions into the ion trap and destabilizing matrix ions, isolating only the pesticide ions. The retention time, peak area and peak height of the sample were compared with those of the standards for quantification.

2.6. Data Handling

External calibration and recovery tests were performed. The residue results were the means from the three replicates of each treatment and all data were analyzed using simple descriptive statistics such as means, standard deviations, using Anova Table: SPSS V-20.

3. Results and Discussion.

The mean concentration of some organochlorine pesticide residues p,p’-DDT.

(2,4-dichlorodiphenyltrichloroethane), ∂-benzene hexachloride BHC), ieldrin, Endrin,Aldrin and Endosulfan II in pumpkin, spinach and sorrel leaves are presented in **Table 1**. The statistical analysis shows that no value has any significant difference.

From **Table 1**, among the organochlorine pesticides studied, the following were detected in different matrices p,p'-DDT, ∂-BHC, γ-BHC, Dieldrin, Aldrin and Endosulfan II (**Figure 1**). Among DDT analogues only the p,p'-DDT was detected in all the samples. **Figure 2** shows that pumpkin has the highest value with the mean value of 0.75 mg/kg (range of 0.605 - 0.902 mg/kg) followed by spinach with the value of 0.319 mg/kg and the least is sorrel with the value of 0.219 mg/kg. All concentrations of the DDT in the three vegetables were much higher than the EU set maximum residue limit (MRL) for total vegetables which is 0.05 mg/kg. The high concentration of DDT and its metabolites, obtained in the result of this study indicates that high concentration of DDT pesticides could have been used in killing pests or other plants that also grow with these vegetables. This also confirms that like other developing countries organochlorine pesticides are still in use here. Although the use of DDT and its metabolites have been banned in Nigeria since 2008, DDT and its metabolites have been classified by NAFDAC as probable human carcinogens, although it is still illegally used by farmers for the control of pests [1].

∂-BHC and γ-BHC were detected only in Pumpkin leaves at a concentration of 0.359 mg/kg and 0.647 mg/kg respectively as it is shown in **Table 1** the concentrations of this pesticide were much higher than the codex 2009 [6] set maximum limits (MRL's) of 0.01 mg/kg for ∂-BHC and γ-BHC. Residues of BHC

Table 1. Mean concentration of organochlorine pesticide residues in three green leafy vegetables. Samples were analyzed in triplicate, the range is displayed in brackets and BDL represents below detection limit.

Pesticide	Vegetable concentration (mg/kg)		
	Pumpkin leaves	Spinach leaves	Sorrel leaves
Endrin	0.732 ± 0.01 (0.537 - 1.035)	BDL -	BDL -
p,p'-DDT	0.751 ± 0.16 (0.605 - 0.920)	0.319 ± 0.07 (0.236 - 0.377)	0.219 ± 0.03 (0.189 - 0.234)
∂-BHC	0.359 ± 0.02 (0.000 - 0.359)	BDL -	BDL -
γ-BHC	0.649 ± 0.01 (0.000 - 0.647)	BDL -	BDL -
Dieldrin	BDL -	0.053 ± 0.01 (0.000 - 0.053)	0.124 ± 0.01 -
Aldrin	BDL -	BDL -	0.095 ± 0.03 (0.064 - 0.127)
Endosulfan II	BDL -	BDL -	0.306 ± 0.01 (0.000 - 0.306)

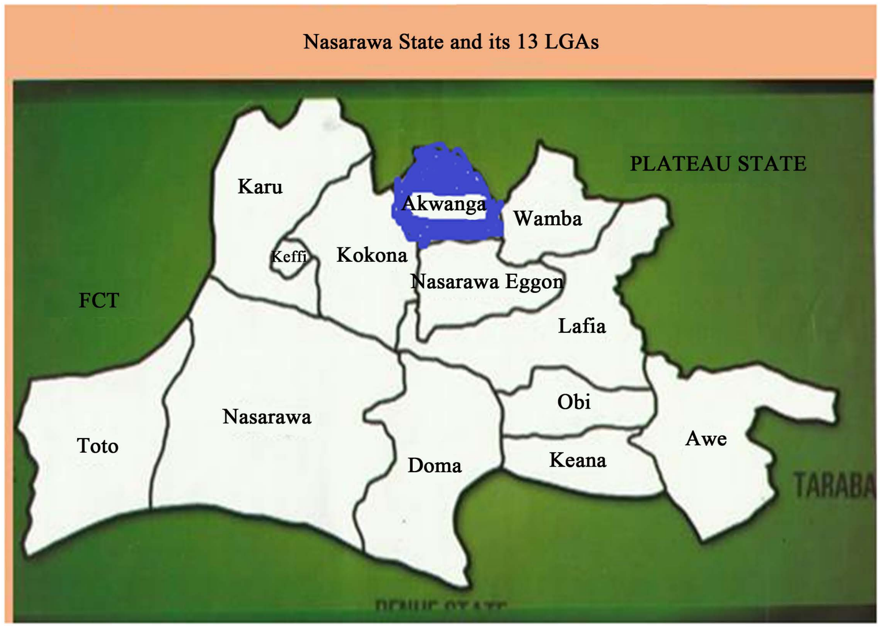

Figure 1. Map of Nasarawa state depicting the location of Akwanga.

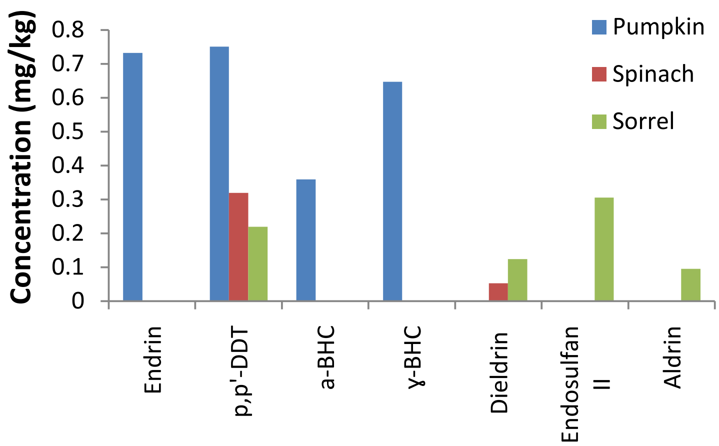

Figure 2. Mean concentrations of some organochlorine pesticide residues in three green leafy vegetables.

isomers in significant concentrations in the vegetable samples may be attributed to the heavy use of this pesticide in the study area. γ-BHC is a reasonably stable compound and only under alkaline condition decomposes to yield trichlorobenzene. It is considered as one of the less persistent organochlorine pesticides. This high value of γ-BHC could be attributed to extensive use of technical Lindane marketed as Gammalin 20 and used by farmers for crop protection in Akwanga and many other places. However, other researchers reported the mean value of 0.002 mg/kg and 0.004 mg/kg for ∂-BHC and γ-BHC in Nigeria and India respectively [7] [8]. However, this was not detected in spinach and sorrel.

Dieldrin was detected in spinach and sorrel, the sorrel had higher concentration (0.124 mg/kg) than the spinach (0.053 mg/kg) however, Dieldrin was not detected in pumpkin (**Table 1**). Dieldrin is one of the organochlorine that is classified as persistent and hence is still detected in the environment even though it has not been used for a very long time. Endrin was found in pumpkin only (0.732 mg/kg) and Aldrin in sorrel only at a concentration of 0.095 mg/kg (**Figure 2**). Aldrin is an alicyclic chlorinated hydrocarbon and is rapidly converted to the epoxide form; Dieldrin [9]. Detection of Dieldrin, Aldrin and Endrin in the vegetable samples in this area indicates that these pesticides are still being used for agricultural and pest control activities. These three are persistent organic pollutants that can be found in the areas where they have not been used, or remain in the soil for a very long time even when their use has stopped. A similar incidence of contamination of vegetables with organochlorine insecticides was published in Nigerian vegetables [1] and [7].

The concentrations of Aldrin, Endrin and Dieldrin were much higher than the EU set maximum residue limits (MRL's) 0.01 mg/kg. This high values could be attributed to intense agricultural activities in the area coupled with excessive usage of pesticides and these also resist degradation and has the ability to bio-accumulate in the environment. Other work by Beena *et al.*, (2002) [10] found p,p'-DDT, and Endosulfan A, Endosulfan B and Endosulfansulphate in cauliflower and Brinjal potato but below the maximum residue limit for vegetables. There has also been a reported contamination of vegetables with organochlorine pesticides in Nigeria by some researchers [11] and in Delhi India vegetables [12].

Endosulfan II was detected in Sorrel at a concentration of 0.306 mg/kg far below EU MRL of 30 mg/kg. Endosulfan II has been considered by the peer review of persistent organic pollutant committee to be added to the list of the "dirty dozen" [13]. These present findings of high values of organochlorine pesticides residues in vegetables are in agreement with that discovered by Akan *et al.*, (2014) [1] in Borno state.

Although the pesticide residues study in this research are organochlorines, the potential hazards to can be reduced from processing like trimming, washing, peeling and cooking by which substantial amounts (80% - 90%) of pesticides other than organochlorine can be degraded. However, consumption of these vegetables over a long period of time could pose a problem to the body system.

4. Conclusions

This study focuses on the three major vegetable leaves consumed in this area. Fresh green leafy vegetables studied in this research are produced and consumed locally with no or minimal preparation which may constitute an important potential source of pesticide residues. Washing under running water is most commonly the only treatment given to many vegetables prior to consumption in Akwanga setting. The pesticide residues will not only affect the nutritional values of the fruits and vegetables but also have deleterious effect on human beings using these food items. Hence, an increasing important aspect of food quality should control the concentration of pesticide residues in food [14].

The results from this study show that pesticide residues were found in pumpkin leaves, spinach leaves and sorrel leaves that were analyzed. These results indicated that majority of growers using agrochemicals is responsible for residue levels in vegetables which are higher than MRL and could pose health problems as these popular or common vegetables are consumed regularly by the population [14].

The concentration of all the pesticide residues was observed to be very high in all the vegetables studied, and above the maximum residue limit set by FAO/WHO and European Union. The objective of this study was to create awareness among the vegetable consumers and producers on safe practices.

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