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DETERMINATION OF PESTICIDE RESIDUES IN COMMONLY PRODUCED VEGETABLES IN MUBI METROPOLIS, ADAMAWA STATE, NIGERIA

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ABSTRACT

Pesticides are hazardous and toxic to human health; any pesticide residues remaining in vegetables can pose danger to humans and cause certain diseases. This study was conducted to determine the pesticide residues in commonly produced vegetables) in Mubi Metropolis these vegetables include *Spinacia Oleracea* (Spinach), *Hibiscus esculentus* (Okra) and *Rumex Acetosa* (Sorrel). Twelve (12) vegetable samples were collected from farms and local markets in Mubi Metropolis, Adamawa, Nigeria. Pesticides residues were extracted from the vegetables using a quick, easy, cheap, effective, rugged, and safe (QuEChERS) method. Extraction of the samples was carried out using acetonitrile containing 1% acetic acid to determine the residual concentration of pesticides which may have been sprayed during seasonal growth. Gas chromatography/mass spectrometry (GC/MS) was used for quantitative and confirmatory analysis of the pesticides. The pesticide residues in vegetable samples were determined and confirmed from their molecular weights. The molecular weights of pesticides were compared with that given in the data bank of GC/MS. The investigation showed that pesticides with low molecular weight were eluted before the high molecular weight pesticides. The factors studied were retention time, relative abundance and molecular weight. The following pesticides were identified during the investigation, dichlorvos, lindane, cyhalothrin and glyophosphate.

Keywords: Pesticides, QuEChERS, GC/MS, acetonitrile and Vegetables

INTRODUCTION

Fruits and vegetables are important components of the human diet because they provide essential nutrients which are required for most of the reactions occurring in the body. The intake of fruits and vegetables are highly encouraged in order to prevent the consequences which occur due to the deficiency of vitamins in the body and also to reduce the incidence of major diseases such as cancer, cardiovascular diseases and obesity [1]. Pest and diseases attacked fruits and vegetables and other crops during production and storage, leading to damages that reduce the quality and the yield. Pesticides together with other pest management techniques are used to destroy pest during cropping and prevent diseases, as well as to reduce the loss and maintain the quality of fruits and vegetables harvested.

The application of pesticides have increased because they have rapid action, in decreasing the toxins produced by food infecting organisms and are less labour intensive than other pest control methods. However, the application of pesticides during production has lead to the presence of pesticide residues in the harvested fruits and vegetables [2].

Pesticides are very hazardous and lethal for organisms as well as for humans. They present danger to consumers, bystanders and workers during manufacture, transport or, during and after use. The presence of pesticide residues is a concern for consumers because pesticides are known to have potential harmful effects to other non-targeted organisms than pests and diseases. The major concerns are their toxic effects such as interfering with the reproductive systems and foetal development as well as their capacity to cause cancer and asthma [3]. Some of the pesticides are persistent and therefore remain in the body causing long term exposure. The concern has led to governments setting up monitoring systems in order to assess the safety situation and make informed decisions when passing legislation.

A number of pesticides are highly toxic and even in small quantities these pesticides can result in the death of humans and animals, while exposure to a sufficient amount of almost any pesticides can initiate long-term illness. Statistics show a 70% increase in the risk of developing Parkinson disease for individuals exposed to low levels of pesticides. Depending upon the duration of exposure of pesticides, short-term adverse, acute health effects include stinging eyes, rashes, blisters, blindness, nausea, dizziness, diarrhea and death, whereas chronic health effects include infertility, developmental toxicity, immunotoxicity and disruption of the endocrine system [4].

Children have been found to be especially susceptible to the harmful effects of pesticides exposure. The major source of pesticides exposure in children and infants is through diet [5]. Early exposure results in brain cancer, leukemia and birth defects. However, children who have adopted an organic diet are less exposed to the harmful effects of organophosphorus pesticides. Due to this the use of organophosphrus pesticides has been increased as they are less persistent and damaging to the environment when compared to organochlorine pesticides [6].

The most common pathway for pesticides to enter the body is orally, through the mouth and the digestive system, dermally through the skin, or by inhalation through the nose and respiratory system. Oral exposure may occur as a result of negligence, eating without proper hygiene after using pesticides, exposure to spills while mixing, and consumption of foods that have been sprayed with a pesticide. The extent of exposure depends upon the oral toxicity of the material and the amount consumed [7]. Dermal exposure accounts for nearly 90 percent of the exposure pesticide uses receive from non-fumigant pesticides. This can occur whenever a pesticide is mixed, applied or handled, and it often goes undetected. Dry materials, as well as liquid pesticides can be absorbed through the skin. Inhalation exposure results from breathing pesticide vapors dust or spray particles. It can also occur by breathing smoke from burning containers; breathing fumes from pesticides while applying without protective equipment, inhaling fumes during the mixing and pouring of pesticides and smoking tobacco products [8].

Pesticides are hazardous and toxic to human health, any pesticide residue remaining in fruits and vegetables can pose danger to humans and cause certain diseases. It is important to identify and quantify the pesticides which can be ingested by fruits and vegetables after pesticides spray [9].

Pesticides belong to different chemical classes but the major ones are Organochlorines, organophosphates, carbamates, and pyrethroids. Several reports show that global pesticide usage has increased significantly during the last three decades consequent with changes in farming practices and increasing intensive agriculture [10, 11]. This extensive use of pesticides for agriculture and nonagricultural purposes has resulted in the presence of their residues in various environmental matrices, especially food stuff providing the high risk of these chemicals to human health and environment [12, 13].

Every pesticide has a withholding period, waiting period, lapse period or Pre Harvest Internal (PHI), which is defined as the number of days required to lapse, between the date of final pesticide application and harvest, for residue to fall below the tolerance level established for that crop or for a similar food type. The PHI differs from pesticide to pesticide and crop to crop. Food products become safe for consumption only after withholding period has lapsed. By this time, the pesticide residues get dissipated. However, the extent and rate of dissipation depends on the nature of the pesticide, crop, cultural practices and various environmental conditions under which the crop is grown or a treated commodity is stored [14].

The objective of this present research study was to determine the pesticide residues in vegetables commonly produced in Mubi Metropolis and also to create awareness about the lethal effects of these pesticides on human beings.

EXPERIMENTAL

The Fresh sample of vegetables *Spinacia Oleracea* (Spinach), *Hibiscus esculentus* (Okra), *RumexAcetosa* (Sorrel),) were randomly collected from markets and farms in Mubi Metropolis of Adamawa State, Nigeria. 2kg of each fresh sample of vegetables were randomly collected, a total of twelve (12) samples were collected, six from market and six from farm. The collected vegetable samples were transported to the laboratory immediately after collection and were stored at -4 degree Celsius for analysis.

SAMPLE PREPARATION AND CLEAN UP

The sample was extracted and analyzed by AOAC Official method. As described by (Lehotay *et al.,* 2005) [15]. Follow multi residue pesticide analysis technique consisting of the QuECHERS based method (quick, easy cheap, effective rugged and safe), QuEChERS was developed using an extraction method for pesticides in fruits and vegetables, coupled with a cleanup method that removes sugars, lipids, organic acids, sterols, proteins, pigment, and excess water.

For each vegetable samples 15g was taken and homogenized in a pestle and mortar to which 15ml of acetonitrile containing 1% acetic acid (v/v) was added into clean 50ml tube. The sample was then shaken vigorously for one minute. 6.0g of $MgSO_4$ anhydrous and 1.5g of sodium acetate anhydrous was added for sample drying and buffering, then it was shaken vigorously and ensured that the salt are not at the bottom of the tube. It was then centrifuge for four minutes at >3500rpm to separate the solid materials. The centrifuged extract resulting from the phase separation stage of sample extract preparation, the supernatant was transfer to the vial tube. 150mg of $MgSO_4$ and 2.5mg of graphite carbon per sample was added to the extract and it was shaken using a vortex mixer for one minute. Then the extract was centrifuged for four minutes at >3500rfc. After the centrifugation step, the supernatant is subjected to GC-MS for further analysis [16].

INSTRUMENTATION

All compounds were determined with the aid of a gas chromatograph equipped with a mass-selective detector (GC-MS), an auto-sampler and a split-split less injector. The DB-5 fused silica capillary column of 30m x 0.25μm i.d. x0.25μm film thickness was coated with cross-linked 5% phenyldimethyl polysiloxane. The carrier gas was helium (99.999% purity) at a flow rate of 1.0ml/min. Oven temperature was maintained initially at 40°C for 1min, increased at 12°C/min to 280°C, then at 20°C/min to 215°C, at 100°C/min to 265°C and finally at 200°C/min to 290°C and held for 8min. Injection volume was1μL, injected in split less mode at injection temperature of 250°C.The mass spectrometer was operated in electron impact (EI)ionization mode with a detector voltage of 700V, ion source temperature of 200°C, GC interface temperature of 320°C and emission current of 150μV. Acquisition mode was selected ion Monitoring (SIM) [17].

RESULTS AND DISCUSSION

The experimental results conducted showed that a large concentration of pesticides is ingested and absorbed into the vegetables which have been exposed to pesticides spray. The amount of pesticides left in vegetables after being sprayed causes harmful health effects. Therefore it is important to determine the amount of pesticides left in vegetable samples after being sprayed. It was also discovered that environmental factors do not necessarily contribute to the absorption of pesticides into vegetables which are not sprayed with pesticides in the vicinity of those sprayed with pesticides

From the spectra of the experimental results conducted, the pesticides residues in vegetable samples were determined and confirmed from their molecular weights. For further confirmation and identification of pesticides, the molecular weights of the pesticides were compared with that given in the data bank of GC/MS. From this investigation, it was found out that the elution time of low molecular weight pesticides were lower than the high molecular weight pesticides on the elution time spectra.

Date presented in Tables 1 and 2 indicated the presence of the pesticides residues dichlorvos and glyophosphate in sorrel vegetable samples obtained from farm with retention time 8.501and 3.425, relative abundance 100% and 24%, molecular weight 220 and 169 respectively, while dichlorovos with retention time 8.543, relative abundance 25.11 and molecular weight 220 was found in sorrel vegetable samples obtained from local market. Dichlorovos was the common pesticide identified in sorrel samples collected from both farm and local market.

Results presented in Tables 3 and 4 indicated the presences of pesticides residues cyhalothrin in spinach samples collected from farm at the rate of 5.642 as the retention time, 6.03% as the relative abundance and 449.9 as molecular weight. Results of the investigation indicated that none of the pesticides residues analyzed was detected in spinach and okra samples collected from the local market. This shows that these (spinach and okra) samples from the local market might have not been sprayed with pesticides.
The results of the investigation presented in table 5 showed the presence of lindane and dichloroves in okra samples collected from farm at the rate of 5.331 and 8.601as the retention time, 19.94% and 34.21% relative abundance, 290.8g/mol and 220.9g/mol molecular weight respectively.

The relative abundance and the values of M/Z ratio of each pesticide were determined from the peaks height of the GC/MS spectrum. The spectrum also recorded the retention time, relative abundance and molecular weight of each extracted pesticide.

The result showed that dichlorvos was the common pesticide residues found in the studied vegetable samples collected from both the farms and the markets. Other pesticides identified in the vegetable samples are presented in the tables 1 to 6 along with their retention time, relative abundance, quality, and molecular weight. However, the pesticides residues identified from the GC/MS spectrum of this study include Dichlorvos, glyophosphate, cyhalothrin, and lindane with molecular weight 220g/mol, 169g/mol, 449.9g/mol and 290.8g/mol respectively.

Table 1: PESTICIDES IDENTIFIED IN SORREL FROM FARM BY GC/MS

Pesticides Identified	Retention Time	Relative Abundance %	Quality %	Molecular Weight
Dichlorvos	8.501	100%	97%	220
Glyophosphate	3.425	24%	91%	169

Table 2: PESTICIDES IDENTIFIED IN SORREL FROM MARKET BY GC/MS

Pesticides Identified	Retention Time	Relative Abundance %	Quality %	Molecular Weight
Dichlorvos	8.543	25.11%	86%	220

Table 3: PESTICIDES IDENTIFIED IN SPINACH FROM FARM BY GC/MS

Pesticides Identified	Retention Time	Relative Abundance %	Quality %	Molecular Weight
Cyhalothrin	5.642	6.03	87%	449.9

Table 4: PESTICIDES IDENTIFIED IN SPINACH FROM MARKET BY GC/MS

Pesticides Identified	Retention Time	Relative Abundance %	Quality %	Molecular weight
BDL	BDL	BDL	BDL	BDL

Table 5: PESTICIDES IDENTIFIED IN OKRO FROM FARM BY GC/MS

Pesticides Identified	Retention Time	Relative Abundance %	Quality %	Molecular Weight
Lindane	5.331	19.94%	94%	290.8
Dichlorvos	8.601	34.21%	89%	220.9

Table 6: PESTICIDES IDENTIFIED IN OKRO FROM MARKET BY GC/MS

Pesticides Identified	Retention Time	Relative Abundance %	Quality %	Molecular Weight
BDL	BDL	BDL	BDL	BDL

Key: BDL Below Detectable Limit

CONCLUSION

From this research it was found that when vegetables are sprayed with pesticides, harmful health effects may occur, due to ingestion and absorption of these pesticides. This study also help to discovered that environmental factors do not necessarily contribute to the absorption of pesticides into vegetables which are not sprayed with pesticides in the vicinity of those sprayed with pesticides. However, the excessive use of pesticide causes negative effects on consumer's health and results in hazardous effect to the environment.

The following pesticide residues were identified in the studied vegetable samples, dichlorvos, glyophosphate, cyhalothrin, and lindane with molecular weight 220g/mol, 169g/mol, 449.9g/mol and 290.8g/mol respectively. The negative effects of pesticide residues to consumers were carcinogenic and mutagenic. On the basis of the above findings, the results recommended the need for continue survey and monitoring programs for pesticide in all food commodities in order to protect the end user for the indiscriminate exposure of pesticides.

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