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Assessment of pesticide residue in *Vigna unguiculata* L. Walp in Iddo Market Lagos State, Nigeria

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Abstract

Food poisoning has been on the increase in Nigeria. This is due to excessive use, poor handling and application by untrained personnel, use of substandard and banned pesticides. This study was carried out to determine the classes and levels of pesticides in *Vigna unguiculata* L. Walp from Iddo Market, which is a major depot for sale, and distribution in Lagos State. Samples were collected during the month of May, June and July 2019 from twenty vendors in a random distribution order and were analysed using Gas Chromatography Mass Spectrometry. Organophosphates (Malathion, parathion and carbophenothion), Pyrethroids (α-Cypermethrin, Cyfluthrin, β-Cypermethrin) and Organochlorines (Parathion, Lindane, Endrin ketone, and Endosulfan II) were detected. Concentration of Parathion was the highest (6578.64 mg/kg) followed by Endosulfan II (745.20 mg/kg) and Baythroid (24.79 mg/kg). These results are above Maximum Residue Limits (MRLs) set for pesticide residues in foods. Also, the detection of Lindane known as gamma hexachlorocyclohexane (ɣ-HCH), a banned pesticide is a serious cause for concern due to its neurotoxic effects occasioned by respiratory distress, convulsions, reproductive disorders, dermatitis and metabolic disorders. The use of green insecticides such as NSPRI Dust™, good agricultural practices would go a long way in addressing this menace. Also, regulatory bodies should sensitise, train and advice stakeholders in the value chain on the dangers of pesticide abuse.

Keywords: pesticides, bioaccumulation, maximum residue limits, diatomaceous earth, prevalence.

1. Introduction

Pesticides are chemical compounds that are either used to kill pests or control their proliferation and reproduction. They have gained widespread use in agriculture, as they are very effective in killing pests that damage crops, these pests interfere with the processing and storage of food. Consequently the use has made pesticides a major environmental contaminant, as by nature they are very toxic to human health and the environment. The amount of pesticides that remain in food crops after application are called pesticide residues, analysing these residues are a way to determine the level of human exposure to these chemicals and hence their potential human hazards. Approximately three million people are poisoned and 200,000 died each year from pesticide poisoning with a majority of them belonging to the developing countries (Sarkar *et al*., 2008)

There are a variety of chemical classes of pesticides namely organochlorines, organophosphates, carbamates and pyrethroids. These pesticides are usually not only toxic but also bioaccumulative as they accumulate in the food chain (Kumar, 2012). Pesticide use varies from dressing of seeds, treatment of soil in the farms to post harvest treatment. Organochlorines are the

most common class of pesticides, due to their adverse effects on the environment and human health they have been banned in most parts of the world. Due to the practicality and convenience of these pesticides it is a challenge for farmers and stakeholders to deter from their use. Furthermore it has been difficult for the government to enforce the strict ban of these chemicals. The high chemical stability and lipid solubility of these compounds leads to chronic toxicity in humans as they easily accumulate in the human body over a long period of time after ingestion (Ogah, 2012).

Health problems linked to pesticide exposure include cancers, neurotoxic disorders, infertility amongst others; these problems mean government all over the world regulate the use of pesticides. The FAO and WHO technical committees on pesticide residues have established Minimum residue limits (MRL) for most pesticides (WHO, 2001). The regulatory agencies in Nigeria lack adequate facilities and infrastructure for monitoring the production and application of these pesticides; despite the ban they remain on sale and are still in use. Abuse of these banned and substandard pesticides cause serious environmental contamination leading to high human exposure. The level of abuse and misuse of these pesticides cannot be assessed without the analysis of pesticide residues in food.

Cowpea *(Vigna unguiculata L.* Walp*)* is an annual legume widely grown in tropical regions; it is a major source of protein especially in the developing world where other sources of protein are too expensive for far-reaching consumption. During harvesting and storage cowpea is usually treated directly with pesticides to avoid heavy pest infestation especially during storage. This direct and indiscriminate application increases the risk of pesticide residues exceeding the MRL set by the regulatory agencies.

The objective of this research was to determine the extent of use of these pesticides residue on cowpea at Iddo Market Lagos, detect and quantify the different classes of pesticides used.

2.0 Materials and Methods

2.1 Area of study and sampling

A survey was carried out in Iddo Market situated in Mainland Local Government Lagos State. It is the major grain depot in Lagos State (cowpea, maize, sorghum and millet). The survey indicates that all the grain dealers apply pesticides and none of them had training on application of storage pesticide. Aluminum phosphide (Phostoxin), Nova, DD Force™ (an organophosphate) and dry pepper were among grains protectants used.

Twenty (20) samples of cowpea were purchased from vendors on a monthly basis (May, June and July) in a random order and were labelled accordingly. The samples were packaged in an analytically cleaned glass jar and kept away for further use. Each sample was coned, quartered and grinded to a powder using a manual blender. The powdered samples were not sieved to prevent loss of the analyte and 5g was taken for analysis.

2.2 Extraction and Clean up

Extraction of samples was carried out according to standard methods (Derek and Sverko, 2006 ; U.S EPA, 1989 ; Singh, 2001 ; Wang *et al*., 2009) 5g portion of each powdered sample was weighed accurately by coning and quartering method into a beaker. 20ml of 1:1 hexane/acetone mixture was added to the beaker and placed in an ultrasonic bath. The sample was extracted by sonicating for 20 minutes in the ultrasonic bath.

The concentrated extract was allowed to cool down to room temperature and then concentrated further to about 2 ml using a rotary evaporator prior to analysis.

0.7 cm of anhydrous sodium sulphate was placed at the top of the column to absorb any water in the sample or the solvent. A column of about 15 cm x 1 cm i.d. was packed with about 5 g activated silica gel prepared in a slurry form in n-hexane. The column was pre-eluted with 15mL of n-hexane without the exposure of the sodium sulphate layer to air in order to prevent drying up and breaking of the adsorbent. The reduced extract was turned into the column and allowed to migrate below the sodium sulphate layer. Elution was carried out with 2 x 10 ml portions of the extracting solvent (Dichloromethane). The eluate was collected, dried with anhydrous sodium sulphate and evaporated to dryness under a stream of analytical grade nitrogen (99.99%).

2.3 Detection and quantification of Organochlorines, Organophosphates and Pyrethroids

Gas chromatography was carried out using Agilent 7820A gas chromatograph coupled to 5975C inert mass spectrometer (with triple axis detector) with electron-impact source (Agilent Technologies). The GC was operated in selective ion monitoring (SIM) and scan mode to ensure low level detection of the target constituents

The stationary phase of separation of the compounds was HP-5 capillary column coated with 5% Phenyl Methyl Siloxane (30m length x 0.32mm diameter x 0.25µm film thickness) (Agilent Technologies). The carrier gas was helium at constant flow of 1.2 mL/min at an initial nominal pressure of 026 psi and average velocity of 40.00 cm/sec, 1.2 mL/min at an initial nominal pressure of 0.71322 psi and average velocity of 40.00 cm/sec and 1.2 mL/min at an initial nominal pressure of 0.23311 psi and average velocity of 40.00 cm/sec respectively for OCPs, OPPs and Pyrethroids respectively. 1µL of the samples were injected in splitless mode at an injection temperature of 250 °C. Purge flow to spilt vent was 30.0 mL/min at 0.35 min with a total flow of 31.24 mL/min; 15.0 mL/min at 0.75 min with a total flow of 16.356 mL/min and 30.0 mL/min at 0.35 minute with a total flow of 31.258 mL/min respectively for OCPs, OPPs and Pyrethroids; gas saver mode was switched off. Oven was initially programmed at 50 °C (1 minute) then ramped at 25 °C/min to 100 °C (3 minutes) and 5 °C/min to 300 °C (5 minutes), at 60 °C (1 min) then ramped at 25 °C/min to 210 °C (1 min) and 20 °C/min to 310 °C (5 min) respectively for OCPs, OPPs and Pyrethroids. Run time was 16 minutes, 51 minutes and 33 minutes for OCPs, OPPs and Pyrethroids with a 3 minutes solvent delay.

2.4 Mass Spectrometry

The mass spectrometer was operated in electron-impact ionization mode at 70eV with ion source temperature of 230 °C, quadrupole temperature of 150 °C and transfer line temperature of 300 °C. Acquisition of ion was via Scan mode (scanning from m/z 50 to 500 amu at 2.0s/scan rate) and selective ion mode (SIM). Prior to calibration, the MS was auto-tuned to perfluorotributylamine (PFTBA) using already established criteria to check the abundance of m/z 69, 219, 502 and other instrument optimal and sensitivity conditions.

After calibration, the samples were analyzed and corresponding OCPs, OPPs and Pyrethroid concentrations obtained.

3.0 Results and Discussion

The analyses showed that all the samples collected from Iddo Grain Market Lagos contains three classes of pesticides namely organochlorine, organophosphate and pyrethroid (Figures 1-3) .

Most prevalent organochlorines (OC) found in cowpeas includes Endrin-Aldehyde with maximum concentration (MC) of 297.4 mg/kg, Endosulfan with MC of 164.94mg/kg and Alpha-Lindane with MC of 30.03mg/kg. Mean concentrations were 126.06mg/kg, 109.93mg/kg and 15.01mg/kg respectively over the course of 3 months of sampling. It is instructive to note that the maximum residue limit for Endrin, Endosulfan and Alpha Lindane is 0.01 mg/kg, 0.05 mg/kg and 0.01 mg/kg respectively (Codex, 2016; GSO, 2016). Similar results were reported by Ogah *et al*., (2012), Gwary *et al*., (2012), Olufade *et al*., (2014).

Organophosphates (OP) found in the samples in high concentrations are Malathion, Carbophenothion and Parathion while Ethion is the list. Maximum concentrations were 264.26 mg/kg, 768.94 mg/kg and 6578.64 mg/kg respectively. Mean concentrations were 130.33 mg/kg, 427.75 mg/kg and 5032.36 mg/kg. Pyrethroids identified in the samples are also prevalent in very high concentrations. The list includes Cyfluthrin, Alpha-Cypermethrin and Beta-Cypermethrin (Baythroid). Maximum concentrations recorded were 12.65 mg/kg, 18.92 mg/kg and 24.79 mg/kg respectively. Mean concentration of 9.2433 mg/kg, 12.72 mg/kg and 15.297 mg/kg respectively was reported. This is clearly above the maximum residue limit of 0.03 mg/kg. 0.30 mg/kg and 0.30 mg/kg for Cyfluthrin, Alpha-Cypermethrin and Beta-Cypermethrin respectively (FAO/WHO,2019).

This high concentration recorded in all the classes of pesticides might probably be attributed to the fact that cowpea is highly susceptible to infestation by weevils *(Callosobruchus maculatus*) on field. However, due to lack of training and awareness, dealers most times, subject cowpea to heavy treatment with pesticides to maintain good physical quality and avoid postharvest losses.

The detection of organochlorine pesticides in the cowpea samples are not only a source of concern as it has been banned but they also occur in excessive quantities. Detected organophosphates and pyrethroids also exceeded permitted quantities. The high prevalence of pesticide residue in cowpea might be as a result of many factors such as multiple treatment over a period of time, multiple or similar active ingredients in formulations, cross contamination and environmental factors among others. All the pesticides studied had residues levels above their Maximum Residue Limits (MRL) The maximum residue limit (MRL) of a pesticide is the maximum concentration of its residue that is legally permitted to remain in any food after it has been treated with the pesticide that will not pose a threat to human or animal health. MRL is not expected to be exceeded in any foodstuff if the pesticide was applied in accordance with directions for its safe use. If a pesticide residue is found to exceed the MRL in any food, the food commodity is termed to be unsafe for consumption.

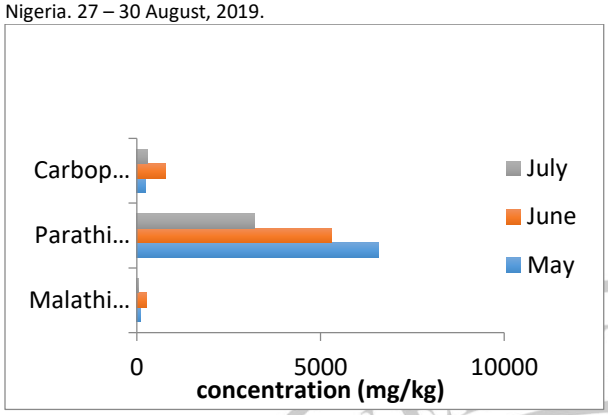

Figure 1: Graph showing concentrations of the 3 most dominant organophosphate pesticides

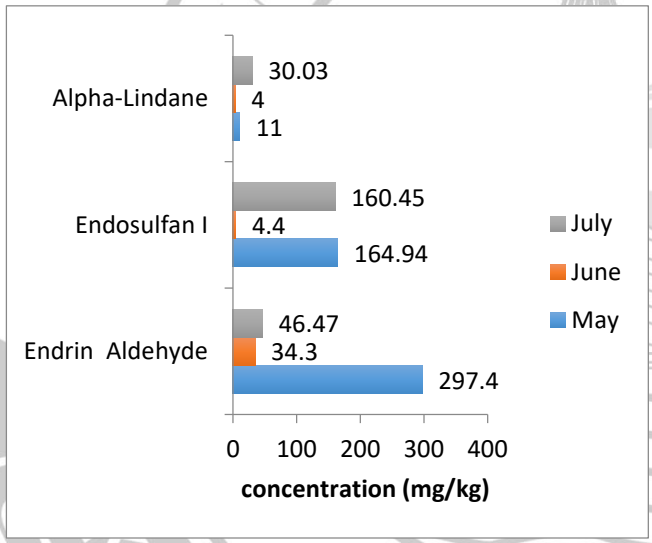

Figure 2: Graph showing concentrations of the 3 most dominant organochloride pesticides

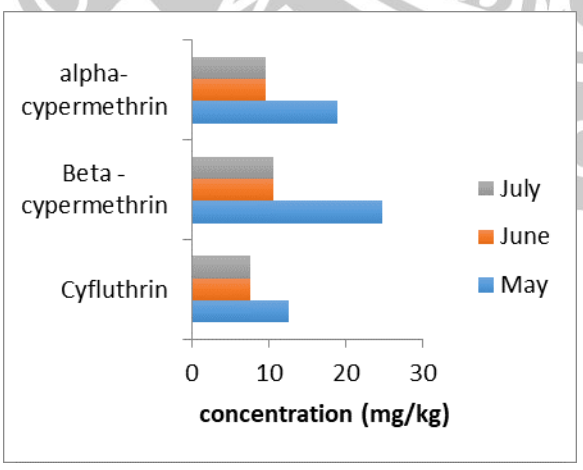

Figure 3: Graph showing concentrations of the 3 most dominant pyrethroid pesticides

Conclusion

The results from this study show that cowpea sample being sold at Iddo market Lagos State contains pesticide residue in in high concentrations (100 % prevalence). Most of the residues tested were found to be above maximum residue limits which are dangerous to human health.

Organophosphate and pyrethroids are recommended for crop protection in Nigeria however strict monitoring and control, enlightenment, training and enforcement is needed by the appropriate agencies. The presence of organochlorines is a worrying case as it has been banned worldwide. The use of natural protectants such as the diatomaceous earth patented by Nigerian Stored Products Research Institute which is a non-toxic, biodegradable, inert dust was tested against insect pests in storage by should be encouraged; the trials results were very satisfactory.

This is one of the very few published studies on the prevalence of three classes of pesticides used on cowpea in Iddo market Lagos State Nigeria. Therefore, the data we have needs to be updated periodically as pesticide use improves.

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