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DETECTION OF INSECTICIDE RESIDUES IN COWPEA AT BAKORI INTERNATIONAL MARKETS, BAKORI LOCAL GOVERNMENT IN KATSINA STATE OF NIGERIA

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Abstract
One kilogram of cowpea sample was collected randomly in Bakori International Market in Katsina State from ten (10) market sellers. Fifty grams (50 g) of the sample were extracted (chopped) from the collected sample, macerated in a blender, dipped in 150 mL of acetone, and the sample was kept overnight until 100 grams (100 g) of powder had been formed. The isolated materials were filtered through anhydrous sodium sulfate. The resulting extracts were evaporated to nearly dryness in a rotary evaporator at a temperature of 26 to 28 degrees Celsius at the Multi User Laboratory at Ahmadu Bello University in Zaria. The residues were redissolved in two milliliters of acetone and chilled for further analysis using Gas Chromatography Mass Spectrometry (GC-MS). The National Research Institute for Chemical Technology (NARICT) GC machine (Shimadzu GC-MS with universal detector (QP 2010 plus)) column RTX, 30 m x 0.25 mm/d, with 0.25 um film thickness (5% diphenyl, 95% dimethyl polysitoxane), was then filled with 1 ul of each sample. Sixteen compounds of the insecticide residue corresponding to the insecticide standards were detected in cowpea. However, among the pesticide residues detected, dichlorvos had the highest residual quantity as compared to EU MRLs in cowpea within the study area. This might be as a result of illiteracy, poor handling of pesticide and dosage rate. Therefore, in order to reduce insecticide residues within the EU MRLS, enhance consumer safety and raise our grains' market worth internationally, the federal government must urgently train extension agents and farmers on pesticide storage, dose, and application timing.

Keywords: Cowpea, Extract, Pesticide Residue, Diclorvos

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INTRODUCTION
Before being moved to its current position on Yashe Road, across from the Bakori local government administration, in 1992, Bakori Market was a part of Bakori Main Market. The market was moved in order to accommodate its quick growth. Maize, guinea corn, millet, beans, rice, groundnuts, soy beans, pepper, cocoyam, and sweet

potatoes are among the main goods traded in the market. Peasants and large-scale farmers from various parts of the local government area, including Tsiga, Barde, Kwantakwaram, Dawan Musa, Kakumi, Guga, Yan'Kwani, and Kurami, provide the majority of the commodities. Marketers utilize storage as a method to store their produce with pesticides. Herbicides, insecticides, nematicides, fungicides, and many other compounds are employed as pesticides (Randall *et al*., 2018). According to the Food and Agricultural Organization, a pesticide is any chemical or combination of chemicals used to prevent, eradicate, or manage pests. Additionally, they are sprayed to crops either before or after harvest to prevent degradation during transportation and storage (Zhang *et al*., 2018). Supermarkets and food storage facilities utilize insecticides to manage rodents and insects that contaminate food, particularly grain (Knutson, 2019).

Nevertheless, pesticides are costly, dangerous, and endanger human health (Weselak *et al*., 2017). Although they are intended to protect the public from pesticide abuse, pesticide safety education and pesticide applicator regulations do not completely prevent misuse. Heavy pesticide use has had a number of detrimental effects on the environment, human health, and the economy (Ashburner *et al*., 2021). According to Oladimeji *et al*. (2023), plants treated with lambda cyhalothrin had the least amount of insect damage to their leaves, but it was still somewhat phytotoxic because the leaves showed signs of deformation.

The Food and Agricultural Organization (FAO) (2017) has expressed concern over numerous reports of pesticide users' poor health. According to estimates from the World Health Organization, a million people are poisoned every year, and 20,000 of those instances end in death (WHO, 2018). The toxicity of the pesticides that many farmers use without sufficient understanding and without wearing the proper protective gear was a major contributing factor to this issue. Pesticide-related health issues are typically attributed to the pesticides themselves, without taking into account how they are applied (PCPB, 2020). Given that the market is global, it is necessary to look at pesticide residue for both consumer safety and to enhance international trade.

From 1,000–2,500 grams of active ingredient per hectare (g/ha) in the 1950s to 40–100 g/ha in the 2000s, pesticide application rates varied (Sparks 2021). Despite this, the quantity used has increased. The amount used rose by 1623% in low-income countries and by 20% in high-income countries during the 1990s and 2010s (Sparks 2021).

MATERIALS AND METHODS

The Bakori market was chosen because to its significance in Nigeria's grain commerce. Laboratory analyses were conducted at the National Agency for Food, Drugs Administration and Control (NAFDAC) in Kaduna, the National Research Institute for Chemical Technology (NARICT) in Zaria, Kaduna State, and the Multi-user Laboratory in the Chemistry Department of Ahmadu Bello University in Zaria, Kaduna State.

One hundred grams (100 g) of cowpea was collected randomly from ten (10) traders in Katsina State. The obtained material was labeled appropriately, placed in a polythene bag, and brought to the lab for additional examination (Islam *et al*., 2009). The following materials used in the laboratory are chemical reagents and solvents were used during the course of extraction and laboratory analysis: Blender, Mechanical shaker, Stainless steel jar, Pestle and mortar, Whatman Filter paper, A clean cotton pad, Graduated cylinder, Rotary evaporator, Refrigerator, Polythene bags. Shimadzu GCMS (QP 2010 plus) with universal detector, Column: RTX, 30m x 0.25mm/d, and 0.25µm film thickness (5% dephenyl, 95% dimethylpolysitoxane) were used to analyze the crop samples. Chemicals with Reagents that were used for the analysis of the insecticide residues were of analytical grade. High grade sodium chloride (NaCl), anhydrous sodium sulphate ($NaSO_4$). Insecticide reference standards (purity above 97%) was obtained from ACCU Standard, USA: Dimethoate 10 ng/µl 1 * 10 ml, Cypermethrin (technical) 10 ng/µl 1 * 10 ml, Dichlorvos 10 ng/µl 1 * 10 ml from NARICT, Zaria, Chlorpyrifos10 ng/µl 1 * 10 ml, Acetone, Methylene chloride, Acetonitrile, n-hexane, Distilled water and tap water.

Techniques for Extraction

Cowpea and maize, each weighing 200 grams (100 g), were processed into powder. From the collected samples, fifty grams (50 g) of each sample were diced, macerated in a blender, dipped in 150 mL of acetone, and left overnight (Singh *et al*., 2008). Anhydrous sodium sulfate was used to filter the extracted materials. In the Multi User Laboratory at Ahmadu Bello University Zaria, the resultant extracts were evaporated to almost dryness using a rotary evaporator at a temperature between 26 and 28 oC. Prior to instrumental analysis, residues were cleaned up and re-dissolved in 2 milliliters of acetone (Barakat *et al*., 1994).

Procedure for extraction

Florisil was cleaned by column chromatography with methylene chloride, n-hexane, and acetonitrile (50: 48.5: 1.5). The residue was quantitatively transferred and filtered over a chromatographic column (2.5 cm) filled with a 7 cm layer of florisil after being dissolved in 10 ml of the eluting solvent. Before continuing, the residue was rinsed three times using roughly 5 ml volumes of the eluting solvent, and each washing was put to the column. The column must have been filled in with the fraction. Elution was carried out at a flow rate of 1.5 ml min-1 until 200 ml of the eluting solvent had been utilized. A rotary evaporator running at 40 oC was used to collect the eluents in a 500 ml rotary evaporator flask and evaporate them under vacuum until they were completely dry. For GC analysis, the residue was dissolved in 10 milliliters of GC-grade ethyl acetate and transferred into a 10 milliliter measuring flask.

Spiked calibration requirement

Acetonitrile was used to generate individual stock standard solutions (1 mg/mL), which were then kept in the dark at -20°C. Before being used, they were stored at room temperature for one hour. Each insecticide was made into a stock standard solution in acetonitrile at 0.2 mg/ml. For each sample (cowpea, maize, kolanut, spinach, and guava), 150 milliliters of the extracted pesticide residue were mixed with fifty milliliters (50 ml) of the 0.2 mg/ml pesticide stock solution. The internal standard was a stock solution of 1 mg/mL of triphenyl methane (TPM) in acetonitrile. As an internal standard, the spiked sample was combined with an aliquot of 20 µL of TPM solution in acetonitrile (1000 mg/L).

Gas chromatography analysis

One ul of sample was injected into the GC machine using a 25 ul glass Hamilton syringe. The plunger was slowly pulled out to extract 1 ul of the liquid, which was then compressed to release it. Following this procedure, the syringe was filled with liquid and slowly drawn up while its needle was in the liquid. It was then injected into the chromatographic injector pot (Shimadzu GCMS (QP 2010 plus with universal detector) column RTX, 30 m x 0.25 mm/d, with 0.25 µm film thickness (5% diphenyl, 95% dimethyl polysitoxane), and the recorder's start button was pressed right away. After a few minutes of observation, the recorder logged multiple peaks and printed out the peaks, retention times, and areas beneath the peaks.

Analyte residues analysed

The samples were analysed for chlorpyrifos, dichlorvos, cypermethrin, dieldrin, dimethoate and profenofos pesticide residues. The average concentration of each pesticides in cowpea was compared with MRLS recommended by (European Union 2011).

RESULTS

Table 1: The matching cowpea sample molecule based on mass spectroscopy data

The study uses mass spectroscopy (MS) data to identify the kind and amount of pesticide residues found in the samples. A comparison of the results with mass spectrometry data from the National Institute of Standards and Technology 2005 Library (NIST05.LIB) revealed that cowpea samples contained sixteen (16) chemicals. Significant occurrences of molecules associated with certain pesticide standards were found in the cowpea sample, as indicated in Table 1. The most common pesticide found in the sample (n = 6) was cypermethrin. Chlorpyrifos followed after cypermethrin which was detected for (n = 4) in the sample. Then dichlorvos which also had equal occurrence just like Profenofos that had three (3).

Table 1: The matching cowpea sample molecule based on mass spectroscopy data

Line	Retention period (min.)	Base peak fragment m/z+	Corresponding molecule	Corresponding pesticides standard
1	12.275	161.15	1-(4-methoxyphenyl)-4-methyl-1-penten-3-one	Cypermethrin
2	13.710	161.15	5-amino-7-ethoxy-quinoxaline	Chlorpyrifos
3	14.678	161.20	5-methoxyindole-3-acetamine	Chlorpyrifos
4	16.230	204.30	1-methyl-3-phenyl-2,4,5-trioxoimidazolidine	Cypermethrin
5	17.140	191.20	3,5-bis(1,1-dimethylethyl), methylesterbezeneacetic acid	Chlorpyrifos
6	17.303	159.15	Carbendazim	Chlorpyrifos
7	20.033	207.25	Trans-3-ethoxy-b-methyl-b-nitrostyrene	Cypermethrin
8	30.102	228.30	5-methyl-2-p-chlorophenylimino-1,3-thiazolidine	Profenofos
9	34.850	227.25	Methylester palmitic acids	Diclorvos
10	39.330	239.30	3-phenyl-2,3-dihydro-1,4-benzoxazepin-5-ol	Cypermethrin
11	42.737	152.25	Methylester-octadecenoic acid	Dichlorvos
12	43.973	298.40	16-methyl-,methylesterheptadecanoic acids	Dichlorvos
13	54.485	185.20	1,2-bis(bromomethyl)-benzene	Profenofos
14	55.488	167.10	Diisootyl phthalate	Profenofos
15	55.745	239.35	1,3-dihydro-1-hydroxy-3,3-dimethyl-1-(m-tolyl)-3,4-benzofuran	Cypermethrin
16	55.920	239.40	3-phenyl-2,3-dihydro-1,4-benzoxazepin-5-ol	Cypermethrin

Pesticide Residue in Cowpea Sample

The analysis of the pesticides residue in the cowpea samples collected from Bakori markets shows that dichlorvos had the highest mean concentrations of 0.0671±0.00876987mg/kg. Cypermethrin (0.0463±0.00153 mg/kg), profenofos (0.0425±0.012527008 mg/kg), and chlorpyrifos (0.0488±0.00494402 mg/kg) are among the pesticide residual values found in the sprayed sample. At probability of ($p<0.05$) Dichlorvos with the highest T-test value of 0.776082783, which was absolutely evidence in the P-value have no significant difference in the level of the residue within the sample. Followed suit was chlorpyrifos T-test value of 0.73994044, profenofos with the T-test value of 0.694082783, while cypermethrin had the least value 0.00802 within the samples.

While the F-test really deals with the variation within each sample array at the same probability of ($p<0.05$) and evaluating the ratio of the variance between the sample and the control. The F-test value ranges from chlorpyrifos (0.74663072) > dieldrin (0.30603137) > profenofos (0.180877535) > dichlorvos (0.18038531) > cypermethrin (0.12483983).

Table 2: The Cowpea sample containing insecticides residue

Analysis	**Organophosphorus esticides**		**Organochlorine Pesticides**	**Pytheroid Pesticides**
Mean value	**Chlorpyrifos**	**Profenofos**	**Dichlorvos**	**Cypermethrin**
Kat (mg/kg)	0.0496	0.05	0.0619	0.0535
Sample Average(mg/kg)	0.0488	0.0425	0.0671	0.0463
EU MRL(mg/kg)	0.05	0.05	0.01	0.05

***EU MRL= European Union Maximum Residue Limit.**

DISCUSSION

In the current research, mass spectrometry (MS) data generated from the SHIMADZU GC–MS were compared with the NIST Chemistry WebBook library in order to validate the detected compounds. The NIST library provides reliable reference spectra, including instrument parameters and EPA MS numbers, which strengthens the accuracy of pesticide identification in the present study. The comparison revealed that several synthetic pyrethroids and organophosphate pesticides occurred in the cowpea samples, which aligns with their widespread use by farmers because of their broad efficacy against a range of insect pests (Parween *et al*., 2013).

However, in the present study a total of sixteen (16) pesticide-related compounds were detected based on their mass spectral matches with the NIST library. Cypermethrin was the most frequently detected pesticide consistent with its routine use for cowpea protection in many West African farming systems. This agrees with Pascual (1992), who described cypermethrin as a broad-spectrum insecticide widely applied by farmers. Chlorpyrifos followed with four occurrences, while both dichlorvos and profenofos each occurred three times in the samples.

The repeated detection of these compounds may reflect inappropriate pesticide application practices, including overdosing and indiscriminate post-harvest treatment, especially during grain storage and marketing. Chedi *et al*. (2010) reported that grain marketers commonly expose stored cowpea to excessive quantities of organophosphates, often exceeding recommended national and international guidelines. Such misuse is known to elevate residue concentrations beyond allowable limits, posing significant risks to consumers and contributing to insecticide resistance in pest populations (Chedi *et al*., 2010; Davies *et al*., 2016; Bardin *et al*., 2015).

Quantitatively, Dichlorvos recorded the highest concentration, this may likely due to routine post-harvest application by grain sellers in the study area. Similar observations were reported by Li (2009) in Zimbabwe, where limited pesticide knowledge and poor handling practices contributed to elevated dichlorvos residues. High dichlorvos levels in the present study suggest a comparable trend among cowpea marketers in Bakori, Katsina State. Cypermethrin, Profenofos, and Chlorpyrifos were also detected, although their concentrations remained below the European Union Maximum Residue Limits (EU MRLs), indicating lower health risk for consumers. However, the markedly elevated Dichlorvos concentration exceeded acceptable limits, reinforcing concerns over its unsafe use and persistence.

The present study Dichlorvos presented the highest concentration, indicating no significant variation in its residue levels across the samples analyzed. Chlorpyrifos and Profenofos similarly showed no significant differences suggesting greater variability among samples. Based on both concentration and statistical precision, the comparative residue trend in relation to the EU MRLs followed the order. This trend highlights dichlorvos as the major contaminant of concern, while the other pesticides, though present, appeared within acceptable international safety thresholds.

CONCLUSION & RECOMMENDATION

Result of the study established that phostoxin (66%) and Dichlorvos (27%) are the major pesticides used to store grains by grain merchants in the study area, while cypermethrin (26.12%) was commonly used as pre harvest pesticides. The least used pesticide in the study area was Chloropyrifos (2%). Also, most pesticide application method was via fumigation, where 88% of the respondents attested to using fumigants to store their harvested produce. However, only few respondents (12%) use admixture method that is applying pesticides directly to the grains.

Additionally, it demonstrates that sixteen (16) distinct chemicals were identified in cowpea in Bakori marketplaces. The study area's cowpea pesticide residues for dichlorvos were found to be higher than EU MRLs. In order to reduce pesticide residues within the EU MRLS, improve consumer safety, and increase the value of our grains on the global market, the federal government must urgently instruct producers on pesticide storage, dosing, and application timing.

Recommendation

Since cowpea is staple crop, all relevant Federal and State agricultural, environmental ministries, departments and agencies should intensify sensitization efforts on the safe use and handling of pesticide.

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Conflicts of Interest:

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