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Heatmap-Based Qualitative Chemical Profiling of Cowpea (*Vigna unguiculata*) from Multiple Nigerian States Indicates Low Pesticide Incidence: Prospect for Lifting the EU Ban II

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Abstract

Purpose: Application of inorganic pesticides in agriculture is a measure often used to mitigate food insecurity due to pest infestation, plant diseases and low weed induced malnutrition of plants. However, with an increasing mortality rate secondary to pesticide poisoning and incidences of novel diseases with idiopathic reference, food safety awareness is on the rise. This study assessed the qualitative incidences of pesticide residues on cowpea seeds randomly sampled from major open markets and storage facilities across 12 Nigerian states where cowpea is predominantly cultivated.

Methodology: Here, we analyzed cowpea samples collected from open markets and storage facilities across 12 States in Nigeria for pesticide residues, using QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) sample preparatory method prior to quantitative analysis by GC-MS. Two hundred and six unique compounds were identified from the sorting and compilation of the 50 most intense chromatographic peaks (>0.5% relative abundance) detected per sample, manually traced to dual databases for benchmarked referencing and categorized into 3 broad classes of chemicals: pesticides, bioactive and inert/ method-associated compounds. The data generated were formatted into a heatmap to enable comprehension at a cursory glance.

Findings: Below 1% of the total number of identified compounds were known pesticides (dichlorvos and chlorpyrifos) with each incidence traceable to two sampling locations out of the 12 Nigerian states covered. The findings indicate low incidence of pesticide contamination on Nigerian cowpea, within the surveyed locations.

Unique Contribution Theory, Policy and Practice: In view of the lingering ban on the export of Nigerian cowpea to the European Union member countries, this study provides information on the adherence of farmers and storers of cowpea to food safety regulations with specific regards to pesticide application prior to harvest and during storage.

Keywords: *Food safety, food security, Maximum Residue Limit (MRL), Integrated Pest Management (IPM), cowpea (Vigna unguiculata).*

1. INTRODUCTION

1.1 History of Plant Protection

The use of pesticides dates to 2500 BC when sulfur compounds were used to control mites and insects by the Sumerians. Before the use of pesticides, mechanical approaches such as manual removal of weeds, pests and other non-chemical methods like burning to control agricultural weeds, diseases or pests were employed in 950 B.C. After the discovery of DDT as a potent insecticide during the second World War, the chemical industry gained substantial global attention by introducing several types of inorganic insecticides for pest control applicable majorly in agriculture. (Edward Crow et al., 2014) Pesticide boom sequel to the 1940's has improved agricultural yield greatly by preserving crop quality and post-harvest longevity of plants and plant products hence there is a perception that prioritizes the availability of nutritious food over hazards posed by pesticide. (Aktar et al., 2009) However, in the past decades, due to increasing rates of pesticide poisoning and other chronic diseases of idiopathic attribution, consumers are more conscious about the safety of food and water. In research conducted by WHO in collaboration with UNEP, it was reported that pesticide poisoning accounted for over 200,000 deaths and about 3 million injuries globally. (WHO, 1990). One of the first recorded incidences of food borne disease dates to 323 B. C., the accounts that led to the demise of Alexander the Great at the age of 32 were described as suggestive of food poisoning. (University Of Maryland Medical Center, 1998) Since that era, countless cases of food poisoning have been reported and probably many such cases went unnoticed. To avert further incidences of food poisoning, novel diseases and comorbidities, global and regional regulatory authorities like WHO, FAO, IPPC, EFSA, FDA, Codex Alimentarius Commission etc., have developed policies over the years that checkmate the quality of food traded locally and internationally. (FAO, 2020) These policies are complimented with scientific guidelines applicable to their facilitation through database creation in research. Different countries comply with world regulatory policies on food at different levels. However, in situations when data from specific locations cannot be obtained, it is permissible to extrapolate with regional data (FAO, 2020). Environmental safety, biodiversity preservation and ecosystem conservation are issues of global concern that require cross-sectoral collaboration in research and development to proffer solutions to current and future challenges (IPPC, 2013).

1.2 Cowpea Cultivation Index in Nigeria

Cowpea is a staple source of protein in Nigeria; most households consume cowpea in different forms; as whole meal or complementary to carbohydrate dish to achieve balanced diet. Nigeria is the highest producers of cowpea with a yield of over 3.6 million tons in 2021 (FAOSTAT, 2023). Yobe, Taraba, Adamawa, Gombe and Kwara are the highest cultivators of cowpea followed by Niger, Benue, Kogi, Kaduna, Bauchi, Jigawa states and Abuja while Kano Sokoto and Borno States are the largest commercial hubs of cowpea in Nigeria. (NAERLS AND FMARD, 2021) cited by (Chibuzo Nwagboso et al., 2024). Moreover, conventional pesticides remain the first line

of insect and plant pest mitigation approach in most cowpea producing states in Nigeria. (Hassan et al., 2018).

1.3 Integrated Pest Management

Integrated pest management (IPM) entails all available pest control techniques and other measures that discourage the development of pest population while minimizing risk to human health and the environment. (WHO, 2023). IPM is an alternative approach to conventional plant protection products (PPPs) which is relatively safer and equally effective, it reduces reliance on the use of inorganic pesticides and enhances the incorporation of diverse pest control methods such as, the use of pheromones (biological), valorization of botanicals into pesticide formulations (biochemical), the practice of basic shifting cultivation and manual barrier creation (mechanical) etc. (Crop Life International, 2014). Recently, the use of modern agricultural techniques like hydroponics and aquaponics which are modifications of conventional greenhouse farming has become widely adopted by many agronomists, and cultivators of fruits and vegetable for commercial and research purposes. Despite Nigeria's strength in cowpea cultivation, chances are high that cowpea value chain is under-reflected on the agricultural economic prospect of the country due to reports of non-compliance with EU's phytosanitary regulation on MRL of ≤0.01 mg/kg as opposed to values ranging from 0.03 mg/kg to 4.6 mg/kg detected on cowpea samples intercepted in the EU in 2013 (Hassan et al., 2018).

The GAP guideline on grain cultivation considers a variety of factors including farm management, worker safety, human rights protection, food safety and environmental conservation when categorizing overall management, risk management, specie management and cultivation management.(Guidelines on International-Level GAP, 2022). However, on a global scale, Nigeria currently struggles to adequately adhere to these guidelines while most affluent countries have been able to secure food security across diverse value chains ("Feeding the Future Global Population," 2024). One of the main factors restricting GAP in Nigeria is stakeholders' lack of exposure to education (Hassan et al., 2018). Furthermore, application of conventional pesticides has high impact on the mitigation of post-harvest losses which helps to achieve high return on investment.

1.4 Sanitary and Phytosanitary Analysis

The agreement on the application of sanitary and phytosanitary measures (The SPS agreement) was enforced upon the establishment of the World Trade Organization in 1995. This agreement was made to ensure global implementation of the trade of safe food and consequent sanctions for non-compliance with the SPS regulations. The SPS agreement operates on a standard guideline. However, it also permits countries to set their own standards on a scientific basis. This implies that affluent countries also have the advantage of utilizing standards that are higher than international standards with appropriate scientific justification. The overall goal of the SPS Agreement is to facilitate international trade of agricultural commodities while ensuring that food safety, food security, plant and animal health are preserved (WTO, 1998). Hence exotic pests, diseases and

contaminants of agricultural products are restricted through the International Standards for Phytosanitary Measures (ISPMs) for plants and World Organization for Animal Health (WOAH) for standards on animal and animal products trade.

1.5 QuEChERS Approach

QuEChERS (Quick, easy, cheap, effective, rugged, and safe) is a widely adopted sample preparation method for pesticide residue analysis in food matrices. Introduced by (Anastasiades et al., 2003a), it combines simplicity with high recovery efficiency for both polar and non-polar pesticides. The technique involves solvent extraction (commonly acetonitrile) followed by dispersive solid-phase clean-up using salts such as magnesium sulfate and buffering agents. Its robustness lies in minimizing matrix interference while preserving analytic integrity, making it suitable for complex agricultural commodities like grains and legumes. In food safety, QuEChERS remains the gold standard for multi residue pesticide extraction.

1.6 Gas Chromatography-Mass Spectrometry (GC-MS)

Gas chromatography mass spectrometry (GC-MS) is a powerful analytical tool that couples chromatographic separation with mass spectral identification. In pesticide residue analysis, GC enables the resolution of volatile and semi-volatile compounds, while MS provides structural confirmation through fragmentation patterns and spectral matching with established databases or direct comparison with peaks from a known standard analyzed under the same parameters. The technique's sensitivity, Specificity, and reproducibility make it indispensable for both qualitative profiling and quantitative monitoring. When applied with spectral libraries such as NIST, GC-MS ensures reliable compound identification which may be further confirmed through quantitative GC-MS by directly matching with known standards under set LoQ and LoD. Its versatility and accuracy explain its prominence in food science research, particularly for assessing chemical safety in agricultural products (Hyötyläinen & Riekkola, 2008).

1.7 General Objective and Scope

This study aims to qualitatively profile pesticide residues and other chemical constituents in cowpea (*Vigna unguiculata*) Samples collected from 12 Nigerian states. Specifically, it seeks to identify the types of pesticides applied, determine the prevalence of individual and multiple residues per sample, and assess the regulatory status of detected compounds, including approved, banned, or pending plant protection products (PPPs), as well as ancillary components such as safeners and synergists. The research focuses on samples prepared using QuEChERS extraction method (Anastassiades et al., 2003) and analyzed via GC-MS, confirmed through quantitative analysis if pesticide incidence is above 5% of total detected compounds, otherwise, conduct qualitative highly sensitive profiling that enables precise cross-referencing with multiple international pesticide databases. By establishing a comprehensive dataset on the chemical composition and pesticide usage patterns of cowpea in Nigeria, this study contributes to building a reference framework for food safety surveillance.

Based on the responses obtained from a preceding survey conducted in the same locations, which involved key stakeholders in the Nigerian cowpea value chain, conventional pesticides were found to be predominantly used by farmers and storage operators. However, the previous study could not assess respondents adhered to the safe concentration limits recommended by pesticide manufacturers or agricultural regulatory agencies during preparation and application. (Idoko et al., 2025)

2. MATERIALS AND METHOD

2.1 Sample Collection

- Different varieties of cowpea (*Vigna unguiculata*) samples were collected from major open markets across 12 Nigerian states to capture specie and regional variability. Three samples weighing 1 kg each were taken from three different vendors per location as a lot (CAC/GL 33-1999). Samples from same location were pooled, homogenized, and milled into fine powder to obtain a representative bulk sample. From each bulk, 15 g was subsampled for analysis into a clean zip lock bag, labeled, and stored at -20°C for further analysis (CAC/GL 33-, 1999)

2.2 Sampling Location

- Locations were selected purposively based on markets in states where cowpea is highly cultivated, stored or traded (Chibuzo Nwagboso et al., 2024; NAERLS AND FMARD, 2021).
- Storage facilities in major markets where aggregators converge to buy grains directly from farmers or suppliers in bulk and transport to other locations.
- Markets close to rural settlements where cowpea is highly cultivated

Table 1. Cowpea Sample Collection Locations

S/N	States	Sampling Locations	Sample Codes
1	Abuja	Wuse, Garki and Utako Markets	AG1, AG2, AG3, AU1, AU2, AU3, AW1, AW2, AW3
2	Adamawa	Lafiya and Tingno Markets	ALF1, ALM1, AM1
3	Benue	Modern and Wurukum Market	BM1, BM2, BM3
4	Borno	Monday market Maiduguri	BRN1, BRN2
5	Cross River	8Miles evening market	CRC1, CRC2, CRC3
6	Gombe	Kauwan Buhana Kaltungo, beti market wange Tula	GT1, GK1, GS1
7	Kwara	Afon Market, Asa LGA Kwara	KI1, KI2
8	Nasarawa	Keffi market	NK1, NK2, NK3
9	Niger	Lambata market, Suleja market	NL1, NL2, NS1
10	Plateau	Jengre market/ store, angwan rukuba market and terminus market	PLA1, PLA2, PLA3, PLJ1, PLJ2, PLJ3
11	Taraba	Tela and maelope markets	TI1, TMB1, TT1
12	Yobe	Kasuwan bayan tasha	YOB1, YOB2

2.3 Qualitative Profiling of Pesticide Residues and Chemical Constituents in Cowpea (Vigna Unguiculata) Using GC-MS

2.3.1 Sample Preparation

Cowpea samples were subjected to pesticide residue extraction using QuEChERS protocol (Anastassiades et al., 2003a). 15 g of cowpea tonight was homogenized into fine powder, from which 10 gram was transferred into a polypropylene centrifuge tube. Extraction was performed by adding 15 ml acetonitrile, vortex-mixing for 10 minutes, and centrifugation at 3500 rpm for 3 minutes. A clean-up matrix consisting of $MgSO_4$ And 1.5 g sodium acetate was added, followed by vortex-mixing for one minute add centrifugation for one minute at 3500 rpm. The clear supernatant (8 ml) was transferred into GC sample vials for analysis.(Anastassiades et al., 2003b; Hyötyläinen & Riekkola, 2008; Ndidi M. Ejoh et al., 2019).

2.3.2 Gas Chromatography Mass Spectrometry

Qualitative chemical profiling was conducted using the GC2010 Shimadzu tandem mass spectrometry equipped with an auto injector (AOC-20i plus) and an Rtx-5ms (30 m, 0.2 mm, 0.25 µm) was used to analyze the pre-extracted cowpea samples for pesticide residues under the conditions listed on the table below. The analysis was programmed as follows: 40°C was maintained for 5 minutes then gradually elevated to 280°C for a minute at the rate of 10 °C/min, held for 1 min. The injectors maintained at 290°C split (60:1). Helium was used as carrier gas at a constant flow of 1.78 ml/min The MS was operated in electronic impact (EI) mode at 70eV with ion source temperature of 200°C, interface temperature of 290°C, and scan acquisition from m/z 35-650 (Jitendra Kelkar et al., 2023; Khammas et al., 2020) as detailed on table 2 below.

Table 2. GCMS Analytical Parameters

GC		**MS**	
Injection temp.	290°C	Ion source temp.	200°C
Colum temp.	40°C	Interface temp.	290°C
Injection mode	Split	Solvent elution time	3.5
Pressure	100 kPa	Start time	4 min
Total flow	111.6 ml/min	End time	30 min
Colum flow	1.78 ml/min	Start mz	35
purge	3 ml/min	End mz	650
Sampling time	1 min	Measurement mode	scan
Linear velocity	48.1 cm/sec	Run time	0.30 sec
Split ratio	60	Scan Speed	2500
Colum size	30 m/ 0.25 mm/ 0.24 µm		

2.3.4 Chromatographic Detection (TIC and MIC)

Data acquisition was performed using both the total ion chromatogram TIC and mass ion chromatogram MIC. TIC provided global chemical fingerprint of all detectable analytes, while

MIC enhanced selective monitoring of diagnostic ions to reduce false positives. The combined use of TIC and MIC improved reliability of compound identification, particularly for pesticide residues present at trace levels.

2.3.5 Compound identification and classification

Compounds were automatically matched against NIST05.LIB my spectral database. Library matches were further validated by retention time consistency and manual inspection of fragmentation patterns. To strengthen accuracy, for each sample, the 50 most intense chromatographic peaks (>0.001% relative abundance) Were considered. corroboratory identification was achieved through multiple database spectral matching (Kim et al., 2021; Stein, 2020; U.S. Department of Agriculture Agricultural Research Service, 2019). Duplicate compounds were removed yielding a total of 206 unique compounds. Identities were manually crossed-verified reference databases to ensure reliability.

Compounds were classified into 4 categories:

1. category 0 - Pesticides
2. category 1 - Vitamins
3. Category 4 – Lipids/fats
4. Category 5 - Inert/ GC-MS derivatives

A total of 206 compounds were identified and classified following this procedure. For illustration, dichlorvos and Phosphorothioic acid, O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) ester (chlorpyrifos) were confirmed as pesticides with high similarity indices (87% and 81% respectively) and clear spectrum match (fig.2).

The study design incorporated a contingency for pesticide quantification: If category 0 (pesticides residues) exceeds 5% of total compounds identified by GC-MS in >5% of the total survey locations then quantitative GCMS would be conducted. However, only 0.97% of the compounds detected are pesticides hence further quantitative analysis was deemed unnecessary.

2.3.6 Data processing and visualization

Datasets from the 12 sampling locations were standardized to remove formatting inconsistencies and ensure uniform compound naming. Each compound was then matched to its assigned category using structured reference tables.

Categorical codes (0,1,4, and 5) We're applied to the data set and visualized through a heat map, with numerical categories represented by distinct color codes (category 0 = red, Category 1 = purple, category 4 = orange and category 5 - blue). This approach allowed comparative assessment of chemical distribution across the 12 states, illustrating the relatively low portion of pesticide residues.

Given the quantitative nature of data set, no formal statistical analysis was done. Compound identification and classification were categorical (categories 0,1,4, or 5), and the primary objective

was to profile chemical constituents and visualize their distribution across locations using a heatmap. Quantitative measurements of the individual compound abundance were not obtained, and pesticide residues were detected in only two compounds (0.97%), representing a negligible portion of the total data set prior to removal of duplicate compounds. Consequently, descriptive summaries and visual representations were deemed sufficient to convey the spatial and categorical patterns of chemical composition among cowpea samples. While statistical comparison of categorical distributions or clustering could be performed, such analyses were considered unnecessary for addressing the primary research objectives.

3. RESULTS AND DISCUSSION

3.1 Analytes from GC-MS Analysis of Cowpea Samples

The list of compounds identified from the GC-MS analysis are shown on Table 3. A final list of 206 compounds was obtained after removing duplicates, the compounds were grouped into 3 broad categories as detailed on Table 3.

Table 3. List of all Compounds Identified by GCMS analysis of Cowpea Samples

Compound/ Common Name	Category	Code	References
(1S,6R,9S)-5,5,9,10-Tetramethyltricyclo[7.3.0.0(1,6)]dodec-10(11)-ene	Inert/GCMS artifact	5	NIST GCMS Library
(E)-9-Octadecenoic acid ethyl ester	Fat/Lipid	4	PubChem / USDA DB
(R)-(-)-14-Methyl-8-hexadecyn-1-ol	Inert/GCMS artifact	5	NIST GCMS Library
(Z)6,(Z)9-Pentadecadien-1-ol	Inert/GCMS artifact	5	NIST GCMS Library
.beta.-Sitosterol	Fat/Lipid	4	PubChem / USDA DB
.gamma.-Tocopherol	Vitamin	1	USDA Nutrient Database
1,1,1-Trifluoroheptadecen-2-one	Inert/GCMS artifact	5	NIST GCMS Library
1,2,6a,6b,9,9,12a-Heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,12,12a,12b,13,14b-octahydropicene-4a-carboxylic acid, methyl ester	Fat/Lipid	4	PubChem / USDA DB
1,2-Benzenedicarboxylic acid, butyl 2-ethylhexyl ester	Fat/Lipid	4	PubChem / USDA DB
1,2-Benzenediol, 3,5-bis(1,1-dimethylethyl)-	Inert/GCMS artifact	5	NIST GCMS Library
1,2-Propanediol, 3-(tetradecyloxy)-	Inert/GCMS artifact	5	NIST GCMS Library
1,4,8-Dodecatriene, (E,E,E)-	Inert/GCMS artifact	5	NIST GCMS Library

1,4-Di-O-acetyl-2,3,5-tri-O-methylribitol	Inert/GCMS artifact	5	NIST Library	GCMS
1,E-8,Z-10-Hexadecatriene	Inert/GCMS artifact	5	NIST Library	GCMS
10-Benzoyloxy-1,2,6a,6b,9,9,12a-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-eicoshydropicene-4a-carboxyli	Inert/GCMS artifact	5	NIST Library	GCMS
10-Octadecenoic acid, methyl ester	Fat/Lipid	4	PubChem / USDA DB	
11-Octadecenoic acid, methyl ester	Fat/Lipid	4	PubChem / USDA DB	
13-Docosenamide, (Z)-	Inert/GCMS artifact	5	NIST Library	GCMS
13-Octadecenoic acid, methyl ester	Fat/Lipid	4	PubChem / USDA DB	
13-Trimethylsilyloxy-9-octadecenoic acid, methyl ester	Fat/Lipid	4	PubChem / USDA DB	
16-Hentriacontanone	Inert/GCMS artifact	5	NIST Library	GCMS
17-(1,5-Dimethylhexyl)-10,13-dimethyl-3-styrylhexadecahydrocyclopenta[a]phenanthren-2-one	Inert/GCMS artifact	5	NIST Library	GCMS
1-Heptatriacotanol	Inert/GCMS artifact	5	NIST Library	GCMS
1-Hexacosanol	Inert/GCMS artifact	5	NIST Library	GCMS
1-Nonadecanol	Inert/GCMS artifact	5	NIST Library	GCMS
1-Octanol, 2-butyl-	Inert/GCMS artifact	5	NIST Library	GCMS
1-Pentadecanamine, N,N-dimethyl-	Inert/GCMS artifact	5	NIST Library	GCMS
1-Tridecanamine, N,N-dimethyl-	Inert/GCMS artifact	5	NIST Library	GCMS
1-Undecanamine, N,N-dimethyl-	Inert/GCMS artifact	5	NIST Library	GCMS
2(1H)Naphthalenone, 3,5,6,7,8,8a-hexahydro-4,8a-dimethyl-6-(1-methylethenyl)-	Inert/GCMS artifact	5	NIST Library	GCMS
2-(2',4',4',6',6',8',8'-Heptamethyltetrasiloxan-2'-yloxy)-2,4,4,6,6,8,8,10,10-nonamethylcyclopentasiloxane	Inert/GCMS artifact	5	NIST Library	GCMS
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	Inert/GCMS artifact	5	NIST Library	GCMS
2,4a,8,8-Tetramethyldecahydrocyclopropa[d]naphthalene	Inert/GCMS artifact	5	NIST Library	GCMS

22-Tricosenoic acid	Fat/Lipid	4	PubChem / USDA DB	
26-Hydroxycholesterol	Fat/Lipid	4	PubChem / USDA DB	
2-Bromo dodecane	Inert/GCMS artifact	5	NIST Library	
2H-1-Benzopyran-6-ol, 3,4-dihydro-2,8-dimethyl-2-(4,8,12-trimethyltridecyl)-, [2R-[2R*(4R*,8R*)]]-	Inert/GCMS artifact	5	NIST Library	
2-Hexyl-1-octanol	Inert/GCMS artifact	5	NIST Library	
2-Pentadecanone, 6,10,14-trimethyl-	Inert/GCMS artifact	5	NIST Library	
3-(1,5-Dimethyl-hexa-1,4-dienyl)-2,2-dimethyl-4-trimethylsilylcyclopentanol	Inert/GCMS artifact	5	NIST Library	
3,3,5-Tributoxy-1,1,1,7,7,7-hexamethyl-5-(trimethylsiloxy)tetrasiloxane	Inert/GCMS artifact	5	NIST Library	
3,5-Dimethyl-3-heptene	Inert/GCMS artifact	5	NIST Library	
3.alpha.-Hydroxy-11-cholenic acid methyl ester	Fat/Lipid	4	PubChem / USDA DB	
3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	Inert/GCMS artifact	5	NIST Library	
3-Ethoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	Inert/GCMS artifact	5	NIST Library	
3-Hexanol, 3-methyl-	Inert/GCMS artifact	5	NIST Library	
3-Isopropoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	Inert/GCMS artifact	5	NIST Library	
4,4,6a,6b,8a,11,11,14b-Octamethyl-1,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-octadecahydro-2H-picen-3-one	Inert/GCMS artifact	5	NIST Library	
4-t-Butoxy-3-hydroxy-butyric acid, ethyl ester	Fat/Lipid	4	PubChem / USDA DB	
5-Cholestene-3-ol, 24-methyl-	Inert/GCMS artifact	5	NIST Library	
5-Eicosene, (E)-	Inert/GCMS artifact	5	NIST Library	
5-Fluoro-1-(.beta.-d-xylofuranosyl)-uracil	Inert/GCMS artifact	5	NIST Library	
5H-3,5a-Epoxynaphth[2,1-c]oxepin, dodecahydro-3,8,8,11a-tetramethyl-, [3S-(3.alpha.,5a.alpha.,7a.alpha.,11a.beta.,11b.alpha.)]-	Inert/GCMS artifact	5	NIST Library	
5-Octadecene, (E)-	Inert/GCMS artifact	5	NIST Library	

6,10,14-Trimethyl-pentadecan-2-ol	Inert/GCMS artifact	5	NIST GCMS Library
6-Octadecenoic acid, methyl ester, (Z)-	Fat/Lipid	4	PubChem / USDA DB
7,10,13-Hexadecatrienoic acid, methyl ester	Fat/Lipid	4	PubChem / USDA DB
7-Hexadecenal, (Z)-	Inert/GCMS artifact	5	NIST GCMS Library
7-Hexadecene, (Z)-	Inert/GCMS artifact	5	NIST GCMS Library
8,11,14-Docosatrienoic acid, methyl ester	Fat/Lipid	4	PubChem / USDA DB
8,11,14-Eicosatrienoic acid, (Z,Z,Z)-	Fat/Lipid	4	PubChem / USDA DB
9,12,15-Octadecatrien-1-ol, (Z,Z,Z)-	Inert/GCMS artifact	5	NIST GCMS Library
9,12,15-Octadecatrienoic acid, 2-[(trimethylsilyl)oxy]-1-[[(trimethylsilyl)oxy]methyl]ethyl ester, (Z,Z,Z)-	Fat/Lipid	4	PubChem / USDA DB
9,12,15-Octadecatrienoic acid, ethyl ester, (Z,Z,Z)-	Fat/Lipid	4	PubChem / USDA DB
9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	Fat/Lipid	4	PubChem / USDA DB
9,12-Hexadecadienoic acid, methyl ester	Fat/Lipid	4	PubChem / USDA DB
9,12-Octadecadienoic acid (Z,Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester	Fat/Lipid	4	PubChem / USDA DB
9,12-Octadecadienoic acid, methyl ester, (E,E)-	Fat/Lipid	4	PubChem / USDA DB
9,12-Octadecadienoyl chloride, (Z,Z)-	Inert/GCMS artifact	5	NIST GCMS Library
9,19-Cycloergost-24(28)-en-3-ol, 4,14-dimethyl-, acetate, (3.beta.,4.alpha.,5.alpha.)-	Inert/GCMS artifact	5	NIST GCMS Library
9,19-Cyclolanost-24-en-3-ol, (3.beta.)-	Inert/GCMS artifact	5	NIST GCMS Library
9,19-Cyclolanost-24-en-3-ol, acetate, (3.beta.)-	Inert/GCMS artifact	5	NIST GCMS Library
9-Eicosyne	Inert/GCMS artifact	5	NIST GCMS Library
9-Hexadecenoic acid, phenylmethyl ester, (Z)-	Fat/Lipid	4	PubChem / USDA DB
9-Methyl-Z-10-pentadecen-1-ol	Inert/GCMS artifact	5	NIST GCMS Library
9-Octadecenal, (Z)-	Inert/GCMS artifact	5	NIST GCMS Library

9-Octadecenamide, (Z)-	Inert/GCMS artifact	5	NIST Library GCMS
9-Octadecene, 1-methoxy-, (E)-	Inert/GCMS artifact	5	NIST Library GCMS
Androstan-3-one, 11,17-dihydroxy-, (5.beta.,11.alpha.,17.beta.)-	Inert/GCMS artifact	5	NIST Library GCMS
Azulene	Inert/GCMS artifact	5	NIST Library GCMS
Benzedrex	Inert/GCMS artifact	5	NIST Library GCMS
Benzene, 1,2,4,5-tetramethyl-	Inert/GCMS artifact	5	NIST Library GCMS
Benzeneethanamine, N-[(pentafluorophenyl)methylene]-.beta.,3,4-tris[(trimethylsilyl)oxy]-	Inert/GCMS artifact	5	NIST Library GCMS
Benzeneethanol, .alpha.-methyl-3-(1-methylethyl)-	Inert/GCMS artifact	5	NIST Library GCMS
Benzoic acid, 2-(dimethylamino)ethyl ester	Fat/Lipid	4	PubChem / USDA DB
Benzoic acid, 2,4-bis[(trimethylsilyl)oxy]-, trimethylsilyl ester	Fat/Lipid	4	PubChem / USDA DB
Bicyclo[10.8.0]eicosa-1(12),14,18-triene	Inert/GCMS artifact	5	NIST Library GCMS
Butanenitrile	Inert/GCMS artifact	5	NIST Library GCMS
Butanoic acid, anhydride	Fat/Lipid	4	PubChem / USDA DB
Campesterol	Fat/Lipid	4	PubChem / USDA DB
Cholest-4-en-3-one	Inert/GCMS artifact	5	NIST Library GCMS
Cholest-4-en-3-one, 26-(acetyloxy)-	Inert/GCMS artifact	5	NIST Library GCMS
Cholest-5-en-3-ol, 24-propylidene-, (3.beta.)-	Inert/GCMS artifact	5	NIST Library GCMS
Cholest-5-ene-3-thiol, (3.beta.)-	Inert/GCMS artifact	5	NIST Library GCMS
Cholesterol 3.beta.-O-[2-chloroethyl]- ether	Fat/Lipid	4	PubChem / USDA DB
Cholesteryl 3-cyclohexylbutyrate	Fat/Lipid	4	PubChem / USDA DB
cis,cis,cis-7,10,13-Hexadecatrienal	Inert/GCMS artifact	5	NIST Library GCMS
Cyclodecasiloxane, eicosamethyl-	Inert/GCMS artifact	5	NIST Library GCMS

Cycloheptasiloxane, tetradecamethyl-	Inert/GCMS artifact	5	NIST GCMS Library
Cyclohexanecarboxylic acid, decyl ester	Fat/Lipid	4	PubChem / USDA DB
Cyclohexanecarboxylic acid, hexyl ester	Fat/Lipid	4	PubChem / USDA DB
Cyclohexanemethanol, 4-t-butyl-2-hydroxy-	Inert/GCMS artifact	5	NIST GCMS Library
Cyclohexasiloxane, dodecamethyl-	Inert/GCMS artifact	5	NIST GCMS Library
Cyclononasiloxane, octadecamethyl-	Inert/GCMS artifact	5	NIST GCMS Library
Cyclooctasiloxane, hexadecamethyl-	Inert/GCMS artifact	5	NIST GCMS Library
Cyclopentaneundecanoic acid, methyl ester	Fat/Lipid	4	PubChem / USDA DB
Cyclotetradecanone oxime	Inert/GCMS artifact	5	NIST GCMS Library
D:A-Friedooleanan-3-ol, (3.alpha.)-	Inert/GCMS artifact	5	NIST GCMS Library
Decanoic acid, 2-oxo-, methyl ester	Fat/Lipid	4	PubChem / USDA DB
Decanoic acid, decyl ester	Fat/Lipid	4	PubChem / USDA DB
Dibutyl phthalate	Inert/GCMS artifact	5	NIST GCMS Library
Dichlorvos	Pesticide	0	FAO/WHO Pesticide Manual
Diethylene glycol monododecyl ether	Inert/GCMS artifact	5	NIST GCMS Library
Di-n-octyl phthalate	Inert/GCMS artifact	5	NIST GCMS Library
d-Mannitol, 1-decylsulfonyl-	Inert/GCMS artifact	5	NIST GCMS Library
Docosanoic acid, methyl ester	Fat/Lipid	4	PubChem / USDA DB
Dodecane, 2,6,10-trimethyl-	Inert/GCMS artifact	5	NIST GCMS Library
Dodecanoic acid, 3-hydroxy-, ethyl ester	Fat/Lipid	4	PubChem / USDA DB
E,E,Z-1,3,12-Nonadecatriene-5,14-diol	Inert/GCMS artifact	5	NIST GCMS Library
E,E-2,13-Octadecadien-1-ol	Inert/GCMS artifact	5	NIST GCMS Library

			PubChem	/
E-11-Hexadecenoic acid, ethyl ester	Fat/Lipid	4	USDA DB	
	Inert/GCM		NIST	GCMS
Eicosane, 7-hexyl-	S artifact	5	Library	
			PubChem	/
Eicosanoic acid	Fat/Lipid	4	USDA DB	
			PubChem	/
Eicosanoic acid, 2,3-bis(acetyloxy)propyl ester	Fat/Lipid	4	USDA DB	
			PubChem	/
Eicosanoic acid, 2-ethyl-2-methyl-, methyl ester	Fat/Lipid	4	USDA DB	
			PubChem	/
Erucic acid	Fat/Lipid	4	USDA DB	
	Inert/GCM		NIST	GCMS
Ethanamine, 2,2'-oxybis[N,N-dimethyl-	S artifact	5	Library	
	Inert/GCM		NIST	GCMS
Ethanol, 2-(2-butoxyethoxy)-	S artifact	5	Library	
	Inert/GCM		NIST	GCMS
Ethanol, 2-(2-butoxyethoxy)-, acetate	S artifact	5	Library	
	Inert/GCM		NIST	GCMS
Ethanol, 2-(9,12-octadecadienyloxy)-, (Z,Z)-	S artifact	5	Library	
	Inert/GCM		NIST	GCMS
Ethanone, 1,1'-(1,3-phenylene)bis-	S artifact	5	Library	
	Inert/GCM		NIST	GCMS
Ethanone, 1,1'-(1,4-phenylene)bis-	S artifact	5	Library	
	Inert/GCM		NIST	GCMS
Ethanone, 1-[4-(1-methylethyl)phenyl]-	S artifact	5	Library	
	Inert/GCM		NIST	GCMS
Floxuridine	S artifact	5	Library	
	Inert/GCM		NIST	GCMS
Friedelan-3-one	S artifact	5	Library	
			PubChem	/
Fucosterol	Fat/Lipid	4	USDA DB	
	Inert/GCM		NIST	GCMS
Glycerol tricaprylate	S artifact	5	Library	
	Inert/GCM		NIST	GCMS
Heneicosane	S artifact	5	Library	
			PubChem	/
Heptacosanoic acid, methyl ester	Fat/Lipid	4	USDA DB	
	Inert/GCM		NIST	GCMS
Heptadecane, 2,6,10,15-tetramethyl-	S artifact	5	Library	
	Inert/GCM		NIST	GCMS
Heptadecane, 3-methyl-	S artifact	5	Library	
Heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl-	Inert/GCM		NIST	GCMS
	S artifact	5	Library	

	Inert/GCMS artifact	5	NIST Library	
Heptasiloxane, hexadecamethyl-				
Hexadecanoic acid, 1-[[[(2-aminoethoxy)hydroxyphosphinyl]oxy]methyl]-1,2-ethanediyl ester	Fat/Lipid	4	PubChem / USDA DB	
Hexadecanoic acid, methyl ester	Fat/Lipid	4	PubChem / USDA DB	
Hexadecanoic acid, trimethylsilyl ester	Fat/Lipid	4	PubChem / USDA DB	
Hexaethylene glycol monododecyl ether	Inert/GCMS artifact	5	NIST Library	GCMS
Hexanoic acid, heptadecyl ester	Fat/Lipid	4	PubChem / USDA DB	
Hexanoic acid, octadecyl ester	Fat/Lipid	4	PubChem / USDA DB	
Hexatriacontane	Inert/GCMS artifact	5	NIST Library	GCMS
Indeno[1,2-b]quinoxalin-11-one, 2-methyl-5-oxy-	Inert/GCMS artifact	5	NIST Library	GCMS
Longiverbenone	Inert/GCMS artifact	5	NIST Library	GCMS
Methyl (Z)-5,11,14,17-eicosatetraenoate	Inert/GCMS artifact	5	NIST Library	GCMS
Methyl tetradecanoate	Inert/GCMS artifact	5	NIST Library	GCMS
N-(3-Methylphenyl)-6-nitro-1,2-benzisothiazol-3-amine 1,1-dioxide	Inert/GCMS artifact	5	NIST Library	GCMS
N-(Trifluoroacetyl)-N,O,O',O''-tetrakis(trimethylsilyl)norepinephrine	Inert/GCMS artifact	5	NIST Library	GCMS
N1-Isopropyl-2-methyl-1,2-propanediamine	Inert/GCMS artifact	5	NIST Library	GCMS
Octacosane	Inert/GCMS artifact	5	NIST Library	GCMS
Octadecane, 1-(ethenyloxy)-	Inert/GCMS artifact	5	NIST Library	GCMS
Octadecane, 3-methyl-	Fat/Lipid	4	PubChem / USDA DB	
Octadecanoic acid	Fat/Lipid	4	PubChem / USDA DB	
Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester	Fat/Lipid	4	PubChem / USDA DB	
Octadecanoic acid, 2-oxo-, methyl ester	Fat/Lipid	4	PubChem / USDA DB	
Octadecanoic acid, 3-oxo-, methyl ester	Fat/Lipid	4	PubChem / USDA DB	

			PubChem /
Octadecanoic acid, methyl ester	Fat/Lipid	4	USDA DB
			PubChem /
Octadecanoic acid, octadecyl ester	Fat/Lipid	4	USDA DB
			PubChem /
Octanoic acid, 3,5-difluorophenyl ester	Fat/Lipid	4	USDA DB
Octasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	Inert/GCMS artifact	5	NIST GCMS Library
Olean-12-en-28-al	Inert/GCMS artifact	5	NIST GCMS Library
Olean-12-en-28-oic acid, 2.beta.,3.beta.,23-trihydroxy-, methyl ester	Fat/Lipid	4	PubChem / USDA DB
Olean-12-en-28-oic acid, 3-(acetyloxy)-, methyl ester, (3.beta.)-	Fat/Lipid	4	PubChem / USDA DB
			PubChem /
Oleic Acid	Fat/Lipid	4	USDA DB
Oxacyclotetradecane-2,11-dione, 13-methyl-	Inert/GCMS artifact	5	NIST GCMS Library
			PubChem /
Oxalic acid, allyl hexadecyl ester	Fat/Lipid	4	USDA DB
Oxirane, [(tetradecyloxy)methyl]-	Inert/GCMS artifact	5	NIST GCMS Library
			PubChem /
Pentadecanoic acid, 14-methyl-, methyl ester	Fat/Lipid	4	USDA DB
Pentadecanoic acid, 2,6,10,14-tetramethyl-, methyl ester	Fat/Lipid	4	PubChem / USDA DB
Pentaethylene glycol monododecyl ether	Inert/GCMS artifact	5	NIST GCMS Library
			PubChem /
Pentafluoropropionic acid, octadecyl ester	Fat/Lipid	4	USDA DB
			PubChem /
Pentafluoropropionic acid, tridecyl ester	Fat/Lipid	4	USDA DB
			PubChem /
Pentanoic acid, 2-methyl-, butyl ester	Fat/Lipid	4	USDA DB
Phenol, 2,4'-isopropylidenedi-	Inert/GCMS artifact	5	NIST GCMS Library
Phenol, 3,5-bis(1,1-dimethylethyl)-	Inert/GCMS artifact	5	NIST GCMS Library
Phosphorothioic acid, O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) ester	Pesticide	0	FAO/WHO Pesticide Manual
Propanoic acid, 2-methyl-, 3-hydroxy-2,4,4-trimethylpentyl ester	Fat/Lipid	4	PubChem / USDA DB
Propenal, 3-(1H-indol-3-yl)-2-phenyl-	Inert/GCMS artifact	5	NIST GCMS Library

Retinol	Vitamin	1	USDA Nutrient Database
Silane, trimethyl(1-methyldodecyloxy)-	Inert/GCMS artifact	5	NIST GCMS Library
Squalene	Inert/GCMS artifact	5	NIST GCMS Library
Stigmasterol	Fat/Lipid	4	PubChem / USDA DB
Tetracontane	Inert/GCMS artifact	5	NIST GCMS Library
Tetracosa-2,6,14,18,22-pentaene-10,11-diol, 2,6,10,15,19,23-hexamethyl-	Inert/GCMS artifact	5	NIST GCMS Library
Tetradecane, 6,9-dimethyl-	Inert/GCMS artifact	5	NIST GCMS Library
Tetratetracontane	Inert/GCMS artifact	5	NIST GCMS Library
Triacontane	Inert/GCMS artifact	5	NIST GCMS Library
Tributyrin	Inert/GCMS artifact	5	NIST GCMS Library
Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16)-diepoxy-	Inert/GCMS artifact	5	NIST GCMS Library
Tridecanoic acid, 3-hydroxy-, ethyl ester	Fat/Lipid	4	PubChem / USDA DB
Triethylene glycol monododecyl ether	Inert/GCMS artifact	5	NIST GCMS Library
Undecanal, 2-methyl-	Inert/GCMS artifact	5	NIST GCMS Library
Urs-12-en-28-oic acid, 3-hydroxy-, methyl ester, (3.beta.)-	Fat/Lipid	4	PubChem / USDA DB
Vinyl caprylate	Inert/GCMS artifact	5	NIST GCMS Library
Vinyl decanoate	Inert/GCMS artifact	5	NIST GCMS Library
Z,Z-2,13-Octadecadien-1-ol	Inert/GCMS artifact	5	NIST GCMS Library
Z,Z-2,5-Pentadecadien-1-ol	Inert/GCMS artifact	5	NIST GCMS Library
Z,Z-8,10-Hexadecadien-1-ol	Inert/GCMS artifact	5	NIST GCMS Library

3.2 Pesticide Detection

Two pesticide residues, dichlorvos and chlorpyrifos were identified representing 0.97% of the total 206 compounds detected. Dichlorvos eluted at RT 5.3 min while chlorpyrifos eluted at 11.6 min. The dichlorvos spectrum displayed characteristic fragment ions (notably m/z 109,220), with the

NIST library indicating dichlorvos (CAS 62-73-7) as the top hit. Similarly, the analyte eluting at RT 11.6 min matched across three independent NIST entries for chlorpyrifos (CAS 2921-88-2), with diagnostic ions at m/z 97,197,258, and 314. Alternative matches such as phorate sulfone, were less consistent with the fragment distribution, supporting the conclusion that the analyte was chlorpyrifos. The spectral library matching has been a reliable method severally reported in research (Kind & Fiehn, 2010; Stein, 1995).

The comprehensive qualitative profile of chemical constituents present in cowpea samples were identified across pooled market samples, enabling a structured categorization into 3 functional classes. Visualization in heatmap format facilitated comparison across sampling locations, emphasizing regional differences as well as shared chemical features.

Key aspect of this study design was the incorporation of a decision rule for pesticide quantification. Quantitative GC-MS would have been conducted if pesticide occurrence exceeded 5% of the total compounds. However, only two pesticide compounds were identified, representing 0.97% of the dataset. This low incidence indicates that pesticide residues, while detectable, were not a dominant chemical feature of the cowpea samples analyzed. Consequently, limiting the study to qualitative profiling was justified and consistent with the primary objective of characterizing the broader chemical landscape. Moreover, the low pesticide residues on the cowpea seed samples extracts could be due to increased adherence to pesticide application guidelines or due to retention of pesticide residues on the hulls of cowpea which may have been significantly reduced by dehulling; likely to reduce pesticide residue levels by about 80% to 100% (Anaemene et al., 2025).

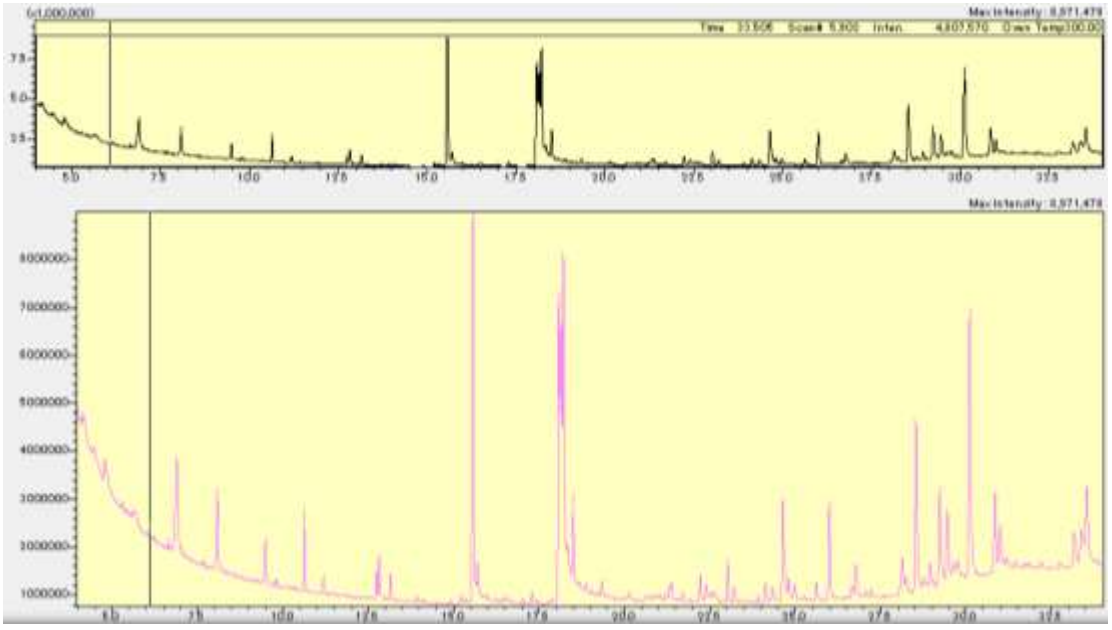

Figure 1. Representative GC-MS Total Ion Chromatogram (TIC) and Mass Ion Chromatogram (MIC) of Cowpea Extract form Location (KI2) Showing Dichlorvos Peak in Relation to The Broader Chemical Profile.

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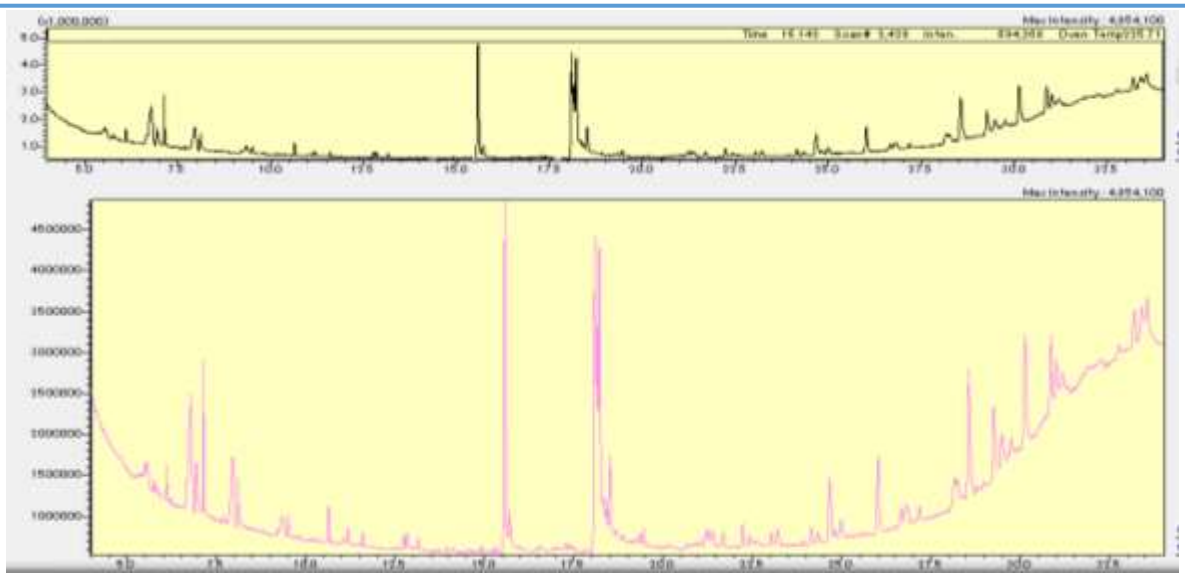
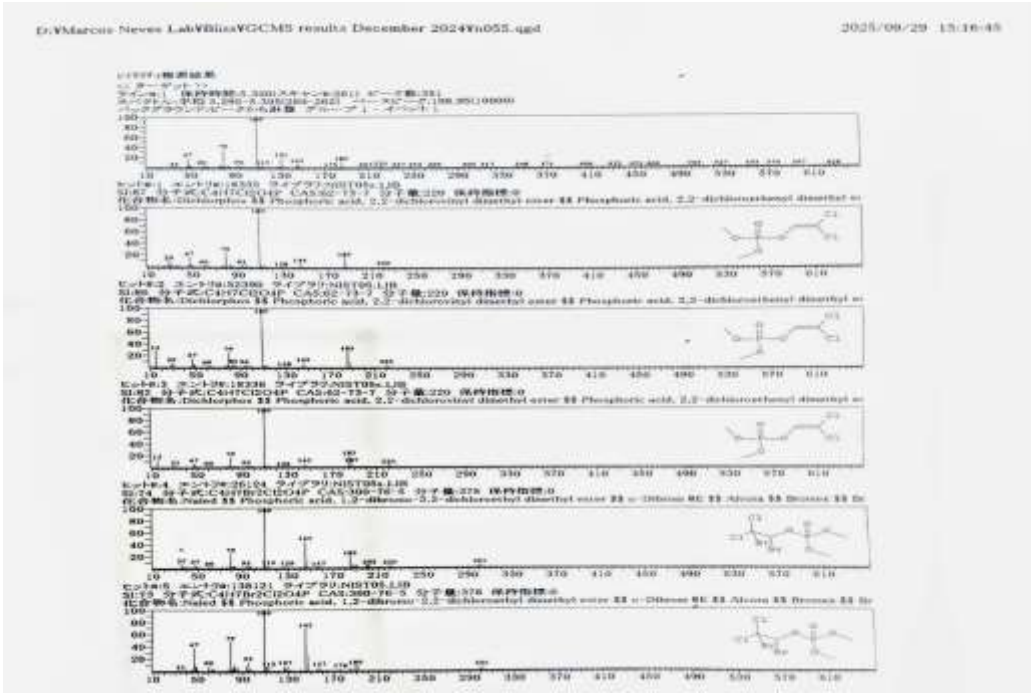


Figure 2. Representative GC-MS Total Ion Chromatogram (TIC) and Mass Ion Chromatogram (MIC) of Cowpea Extract form Location (NK1) Showing Chlorpyrifos Peak in Relation to The Broader Chemical Profile.



Source: Raw data

Figure 3. Mass Spectrum of Analyte at RT 5.3 min NIST Library Match Confirming Identification as Dichlorvos (CAS 62-73-7). Diagnostic Fragment Ions Include m/z 109 and 220.

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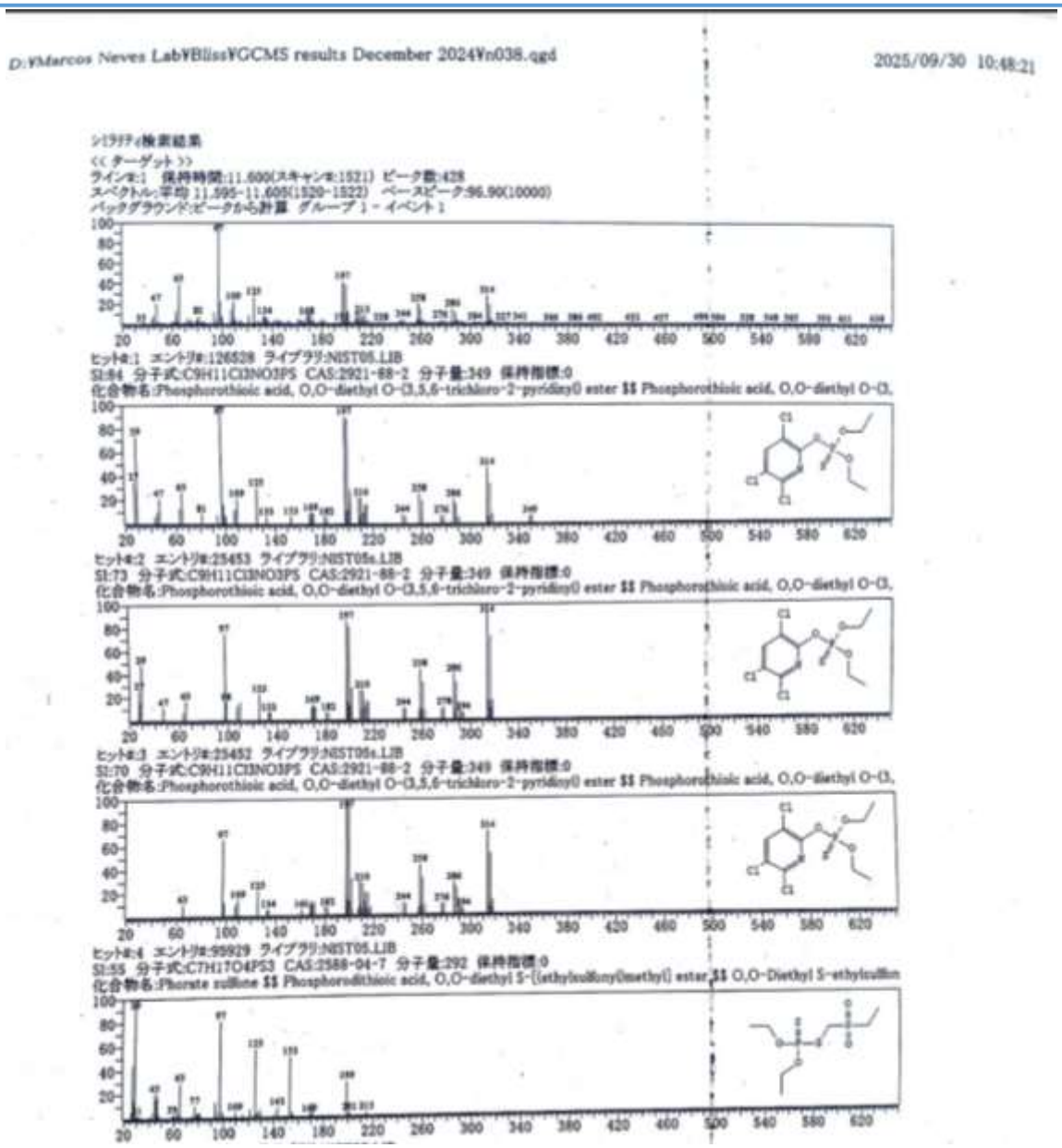

Figure 4. Mass Spectrum of Analyte at RT 11.6 min NIST library match Confirming Identification as Chlorpyrifos (CAS 2921-88-2). Characteristic ion include m/z 97, 197,258 and 314.

3.3 Chemical Profile of Cowpea Extracts

The predominance of non-pesticide compounds is particularly of relevance. Category 0 contained compounds of potential toxicological concern. The variation in categorical distribution between markets suggests that environmental factors, storage conditions, and handling practices may contribute to chemical differences observed across states. Categories 1 and 4 included naturally occurring bio-active constituents (vitamins and fat/lipids) consistent with cowpeas and detectable by GCMS which corroborates established nutritional micronutrients reported by (Odion & Usifoh,

2024). Category 5 were compounds with inert or intermediate biological significance which may be derivatives of industrial sources or by products of GCMS analytical reagents.

The relatively low incidence of pesticides contrasts with previous reports of significant residue burden in other legumes and cereals in sub-Saharan Africa (Eimiomodebheki Odion et al., 2020; Ndidi M. Ejoh et al., 2019) suggest that pesticides are being applied at the point of aggregation at major central storage facilities, hence the high MRLs previously recorded may not be due to PPPs applied majorly by the farmers. Also, the current data reflects an improvement in local pest management practices, variations in pesticide regulation, or differences in post-harvest handling. Nonetheless, even limited pesticide occurrence reinforces the importance of continued monitoring, given Nigeria's historical challenges with pesticide misuse and regulatory enforcement. (Akinyemi et al., 2024; Hassan et al., 2018; Oshatunberu et al., 2023)

The overall outcome reflects the analytical selectivity of GCMS rather than the complete nutritional composition of cowpea. GC-MS technique favors the detection of volatile and thermally stable compounds, such as fatty acid methyl esters, sterols, hydrophobic vitamins, and small xenobiotics. In contrast, proteins, polysaccharides, and minerals even though the major constituents of cowpea are nonvolatile and thermally labile hence may not be observed without extensive hydrolysis and derivatization. The extraction protocol, optimized for non-polar metabolites, further biases the output towards lipid and fat-soluble constituents. Although pesticide residues appeared sporadically, their detection is consistent with the known sensitivity of GC-MS for semi-volatile agrochemical contaminants. The clustering of vitamin E (gamma tocopherol) which is a fat-soluble antioxidant and retinol (vitamin A1) another fat-soluble vitamin consistent with seeds, nuts and some vegetables suggest the partial detectability of small bio active compounds, but water-soluble vitamins remain undetectable. The substantial fraction of inert or analytical derivatives/ artifact emphasizes the importance of critical data curation. GCMS provides high resolution insight into the lipidome and xenobiotic residues, complementary techniques such as LC-MS/MS, for amino acids, and sugars, ICP-MS for minerals, are essential for a holistic biochemical characterization of cowpea.

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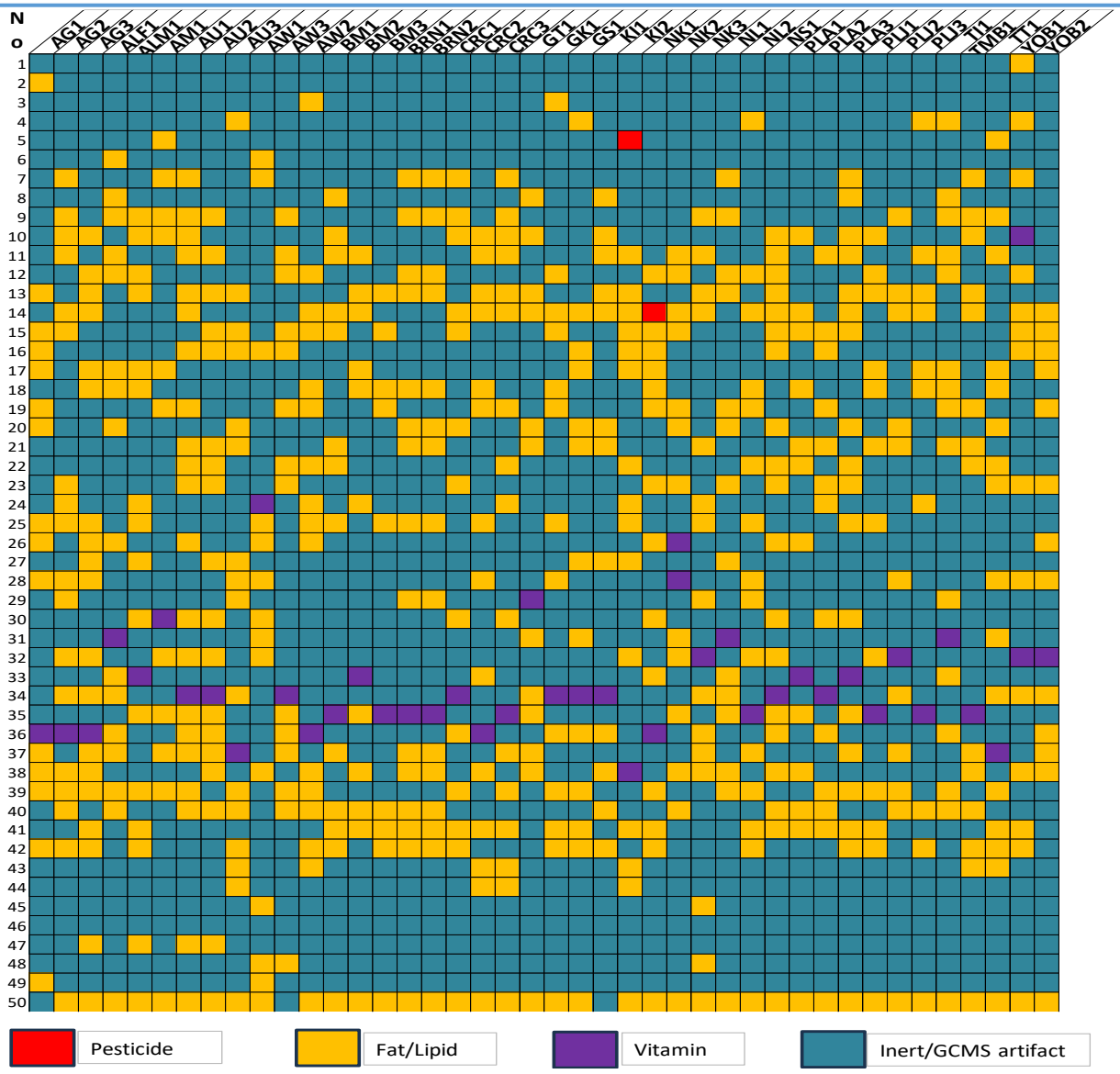

Figure 5. Heatmap of Compound Categories Identified by GCMS in Cowpea Samples from 12 Nigerian States

3.4 Accuracy and Reliability of the Methods

Several methodological features enhanced the accuracy of compound identification:

- QuEChERS extraction ensured effective recovery of polar and non-polar pesticides while minimizing matrix interference. (Anastassiades et al., 2003)
- Dual chromatographic monitoring (TIC + MIC) Reduced false positives and provided confirmatory evidence for pesticide residues.(Kind & Fiehn, 2010)
- NIST library machine gives robust Spectra identifications, strengthened by high similarity indices (Kind & Fiehn, 2010; Stein, 1995).

- PubChem cross-validation Provided A secondary layer of verification, allowing chemical classification into meaningful categories.
- Heat map visualization summarizes the chemical occurrence pattern, reinforcing the conclusion that pesticide residues were minor relative to bio active/natural compounds.

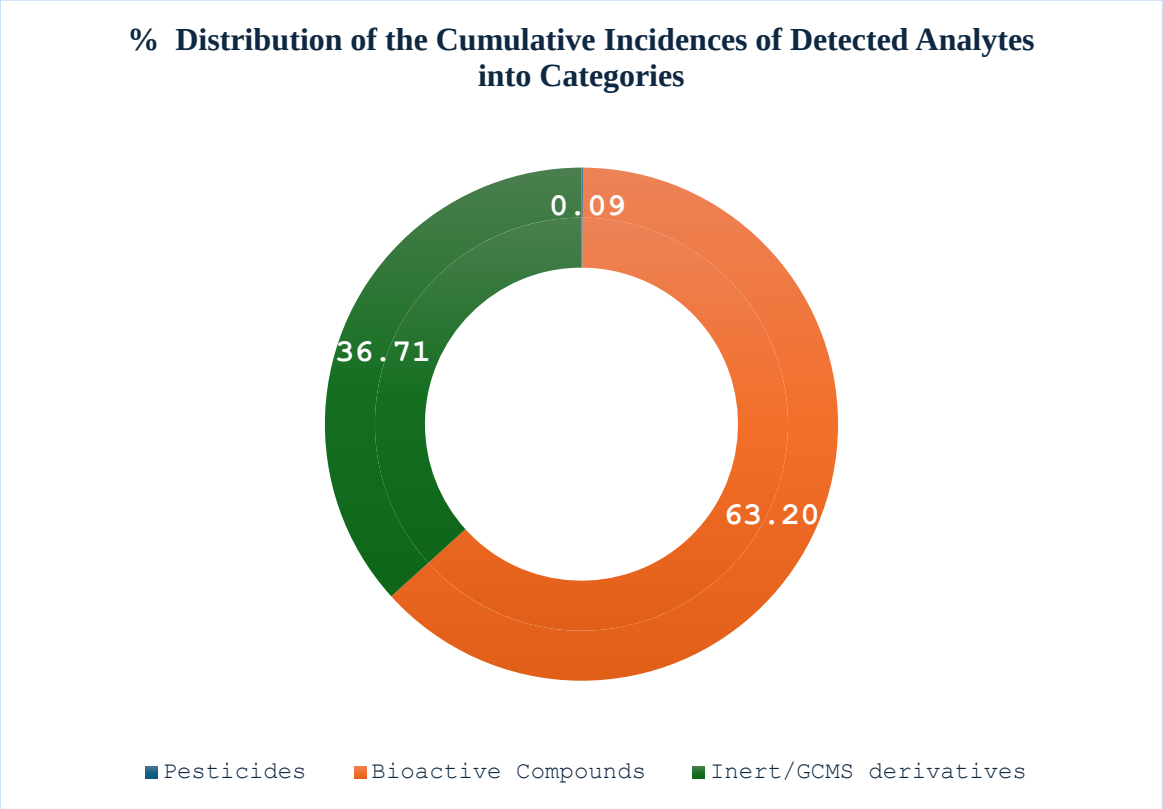

Figure 6. Cumulative Percentages of Chemical Categories of all GC-MS-identified Analytes

Collectively, this tiered strategy provided strong qualitative accuracy despite the study not being designed for quantification. The very low pesticide incidence (<1%) justified limiting the analysis to qualitative profiling, aligning with tiered surveillance strategies in food safety monitoring where quantitative confirmation is reserved for samples with high contaminant levels. Moreover, findings from this study corroborates recent reports of cowpea sampling and analysis using GC-MS/MS in some Nigerian states where pesticide incidences were within the EU stipulated MRLs (Okoro et al., 2025).

Methodologically, this study demonstrates the utility of qualitative GCMS combined with structured categorization and heatmap visualization. The approach allowed for rapid interpretation of complex datasets and identification of regional patterns. Although library-based identification provides valuable insights, (Stein, 1995) limitations include potential ambiguity with structural isomers or uncharacterized compounds. Continuous quality assurance monitoring is encouraged by researchers and food regulatory authorities to ensure timely detection of pesticides exceeding MRLs through strategic routine surveillance. Future research should incorporate confirmatory

analysis using authentic standards and extend to quantitative assays for compounds of toxicological interests especially when qualitative analyses are suggestive of high MRL incidence or unclear spectra of analytes.

The findings from this study express the importance of coupling broad spectrum chemical profiling with target contaminant surveillance. This dual strategy, which can be modified to accommodate more qualitative and quantitative data, ensures both nutritional insight and food safety assurance in staple crops such as cowpea.

4. CONCLUSIONS

This study characterized the chemical composition of cowpea samples across key cowpea producing Nigerian states using qualitative GC-MS, revealing a rich and diverse chemical profile with minimal evidence of pesticide contamination. The findings reinforce the safety and nutritional potential of cowpea across the analyzed samples. The standardized analytical procedures applied here provides a framework for chemical surveillance that can be extended beyond the cowpea value chain to other crops for nutritional value analysis and HACCP in food safety monitoring.

Recommendations

Generally, it is recommended that frequent pesticide residue analysis is conducted on staple food value chains across Nigeria to enable ease of traceability to the critical control points of pesticide induced contamination amongst other sources of food contaminant. It is ideal that educational and research institutions are mandated and funded to jointly conduct regular randomized quality assurance on diverse value chains, to create a reliable and consistent MRL database in Nigeria.

Further to this study, I recommend that subsequent studies on cowpea MRL with regards to resolving the EU ban on Nigerian cowpea should expand its scope to include quantitative analyses, seasonal variations, specie-pest susceptibility indices, post-harvest handling factors, and wider coverage of survey locations/ sample collection. As a matter of national priority, I recommend that relevant quality control regulatory Ministries, Departments and Agencies (MDAs) should identify, isolate and register farmers and storers who are specifically interested in producing in large scale for export purposes as an association of producers overseen and coordinated by such MDAs. This approach assures a secured value chain that can mitigate the risks of aggregator-induced adulterations, storage facility fumigation-induced contamination, batch compliance inconsistencies, and traceability ambiguities in Nigeria's export readiness and quality assurance.

Acknowledgement

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