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Concentration levels of organochlorine pesticides (OCPs) residue in soils of selected maize farms within Enugu State, Nigeria

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Abstract
This study was conducted to determine the concentration level of organochlorine pesticide residues in soils of selected maize farms in Enugu State, Nigeria. Composite soil samples (1 kg each) were taken from Glory maize farm, Nkwubor Road; Ogbodo maize farm, Akpuoga Nike; Igboanugo maize farm, Ugwuoba; and Agbo maize farm, Opi Nsukka. The samples, ground into powdered form, stored in appropriately labeled hermetic polyethylene bags prior to analysis. The soil samples were analyzed for organochlorine pesticide residue using gas chromatography coupled with an electron capture detector and according to the method of the Association of Analytical Chemistry. The data analysis was done using Ms-Excel 2007. The results obtained revealed that the total organochlorine pesticide residue in the studied soils was in the order: Ogbodo maize farm > Igboanugo maize farm > Agbo maize farm > Glory maize farm. Furthermore, the OCPs residue levels exceeded the Food and Agriculture Organization and the World Health Organization's acceptable limit for OCPs in agricultural soils. Also, the high levels could be due to the differences in the pesticide type, concentration, and accumulation. Correlation analysis revealed a weak and negative/inverse correlation between samples A and B ($r = -0.28013$), samples A and C ($r = -0.28438$), samples A and D ($r = -0.14569$), samples B and C ($r = -0.20784$), samples B and D ($r = -0.32812$), and samples C and D ($r = -0.09325$). Analysis of variance (ANOVA) showed that the organochlorine pesticides (OCP) residue variation is significant between the studied agricultural farmland soils ($p>0.05$). Based on the findings of this study, there is a dire need for promoting organic farming, proper implementation and amendment of pesticide-related laws.

Keywords: pesticides, accumulation, soil, organochlorine pesticides (OCPs), Enugu State

Introduction

Pesticides are chemical substances mainly used in agriculture to prevent, destroy, repel, and mitigate pests, weeds or diseases, and improve crop yield (Quintero et al., 2008; Qu et al., 2016; Mahugija et al., 2017). They have significantly contributed to the increased food production over the last few decades. However, the continuous use of pesticides in agriculture has led to increased environmental pollution of the soil, air and water, due to their toxicity, highly stablity, bio-accumulation, and a high affinity for lipids (Osibanjo & Adeyeye, 1995; Tao et al., 2009; Agboyi et al., 2015).

One of the most common pesticides used in developing countries such as Nigeria is the organochlorine pesticides (OCPs) which constitute about 35% of the pesticides used in farmlands (Mahugija et al., 2017). Historically, organochlorine pesticides (OCPs) such as dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs) have been extensively used globally between 1950 and 1980 as agricultural and domestic pesticides (Tieyu et al., 2005; Aktar *et al*., 2009; Zhang et al., 2012, Qu et al., 2017). The OCPs are a class of persistent organic pollutants (POPs) that are ubiquitous due to their inability to break down in the environment; resisting degradation by chemical, physical, microbiological, and biological means (National Center for Environmental Health (NCEH), 2005; Darko & Acquaah, 2007). Additionally, OCPs have half-lives ranging from months to years, and are a class of non-polar toxic chemical compounds containing carbon, hydrogen and chlorine, and are composed of five broad groups namely: the Dichloro-diphenyl-trichloro ethane (DDT) and analogues (e.g. dicofol, methoxychlor); the Hexacholrocyclohexane or Benzene hexachloride and their isomers (e.g. lindane, the Y- isomer); the Cyclodienes (e.g. chlordane, heptachlor, aldrin, dieldrin, endrin, endosulfan, isobenzan); the Chlordecones, Kelevan, Murex; and the Toxaphenes (Townsend & Specht, 1975; Pope et al., 1994; Castilho et al., 2000).

Furthermore, there are empirical evidences that OCP residues are toxic, bio-accumulates in the fatty tissues of exposed animals and humans and may be responsible for a wide variety of health effects even at low concentrations (USEPA, 2012; Agboyi et al., 2015; Eze et al., 2020). Moreso, acute and chronic health effects such as irritation of the skin and eyes, affecting the nervous system, mimicking hormones, causing reproductive problems, cancer, neurological effects, birth defects, fetal death, and neurodevelopment disorders, are short-term or long-term health effects associated with the OCPs (Castilho et al., 2000; Ngowi, 2002; Aktar et al., 2009; Sarwar, 2015; Eze et al., 2021).

A review of literature suggests that many studies on the adverse effects of accumulation of the OCP residues in soils and food crops have been carried out by Nigerian researchers (Tao et al., 2009; Aktar et al., 2009; Agboyi et al., 2015; Qu et al., 2016; Mahugija et al., 2017). However, there are only a few documented studies on the concentration level of organochlorine pesticide residues in agricultural soils and this study was conducted to fill the knowledge gap.

Materials and Methods

Description of the study area

Experimental farmlands are located in some selected local government areas in Enugu State, which is located in the southeastern region of Nigeria (Figure 1). Farmland soil samples were obtained from four popular maize farms in Enugu State: Glory maize farm (Sample A), Nkwubor; Ogbodo maize farm (Sample B), Akpuoga Nike; Igboanugo maize farm (Sample C), Ugwuoba; and Agbo maize farm (Sample D), Opi Nsukka.

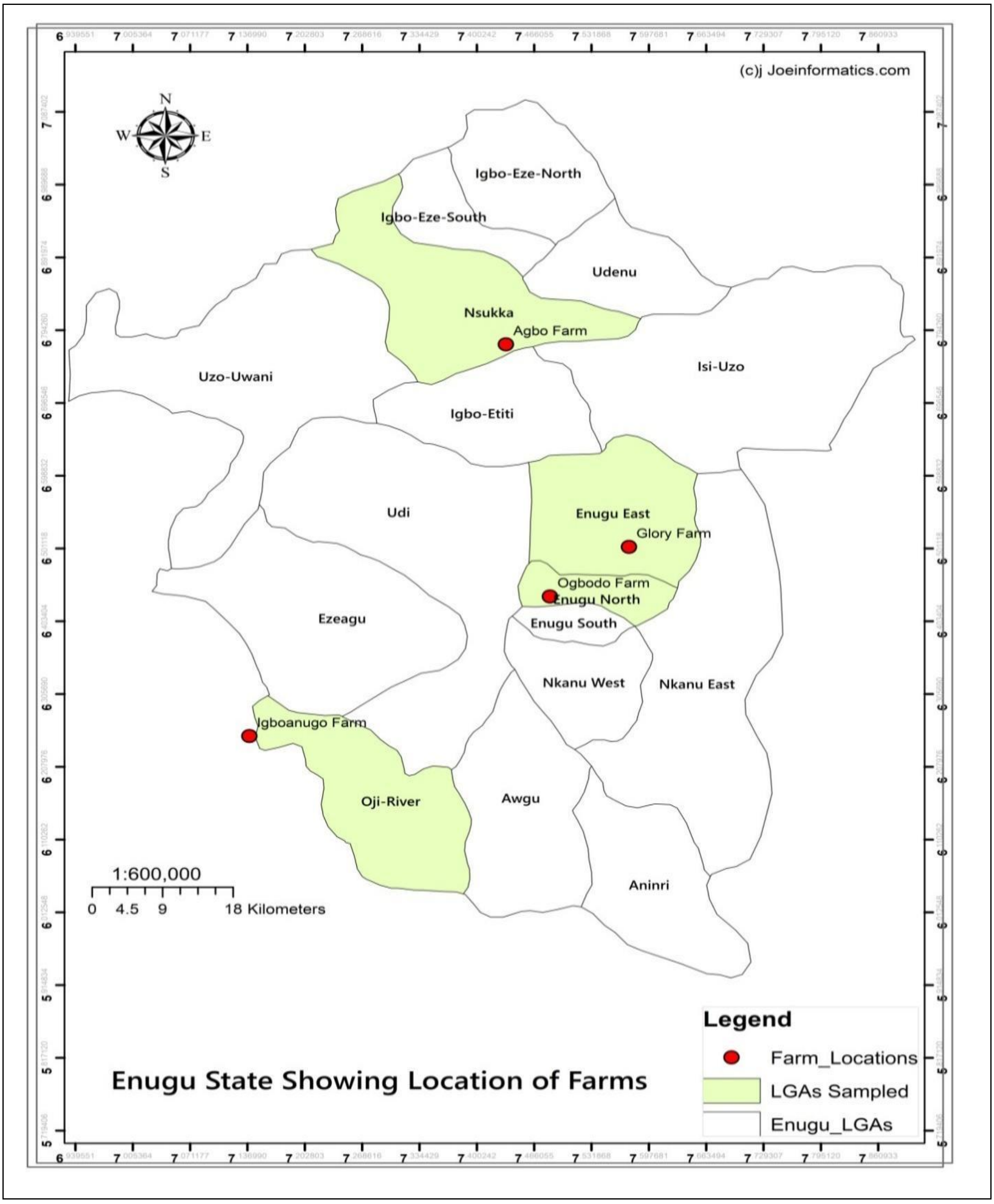

Fig 1: Map of Enugu State showing the farmland locations

Sample Collection and Preparation
Soil samples (1 kg each) were taken from the selected farmlands within the sampling locations in the study area. The selected farms were: Glory maize farm, Nkwubor; Ogbodo maize farm, Akpuoga Nike; Igboanugo maize farm, Ugwuoba; and Agbo maize farm, Opi Nsukka. The samples were bagged in hermetic polyethylene bags, labeled appropriately.These samples were air-dried and later ground into powdery form, and then properly labelled and stored in clean, separate hermetic polyethylene bags until required for analysis. At each sampling site, a representative 1 kg sample was bagged for that farm and appropriately labelled.

Sample Extraction and Clean-up
A wide range of extraction techniques have been used for the extraction of pesticides from various samples. In this study, the extraction of the pesticide residues from the soil samples was done by the modified version of the quick, easy, cheap, effective, rugged, and safe (QuEChERS) method at the pesticide residue laboratory of Standard Authority. Composite samples were collected from each of the maize farms. About 20 g was homogenized and pulverized to powdered form and weighed using a Mettler Toledo PG 1003-S mass balance into a 50 mL centrifuge tube. After that, 10 ml of cold, deionized water and acetonitrile were added. The mixture was then vortexed for one minute using a Thermolyne max mix plus. A mixture of QuEChERS salts was then added [4 g of anhydrous MgSO4 plus 1 g NaCl, 1 g Trisodium Citrate Dihydrate (TSCD), and 0.5 g of disodium hydrogen citrate sesquihydrate (DHS)]. The mixture was vortexed for a further one minute and then centrifuged for five minutes at 3000 rpm. Furthermore, the sample extracts were then purified using the Dispersive Solid Phase Extraction (SPE) method. An aliquot (6 ml) of the extracts were transferred into a polypropylene (PP) centrifuge tube containing 150 mg of primary and secondary amine (PSA) and 900 mg of $MgSO_4$. The mixture was vortexed for 1 minute and centrifuged for 5 minutes at 3000 rpm. Then, 4 ml of the supernatant (clean extract) was transferred into a volumetric flask. To adjust the pH, 40 µL of 5% formic acid in acetonitrile (v/v) was added. The filtrate was then concentrated to dryness at about 35 ^{0}C in a rotary evaporator. The dry concentrate was then redissolved in ethyl acetate (1 ml) plus 20 L of 1% polyethylene glycol, then transferred into a 2 ml standard opening auto sampler vials for quantification by GC-ECD for organochlorines and GC-MS for atrazine.

Sample Analysis using GC-FID
The soil samples were analyzed using the method of the Association of Analytical Chemistry, AOAC (1990). 1ml of filtered residue was dissolved in 50 ml of chloroform and transferred to a 100 ml volumetric flask and dilute to the mark. Most of the chloroform was evaporated at room temperature. This was followed by the addition of 1 ml of the reagent (20 vol% benzene and 55 vol% methanol). It was then sealed, and heated at a temperature of 40^{o}C in a water bath for 10 minutes. After heating, the organic sample was extracted with hexane and water so that the final mixture of the reagent, hexane and water, was in the proportion of 1:1:1 (that is,1 ml each of hexane and water was added to the reaction mixture). The mixture vigorously shaken by hand for 2 min. until a stable emulsion was formed; then broken by centrifugation means. About half of the top hexane phase was transferred to a small test tube for injection. Care was taken to remove only the organic layer. Direct injection from the reaction vial was avoided because of the risk of injecting water. Water can ruin the GC column. Similarly, a standard was prepared by injecting 10ul of the sample into the gas chromatographic column and the retention time compared with retention time of standard.

Quality Control/Quality Assurance
Quality control and quality assurance as prescribed by the CODEX Alimentarius Committee were incorporated into the analytical scheme. Quality assurance measures applied in the laboratory include rigorous contamination control procedures (strict washing and cleaning procedures), monitoring of blank levels of solvents, equipment, and other materials, and including blanks and duplicates in the analysis and re-calibration standards run frequently to check the integrity of the calibration curve. An aliquot (50 ml) of each solvent was concentrated to 1 ml and analysed to check the contamination from the reagents. The quality of analytical methods was assessed by recovery experiments. Sand matrices that had been assayed and were known to have no detectable levels of pesticides were used for recovery tests. The validation and chemical recoveries were estimated by spiking pesticides-free soil sample blanks with pesticides standards overnight before extraction. Samples were extracted and cleaned-up as described above and subsequently analysed by GC-ECD. The percentage recovery was calculated using the formula:

$$\text{Recovery (\%)} = \frac{\text{Conc. of pesticide residue recovered from spiked sample}}{\text{Conc. of pesticide added to sample}} \times 100$$

Data analysis
The data analysis in this study was done using Ms-Excel 2007. At a 5% level of significance, analysis of variance (ANOVA) was used to establish a relationship between the OCP residue concentrations in the studied farmland soils.

Results and Discussions

Concentration levels of the Organochlorine Pesticide (OCP) Residues in Soils

The concentration of the pesticides in agricultural soils from Glory maize farm (sample A), Ogbodo maize farm (sample B), Igboanugo maize farm (sample C), and Agbo maize farm (sample D) are presented in Table 1. The organochlorine pesticide residues detected are Isopropylamine, 2,4- Dichoro Ethane, Hcb, Lindane, G-Chlorodane, Carbufuran, Chloropyfos and Glyphosphate. The mean concentrations of Isopropylamine in Glory maize farm, Ogbodo maize farm, Igboanugo maize farm and Agbo maize farm are 0.111 ug/g, 0.004 ug/g, 0.016 ug/g and 0.123 ug/g respectively. 2,4- dichoro ethane concentrations in the studied soils are 0.072 ug/g, 0.096 ug/g, 1.138 ug/g and 0.030 ug/g respectively. Hcb concentrations in the studied soils are 0.046 ug/g, 0.220 ug/g, 0.397 ug/g and 0.574 ug/g respectively. Lindane concentrations in the studied soils are ND, 0.765 ug/g, 0.456 ug/g and 0.030 ug/g respectively. G-Chlorodane concentrations in the studied soils are 0.055 ug/g, 0.220 ug/g, 0.378 ug/g and 0.034 ug/g respectively. Carbufuran concentrations in the studied soils are 0.056 ug/g, 0.978 ug/g, 0.235 ug/g and 0.020 ug/g respectively. Chloropyfos concentrations in the studied soils are 0.081 ug/g, 0.657 ug/g, 0.345 ug/g and 0.053 ug/g respectively. Glyphosphate concentrations in the studied soils are 0.178 ug/g, 0.456 ug/g, 0.234 ug/g and 0.048 ug/g respectively. Generally, the organochlorine pesticide levels exceeded the Food and Agriculture Organization and the World Health Organization’s acceptable limit for pesticides in agricultural soils (WHO, 2010). It is worth noting that the variations in the OCPs residue in the studied soils were influenced by the differences in pattern of pesticide usage; and that could determine the fate of the pesticides in the soil and environment. Furthermore, the total organochlorine pesticide residue in the studied soils was in the order: Ogbodo maize farm (sample B) > Igboanugo maize farm (sample C) > Agbo maize farm (sample D) > Glory maize farm (sample A). Additionally, the total concentration of organochlorine pesticide residue was highest in Ogbodo maize farm. This could be due to the differences in the pesticide type, concentration, and accumulation, which subsequently resulted in pollution of the soils within and around the maize farm (WHO, 2010; Onuwa et al., 2017; Mwanja et al., 2017).

Table 1: Concentrations of organochlorine pesticide residue in soil samples (ug/g)

Pesticides	Sample A	Sample B	Sample C	Sample D	Mean±SD	Minimum	Maximum
Isopropylamine	0.111	0.004	0.016	0.123	0.063±0.06	0.004	0.123
2,4- Dichoro Ethane	0.072	0.096	1.138	0.030	0.334±0.54	0.030	1.138
Hcb	0.046	0.220	0.397	0.574	0.309±0.23	0.046	0.574
Lindane	ND	0.765	0.456	0.030	0.313±0.37	0.00	0.765
G-Chlorodane	0.055	0.220	0.378	0.034	0.172±0.16	0.034	0.378
Carbufuran	0.056	0.978	0.235	0.020	0.322±0.45	0.978	0.020
Chloropyfos	0.081	0.657	0.345	0.053	0.284±0.28	0.053	0.657
Glyphosphate	0.178	0.456	0.234	0.048	0.229±0.17	0.456	0.048

ND- Not Detected (Below Detection Limit)

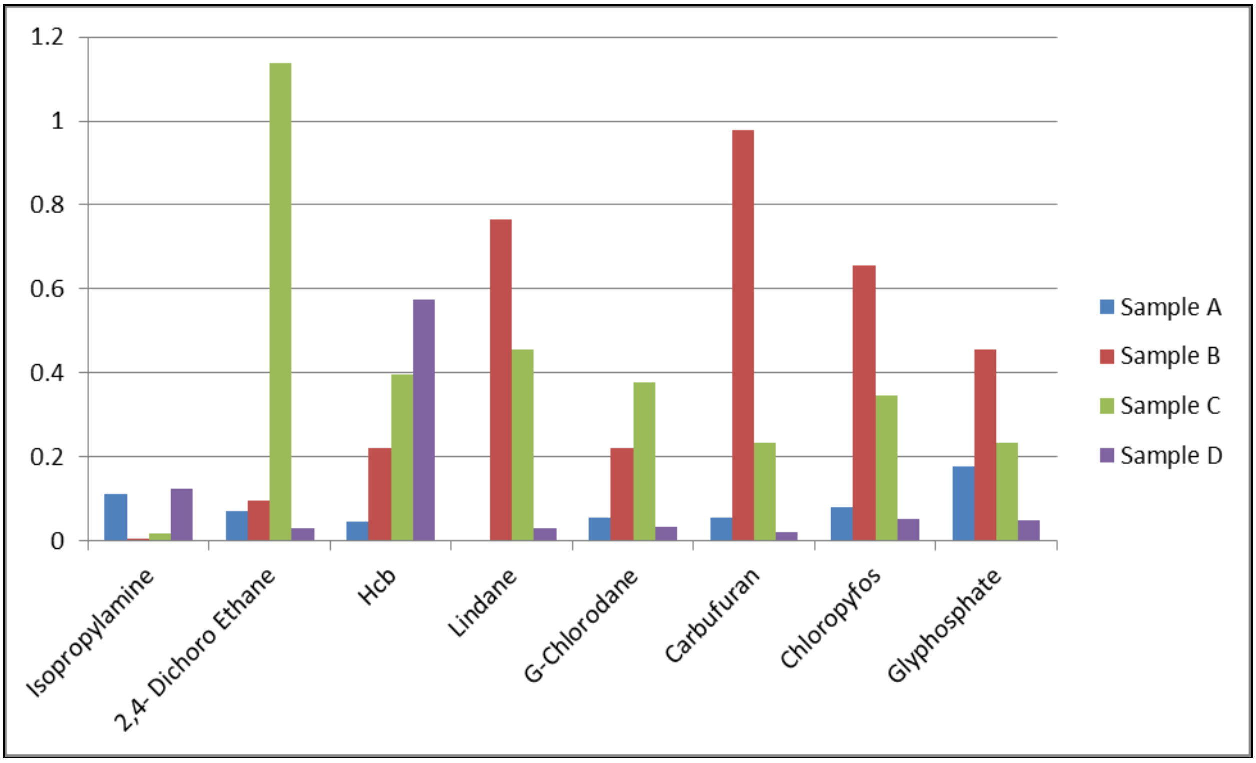

Fig 2: Organochlorine pesticide residue in soils

Correlation analysis

In this study, the degree of linear association between the pesticides in the studied agricultural soils was measured by the simple correlation coefficient (r), and the values are presented in Table 2. The results of the correlation analysis revealed a weak and negative/inverse correlation between samples A and B (r = -0.28013), samples A and C (r = -0.28438), samples A and D (r = -0.14569), samples B and C (r = -0.20784), samples B and D (r = -0.32812), and samples C and D (r = -0.09325). A strong and positive correlation (0.50 – 0.99) between two variables implies that an increase in one variable causes the other variable to increase.

Table 2: Correlation between the soils in the maize farms

	Sample A	Sample B	Sample C	Sample D
Sample A	1			
Sample B	-0.28013	1		
Sample C	-0.28438	-0.20784	1	
Sample D	-0.14569	-0.32812	-0.09325	1

Analysis of variance (ANOVA)

The results of the two-way analysis of variance ANOVA showed that the organochlorine pesticide (OCP) residues variation is significant between the studied agricultural farmland soils ($p>0.05$).

Conclusion

Organochlorine pesticide residues were found in high concentrations in all the studied maize farms in Enugu State, Nigeria. The total concentration of organochlorine pesticide residue was highest in Ogbodo maize farm (sample B), while the least was observed in Glory maize farm (sample A). Furthermore, the organochlorine pesticide concentrations exceeded the Food and Agriculture Organization and the World Health Organization's acceptable limit for pesticides in agricultural soils. This implies that consumption of food crops such as maize, cassava, rice and yam, cultivated on the studied soils poses health hazards due to translocation of pesticides to the plants. Based on the findings of this study, there is a dire need for promoting organic farming, proper implementation and amendment of pesticide-related laws.

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