

**Determination of Pesticide Residues in Edible Crops and Soil from University of
Agriculture Makurdi Farm Nigeria
Part 1 in the series of pesticide residues**

Abstract

Aims: To extract pesticide residues in some edible crops and soils from farm lands so as to determine their concentration in order to assess their safety status

Study Design: Solid-Phase extraction technique was used to extract pesticides content mainly of organochlorine class from some edible crop plants and soils as well as determining some main physicochemical parameters of the soils.

Place and Duration of Research: University of Agriculture, Makurdi commercial crop farms from in the month of July, 2015.

Methodology: Pesticide residues were extracted from edible crops (*Daucus carota*, *Capsicum Anuum*, *Telfairia occidentalis*, *Solanum lycopersicum*, *Amaranthus Hybridus*, *Solanum macrocarpon*) and soils using dispersive solid-phase extraction method. The extracts were analysed using GC-MS technique

Results: The mean concentration (mg/kg) of pesticides in soil samples were 12.1 ± 0.1 , 0.09 ± 0.02 , 0.12 ± 0.02 , 14.9 ± 0.2 and 5.05 ± 0.2 for butachlor, aldrin, dieldrin, pendimethalin and propanil, respectively. Pesticides concentration in vegetables ($\mu\text{g/kg}$) generally ranged from 0.001 ± 0 - 1.64 ± 0.6 , the highest value being cypermethrin and the least alpha-HCH. Their concentrations in each sample ranged in this order; *D. carota* (1.62 ± 0.01 - 0.001 ± 0); *C. Anuum* (1.63 ± 0.7 - 0.002 ± 0.001); *T. occidentalis* (1.64 ± 0.6 - 0.001 ± 0.001); *S. lycopersicum* (0.84 ± 0.7 - 0.002 ± 0.01); *A. Hybridus* (1.61 ± 0.5 - 0.001 ± 0); *S. macrocarpon* (1.62 ± 0.01 - 0.001 ± 0), respectively.

Conclusion: Cypermethrin showed the highest concentration values in all vegetable samples while alpa-HCH has the least. Although all samples showed values within WHO maximum residue limits (MRLs) for spices, indicating that they are transiently safe, but it is necessary to have prolonged seasonal monitoring.

..

Keywords: Edible crops, Organochlorine, residues, soil, solid phase extraction

1. Introduction

Much Concerns have been raised about risks of pesticide residues in food as most pesticides show a high degree of toxicity, especially in developing countries like Nigeria, where the European Union places a ban on some agricultural commodities for some times now. Food items banned from Europe till June 2016 include beans, sesame seeds, melon seeds, dried fish and meat, peanut chips and palm oil [1]. According to the European Food Safety Authority, the prohibited beans were found to have concentration of dichlorvos ranging from 0.03 to 4.6 mg/kg, where as the acceptable maximum residue limit is 0.01mg/kg [1]. Pesticides are formulated to eliminate certain organisms but they also generate some risks within the environment. Human health is often threaten by the presence of pesticides in vegetables and soils. Some of the pesticides of interest include cypermethrin (α -cyano-3-phenoxybenzyl-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarbo- ylate), butachlor, aldrin, dieldrin, pendimethalin and propanil and alpa-HCH. Cypermethrin belongs to a class of pesticides known as synthetic pyrethroid and it is generally used in combating insects in commercial agricultural practice. It is also used in consumer products for subsistence purposes [2]. Ectoparasites of cattle, sheep, and poultry are sufficiently controlled by the application of cypermethrin [3]. It is applicable in veterinary medicine for effective control of ticks on dogs (Somasani, 2014). It acts as a neurotoxin in insects. It can be broken down with ease on soil and plants but its effects can be felt for some weeks if it is applied to indoor inert surfaces [2]. When it is exposed to sunlight, water and oxygen, its rate of decomposition is facilitated. Cypermethrin is a very toxic pesticide to fish, bees and aquatic insects. Cypermethrin has relatively low dermal toxicity or when ingested. High exposure to it causes nausea, headache, muscle weakness, salivation, shortness of breath and seizures [4]. Measurement of metabolites of the urine serves as means of monitoring how much workers are exposed to the pesticide, while quantitation of cypermethrin present in blood or plasma may be confirmed by excessive dosage [5]. Aldrin as an organochlorine insecticide was generally available until the 1970s, when its use was sanctioned in most countries. However, it is still in use till now especially in some developing countries. Before aldrin was phased out, it was seriously deployed as a pesticide for treating seed and soil. Aldrin and related "cyclodiene" pesticides were well known as persistent organic pollutants [6]. Dieldrin is an organochloride originally produced as an insecticide in 1948. Dieldrin is similar to aldrin, which reacts further to form dieldrin [7]. Alpha-Hexachlorocyclohexane (α -HCH) is also an organochloride which is

one of the isomers of hexachlorocyclohexane (HCH) [3]. It results from the production of lindane (γ -HCH) and it is still contained in commercial grade lindane which is used as insecticide. Lindane. United States has stopped the use of lindane for more than 20 years [8]. Lindane is a white, powdery solid substance, stable at ambient temperatures. The Stockholm Convention on Persistent Organic Pollutants classified (α -HCH) and (β -HCH) as Persistent organic pollutants (POPs), since 2009 due to the chemical's ability to remain for a long time in the environment, bioaccumulative, biomagnifying, and long-range transport capacity. Solid phase extraction (SPE) is one of the most commonly used sorbent techniques in analyzing pesticide residues. It has to do with the omission of extracts containing target analytes through a column filled with the desirable sorbent (which was previously conditioned by an appropriate solvent or solvent mixture), or passing the required solvent through the SPE column to which a suitable amount of sample was previously added) [9]. The coextractants from the SPE column can be eluted successfully if selective solvent are used, and then the target analytes or the elution of analytes can be direct, where undesirable coextractants derived from the sample matrix remain in the SPE column. SPE has many attractive features when compared with the traditional methods of extraction. It is easy to operate, less costly; it is being automated and uses small amounts of solvent [9]. Apart from this, SPE is the multifunctional techniques, since the purification and the concentration occur in the same step. However, some limitations are associated with, SPE technique. This has to do with lower yields (recovery), i.e. slightly lower sensitivity, in situations where there is "clogging" of the SPE column (blocking of the sorption centers by solid and oily components originating from the sample) [9]. The matrix nature has much influence on the SPME efficiency. Since the analytes distribution coefficients are partially determined by analytes-matrix interaction, appropriate matrix modification can increase the analytes partition coefficients. For instance, the presence of chloride and sulfate ion increases the ionic strength of the solution, which makes a large number of compounds less soluble [10]. The amount of analytes that would be adsorbed on the fiber will depend on the thickness and polarity of the active fiber layer, sampling mode (direct sampling -microextraction (DM-SPME) from solution, and headspace sampling-microextraction (HS-SPME) from gas phase, the nature of the sample and the analyte (analyte polarity, its molecular weight, pH value, nature of matrix), the mode and speed of the sample mixing, the solid phase micro-extraction (SPME) duration, the temperature at which it is performed, [11]. The most commonly used SPE sorbents in pesticide residues

determination are: reverse-phase octadecyl (C_{18}), normal-phase aminopropyl ($-NH_2$) and primary-secondary amine (PSA), anion-exchanger three-methyl ammonium (SAX) and adsorbents such as graphitized carbon black (GCB). Normal-phase sorbents such as florisil ($MgSiO_3$), aluminum oxide (Al_2O_3) and silica (SiO_2) are usually used in combination with the previously mentioned sorbents. The SPE cartridge should be chosen depending on the physicochemical properties of pesticides that are searched for in a particular sample, and the nature of the sample matrix. Researches indicate that the GCB sorbent is suitable for extraction of compounds of different polarity, and that it causes retention of pigments (carotenoids and chlorophylls) and sterols, and now are widely used for purification of plant extracts [12; 13]. On the other side, PSA sorbent proved to be effective in removing polar compounds and fatty acids, while the SAX is suitable for the removal of fatty and other organic acids and sugars [14]. Activated charcoal proved to be a good solution for removal of pigments from tomato extracts [15], and cabbage and carrots [16], while the florisil gave good results in pyrethroids determination in lettuce, cabbage, cauliflower, carrot, green pepper and green beans [17]. The most of the SPE methods are based on a combination of two or three cartridges. As GCB is suitable for removal of lipids, waxes and other nonvolatile, non-polar coextractants with high molecular weight, it is usually used in combination with other sorbent. SPE technique was used by [18] for determination of 446 pesticides in some vegetable crops in Ghana and found out that the C_{18} /GCB/ $-NH_2$ combination was the best. Except for slightly lower recoveries obtained for onion and leeks, the method was shown as good choice for all other samples) [9]. Pesticide residues have been determined in several food crops in Nigeria. This study aimed at adding another step in pesticide residues determination in commonly cultivated food crops within the university community as to ascertain their consumption safety and potential efficacy in agricultural markets as income drive of the university and state so as to advise the targeted consumers appropriately.

2. Study Area

The study was carried out at University of Agriculture commercial rice and vegetable farm sites designated as study site 'A' and 'B' respectively which are about 500 m apart. 'A' covers an area of 210 m (700 ft) long and 180 m (600 ft) width, while site 'B' covers an area of 77 m (258 ft) in length and 76 m (265 ft) width. The two sites A and B lie within latitude $7^{\circ} 47' 0''N$, longitude $8^{\circ} 44' 40''E$ and latitude $7^{\circ} 39' 10''N$, longitude $8^{\circ} 49' 46''E$, respectively. These areas are

found in the flood plain of river Benue which are usually surrounded by a large mass of sand stone and alluvium. The study areas were also found to be covered by a large deposits sandy soil, silt and laterites. The main crops commonly cultivated in sample site B include *Telfaria occidentalis* (Fluted Pumpkin) locally called *Ugwu*, *Solanum lycopersicum* (tomatoes), *Amaranthus hybridus* (African spinach) commonly called 'green', *Solanum macrocarpon* (Garden egg), *Daucus carota* (Carrot plant), *capsicum* (red bell pepper) [fruits and leaves] locally called *Tar tase* soya beans etc.

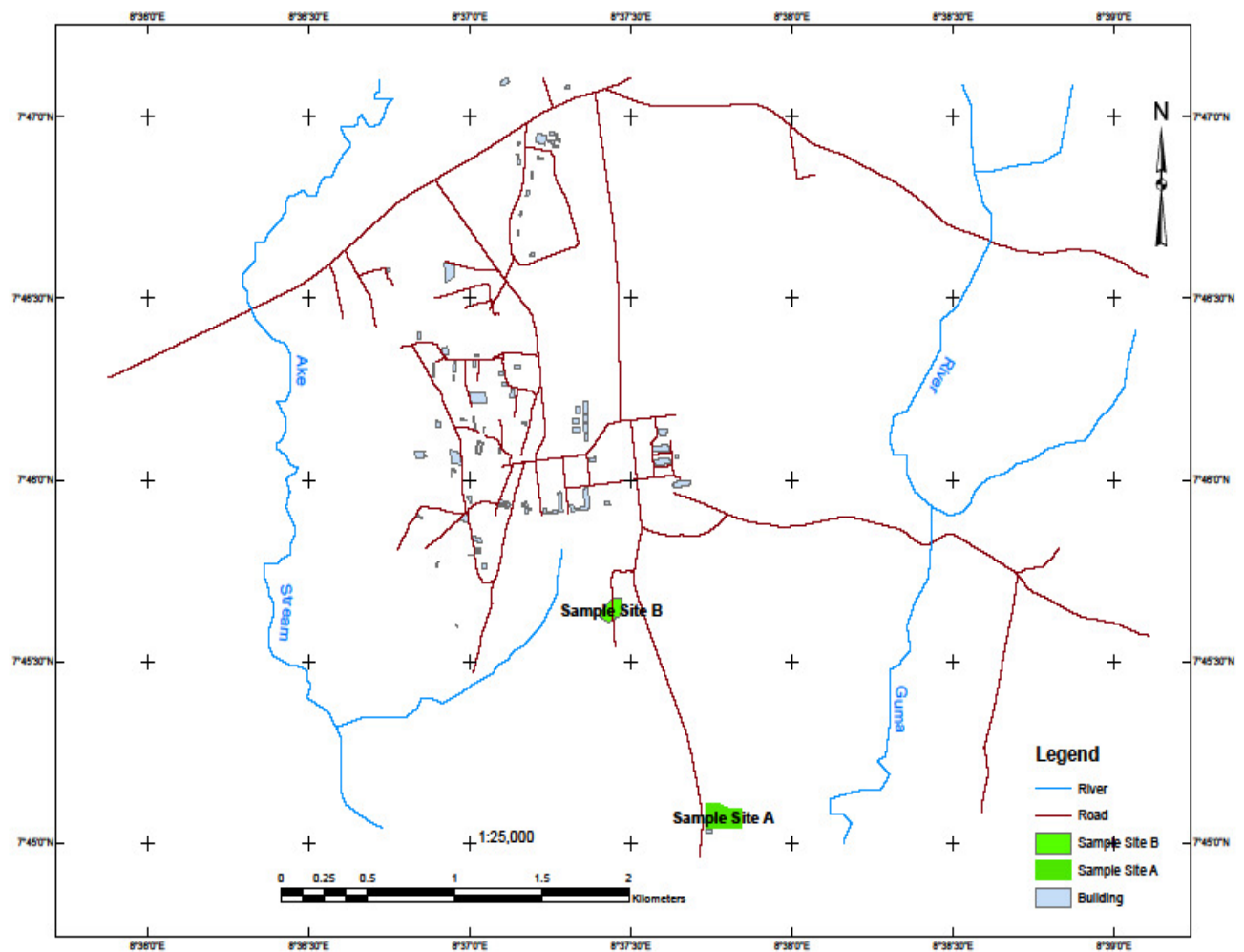


Figure 1: Map of South Core, University of Agriculture, Makurdi showing the Sampling Sites

3. Materials and Methods

Analytical grade acetone, sodium sulphate, ethyl acetate, n-hexane, sodium bicarbonate, silica gel and Florisil were supplied by Central Drug House (CDH), India. Pesticide quantification was achieved by using a GC-MS (Shimadzu QP-2010).

Laboratory Materials

All reagents were of analytical grade except otherwise stated

Sample Collection

(a) Soil Samples

Multiple soil samples were collected in July, 2015, within a depth of 0-15 cm layer using soil auger of 20.7 cm or 8.2'' claw length. Each soil sample was a composite of fifteen subsamples of soil collected using random sampling method within a grid from a particular sample point and was mixed thoroughly together to obtain a homogenized representative sample. A grid was also established by locating the approximate centre of the field (rice farm) and dividing the farm in to three rows and columns, respectively, having a total of nine (9) paces apart according to a method by [19] was established. Materials like roots, stones and pebbles were removed and bulked. The bulk sample was reduced to about 1 kg by dividing the thoroughly mixed sample into four equal parts. The two opposite quarters were discarded while the remaining two quarters were remixed and the process was repeated until the desired sample size was obtained. Nine soil samples were collected from sample site A' i.e. rice farm while one sample was taken from vegetable plot, sample site 'B'. Two control samples were obtained about 16 cm (54 ft) each away ahead and before the sampling station, respectively from sample site 'A' where no farming activity was expected to have taken place. Samples obtained were wrapped in aluminum foil, well labelled and transported to the laboratory in a bucket and stored at ambient temperature for further treatment.

(b) Vegetable Samples

Two replicate vegetable samples were obtained from tomato leaves and fruits (*S. lycopersicum*), pepper leaves and fruits [red bell pepper fruit locally called 'tartase' (*Capsicum*), Ugwu leaves (*T. occidentalis*), garden egg leaves and fruits (*S. macrocarpon*), carrot leaves (*D. carota*) and African spinach called 'Green' (*A. hybridus*) randomly from each of the selected points as distributed in the farm. A total of fourteen samples of food crops were obtained, wrapped in aluminium foil, clearly labeled and placed in polythene bags and then transported in a cooler to the laboratory.

3.1 Extraction of Pesticides

3.1.1 Soil

Extraction of soil samples was carried out by the method described by [20]. Exactly 10 g of each sample and 20 g of anhydrous sodium sulphate (Na_2SO_4) was ground into dry powder. The ground powder sample was extracted with 150 mL of a mixture of acetone and n-hexane (2:1). After extraction, the extract was transferred into a round bottomed flask connected to a pre-weighed receiver through a Liebig condenser and concentrated to about 20 mL on a water bath maintained between 50 and 55⁰ C. The remaining solvent in the concentrated extract was evaporated using a rotary evaporator. The almost-dry extracts were cleaned up in a micro-column as described in ASTM [21]. Two (2) grams of activated silica gel was packed into a chromatographic micro-column of 10 mm internal diameter and approximately 10 cm long. The silica gel was conditioned with 10 mL n-hexane while the sample extracts were dissolved in 5 mL n-hexane before they were loaded on to the separate micro-column. Elution of each of the sample was carried out with 50 mL of ethyl acetate: n-hexane mixture (9:1). The eluents were then concentrated on a rotary evaporator at about 45⁰ C and under a gentle stream of nitrogen gas. The almost-dry concentrates were then dissolved in 2 mL acetone and transferred into vials for injection into the Gas Chromatograph.

3.1.2 Vegetable

A method described by Ize-Iyamu [20] was adopted and modified. Each sample was chopped with a sharp knife on a chopping board. This was blended in a salton elite glass blender to obtain a homogenous representative sample. The knife, chopping board and blender were washed with distilled water to avoid cross contamination. Twenty (20) grams of sodium sulphate (Na_2SO_4) and 5 g of sodium hydrogen carbonate (IV) (NaHCO_3) were weighed and added to a separatory funnel. Samples to be blended (10 g) were added followed by 40 mL of ethyl acetate ($\text{CH}_3\text{COOCH}_2\text{CH}_3$). The mixture was shaken for ten minutes and allowed to settle. The supernatant (extract) was decanted into a round bottomed flask. This was evaporated in a BUCHI Rotavapor R-200 rotary evaporator [20].

3.1.3 Cleanup Process

Ize-Iyamu *et al.* [20] described a method of clean up which was adopted. In order to remove any interfering substances co-extracted with the pesticide residues, the extract will be cleaned up. Activated florisil (1.5 g) was packed into a column that was plugged with glass wool. The column was further packed with 0.5 and 1.0 g of activated charcoal and sodium sulphate (Na₂SO₄), respectively. 10 mL of ethyl acetate was used to condition the column prior to clean up. Extract was transferred unto a florisil column using a Pasteur pipette and then waited until it was eluted. The sample tube (round bottomed flask) was rinsed with 2 mL ethyl acetate and was repeated twice to get all the extract from the tube. 9 mL of ethyl acetate was put on the column after the last rinse. The solvent (extract) was concentrated (evaporated) to dryness in a Rotavapor R- 200 rotary evaporator. The dried residue for each sample was dissolved in 1.5 mL of isooctane and picked into GC vials for analysis.

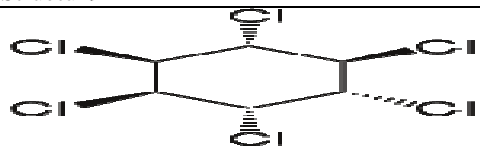
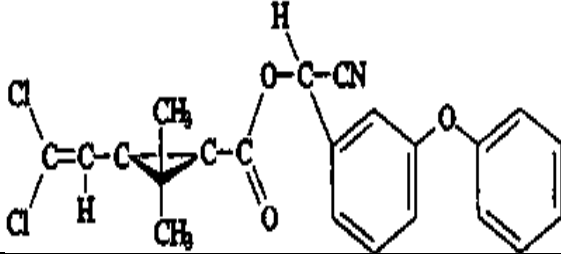
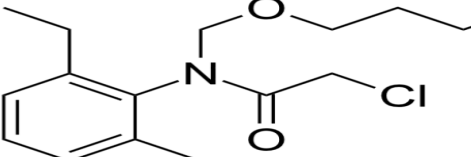
Quality Assurance Parameters

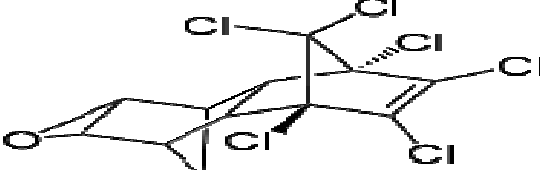
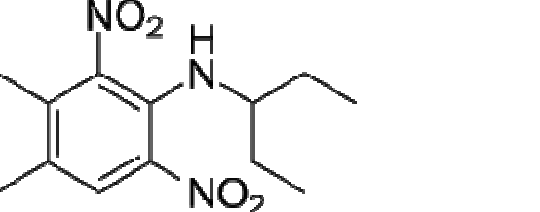

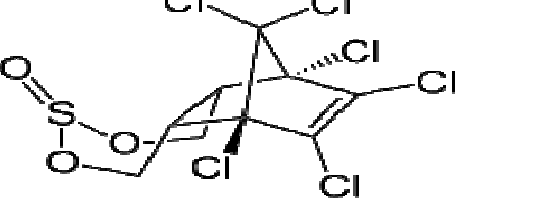
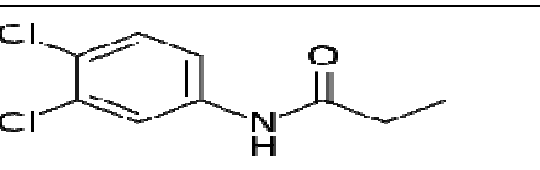
To ensure good data quality, the efficiency of the analytical method (the extraction and clean- μ L of 100 ng/mL internal standard (isodrin) and extracted under the same conditions as the analytes.

To check for cross contamination and interferences, a blank sample was determined.

4. Results and Discussion

Table 1: Selected Properties of Pesticide Residues Determined

Pesticide	Structure	Properties
^[22] (α -HCH): α -1,2,3,4,5,6-hexachlorocyclohexane		Formula: C ₆ H ₆ Cl ₆ , molar mass: 290.83 g/mol, melting point: 156-161 ⁰ , assay: 99 %, solubility: 1000 μ g/mL in methanol
^[22] Cypermethrin: (R,S)-alpha-Cyano-3-phenoxybenzyl-2,2-dimethyl(1R, 1S)-cis,trans-3-(2,2-dichlorovinyl) cyclopropane-carboxylate)		Formula: C ₂₂ H ₁₉ Cl ₂ NO ₃ , Molar mass: 416.30 g/mol, Purity: commercial preparation (94.2%). Melting point: 80.5°C, Vapour pressure: 1.9x10 ⁻⁷ pascals at 20°C, Solubility (g/l at 20°C): Density: 1.23 kg/l at 20°C, Octanol-water partition coefficient (P): 2.0 x 10 ⁶
^[22] Butachlor :N-(Butoxymethyl)-2-chloro-N-(2,6-diethylphenyl)acetamide		Formula: C ₁₇ H ₂₆ ClNO ₂ , molar mass: 311.85 g mol ⁻¹ , appearance: Light yellow oil, density: 1.0695 g/cm ³ , solubility in H ₂ O: 20 mg/L (20 °C), LD ₅₀ (median dose) 1740 mg/kg.

^[23] Dieldrin: 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo,exo-5,8-dimethanonaphthalene		Formula: C ₁₂ H ₈ Cl ₆ O, molar mass: 380.91 g/mol, appearance: colourless to light tan crystals, density: 1.75g/cm ³ , melting point: 176 to 177 °C, boiling point: 385 °C, solubility in H ₂ O: 0.02 %
Pendimethalin (3,4-Dimethyl-2,6-dinitro- <i>N</i> -pentan-3-yl-aniline)		Formula: C ₁₃ H ₁₉ N ₃ O ₄ , molar mass: 281.31 g·mol ⁻¹ , density: 1.17g/cm ³ , melting point: 47 to 58 °C (117 to 136 °F; 320 to 331 K); boiling point: 330 °C (626 °F; 603 K); solubility in H ₂ O: 0.275 ppm
^[23] Aldrin (1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene)		Formula: C ₁₂ H ₈ Cl ₆ , molar mass: 364.90 g·mol ⁻¹ , density: 1.60 g/mL, appearance: colourless, melting point: 104 °C (219 °F; 377 K), solubility in H ₂ O: slightly soluble (0.003, vapour pressure: 7.5 × 10 ⁻⁵ mmHg @ 20 °C
Endosulfan: (6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine-3-oxide)		Formula: C ₉ H ₆ Cl ₆ O ₃ S, molar mass: 406.90 g·mol ⁻¹ , appearance: Brown crystals, odour: slight sulfur dioxide odour, density: 1.745 g/cm ³ , melting point: 70 to 100 °C (158 to 212 °F; 343 to 373 K), Boiling point: decomposes, solubility in H ₂ O: 0.33 mg/L, vapour pressure: 0.00001 mmHg (25 °C)
Propanil: <i>N</i> -(3,4-Dichlorophenyl)propanamide		Formula: C ₉ H ₆ Cl ₂ NO, molar mass: 218.08 g/mol, appearance: White crystalline solid (pure), Brown powder (impure), melting point: 91 to 93 °C (196 to 199 °F; 364 to 366 K), solubility in H ₂ O: 225 ppm

The physico-chemical properties of selected pesticides and their chemical structures are presented in **Table 1**.

Table 2: Physico-chemical properties of soil from Sampling Sites

S/No	Sample ID	pH [†]	Particle size distribution			Cond. μScm ⁻¹	CEC (Cmolk ⁻)	Bulk Density (g.cm ⁻³)
			% sand	% clay	% silt			
1	A	7.16	65.4	20.6	14.0	872	7.79	1.40
2	B	7.30	75.4	16.6	8.00	116	8.12	1.36

pH[†]: pH of samples in water, Cond.: Conductivity

Table 2 shows some major physico-chemical parameters of soil samples taken from both sites. Particles size distribution was determined using a method described by Gee and Or [24] . Bulk density determination was also carried out according to standard procedure described by Blake and Hartge [25]. The pH in both sites was determined to be comparatively close and remained slightly alkaline (7.16 and 7.30). A neutral to moderately alkaline (6.5 to 8.0) pH value was also reported by [26]. The physical and chemical characteristics of the soil system includes moisture content, organic matter, clay contents, and pH, which have influence on the sorption/desorption and degradation of pesticides and their access to groundwater and surface waters [27]. The bulk density (gcm^{-3}) have close values of 1.40, 1.36, for sites ‘A’ and ‘B’ respectively. Nwite [28] reported values of 1.2 ± 1.00 for forest land and 1.30 ± 0.15 for continuous cropping system within a soil profile depth of 0-15 cm in a similar research carried out in Abakaliki, Nigeria. Cation exchange capacity, CEC ($\text{Cmol} \text{kg}^{-1}$) have very close range of values and 7.79, 8.12 for sample sites A and B, respectively. AariffKhan and Kamalakar [26] also reported low to medium in CEC ($11.5 - 26.5 \text{ C mol (p+) kg}^{-1}$) which was only slightly higher. Electrical conductivity ranged between $116 - 872 \mu\text{Scm}^{-1}$ for sites A and B. Soil sample in site A has high sandy content (65.4 %) with relatively higher percentage of clay and silt (20.6 and 14.0 %) as compared to site B. Perhaps, this necessitates its use for growing of paddy rice, a rice variety commonly known as ‘‘CP Farrow 44’’ as reported by the farmer officially in charge of the university rice farm in the site. Soil sample in site B has higher percentage of sandy soil (75.4 %) than A with relatively lower clay content (16.6 %) followed by silt (8.00 %). Nwite [28] also reported values of 38 ± 0.7 , 14 ± 0.7 and 48 ± 0.7 for sand, clay and silt for continuous cropping system in Ghana within same soil depth. Variations in soils properties could be attributed to the nature of parent materials [29]. The physical properties of Soil influence the occurrence and growth the movement through soil of water and its dissolved nutrients and chemical pollutions [20, 31]. The fate of pesticides in soil and water environments is influenced by the physico-chemical properties of the pesticide, the properties of the soil and water systems (presence of clay materials, organic matter, pH), climate, biology, and other factors [32].

Table 3 shows the mean concentration (mg/kg) of pesticides residues present in Edible crops. In *D. carota* (carrot), Cypermethrin has the highest residue concentration of $1.62 \pm 0.01 \text{ mg/kg}$, while pendimethalin has a close concentration of $(0.58 \pm 0) \text{ mg/kg}$. Alpha-HCH has the least concentration of residues in this sample (0.001 ± 0); they are in order of; Cypermethrin >

pendimethalin > propanil > butachlor > Alpha-HCH. However, aldrin, dieldrin and endosulfan residues were not detected. The entire pesticide residues concentration (mg/kg) were distributed to range between 1.62- 0.001. **Table 3** also shows the mean concentration (mg/kg) of pesticide residues in *C. annuum* (fruits and leaves). The pesticide residue concentration (mg/kg) ranged between 1.63 ± 0.66 - 0.002 ± 0.001 . Cypermethrin indicated the highest mean concentration (1.63 ± 0.66) while alpha-HCH gave the lowest residual concentration (0.002 ± 0.001) mg/kg. Aldrin, dieldrin and endosulfan were not detected as well. Others with residual concentration (mg/kg) decreasing progressively are pendimethalin, propanil and butachlor (0.61 ± 0.24 , 0.07 ± 0.03 and 0.03 ± 0.01), respectively. Cypermethrin exceeded the maximum residue limits of 0.1 mg/kg in fruits or berries [33]. Cypermethrin is not soluble in water and has a strong tendency to adsorb to soil particles [34]. There are four major routes through which pesticides reach water body, it may percolate, or leach, through the soil, it may be carried to the water as runoff, or it may be spilled. Factors that affect a pesticide's ability to contaminate water include its water solubility, the distance from an application site to a body of water, weather, soil type, presence of a growing crop, and the method used to apply the chemical [35, 36, 37]. *Telfaria occidentalis* was analysed for pesticide residual content. *T. occidentalis* was analysed for pesticide residual content. The mean concentration (mg/kg) of each pesticide residue in the sample is also presented in **Table 3**. The pesticides ranged from concentrations (mg/kg) of 1.64 ± 0.6 - 0.001 ± 0.001 , which represents cypermethrin and alpha-HCH, respectively. The concentrations (mg/kg) of other pesticide residues in order of magnitude are 0.55 ± 0.2 , 0.06 ± 0.02 , and 0.02 ± 0.01 for pendimethalin, propanil and butachlor, respectively. Rao *et al.* [38] also observed that very low levels of butachlor residues were detected in rice grain below the maximum residue limit of 0.5 mg/kg. Maximum residue value of 0.0095 mg/kg was observed at 2 kg/ha of herbicide (with poultry manure) during wet season. However, in both seasons and in all the treatments, the detected residues were below maximum residue limits of 0.05 µg/g [39]. Aldrin, dieldrin and endosulfan were not detected in any of the *T. occidentalis* (ugwu leaves) and fruits designated as UL. **Table 3** shows the mean concentration (mg/kg) of pesticide residues in *S. lycopersicum* (garden egg). Pesticides ranged from a concentration (mg/kg) of 0.84 ± 0.7 - 0.002 ± 0.001 . The highest concentration being cypermethrin and the lowest being alpha-HCH. Other concentration (mg/kg) in order of magnitude are 0.29 ± 0.2 , 0.07 ± 0.02 , and 0.03 ± 0.01 for pendimethalin, propanil and alpha- HCH, respectively. Aldrin, dieldrin and endosulfan were not detected in any

of the tomato leaves and fruits designated as TL and TF. The residual concentration (mg/kg) of pesticides in *A. hybridus* (African spinach) is shown in **Table 3**. The concentration of the pesticide residues ranged from $1.61 \pm 0.5 - 0.001 \pm 0.001$, which represents cypermethrin and alpha-HCH pesticides, respectively. The concentration of other pesticides in decreasing order are 0.58 ± 0.2 , 0.06 ± 0.02 and 0.02 ± 0.01 for pendimethalin, propanil and butachlor, respectively. Aldrin, dieldrin and endosulfan were not detected in the vegetable sample, meaning that it was absent in the cultivated soil and consequently the crop. Pesticide residues analysis was also carried out to find out the residual concentration in *S. macrocarpon* (garden egg fruits and leaves). The mean concentration of each incipient is presented in **Table 3** as well. The concentration (mg/kg) decreases from cypermethrin (1.62 ± 0.01), pendimethalin (0.57 ± 0.01), propanil (0.06 ± 0.01), butachlor (0.02 ± 0.01) and alpha-HCH (0.001 ± 0), being the least. Aldrin, dieldrin and endosulfan were also not detected in this sample. A two-tailed Pearson correlation analysis was carried out (at $p = 0.01$ and 0.05) to show relationships among individual pesticides in various vegetable crops. The results were significant between butachlor and alpha-HCH, pendimethalin and cypermethrin ($p = 0.01$) with a very high positive values ($r = 1.000$ and 0.985), respectively while it was significant between prapanil and alpha-HCH, propanil and butachlor ($p = 0.05$) with high positive correlation value ($r = 0.857$), respectively. The high positive values obtained suggest strong interaction between these pesticides in the crops, indicating that the presence of one quantitatively induces the availability of its pairs. Others pesticides showed high negative correlation values indicating absence of meaningful interaction among them. The presence of these pesticides may not be wholly attributed to only direct application within the farm site. Aldrin, dieldrin, endrin, heptachlor, hexachlorobenzene are Persistent organic pollutants (POPs) which resist degradation and thus remain in the environment for years. Some POPs have the ability to volatilize and travel great distances through the atmosphere to become deposited in remote regions. Such chemicals may have the ability to bioaccumulate and biomagnify and can bioconcentrate up to 70,000 times their original concentrations [40]. These can affect non-target organisms in the environment and increase risk to humans by disruption in the endocrine, reproductive, and immune systems. Other plant (branching habit, plant Surface, plant species and varieties, Plant Maturity or Age of the Plant) as well as environmental (temperature and Humidity, rain fall, wind, light) factors also influenced pesticides distribution in crops [40].

314 **Table 3: Mean Concentration of Pesticides residues present in Edible Crops**

Pesticide	Mean Concentration (mg/kg) in Edible Crops					
	<i>Daucus carota</i>	<i>Capsicum anuum</i>	<i>Telfaria Occidentalis</i>	<i>Solanum lycopersicum</i>	<i>Amaranthus Hybridus</i>	<i>Solanum macrocarpon</i>
Alpha-HCH	0.001 ± 0	0.002 ± 0.001	0.001±0.001	0.002 ± 0.001	0.001±0.001	0.001±0
Butachlor	0.02 ± 0.01	0.03 ± 0.01	0.02 ±0.01	0.03 ± 0.01	0.02±0.01	0.02 ±0.01
Aldrin	ND	ND	ND	ND	ND	ND
Cypermethrin	1.62 ± 0.01	1.63 ± 0.7	1.64 ± 0.6	0.84 ± 0.7	1.61±0.5	1.62 ± 0. 01
Dieldrin	ND	ND	ND	ND	ND	ND
pendimethalin	0.58 ± 0	0.61 ± 0.2	0.55 ± 0.2	0.29 ± 0.2	0.58±0.2	0.57 ± 0.01
Endosulfan	ND	ND	ND	ND	ND	ND
Propanil	0.05 ± 0	0.07 ± 0.03	0.06 ± 0.02	0.07 ± 0.02	0.06±0.02	0.06 ± 0.01

315 ND: Not detected

316 The total mean concentration (mg/kg) of pesticide residues in soil for sites ‘A’ and ‘B’ are
317 presented in **Table 4**. Organochlorine pesticide residues were detected in almost all the soil
318 sample except Alpha-HCH, cypermethrin and endosulfan which were not detected in all soil
319 sample from site A but were detected in samples from site B. Endosulfan was only determined in
320 very small quantity in soil from the vegetable farm but was not detected in any of the vegetable
321 crops. This indicates that the pesticide was probably applied on soil from site B or washes off
322 from nearby vicinity where micro-farming and students’ domestic activities from residence take
323 place but was not used on the commercial rice farm (site A). Endosulfan was present in similar
324 research conducted in Ghana, where human health risk assessment was performed on the results
325 obtained. The analysis indicated cancer risk for adults and children as a result of the presence of
326 endosulfan and chlopyrifos. Endosulfan is not registered in Ghana as a pesticide for use on
327 vegetables, therefore the detection of endosulfan in several samples indicates misuse of
328 agrochemicals among Ghanaian farmers [41]. Conversely, aldrin and dieldrin were not detected
329 in soil from sample site B, but were present in all soil samples from site A (rice farm), meaning
330 that they were preferably applied only to the rice during cultivation but not applied to the
331 vegetable crops. However, hazards associated with aldrin are that they are potential occupational
332 carcinogen [42]. The predominant pesticides analysed were propanil, butachlor and
333 pendimethalin. Pendimethalin gave the highest mean concentration (mg/kg) of 13.8 ± 3.8 ,
334 followed by butachlor (11.0 ± 3.3) and propanil (4.76 ± 0.94). Both butanol and propanil were
335 above the residue limits. Cypermethrin, which was absent in soil samples from site ‘A’ was
336 sufficiently present and ranged the highest in soil samples from site ‘B’. Two control soil
337 samples (CA1 and CA 2) were taken from extremes sides of site A, where farming activities
338 were expected to be low or has not taken place over a long period of time. No significant
339 pesticides concentration was obtained as they were below the instrument detection limit except

butachlor, propanil and pendimethalin having the concentration of 0.01, 0.01 and 0.02, respectively in CA1 only. The farmer in charge of the university rice farm reported that 2,4, D-amine combined with Nominee gold (a post emergent, broad spectrum systemic herbicide for all types of rice cultivation i.e. direct sown rice, rice nursery and transplanted rice) were regularly used in the farm as selective post emergence weed control pesticides against rice within cropping seasons. Two-tailed Pearson's correlation analysis was carried out to infer possible interactions among pesticides in different soil sites ($p = 0.01, 0.05$), respectively. The concentration of butachlor and alpha-HCH was significant but high negative value (-0.999 at $p = 0.01$) as presented in **Table 5**. This indicates that as the concentration of one increases, the other reduces, a negative interaction. This could possibly suggests a side reaction or chelating property that limits availability of the other within the substrate or the vicinity. The same effect was observed between aldrin and alpha-HCH, pendimethalin and alpha-HCH, endosulfan and butachlor, endosulfan and aldrin, propanil and alpha-HCH, propanil and endosulfan. A significant positive correlation values were observed ($r = 1, 0.999, 1$) between cypermethrin and alpha-HCH, pendimethalin and butachlor as well as endosulfan and cypermethrin), respectively. This shows active interaction within the soil. How long the pesticide remains in the soil depends on how strongly it is bound by soil components and how readily it is degraded [27]. It also depends on the environmental conditions at the time of application, *e.g.*, soil water content, temperature and Humidity, rainfall, wind, light.

Table 4: Total Concentration (mg/kg) of Pesticide Residues in Soil for both Sites

Pesticide	Sampling Sites										Mean \pm SD
	A1	A2	A3	A4	A5	A6	A7	A8	A9	B1	
Alpha-HCH	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.51	0.51 ± 0
Butachlor	12.0	12.0	12.0	11.9	12.3	12.1	12.1	12.2	12.2	1.73	11.0 ± 3.3
Aldrin	0.09	0.10	0.12	0.09	0.05	0.11	0.10	0.06	0.08	ND	0.09 ± 0.02
Cypermethrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.45	4.45 ± 0
Dieldrin	0.12	0.13	0.13	0.14	0.11	0.09	0.12	0.1	0.13	ND	0.12 ± 0.02
pendimethalin	14.6	15.2	15.0	14.7	15.1	15.1	15.1	15.0	14.8	3.05	13.8 ± 3.8
Endosulfan	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01	0.01 ± 0
Propanil	4.83	5.23	5.13	4.57	5.09	5.16	4.94	5.33	5.15	2.15	4.76 ± 0.94

ND: Not detected

Table 5: Pearson correlation analysis of pesticides in soil sampling sites

	Alpha-HCH	Butachlor	Aldrin	Cypermethrin	Dieldrin	Pendimethalin	Endosulfan	Propanil
Alpha-HCH	1							
Butachlor	-0.999 **	1						
Aldrin	-0.797**	0.781**	1					
Cypermethrin	1.000**	-0.999**	-0.797**	1				
Dieldrin	-0.124	0.103	0.110	-0.124	1			
Pendimethalin	-0.999**	0.999**	0.798**	-0.999**	0.100	1		
Endosulfan	1.000**	-0.999**	-0.797**	1.000**	-0.124	-0.999**	1	
Propanil	-0.973**	0.977**	0.756*	-0.973**	-0.058	0.979**	-0.973**	1

366

367 ** Correlation is significant at the 0.01 level (2-tailed)

368 * Correlation is significant at the 0.05 level (2-tailed)

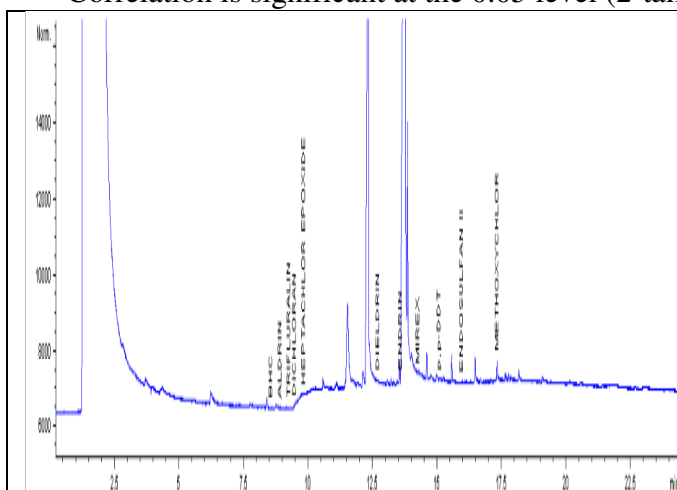


Figure 2: GC-MS Chromatogram of Soil Sample in Site A1

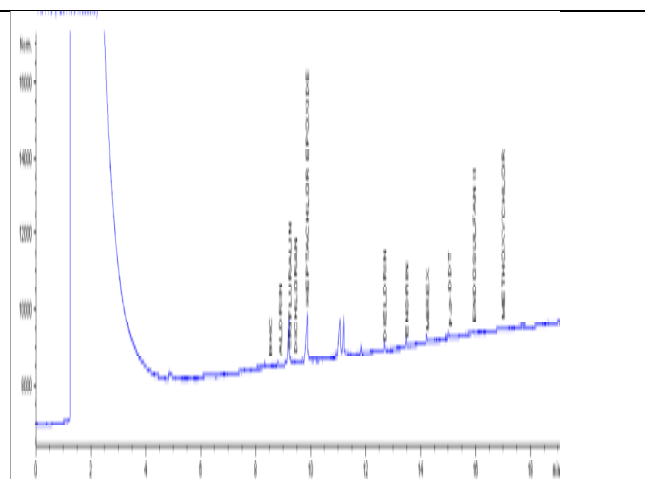
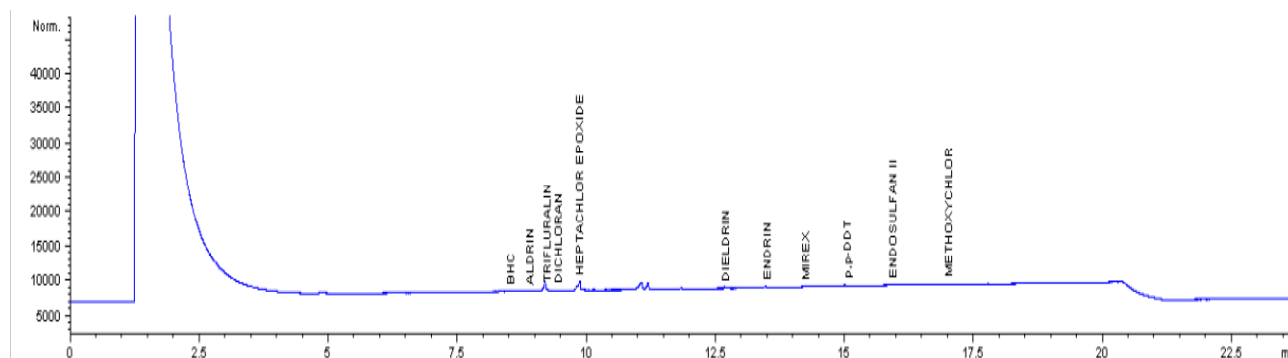


Figure 3: GC-MS Chromatogram of Soil Sample B1

369



370

Figure 4: GC-MS Chromatogram of Control Soil Sample (A1)

371

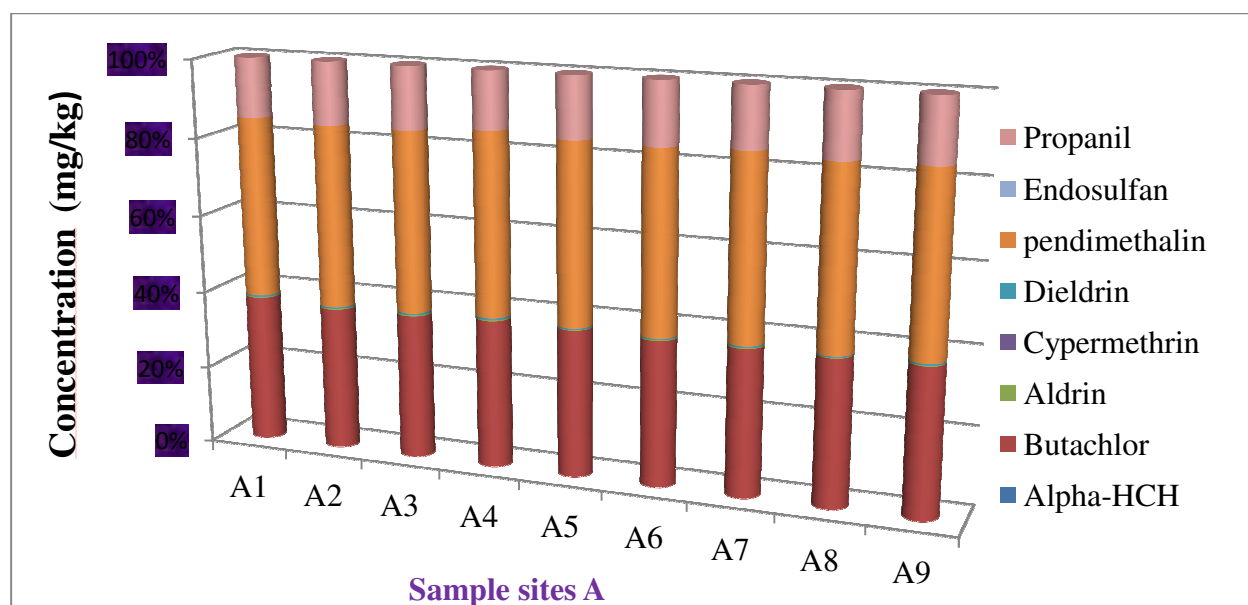
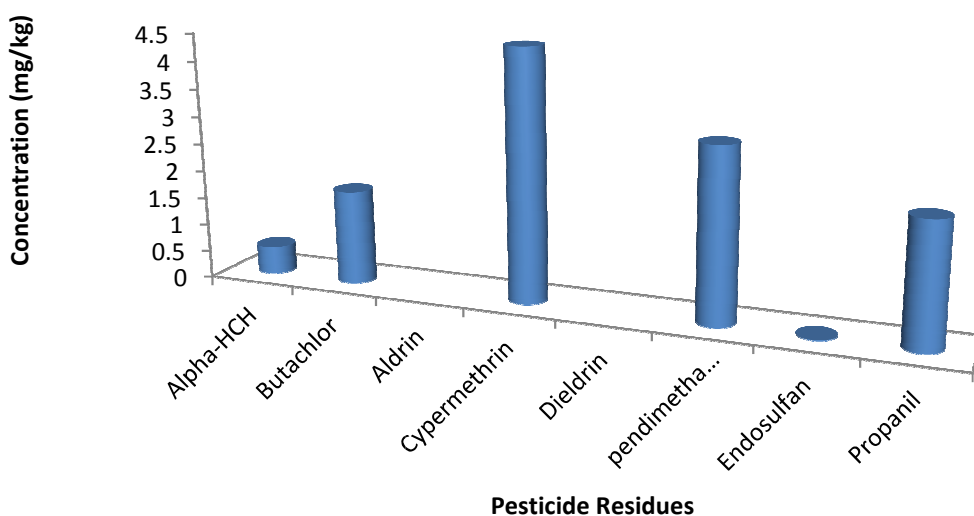


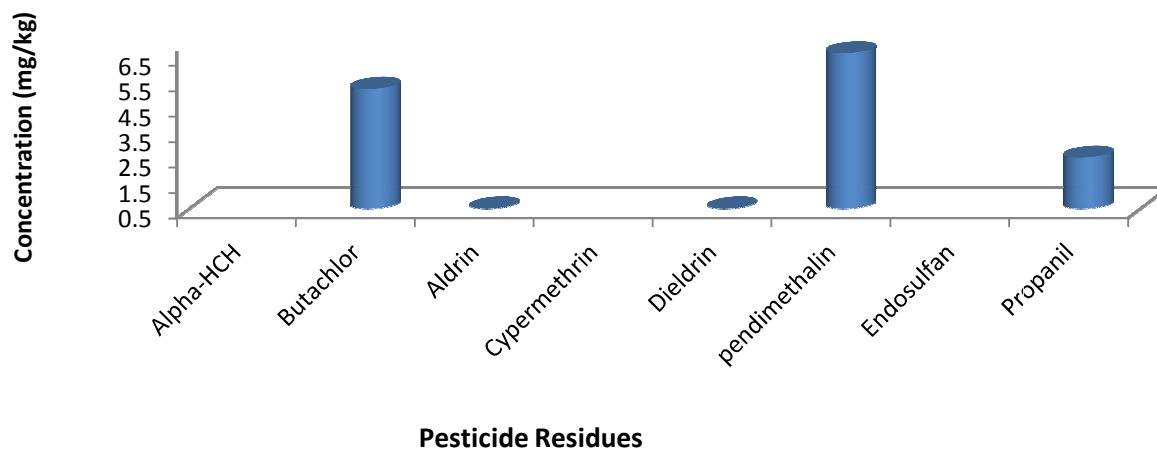
Figure 5: Concentration (mg/kg) of pesticide residues in each soil sample in Site A

Figure 2 shows the Chromatogram of Soil Sample in Site A. The chromatogram of soil sample taken from Sample B is shown in **Figure 3**. **Figure 4** shows the chromatogram of control soil Sample (A1) also taken from the sampling site A.

The mean concentration of pesticide residues in individual soil sample taken from site A is presented in **Figure 5**. The mean concentration (mg/kg) of pesticide residues in soil sample in site B is shown in **Figure 6**. Cypermethrin showed the greatest peak, indicating highest concentration followed by pendimethalin, propanil, butachlor and alpha-HCH. Aldrin and dieldrin were not detected in all the soil samples from this site as they were reportedly not applied. No good linear relationship was statistically observed between pesticide concentration and distribution as the square of correlation coefficient was ($r = -0.08$), indicating a very low negative correlation. This is because the concentration of pesticides was only based on those ones selectively applied and consequently present in the soil for adsorption.



387
388 **Figure 6:** Mean Concentration (mg/kg) of pesticide residues in soil samples in Site B



389
390 **Figure 7:** Mean Concentration (mg/kg) of pesticide residues in soil samples in Site A

391 **Figure 7** shows the mean concentration (mg/kg) of all the pesticide residues present in soil
392 samples in site A. Pendimetalin gave the highest concentration peak followed by butachlor,
393 propanil, dieldrin and aldrin which are close in terms of the magnitude of their values. Alpha-
394 HCH, cypermethrin and endosulphan were not detected. The consistent absence of these
395 pesticides in sample site A indicated that they were not applied to the commercial rice farm
396 within cropping seasons. Conversely, aldrin and dieldrin which were completely not detected in
397 site B were present in small quantities in the rice farm (Site A).

398

5. Conclusion

Alpha-HCH, cypermethrin and endosulphan were not detected in all soil samples within the commercial rice farm (Site A) but were detected in the vegetable farm plot (Site B). Aldrin and dieldrin were not detected in site B were present in the rice farm in comparatively little amount. This generally indicates the selective use of these pesticides is based on the crops grown in each of these locations. However, run offs of effluents from the neighbouring farming environment can not be over ruled. Therefore, the university farmers who are expected to be more enlightened and should be well disposed to sensitise the neighbouring communities as how to apply these chemicals to alleviate their residual toxicity to unsuspected consumers. The mean concentration (mg/kg) of all the pesticides of interest were within MRL, except cypermethrin in edible crops meaning that the concentrations of these pesticide residues are safe for now in many of the food crops, however, continuous research should be endorsed.

References

1. Vanguard News Paper (2015). EU bans Nigeria from exporting beans, melon seeds, dried fish, meat, others. 10th August, 2015. <http://www.vanguardngr.com/2015/08/eu-bans-nigeria-from-exporting-beans-melon-seeds-dried-fish-meat-others-containing-pesticide-con>
2. (FAO, 2017). Residues of some veterinary drugs in animals and foods. Abamectin, (FAO Corporate Document Repository). [Http://www.fao.org/home/en/](http://www.fao.org/home/en/) accessed 14th June, 2017
3. Hutson, D.H. and Stoydin, G., (1987). Excretion and residues of the pyrethroid insecticide Cypermethrin in laying hens, *Pesticide Science*. 18(3): 157-168.
4. Schulze, Larry D.; Ogg, Clyde; and Vitzthum, Edward F. (1997). "EC97-2505 Signs and Symptoms of Pesticide Poisoning". Historical Materials from University of Nebraska-Lincoln Extension. Paper 1225. 16 pp. <http://digitalcommons.unl.edu/extensionhist/1225>
5. Baselt, R. (2008). *Disposition of Toxic Drugs and Chemicals in Man*, 8th edition, Biomedical Publications, Foster City, CA, pp. 389-391
6. Metcalf, R.L. (2002). Insect Control" in Ullmann's Encyclopedia of Industrial Chemistry" Wiley-VCH, Weinheim,. doi:10.1002/14356007.a14_263

- 428 7. Jubb, A. H. (1975). *Basic Organic Chemistry, Part 5 Industrial products*. London: Wiley.
429 ISBN 0-471-85014-4
- 430 8. Croucher, A., Hutson, D.H. and Stoydin, G. (1985). Excretion and Residues of the Pyrethroid
431 Insecticide Cypermethrin in Lactating Cows, *Pesticide Science*, 16, 287-301
- 432 9. Đurović, R. and Đorđević, T. (2011). Modern Extraction Techniques for Pesticide Residues
433 Determination in Plant and Soil Samples, *Pesticides in the Modern World - Trends in*
434 *Pesticides Analysis*, Dr. Margarita Stoytcheva (Ed.), ISBN: 978-953-307-437-5, InTech,
435 Available from: [http://www.intechopen.com/books/pesticides-in-the-modern-world-](http://www.intechopen.com/books/pesticides-in-the-modern-world-trends-in-pesticides-analysis/modern-extraction-techniques-for-pesticide-residues-determination-in-plant-and-soil-samples)
436 [trends-in-pesticides-analysis/modern-extraction-techniques-for-pesticide-residues-](http://www.intechopen.com/books/pesticides-in-the-modern-world-trends-in-pesticides-analysis/modern-extraction-techniques-for-pesticide-residues-determination-in-plant-and-soil-samples)
437 [determination-in-plant-and-soil-samples](http://www.intechopen.com/books/pesticides-in-the-modern-world-trends-in-pesticides-analysis/modern-extraction-techniques-for-pesticide-residues-determination-in-plant-and-soil-samples), 246 pp
- 438 10. Arthur, C. L.; Killam, L. M.; Buchholz, K. D.; Pawliszyn, J. and Berg, J. R. (1992).
439 Automation and Optimization of Solid-Phase Microextraction. *Analytical Chemistry*,
440 64(17): 1960-1966
- 441 11. Fernández Moreno, J. L., Garrido Frenich, A., Plaza Bolaños, P. and Martínez Vidal, J. L.
442 (2008). Multiresidue Method for the Analysis of More Than 140 Pesticide Residues in
443 Fruits and Vegetables by Gas Chromatography Coupled to Triple Quadrupole Mass
444 Spectrometry. *Journal of Mass Spectrometry*, 43(9): 1235-1254
- 445 12. Schenck, F. J., Lehotay, S. J. and Victor, V. (2002). Comparison of Solid-Phase Extraction
446 Sorbents for Cleanup in Pesticide Residue Analysis of Fresh Fruits and Vegetables.
447 *Journal of Separation Science*, 25(14): 883–890.
- 448 13. Anastassiades, M., Lehotay, S. J., Štajnbaher, D. and Schenck, F. J. (2003). Fast and Easy
449 Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive
450 Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce. *The*
451 *Journal of AOAC International*, 86(2): 412-431
- 452 14. Okihashi, M.; Kitagawa, Y.; Akutsu, K.; Obana, H. and Tanaka, Y. (2005). Rapid Method
453 for the Determination of 180 Pesticide Residues in Foods by Gas Chromatography/Mass
454 Spectrometry and Flame Photometric Detection. *Journal of Pesticide Science*, 30 (4):
455 368–37

15. Kaipper, B. I. A.; Madureira, L. A. S. and Corseuil, H. X. (2001). Use of Activated Charcoal in a Solid-Phase Extraction Technique for Analysis of Pesticide Residues in Tomatoes. *Journal of the Brazilian Chemical Society*, 12(4): 514-518
16. Wang, L.; Liang, Y. and Jiang, X. (2008). Analysis of Eight Organophosphorus Pesticide Residues in Fresh Vegetables Retailed in Agricultural Product Markets of Nanjing, China. *Bulletin of Environmental Contamination and Toxicology*, 81(4): 377–382
17. Chen, T. and Chen, G. (2007). Identification and Quantitation of Pyrethroid Pesticide Residues in Vegetables by Solid-Phase Extraction and Liquid Chromatography/Electrospray Ionization Ion Trap Mass Spectrometry. *Rapid Communications in Mass Spectrometry*, 21(12): 1848–1854.
18. Pang, G. F.; Fan, C. L.; Liu, Y.M.; Cao, Y. Z.; Zhang, J. J.; Li, X. M.; Li, Z. Y. & Guo, T. T. (2006). Determination of Residues of 446 Pesticides in Fruits and Vegetables by Three- Cartridge Solid-Phase Extraction-Gas Chromatography-Mass Spectrometry and Liquid Chromatography-Tandem Mass Spectrometry. *The Journal of AOAC International*, 89(3): 740-771
19. Dem, S.B., Cobb, J.M. and Mullins, D.E. (2007). Pesticide Residues in Soil and Water from Four Cotton Growing Areas of Mali, West Africa, *Journal of Agricultural, Food and Environmental Sciences*, 1(1):1-12
20. Ize-Iyamu, O.K., Asia, I. O. and Egwakhide, P. A. (2007). Concentrations of residues from organochlorine pesticide in water and fish from some rivers in Edon State Nigeria, *International Journal of Physical Sciences* 2 (9): 237-241
21. ASTM (1979). Annual Book of America Society for Testing and Materials Standards, 1289, Philadelphia, ASTM Tech. Publ. 630pp.
22. Toxicological Profile for Alpha-, Beta-, Gamma-, and Delta-Hexachlorocyclohexane, U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, August 2005
23. Agency for Toxic Substances and Disease Registry (ATSDR). (2002). Toxicological profile for Aldrin/Dieldrin. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service
24. Gee, G.W. and Or, D. (2002). Particle size Analysis. In: Dane. J. H. and Topp, G.C. (eds). *Methods of Soil Analysis. Soil Science Society of America* 5(4): 255-293.

- 488 25. Blake, G. R. and Hartage, K.H. (1986). Bulk density. In: Klute, A. (ed). Methods of Soil
489 Analysis. *American society of Agronomy* 9(1): 365-375
- 490 26. Aariff Khan, M.A. and Kamalakar, J. (2012). physical, physico-chemical and chemical
491 properties of soils of newly established agro-biodiversity park of acharya ng ranga
492 agricultural university, hyderabad, andhra Pradesh, *International Journal of Farm*
493 *Sciences* 2(2) :102-116.
- 494 27. Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J.
495 and García-Río, L. (2008). The mobility and degradation of pesticides in soils and the
496 pollution of groundwater resource, *Agriculture, Ecosystems and Environment*, 123(4):
497 247–260
- 498 28. Nwite, J. N. (2015). Profile Distribution of Soil Physicochemical Properties under Two Land
499 Use Systems in Abakaliki, Southeastern Nigeria, *Journal of Biology, Agriculture and*
500 *Healthcare* 5(.22): 107-114.
- 501 29. Ibanga, I.J. (2006). Soil Studies: The pedological Approach, Maesot Printing and Computers,
502 Calabar Nigeria.
- 503 30. Brady, N.C. and Weil, R.R. (2002).Elements of the nature and properties of soils. Abridged
504 ed. of: The nature and properties of Soils 13th ed
- 505 31. Ihem, E.E., Ahukemere, C.M., Nkwopara, U.N., Chris-Emenyonu, C., Okoli, N.H. and Osi, A.
506 (2014). Differences in Particle Size Distribution of Soils of Northern Niger Delta of
507 Nigeria as Affected by Crude Oil Pollution, *International Journal of Research in*
508 *Agriculture and Forestry*, 1(1): 16-20
- 509 32. Singh, R.P. (2001). Comparison of organochlorine pesticide levels in soil and groundwater of
510 Agra, India. *Bull. Environ. Contam. Toxicol.* 67: 126-132.
- 511 33. CODEX International Food Standards, Maximum Residue Limits for Spices (2012).
512 Retrieved on October 28, 2012
- 513 34. U.S. Environmental Protection Agency. (1989). Pesticide Fact Sheet Number 199:
514 Cypermethrin. US EPA, Office of Pesticide Programs, Registration
515 Div.Washington, DC.
- 516 35. Papendick, R.I, Elliott, L.F, Dahlgren, R.B. (1986). "Environmental consequences of modern
517 production agriculture: How can alternative agriculture address these issues and
518 concerns?". *American Journal of Alternative Agriculture*, 1 (1): 3–10.
- 519 36. Pimentel, D., McLaughlin, L., Zepp, A., Lakitan, B., Kraus, T., Kleinman, P., Vancini, F.,
520 Roach, W.J., Graap, E., Keeton, W.S. and Selig, G. (1991). Environmental and economic

- 521 impacts of reducing U.S. agricultural pesticide use. In: D. Pimentel (Editor), Handbook
522 of Pest Management in Agriculture, Second Edition. Vol. I. CRC Press, Boca Raton, FL,
523 679-718.
- 524 37. Barbash, J.E. and Resek, E.A. (1996). Pesticides in Ground water. Volume 2 of the series
525 Pesticides in the Hydrologic Environment. Ann Arbor Press, Inc. Chelsea, Mich. pp 425
- 526 38. Rao, P.C., Rama Lakshmi, Ch.S., Madhavi, M., Swapna, G. and Sireesha, A. (2012).
527 Butachlor dissipation in rice grown soil and its residues in grain, *Indian Journal of Weed*
528 *Science*, 44(2): 84–87
- 529 39. The Pesticide Chemical News Guide. 1985. Food Chemical News, INC. 1982 (202): 544-198
- 530 40. Ritter, L., Solomon, K.R., Forget, J., Stemmerhoff, M. and O'Leary, C. (2007). Persistent
531 organic pollutants: An Assessment Report on: DDT, Aldrin, Dieldrin, Endrin,
532 Chlordane, Heptachlor, Hexachlorobenzene, Mirex, Toxaphene, Polychlorinated
533 Biphenyls, Dioxins and Furans. Prepared for The International Programme on
534 Chemical Safety (IPCS), within the framework of the Inter-Organization Programme
535 for the Sound Management of Chemicals (IOMC). Retrieved on April, 28, 2017
- 536 41. Essumang, D.K., Dodoo, D.K., Adokoh, C.K. and Fumador, E.A. (2008). Analysis of
537 Some Pesticide Residues in Tomatoes in Ghana, *Human and Ecological Risk*
538 *Assessment: An International Journal*, 14(4): 796-806.
- 539
- 540 42. "NIOSH Pocket Guide to Chemical Hazards #0016". National Institute for Occupational
541 Safety and Health (NIOSH). page last updated April 11, 2016