Determination of Some Organochlorine Pesticide Residues in Vegetable and Soil Samples from Alau Dam and Gongululong Agricultural Sites, Borno State, North Eastern Nigeria

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Abstract—Five vegetables (spinach, lettuce, cabbage, tomato, and onion) were freshly harvested from the Alau Dam and Gongululong agricultural areas for the determination of some organochlorine pesticide residues (α, p-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT, α-BHC, γ-BHC, methoxychlor, lindane, endosulfan dieidrin, and aldrin.) Soil samples were also collected at different depths for the determination of the above pesticides. Samples collection and preparation were conducted using standard procedures. The concentrations of all the pesticides in the soil and vegetable samples were determined using GC/MS SHIMADZU (GC-17A) equipped with electron capture detector (ECD). The highest concentration was that of p,p'-DDT (132.4±13.45µg/g) which was observed in the leaf of cabbage, while the lowest concentration was that of p,p'-DDT (2.34µg/g) was observed in the root of spinach. Similar trends were observed at the Gongulong agricultural area, with p,p'-DDD having the highest concentration of 153.23µg/g in the leaf of cabbage, while the lowest concentration was that of p,p'-DDT (12.45µg/g) which was observed in the root of spinach. α-BHC, γ-BHC, Methoxychlor, and lindane were detected in all the vegetable samples studied. The concentrations of all the pesticides in the soil samples were observed to be higher at a depth of 21-30cm, while the lowest concentrations were observed at a depth of 0-10cm. The concentrations of all the pesticides in the vegetables and soil samples from the two agricultural sites were observed to be at alarming levels, much higher than the maximum residue limits (MRLs) and acceptable daily intake values (ADIs). The levels of the pesticides observed in the vegetables and soil samples investigated, are of such a magnitude that calls for special attention and laws to regulate the use and circulation of such chemicals. Routine monitoring of pesticide residues in these study areas is necessary for the prevention, control and reduction of environmental pollution, so as to minimize health risks.

Keywords—Alau Dam, Gongululong, Organochlorine, Pesticide Residues, Soil, Vegetables.

I. INTRODUCTION

PESTICIDES is an extremely diverse group of substances with a wide potential for a variety of toxic effects. They can range in acute toxicity from being lethal at low doses, such as strychnine, to the relatively large quantities, such as sodium chloride, which is also edible in measured quantities. Pesticides have helped to increase crop production by controlling the pests that destroy the crops. However, some of the pesticides have adversely affected the non-target species by inducing carcinogenic, tetratogenic, mutagenic, neuro-toxic effects as well as alterations of reproductive processes or functions in experimental animals and in man [1]. Like op-DDT have been able to modulate the endocrine system by augmenting the sex steroid burden and have therefore been termed as endocrine disrupters [2]. Pesticides have sustained the growth in food production and preservation, although, their increased usage for good reasons, in both the developed and in the developing countries, has resulted in contamination of food and the environment, through pesticide residues [3]. Environmental pollution by pesticides has been identified as one of the major environmental impacts of agriculture [4]. Parent compounds, as well as metabolites of pesticides have been identified in air [5], water [6] and soil [7]. Reference [8] reported on the many environmental chemicals which are carcinogenic and 90% of these chemicals were pesticide related. Some of the most commonly used insecticides like toxophene, DDT, aldrin and dieldrin were found to be both carcinogenic and mutagenic, while carbaryl, ethylene dibromide and parathion were mutagenic. The herbicide, nitrofen, and the fungicide, captan, also possess similar properties. Pesticides differ in their mode of action, uptake by the body, metabolism and elimination from the body and toxicity potential. Because of these differences, some pesticides show acute short term effects, while others tend to accumulate in the body and with time demonstrate sub-lethal adverse health effects. Many of these compounds also persist in the environment and bioaccumulate in the animal and human tissues [9]. The degradation and transformation of the non-persistent chemicals in the environment are dependent on their physicochemical properties, the environment in which they reside and the threshold levels of these chemicals in the environment. Non-persistent chemicals degradation and transformation processes do not always result in decreased activity or dilution of the parent compound, for the degraded or transformed products are at times more toxic, resulting in biomagnification of the toxicity of the parent compound.

Plants obtain pesticide residues directly from application and indirectly by aerial drift, soil dust, volatilization and root uptake. Pesticides applied to the shoots of plants can migrate through the cuticular layer by two routes: a lipid and aqueous...
pathway. Compounds that penetrate the cuticle in the lipid soluble form are non-polar, undissociated compounds, while those which enter through the aqueous route have a polar nature. Both types of compounds penetrate the cuticle better in conditions of increased humidity. The compounds absorbed by the plant may remain bound to the plant tissue, are stored in the vacuoles of the plant cells, form conjugates with the plant constituents or undergo degradative processes in the plant material. The unabsorbed materials on plant surface may be volatilized, washed down from the leaf surface by rainfall, or remain on the outer surface where it dries to crystalline form or concentrates to form a viscous liquid. Pesticides which are washed down are deposited in the soil and may be absorbed through the roots.

Loamy sands with low pH tend to have high pesticide dissipation rates [10], and warm moist soils containing high organic matter generally accelerate the decomposition process. The climatic factors which influence pesticide persistence in soil include air temperature, light intensity, rainfall and wind direction. Pesticide residues in soils expose the crops grown in rotation to additional residues and inhibit beneficial microorganisms to critical levels. Excessive amounts of pesticide residues could alter the soil ecology, threaten the soil flora and fauna, and destroy the metabolic integrity of the soil. Pesticide residues in soils enter the food chain through the soil flora and fauna and bioaccumulate in the higher members of the food chain. Disposal of pesticide waste and used containers has been identified as one of the major causes of soil contamination other than for agricultural contamination. In the case of agricultural contamination, the top soils have been found to be the most contaminated. These pesticides could readily partition into the air, thereby increasing the risk of exposure in agricultural workers. Degradation of biodegradable pesticide residues in the soil takes place by first order kinetics. In contrast, non-biodegradable residues accumulate and enter the food chain [11].

Alau Dam and Gongulong agricultural areas have a long history of large scale production of vegetables for human consumption, as well as use of pesticides. Commercial vegetable production takes place in the two agricultural sites, where farmers use persistent organochlorine pesticides to control pests on the vegetables. Lack of knowledge of the use and the effects of these pesticides among the farmers has resulted in their misuse and consequently bioaccumulation in the various parts of the plants. The uptake of these pesticides by plants especially leafy vegetables is an avenue for their entry into the human food chain which will eventually affect humans and other species that depend on such plants as food. This calls for the need of epidemiological data concerning the risk of farmers and consumers of Vegetables from the two agricultural areas.

II. MATERIALS AND METHODS

A. Study Area

Vegetable and soil samples were collected from Alau Dam agricultural area within Jere local government area and Gongulong in Konduga local government, Borno State, Nigeria.

B. Collection of Vegetable and Soil Samples

At each sampling sites, 20g each of the five vegetables namely, spinach, lettuce, cabbage, tomato and onion were collected from three different locations in each area to provide replicate samples of each crop. The Vegetables samples were collected in clean polyethylene bag, labeled and transported to the laboratory and preserved in a refrigerator at 4 OC, pending extraction.

Soil samples were collected from ten plots, from Alau Dam and Gongulong Agricultural areas. In each plot, three soil samples were collected at three depths (0-10cm, 10-20cm and 20-30cm), using spiral auger of 2.5cm diameter. The Soil samples were then randomly selected and bulked together to form a composite sample before being placed in clean plastic bags and transported to Chemistry Laboratory University of Maiduguri.

C. Extraction of Vegetable Samples

The method of extraction used for the vegetables was the USEPA method 3510 for extracting pesticide residues in non-fatty crops, using ethyl acetate as the solvent. Sodium hydrogen carbonate (NaHCO3) was used to neutralise any acid that may be present and the vegetable samples were washed thoroughly with distilled water. Twenty grams (20g) of each of the samples was placed in a mortar and anhydrous sodium sulphate (Na2SO4) was used to remove water from the sample matrix. After weighing, the samples were washed thoroughly with distilled water and placed in a mortar and ground to a paste using a pestle. The paste was transferred into a conical flask with the help of a spatula and 40ml of Ethyl acetate was added and shaken thoroughly. A 5g portion of sodium hydrogen carbonate (NaHCO3) was added to the mixture followed by 20g of anhydrous sodium sulphate (Na2SO4) and the entire mixture was shaken vigorously for one hour. This process was to ensure that enough of the pesticide residue dissolved in the ethyl acetate. The procedure was repeated for the samples from each area and the mixture was filtered into a labeled container before being centrifuged at a speed of 1800 rpm for 5 mins. The organic layer was decanted into a container and a 1:1 mixture of 5 ml ethyl acetate and cyclohexane was added.

D. Cleaning up of Vegetable Extract

The vegetable extracts were cleaned up as follows; A 10mm chromatographic column was filled with 3g activated silica gel and topped up with 2 to 3g of anhydrous sodium sulphate, and 5ml of n-hexane was added to the column. The residue in 2ml n-hexane was transferred onto the column and the extract was rinsed thrice with 2ml hexane. The procedure was repeated for all the samples. The sample was collected in a 2ml vial, sealed and placed in the refrigerator in the laboratory with temperature below normal room temperature, to prevent evaporation of the ethyl acetate.

E. Extraction of Soil Sample

The Soil samples were extracted using a soil-packed bulb.
column, and 25g of each sample was weighed into a glass jar, and fortified at this step, before adding 25g of pre-cleaned sand and 50g of granular sodium sulfate. The sample mixture was manually shaken for 30 seconds, placed on a roller for 30 seconds, and then allowed to stand for 20 minutes to provide time for the sodium sulfate to adsorb any residual moisture from the soil. The sample mixture was then transferred to a 250ml bulb column and the sample jar was triple rinsed with small amounts of 5ml of hexane and transferred to the bulb column. The soil content was extracted with acetone:hexane (1:1 v/v, 250ml) and the eluate collected and concentrated to 100ml using a rotary evaporator. The soil extract was then subjected to additional cleanup.

F. Cleaning up of Soil Extracts

The concentrated soil eluate was washed by liquid-liquid partitioning with saturated sodium sulfate (25ml) and distilled water (300ml) in a separatory funnel (500ml). After shaking, the aqueous layer was transferred to a separatory funnel (250ml). The aqueous layer was returned to the 500ml separatory funnel and re-extracted with 15% dichloromethane in hexane (40ml). The organic layer was combined in the 250ml separatory funnel and gently washed with distilled water (100ml) for about 30 seconds. After discarding the aqueous layer, the organic layer was filtered through sodium sulfate evaporated to near dryness on a rotary evaporator; rinsed the sides of the flask with hexane (20ml), and evaporated to about 1ml. The sample extract was quantitatively transferred to a centrifuge tube, concentrated on a nitrogen evaporator to 0.5ml, and diluted to 2.0ml final volume in hexane prior to Gas chromatography analysis.

G. Determination of Pesticide Residues

The SHIMADZU GC/MS (GC – 17A), equipped with fluorescence detector was used for the chromatographic separation and was achieved by using a 35% diphenyl, 65% dimethyl polysiloxane column. The oven was programmed as follows: initial temperature 40 OC, 1.5min, to 150 OC, 15.0 min, 5 OC/min to 200 OC, 7.5min, 25 OC/min to 290 OC with a final hold time of 12 min and a constant column flow rate of 1 ml/min. The detection of pesticides was performed using the GC-ion trap MS with optional MSn mode. The scanning mode offer enhances selectivity over either full scan or selected ion monitoring (SIM). At the elution time of each pesticide using selected ion monitoring, the ration of the intensity of matrix ions increase exponentially versus that of the pesticide ions as the concentration of the pesticide approach the detection limit, decrease the accuracy at lower levels. The GC-ion trap MS was operated in MSn mode and perform tandem MS function by injecting ions into the ion trap and destabilizing matrix ions, isolating only the pesticide ions. The retention time, peak area and peak height of the sample was compared with those of the standards for quantization.

H. Data Handling

Data collected were subjected to a one-way analysis of variance (ANOVA) and least significant Difference (LSD) to assess whether or not pesticide residues varied significantly within and between the vegetables and soil samples. The statistical significance tests were carried at 5% confidence level (p<0.05).

III. RESULTS

A. Organochlorine Pesticide Residues in Different Parts of Vegetable Samples from Alau Dam Agricultural Area

The concentration of some organochlorine pesticide residues (dichlorodiphenyl dichloroethylene (o,p'-DDE), 4,4’-dichlorodiphenyldichloroethan, 2,4’-dichlorodiphenyldichloroethan (o,p’-DDD), 2,4’,dichlorodiphenyltrichloroethane (p,p’-DDT), α-BHC, γ-BHC, metoxichlor, lindane, endosulfan, dieldrin and aldrin) in different parts of tomato samples from Alau Dam agricultural site are presented in Table I. The levels of these pesticides in root samples of tomato ranged between 9.23±0.54 and 66.34±1.23 µg/g; 14.44±0.23 and 83.56±8.45 µg/g stem, and 22.55±0.67 and 132.87±24.54 µg/g leaf. The maximum concentration of 132.87±24.54 µg/g was observed in the leaf sample while the root had the least value of 9.23±0.54 µg/g. Table II presents the concentrations of some organochlorine pesticide residues (o, p’-DDE), (p,p’-DDD), (o,p’-DDD), (p,p’-DDT), α-BHC, γ-BHC, metoxichlor, lindane, Endosulfan, dieldrin and aldrin) in different part of onion samples from Alau Dam agricultural areas. The levels of this pesticide in root sample of onion ranges between 8.93±0.11 and 66.56±0.77 µg/g; 12.34±0.75 and 79.45±0.45 µg/g stem, and 18.63±1.02 and 121.53±7.13 µg/g leaf. The maximum concentration of 121.53±7.13 µg/g was observed in the leaf, while the root shows the least value of 8.93±0.11 µg/g.

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>MEAN CONCENTRATIONS OF ORGANOCHLORINE PESTICIDE RESIDUES IN DIFFERENT PARTS OF TOMATO SAMPLES FROM ALAU DAM AGRICULTURAL SITE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SITE</strong></td>
<td><strong>ROOT</strong></td>
</tr>
<tr>
<td><strong>Concentrations (µg/g)</strong></td>
<td></td>
</tr>
<tr>
<td>α, p’-DDE</td>
<td>23.65a±2.98</td>
</tr>
<tr>
<td>p,p’-DDD</td>
<td>65.34a±1.23</td>
</tr>
<tr>
<td>o,p’-DDD</td>
<td>41.17a±2.07</td>
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<tr>
<td>p,p’-DDT</td>
<td>12.34a±0.56</td>
</tr>
<tr>
<td>Alpha BHC</td>
<td>66.34a±1.23</td>
</tr>
<tr>
<td>Gamma BHC</td>
<td>58.34a±1.65</td>
</tr>
<tr>
<td>Metoxichlor</td>
<td>13.12a±2.43</td>
</tr>
<tr>
<td>Lindane</td>
<td>22.34a±3.23</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>15.23a±5.23</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>48.55a±12.34</td>
</tr>
<tr>
<td>Aldrin</td>
<td>9.23a±0.54</td>
</tr>
</tbody>
</table>

Within rows, mean and standard deviation with different letters are statistically significant (p<0.05).
TABLE II
MEAN CONCENTRATIONS OF ORGANOCHLORINE PESTICIDE RESIDUES IN DIFFERENT PARTS OF ONION SAMPLES FROM ALAU DAM AGRICULTURAL SITE

<table>
<thead>
<tr>
<th></th>
<th>Concentrations (µg/g)</th>
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<tbody>
<tr>
<td></td>
<td>ROOT</td>
</tr>
<tr>
<td>α, p’,DDE</td>
<td>10.42±2.12</td>
</tr>
<tr>
<td>p,p’,DDT</td>
<td>27.34±0.54</td>
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<tr>
<td>o,p’,DDE</td>
<td>15.43±1.08</td>
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<tr>
<td>p,p’,DDT</td>
<td>42.13±2.34</td>
</tr>
<tr>
<td>Alpha BHC</td>
<td>28.64±2.34</td>
</tr>
<tr>
<td>Gamma BHC</td>
<td>66.56±0.77</td>
</tr>
<tr>
<td>Metoxichlor</td>
<td>55.87±6.45</td>
</tr>
<tr>
<td>Lindane</td>
<td>8.93±0.11</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>22.87±3.87</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>32.34±1.09</td>
</tr>
<tr>
<td>Aldrin</td>
<td>25.65±2.24</td>
</tr>
</tbody>
</table>

Within rows, mean and standard deviation with different letters are statistically significant (p<0.05).

TABLE III
MEAN CONCENTRATIONS OF ORGANOCHLORINE PESTICIDE RESIDUES IN DIFFERENT PARTS OF CAULIFLOWER SAMPLES FROM ALAU DAM AGRICULTURAL SITE

<table>
<thead>
<tr>
<th></th>
<th>Concentrations (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ROOT</td>
</tr>
<tr>
<td>α, p’,DDE</td>
<td>42.33±0.61</td>
</tr>
<tr>
<td>p,p’,DDT</td>
<td>66.56±3.34</td>
</tr>
<tr>
<td>o,p’,DDE</td>
<td>73.45±6.44</td>
</tr>
<tr>
<td>p,p’,DDE</td>
<td>11.34±0.12</td>
</tr>
<tr>
<td>Alpha BHC</td>
<td>14.34±0.32</td>
</tr>
<tr>
<td>Gamma BHC</td>
<td>93.23±5.65</td>
</tr>
<tr>
<td>Metoxichlor</td>
<td>6.34±0.23</td>
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<tr>
<td>Lindane</td>
<td>15.34±2.07</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>4.56±0.02</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>43.56±0.16</td>
</tr>
<tr>
<td>Aldrin</td>
<td>13.45±0.21</td>
</tr>
</tbody>
</table>

Within rows, mean and standard deviation with different letters are statistically significant (p<0.05).

TABLE IV
MEAN CONCENTRATIONS OF ORGANOCHLORINE PESTICIDE RESIDUES IN DIFFERENT PARTS OF LETTUCE SAMPLES FROM ALAU DAM AGRICULTURAL SITE

<table>
<thead>
<tr>
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<th>Concentrations (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ROOT</td>
</tr>
<tr>
<td>α, p’,DDE</td>
<td>33.45±0.43</td>
</tr>
<tr>
<td>p,p’,DDT</td>
<td>35.85±0.64</td>
</tr>
<tr>
<td>o,p’,DDE</td>
<td>5.65±0.21</td>
</tr>
<tr>
<td>p,p’,DDT</td>
<td>15.34±0.32</td>
</tr>
<tr>
<td>Alpha BHC</td>
<td>4.34±0.02</td>
</tr>
<tr>
<td>Gamma BHC</td>
<td>16.34±0.12</td>
</tr>
<tr>
<td>Metoxichlor</td>
<td>24.56±0.26</td>
</tr>
<tr>
<td>Lindane</td>
<td>43.85±1.07</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>30.43±0.23</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>33.23±4.13</td>
</tr>
<tr>
<td>Aldrin</td>
<td>12.34±3.65</td>
</tr>
</tbody>
</table>

Within rows, mean and standard deviation with different letters are statistically significant (p<0.05).

Fig. 1, presents the mean concentrations of some organochlorine pesticide residues (α, p-DDE, p,p’-DDT, o,p’-DDD, p,p’-DDT, α-BHC, γ-BHC, metoxichlor, lindane, endosulfan, dieldrin and aldrin) in different part of spinach samples from Alau Dam agricultural site. The concentrations of these pesticides in the root of spinach ranged between 1.98 and 43.22 µg/g; 3.87 and 48.34 µg/g stem, and 6.94 and 53.85 µg/g leaf. The maximum concentration of 53.85 µg/g was observed in the leaf, while root shows the least value of 1.98 µg/g.

B. Organochlorine Pesticide Residues in Different Parts of Vegetable Samples from Gongulong Agricultural Site

Fig. 2, shows the mean concentrations of some organochlorine pesticides residues (α, p-DDE, p,p’-DDT, o,p’-DDD, p,p’-DDT, α-BHC, γ-BHC, metoxichlor, lindane, endosulfan, dieldrin and aldrin) in different part of tomato samples from Gongulong agricultural site. The levels of these pesticides in the root samples of tomato ranged between12.45 and 84.34 µg/g; 18.96 and 98.34 µg/g stem, 34.19 and 142.81 µg/g leaf. The highest concentration of 142.81 µg/g was observed in the leaf sample, while root shows the lowest value of 12.45 µg/g. Fig. 3, presents the mean concentration of some organochlorine pesticide residues (α, p-DDE, p,p’-DDD, p,p’-DDT, α-BHC, γ-BHC, metoxichlor, lindane, endosulfan, dieldrin and aldrin) in different part of onion samples from Gongulong agricultural site. The levels of these pesticides in the root sample of onion ranged between 15.56 and 74.56 µg/g; 20.45 and 89.45 µg/g stem, and 23.65 and 133.76 µg/g leaf. The highest concentration of 133.76 µg/g was observed in the leaf sample, while root shows the lowest value of 15.56 µg/g. Fig. 4, present the mean concentration of some organochlorine pesticide residues (α, p-DDE, p,p’-DDD, p,p’-DDT, α-BHC, γ-BHC, metoxichlor, lindane, endosulfan, dieldrin and aldrin) in different part of cabbage samples from Gongulong agricultural site. The levels of these pesticides in root samples of cabbage ranged between 10.41 and 104.58 µg/g; 13.23 and 121.23 µg/g stem; and 17.45 and 142.08 µg/g leaf. The highest concentration of 142.08 µg/g was observed in the leaf sample, while root shows the lowest value of 10.41 µg/g. Fig. 5, presents the mean concentration of some organochlorine pesticides residues (α, p-DDE, p,p’-DDD, p,p’-DDT, α-BHC, γ-BHC, metoxichlor, lindane, endosulfan, dieldrin and aldrin) in different part of lettuce samples from Gongulong agricultural site. The levels of these pesticides in the root sample of lettuce ranged between 8.34 and 55.45 µg/g, 15.75 and 58.34 µg/g stem, and 21.23 and 65.43 µg/g stem.
µg/g leaf. The highest concentration of 65.43 µg/g was observed in the leaf sample, while roots show the lowest value of 8.34 µg/g. The mean concentrations of some organochlorine pesticides residues (o, p-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT, α-BHC, γ-BHC, metoxichlor, lindane, Endosulfan, dieldrin and aldrin) in different part of spinach samples from Gongulong agricultural site are presented in Fig. 6. The levels of these pesticides in the root samples of spinach ranges between 6, 6.45 and 53.34, 9.72 and 58.47 µg/g stem, and 11.03 and between 64.02 µg/g. Highest concentration of 64.02 µg/g was observed in the leaf, while roots shows the lowest values of 6.45µg/g.

![Fig. 2 Mean concentrations of some organochlorine pesticide residues in different parts of Tomato samples from Gongulong agricultural site](image2)

![Fig. 3 Mean concentrations of some organochlorine pesticide residues in different parts of Onion samples from Gongulong Agricultural site](image3)

![Fig. 4 Mean concentrations of some organochlorine pesticide residues in different parts of Cabbage samples from Gongulong agricultural site](image4)

![Fig. 5 Mean concentrations of some organochlorine pesticide residues in different parts of lettuce samples from Gongulong agricultural site](image5)

![Fig. 6 Mean concentrations of some organochlorine pesticide residues in different parts of spinach samples from Gongulong agricultural site](image6)

C. Organochlorine Pesticide Residues in Soil Samples at Different Depth at Alau Dam and Gongulong Agricultural Areas

The mean concentrations of some organochlorine pesticide residues (o,p-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT, α-BHC, γ-BHC, metoxichlor, lindane, Endosulfan, dieldrin and aldrin) indifferent depth of soil samples from Alau Dam agricultural site are as presented in Fig. 7. The levels of this pesticide in soil sample from depth 0-10cm ranged from 65.45 to 176.45 µg/g.
82.13 to 234.23 µg/g at 11-20cm and 97.34 to 265.34 µg/g for soil at a depth of 21-30cm. The highest concentration of Gamma BHC with value of 265.34 µg/g was observed in the soil sample at a depth of 21-30cm, while 0-10cm depth shows the lowest value of 65.45 µg/g. Fig. 8 present the mean concentration of some organochloride pesticide residues (α, β, p'-DDD, α, β, p'-DDD, α, p'-DDT, α-BHC, γ-BHC, metoxichlor, lindane, Endosulfan, dieldrin and aldrin) from different depth of soil samples within Gongulong Agricultural site. The concentrations of these pesticides for depth 0-10 cm ranged from 74.56 to 193.45 µg/g; 92.34 to 256.87 µg/g 11-20cm depth and 107.84 to 288.45 µg/g for soil sample ranging from 21-30cm depth. The highest concentration of 288.45 µg/g was observed in the soil sample at depth 21-30cm, while 0-10cm depth shows the lowest value of 74.56 µg/g.

Fig. 7 Mean concentrations of some organochlorine pesticide residues in soil samples from different depth from Alau Dam agricultural site

Fig. 8 Mean concentrations of some organochlorine pesticide residues in soil samples from different depth from Gongulong agricultural site

IV. DISCUSSION

A. p,p'-DDT, α,p'-DDD, p,p'-DDD and α,p'-DDE in Vegetable Samples from Alau Dam and Gongulong Agricultural Areas

In Alau Dam agricultural site, the concentration of organochloride pesticide residue (α,p'-DDE, p,p'-DDD, α,p'-DDD, p,p'-DDT) were detected in all the vegetable samples. The highest concentration (132.4±13.45µg/g) was that of p,p'-DDD which was observed in the leaf of cabbage Table III, while the lowest concentration (2.34µg/g) was that of p,p'-DDT which was observed in the root of spinach in Fig. 1. A similar trend was observed in the Gongulong agricultural area, with the highest concentration of 153.23µg/g being that of p,p'-DDD in the leaf of cabbage Fig. 4, while the lowest concentration of 12.45µg/g p,p'-DDT was observed in the root of spinach Fig. 6. The pesticide DDT gradually degrades to DDE and DDD through biological and photochemical transformations under both aerobic and anaerobic conditions [12]. The DDT (DDE and DDD) ratio is usually used to know whether DDT input has occurred recently [13]. The total DDT, DDD and DDE in all the vegetable samples from the two agricultural areas were much higher than the EU set maximum residue limit (MRL) for total DDT, DDD and DDE in vegetables plants which are 0.05µg/kg. Giving the lipophilic nature of organochlorine compounds, vegetables having less water and greater lipid contents, have greater potential to accumulate the organochlorine pesticides. The high accumulation of DDT and its metabolites, obtained in the results of this study indicates that very high levels of DDT and DDD had been used. The low level of DDT instead of DDE as seen on Table III suggests that DDT have been metabolized to DDD over time, and is currently in use for control of pests in the two agricultural areas. This wide difference of DDT residue 33.21±1.45µg/kg and its metabolites levels 132.4±13.45µg/kg indicates the differences in the level of this pesticide usage by farmers. The difference in the parts of these vegetables that is root, stem and the leaf is as a result of uptake of nutrients from the root to the leaf for photosynthesis. The detection of high residual level of organochlorine pesticides in vegetable samples collected from the two agricultural areas shows that, like other developing countries, such pesticides are still in use here. Although the use of DDT and its metabolites have been banned in Nigeria since 2008, it is still being used. DDT and its metabolites have been classified by NAFDAC as probable human carcinogens. However, because of their easy accessibility to the farmers, it is illegally used by farmers within the study area for the control of pest. The concentrations of all the pesticides were significantly higher in the leaf of all the vegetables when compared with other parts. The higher concentration might be due to photosynthesis within the plant leaf.

B. Dieldrin and Aldrin in Vegetable Samples from Alau Dam and Gongulong Agricultural Areas

The highest concentrations of dieldrin and aldrin in vegetable samples from the Alau Dam agricultural area are observed in the leaf of tomatoes 132.87±24.54 µg/g, while the lowest concentrations 1.98µg/g were observed in the root of spinach in Fig. 1. For Gongulong agricultural area, the concentrations of dieldrin and aldrin were also observed to be higher in tomatoes samples, while spinach accumulated the lowest concentration as shown in Fig. 6. The concentration of dieldrin was significantly higher that of aldrin in all the vegetable samples studied for both areas, such high concentration is an indication that there is more dieldrin in the
environment compared to aldrin. This trend is supported by the fact that aldrin photolysis to dieldrin in the environment. These results are in agreement with those of the United States Department of Health and Human services [14], which shows that aldrin is rapidly converted into dieldrin in plant and animal tissues. This is so because dieldrin is extremely non-polar and therefore has a strong tendency to adsorb tightly to plant waxes. Detection of dieldrin and aldrin in the vegetable samples from the two agricultural sites indicate that these pesticides are still being used for agricultural and pest control activities. This observation is in confirmation with the findings in research carried out on soil samples from Awash Basin in Ethiopian state farm soil, which indicated the presence of aldrin in soil [15] and it is illegal availability and use. The concentrations of aldrin and dieldrin found in all the vegetable samples from the two agricultural sites were much higher than the EU set maximum residue limits (MRLs) of 0.01 µg/kg and the Acceptable Daily intake values (ADIs) of 0.0001 µg/kg. The fact that the concentrations of all the pesticides were higher in the Gongulong Agricultural area than the Alau Dam area could be due to intense agricultural activities in the area, coupled with excessive usage of pesticides.

C. α-BHC, γ-BHC, Methoxychlor, and Lindane in Vegetable Samples from Alau Dam and Gongulong Agricultural Site

α-BHC, γ-BHC, methoxychlor, and lindane were detected in all the vegetable samples studied. The concentrations of α-BHC, γ-BHC, Methoxychlor, and lindane were observed to be highest in the leaf of cabbage, while the lowest value of α-BHC, γ-BHC, Methoxychlor, and lindane were observed in the root of Spinach. The concentrations of this pesticide in all the vegetables were much higher than the Codex 2009, set maximum residue limits (MRLs) of 0.01 µg/kg for α-BHC, γ-BHC, Methoxychlor, and lindane. The Acceptable Daily Intake value (ADI) of lindane in leafy vegetables is 0.0001 µg/kg, the result in this study exceeded these limits, indicating that there is severe contamination of these vegetables by lindane. Residues of BHC isomers in significant concentrations in the vegetable samples may be attributed to the heavy use of this pesticide in the study area. Methoxychlor concentration in vegetable samples was high 72.77±2.34µg/g for Alau Dam agricultural area and 82.45µg/g for Gongulong Agricultural area, this might be as a result of historical use of DDT with technical methoxychlor containing about 88% of the p,p’-isomer together with more than 50 structurally related contamination, which might have been added to the actual amount of methoxychlor present [16].

D. Organochlorine Pesticide Residues in Soil Samples from Alau Dam and Gongulong Agricultural Sites

In the Alau Dam and Gongulong agricultural sites, the concentration of organochloride pesticide residue (α-BHC, γ-BHC, methoxychlor, lindane, endosulfan, aldrin, dieldrin, p,p’-DDT, o,p’-DDD p,p’-DDD and o,p’-DDE) were detected in all the soil samples. The highest concentration of p,p’-DDD was observed at a depth of 21-30cm, while p,p’-DDT shows the lowest concentration at a depth of 0-10cm. The concentrations of DDT and its metabolites were all higher at a depth of 21-30cm, while the lowest detectable levels were observed at depth 0-10cm. The highest concentration of γ-BHC was observed at a depth of 21-30cm, while the lowest concentration of Lindane was observed at a depth of 0-10cm The highest concentrations of endosulfan, dieldrin and aldrin were observed at a depth of 21-30cm, while the lowest concentrations were observed at a depth of 0-10cm. DDT can be biodegraded to DDE under aerobic conditions and to DDD under anaerobic conditions. The relative concentration of the parent DDT to its metabolites, DDD and DDE, can therefore be used as indices for assessing the possible pollution sources [13]. In the present study DDT compositions varied significantly with agricultural area at 5% confidence level (p<0.05). All the pesticides used are mostly synthetic organic compounds. The soil may act as an important sink for persistent organic pollutants including many pesticides used presently or in the past. They are relatively insoluble in water and are retained strongly by the soil. Soil acts as filter buffer and degradation of pollutants with respect to storage of pollutants with the help of soil organic carbon. Soil acts as a pathway of pesticide transport to contaminate ground/surface water, plants, food and effect on human via runoff, leaching, transfer of mineral nutrients and pesticides from soil into the plants and animals that constitute human food chain. Persistent pesticides slowly break down into the soil and lead to contamination which is closely correlated to human activities agricultural applications and deforestation which leads to soil erosion [6]. Several studies [17] have reported the detection of pesticides in soil and the most frequent pesticides detected were of organochlorine (OC) group which is more persistent and stay in the soil, decomposed very slowly and may persist for several years as they are insoluble in water and are retained by the soils. Studies of pesticide residues have been reported by several researchers [18], [19]. The detection of pesticides in soil and their findings was lower than results obtained in the present study. Reference [19] studied the hydrophobicity and persistence of pesticides that controlled the accumulation in different soil series of Pakistan. It was observed that less water soluble (<1 mg/l) pesticides have the potential to accumulate in sediment and aquatic biota, which is in full agreement with present study that most pesticides used in the two agricultural sites are insoluble in water that is why they persist in the soil without any influence of temperature, humidity and microbial activity.

V. CONCLUSION

The results from the present study shows that organochlorine pesticide residues are present in all the vegetable and soil samples collected from Alau Dam and Gongulong agricultural sites. The concentrations of all the pesticides were observed to be higher in the leaf of all the vegetable samples studied, while the root had the lowest concentrations in both study sites. The concentrations of all the organochlorine pesticides in the soil samples were observed to be higher at the depth of 21-30cm,
while the lowest concentrations were observed at the depth of 0-10cm. The concentrations of all the pesticides in the vegetables and soil samples from the two agricultural sites studied were observed to be at alarming levels, much higher than the European Union (EU) set maximum residue limits (MRLs) and acceptable daily intake values (ADIs) set for vegetables and soil by the European Union (EU).

REFERENCES