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Gas-Chromotography- Mass Spectrometric Determination Of Organochlorine Pesticides Residues In Water And Fish Samples From Lake Njuwa, Yola Adamawa State, Nigeria

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***Abstract*:** *This study was aimed to determine the levels of pesticides residues in water and fish from lake Njuwa Yola Adamawa State Nigeria. The water sample was subjected to liquid- liqiud extraction method while the fish samples were subjected to soxhlet extration for eight hours using dichloromethane and n-hexane mixture. The extrats were later analysed for organocholorine pesticide residues using Gas-Chromotography coupled with mass spectrometer (GS-MS). The result of insectides shows mean concentration (µg/L) of pesticides residues in water were Endosulfan 1 (0.92µg/l), Endrin (0.82µg/l), Alpha-BHC (0.57µg/l), Carbaryl (0.37µg/l), Diazinon (0.19µg/l) and Cypermethrin (0.15µg/l). However, in herbicides Di-allate was detected (0.55µg/l), Simazine (0.41µg/l) and Butachlor (0.28µg/l). concentration of pesticide residues of Tilapia Galilaea were Atrazine (1.17 µg/g), Endrin (1.13 µg/g), Methabenzthiazuron (1.07 µg/g), Di-allte (1.07 µg/g), Simazine (1.03 µg/g), carbaryl (0.89 µg/g) and Endosulfan 1 (0.76 µg/g). lastly, in Clarias Gariepinus pesticide recidues concentrations were given as follows, Methabenzthiazuron (1.86 µg/g), Carbaryl (1.07 µg/g), Simazine (0.86 µg/g), Trifluralin (0.74 µg/g), Endosulfan II (0.53 µg/g), Diazinon (0.45 µg/g) and Alpha-BHC (0.17 µg/g) respectively.The pesticide residues found in the present study are generally above the maximum residues limit (MRL) set by FAO/WHO bodies. This indicate that the pesticides residues could pose a health risk to the consumers of the fish from lake Njuwa. However emphasis should be laid on a continuous monitoring programme to safe guard the consumer of fish and animal products from lake Njuwa.*

Keywords: *pesticides,Herbicides, Insectides,Gas Chromatography, Mass Spectrometry.*

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I. Introduction

Man employs pesticide as purposeful environmental contaminants in order to improve environmetal quality for him self and his domisticated animals and plants.Pesticide is the general term for insecticides, acaricides, rodenticides, molluscicides, herbicides, fungicides and similar active compounds. A wide range of compounds are used as pesticides and a correspondingly wide methods are used in the analysis of their residues.Pesticides are synthetic and natural compounds used to control animal and plant life considered adverse to human society. Only natural pesticide compounds, such as rotenone, pyrethrum, lead arsenate and arsenic tri-chloride, were used prior to 1900. Several synthetic pesticides had been incorporated into thousands of different formulations for control of pests.

Pesticides have assisted human survival in many ways: increased crop yields; reduced losses of crops in storage or transit; improved quality of food and fiber; reduced human death rates in many parts of the world; protected clothing, carpeting, wood and other products from termites and other destructive organisms; controlled bad odor and tastes in municipal water. The examples are endless. The honest and intelligent use of pesticides has made tremendous contributions to human welfare. These compounds have, on occasion, been responsible for adverse effects on both plants and animals, including fishes.The major source of pesticides in water is from runoff from treated land, industrial discharges and domestic wastes. Other sources include fallout from atmospheric drift and precipitation, and application of pesticides to water surfaces either intentionally or accidentally. Many of the pesticides have relatively low solubility in water and tend to absorb onto suspended or sedimentary materials or organisms in water bodies. Many have an affinity for, and accumulate in, animal and plant lipids. Some are extremely stable and remain in ecosystems for exceptionally long times. Fishes may accumulate these compounds either by direct absorption or through the food chain. The transfer of pesticide residues from prey to predator in the food chain can result in residues in higher trophic levels many times

greater than residues in water or sediments [1].The majority of pesticides are insecticides or herbicides [3].Probably insecticides have had more inadvertent adverse effects on fishes than any other pesticides. Therefore, the discussion which follows is a brief examination of a few insecticidal and herbicidal compounds to demonstrate toxic effects on fishes.

The toxicity of chlorinated hydrocarbon insecticides is partly because of their fat solubility and accumulation in tissues high in lipids. Fishes may accumulate relatively large quantities of these compounds over a summer season with little or no toxic effect, because the compounds accumulate in adipose tissue. Body fats mobilized from adipose cells during periods of reduced availability of food release stored chlorinated hydrocarbon insecticides or their metabolites [4].They may then be absorbed by tissue with the next higher lipid content, often nervous tissue. The result may be destruction of nerve cells, causing partial or complete paralysis. Some may be absorbed into other vital tissues (liver, kidney, or spleen) and cause foci of necrosis or general toxemia within the organ. Death may result, or anatomical or physiological changes which may lead to death [7].Organophosphate compounds used as insecticides are oily, relatively volatile, relatively insoluble in water and soluble in organic solvents. Most are absorbed through unbroken skin, respiratory tissue and from the digestive tract of animals. Many of those used as insecticides are non-persistent, losing toxicity within a short time after application, especially in warm, moist conditions [8].Carbamate insecticides are highly toxic to a wide variety of insects and crustaceans but have a relatively low toxicity to most vertebrates. These compounds have intermediate persistence when compared to persistent chlorinated hydrocarbon and non-persistent organophosphate insecticides." Applications of carbaryl to maintain insecticidal activity up to three weeks. Furthermore, its toxicity to fishes is up to 250 times less than DDT.

There are a large number of terrestrial herbicidal compounds in use, each a possible pollutant to aquatic ecosystems. Several aquatic herbicides are used to remove unwanted aquatic plants from waterways (streams, ponds, lakes, and other bodies of water).Many of the aquatic herbicides are relatively persistent. Diquat and paraquat, for example, may be found in bottom sediment or bottom soil for up to six months after application [5].Some aquatic herbicides are applied to water bodies in granular form, the formulations being designed for slow and continuous release of the herbicide to the water. The solubility of most herbicides is quite low, but granular formulations tend to maintain maximum concentration of the herbicide for longer periods of time than those formulations applied to the water surface. Bottom-feeding fishes may be subjected to contact with herbicidal compounds continuously for several weeks or months [13].

Analysis of organochlorine pesticides can be done by gas chromatography [6]. Has listed BHC, lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin, DDT, DDE, DDD, etc. which could be analysed by a gas chromatograph. In the gas chromatograph there are two phases: a stationary phase and a mobile phase [9]. The stationary phase is a liquid content on an inert granular solids packed in a borosilicate glass tube known as column packing. The mobile phase is a carrier gas like argon, hydrogen, helium or nitrogen. The column has an inlet and an outlet and it is fitted in an oven. The water sample to be analysed for pesticides is injected into the column through a silicon rubber septum by means of a microsyringe. The column, being kept at a high temperature, the injected sample gets vapourised [10]. Carrier gas from the mobile phase carries with it vapourised pesticides through the column at different rates [17]. There is a detector device to measure as electrical signal of the different peaks of different pesticides and a recorder device prints it on a strip chart. The peak height is proportional to the quantity of the pesticide. The detector system, being based on electron capture device, is very sensitive to organo-chlorines. There are possibilities of interfaces due to the presence of polychlorinated biphenyls (PCB) and some other compounds [18]. It is essential to clean all glassware and flush out the column very carefully before using the gas chromatographs. Different marks of the instrument provide working manuals for proper handling and [6] has also described the details of preparing the chemicals and calculations.This present study is intended to determine the organochlorine pesticide residues in water and two fish species in Lake Njuwa Yola, Adamawa State, Nigeria.

II. Materials And Methods

2.1 Study Area: Lake Njuwa is locate at near Rugange, Yola, Adamawa State it lies on latitude 09º 18’ 11” N and longitude 12º 25’ 26” E. Lake Njuwa occupies natural depression near the upper River Benue in the north east Nigerian. The lake Njuwa is flooded by the river during the raining season such that it receive influx of water which pollution load originated from river Benue upstream lekdo dam from Cameroon Republic. The water from the lake is primarily used for fishing and a source of water large cattle farmer in the areas. Show in figure 1. The surrounding farmlands rely entirely on the lake for irrigation faming during dry season. According to the information from the Rugange village head and head of the local fishermen, the lake formed naturally from river Benue that was cut off as a result of heavy siltation about 100 years ago, thereby forming a lake. It is a shallow water body of about 250 hectares in size with mean depth of about 3 meters. Aquatic vegetation on the lake consists of mass of floating weeds such as Typha sp an aquatic emergent plant, Pistia sp is a water floating plant and Salvinia sp a floating plant are very commonly found in the lake. The area is characterised by Sahel

Savannah vegetation of north eastern part of Nigerian in Adamawa to be specific.It is a semi-arid with low rainfall, low humidity and high temperature. The area experiences two distinctive wet and dry seasons. The rain season starts from May to October, while the dry season commences from November to April and mean daily temperature fluctuates with season normally from 25ºC to 45ºC, and mean annual rainfall received from the range of 150-1000m. Cold and dusty weather is from December to January and then followed by intense heat of March to April. The climate is characterised by high evaporation especially during the dry season.

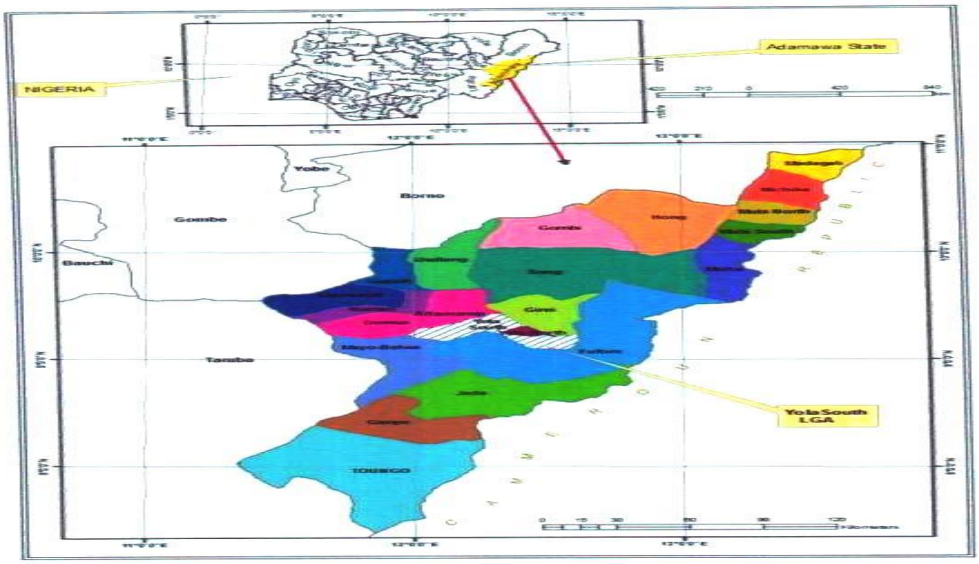

Figure 1. Map of Adamawa State Showing the Location of Njuwa lake.

2.2 Sample collection: Water and fish samples were collected from various sites of the lake (Figure 1). Sample were collected from surface parts of the water. Also, each sampling was carried out in three replicates, so as to enable statistical analysis. A total of 12 sample each of water were collected randomly. Two common species of fishes were collected from the fishermen in the lake Njuwa during study period. One species of these was omnivore *Tilapia galilae* and the other was carnivore *Clariasgariepinus.* The fishes selected were among the fish species commonly found in the lake Njuwa. Extraction of pesticide residues in fish and water samples was done as described by [13, 19] with some modifications.

2.3 Extraction of pesticide residues in fish: Ten grams of homogenized fish sample was placed into a 100ml conical flask followed by addition of 20.0g of activated anhydrous sodium sulfate and mixed. The 30ml 2:1(v/v) hexane / acetone mixture was added and thoroughly mixed by shaking. The sample was then sonicated for 20 min using Bransonic ultrasound sonicator. The supernatant was filtered into a 250 ml round bottom flask. The extraction was repeated twice and the supernatants was combined and concentrated at 40ºC to near dryness using Vacuum Rotary Evaporator (Buchrotavapor R-200, Bushi heating bath B-490).

2.4 Extraction of pesticide residuesWater Samples: Extraction of pesticide residues in water samples was done using 50 ml *n*-hexane which was introduced into a 1 L separating funnel containing 100ml of filtered water. The mixture was shaken vigorously for 5 min and allowed to settle. After complete separation, the organic phase was drained into 250ml conical flask while the aqueous phase was re-extracted twice with 50 ml of *n*- hexane. The extracted organic phase was then dried by passing through a glass funnel packed with activated anhydrous sodium sulfate. The organic fraction was then concentrated to near dryness using vacuum rotary evaporator at 40ºC.

2.5 Sample Clean up procedure: The clean-up procedure is required for the pesticide residues analysis in fish samples in order to avoid interferences. The extracts from thefish samples were clean up using acolumn packed with 2 g of octadecyl (C_{18})\ modified silica gel and 2 g of anhydrous sodium sulphate (Na_2SO_4). Prior to the clean-up, the column was conditioned with 20 ml of n-hexane/acetone. The extract was introduced into the column and eluted using a mixture of n-hexane and diethyl ether (1:1 v/v). The eluates was concentrated to 5 ml using a rotary evaporator at a temperature of 45°C, during concentration the solvent is exchanged with n-hexane.

2.6 GC Analysis: The GC analysis of the organochlorine pesticide residues was conducted using a model 2010 shimadzu GC whish was equipped with an EC, a capillary column (SGE BPX-5) 60m with 0.25mm internal diameter and 0.25µm film thickness with 1m retention gap. Oven temperature was set at 90ºC at a rate of 3min. and ramped at 30ºC / min to 200ºC for 15min and then to 265 ºC at 5 ºC/ min for 5min, to 275 ºC at 3 ºC/min. and allowed for 15min. the injector was a pulsed split less mode with temperature setting of 250 ºC at a pressure of 1.441bar. Then pulsed pressure was at 4.5 bar, while pulsed time was set at 1.5min, purge flow was 55.4 ml/ min and purge time 1.4 min. Detector was set at 300 ºC and nitrogen was the carrier gas at flow rate 30ml/min.The organochlorine pesticide residues level was measure using a Varian Cp-3800 GC equipped with a CombiPAL auto sampler. A column of 30m x 0.25mm internal diameter fused silica capillary coated with VF-1701 (0.25µm film) was used. The oven temperature was programed as follows initial temperature was set at 65 ºC for 3min and ramped at 25 ºC/min to 210 ºC for 6 min and then to 230 ºC at 20 ºC/min and allow to stay for 20min.the injector setting is a pulsed split less mode at a temperature of 230 ºC detector was set at 250 ºC in "constant make flow" mode helium was used as carrier gas at flow rate of 2ml/min.

2.7Data analyis and calculations: The following informations were provided for data analysis and calculation of pesticides residues concentrationsfor aqueous and non-aqueous samples matrices.

Concentration (µg/l) = $\frac{(A_x)\,(V_t)(D)}{(\overline{CF})(V_i)(V_s)}$

Where:

A_x = Area (or height) of the peak for the analyte in the sample.

V_t = Total volume of the concentrated extract (µL).

D = Dilution factor, if the sample or extract was dilluted prior to analysis. If no dillution was made, D=1. The diluted factor is always dimensionless.

$\overline{CF}$ = Mean callibration factor from the initial calibration (area/ng).

V_i = volume of ther exact injected (µL). The injection volume for sample and callibration starndards should be the same, unless the analyst can demostrate acceptable performance using different volume or conditions.

V_s = volume of the aqueous sample extracted im mL. If units of liters are used for this term, multiply the result by 1000.

Using the unit given here for these terms will result in a concentration in units of ng/ml, which is equivalent to µg/L.

Fumular For Non- Aqueous solid samples:

Concentration (µg/g) = $\frac{(A_x)\,(V_t)(D)}{(\overline{CF})(V_i)(W_s)}$

Where A_x, V_t, D, $\overline{CF}$ and V_i are the same for aqueous sample, and

W_s = weight of the sample extracted (g). The wet weight or dry weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the result by 1000.

III. Results

The concentration of pesticde residues of water in the four sample sites of the lake range from (0.15 – 0.92), is presented on Table 1.

Table 1 – Concentration in (µg/l) of pesticide residues in *water sample at Njuwa Lake sampling site*.

Pesticide residue	Types of residue	Molecular formula	Molecular mass	RT (min)	Concentration (µg/l)
Simazine	Herbicide	$C_7H_{12}ClN_5$	201	6.25	0.41
Trifluralin	Herbicide	$C_{13}H_{16}F_3N_3O_4$	335	ND	Nil
Alpha-BHC	Insecticide	$C_6H_6Cl_6$	290	7.26	0.57
Endrin	Insecticide	$C_{12}H_8Cl_6O$	380	9.64	0.82
Isofenphos-methyl	Insecticide	$C_{14}H_{22}NO_4PS$	331	ND	Nil
Attrazine	Herbicide	$C_8H_{14}ClN_5$	215	ND	Nil
Diazinon	Insecticide	$C_{12}H_{21}N_2O_3PS$	304	10.99	0.19
Carbaryl	Insecticide	$C_{12}H_{11}NO_2$	201	14.15	0.37
Endosulfan 1	Insecticide	$C_9H_6Cl_6O_3S$	406	14.61	0.92
Endoulfan II	Insecticide	$C_9H_6Cl_6O_3S$	406.91	ND	Nil
Di-allate	Herbicide	$C_{10}H_{17}C_{l2}NOS$	270	16.17	0.55
Diphenamid	Herbicide	$C_{16}H_{17}NO$	239	ND	Nil
Cypermethrin	Insecticide	$C_{22}H_{19}C_{l2}NO_3$	416	19.17	0.15
Fluopicolide	Fungicide	$C_{14}H_8C_{l3}F_3N_2O$	383	ND	Nil
Butachlor	Herbicide	$C_{17}H_{26}ClNO_2$	311	20.75	0.28
Metamitron	Herbicide	$C_{10}H_{10}N_4O$	202	ND	Nil
Metabenzthiazuron	Herbicide	$C_{10}H_{11}N_3O_5$	221	ND	Nil

ND = Not Detected, RT = Retention Time

Table 2, presents the concentration of pesticide residues in Tilapia Galilaea which range between (0.76 – 1.17).

Table 2 – Concentration in (µg/g) of pesticide residues in *Tilapia Galilaea (Omniovorous fish).*

Pesticide residue	Types of residue	Molecular formular	Molecular mass	RT (min)	Concentration (µg/g)
Simazine	Herbicide	$C_7H_{12}ClN_5$	201	5.91	1.03
Trifluralin	Herbicide	$C_{13}H_{16}F_3N_3O_4$	335	ND	Nil
Alpha-BHC	Insecticide	$C_6H_6Cl_6$	290	ND	Nil
Endrin	Insecticide	$C_{12}H_8Cl_6O$	380	9.04	1.13
Isofenphos-methyl	Insecticide	$C_{14}H_{22}NO_4PS$	331	ND	Nil
Attrazine	Herbicide	$C_8H_{14}ClN_5$	215	9.93	1.17
Diazinon	Insecticide	$C_{12}H_{21}N_2O_3PS$	304	ND	Nil
Carbaryl	Insecticide	$C_{12}H_{11}NO_2$	201	13.94	0.89
Endosulfan 1	Insecticide	$C_9H_6Cl_6O_3S$	406	14.68	0.76
Endosulfan II	Insecticide	$C_9H_6Cl_6O_3S$	406.91	ND	Nil
Di-allate	Herbicide	$C_{10}H_{17}C_{l2}NOS$	270	17.72	1.07
Diphenamid	Herbicide	$C_{16}H_{17}NO$	239	ND	Nil
Cypermethrin	Insecticide	$C_{22}H_{19}C_{l2}NO_3$	416	ND	Nil
Fluopicolide	Fungicide	$C_{14}H_8C_{l3}F_3N_2O$	383	ND	Nil
Butachlor	Herbicide	$C_{17}H_{26}ClNO_2$	311	ND	Nil
Metamitron	Herbicide	$C_{10}H_{10}N_4O$	202	ND	Nil
Metabenzthiazuron	Herbicide	$C_{10}H_{11}N_3O_5$	221	23.95	1.09

ND = Not Detected, RT = Retention Time

Table 3, show the concentration of pesticide resudues in Clarias Gariepinus which range between (0.17 – 1.86).

Table 3 – Concentration in (µg/g) of pesticide residues Clarias Gariepinus (Carnivorous fish)

Pesticide residue	Types of residue	Molecular formular	Molecular mass	RT (min)	Concentration (µg/g)
Simazine	Herbicide	$C_7H_{12}ClN_5$	201	6.14	0.86
Trifluralin	Herbicide	$C_{13}H_{16}F_3N_3O_4$	335	7.60	0.74
Alpha-BHC	Insecticide	$C_6H_6Cl_6$	290	8.55	0.17
Endrin	Insecticide	$C_{12}H_8Cl_6O$	380	ND	Nil
Isofenphos-methyl	Insecticide	$C_{14}H_{22}NO_4PS$	331	ND	Nil
Attrazine	Herbicide	$C_8H_{14}ClN_5$	215	ND	Nil
Diazinon	Insecticide	$C_{12}H_{21}N_2O_3PS$	304	12.52	0.45
Carbaryl	Insecticide	$C_{12}H_{11}NO_2$	201	12.79	1.07
Endosulfan 1	Insecticide	$C_9H_6Cl_6O_3S$	406	ND	Nil
Endosulfan II	Insecticide	$C_9H_6Cl_6O_3S$	406.91	15.61	0.53
Di-allate	Herbicide	$C_{10}H_{17}C_{l2}NOS$	270	ND	Nil
Diphenamid	Herbicide	$C_{16}H_{17}NO$	239	ND	Nil
Cypermethrin	Insecticide	$C_{22}H_{19}C_{l2}NO_3$	416	ND	Nil
Fluopicolide	Fungicide	$C_{14}H_8C_{l3}F_3N_2O$	383	ND	Nil
Butachlor	Herbicide	$C_{17}H_{26}ClNO_2$	311	ND	Nil
Metamitron	Herbicide	$C_{10}H_{10}N_4O$	202	ND	Nil
Metabenzthiazuron	Herbicide	$C_{10}H_{11}N_3O_5$	221	22.06	1.86

ND = Not Detected, RT = Retention Time

The following figures (1-11) were Mass Spectra detected for the compounds seperated by gas Chromotography.

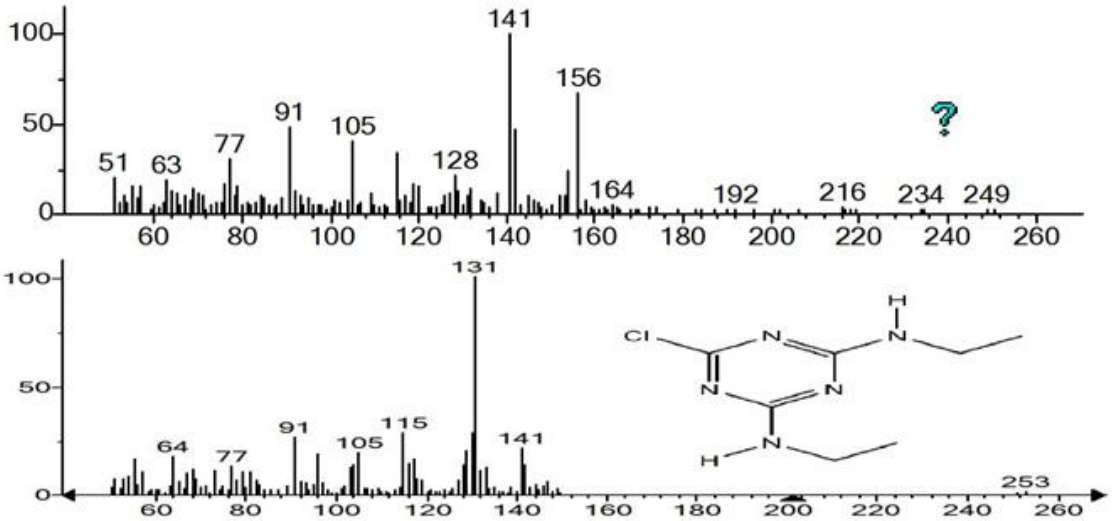

Figure 1: Mass spectra of Simazine pesticide concentration detected in surface Water and Fish of Njuwa Lake.

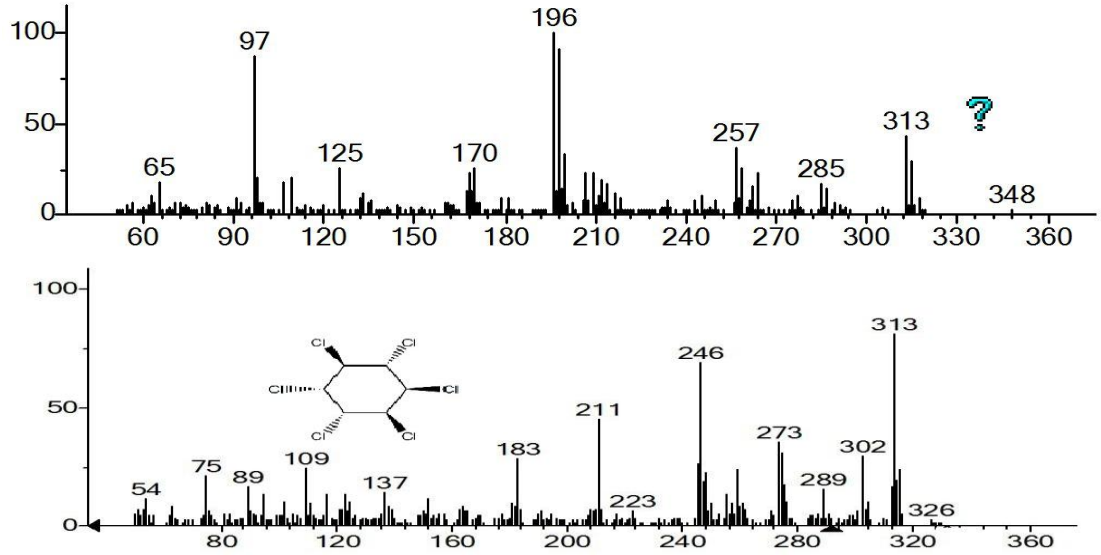

Figure 2: Mass spectra of Alpha-BHC pesticide concentration detected in surface Water and Canivorous Fish of Njuwa Lake

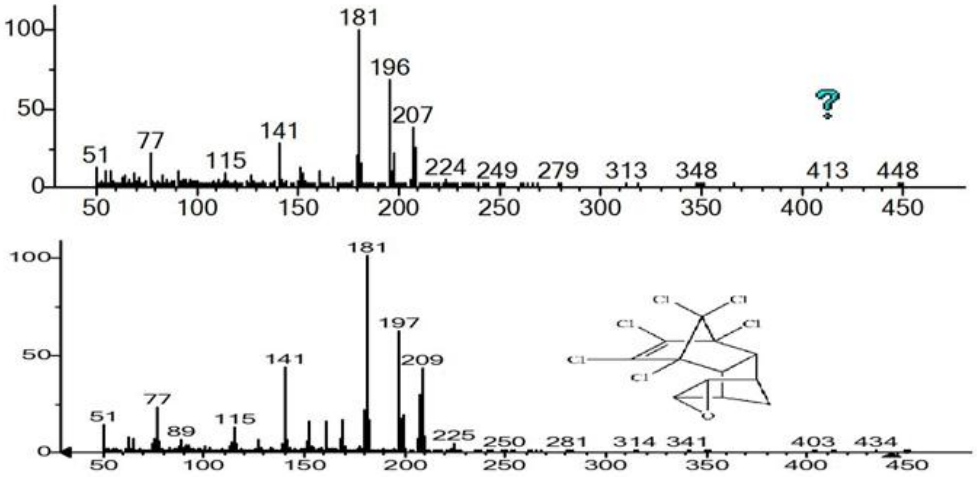

Figure 3: Mass spectra of Endrin pesticide concentration detected in surface Water and omnivorous Fish of Njuwa Lake.

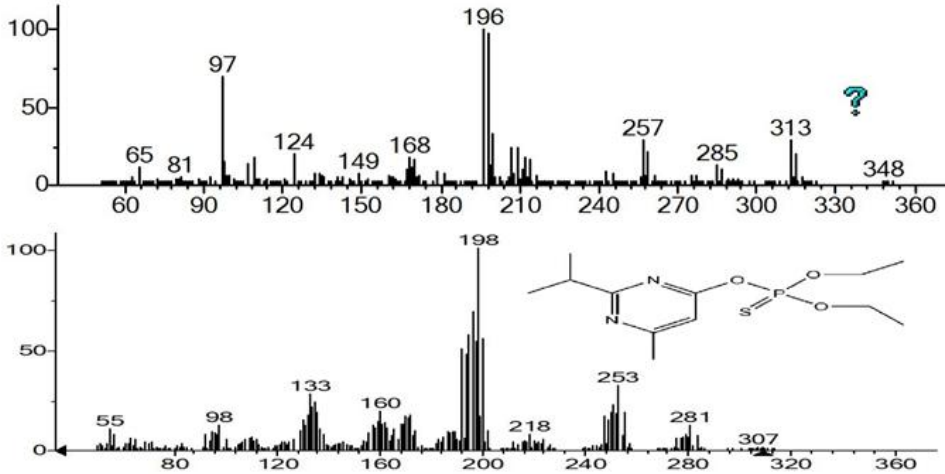

Figure 4: Mass spectra of Diazinon pesticide concentration detected in surface Water and Canivorous Fish of Njuwa Lake

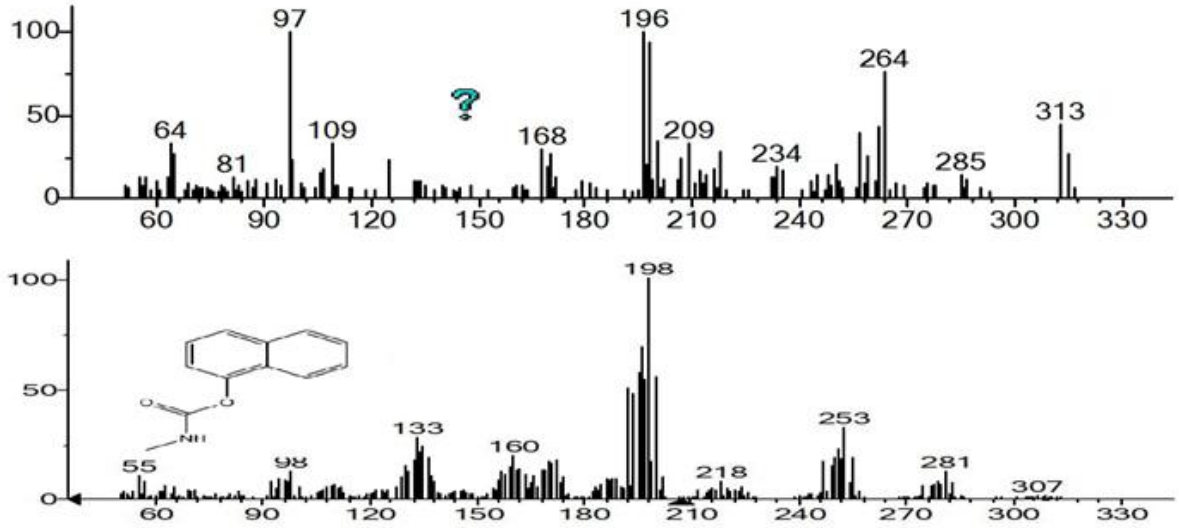

Figure 5: Mass spectra of Carbaryl pesticide concentration detected in surface Water and Fish samples of Njuwa Lake

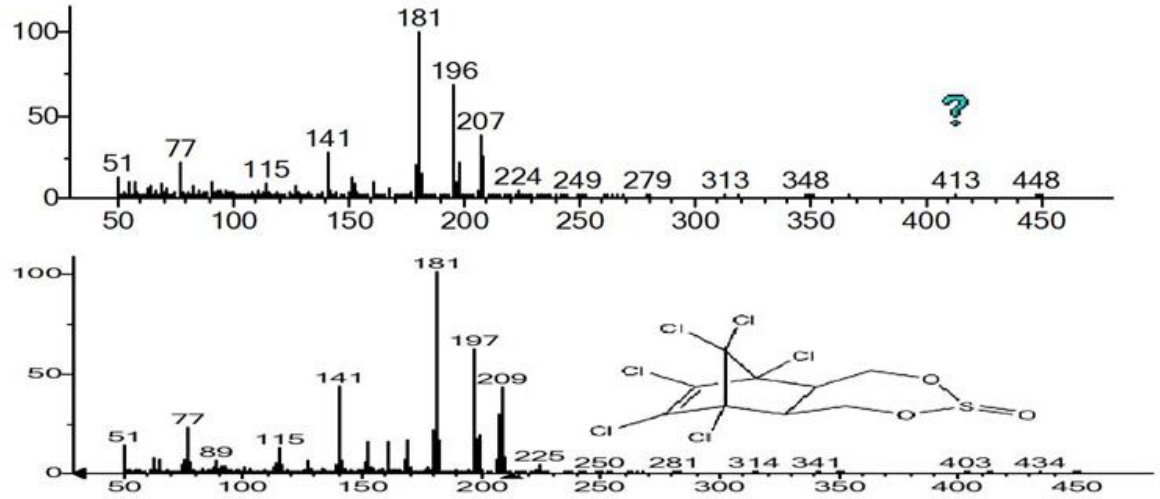

Figure 6: Mass spectra of Endosulfan 1 pesticide concentration detected in surface Water and Omnivorous Fish sample of Njuwa Lake

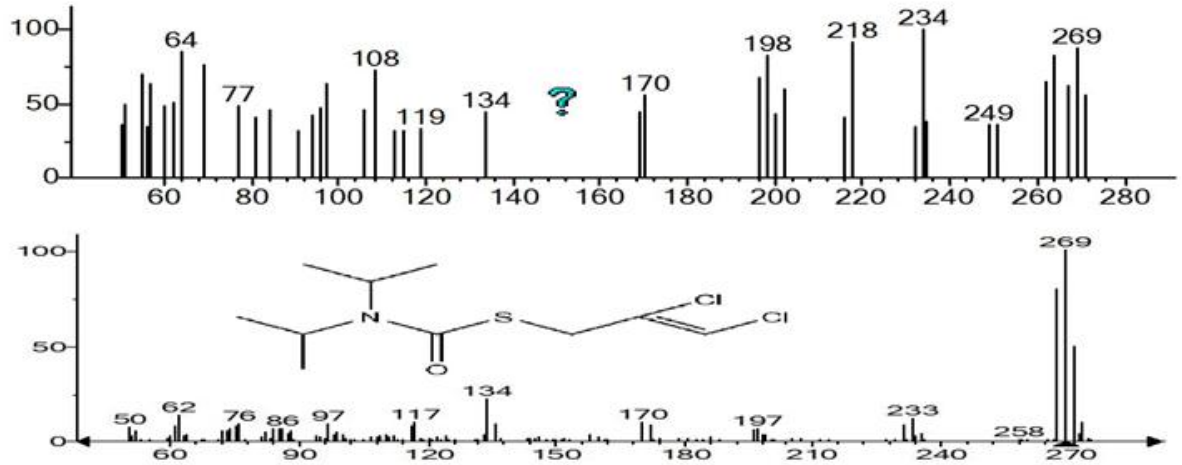

Figure 7: Mass spectra of Di-Allate pesticide concentration detected in surface Water and Omnivorous Fish sample of Njuwa Lake.

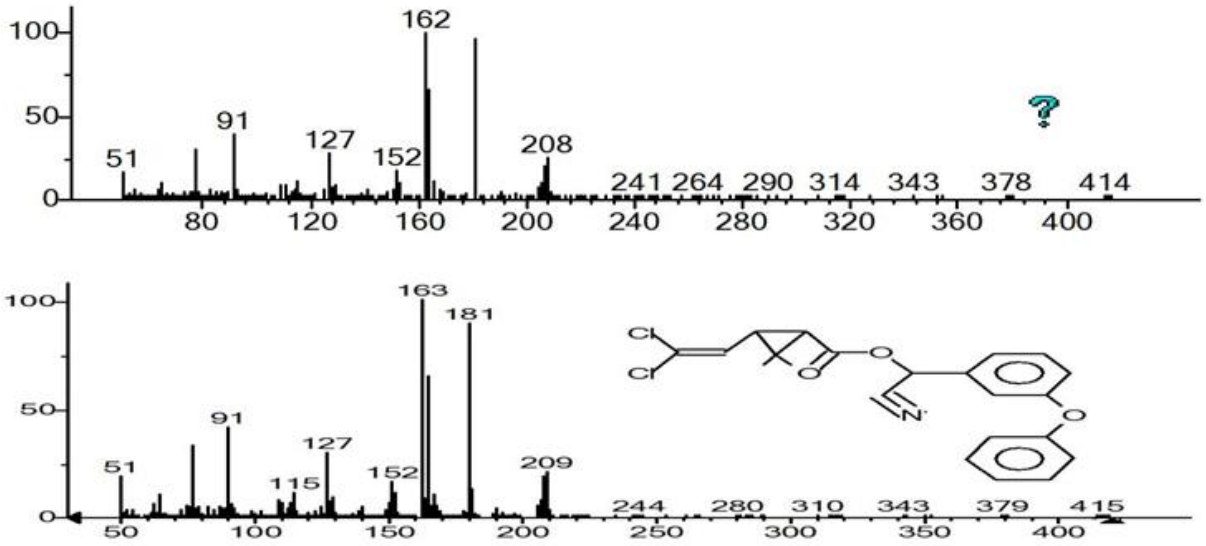

Figure 8: Mass spectra of Cypermethrin pesticide concentration detected in surface Water sample only of Njuwa Lake

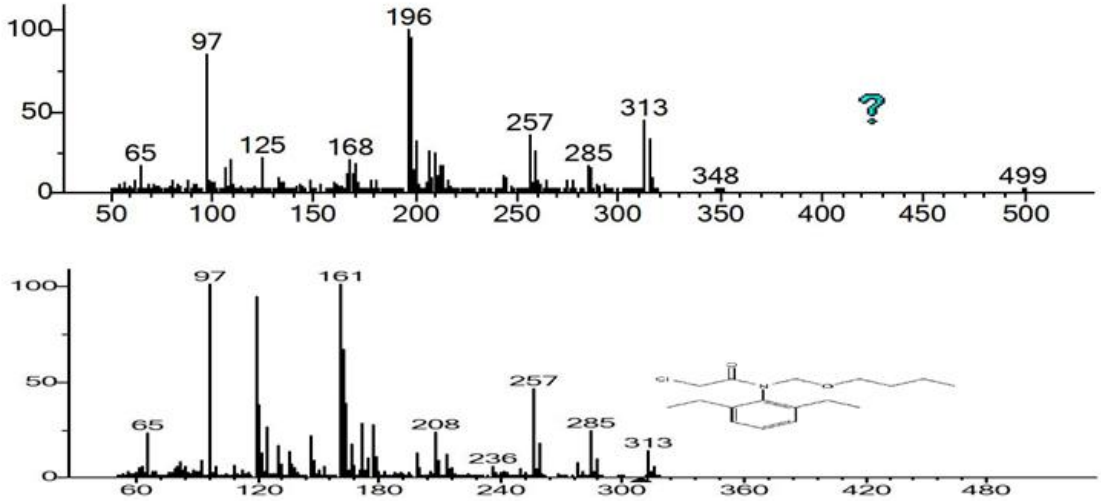

Figure 9: Mass spectra of Butachlor pesticide concentration detected in surface Water sample only of Njuwa Lake

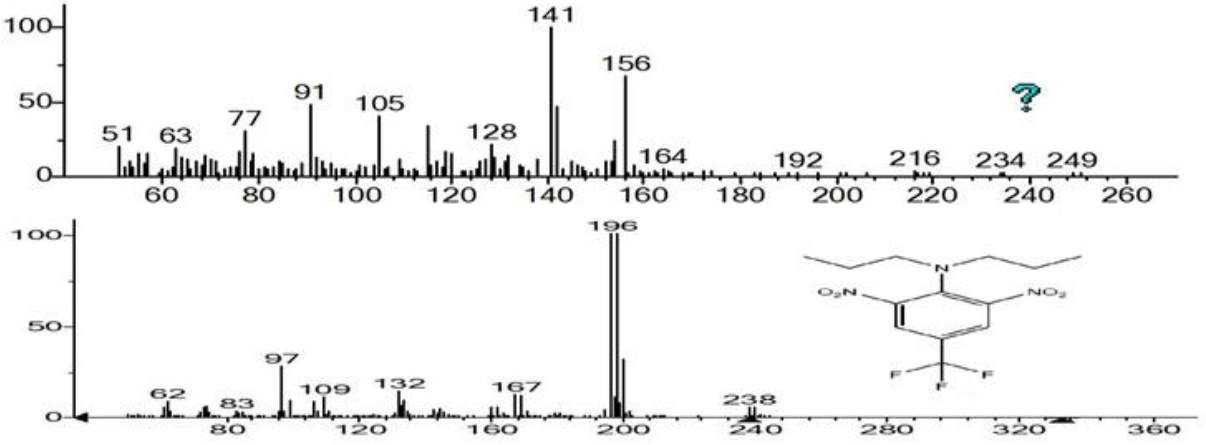

Figure 10: Mass spectra of Trifluralin pesticide concentration detected in Fishes sample of Njuwa Lake.

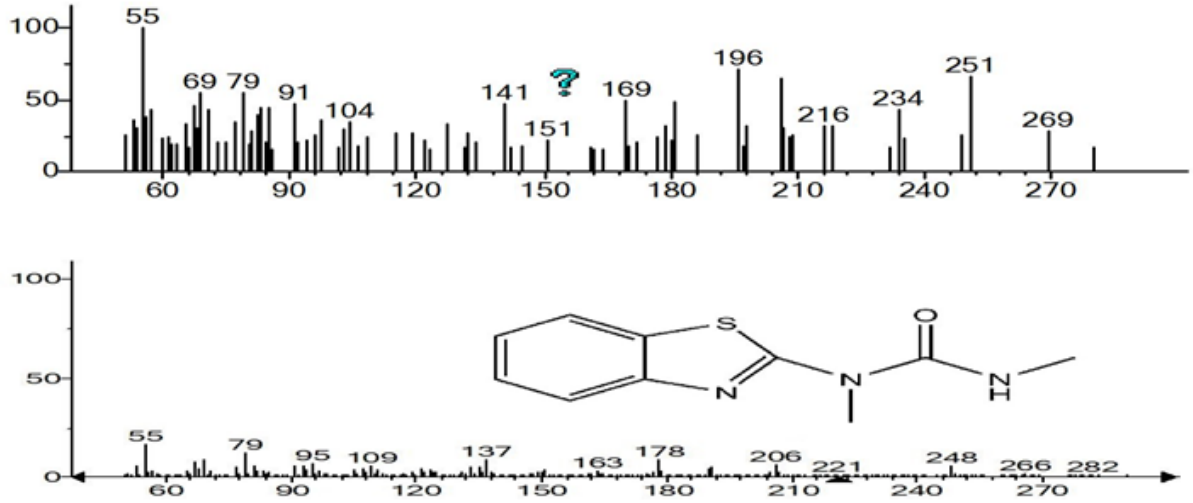

Figure 11: Mass spectra of Methabenzthiazuron pesticide concentration detected in Fish only of Njuwa Lake.

IV. Dicussion

Table 1 shows result of the occurrence and concentration of pesticides residue detected in the water samples collected at the four sampling points in the lake of Njuwa, Adamawa state. Out of nine pesticides determined, six were insecticides namely: alpha-BHC, Endrin, Diazinon, Carbaryl, Endosulfan 1 and Cypermethrin. Only three herbicides were detected which include Simazine, Di-allate, and Butachlor respectively. Insecticides that were present in higher concentration in the surface water were Endosulfan 1(0.92µg/l), Endrin (0.82µg/l), Alpha-BHC (0.57µg/l), Carbaryl (0.37µg/l), Diazinon (0.19µg/l) and Cypermethrin (0.15µg/l). However, in herbicides Di-allate was detected (0.55µg/l), Simazine (0.41µg/l) and butachlor (0.28µg/l).

The higher concentration of Endosulfan 1 detected in the water sample relative to those of Endosufan II may be attributed to the following reasons: Firstly, the manufactured technical endosulfan normally contains about 67% Endosulfan 1 by weight of the total Endosulfan content, while Endosulfan II constitutes only32 % [18].It is therefore, not unexpected that more of Endosulfan would be found in the environment when the pesticide is applied. Secondly, Endosulfan 1 is thermally stable, while Endosulfan II is unstable and is converted to Endosulfan 1 in the environment [17]. However, the high concentration of Endosulfan 1 compounds in the water sample may be an indication of recent application of the pesticide, as Endosulfan 1 is easily degraded and does not accumulate in the environment like most other Organo-chlorines [5].Endrin, Alpha-BHC, Carbaryl, Diazinon, Cypermethrin, Di-allate, Simazine and Butachlor were also detected in the water sample. The different concentrations found suggest that the pollution of the water emanates from diverse non-point sources, and possibly from varied applications of pesticides on the farms in the area.

Pesticides Residue Levels in Fish Samples from Njuwa Lake.Fish are used extensively for environmental monitoring because they take contaminants directly from water and diet [3]. Generally, the ability of fish to metabolize pesticides is moderate; therefore, contaminants loading in fish is reflective of the state of pollution in the surrounding environment [6].

Pesticides residues were analyzed in tilapia galilaea, presented in Table 2. The following compounds were detected in *Tilapia galilaea* and omnivorous fish. Atrazine a herbicides pesticide recorded at concentration of (1.17µg/g), Endrin, an insecticides pesticides residue was recorded at (1.13µg/g), methabenzthiruzon is also a herbicide which showed concentration of (1.09µg/g) and Di-allate a herbicide by formation indicated pesticide residue concentration at (1.07µg/g). simazine a herbicide had a concentration (1.03µg/g), Carbaryl an insecticide had (0.89µg/g) and Endosulfan 1 used as an insecticide om vegetable and crops had residue concentration of (0.76µg/g) respectively. The presence of the detected pesticide residues is evident by their use on irrigation farms around lake of Njuwa. The pesticides residue were above the prescribed MRL set by FAO/WHO in the fish sample. Similar studies was carried out by [8]. who reported significantly higher concentration of pesticides in fish tissues as was detected in this study.

From the results of the pesticides residues analyzed in *Clarias gariepinus*fish sample from the Njuwa lake.Table 3 showed that the fish sample was contaminated to some degree with highly significant concentration of Methabenzthiazuron, a herbicide (1.86µg/g), carbaryl (1.07µg/g), Simazine (0.86µg/g), trifluralin (0.74µg/g), Endosulfan II (0.53µg/g), Diazinon (0.45µg/g) amd alpha –BHC (0.17µg/g). The levels of these pesticides residue concentrations were ordered methabenzthiazuron>carbaryl>Simazine>Trifluralin>Endosulfan II

>Diazinon> alpha – BHC. The presence of pesticides in clarias gariepinus could be attributed to uptake either through bio concentration from water through gills or epithelial tissues and through bio-accumulation through water and through food leading to eventual bio-magnification in different organism, occupying successive trophic levels [6]. Hence, the presence of pesticide residues implies that there is clear evidence of the bio-concentrations and bio-accumulation of pesticides from the surrounding environment. The levels and occurrence of residues in fish samples seem to be governed by feeding mode, age and mobility of the biota; consequently, higher concentrations of pesticide residue observed in *Clarias gariepinus* may be attributed to the feeding mode of the fish [9]. This result is corroborated by [3]. who related to habitation and feeding habit of *Clarias gariepinus* to an increased concentration of pesticide residues compared with other pelagic fish species. [15], equally adds that pesticides accumulation in fish was due to their lipid content; this implies that due to the high lipid content in clariasgariepinus, more pesticide residues tend to be trapped in their lipid stores.

V. Conclusion

This study has presented information on the different pesticides residues contamination and their levels in water and fish species around lake Njuwa Yola, Adamawa state. Carbaryl, Di-allate and cypermethrin was found frequently in the water and fish samples, which is believed to be connected with the high concentations of the compounds as was reported in the water and fish samples from lake Njuwa. The results also showed that the concentations of the pesticides residues in the lake is associated with the pollution load from diverse non-point sources. The high concentrations of the pesticides found in the water and fish samples would pose a risk to human and aquatie life and this also pointed and indication of wrong use of the aforementioned pesticides residues in the vicinity of the lake Njuwa. This work will provide a reference with which future levels of pesticides residues in lake Njuwa, fish can be strictly monitred.

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