

## **Herbicide Residues in Water, Sediment and Fish Samples from Lake Alau Dam, Borno State, Nigeria**

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**Abstract:** *This study aimed at determining the levels of eight herbicide residues (atrazine, propanil, alachlor, metolachlor, paraquat, propachlor, butachlor and glyphosate) in fish, water and sediment samples from Lake Alau Dam Borno State, Nigeria. All the herbicides were detected in water, sediment and four tissues (flesh, liver, intestine and gills) of fish (*Tilapia dageti*) species at different sampling points. The total concentrations of all the herbicides studied were observed to be significantly higher in the fish sample with a value of  $8.16E-03$  mg/kg when compared with sediment and water sample with a value of  $7.50E-01$  mg/L and  $7.75E-2$  from all the sampling points. The results of these studies also indicate that the concentrations of the studied herbicides in fish, water and sediments were below the WHO set maximum residue limit (MRL) 0.01 mg/kg and the acceptable daily intake value (ADI) of 0.006 mg/kg in water and fish, and 5 mg/kg in sediment. Also, the observed concentrations of the studied herbicides in the water, fish and sediments suggest a relatively clean aquatic environment that has not yet been significantly contaminated by herbicide residues. Hence, consumption of these species of fish from the study area would not pose any problem on human health for now.*

**Keywords:**

**Keywords:** *Herbicide, Sample, Sediment, & Water*

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### **INTRODUCTION**

#### **1.1 Background of the Study**

Herbicides, commonly known as weedkillers, are chemical substances used to control unwanted plants. Selective herbicides control specific weed species, while leaving the desired crop relatively unharmed, while non-selective herbicides (sometimes called "total weedkillers" in commercial products) can be used to clear waste ground, industrial and construction sites, railways and railway embankments as they kill all plant material with which they come into contact. Apart from selective/non-selective, other important distinctions include persistence (also known as residual action: how long the product stays in place and remains active), means of uptake (whether it is absorbed by above-ground foliage

only, through the roots, or by other means), and mechanism of action (i.e how it works). Historically, products such as common salt and other metal salts were used as herbicides, however, these have gradually fallen out of favor and in some countries a number of these are banned due to their persistence in soil, and toxicity and groundwater contamination concerns. Herbicides have also been used in warfare and conflict (EPA, 2011).

Herbicides represent the largest proportion of pesticides used in agriculture. Worldwide use of pesticides in 2007 was estimated at 2.4 billion kg, of which the largest proportion, 40% or 950 million kg, was herbicides (USEPA, 2012). Herbicides are used in agriculture, forestry, and for other functions such as the control of vegetation on rights of way, industrial and urban sites, but agricultural uses dominate the market. With the number and variety of crops that have been genetically modified (GM) to be tolerant to herbicides, the use of GM products will increase in the future. Until now, the herbicide most widely used on GM crops has been glyphosate (Duke and Powels, 2008), but other crops have been modified for resistance to other classes of pesticides such as the auxin mimic, 2,4-D, and related products (Mortensen *et al.*, 2012). Increased uses on GM crops will result in increased inputs to agro-ecosystems with concomitant increases in the potential for exposures in the environment particularly in aquatic organisms.

Herbicides are actively used in terrestrial and aquatic ecosystems to control unwanted weeds and their use has generated serious concerns about the potential adverse effects of these chemicals on the environment and human health (Oleh *et al.*, 2009). The herbicides 2, 4-D Sodium salt is selective in nature, glyphosate and paraquat are non-selective; all are used as post-emergence herbicides. The 2,4-D Sodium salt is dichlorophenoxy-acetic acid, Phenoxy acids group, glyphosate is N-(Phosphonomethyl) Glycine, organophosphorus group and Paraquat is 1,1-dimethyl-4, 4-bipyridilium dichloride, bipyridylum group (Robert, 2007). These herbicides are used in aquatic ecosystem and are easily degraded in water system compared to other herbicides.

Fisheries and aquatic resources (ponds, lakes, rivers, streams, and oceans) are exceptionally valuable natural assets enjoyed by millions of Americans. They provide citizens with generous long-term benefits in return for minimal care and protection. These benefits can be direct financial ones that provide employment, profit, and dollar savings. For example, the seafood industry provides jobs for commercial fishers, wholesalers, and retailers. More indirect, but equally valuable, benefits of fish and aquatic ecosystems include recreational boating, sport fishing, swimming, relaxation, and natural beauty (Spradley, 1985). Appreciation of fisheries and aquatic systems has been accompanied by increasing concern about the effects of growing human populations and human activity on aquatic life and water quality. Pesticides are one group of toxic compounds linked to human use that have a profound effect on aquatic life and water quality (Lal, 1994).

Sediment from erosion is a major concern in our waterways not only because it shows rural areas are losing precious topsoil, but also because large amounts of sediment can kill aquatic plants and animals and fill the stream making flooding more frequent. Sediment is also problematic because it must be filtered out of water before drinking, even raindrops erode soil. If there is no canopy to intercept the energy of a raindrop as it falls to earth, soil particles are blown in every direction as the drop impacts the soil. Sediment refers to the conglomerate of materials, organic and inorganic, that can be carried away by water, wind or ice (Johnson and Finley, 1980). While the term is often used to indicate soil-based, mineral matter (e.g. clay, silt and sand), decomposing organic substances and inorganic biogenic material are also considered sediment. Most mineral sediment comes from erosion and weathering,

while organic sediment is typically detritus and decomposing material such as algae. Sediment transport is the movement of organic and inorganic particles by water. In general, the greater the flow, the more sediment that will be conveyed, water flow can be strong enough to suspend particles in the water column as they move downstream, or simply push them along the bottom of a waterway. Transported sediment may include mineral matter, chemicals and pollutants, and organic material (Czuba *et al.*, 2011). Alau Dam is located in Maiduguri, Borno State, Nigeria. Alau Dam is use for commercial fishing activities and the main source of fish and vegetables to the State and neighboring States within the country. The Dam is nine meter high with a square reservoir area of about 50 square kilometer. The maximum storage capacity is 112 million meter cube. Alau Dam received water from River Yedzram and River Gombole which meet at a confluent at Sambisa and flow as River Ngada into Alau Dam. Within the two rivers, intensive agriculture activities take place couple with the used of synthetic herbicides to control weed on vegetables and other farm products.

## **2.0 Material and Methods**

### **2.1 Collection of Fish Samples**

Fish samples *Tilapia dageti* (Coptodon fish) was collected according to method adopted by Akan *et al.* (2014) from fisher men in Lake alau Dam at early hours of the day. Fish samples of uniform size were collected in order to avoid the possible error due to size differences. Samples of fishes were transported to the laboratory on the same day, and identified by an expert in Agric. Department Ramat Polytechnic Maiduguri Borno State and later dissected to remove the flesh, liver, intestine, and gills of each specie of fish. The tissues were placed in a well sterilized 200g amber glass bottle and labelled with unique identification number and stored in an ice box at 10°C pending extraction and analysis.

### **2.2 Extraction of Fish Samples**

Extraction of herbicide residues from fish samples were performed using a method adopted by Anastassiades *et al.*, 2003. Each of the fish samples were chopped in an electrical chopper and 50g of the chopped samples was placed in an Erlenmeyer flask. 7.5 g of the chopped samples were weighed and transferred into a beaker, 75 ml of acetonitrile was added and shaken for 30 mins using a reciprocal shaker. The mixture was then filtered by vacuum suction and the beaker was rinsed with 5 ml while the residual cake was washed using 20 ml acetonitrile.

### **2.3 Collection of Sediment Samples**

Sediment samples were collected from four (4) sampling points designated S<sub>1</sub>- S<sub>4</sub>. Point S<sub>1</sub> was the point of flow of water into Alau Dam. Point S<sub>2</sub> to S<sub>4</sub> are 0.10km away from each other, making a total of 3.4 km for the study. Three samples were collected at each sampling points and pooled. The sediment samples were collected using plastic hand trowel by scooping 0-5 cm of the top layer of the sediment and placed in an amber glass bottle and stored in an ice-block cooler as described by (Boy'd and Tucker, 1992). The samples were transported to the Department of Science Laboratory Technology, Ramat polytechnic Maiduguri and stored in a refrigerator pending extraction and analysis.

## 2.4 Collection of Water Samples

Water samples were collected from four (4) sampling points designated S<sub>1</sub>- S<sub>4</sub>. The distance from each sampling points are 0.10km away from each other. The water samples were collected using plastic containers by dipping 1-5 cm below the top layer of the water and placed in an amber glass bottle and stored in an ice-block cooler as described by (Boy'd and Tucker, 1992). Three samples were collected at each sampling points and pooled. The samples were transported to the Department of Science Laboratory Technology, Ramat polytechnic Maiduguri and stored in a refrigerator pending extraction and analysis.

## 2.5 Extraction of Water Samples

According to the method adopted by Anastassiades *et al.* (2003) two hundred and fifty mill, (250ml) of water sample were measured using measuring cylinder and then transferred into separation funnel, then 25ml of dichloromethane was added and shaken for 30s and allowed to stand for 30s, the mixture was separated into clean glass container pending analysis (Anastassides *et al.*, 2003).

## 2.6 Extraction of Sediment Samples

According to method adopted by Cho *et al.* (2007), 25g of sediment samples weighed into a glass jar and 50g of sodium sulphate was added, the mixture were shake manually for 30s, placed on a roller for 30s and allowed to stand for 20 min to provide time for the sodium sulphate to absorbed any residual moisture from the sediment. The sample mixture was transferred into 250 ml bulb column and the sample and the sample jar were triple rinsed with 5 ml of hexane and transferred to the bulb column. The sediment contents were extracted with acetone: hexane (1:1v/v, 250 ml mixture) and the eluate was collected and concentrated to 100 ml using rotary evaporator (Cho *et al.*, 2007).

## 2.7 Clean-Up for Sediment Samples

Clean-up of extracts were performed on Florisil cartridges. Florisil cartridges were preconditioned with ethyl acetate and petroleum ether. The cartridges were loaded with 2 mL petroleum ether extract above. The cartridges were washed with petroleum ether (2 mL), and discarded. The cartridges were re-washed with 2 mL petroleum ether-ethyl acetate (98/2, v/v), and discarded. The analyte was eluted with 2 mL petroleum ether-ethyl acetate (95/5, v/v), and concentrated in a rotary evaporator (40°C) and completely dried under a nitrogen purge. The residue was re-dissolved with 2 mL methanol for HPLC analysis (Boyd and Toker 1992).

## 2.8 Determination of Herbicide Residues

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°C, 1.5 min, to 150°C, 0.0 min, 5 °C/min to 200°C, 7.5 min, 25 °C/min to 290°C with a final hold time of 12 min and a constant column (flow rate of 1 ml/min). The detection of herbicides 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). In SIM at the elution time of each herbicide, the ration of the intensity of matrix ions increase exponentially versus that of the herbicide ions as the concentration of the herbicide approach the detection limit, decrease the accuracy at lower levels. The GC-ion trap MS were operated in MSn mode and perform tandem MS function by injecting ions into the ion trap and destabilizing matrix ions,

isolating only the herbicide. The retention time, peak area and peak height of the sample were compared with those of the standards for quantization (Bartels, 1994).

## RESULTS

### Mean Concentrations of Some Herbicide Residues in Water and Sediment Samples

The mean concentrations of some herbicide residues in water samples at different sampling points from Lake Alau Dam are shown in Table 4.1. The mean concentration of glyphosate ranges from 1.00E-02 to 3.00E-02 mg/L; 1.00E-02 to 2.00E-02 mg/L butachlor; 1.00E-02 to 2.00E-02 mg/L metolachlor; 1.00E-02 to 2.00E-02 mg/L paraquat; 1.00E-02 to 2.50E-02 mg/L propachlor; 1.00E-02 to 2.50E-02 mg/L atrazine; 1.00E-02 to 3.00E-02 mg/L propanil and 1.00E-02 to 5.00E-02 mg/L alachlor. The highest total concentration of 2.00E-02 mg/L was recorded at point S<sub>2</sub>, while the lowest total concentration of 1.10E-02 mg/L was recorded at point S<sub>1</sub>. The mean concentrations of some herbicide residues in sediment samples from Lake Alau Dam at different sampling points are presented in Table 4.2. Glyphosate concentration ranged from 1.00E-01 to 4.00E-01 mg/kg; 1.00E-01 to 3.00E-01 mg/kg butachlor; 1.00E-01 to 3.00E-01 mg/kg metolachlor mg/kg; 1.00E-01 to 2.00E-01 mg/kg paraquat; 1.00E-01 to 3.00E-01 mg/kg propachlor; 1.00E-01 to 3.00E-01 mg/kg atrazine; 1.00E-01 to 3.00E-01 mg/kg propanil and 1.50E-02 to 3.00E-02 mg/kg alachlor. The highest total concentration of 2.30E-01 mg/kg was recorded at point S<sub>2</sub>, while the lowest total concentration of 1.40E-01 mg/kg was recorded at point S<sub>1</sub>.

Table 4.1: Mean Concentrations of Some Herbicide Residues (mg/L) in Water Samples.

Herbicides	Concentrations (mg/L)			
	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>
Glyphosate	1.00E-02	3.00E-02	1.00E-02	3.00E-02
Butachlor	1.00E-02	1.50E-02	1.00E-02	2.00E-02
Metolachlor	2.00E-02	1.10E-02	2.00E-02	1.00E-02
Paraquat	1.50E-02	1.00E-02	1.10E-02	2.00E-02
Propachlor	1.00E-02	2.00E-02	1.23E-02	2.50E-02
Atrazine	1.00E-02	1.50E-02	2.50E-02	2.00E-01
Propanil	2.50E-02	3.00E-02	2.00E-01	1.00E-01
Alachlor	1.00E-02	5.00E-01	2.00E-02	2.00E-01

$S_1 = 1^{\text{st}}$  Sampling point (is the point of flow of water into Gubi Dam),  $S_2 = 2^{\text{nd}}$  Sampling point is 0.10km away from  $S_1$ ,  $S_3 = 3^{\text{rd}}$  Sampling point is 0.10km away from  $S_2$ ,  $S_4 = 4^{\text{th}}$  Sampling point is 0.10km away from  $S_3$

Table 4.2: Mean Concentrations of Some Herbicide Residues (mg/kg) in Sediment Samples.

Herbicides	Concentrations (mg/kg)			
	$S_1$	$S_2$	$S_3$	$S_4$
<b>Glyphosate</b>	2.00E-01	4.00E-01	1.00E-01	3.00E-01
<b>Butachlor</b>	3.00E-01	2.00E-01	1.00E-01	2.00E-01
<b>Metolachlor</b>	1.00E-01	1.00E-01	3.00E-01	1.00E-01
<b>Paraquat</b>	1.00E-01	2.00E-01	2.00E-01	1.00E-01
<b>Propachlor</b>	2.00E-01	1.00E-01	2.00E-01	3.00E-02
<b>Atrazine</b>	1.00E-01	2.00E-01	3.00E-01	1.00E-02
<b>Propanil</b>	1.00E-01	1.00E-01	2.00E-02	3.00E-02
<b>Alachlor</b>	3.00E-01	1.50E-01	2.50E-02	1.00E-02

$S_1 = 1^{\text{st}}$  Sampling point (is the  $1^{\text{st}}$  sediment sample obtained from the  $1^{\text{st}}$  point of flow of water into Lake Alau Dam),  $S_2 = 2^{\text{nd}}$  Sampling point is 0.8km away from  $S_1$ ,  $S_3 = 3^{\text{rd}}$  Sampling point is 0.10km away from  $S_2$ ,  $S_4 = 4^{\text{th}}$  Sampling point is 0.8km away from  $S_3$

Table 4.3 shows the mean concentrations of some herbicide residues in different tissues of *Tilapia dageti* from Alau Dam. The mean concentration of glyphosate ranges from 1.54E-03 to 3.60E-03 mg/kg; 1.50E-03 to 2.50E-03 mg/kg butachlor; 1.00E-03 to 3.00E-03 mg/kg metolachlor; 1.50E-03 to 3.00E-03 mg/kg paraquat; 1.00E-03 to 2.00E-03 mg/kg propachlor; 1.00 E-03 to 3.00E-03 mg/kg atrazine; 1.20E-03 to 3.00E-03 mg/kg propanil and 1.00E-03 to 3.00E-03 mg/kg alachlor. The highest total concentration of 3.60E-03 mg/kg was recorded in the liver, while the lowest total concentration of 1.00E-03 mg/kg was recorded in the flesh.

Table 4.3: Mean Concentrations of Some Herbicide Residues (mg/kg) in Different Tissues of *Tilapia dageti*.

Herbicides	Concentrations (mg/kg)			
	Liver	Flesh	Intestine	Gills
<b>Glyphosate</b>	2.60E-03	2.00E-03	1.54E-03	3.50E-03
<b>Butachlor</b>	1.91E-03	1.50E-03	2.10E-03	2.50E-03
<b>Metolachlor</b>	1.91E-03	1.00E-03	2.00E-03	3.00E-03
<b>Paraquat</b>	1.50E-03	2.00E-03	3.00E-03	2.53E-03
<b>Propachlor</b>	1.10E-03	1.50E-03	1.00E-03	2.00E-03
<b>Atrazine</b>	1.00E-03	2.50E-03	2.00E-03	3.00E-03
<b>Propanil</b>	2.30E-03	1.20E-03	3.00E-03	1.50E-03
<b>Alachlor</b>	2.50E-03	1.00E-03	2.00E-03	3.00E-03

#### Comparison of total Concentrations of Some Herbicide Residues in Fish, Water and Sediment Samples

Table 4.4 shows the comparison in total concentrations of some herbicide residues in Fish, water and sediment samples from Lake Alau Dam. The concentration of glyphosate ranges from 9.64E-3, 8.00E-02 and 10.00E-01mg/kg; 8.01E-3, 5.50E-02 and 8.00E-01 mg/kg butachlor; 7.91E-3, 6.10E-02 and 6.00E-01 mg/kg metolachlor; 9.03E-3, 5.60E-02 and 6.00E-01 mg/kg paraquat; 5.60E-3, 6.730E-02 and 8.00E-01 mg/kg propachlor; 8.50E-3, 7.00E-02 and 7.00E-01 mg/kg atrazine; 8.00E-3, 8.50E-02 and 7.00E-01 mg/kg propanil and 8.50E-3, 10.00E-02, 8.00E-01 alachlor. The highest total herbicide concentration of 10.64E-02 mg/kg was recorded in fish samples, while the lowest total herbicide concentration of 6.00E-01 mg/L was recorded in sediment samples.

Table 4.4: Total Concentrations (mg/kg) of Some Herbicide Residues in Fish, Water and Sediment Samples from Different Sampling Points.

Herbicides	Water Samples	Sediment Samples	Tilapia Dageti
	Con.(mg/kg)	Con.(mg/kg)	Con.(mg/kg)
Glyphosate	8.00E-02	10.00E-01	9.64E-3
Butachlor	5.50E-02	8.00E-01	8.10E-3
Metolachlor	6.10E-02	6.00E-01	7.91E-3
Paraquat	5.60E-02	6.00E-01	9.03E-3
Propachlor	6.73E-02	8.00E-01	5.60E-3
Atrazine	7.00E-02	7.00E-01	8.50E-3
Propanil	8.50E-02	7.00E-01	8.00E-3
Alachlor	10.00E-02	8.00E-01	8.50E-3
TOTAL	<b>7.75E-2</b>	<b>7.50E-1</b>	<b>8.16E-3</b>

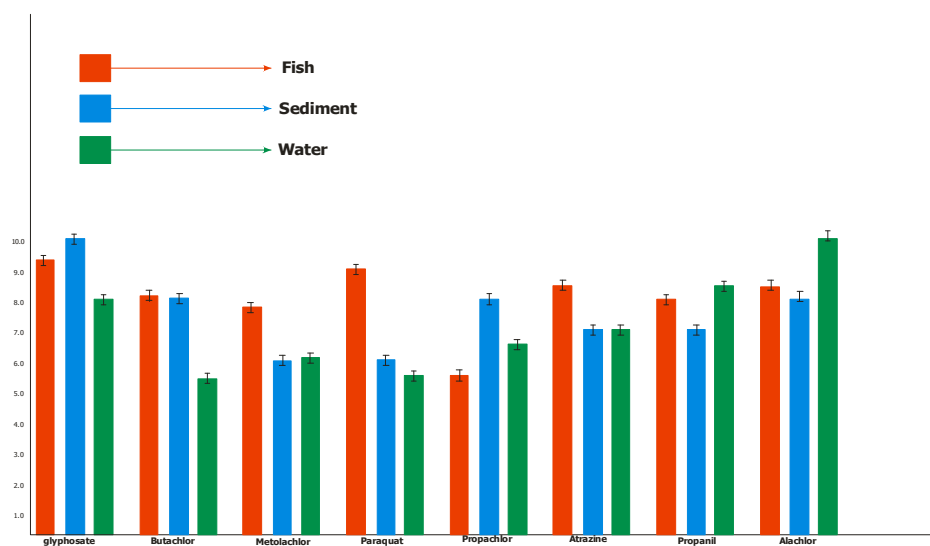


Fig. 4.2: Comparison of the Concentrations of Herbicide



#### **4. DISCUSSION**

##### **Herbicide Residues (glyphosate, butachlor, metolachlor, paraquat, propanil, atrazine, propanil and alachlor) in Water and Sediment Samples**

The highest concentration of glyphosate in the water samples was detected at point  $S_4$  with a value of  $3.00E-02$  mg/L, while the lowest concentration was detected at point  $S_1$  with a value of  $1.00E-02$  mg/L. For butachlor the highest concentration of  $2.00E-02$  mg/L was observed at point  $S_4$ , with point  $S_1$  showing the lowest concentration of  $1.00E-02$  mg/L. The concentration of butachlor in water samples was in agreement with the study conducted at All India Coordinated Research Project (AICRP) weed control in water system which revealed that butachlor residues ranged between 0.001 and 0.093 mg/L in the water of rice field (AICRP 2009). Metolachlor had the highest concentration of  $2.00E-02$  mg/L at point  $S_1$  and the lowest concentration was detected at point  $S_4$  with a value of  $1.00E-02$  mg/L. Also paraquat highest concentration was observed at point  $S_4$  with a value of  $2.00E-02$  mg/L, while the lowest concentration was detected at point  $S_2$  with a value of  $1.00E-02$  mg/L. The highest concentration of propachlor in water samples was detected at point  $S_4$  with a value of  $2.50E-02$  mg/L and the lowest concentration of  $1.00E-02$  mg/L was recorded at point  $S_1$ . The highest concentration of atrazine with a value  $2.50E-02$  mg/L was recorded at point  $S_3$  and the lowest concentration of  $1.00E-02$  mg/L was observed at point  $S_1$ . The highest concentration of propanil in water samples was detected at point  $S_2$  with a value  $3.00E-02$  mg/L, while the lowest concentration of  $1.00E-02$  mg/L was observed at point  $S_4$ . For alachlor the highest concentration of  $5.00E-02$  mg/L was recorded at point  $S_2$ , whereas the lowest concentration of  $1.00E-02$  mg/L was observed at point  $S_1$  as presented in Table 4.1. Among all the herbicide residues studied, alachlor, glyphosate and propanil were observed to be the most dominant herbicides in the present study. Levels of herbicide in the water samples indicates that the herbicides detected are presently used in the study area despite the fact that most of this herbicides were banned in many countries around the world including Nigeria by (NAFDAC, 2008). These herbicides are extensively used in the study area to check and control weeds in an effort to reduce or eliminate yield losses and preserved high produce quality. The high concentration of these herbicides in the study area might be as a result of run-off, atmospheric deposit, these herbicides usually find their way into surface water and sediment which act as a sink for vast varieties of pollutants including herbicide. The concentration of herbicide residues in the present study were below the maximum residue limit (MRL) of 0.1 mg/L in water, hence, the result of this findings indicate that the water samples within the study area will not cause harm to the aquatic and benthic organism.

The highest concentration of glyphosate in the sediment samples was observed at point  $S_2$  with a concentration of  $4.00E-01$  mg/kg, while the lowest concentration of  $1.00E-01$  mg/kg was observed at point  $S_3$ , for butachlor the highest concentration was recorded at point  $S_1$  with a value of  $3.00E-01$  mg/kg, whereas the lowest concentration of  $1.00E-01$  was observed at point  $S_3$ , also for metolachlor, the highest concentration was detected at point  $S_3$  with a value of  $3.00E-01$  mg/kg and the lowest concentration of  $1.00E-01$  mg/kg was observed at point

S<sub>1</sub>. Also the highest concentration of paraquat with a value 2.00E-01 mg/kg was recorded at point S<sub>3</sub>, while the lowest concentration of 1.00E-01 mg/kg was recorded at point S<sub>1</sub>. Similarly, the highest concentration of propachlor (3.00E-01 kg/kg) was detected at point S<sub>4</sub>, while the lowest concentration of 1.00E-01 mg/kg was recorded at point S<sub>2</sub>. The highest concentration of atrazine with a value of 3.00E-01 mg/kg was recorded at point S<sub>3</sub>, while the lowest concentration of 1.00E-01 mg/kg was recorded at point S<sub>1</sub>. For propanil the highest concentration of 3.00E-01 mg/kg was detected at point S<sub>4</sub>, whereas the lowest concentration of 1.00E-01 mg/kg was detected at point S<sub>1</sub>. The highest concentration of alachlor with a value of 3.00E-01 mg/kg was recorded at point S<sub>1</sub> and the lowest concentration of 1.00E-01 mg/kg was observed at point S<sub>4</sub>. The comparison of the results in water and sediment samples revealed higher concentrations of the herbicides in sediment, while water had the lowest concentration. The lower levels of herbicide residues found in the water bodies than in the sediment might be attributed to the fact that the input of herbicides in water is a function of suspended particulate concentrations, where the residues are absorbed in the sediment and transported, as also commented by Bishnu *et al.* (2009).

The highest levels of herbicide in the sediments than water samples were because sediments are important sinks for various pollutants which also play a significant role in the remobilization of contaminants in aquatic systems under favorable conditions and in interactions between water and sediment also commented by Ntow (2005). Sediments act as secondary contamination source after water in the ecosystem. Sediments are the principal reservoirs of environmental pesticides, representing a source from which residues can be released to the atmosphere, groundwater and living organisms.

## **5.2 Distribution of Herbicide Residues (glyphosate, butachlor, metolachlor, paraquat, propanil, atrazine, propanil and alachlor) in Tissues of Fish Samples from Gubi Dam**

Eight herbicide (glyphosate, butachlor, metolachlor, paraquat, propanil, atrazine, propanil and alachlor) residues were determined in the liver, flesh, intestine and gills of, *Tilapia dageti* caught from Lake Aau Dam. According to Kammann *et al.* (1992), herbicides tend to accumulate in living organisms especially in aquatic organisms and they substantially settle on the sediments. The highest value of glyphosate was observed in the liver of *Tilapia dageti*. Despite the adverse side effect of herbicide, herbicides form an integral component of modern agriculture practice all over the world. The benefits are increase supply of food, but problems arise when significant amount of the chemicals are left on the field as residue which tend to affect non target organisms and river bodies are one of the main recipient of herbicide as a residues generated on the field. Atrazine is one of the most widely used herbicide globally, commonly used in Nigeria for the control of weeds in most farms (Ezemonye and Tongo, 2009). Despite its intensive use, atrazine has been implicated in a number of health effects (Hopenhayn-rich *et al.*, 2001). In the present study the highest concentration of atrazine was observed in the gill of *Tilapia Dagede* with a value of 3.00E-3 mg/kg, while the flesh of *Tilapia dageti* was observed to shows the lowest value of 1.00E-03 mg/kg. The high levels of atrazine in the liver might be attributed to the fact that liver as a storage organ for vast variety of nutrient.

The concentration of butachlor was higher in the gills, while the flesh shows the lowest value. A study carried out by He *et al.* (2013) shows that butachlor poses potential threat to the aquatic ecosystem.

Suseela (2001), reported that the herbicide, as toxicant, did not have any adverse effects but it accelerated the nitrogen fixation. Hashimoto and Nishituchi, 1983, studied the toxic effects of butachlor not only in fish but also in *Daphnia* and other aquatic organisms and concluded that it is toxic. Wang *et al.* (1991), also reported that the residues of butachlor in paddy field, even though lower than the safe concentration, caused toxic effect to *Cyprinus carpio*. Butachlor has been proven to be genotoxic and cytotoxic in catfish (*Clarias gariepinus*) and the concentration of butachlor was found proportional to the extent of DNA damage (Zheng *et al.*, 2012). In another study, butachlor was found to cause remarkable protein loss in *Clarias batrachus* at both lethal and sub-lethal concentration which might be due to increased proteolysis (Muley *et al.*, 2007) or by metabolic utilization of ketoacids to glucogenesis pathway for synthesis of glucose (Rajput *et al.*, 2012). The results demonstrated adverse effects of butachlor on the normal reproductive process of zebra fish and also found to disrupt the thyroid and sex steroid endocrine systems when exposed to butachlor for 30 days (Chang *et al.*, 2013). Results from the present study show that, the maximum concentration of 7.00E-04 mg/kg was detected in *Clarias gariepinus*, which is in conformity with study conducted by Yadav *et al.* (2013), which revealed levels of butachlor in all the fish samples analysed. This study is in agreement with the study carried out by Akan *et al.* (2013), which revealed some levels of pesticide residues in tissues of fish samples from Alau Dam, Maiduguri, Borno State Nigeria.

The highest mean concentration of 3.00E-03 mg/kg paraquat in the present study was detected in the intestine of the *Tilapia Dageti*. Irrespective of the route of administration of herbicides in mammalian systems, paraquat is rapidly distributed in most tissues, with the highest concentration was found in the lungs and kidneys (Suntres, 2002). This trend contradicts the present study, where the concentrations of paraquat was significantly higher in the liver and gills. The inability of the fish to detoxify the toxicant and excrete the resultant metabolites, besides direct damage by the toxicant to the epithelial cells of gills, possible destruction of liver (Omeregbe *et al.*, 1996) and internal asphyxiation (Duffus, 1980), may account for the rapid mortality recorded in acute lethal studies of this nature.

Sublethal effects on fish include adverse effects on the immune system, with the effect enhanced by elevated temperatures (Salazar-Lugo *et al.*, 2009); alterations to gonads likely to affect reproductive activity particularly in males (Figueiredo-Fernandes *et al.*, 2006); and oxidative stress (Stephensen *et al.*, 2002). Generally, the studied herbicide residues in the fish samples were higher in the liver and gills of *Tilapia Dageti* studied when compared with other organs. The high level of these herbicides in the liver and gills might be due to the fact that fresh water fishes gills might be expected to be the primary route for the uptake of water pollutants; while the liver serve as a storage organs for vast variety of nutrient. High accumulation of these herbicides in the gills and liver can also be as a result of detoxicating mechanisms and may originate from herbicides deposited in the sediments and food in the aquatic environment. However, the liver is the preferred organ for pollutants accumulation as could be deduced from the present study which is in line with the study carried out by Risbourg

and Bastide (1995), which revealed that the exposure of fish to herbicide increased in the size of lipid droplets, vacuolization in the liver. Accumulation of herbicides in different species is the function of their respective membrane permeability and enzyme system, which is highly species specific and because of the fact that herbicide residues accumulated in different organs in the fish as observed in the study. The present study revealed that herbicide accumulation in tissues of fish samples were in order of liver > gills > intestine > flesh, this research work is in agreement with the study carried out by (Akan *et al.*, 2014), which revealed that the variations in the residue analysis are due to factors like difference in uptake rate, lipid content of respective animal tissue, chemical structure, solubility, and metabolic pattern. The concentrations of the studied herbicides in the fish samples were observed to be lower than the WHO and FAO (Codex, 2009) set maximum residue limit (MRL) 0.01 mg/kg and the Acceptable Daily Intake value (ADI) of 0.006 mg/kg which is considered safe for consumption as at the time of the present research work.

## CONCLUSION

In View of the finding of this research work, the herbicides residues found in fish, water and sediment sample relatively clean aquatic environment, consumption of this species of fish from the study area would not pose any problem on human health for now. Other suitable methods of analysis should be employed on the same samples to further confirm the level of herbicide residues as claimed by the result of this study.

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