Organochlorine Pesticides Residues in Water, Sediment, and Various Species of Fish from Komadugu River Basin, Yobe State, Nigeria

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ABSTRACT

Water, sediment and fish (*Claria sanguillaris, Tilapia zilli, Synodontisbudgetti,* and *Heterotisniloticus*) samples from Komadugu River basin of Yobe State, Nigeria were collected on a seasonal basis (rainy, dry seasons, and Harmattan period) for the determination of the levels of organochlorine pesticide residues (OCPs). Extraction and clean-up of water, sediment, and fish samples for OCPs was carried out using standard procedures. The concentrations of all the OCPs in water, sediment and fish samples were determined using GC/MS SHIMADZU (Agilent 7890A).

The total concentration of OCPs in water samples from the study area ranged from 6.70E-01 µg/L to 2.55E+00 µg/L. The concentrations of OCPs in the different species of fish samples ranged from2.00E-02 to 1.42E+00 mg/kg. Alderin shows the highest concentration (1.42E+00 mg/kg) during the rainy season**.** The total OCPs (7.26E+00mg/kg) was obtained during the rainy season, while the lowest concentration of 5.68E+00 mg/kg was recorded during the dry season**.** The concentrations of OCPs residues in sediment samples studied ranged from 1.03E+00 to 1.20E+01 mg/kg, with dieldrin showing the highest total concentration of 1.20E+01 mg/kg during the rainy season.

Dieldrin was the most abundant pesticide residues in the studied water, sediment and fish samples. The highest levels of all the studied pesticides were observed during the rainy season when compared to Harmattan period and the dry season. This study revealed that pesticide residues levels in the fish samples studied were above the maximum residue limits (MRLs) and acceptable dietary intake (ADI) and could be an important process of transferring pesticides to humans.

(Keywords: Komadugu River basin, water, sediment, fish, extraction, cleanup, contamination)

INTRODUCTION

Pesticides are substances or mixtures of substances intended to prevent, destroy, repel or mitigate pests. Pests can be insects, mice, unwanted plants (weeds), fungi, or microorganism such as bacteria and viruses. Though often misunderstood to refer only to insecticides, the term pesticides also applies to fumigants, fungicides, herbicides, rodenticides, and various other substances used to control pests.

Chemical classification of pesticides can be based on the functional groups on their molecular structures or their specific biological activity on target species (Van-der and Van-Zoonen, 1999). Some examples of chemically-related pesticides follow other examples are available in sources such as *Recognition and Management of Pesticide Poisonings*. Pesticides are often referred to according to the type of pest they control. Another way to describe pesticides is to consider those that are chemical pesticides or are derived from a common source or production method. Other categories include bio pesticides, antimicrobials, and pest control devices.

Numerous studies on both human and laboratory animals provide strong evidence of the toxic potential of exposure to pesticides residues (Gladen and Rogan, 1995; Longnecker *et al.,* 2001; Torres – Areola *et al.,* 2003). Therefore risk characterization of pesticides in environmental

samples, foods and dietary products is an important step and a vital tool in the assessment of food safety risk (Renwick, 2002; Duffus and Worth, 2006; Granby *et al.,* 2008). The toxic effects of pesticides to man and the environment is a major issue that gives rise to concerns at local, national, regional and global scales and is the basis for the control, monitoring and prohibition of pesticides in food (UNEP, 2002). A number of pesticides residues monitoring research has been conducted on various samples, such as eggplant (Islam *et al.,* 2009), drinking water from household wells (Sabdono *et al.,* 2008), and in human breast milk (Ebadi and Shokerzadeh, 2006).

These pesticides are used widely to improve agricultural production and also to prevent arthropod-borne diseases. But they are used improperly due to the lack of appropriate knowledge about their applications and untoward effects. The excessive usage is harmful to eco-system and they contaminate soil, surface and under-ground water resources (Khodadadi *et al.,* 2010). The relevant fulfilled researches have shown that each year 2.5 million tons of pesticides are released 50% of them penetrate to soil, water and other sources and also to the bodies of living creatures (Rao and Northup, 2009). Relevant poisoning in many countries, especially developing countries is considered the second causes of mortalities after infectious diseases.

The organochlorines are the most important group of persistent organic pollutants. These compounds are noted for their environmental persistence, long half-lives, and their potential to bio-accumulate and bio-magnify in organisms once dispersed in to the environment. Twelve of the known persistent organic pollutants, referred to as the "dirty dozen", have been officially registered by the United Nations Environmental Programme (UNEP, 2002) under the Stockholm convention in 2001 as priority pollutants. The member states of the convention aimed to eliminate or reduce levels of these compounds in the environment.

DDT is classified as a restricted compound and only be used for disease vector control in the indoor residual's spraying (IRS) program initiated by the World Health Organization (WHO). The IRS program rolled out to all epidemiologic settings including unstable, epidemic-prone areas with seasonal transmissions, and stable-hyperendemic areas with seasonal or perennial transmission (WHO, 1993). Sufficient contact with DDT-sprayed surfaces kills malaria vectors. More importantly, DDT has an exitorepellent effect, deterring entry into and promoting exit from sprayed dwellings (Roberts and Andre, 1994). It is argued that the combined mosquito toxicity and excite to repellent effects of DDT may maintain its continued efficacy in areas where there is resistance against the insecticides (Roberts and Andre, 1994; Curtis, 2002).

A study in India which assessed the impact of IRS with DDT on malaria transmission corroborated the results of earlier studies which reported marked reductions in vector densities and malaria incidences (Sharma *et al.*, 2005). Chlorinated compounds registered by the Stockholm convention as priority persistent organic pollutants where highlighted in Table 6 below. Nine of the Stockholm convention priority pollutants compounds (DDT, dieldrin, toxaphene, endrin, aldrin, hexachlorobenzene, chlordane, heptachlor and mirex) are insecticides and are used in agriculture as pesticides.

Pesticides have contributed greatly in the increase of food production in agriculture and improved both human and animal health. However, these successes have been marred by side-effects resulting from the action of pesticides on non-target species (Barlas, 2002). Some toxic effects associated with pesticides residues include cancer, immunosuppression, reproductive, and developmental disorders (Garabrant *et al*., 1992). Studies have shown that dieldrin, DDT and its metabolites are some of the numerous endocrine disrupting chemicals (EDCS) that exhibit estrogenic and anti-androgenic effects (Mckinney and Walker, 1994).

The effects on the health due to exposed organism. Similarly, epidemiological studies have suggested on etiological relationship between exposure to organochlorine pesticides and Parkinson's disease (Fleming *et al*., 1994). The observed adverse effects of DDT exposure on wildlife include: reproductive abnormalities in birds, mammals and the feminization of males (Guiletti *et al.*, 1995).

Pesticides contamination pathways to water bodies are likely to be nonpoint sources via runoff, atmospheric deposition and leaching due to agricultural applications, vector pest control and improper waste disposal. Sediments act as a sink for persistent organic pollutants; hence

increase the compounds bioavailability and accumulation in the food chain through re-suspension. This exposes fish and other aquatic organisms to the pollutants through ingestion, dermal absorption and respiration. Consumption of fish from polluted water systems is considered to be one of the important routes through which humans get exposed to pesticides (Johansen *et al.,* 1996).

The majority of pesticides are sprayed onto crops while the rest are channeled through water and manure into the soil. The ubiquitous nature of the biological and chemical processes which occur with pesticides once they are applied make it unlikely that even highly specific pesticides will not affect the non-target organisms. Some of the ecological changes brought about by the pesticides are transient, while others are more permanent and lead to the biomagnification of the contaminant in the food chain and amplification of the adverse effects (Tanabe *et al.,* 1994).

Persistence, mobility, toxicity, and ability to biomagnify are some of the important factors which need to be considered in assessing the environmental impact of pesticides. Persistent compounds that readily move from their application site and ultimately bio-concentrate into the fatty tissues of various aquatic and terrestrial food chains, offer the greatest environmental problems.

METHODOLOGY

Study Area

Yobe State covers an estimated area of about 47,l53 km^2 and supports a human and livestock population of over 1.4 million and I million, respectively (NPC, 199I; RIM, 1992). The Komadugu-Yobe basin from which the State derived its name, supplies up a source of over 1.12 billion cubic meters of surface water per year. It is located between latitude 10^oN and 13^oN and longitude 9.45°E and 12.30^oE^o (GIS, 2015).

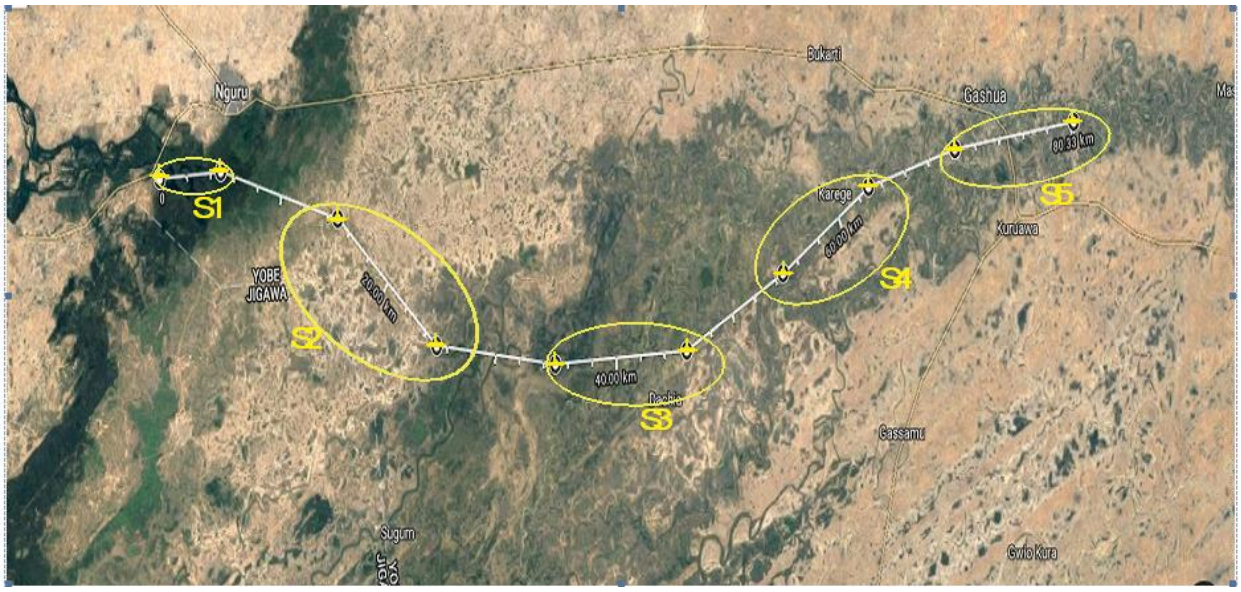
The Komadugu - Yobe River originates from the Jos Pleateau and Kano ends up in the Lake Chad, the river was formed by the confluence of the Hadejia and Jam'are Rivers. The curvature is of advantage because it provides a large increase in river, frontage and easier abstraction of irrigation water for a large area. The geological formation of the upstream part of the basin consists largely of impermeable basement complex rocks, which dips away to the east where it is covered by the permeable lakes sediments of the Chad formation. In some areas, the sediments are covered with oriented longitudinal dunes (Schultz, 1976).

The three main rivers in the Hadejia- Jamaare - Yobe River System are the Rivers Hadejia, Jarnaare, and Komadugu-Yobe. The Hadejia River is formed by the confluence of the River Kano and Challawa at Tamburawa. It has a poorly defined channel and characterized by numerous oxbow lakes. The rivers pass through Hadejia and Madachi towns and enter a number of lakes and swamps. The Hadejia River bifurcates into two channels between Hadejia and Likori. One channel, the old Hadejia joins the Jamaare River upstream at Gashua near Karage to form the River Yobe. The other channel feeds the Marma channel, which flows into the Nguru Lake and the relatively small Burun Gana River. Rivers Hadejia, Marma and Burun Gana leave the swamps with an estimated flow of about 50%, 30% and 20% of the outflow, respectively (Kalachiwi, 1996).

Collection of Water, Sediment and Fish Samples

Water and sediment samples were collected in accordance with method described by (Boyd and Tucker, 1992). Water samples were collected within the Komadugu River basin from Nguru to Gashua points S_1 to S_5 (Map 1). Water samples were collected in glass at a depth of 3 cm in a 1.5 liters amber glass bottle previously clean with non-ionic detergent (ethoxylates) and rinsed thoroughly with sample water prior to collection. Water samples were preserved in an ice box.

Fish samples were collected in accordance with method described by (Boyd and Tucker, 1992), four fish species (*Tilapia zillii, Clarias angullaris, Synodontis budgetti and Heterotis niloticus)* were caught within the Komadugu River basin in Nguru and Gashua were commercial fishing activities take place through local fishermen of the area. Fish samples of uniform size and weight were collected in order to avoid the possible error due to size differences. The samples were transported to the Chemistry Laboratory, University of Maiduguri and stored in a refrigerator at 4°C for further analysis.



Map 1: Map Showing 5 Sampling Points.
Source: GIS, 2015

Water samples were collected 10 meters away from the bank of the river on seasonal basis (dry, rainy seasons and Harmattan period).

Extraction of Water Samples for Organochlorine Pesticides

Liquid–liquid extraction method was used for the determination of pesticide residue according to the procedure described by Pandit *et al.,* (2006). A 50 mls volume of n-hexane was introduce into a 2 liter separating funnel containing 1 liter of filter water and were shake manually for 5 minute and allow to settle. After complete separation, the organic phase was drained into a 250 mls conical flask, while the aqueous phase was re-extracted twice with 50 mls of n-hexane. The three extracted organic phases were combined and dried by passing through a glass funnel containing anhydrous sodium sulfate. The organic fraction were concentrated using rotary evaporator.

Extraction of Sediment Samples for Organochlorine Pesticides

Dry sediment samples were extracted according to Darko *et al.,* (2008). A 10g portion of Sediment samples were transferred into an extraction thimble that had been previously washed with n-hexane and acetone and oven dried. The sample were extracted using 150 mls of n-hexane/acetone mixture 4:1 v/v for eight hours (8 hrs) using soxhlet extractor. The extract was evaporated to dryness using a rotary evaporator at 40^{o}C. Each extract was dissolved in 10 mls n-hexane and subject to clean-up procedure.

Sample Clean-Up of Sediment for Organochlorine Pesticides

Sediment samples clean-up for organochlorine pesticides residues were carried out according to method described by Michelle and Megan, (2012). The residue of the extraction step of each sediment samples were dissolved in 4 mls n-hexane and transferred into a Florisil mini-column (8 mm, filled with 3.5g of 7% deactivated Florisil with distilled water, and a 1cm layer of anhydrous sodium sulfate was used to cork the Florisil from both sides).

The Florisil column was washed with 10 mls n-hexane before use. The pesticides were eluted from the column with 150 mls of 30% diethyl ether in n-hexane (v/v). The eluate was evaporated at ≤40°C to dryness using a rotary evaporator and dissolved in 1mls of ethyl acetate for gas chromatograph analysis.

Extraction of Organochlorine Pesticides from Fish Samples

Extraction of fish samples were carried out according to method described by (Michelle and Megan, 2012). The fish samples (20g) were weigh into a 150 mls conical flask followed by the addition of 20 g and 5 g of anhydrous sodium sulfate and sodium hydrogen carbonate, respectively. 100 mls of 1:1 (v/v) ethyl acetate/dichloromethane mixture was transferred into the 20 g fish samples and were thoroughly mixed by shaking the conical flask while cork. 20 g of anhydrous sodium sulfate were added to the content of the conical flask followed by addition of 20 g of sodium hydrogen carbonate.

The conical flask was cork tightly and the mixture was shaken thoroughly for 10 min. The content was allowed to stand for 3h. The organic layer was decanted into a 200 mls round bottom flask and was evaporated using the rotary evaporator at 40 °C. The pesticide in the rotary flask were dissolved and was collected with 2 mls of ethyl acetate and transferred into a 2 mls vial and ready for the clean-up.

Silica Gel Clean-Up of Fish Sample Extracts for Organochlorine Pesticides

Extraction of sediment samples were carried out according to method described by (Michelle and Megan, 2012). Ten grams (10g) portion of deactivated silica gel was weigh and transferred into a 10 mm glass chromatographic column followed by addition of 3g of anhydrous sodium sulfate. Ten (10mls) of the 1:1 (v/v) ethyl acetate/dichloromethane mixture were used to wet and rinsed the column. The extract residue that is water and fish in 2 mls ethyl acetate was transferred into the column and the extracted vial rinsed (three times) with 2 mls ethyl acetate.

The columns were elute with 80 mls portion of ethyl acetate/dichloromethane at a rate of 5 mls/min into a conical flask as fraction one. The column was elute again with 50 mls portion of ethyl acetate/dichloromethane for the second elution and added to the first extract. All the fractions of each sample were concentrated to dryness using a rotary evaporator at 40 °C. Each residue was dissolved and collected in 2 mls ethyl acetate for gas chromatograph analysis.

De-fattening of the Fish Sample Extracts for Organochlorine Pesticides

De-fattening of fish samples were carried out according to method described by (Michelle and Megan, 2012). Fifty (50) mls of 1:1 (v/v) hexane/acetonitrile solution were added to 2 mls pesticide extracted from the fish samples in a 100 mls separator funnel. The separator funnel was shaken gently for 3 min while releasing the gas pressure. The separator funnel was allowed to stand for 20 min to allow for phase separation of the organic solvents. The acetonitrile fractions containing the pesticides were collected into a 50 mls beaker while the fat containing hexane solvent phase was discarded.

The acetonitrile solvent extract obtained was further clean-up using 25 mls of the pure hexane. The acetonitrile fraction was concentrated with rotary evaporator at 40 °C and the content of the flask dissolved and collected with 2 mls of ethyl acetate into a 2 mls vial. The vial containing the pesticides extracts was stored in the refrigerator at 4 °C for GCMS analysis.

RESULTS

Means Concentrations of Organochlorine Pesticide Residues in Water and Sediment Samples from Different Sampling Points During the Rain, Dry Seasons and Harmattan Period

The mean concentrations of some organochlorine pesticide (OCPs) (endosulfan, dieldrin, aldrin, and metoxichlor) residues in water samples from Komadugu River basin, Yobe State, Nigeria from different sampling points during the rainy, dry seasons and Harmattan period are as presented in Figures 1 to 3.

The concentration of endosulfan ranged from 1.00E-02 to 1.01E+00 µg/L; 1.00E-02 to 8.60E-01µg/L dieldrin; 1.00E-02 to 1.51E+00 µg/L aldrin and 3.00E-02 to 3.30E-01µg/L metoxichlor. Sampling point S4 recorded the highest total concentration with a value of 2.55E+00 µg/L during the rainy season, while points S5 recorded the lowest concentration with a value of 6.70E-01 µg/L during the dry season.

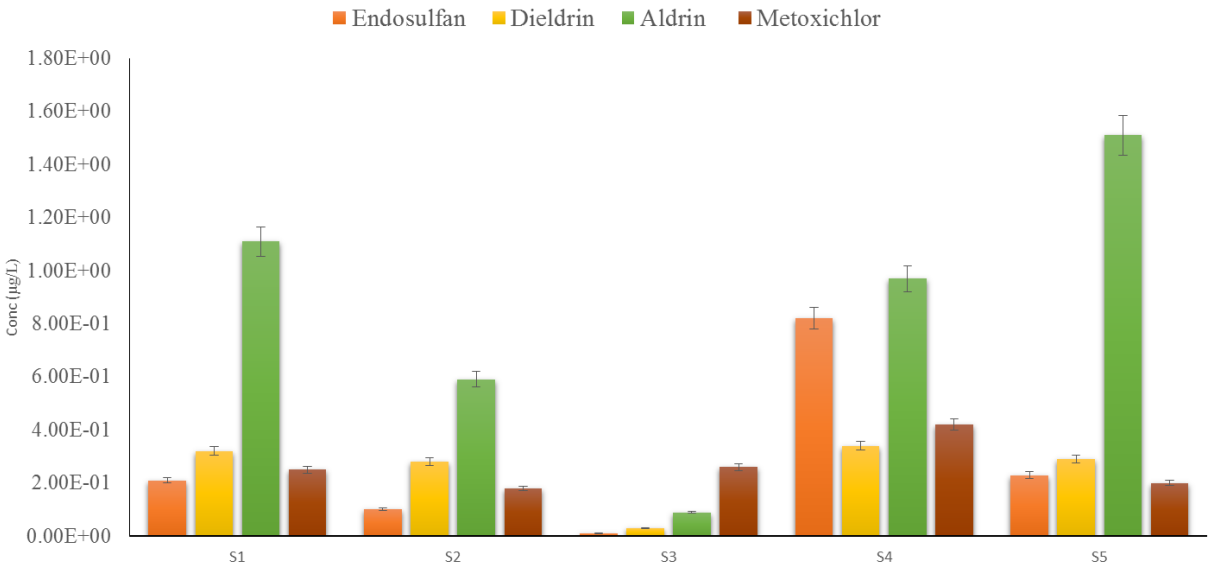


Figure 1: Mean Concentrations of Organochlorine Pesticide Residues in Water Samples from Komadugu River Basin, Yobe State, Nigeria During the Rainy Season

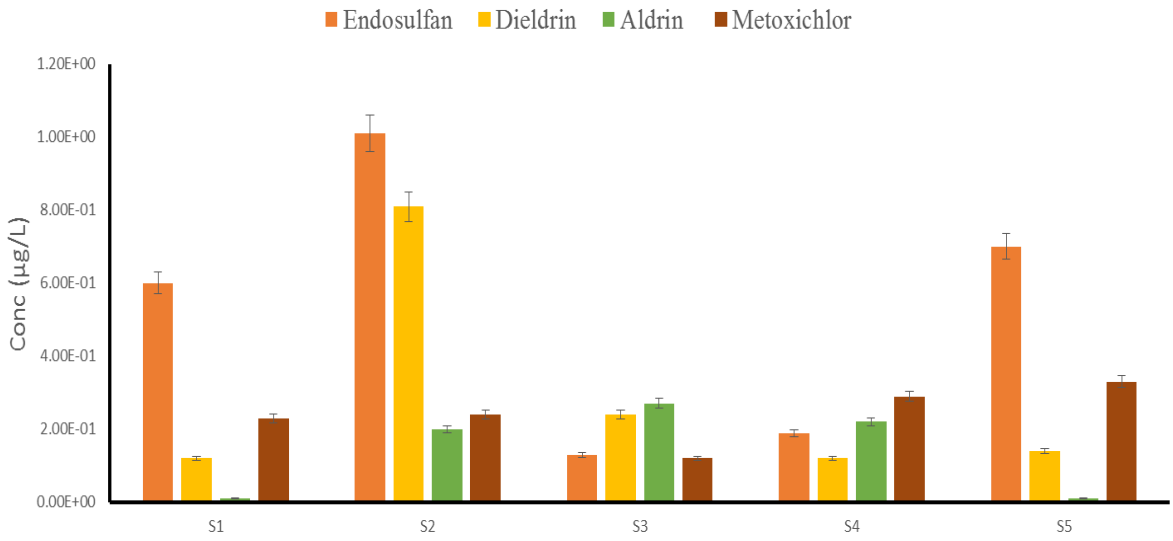


Figure 2: Mean Concentrations of Organochlorine Pesticide Residues in Water Samples from Komadugu River Basin, Yobe State, Nigeria During the Harmattan Period

For sediment samples, the concentration of endosulfan ranged from 1.34E+00 to 7.03E+00 mg/kg; 1.08E+00 to 1.20E+01mg/kg dieldrin; 1.03E+00 to 8.05E-+00 mg/kg aldrin and 2.11E+00 to 6.41E+00 mg/kg metoxichlor (Figures 4 to 6).

Sampling point S4 recorded the highest total concentration with a value of 2.72E+01 mg/kg during the rainy season, while points S2 recorded the lowest concentration with a value of 1.22E+01 mg/kg during the dry season.

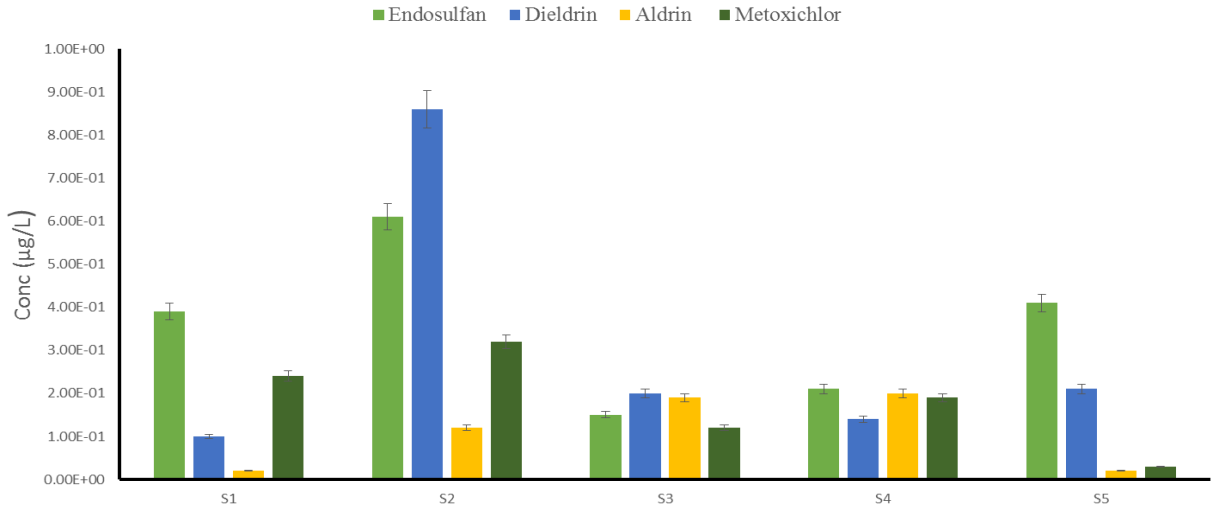


Figure 3: Mean Concentrations of Organochlorine Pesticide Residues in Water Samples from Komadugu River Basin, Yobe State, Nigeria During the Dry Season

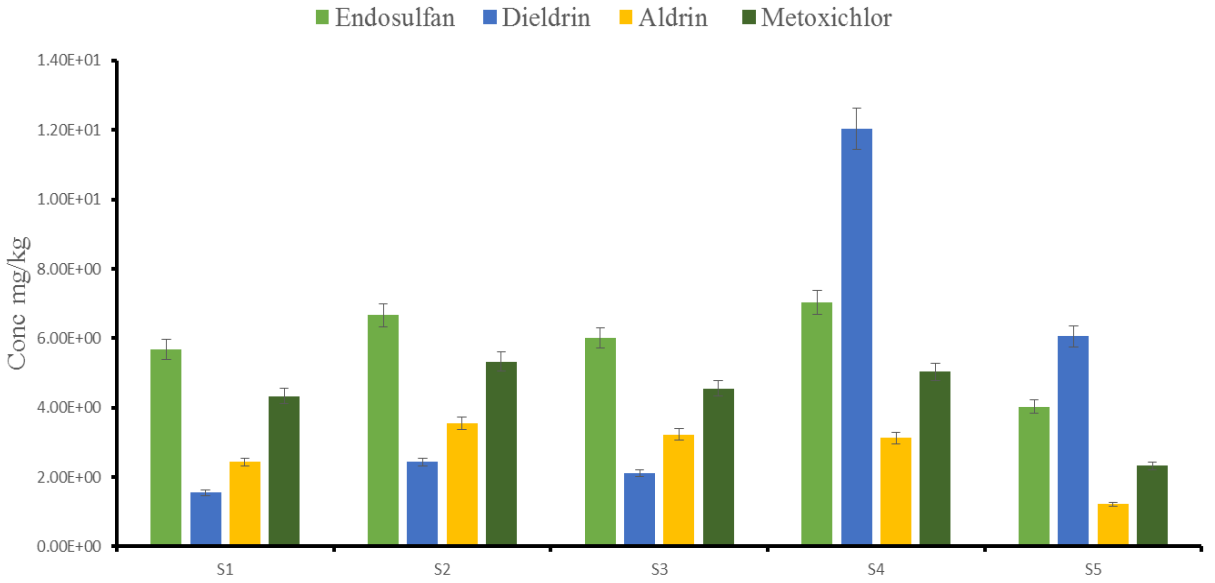


Figure 4: Mean Concentrations of Organochlorine Pesticide Residues in Sediment Samples from Komadugu River Basin, Yobe State, Nigeria During the Rainy Season

Means Concentrations of Organochlorine Pesticide Residues in Different Fish Samples During the Rain, Dry Seasons and Harmattan Period

The mean concentrations of some organochlorine pesticide (endosulfan, dieldrin, aldrin and metoxichlor) residues in *Clarias anguillaris, Tilapia zilli, Heteroutis niloticus and Synodontis budgetti* from Komadugu River basin, Yobe State, Nigeria during the rainy seasons are as presented in Figure 7.

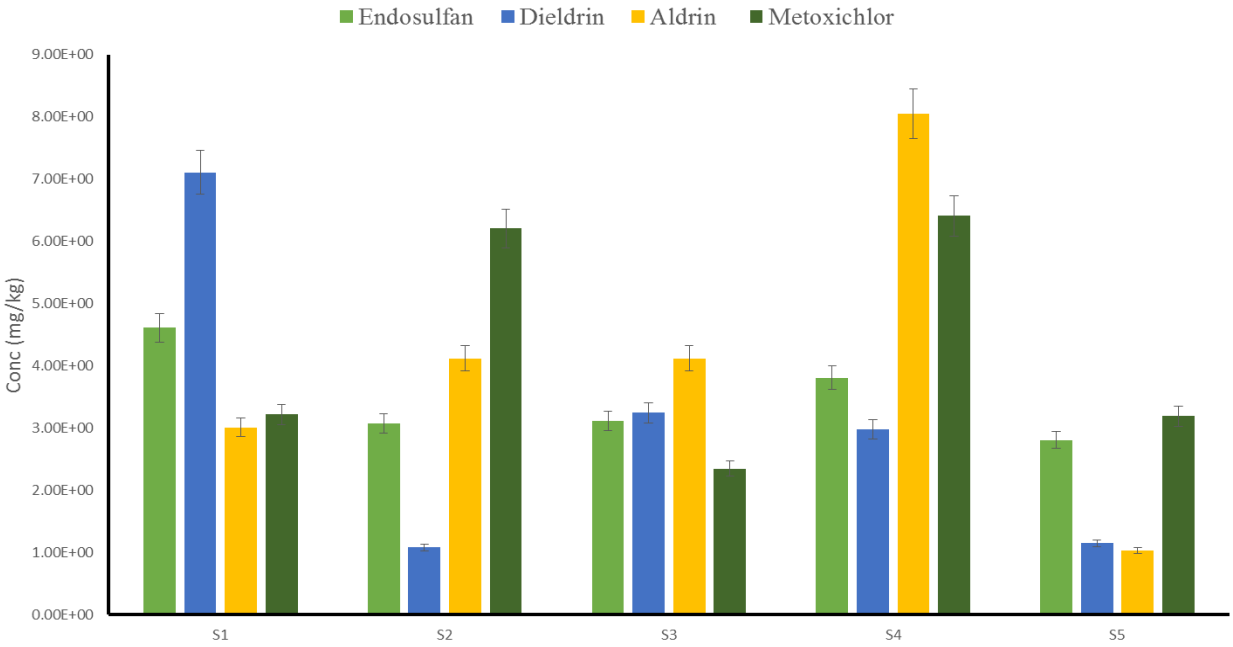


Figure 5: Mean Concentrations of Organochlorine Pesticide Residues in Sediment Samples from Komadugu River Basin, Yobe State, Nigeria During the Harmattan Period

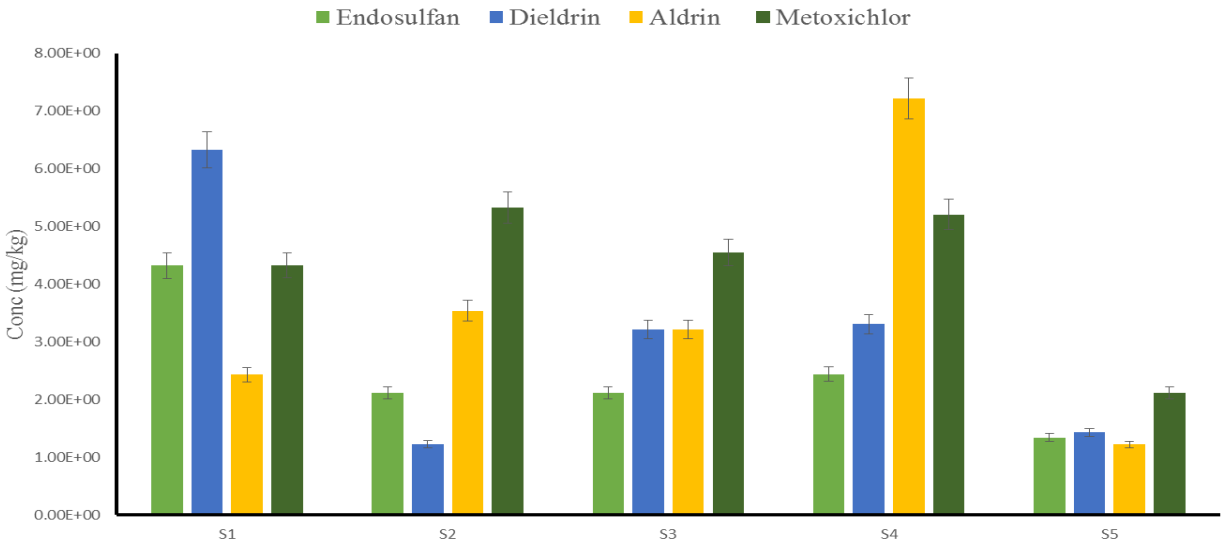


Figure 6: Mean Concentrations of Organochlorine Pesticide Residues in Sediment Samples from Komadugu River Basin, Yobe State, Nigeria During the Dry Season

The concentration of endosulfan ranged from 2.00E-02 to mg/kg; 4.00E-02 to 4.50E-01mg/kg dieldrin; 1.10E-01 to 1.42E-+00 mg/kg aldrin and 2.30E-01 to 5.50E-01 mg/kg metoxichlor. *Synodontis budgetti* recorded the highest total concentration with a value of 3.36E+00 mg/kg, while *Heteroutis niloticus* recorded the lowest concentration with a value of 5.01E-00 mg/kg. For the dry season, the concentration of endosulfan ranged from 1.70E-01 to 8.90E-01 mg/kg; 1.90E-01 to 1.33E+00 mg/kg dieldrin; 4.00E-02 to 3.00E-01 mg/kg aldrin and 1.50E-01 to 4.10E-01 mg/kg metoxichlor (Figure 8).

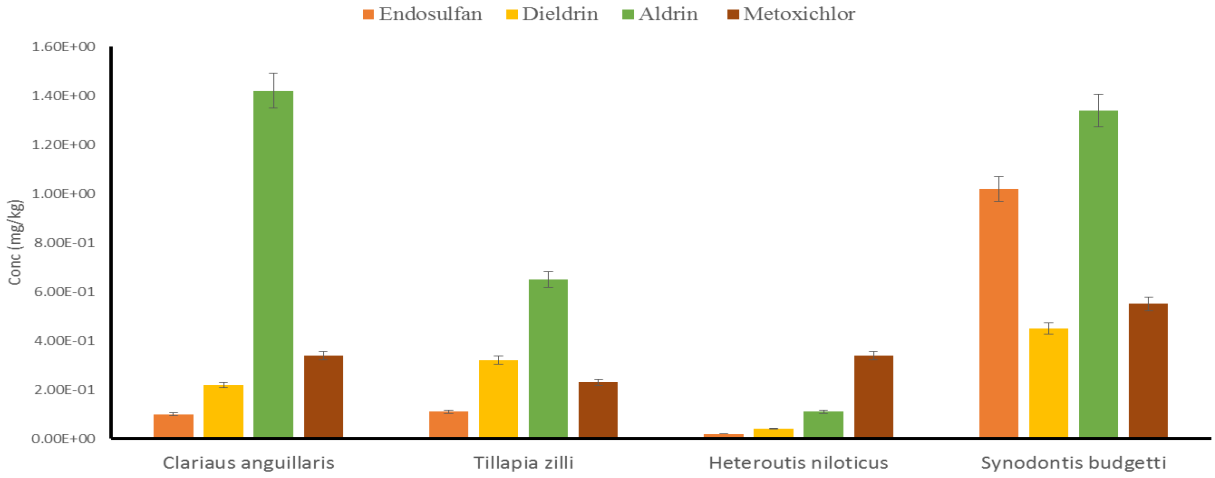


Figure 7: Mean Concentrations of Organochlorine Pesticide Residues in Tissues of Four Species of Fish Samples frome Komadugu River Basin, Yobe State, Nigeria During the Rainy Season

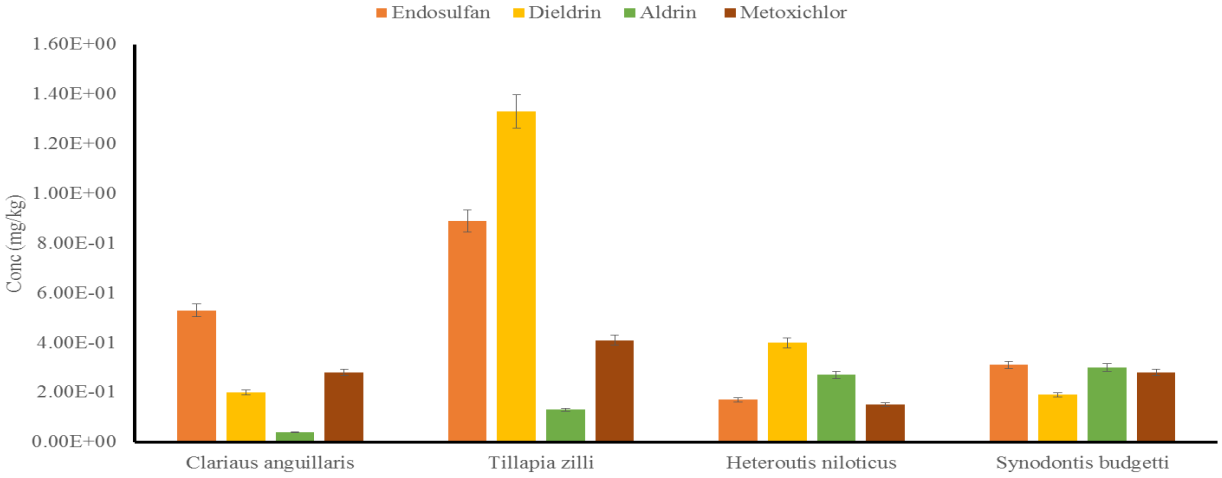


Figure 8: Mean Concentrations of Organochlorine Pesticide Residues in Tissues of Four Species of Fish Samples frome Komadugu River Basin, Yobe State, Nigeria During the Harmatta Period

Tilapia zilli recorded the highest total concentration with a value of 2.76E+00 mg/kg, while *Heteroutis niloticus* recorded the lowest concentration with a value of 9.90E-01 mg/kg. For Dry season the concentration of endosulfan ranged from 1.10E-01 to 1.04E+00 mg/kg; 1.10E-01 to 1.23E+00 mg/kg dieldrin; 2.00E-01 to 3.30E-01 mg/kg aldrin and 1.10E-01 to 3.40E-01 mg/kg metoxichlor (Figure 9). *Tilapia zilli* recorded the highest total concentration with a value of 2.72E+00 mg/kg, while *Heteroutis niloticus* recorded the lowest concentration with a value of 8.70E-01 mg/kg.

Total Percentage Accumulation of Some Organochlorine Pesticide Residues in Water, Sediment and Fish Samples

The total percentage accumulation of some organochlorine pesticide residues in water samples for rainy, dry seasons and Harmattan period from points S1 to S5 of Komadugu River basin, Yobe State, Nigeria are as presented in Figure 10. Rainy season shows the total percentage accumulation of 25%; Harmattan period with 25% and the dry season with 50%.

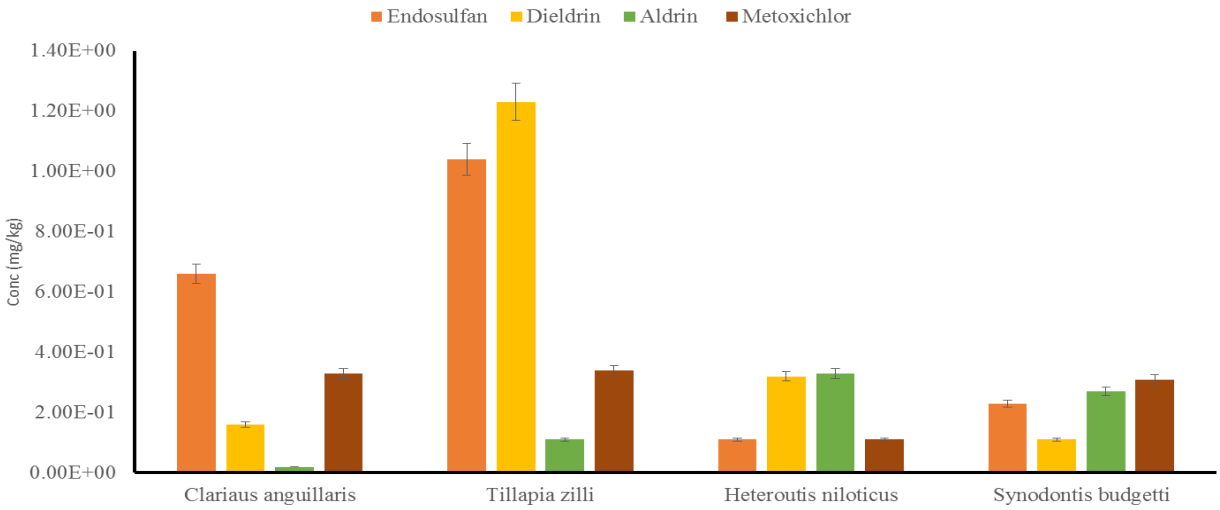


Figure 9: Mean Concentrations of Organochlorine Pesticide Residues in Tissues of Four Species of Fish Samples frome Komadugu River Basin, Yobe State, Nigeria During the Dry Season

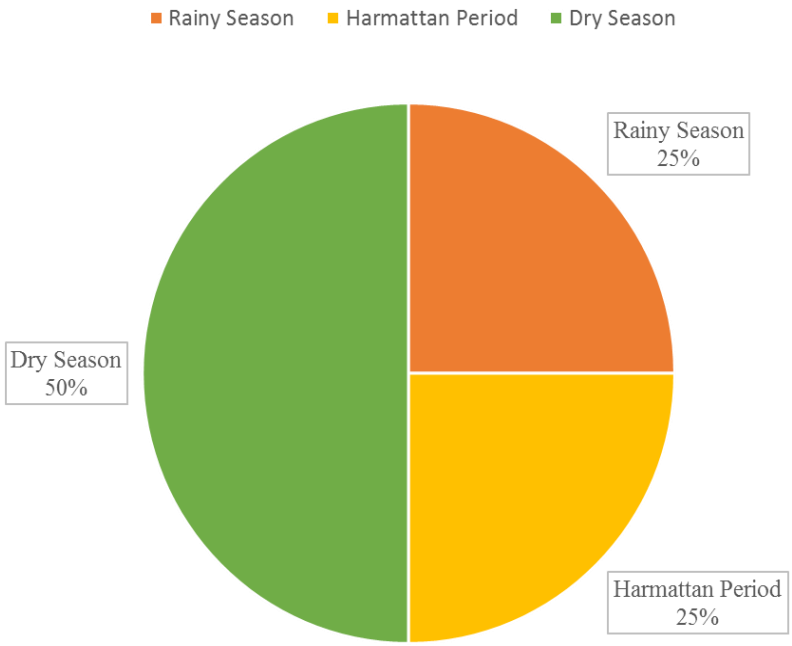


Figure 10: Percentage Accumulation of Organochlorine Pesticide Residues in Water Samples During the Rainy, Dry Seasons and Harmattan Period.

For the sediment samples, rainy season shows 39%; Harmattan period with 32% and dry season with 29% (Figure 11). The highest and the lowest percentage accumulations were observed during the rainy and dry seasons, respectively. The total percentage accumulation of some organochlorine pesticide residues in Fish samples for rainy, dry seasons and Harmattan period of Komadugu River basin, Yobe State, Nigeria are as presented in Figure 12. The total percentage accumulation for fish samples during the rainy season is 39%; Harmattan period 31% and the dry season 30%. Rainy season were observed to show the highest percentage accumulation, while the dry season shows the lowest percentage accumulation.

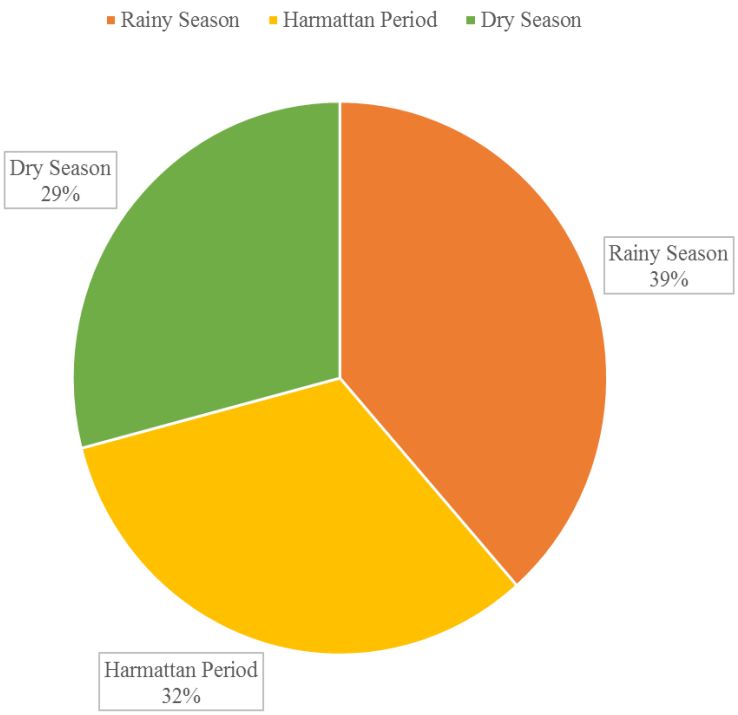


Figure 11: Percentage Accumulation of Organochlorine Pesticide Residues in Sediment Samples During the Rainy, Dry Seasons and Harmattan Period.

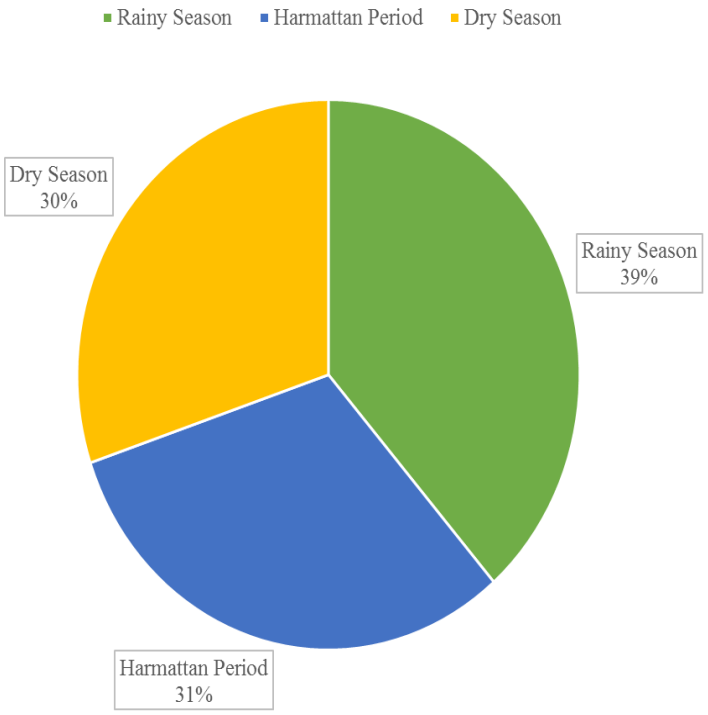


Figure 12: Percentage Accumulation of Organochlorine Pesticide Residues in Fish Samples During the Rainy, Dry Seasons and Harmattan Period.

DISCUSSION

Organochlorine Pesticide Residues in Water, Sediment, and Fish Samples

As at December 2008, the organochlorine pesticides namely: aldrin, dieldrin, and endosulfan were among the banned pesticides by Environmental Protection Agency of Nigeria and National Agency for Food and Drug Administration and Control (NAFDAC, 2008) because of their toxicity and its ability to cause cancer. The total concentration of OCPs in water samples from Komadugu River basin, Yobe State, Nigeria ranged from 6.70E-01 to 2.55E+00 µg/L (Figures 1 to 3).

Alderin shows the highest organochlorine concentration of 1.51 µg/L at sampling point S5 during the rainy season, the concentrations of OCPs were observed to be significantly higher during the rainy season when compared to the dry season and Harmattan period, this could be attributed to the excessive usage of this compound in the study area coupled with agricultural run-off as well as discharges from river sources of Kano and Jos.

In general terms, the concentrations of OCPs detected showed slightly higher levels in the fish compartment compared to those in the water compartment. The negligibility of OCPs residues in water was due to the fact that organochlorines are scarcely soluble in water (Imo *et al*. 2013). Veljanoska-Sarafiloska *et al.* (2013) similarly, reported higher OCPs concentrations in the muscle tissue of fish than in water compartments.

This trend of this result was anticipated as organochlorines are hydrophobic in nature and therefore they are prone to concentrating in fatty tissues of living systems like fishes and other related aquatic organisms. Sediment plankton and microflora are used as a main source of food for young fishes, which are eaten by larger fishes, which are then used by humans. In this cycle, the repetitive accumulations of such compounds increase the rate of breast cancer in the female population that live near the coastal areas and these compounds will be subsequently transferred to new generations via mother's milk as a result of their high lipophilic storage (Iscan *et al*., 2002; Alpay *et al*., 2008). The concentrations of organochlorine pesticides ranged from 2.00E-02 to 1.42E+00 mg/kg in fish samples studied.

The highest concentration (1.42E+00 mg/kg) was recorded for alderin during the rainy season**.** The OCPs loads (sum of all detected pesticides) all fish species studied was obtained during the rainy season with a value of 7.26E+00 mg/kg, while the lowest load of 5.68E+00 mg/kg was recorded during the dry season**.** The concentrations of OCPs residues in sediment samples studied ranged from 1.03E+00 to 1.20E+01 mg/kg, with the highest total concentration of 1.20E+01 mg/kg which was recorded for dieldrin during the rainy season and 8.87E+01 mg/kg which were observed during the rainy season, while the lowest value of 6.07E+01 mg/kg was recorded during the dry season. The highest pesticide load recorded during the rainy season could be linked possibly to its higher usage during the rainy season for agricultural production couple with discharge from river source and agricultural run-off.

Endosulfan

Organochlorine pesticides tend to accumulate in living organisms especially in aquatic organisms and they substantially settle on the sediments (Kamman *et al*., 1992). Endosulfan accumulation was the highest in all the fish samples studied and was observed during the rainy season, while the lowest value was observed during the Harmattan period Figure 12.

Despite the adverse side effect of pesticides, OCPs form an integral component of modern Agriculture. The benefit 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 pesticide residues generated on the field. These results of the present study are in agreement with the study carried out by (Afful *et al*., 2010) which indicate high level of endosulfan residue in fish. However, level of this pesticide residues were also reported in Lagos Lagoon (Adeyemi *et al*., 2008) were extremely low compared to the level recorded in this work.

The concentrations endosulfan in all the fish samples were much higher than the WHO and FAO (Codex, 2009) set maximum residue limit (MRL) 0.1 mg/kg and the Acceptable Daily Intake value (ADI) of 0.006 mg/kg. Agricultural runoff is the primary source of this pesticide in aquatic

ecosystems. Endosulfan has been shown to be highly toxic to fish and marine invertebrates and is readily absorbed in sediments. It therefore represents a potential hazard in the aquatic environment (Sittig, 1980).

Dieldrin and Aldrin

The highest level of dieldrin and aldrin were recorded in all the samples of fish studied, similar observation was reported by Gitau, (1994). Other work also reported the highest level of aldrin and dieldrin in the aquatic environment (Schmitt *et al*., 1990), dieldrin is a chlorinated cyclodiene that was widely used in the Nigeria. The National Agency for Food and Drug Administration and Control (NAFDAC) has banned the sale and supply of 30 different agrochemical products in the country which include dieldrin and aldrin.

Because the toxicity of this persistent pesticide posed an imminent danger to human health, NAFDAC banned the most major uses of dieldrin and aldrin in 2008, but the product is still in used because the low cost and affordability. In 1984 and 1985, the U.S. Fish and Wildlife Service collected 321 composite samples of whole fish from 112 stations nationwide as part of the National Contaminant Biomonitoring Program.

Maximum and geometric mean tissue concentrations of dieldrin and aldrin in 1984 were 1.39 and 0.04 ppm (wet weight), respectively (Schmitt *et al*., 1990). The present data also indicated the accumulation levels of dieldrin and aldrin in the fish species study. The concentrations of aldrin and dieldrin in most of the fish samples were much higher than the WHO and FAO (Codex, 2009) set maximum residue limit (MRL) of 0.2 mg/kg and the acceptable daily intake values (ADIs) of 0.0001mg/kg.

The concentration of dieldrin was slightly significantly higher than that of aldrin in all the species of fish studied. This could be an indication that there is more dieldrin in the environment compared to aldrin. This trend is supported by the fact that aldrin undergoes photolysis to dieldrin in the environment. These results are in agreement with Akan *et al*. (2013), United States Department of Health and Human services (USDHHS), 1993 who reported that aldrin is readily and 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 lipids such as animal fat and plant waxes. It is for this reason that dieldrin bioconcentrates and biomagnifies through the terrestrial and aquatic food webs. (Matsumura, 1985) pointed out that dieldrin is one of the most persistent chemicals known. He also reported that dieldrins bioaccumulation in animal tissue is due to its resistance to degradation and biologic metabolism. Similar to DDT and its metabolites, dieldrin is not easily metabolized in water and has limited capacity of being digested and excreted from the body. It is, however, easily absorbed and transported throughout the blood of vertebrates and hemolymph of invertebrates.

Methoxichlor

The maximum concentration of methoxichlor was detected during the rainy season with a value of 1.46E+00, while the lowest value was recorded during the dry season with a value of 0.01µg/L in water samples. Methoxychlor is used to protect crops, ornamentals, livestock, and pets against fleas, mosquitoes, cockroaches, and other insects. It was intended to be a replacement for DDT, but has since been banned based on its acute toxicity, bioaccumulation, and endocrine disruption activity.

The amount of methoxychlor in the environment changes seasonally due to its use in farming and foresting. It does not dissolve readily in water, so it is mixed with a petroleum-based fluid and sprayed, or used as a dust. Sprayed methoxychlor settles on the ground or in aquatic ecosystems, where it can be found in sediments. Its degradation may take many months.

Methoxychlor is ingested and absorbed by living organisms, and it accumulates in the food chain. Some metabolites may have unwanted side effects.

RECOMMENDATIONS

Four OCPs were detected in water, sediment and tissues of fish samples (*Clarias anguillaris, Tilapia zillii, Synodontis budgetti and Heterotis niloticus)* in Komadugu River basin on seasonal variation. The results of these studies also indicate that the some of the concentrations of the studied PCBs in fish were above the maximum residue limit (MRL) of 2 mg/kg set by the European Union.

The levels of dieldrin were the most abundant pesticide residues in the studied water, sediment and fish samples studied. The highest levels of these pesticides were observed during the rainy season when compared to Harmattan period and the dry season. This study revealed that pesticide residue levels in the fish samples study were above the maximum residue limits and acceptable dietary intake and could be an important process of transferring pesticides to humans. It also indicated the extensive presence and usage of these pesticides in the study environment, which include recent use of this pesticide for pest control. Thus, the use of these pesticides to control pest by farmers within the study area with little or no knowledge must be checked through adequate control of the trade and use of pesticides and the enforcement of appropriate sanctions.

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