ChemSearch Journal 13(1): 157 – 165, June, 2022
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 28/05/2022 Accepted: 16/06/2022
http://www.ajol.info/index.php/csj

Levels of Organochlorine Pesticide Residues in Tissues of Fish Samples from River Benue, Vinikilang, Adamawa State, Nigeria

Mshelia, J. U., Jatau, A. M., Zakari, M., Akan J. C., *Yakubu, J. and Abba, A.
Department of Pure and Applied Chemistry, Faculty of Science, University of Maiduguri, P.M.B. 1069, Maiduguri, Borno State, Nigeria
***Correspondence Email:** jamesyakubu96@gmail.com

ABSTRACT

This study aimed to determine organochlorine pesticide residues which include dichlorodiphenyldichloroethylene (o,p-DDE), 4,4'- dichlorodiphenyldichloroethan (p,p'-DDD), 2,4'dichlorodiphenyldichloroethan (o,p'-DDD), 2,4'-dichlorodiphenyltrichloroethane (o,p'-DDT), 4,4'dichlorodiphenyltrichloroethane (p,p'-DDT), metoxichlor, dieldrin and aldrin in the flesh, liver, bones and gills of five commercially available species (*Bagrusbayad, Clariasanguillaris, Latesniloticus, Hetorosisniloticus, and Auchenogianis occidentals*)within River Benue in Vinikilang, Adamawa State, Nigeria.The sample collection and preparation were carried out using standard procedures. The concentration of all the analytes in the samples were analyzed using Gas Chromatography-ion trap Mass Spectrometer with optional Msn mode. The study revealed that all the organochlorine pesticides analyzed (p,p'-DDT, o,p'-DDE, p,p'-DDD, o,p'-DDD, Metoxichlor, dieldrin and aldrin), were detected in all the studies fish samples. Highest levels of these pesticides were observed in the gills of *Auchenogianis occidentals* compared to other tissues. This study revealed that pesticide residue levels in the fish samples studied were lower than the maximum residue limits (MRLs) and acceptable dietary intake (ADI), with the exception of dieldrin and aldrin which were higher than the WHO and FAO set maximum residue limit (MRL) of 0.2 mg/kg and the Acceptable Daily Intake values (ADIs) of 0.0001mg/kg. 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.

Keywords: Fish Tissues, Organochlorine, Pesticides, River Benue

INTRODUCTION

Pesticides use has increased worldwide, particularly in its use to salvage the food supply to the ever increasing global population. Although it is undisputed that pesticides are essential in modern agriculture. There is growing concern about possible environmental contamination from agrochemicals, industries, and household and rain water runoff from agricultural systems, disposal of outdated stocks, containers and packets (Domagalski and Kuivila, 1993; Satya *et al.*, 1995. Thurman *et al.*, 2000).

Agricultural practices are the largest consumer of pesticides to chemically control various pests. Moreover, pesticides are also used in public health to control vector-borne diseases which includes malaria and dengue as well as unwanted plants such as grass and weeds in ornamental landscaping, parks and gardens. They are also useful in suppressing or avoiding the proliferation of insects, pests, bacteria, fungi, and algae in electrical equipment, refrigerators, paint, carpets, paper, cardboard, and food packaging materials (Gilden *et al.*, 2010).

However, unintended exposure to pesticides can be extremely hazardous to humans and other living organisms as they are designed to be poisonous (Sarwar, 2015). They may also be harmful to people who are exposed to pesticides through occupational (or home) use, eating foods or liquids containing pesticide residue, or inhalation (or contact) of pesticide-contaminated air (Pimentel *et al.*, 2013). Even a very low concentration level of exposure may have negative health effects at early stages (Damalas and Eleftherohorinos, 2011).

Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) or pesticides including dichlorodiphenyltrichloroethane (DDTs) and its metabolites, hexachlorobenzene (HCB) or isomers of hexachlorocyclohexane (HCHs) have been known as global contaminants of the environment for decades. Some pesticides (e.g., aldrin, chlordane, dichlorodiphenyltrichloro-ethane (DDT), dieldrin, endrin, heptachlor, and hexachlorobenzene) contain persistent organic pollutants (POPs) that resist degradation and thus remain in the environment for years (Yadav *et al.*, 2015).

Pesticides residues problems in the fish tissue are serious, as reflected by the high pesticides concentration recorded in the water and sediments (Hussein *et al*., 2009). The gills are directly in contact with water. Therefore, the concentration of pesticides in gills reflects their concentration in water where the fish live, whereas the concentration in live represent storage of pesticides in the water (Babu *et al.,* 2003). Fish are used extensively for environmental monitoring (Lan Franchi *et al.,* 2006). Because they uptake contaminants directly from water and diet. Generally, the ability of fish to metabolize organochlorines is moderate; therefore, contaminant loading in fish is a reflection of the state of pollution in surrounding environments (Guo *et al.*, 2008).

Organochlorine pesticides are pesticides that act primarily by altering the movement of ions across the nerve cell membrane, thus changing the ability of the nerve to fire. For example, organisms exposed to low doses of DDT exhibit tremors and in-coordination as a result of repetitive discharge (over-firing) of the nerves. Studies showed inhibition of brain activity in Juvenile bluegill sunfish exposed to endosulfan (organochlorine pesticide). Pesticide exposure is linked with various diseases including cancer, hormone disruption, asthma, allergies, and hypersensitivity (Van Maele-Fabry *et al*., 2010). A line of evidence also exists for the negative impacts of pesticide exposure leading to birth defects, reduced birth weight, fetal death, etc. (Wickerham *et al*., 2012).

Vinikilang is a fast growing community located on the slope of Bagale hill and close to River Benue. River Benue flows through Vinikilang in Adamawa State, Nigeria. The River cover the long distance from Damare, Labong to Vinikilang and Greng, River Benue received a wide variety of waste from agricultural land. These wastes generated contaminate the River Benue with a variety of pesticides acting as point sources. This river is also used for commercial fishing. Most farmers within the shores of river Benue area used fertilizers, synthetic chemicals and pesticides to increase crop yield and control pests on vegetables including a number of highly persistent organochlorine and organophosphorus pesticides to check and control pests, diseases, weeds and other plants pathogens in effort to reduce or eliminate yield losses and preserve high product quality.

This study aimed to determine organochrlorine pesticide residues which include dichlorodiphenyldichloroethylene (o, p-DDE), 4,4'- dichlorodiphenyldichloroethan (p,p'-DDD), 2,4'dichlorodiphenyldichloroethan (o,p'-DDD), 2,4'-dichlorodiphenyltrichloroethane (o,p'-DDT), 4,4'dichlorodiphenyltrichloroethane (p,p'-DDT), dieldrin and aldrin in the flesh, liver, bones and gills of five commercially important species of fish such as *Bagrusbayad, Clariasanguillaris, Latesniloticus, Hetorosisniloticus, and Auchenogianis occidentals* caught within River Benue in Vinikilang, Adamawa State, Nigeria.

MATERIALS AND METHODS

Sampling and Sample Preparation

Sampling Area

Fish samples were collected from River Benue in Vinikilang, Girei Local Government Area of Adamawa State, Nigeria (Figure 1).

Sample Collection

Fish samples were caught using gill nets from River Benue in Vinikilang, Adamawa State, Nigeria. Different fish samples (*Bagrusbayad, Clariasanguillaris, Heterosisniloticus, Latesniloticus and Auchenogianis occidentals)* of uniform sizes were collected in order to avoid the possible error due to size differences. The fishes were transported to the Fisheries Department, University of Maiduguri for identification. The samples were subsequently transported to the laboratory on the same day and later dissected to remove the flesh, intestine, liver, bone and gills of each species of the fish and stored at 4°C in a refrigerator for further extraction and analysis.

Extraction of Organochlorine Pesticide Residues from Fish Samples

For the extraction of pesticides from fish samples, 20g of the fish samples were weighed into a 150ml conical flask followed by the addition of 20g and 5g of anhydrous sodium sulfate and sodium hydrogen carbonate respectively. A mixture, 100ml of 1:1 (v/v) ethyl acetate/dichloromethane was transferred into the 20g fish samples and mixed thoroughly by shaking the conical flask while corked. Again, 20g of anhydrous sodium sulfate was added to the content of the conical flask followed by 20g of sodium hydrogen carbonate. The conical flask was corked tightly and the mixture shaken thoroughly for 10min. The content was allowed to stand for 3hrs. The organic layer was decanted into a 200ml round bottom flask and evaporated using the rotary evaporator at 40°C. The pesticide in the rotary flask was dissolved and collected with 2ml of ethyl acetate and transferred into a 2ml vial and ready for the clean-up.

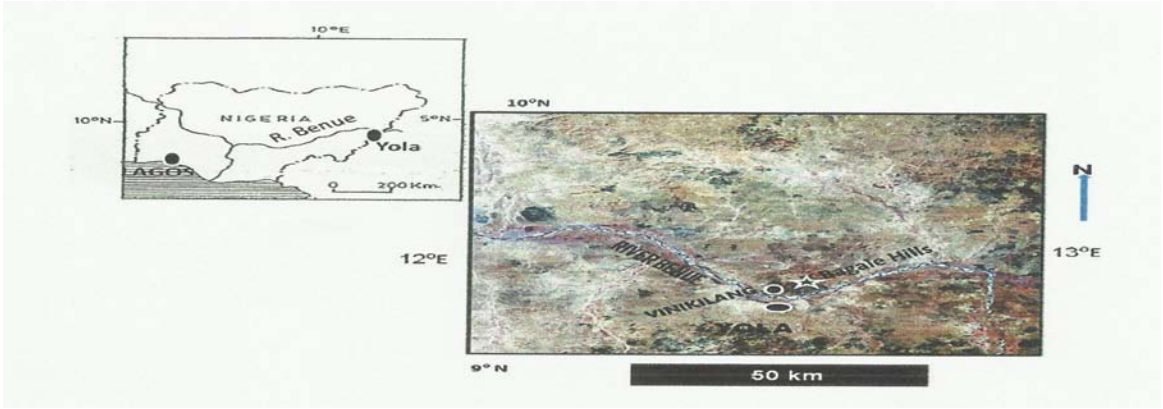

Figure 1: Map showing location of Vinikilang on satellite imagery of Yola area. River Benue exhibit "V" shaped channel due to control by conjugate NE-SW and NW-SW fracture
(source of imagery: Federal Dept. of Forestry, Abuja Vintage: Jan 1993). Upper left is map of Nigeria showing location of Yola

Silica Gel Clean-Up of Sample Extracts

An inherent difficulty in the extraction of biological samples is the co-extraction of matrix components that are also soluble in the extraction solvent. A common example is the co-extraction of lipids during the extraction of non-polar compounds from animal and vegetable matrices (Bjorklund *et al.*, 2000; Kayali–Sayidi *et al.*, 2000, Ali and Cole, 2001). The presence of matrix interferences in sample extracts can result in a multitude of challenges including; formation of emulsions, sample turbidity, contamination or plugging of the analytical instrument, masking of the analytical signal for the target analyte and the consequent increase in the method limit of detection.

Co-extractives are frequently removed during the post-extraction clean up step. The co-extracted substance in the extracts can be removed by destructive or non-destructive methods. Destructive methods e.g. sulphuric acid treatment or saponification efficiently removes the bulk lipids (triglycerides) from the extracts. However, some pollutants such as dieldrin and aldrin degrade under strong acidic conditions. Saponification can cause dechlorination of higher polychlorinated biphenyls and hexachlorobenzene from sewage slug during alkaline saponification (van der Valk and Dao, 1988). Efficient non-destructive removal of lipids can be obtained by adsorption on alumina (Hess *et al*., 1995).

Ten gram (10g) portion of deactivated silica gel were weighed and transferred into a 10mm internal diammeter (i.d.) glass chromatographic column followed by the addition of 3g of anhydrous sodium sulfate. A 10ml mixture of the 1:1 (v/v) ethyl acetate/dichloromethane was used to wet and rinse the column. The extract residue in 2ml ethyl acetate was transferred into the column and the extract vial rinsed three times with 2ml ethyl acetate and added to the column. The column was eluted with 80ml 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 2ml ethyl acetate for gas chromatograph analysis. The vials containing the pesticide extract were stored in the refrigerator at 4°C for GC/MS analysis.

De-fattening of the Fish Sample Extracts

De-fattening of the sample extracts was carried out by method adopted by Domagalski and Kuivila, (1993) in which 50ml of 1:1 (v/v) hexane/acetonitrile solution was added to 2 ml pesticide extracted from the fish samples in a 100ml separatory funnel. The separatory funnel was shaken gently for 3 min while releasing the gas pressure. The separatory funnel is allowed to stand for 20 min to allow for phase separation of the organic solvents. The acetonitrile fraction containing the pesticide was collected into a 50 ml beaker while the fat containing hexane solvent phase will be discarded. The acetonitrile solvent extract obtained was further cleaned-up using 25 ml 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 ml of ethyl acetate into a 2 mL vial. The vial containing the pesticide extract was stored in the refrigerator at 4°C for GCMS analysis.

Determination of Organochlorine Pesticide Residues

The determination of organochlorine pesticide residues was carried out using method adopted by David *et al*., (2008).The SHIMADZU GC/MS (GC-17A), equipped with fluorescence detector was used for the chromatographic separation. This was achieved by using a 35% diphenyl/65% dimethyl polysiloxane material in the column. The oven was programmed as follows; initial temperature 40^{o}C, 1.5min, to 150^{o}C, 5.0min, 5^{o}C/min to 200^{o}C, 7.5min, 25^{o}C/min to 290^{o}Cwith a final hold time of 12min and a constant column flow rate of 1ml/min. The detection of pesticides was perform 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 pesticide, the ratio of the intensity of matrix ions increase exponentially versus that of the pesticide ions as the concentration of the pesticide approach the detection limit, decrease the accuracy at lower levels. The GC-ion trap MS was operated in MSn mode and perform tandem MS function by injecting ions into the ion trap and destabilizing matrix ions, isolating only the pesticides ions. The retention time, peak area and peak height of the sample were compared with those of the standards for quantization.

Data Handling

Data collected were subjected to Pearson's correlation analysis, one-way analysis of variance (ANOVA) was used to assess whether pesticide residues varied significantly between fish samples. Possibilities less than 0.05 ($p<0.05$) were considered statistically significant. All statistical calculations were performed with SPSS 9.0 for windows.

RESULTS AND DISCUSSIONS

Concentrations of Organochlorine Pesticide Residues in Fish

The mean concentrations of o,p'-DDE, p, p'-DDD, o,p'-DDD, p,p'-DDT, metoxichlor, dieldrin and aldrin in the liver, gills, flesh and bones of *Bagrusbayad* from river Benue in Vinikilang are as presented in Figure 2. The concentrations of these pesticides in the liver of *Bagrusbayad* range between 0.04 and 0.62 mg/kg; 0.06 and 0.71 mg/kg gills; 0.02 and 0.42 flesh and 0.01 and 0.32 bones. The highest concentrations of all the pesticides were recorded in the gills, while the bones recorded the lowest value. The concentrations of o,p'-DDE, p, p'-DDD, o,p'-DDD, p,p'-DDT, metoxichlor, dieldrin and aldrin in the liver, gills, flesh bones of *Latesniloticus* from river Benue in Vinikilang are as presented in Figure 3. The levels of these pesticides in the liver range between 0.02 and 0.57 mg/kg; 0.03 and 0.64 mg/kg gills; 0.01 and 0.26 mg/kg flesh and 0.01 and 0.17 mg/kg bones. The maximum concentrations of all the pesticides were significantly observed in the gills, while bones show the minimum value. The concentrations of o,p'-DDE, p, p'-DDD, o,p'-DDD, p,p'-DDT, metoxichlor, dieldrin and aldrin in the liver, gills, flesh and bones of *Clariasangularis* from river Benue in Vinikilang are as presented in Figure 4. The concentrations of pesticides in the liver of *Clariasangularis* ranged between 0.07 and 0.73 mg/kg; 0.04 and 0.33 mg/kg gills; 0.01 and 0.26 mg/kg flesh and 0.01 and 0.14 mg/kg bones. Figure 5 represent the mean concentrations of o,p'-DDE, p, p'-DDD, o,p'-DDD, p,p'-DDT, metoxichlor, dieldrin and aldrin in the liver, gills, flesh and bones of *Hetrotisniloticus* from river Benue in Vinikilang. The concentrations range between 0.03 and 0.0.46 mg/kg liver; 0.04 and 0.33 mg/kg gills; 0.01 and 0.26 mg/kg flesh and 0.01 and 0.14 mg/kg bones.

The mean concentrations of o,p'-DDE, p, p'-DDD, o,p'-DDD, p,p'-DDT, metoxichlor, dieldrin and aldrin in the liver, gills, flesh bones of *Auchenogianis occidentals* from river Benue in Vinikilang are as presented in Figure 6. The concentrations of the studied pesticides in the liver of *Auchenogianis occidentals* ranged between 0.08 and 0.76 mg/kg; 0.14 and 0.82 mg/kg gills; 0.06 and 0.57 mg/kg flesh; 0.03 and 0.51 mg/kg bones.

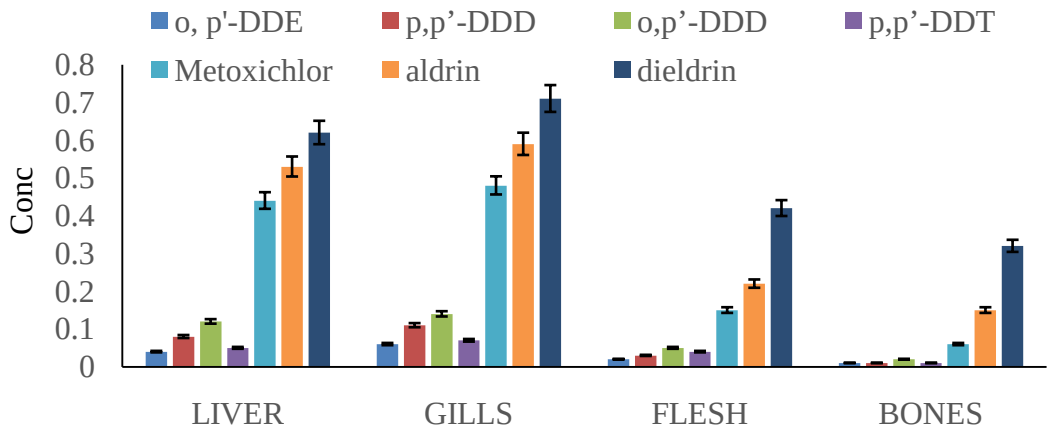

Figure 2: Mean Concentrations of Some Organochlorine Pesticides in

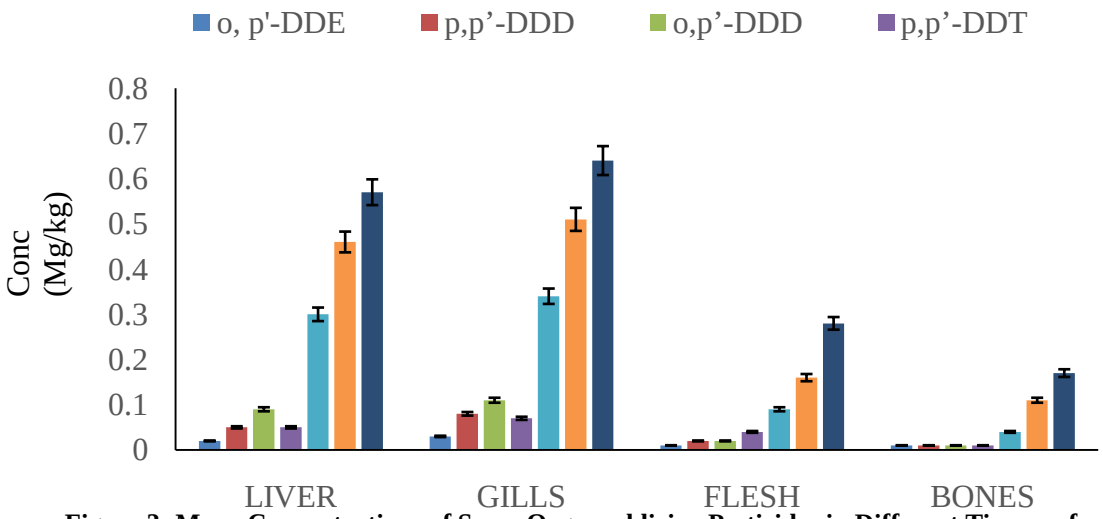

Figure 3: Mean Concentrations of Some Organochlirine Pesticides in Different Tissues of *Lates niloticus*

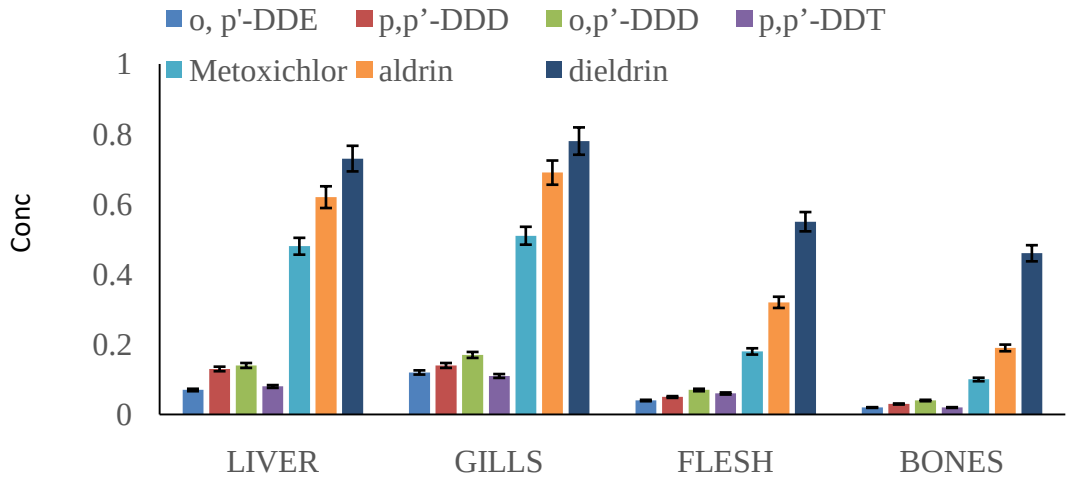

Figure 4: Mean Concentrations of Some Organochlirine Pesticides in Different Tissues

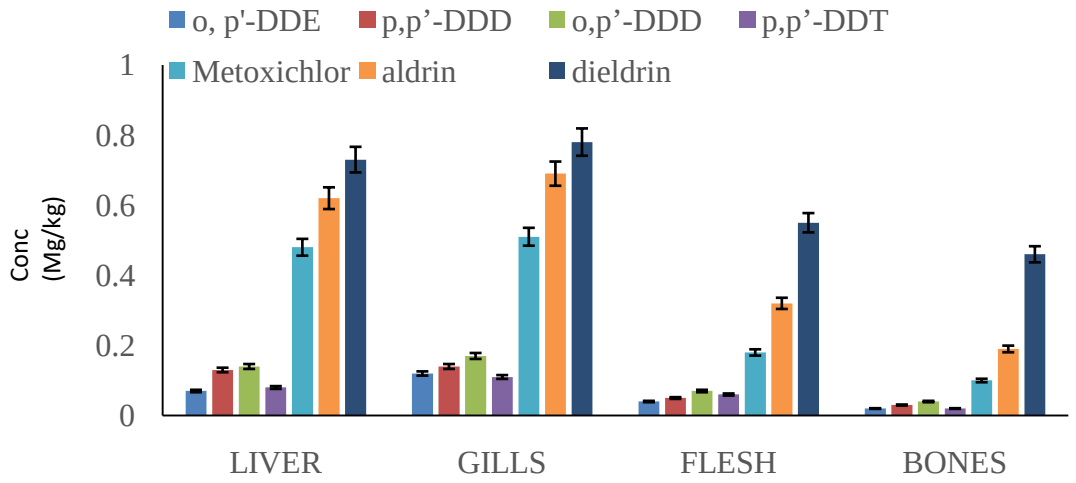

Figure 4: Mean Concentrations of Some Organochlirine Pesticides in Different Tissues

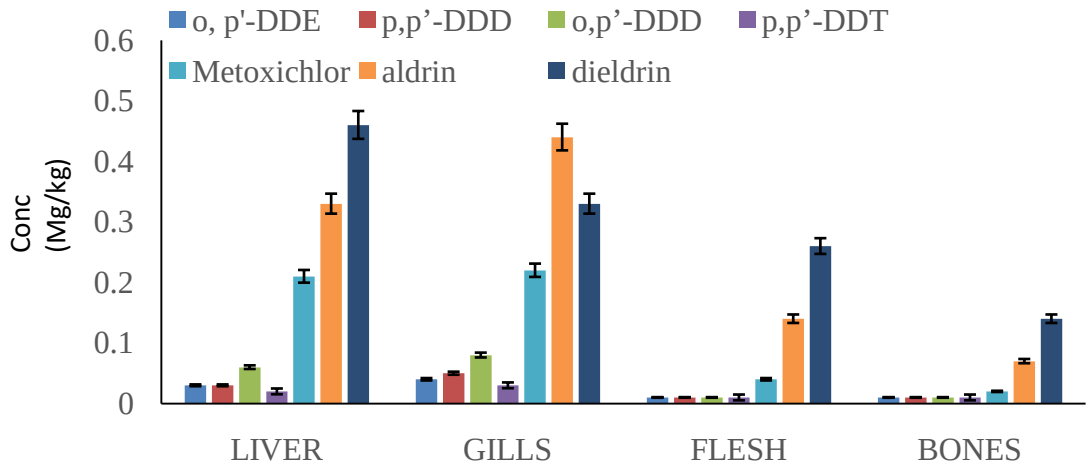

Figure 5: Mean Concentrations of Some Organochlirine Pesticides in Different Tissues of *Heterotis niloticus*

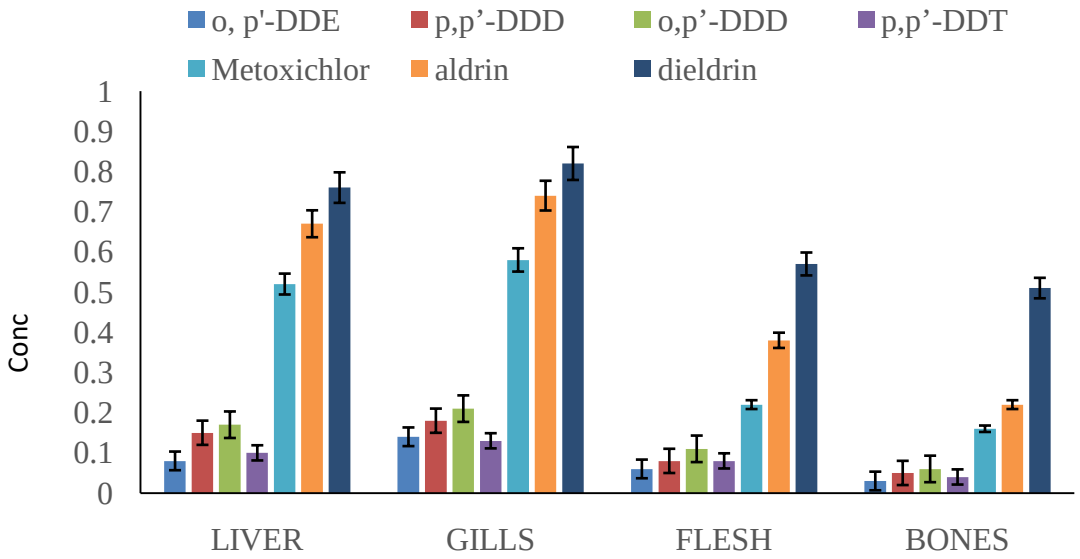

Figure 6: Mean Concentrations of Some Organochlirine Pesticides in Different Tissues of *Auchenogiasis occidentals*

The highest levels of p,p'-DDT and its metabolites in the present study were observed in the gills of *Auchenogianis occidentals*, while the bones of *Bagrusbayad* recorded the lowest value, This outcome is expected because of the high lipophilic and hydrophobic nature of the compound, and the possibility of being retained on the organic phase of sediment and organisms (Sakar *et al*., 1997; Adeyemi *et al*., 2008). The detection of p,p'-DDE is an indication of photochemical degradation of p,p'-DDT (Wandinga, 1995.) Although the use of DDT has been banned in Nigeria in 2008, but still in used. DDT and its DDE and DDD metabolites persist in the environment and are known to bioaccumulate in aquatic organism (Ware, 1978). DDT, DDD, and DDE have all been classified by the National Agency for Food and Drug Administration and Control (NAFDAC) as probable human carcinogens. DDT or its metabolites have been included as target pesticides residues in five species of fish; similar studies reported that there is a widespread of DDT and its metabolites in tissue of fish samples (NOAA, 1987, 1989; Schmitt and Linder, 1990). The concentrations of DDT and its metabolites in all the fish tissues were lower than the WHO and FAO (Codex, 2009) set maximum residue limit (MRL) of 1.0 mg/kg, with exception of *Hetrosisniloticus* indicating contamination of the aquatic environment by pesticides.

The highest level of dieldrin and aldrin were recorded in the gills of *Auchenogianis occidentals*, while the least value was recorded in the bones of *Bagrusbayad*. Schmitt and Linder (1990) reported the highest level of aldrin and dieldrin in the aquatic environment. Dieldrinis a chlorinated cyclodiene that was widely used in Nigeria. 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 and Linder, 1990). The present data also indicated the accumulation levels of dieldrin and aldrin in the fish species studied. The concentrations of aldrin and dieldrin in all 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 photolysis to dieldrin in the environment. These results are in agreement with those of the 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 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 metabolised 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

The maximum concentration of metoxichlor was detected in gills of *Aucherogianis occidentals*, while the least value was recorded in the bones of *Bagrusbayad*. 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 (Dong *et al.*, 2003).

CONCLUSION

The study revealed that all the Organochlorine Pesticides analyzed (p,p'-DDT, o,p'-DDE, p,p'-DDD, o,p'-DDD, Metoxichlor, dieldrin and aldrin), were detected in all the studies fish samples. Highest levels of these pesticides were observed in the gills of *Auchenogianis occidentals* compared to other tissues. This study revealed that pesticide residue levels in the fish samples studied were lower than the maximum residue limits (MRLs) and acceptable dietary intake (ADI), with the exception of dieldrin and aldrin which were higher than the MRLs values. 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.

REFERENCES

Adeyemi D, Ukpo G, Anyakora C, Unyimandu J (2008). Organochlorine pesticides residues in fish samples from Lagos Lagoon, Nigeria. *Am. J. Environ. Sci*.,4:649 – 653.

Ali, M.Y. and Cole, R.B. (2001). Supercritical fluid extraction-plus-c (18) lipid clean-up and selective extraction method for GC/MS quantization of cyclic aromatic hydrocarbons in smoked meat. *J. Agric. Food Chem.*, 49(9): 4192-4198.

Babu, K.N., Padmalal, D., Maya, K., Sreeja, R. and Arun, P.R. (2003). Quality of surface and ground water around tile and brick clay mines in the chalakudy River basin, southwestern India. *J. Geol. Soc. India*, 69(**2**): 279-284.

Barlas, N. E. (2002). Determination of organochlorine pesticide residues in water and sediment samples in inner Anatolia in Turkey. *Bull. Environ. Contam. Toxicol*., 69: 236 -242.

Bjorklund, E., Jaremo, M. and Mathiasson, L. (2000). Simultaneous determination of polychlorinated biphenyls and triglycerides in a model fat sample using selective supercritical fluid extraction. *J. Liq. Chrom. Rel. Technol*., 23: 2337-2344

Codex Alimentarius Commission (2009): Pesticide residues in food: Maximum Residue Limits.

Damalas, C. A. and Eleftherohorinos, G. E. (2011). Pesticide exposure, safety issues, and risk assessment indicators. *Int. J. Environ. Res. Public Health*, 8 (5): 1402–1419.

David, R. B., Alan, B. and Neil, F. (2008). Shimadzu Pesticide MRM Library Support for LC/MS/MS Shimadzu corporation, UK.

De-Boer, J., Allehin, C., Law, R., Zegers, B. and Boon, J. P. (2001). Method for the analysis of polybrominated diphenylethers in sediments and biota. *Trends Anal. Chem.*, 20: 59-99.

Domagalski, J. L. and Kuivila, K. M. (1993). Distributions of pesticides and organic contaminants between water and suspended sediments, San Francisco Bay, Califonia, *J. Env. Qual*., 16 pesticide residues in sediments from selected rivers in Taiwan. *Chemo*, 48: 237 -246.

Dong, R. A., Sun, Y. C., Liao, P. L., Peng, C. K. and Wu, S. C. (2003). The distribution and fate of organochlorine pesticides residues in fish from the selected rivers in Taiwan. *Chemosphere* 48: 237-246.

Fleming, L., Mann, J.B., Briggle, T. and Sanchez-Ramos, J.R. (1994). Parkison's disease and brain levels of organochlorine pesticides. *Ann. Neurol.*, 36: 100 -103.

Garabrant, D. H., Held, J., Langholz, B., Peter, J.M. and Mark, T.M. (1992). DDT and related compounds and risks of pancreatic cancer. *J. Natl. Cancer Inst.*, 84(10): 764 - 771.

Gilden, R.C., Huffling, K. and Sattler, B.(2010). Pesticides and health risks. *J. Obstet. Gynecol. Neo-natal. Nurs*. 39(1):103–110.

Guillet P, N'Guessan, R., Darriet, F., Traore-Lamizana, M., Chandre, F. and Carnevale, P. (2001). Combined Pyrethroid and carbamate: two-in-one' treated mosquito nets: field efficacy against pyrethroid resistant *Anopheles gambiae* and *Culexquinquefasciatus*. *Medical and Veterinary Entomology*, 155: 105-112.

Guo, Y., Meng, X. Z., Tang H. L. and Zeng, E.Y. (2008). Tissue distribution of organochlorine pesticides in fish collected from Pearl River delta, china: implications for fishery input source and bioacculation. *Environ. Pollut*, 155: 150-156.

Hess, P., deBoer, J., Cofino, W.P., leonards, P.G.E. and Wells, D.E (1995) critical review of the analysis of non and mono-ortho-chlorodiphenyls, *J. Chromatogr*. A. 703: 417-465.

Hussein, El-M., Magdy, D., Mohammed, Z. and Ayman, H. (2009). Determination of chlorinated organic pesticide Residues in water, sediments, and fish from private fish farms at Abbassa. *J. Basic Applied Sci.*, 3(4): 4376-4383.

Kayali-Sayadi, M. N., Rubio-Barraso, S., Garcia-Iranzo, R. and Polo-Diez, L.M. (2000). Determination of selected polycyclic aromatic hydrocarbons in toasted bread by supercritical fluid extraction and HPLC with fluorimetric detection. *J. Liq. Chromotogr. Relat-Technol*, 23: 1913-1925.

Lan Franchi, A. L., Miglioranza, M. L., Menone, K. S. B., Janiot, L. J., Aizpun, J. E. and Moreno, V. J. (2006). striped weakfish (*Cynoscionguatucupa*): a biomonitor of organochlorine pesticides in estuarine and near- coastal zones. *Mar. Pollut. Bull.*, 52: 74-80.

Matsumura Fumio (1985). General Principles of insecticide toxicology. Second edition. New York N.Y plenum press, pp111 – 564.

Mckinnney, J. D. and Walker, C.L. (1994). Polychlorinated Biphenyls as hormonally active structural analogues. *Environ. Health Perspect*, 102: 290 - 297.

NOAA (National Oceanic and Atmospheric Administration). (1987). National Status and Trends Program for Marine Environmental Quality—Progress Report: A Summary of Selected Data on Chemical Contaminants in Tissues Collected During 1984, 1985 and 1986. NOAA Technical Memorandum NOS OMA 38. U.S. Department of Commerce, Rockville, MD.

NOAA (National Oceanic and Atmospheric Administration). (1989). National Status and Trends Program for Marine Environmental Quality – Progress Report: A Summary of Selected Data on Tissue Contamination from the First Three Years (1986-1988) of the Mussel Watch Project. NOAA Technical Memorandum NOS OMA 49. U.S. Department of Commerce, Rockville, MD.

Ntow, W. J. (2001). Organochlorine pesticides in water, sediment, crops, and human fluids in a farming community in Ghana. *Arch. Environ. Contam. Toxicol*. 40: 557-563.

Pimentel, D., Culliney, T. W. and Bashore, T.(2013).Public Health Risks Associated with Pesticides and Natural Toxins in Foods. IPM World Textbook. Regents of the University of Minnesota.

Racke, K., Skidmore, M. and Hamilton, D. (1997). Pesticides fate in Tropical Soils. *Pure Appl. Chem.* 69(6): 1349-1371.

Sarkar, A., Nagarajan, R., Chaphadkar, S., Pal, S. and Singbal, S. Y. S. (1997). Contamination of organochlorine pesticides in sediments from the Arabian Sea along the west coast of India. *Water Res*, 31(2):195-200.

Sarwar, M., (2015). The dangers of pesticides associated with public health and preventing of the risks. *Int. J. Bioinfor. Biomed. Eng*, 1 (2): 130–136.

Satya, P. M., Vlay, T. G., Narendor, P. A. and Mangu, R. (1995). Environmentalist. *Int. J. Environ*, 15(1): 41-44.

Thurman, E.M., Bastian, K.C and Mollhagan, T. (2000). Occurrence of cotton herbicides and insecticides in playa lakes of high plain and West Texas. *Sci. Total Environ*, 248(2-3): 189-200.

USDHHS (1993). United States Department of Health and Human services. National Center for Health Statistics. In: *Health*, United States. Library of Congress Catalog Number: 76-641496.

Van der Valk, F. and Dao, Q. T. (1988). Degradation of PCBS and HCBs from sewage sludge during alkaline saponification. Chemo, 17(9): 1735-1739.

Van Maele-Fabry, G., Lantin, A. C., Hoet, P. and Lison, D. (2011). Residential exposure to pesticides and childhood leukaemia: a systematic review and meta-analysis. *Environ. Int*, 37 (1), 280–291.

Wandiga, S.O. (1995). Organochlorine pesticides: curse or blessing in tropical agriculture. *Proceedings of the 6th International Chem*. Conf. in Africa. Accra, Ghana,220-223**.**

Ware, G. W. (1978). The Pesticide Book (San Francisco: W. H, Freeman and Company), p197.

Wickerham, E. L., Lozoff, B., Shao, J., Kaciroti, N., Xia, Y. and Meeker, J. D.(2012). Reduced birth weight in relation to pesticide mixtures detected in cord blood of full-term infants. *Environ. Int.*, 47: 80–85.

Yadav, I. C., Devi, N. L., Syed, J. H., Cheng, Z., Li, J. and Zhang, G. (2015). Current status of persistent organic pesticides residues in air, water, and soil, and their possible effect on neighbouring countries: a comprehensive review of India. *Sci. Total Environ*, 511: 123–137.