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PESTICIDE RESIDUE ANALYSIS IN TILAPIA ZILLI, SOLD IN WUKARI MARKET

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Abstract: *This research reports the concentrations of pesticide residues in Tilapia zilli sold within Wukari Market using gas chromatography equipped with electron capture and flame photometric detectors.The organochlorine pesticides OCPs determined included:* α-BHC, β-BHC, Lindane, Chlorothalonil, Heptachlor, Aldrin, o,p’-DDE, Endusulfan I and II, p,p’-DDE, PCB 153, PF-38, p,p’-DDT, Cypermethrin a, b and z.
Of these only β-BHC and Endusulfan II were detected at 0.386±0.0014 *µg/g* and 0.413±0.00071 *µg/g*, respectively. *The organophosphates: Mevinphos, Dichlorvos, Dimethoate, Pirimiphos methyl, Malathion, Methyl parathion, Dichlofenthion, Pirmicarb, Diazinon, Carbofurane, Ethion, Carbofenothion, PF-38, Bromophos ethyl, Isofenphos, Parathion, Chloropyrifos, Fenthion. Of these only dichlorvos (0.032±0.012 µg/g) was found within the limit of detection.*

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INTRODUCTION

Organic contaminants present in the environment are a result of different sources of pollution from anthropogenic activities (Reemtsma and Jekel, 2006). Organochlorine pesticides are still in use in developing countries despite their ban in many countries as a result problems of indiscriminate potency and persistency associated with their use. The chemical stability of these compounds, their high lipid solubility and toxicity to human and animals (Aulakh *et al.,* 2006), has warranted the concern of government and researchers with their presence in the environment. Organochlorines continue to be the potential group of chemicals used in control of agricultural pests and vectors of diseases like malaria (David, *et al*., 2003), although many new broad spectrum pesticides have been developed in recent years. The pesticides applied on land eventually find their way to the aquatic environment, thus contaminating soil and water for several years and subsequently get accumulated in aquatic organisms (Singh, *et al.*, 2005). The aquatic organisms like fish are able to accumulate several fold higher concentration of pesticide residues than the surrounding water (Siddiqui, *et al.*, 2005). It has been found that greater than 80% of the total intake of pesticide residues in human beings is through the food chain (Martinez, *et al.*, 1997) and considerable amount of residues find their way into humans through consumption of contaminated fishes (Mwevura, *et al.*, 2002).

As many of the organochlorine pesticides became banned in the 1970s, the agrochemical industry turned to the less persistent, but more acutely toxic, organophosphorus pesticide (OPP) compounds to control insect pests. Nowadays, OPPs are the class of agricultural insecticides most widely used in the world. Their extensive use, especially for crop protection, implies an environmental risk, which has risen to an increasing social concern with respect to the presence of OPPs in a wide range of surface and ground waters, drinking waters, fruits, vegetables, and foodstuffs in general (Sun *et al.,* 2006, Abdel-Halim *et al.,* 2006, Liu *et al*., 2005).

In this study, the researchers aim to identify and quantify the pesticide residue found in *Tilapia zilli* samples collected from Wukari Market using different GC equipped with

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detectors flame photometric detector (FPD) for OPPs and GC equipped with electron capture detector (ECD) for OCPs.

Wukari Town the study area is located on a Geographic grid reference longitude 7°51′ N and latitude 9°47′ E.

Materials and Methods

Organic solvents especially dichloromethane which is toxic, were handled with care observing safety precautions, using efficient fume hoods and protective gloves. Silica gel (60-100 mesh ASTM) was purchased from Merck, Germany. Standard stock solutions of α, β, δ BHC (99.9 % w/w), lindane (99.3 % w/w), DDT, DDD (99.7 % w/w), aldrin (99.9 % w/w), dichlorvos (99.2 % w/w), endosulfan I and endosulfan II (73.2 % w/w), dieldrin (94.2 % w/w), diazinon (94.2 % w/w), mevinfos (94.2 % w/w), purchased from Restek Corporation U.S.A., chlorpyrifos (99.0 % w/w), purchased from Chem Service (West Chester, PA, USA were prepared in acetonitrile at a concentration of 1000 mg L^{-1} and stored at 4 °C. From the dilution of stock, solutions were prepared containing the two pesticides (organochlorine and organophosphate) at concentrations of 10 and 20 mg L−1 in the same solvent. Anhydrous sodium sulphate with a purity superior to 99% was also purchased from Vetec.

Sampling

Tilapia zilli was selected for analysis in this study owing to its wide consumption. Smoked species of the fishes were bought from the market to asses the pesticide residue in them. The fish samples were crushed and pulverized to very fine particles. The samples were then sieved using mesh 2mm sieve size. Each of the crushed samples were transferred separately into a thermo insulator box and transported to the laboratory where they were stored in a freezer pending time for analysis.

Liquid-Liquid Extraction

5g of three replicate samples of the crushed *Tilapia zilli* were placed in extraction flasks separately. 25 mL of water were poured into each of the samples followed by 25mL each of dichloromethane (for *Tilapia zilli*) and ethyl acetate. The mixtures were allowed to

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settle for 15 minutes in a separating funnel before the aqueous layer was carefully poured into a 200 mL round bottom flask. 5g of anhydrous sodium sulfate was added to each of the three solutions which were then transferred to the rotary evaporator. The extracts were collected using a 2 mL Vial for each of the samples and ready for silica gel clean up.

Silica Gel Clean up

The clean-up column was packed with 2 g of activated silica gel and 3 g anhydrous sodium sulphate. The packed column was clamped with a retort stand and conditioned using 10 mL of hexane (99%). The extract was passed through the conditioned column with a receiving flask beneath the column. The sample (analyte) put in the column was eluted with 10 mL hexane (99%) and eluted further with 20 mL 2:1 Hexane:Acetone to recover the pesticide residues. The sample was collected into a round bottomed flask and concentrated using a rotary evaporator fitted to a vacuum pump to almost dryness and 2 mL ethyl acetate (99%) was added. The mixture was then transferred to an auto sampler vial ready for Gas chromatographic analysis.

GC-FPD Analysis

An Agilent 7890 Gas chromatograph (GC) with Agilent 7693 Auto sampler equipped with electron capture detector and flame photometric detector were used for quantification. OC and OP compounds were completely separated using a HPS MS fused silica capillary column (30 m × 0.25 µm × o.32 mm id). 1.0 µL of analyte was injected into the GC on splitless mode with a 0.75 min vent delay. The injector temperature was maintained at 240°C and the initial oven temperature was set at 60°C for 1 min and then increased at a rate of 10°C/min until it reached 200°C, where it remained for 2 min. The temperature was then increased at a rate of 10°C/min until it reached 280°C, where it remained for 3 min using this temperature program (Ogah *et al.*, 2016). The concentrations determined in parts per million by the instrument were divided by 5 to obtain the actual concentrations of the various pesticides.

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Quantification

When using GC-MS analysis, samples were confirmed to contain a pesticide if the observed retention times of peaks of sample solutions were the same as the peaks for the standards in solvent and the observed abundance ratio of ions was identical to that of the standard ions. Instru- mental and procedural blanks were analyzed to avoid laboratory contamination and analytical interferences, and the blank value deducted from the results.

Results and Discussion

The retention times of the various pesticides are presented in Table 1.1. while the results for the analyses of organochlorine and organophosphorus in *Tilapia zilli* are as shown in Table 1.2 and 1.3, respectively.

Table 1.1: Retention Time of the various Pesticides Analyzed.

Pesticide	Retention time (Min)
Endusulfan II	18.386
a-cypermethrin	23.911
b-cypermethrin	23.995
z-cypermethrin	24.270
Dichlorvos	6.6070
Dieldrin	17.580

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Table 1.2: Mean concentration of Organochlorine pesticide levels (µg/g) in *Tilapia zilli*

Organochlorine	***Tilapia zilli***
α-BHC	-
β-BHC	0.386±0.0014
Lindane	-
Chlorothalonil	-
Heptachlor	-
Aldrin	-
Heptachlor epoxide	-
o,p'-DDE	-
Endusulfan I	-
p,p'-DDE	-
Dieldrin	-
Endosulfan II	0.413±0.00071
PCB 153	-
PF-38	-
p,p'-DDT	-
a-Cypermethrin	-
b-Cypermethrin	-
z-Cypermethrin	-

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Table 1.3: Mean Concentration of Organophosphate Pesticide (µg/g) in *Tilapia zilli*

Organophosphate	***Tilapia zilli***
Dichlorvos	*0.032±0.012*
Mevinphos	-
Dimethoate	-
Carbofurane	-
Diazinone	-
Pirmicarb	-
Dichlofenthion	-
Methyl parathion	-
Pirimiphos methyl	-
Malathion	-
Chloropyrifos	-
Fenthion	-
Parathion	-
Isofenphos	-
Bromophos ethyl	-
Ethion	-
Carbofenothion	-
PF-38	-

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Concentration of Organochlorine Pesticides in Fish Samples

From Table (1.2) it can be observed that apart from β-BHC (0.386±0.0014) and endosulfan II (0.413±0.00071) all other organochlorine pesticides were below limit of detection (LOD). Concentrations of β-BHC below LOD were reported in Rivers of the cocoa producing parts of Ondo State, Nigeria (Idowu *et al*, 2013). Concentration of 0.005 µg/mL for endosulfan II which is lower than concentrations detected in this study has also been reported (Idowu *et al*, 2013). The WHO MRL for endosulfan II is 62 µg/mL which is higher than th concentraton determined in this work.

Endosulfan (CAS No. 115-29-7) is an insecticide used in countries throughout the world to control pests on fruit, vegetables and tea and on non-food crops such as tobacco and cotton. In addition to its agricultural use, it is used in the control of the tsetse fly, as a wood preservative and for the control of home garden pests. Endosulfan contamination does not appear to be widespread in the aquatic environment, but the chemical has been found in agricultural runoff and rivers in industrialized areas where it is manufactured or formulated, as well as in surface water and groundwater samples collected from hazardous waste sites in the USA. Surface water samples in the USA generally contain less than 1mg/litre. The main source of exposure of the general population is food, but residues have generally been found to be well below the FAO/WHO maximum residue limits. Another important route of exposure to endosulfan for the general population is the use of tobacco products. JMPR concluded that endosulfan is not genotoxic, and no carcinogenic effects were noted in long-term studies using mice and rats. The kidney is the target organ for toxicity. Several recent studies have shown that endosulfan, alone or in combination with other pesticides, may bind to estrogen receptors and perturb the endocrine system. A health-based value of 20mg/litre can be calculated for endosulfan on the basis of an ADI of 0.006 mg/kg of body weight, based on results from a 2-year dietary study of toxicity in rats, and supported by a 78-week study in mice, a 1-year study in dogs and a developmental toxicity study in rats.

Concentration of Organophosphate Pesticides in Fish Samples

The result presented in Table 1.3 shows that of the organophosphates analyzed, only dichlorvos (0.032±0.012) was detected. From the Table (1.3), it can be observed that all

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the organophosphate pesticides were below limit of detection (LOD). However, a mean dichlorvos concentration of 1.02 µg/g in *Tilapia zilli* sample from Alau dam in Borno State was reported by Joseph *et al*., (2013). The <LOD mean concentration recorded in this study fell below the 0.04 µg/g MRL set by WHO and FAO in fish samples and as such the result deviates from that reported by Joseph *et al*., 2013 due to low distribution of dichlorvos in the studied area.

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CONCLUSION

The present study is the first to be carried out within Wukari metropolis and the study revealed that the fish samples analyzed (*Tilapia zilli*) are contaminated by organochlorine and organophosphate pesticides. From the discussion above, it is clear that the order and concentration of these pesticides varied in the fish species. From the results obtained throughout the entire course of the study, it can be concluded that the river from which these fish samples are harvested are reasonably free from contamination with pesticide runoffs from nearby agricultural lands. Regular monitoring of the fish bearing water bodies in Wukari should however be carried out. Unhealthy methods of harvesting and preserving fish should be discouraged forestall a build up of pesticides in the aquatic environment within the study location.

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REFERENCES

K.Y. Abdel-Halim, A.K. Salama, E.N. El-Khateeb, and N.M. Bakry(2006). organophosphorus pollutants (OPP) in aquatic environment at Damietta Governorate, Egypt: implications for monitoring and biomarker responses. *Chemosphere* **63(9):** 1491–98.

Aulakh R S, Gill J P, Bedi J S, Sharma J K, Joia B S, Ockerman H.W.(**2006**). Organochlorine pesticide residues in poultry feed, chicken muscle and eggs at a poultry farm in Punjab, India. J Science Food Agric, 86(5):741–744.

David M, Mushigeri S B, Philip G H. (**2003**). Alterations in the levels of ions in tissues of fresh water fish Labeo rohita exposed t fenvalerate. Pollut Res, 223:359–363.

FAO/WHO (1999) *Pesticide residues in food – 1998 evaluations. Part II – Toxicological*. Geneva, World Health Organization, Joint FAO/WHO Meeting on Pesticide Residues (WHO/PCS/99.18).

Idowu GA, Aiyesanmi AF and Owolabi BJ (2013). Organochlorine pesticide residue levels in river water and sediment from cocoa-producing areas of Ondo State central senatorial district, Nigeria. *J Environ Chem Ecotoxicol* 5(9): 242- 249.

Joseph, A., Mohammed, Z., Jafiya, L., Ogugbuaja, VO., (2013) Organochlorine Pesticide Residues in Fish Samples from Alau Dam, Borno State, North Eastern Nigeria. *Journal of Environ Anal Toxicol* 3: 171.

Liu W., Y. Hu, J. Zhao, Y. Xu, and Y. Guan. (2005). Determination of organophosphorus pesticides in cucumber and potato by stir bar sorptive extraction. *J. Chromatogr. A* **1095(1-2):** 1–7 (2005).

Martinez M P, Angulo R, Pozo R, Jodral M. (**1997**). Organochlorine pesticides in pasteurized milk and associated health risks. Food Chem Toxicol, 35:621

Mwevura H, Othman O C, Mehe G L. (**2002**). Organochlorine pesticide residues in edible biota from the coastal area of Dares Salaam city. J Mar Sci, 1:91–96.

Ogah, E., Ushie, A. O., Nkom, P. Y., Amah, S. O., Ugwuja, D. I., & Abiaziem, C. V. (2016). Determination of organochlorine pesticides in river Benue at Agatu

ISSN 2320-9186

using gas-chromatograph equipped with electron capture detector. *Ewemen Journal of Analytical & Environmental Chemistry,* 2(1), 45-50.

Siddiqui M K J, Anand M, Mehrotra P K, Sarangi R, Mathur N. (**2005**). Biomonitoring of organochlorines in women with benign and malignant breast disease. Environ Res, 98:250–257.

Singh KP, Malik A, Mohan D, Takroo R. (**2005**). Distribution of persistent organochlorine pesticide residues in Gomti River, India. Bull Environ Contam Toxicol, 74(1):146–154.

Sun Q., L. Zhu, andM. Dong.(2006). Risk assessment of organic pesticides pollution in surface water of Hangzhou. *Environ. Monit. Assess.* **117 (1-3):** 377–85.

WHO (2003) *Endosulfan in drinking-water. Background document for preparation of WHO Guidelines for drinking-water quality*. Geneva, World Health Organization (WHO/SDE/WSH/03.04/92).

Reemtsma T. and M. Jekel, “Organic Pollutants in the Water Cycle, Wiley-VCH VerlagGmBH& Co. KGaA, Weinheim,” *Journal of Chromatography A*, Vol. 1150, 2006, pp. 267-278.