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Organochlorine Pesticide Residuals in Mud Fish Samples (Neoxhanna Galaxiidae) from Onyedega River, Kogi State North Central, Nigeria

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***Abstract* – The levels of organochlorine (gamma – BCH, Alpha – BCH, aldrin, O, P DDE, endosulfan, dieldrin, P,P = DDT, lindane, P, P = DDD, O, P = DDD and methoxychlor) pesticide residues in Onyedega River from Ibaji Local Government Area, Kogi State, Nigeria was investigated using fish samples as a case study. The fish specy, mud fish (*Neoxhama Galaxiidae*) of uniform size were collected in order to avoid possible errors due to size differences. The fish samples were labeled with a unique identification number. Samples of fishes were stored in a refrigerator the same day pending extraction and analysis. The fish samples were later dissected to remove the fish. The extractions, clean up and de-fattening of the fish muscle were carried out using standard procedures. The levels of all pesticides residues were determined using GC equipped with electron capture detector (ECD). Twenty-two organochlorine pesticides were detected in all fish samples. The result showed that all the pesticide residues identified were below the maximum residual limits (MRLs) and dietary intake (ADI) (see table 1) suggesting that the fishes are safe for human consumption. Despite the positive risk assessment results obtained in this study, the potential health risks associated with fish consumption cannot be neglected, hence the need for continuous monitoring to ensure the long-term safety of consumers.**

***Keywords* – Organochlorine Pesticide, Residues, Onyedega River, Continuous – Monitoring, Mud-Fish.**

I. INTRODUCTION

The widespread use of pesticides and other noxious organic compounds in agriculture since the World War II has resulted in extensive environmental expression of toxic symptoms amongst biological concentrators of these pesticides in a serious problem because it is insidious. It goes unnoticed until mortality results and even then the cause of mortality may be suspected. Although claims have been made on ill effects of these channels on human health, according to Bentum, et al, (2006), none of them has yet been conclusively confirmed. According to Bentum, et al, 2006, pesticide residue levels are too low to detect in diet but are often concentrated in the adipose tissue of the human body and in breast milk of mothers.

Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) or pesticides including dichlorophenyl ← trichloro ← ethane and its metabolites (DDTs), hexachlorocyclohexane (HCHs) have been known as global contaminants of the environment for decayeds. Pesticide is a general classification that indicates insecticides, rodenticides, fungicides, herbicides and fumigants etc. Although pesticides may be selectively toxic to those forms of life, they may still be toxic to man if food contaminated by them is ingested. (Ademoroti, 1996). DDT in particular can block potassium influx across the membranes of nerve fibres and causes increase negative after potentials. DDT also induces the mixed function oxidize system thereby altering the metabolism of xenobiotics and steroid hormones (Ademoroti, 1996).

Organochlorine pesticides are among the agrochemicals that have been used extensively for long periods. They have been used widely in agriculture, as well as, in mosquito, termite and tsetse fly control programs (Guo, et al, 2008). Organochlorine pesticides (OCs) are characterised by low polarity, low aqueous solubility and high lipid solubility (lipophilicity) and as a result they have a potential for bioaccumulation in the food chain posing a great threat to human health and the environment globally (Afful, et al, 2010). Residues and metabolites of many OC pesticides are very stable, with long half lives in the environment, (El – Mekkawi et al, 2009). It is a hydrophobic molecule which disrupts ionic channels like Na^+- K^+ pumps in nervous cell membrane leading to automatic stimulation of neurons and involuntary contraction of muscles, (Esmailisari, 2003).

Fish are used extensively for environmental monitoring (Lanfranchi, et al, 2006). They uptake contaminants directly from water and diet. Generally, the ability of fish to metabolise organochlorines is moderate, therefore contaminant loading in fish is well reflective of the state of pollution in surrounding environments, (Onojah, et al, 2013). The use of pesticide introduces some risk to the environment, the degree of risk depending upon the pesticide persistence, mobility, non-target toxicity and volume of use.

The toxicity level of a pesticide also depends on the deadlines of the chemical, the length of exposure, the health status of the recipient and the route of entry into the body (Onojah, et al, 2014). OCPs contribute to many acute and chronic health effects, including cancer, neurological damage, birth defects, tremors, headache, dermal irritation, respiratory problems and dizziness. Animal studies have also shown the potential for reproductive and developmental effects and disruption of normal hormone function. Residues of these toxic chemicals found in water, sediments and aquatic biota pose a risk to aquatic organisms, predators and humans. OCPs act as central nervous system stimulants in aquatic fishes. In order to minimise the health risks from the ingestion of food

contaminated with these chemicals, environmental protection agencies and public health authorities, including the World Health Organisation (WHO), have set maximum residue levels (MRL) for OCPs in water, fishes and shell fishes (UNEP/FAO/WHO, 1988).

Fishes are suitable indicators for environmental pollution monitoring because they concentrate pollutants in their tissues directly from water and also through their diet, thus enabling the assessment and transfer of pollutants through the trophic web (Lanfranchi, et al, 2006). This offers the opportunity to study the influence of environmental and biological factors on the bioaccumulation of pollutants (Sarkar, et al, 2008). Organisms that live in aquatic environments are suitable representatives for assessing pollution. Literature data on the concentrations of OCPs residues in the Nigerian environment are inadequate. There is need for continuous monitoring to identify the occurrence and the levels of OCPs in fishes, water and sediment of aquatic ecosystem in Nigeria. This research report serves to provide data on the prevailing levels of these persistent pollutants in biotic and abiotic media in Onyedega River.

Onyedega River is located in Ibaji Local Government Area of Kogi State, Nigeria (fig. 1) which has between latitude 6^{o}, 53^{1} N and longitude 6^{o}, 41^{1} E on the Southern part of Kogi State. The local government was created out of Idah Local Government on the 415 of December, 1996 with a total area of 1, 377km^2 and population of 128, 129 according to 2006 census. The river receives water from the River Niger during the dry season and in the rainy reason, it receives water from the surface run off of water. Human activities associated in the area include fishing and farming. The River also receives a wide variety of waste from the agricultural land. The waste generated contaminates the river withy a variety of pesticides acting as a point source. The River is also used for commercial fishing and also received a wide variety of waste from agricultural activities within the area. Most farmers within the Onyedega River area used synthetic chemical pesticides to control pests on vegetables, crops etc including a number of highly persistent organochlorine pesticides. Pesticides are extensively used in agricultural production to check or control pests, diseases, weeds and other plant pathogens in an effort to reduce or eliminate yield losses and preserve high product quality. Lack of knowledge of the use and effects of these pesticides among small and large scale farmers has resulted in their misuse and consequently the waste generated flows into the river and may contaminates the river with a variety of pesticides acting as point source.

II. MATERIALS AND METHODS

Sample Collection

Fish samples (*Neoxhanna Galaxiidae*) were caught using gill nets from Onyedega River, Ibaji Local Government Area, Kogi State, Nigeria. Fish samples of uniform size were collected in order to avoid the possible error due to size differences. Samples were transported to the laboratory on the same day, identified by on expert in the Department of Fisheries, Kogi State University, Anyigba and later stored in the refrigerator the same day.

Extraction of Pesticides from Fish Samples

The extraction was carried out following the methods of Osibanjo and Adeyeye (1995) with some modifications. The fish samples were disserted and filtered to obtain the fish flesh. 10g of the fish fillet was wrapped in a labeled aluminum foil paper. Each fish flesh sample was removed from the foil paper and put into a mortar. 10g anhydrous sodium sulfate was added to it and a pestle was used to homogenise the mixture. The homogenous blend was allowed to dry overnight for a period of 18hours. Cold solvent extraction was performed. Petroleum ether/acetone (I: IV/V) mixture was used for the extraction because a more aggressive chemical is required for the extraction of fats. 50ml of the mixture was added to the homogenous blend in a conical flask. The mixture was shaken and allowed to stand for 30mins and the reagent was allowed to be absorbed by the blend and then filtered (USEPA, 2002). At the end of the extraction process, the extract was transferred into a round bottom flask connected to a pre-weighed receiver through a liebig condenser, and connected to about 10ml on a water bath maintained at 90^{o}C. The remaining solvent in the concentrated extract was evaporated using a rotary evaporator. The receiver contaminated the fat extract of about km^3. The extract was stored in a sample bottle.

Silca Gel Clean-Up of Sample Extract

Silca gel clean-up was carried out according to the USEPA, (2002) standard Using Column Chromatography. The glass separating column was packed with activated silca gel (90% < 45um) and washed down with n-hexane to remove dirts. The extracts were demoisturised over 1g of an hydrous granulated Na_2SO_4 and separated into two eluted fractions using mixtures of dichloromethane, hexane and acetronitriles as eluting solvents. For the first fraction, $30cm^3$ of a dichloromethane / hexane (20/80) mixture was used, while $30cm^3$ of a dichloromethane/hexane/acetonitrile (50/49.5/0.5) mixture was used for the second fraction to ensure that the polar acetonitrile eluted any remaining residue. The fractions were combined, concentrated to $1cm^3$ and subsequently analysed.

Identification and Determination of Pesticide Residues

A gas chromatograph equipped with an electron capture detector (GC – ECD) was used for the analysis of the OCP residues. The clean-up extracts were dried and re-dissolved in $1.0cm^3$ of analar grade Iso octane for injection into the gas chromatograph (Pandit et al, 2002). Blank runs were made for background correction and performance of the system. The detection and determination of the residues were performed by infecting 1μL of the $1.0cm^3$ purified extract into infection port as a gas chromatograph with a Ni electron capture detector (GC – NECD) Agilent Technology 7890A) equipped with the chemstation software. The column consisted of a DB – 5 fused silica capillary column (30m length x 0.32mm i.d x 0.25μm film thickness). The column temperature was programmed from 50^{o} C /min to 300^{o} C, held for 5mins.

The temperature of the injector and detector are 250°C and 300°C, respectively. The injection was carried out on a splitless injector at 250°C and the purge activation time was 30s. The carrier gas was helium while nitrogen gas used for the make up flow. The run time was 17mins. Identification of pesticide residues was accomplished using reference standards and relative retention time techniques, while the concentration of the residues was determine by comparing the peak of the heights of the sample with the corresponding peak heights of the reference standards of known concentrations. All the extracts from fish samples were analysed for aldrin, die (drin) endrin, DDT, heptachlor and metabolities, HCH and endosulfan isomers, X, Y – chlordane and methoxychlor. The concentration of the OCP residues were calculated directly by the gas chromatograph after inputting the weight of the samples. (David, et al, 2011).

III. Analysis of Data

The fish extracts were analysed fro aldrin, endrin, dieldrin, DDT, heptachlor, HCH, endosulfan, chlordane and methoxychlor. Concentrations of OCP residues were calculated individually and as the sum of their Isomeric forms. Description of data was performed using a stategraphics centurion XV statistical software, with the level of significance maintained at 95% for each test. The mean and standard deviation were calculated from the detectable values, and values below the detectable limit were considered not detected (ND).

IV. Results and Discussion

The result in Table (1) showed the distribution concentrations (PPM) of organochlorine pesticide residues detected in tissue fish samples collected from Onyedega River. Although the tissue fish samples of Mud fish (Neoxhanna Galaxiidae) had pesticide residues such as aldrin, dieldrin, endrin, DDT, heptachlor, HCH, endosulfan, chlordane and methoxychlor etc but its concentration were eighter no detected (ND) or have their concentrations lower than the permissible limits (PPM). (FAO, 1996).

From the results, it can be concluded that although the incidences of pesticides were relatively high, mean concentrations were below the permissible limits purposed by FAO, 1996. On the other hand, the organochlorine pesticides were predominant in the fish samples, but in low concentrations which might be attributed to the association of organochlorine pesticide residues with the fat phase in fish. However, some types of organophosphorus pesticides were not found. The cafdiment areas are largely sites of agricultural activities. They were characterised by the presences of intense farming activities, fishing activities and Inland water transportation. Onyedaga River is a semi-enclosed water body which receive water from River Niger.

Organochlorine pesticides tend to accumulate in living organisms especially in aquatic organisms and they substantially settle on the sediments (Kammann, et al, 1992). The result of the work indicates that Endrin Aldehyde and Heptachlor epoxide were the most abundant pesticide residue in fish sample. Despite the adverse side effects of pesticides, organochlorine pesticides (OCPs) form an integral component of modern agriculture. The benefits are increased supply of food, but problems arise when significant amount of the chemicals are left on the field as residues which tend to effect non-target organisms and river bodies are one of the main recipient in pesticide residues generated on the field. Agricultural run off is the primary source of this pesticide in aquatic ecosystem. Levels of residues in the fishes were below the recommended maximum residue limits (MRLs), suggesting that the fishes are safe for human consumption. Despite the positive risk assessment results obtained in this study, the potential health risk associated with fish consumption can not be neglected, hence the need for continuous monitoring to ensure the long-term safety of consumers. (Akan, et al, 2013).

Table 1: Mean Concentration of Organochloride Pesticide Residues (OCPs) in two Specimen of Mud Fish from Onyedega River in Ibaji Local Government Area, Kogi State, Nigeria.

Pesticides	Specimen A (mg/g)	Specimen B (mg/g)	Standard Deviation
Aldrin	0.00	0.00	±0.00
Dieldrin	0.00	0.00	±0.00
α – chlordane	0.00	0.00	±0.00
ɤ - chlordane	0.00	0.00	±0.00
Endrin	0.00	0.00	±0.00
Endosulfan I	0.00	0.00	±0.00
Endosulfan II	0.00	0.00	±0.00
Endosulfan sulfate	0.00	0.00	±0.00
Heptachlor	0.00	0.00	±0.00
Heptachlor epoxide	0.12	0.12	±0.00
Methoxychlor	0.00	0.00	±0.00
HCB	0.00	0.00	±0.00
α – HCH	0.00	0.00	±0.00
Y – HCH	0.00	0.00	±0.00
β – HCH	0.00	0.00	±0.00
HCH	0.00	0.00	±0.00
$P_1\ P^1$ *DDD*	0.00	0.00	±0.00
$P^1\ P^1$ *DDE*	0.00	0.00	±0.00
$P_1\ P^1$ *DDT*	0.00	0.00	±0.00
Endrin	0.00	0.00	±0.00
Endrin Aldehyde	0.15	0.15	±0.00
Endrin Ketone	0.00	0.00	±0.00

V. Conclusion

The study revealed that the pesticide residue levels in the fish samples study were below the maximum residue limits (MRLs) and acceptable dietary intake (ADI) suggesting that the fishes are safe for human consumption. However, the results showed that a total of twenty-two organochlorine pesticide residues were detected in all the

samples though the frequency of detection of most of the residues was less than 100% except for Heptachlor epoxide with concentration of 0.12 mg/g and Endrin Aldehyde with concentration 0.15 mg/g. 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.

Therefore, since the improvement in crop yield by pesticides application is always concomitant with the occurrence of pesticide residues in soil, water and fish samples, there is need for regulatory control on application and point sources of pesticides in order to forestall serious health hazards on the environment (Enbaia, et al, 2014).

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