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EVALUATION OF THE EFFECT OF ORGANOPHOSPHATE PESTICIDE RESIDUES IN SEDIMENTS, WATER AND FISH TISSUES FROM RIVER BENUE AND THEIR HEALTH RISK IMPLICATIONS

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ABSTRACT

Modern agriculture relies to a great extent on pesticides application to feed the ever growing large populations around the world. The wide and increased pesticides usage in both agriculture and sanitation sectors for combating pests and vectors of diseases brings with it environmental hazards and health risks arising from indiscriminate use and inappropriate handling of these chemicals. Pesticides use can leave behind unwanted residues that may contaminate food, the environment, and living tissue. They may be readily absorbed into fish bodies where they entire food chain inducing harmful impacts on human health when consumed. Levels of Organophosphate pesticide residues (OPPs) in sediments, water and fish tissues from River Benue at the Makurdi axis in Benue State, North Central Nigeria were analysed for possible contamination of the aquatic ecosystem for possible health effects. Water and sediment samples were collected from the river at three (3) different locations, while fish caught in the river were bought from fishermen at the river bank. The extraction, clean up and de-fattening of the fish samples were carried out using Standard procedures. Pesticide residues in the various samples were determined using GC/MS SHIMADZU (GC-17A) equipped with electron capture detector (ECD). Concentration of OPPs ranged from 0.08±0.06 to 1.68±0.02; 0.08±0.03 to 1.60±0.02; 0.01 to 1.69µg/kg in sediments, water and fish respectively. Level of OPPs Analysis of variance (ANOVA) shows that concentrations of OPPs in sediments and fish were not significantly different (P≤0.05) except for dichlovos, chloripyrifos and fenitrothion. Correlations for OPPs in sediments and water were almost perfectly positive (0.717-0.777). While between sediment and fish samples, correlations varied from negatively strong to moderately positive were weak and negative (-0.38 to 0.500). Concentrations of OPPs were within WHO/FAO set maximum Residue limits (MRLs). The results however, indicate the usage of these pesticides in the study area. These calls for regular monitoring of the OPPs in aquatic ecosystem in order to avert any unprecedented health hazard that might arise overtime from consumption of fish as well as use of water from this environment.

Keywords: Organophosphates, Pesticides, Residues, Aquatic ecosystem, Health Effect

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INTRODUCTION

The increasing human population around the world necessitates more agricultural products and foodstuffs that consequently need more pesticide usage to destroy any pests. Pesticide application has therefore become a crucial component for Agricultural productivity. Increased usage of pesticides has significantly increased Agricultural output, reduced grain loses in storage, and overall enhanced human wellbeing. The usage of such chemicals usually achieves the goal, but the accompanying environmental consequences with regards to the compounds are of a great concern worldwide (Rani L, *et al.,* 2021; Tang FHM *et al.,* 2021).

The term pesticide refers to Agrochemicals design to combat the attack of pests on Agricultural crops...' (American Chemical Society, 2000). Hence they are widely used to improve Agricultural production and also to prevent arthropod-borne diseases. Pesticide can leave behind unwanted residues that may contaminate food, the environment and living tissues. They are known to spread from Agricultural regions where they have been used into the wider environment, where they affect non-target organisms such as fish. The increase in pesticide usage brings with it environmental and health ills arising from indiscriminate use and inappropriate handling of the chemicals. Relevant poisoning from these chemicals in many countries, especially in developing countries like Nigeria is considered the second causes of mortalities after infectious diseases (Osuegba *et al.,* 2021).

Pesticides may enter surface water and ground water through runoffs, from treated soils, leaching processes, aerial drift and inappropriate disposal methods. The presence of Organophosphate in sediments samples suggests that these environmentally persistent compounds have been resident in the water bodies for a long time and may have contaminated the aquatic flora and fauna. The most striking effect of some of the pesticides in water is their ability to concentrate in the fatty tissues of successively higher components of the aquatic food chain. The accumulation of such pollutants in food chain may restrict the consumption of such valuable food resource (Bhat *et.al.,* 2012).

The frequent presence of pesticides and their high toxicity along with considerable bioaccumulation in fresh water fishes make then toxicants that should be given due consideration in aquatic toxicology. Fish accumulate xenobiotic chemicals, especially those with poor water solubility because of very intimate contact with the medium that carries the chemicals in solution or suspension and also because fish have to extract oxygen from the medium by passing enormous volumes of water over their gills. Fish kill or injure due to pesticides contamination is considered the primary cause of reducing fish populations and other animals through the food chain, an additional cause of reduced fish populations (Akueshi, et. al., 2003).

Environmental disturbances by pesticides have been identified as one of the major environmental impacts from agriculture (Skinner *et, al.,* 1997). Parent compounds as well as metabolites of pesticides have been identified in the air (Rudel, 1997), water (Boonyatumanond *et, al.,* 1997), and soil (Redondo, *et, al.,* 1997). The list of pesticide related compounds which have been carcinogenic is growing as new methods of detection have been developed and sensitivities and specifications of assays have been improved. Environmental contamination have been reported even when pesticides have been applied at recommended doses for example following the treatment of African rivers with Abate for black fly control, even in the absence of mortality of fish, behavioral changes appeared to have caused a change in population structure, with certain species being more prone to capture (Kerswills Edwards 1967) & (Ochulu 2002).

Organophosphate pesticides (OPPS) are chemical compounds that were produced shortly after the second world war in 1945 to control the activities of pests and insects (Adeyinka, *et.al.,* 2020). They are mostly insecticides containing phosphorus. They are often called organic phosphates, phosphorus insecticides, nerve gas relatives, phosphate insecticides or phosphorus acid esters. Their ability to control the activities of pest in crops implies that there would be viable and good Agricultural products during planting and harvesting seasons. Of no doubt, they have greatly lessen the human efforts on how to control pests and insects in all applicable sectors (Waddell *et. al.,* 2001). Common examples of Organophosphate pesticide include Diazinon, dichlorvos, chlorpyrifos, malathion, parathion, nerve gasses and a host of others (Adeyinka *et. al.,* 2022).

Side Effects of Organophosphate Pesticides on Living Organisms

The toxicity induced by organophosphate pesticides results from inhibition of the enzyme (acetylcholineterase) in the nervous system of the exposed organisms which makes the central nervous system functional disturbance. Long-term exposure to organophosphates can cause confusion, anxiety, loss of memory, loss of appetite, disorientation. Organophosphates are acutely neurotoxic, they make people sick with symptoms like headaches, nausea, dizziness, breathing difficulty, and at a very high exposures seizures and even death. They also cause more troubles to children at risk of reducing their intellectual quotient, autism and attention deficit disorder at very low levels of exposure.

When the organophosphate enter the environment (often sprayed on crops and plants) small particles of the chemicals may be carried away from the field before falling to the ground. The applied chemical may also be present in soil, surface waters and on the surface of the plant. They can move through the soil and contaminate ground water. Rain can wash these chemicals on soil and plant surface into surface waters where they constitutes great environmental hazards. OPPs are not likely to build up to high or dangerous levels in animals and plant foods that man might eat. This is because, they are less persistent in the environment than the Organochlorine pesticides, due to the fact that they are relatively soluble in water, and are mobilized by precipitation.

Effects of Pesticides on Aquatic Environment

The environmental impact of pesticide consist of the effects of the pesticides on non-target species. Over 98% of sprayed insecticide and 95% of herbicides reach a destination other than their target species, because they are sprayed or spread across entire Agricultural field (Miller, 2004). Each pesticide comes with specific set of environmental concerns, the effect of which have lead many pesticides to be banned, while regulations have limited less persistent and more species-specific. However, the global spread of pesticide use, including the use of obsolete pesticides that have been banned in some developed countries has overall increased (Lamberth, *et. al.*, 2013).

Pesticides may change the ecological systems of water bodies and interfere with the fish food chain (Uddin, *et.al.,* 2016). The availability of water plants and insects that provide meals for fish and other aquatic organisms may decline when pesticides concentration rise. In addition, pesticides toxicity, causes mortality, reproduction failure, egg shell thinning, suppression of the immune system, and other fish health complications such as excessive health slime on fish scales and gills, cancers, tumors and lesions.

Effects of Pesticides on Fish

The risk posed by pesticide to aquatic life is relative and depends on several factors including landscape, application methods, application rates, erosion, irrigation, topography, soil type

and management practices (Usepa, 2004). Invariably, an increase in concentration of pesticides residues in fish and sediments, is an indication of the high level of pollution of the water throughout its food web (Kafizadeh, 2015).

Fish can be directly or indirectly impacted by pesticides. Some long exposures cause abnormalities or mutation in developing fish larvae, while acute exposure may cause immediate fish die-offs. The liver, kidney, brain and gills of exposed fish are extremely vulnerable to chemical exposure. Chemical pesticides are double-edges weapons that have the potentials to harm both humans and the environment just as much as they can harm target pests. As a result, eating fish that has been subjected to these pesticide can be considered a major cause of human exposure to environmental toxins. When exposed to contamination stress, specimens experience considerable changes in their molecular, cellular, histological, and physiological characteristics, fish are exposed to environmental contaminants through their gills, skins and food. The bioaccumulation found in fish organs is used as a measure of the health of the aquatic system.

Maximum Residue Limits (MRL) for Pest

MRL refers to the maximum concentration of pesticide residue that may remain in food or on soil after a pesticide is applied per labelled direction and which can safely be consumed. This can be expressed as mg of active residue per kg, (mg/kg) (Kennedy, *et.al.*, 2015). When pesticide is applied to a crop, a residue may still remain on that crop at harvest time. The MRL is determined by a small-scale farm study in which the pesticide under study is applied to the particular crop, the appropriate withdrawal period is allowed (that is the time necessary between application of pesticide and harvest), the crop is harvested and residue determined (Tay, *et.al.*, 2007). Also, a maximum residue limit is the highest level of pesticide residue that is legally tolerated in or on food or feed when pesticides are applied correctly in accordance with good Agricultural practice. To protect population health, international agencies regulate pesticides (MRL) which are legal limits that must not be exceeded. Worldwide, about 114 countries like European Union, India, China, Germany, South Africa and many have regulated MRLs on not less than 100 of Agricultural commodities such as fruits, vegetables, grains, seeds, meats, fish and dairy products (Skawsang, *et. al.*, 2019).

Lethal Dose 50 (LD_{50}) of Organophosphorus Pesticides

The term LD_{50} refers to an estimate of the amount of poison that, under control condition will be a lethal dose to 50% of the large number of test animals of a particular species. The value is expressed in milligram of the substance been tested per kilogram of animal body weight (mg/kg). Some acute toxicity tests (such as the "classical" LD_{50} test) are designed to determine the mean lethal dose of the test substance. The median lethal dose (or LD_{50}) is also defined as the dose of a test substance that is lethal for 50% of the animals in a dose group. (Rand Hawaii, *et.al.*, 2009). According to Sanganuwan, (2016), LD_{50} can be calculated using the formula $LD50=ED_{50}/3 \times Wm \times 10^{-4}$. It is expressed in mg/kg bw/d or milligram of the substance per kilo of body weight administered per day.

Extraction Methods of Pesticide Residues: The method of liquid-liquid extraction has been used for organophosphorous pesticide residues in environmental waters in which a nitrogen–phosphorus detector (NPD) was used to selectively detect trace amounts of organophosphates in the water. This is a method also developed by the Chinese Ministry of the Environment, regarded as Method GB 5750.9-2006 (Chaoying *et al.*, 2007). The method principally makes use of liquid–liquid extraction (LLE) to eliminate the residues but automated SPE can replace the use of LLE to reduce the quantity of organic solvent. There are various methods which

have evolved in extraction of pesticide residues in both soil and food crops. Some of these are chromatographic methods used for either organophosphates or organochlorine pesticide analysis. The chromatographic methods for OPP pesticides analysis include some of the promising techniques: solid-phase extraction, solid-phase micro-extraction, stir-bar sorbent extraction, matrix solid-phase dispersion, solvent extraction, liquid-phase micro-extraction, super critical fluid extraction, ultra-sonication extraction, microwave- accelerated extraction, and membrane-assisted methods, applied to various matrices (Pico *et al*., 2007; Hyötyläinen and Riekkola, 2008; Pinto *et al*., 2010; Wang and Du, 2010). Solid Phase Extraction (SPE) is one of the most commonly used sorbent techniques in analyzing pesticide residues. It is easy to operate, less costly; it is being automated and uses small amounts of solvent (Stoytcheva and Zlatev, 2011).

Determination of Pesticides Concentration

Concentration of pesticides in different matrices can be adequately determined by several methods like chromatographic, electrochemical, immunochemical and biosensors analytical methods. Gas Chromatography (GC) and Carbon Fibre Micro Electron (CFM) have been used for selected organochlorine determination (Sbaï *et al*., 2007; Wang and Li, 2008). Organophosphorus pesticides can be analysed by the application of several chromatographic methods such as gas chromatography-mass spectrometry, gas chromatography-tandem mass spectrometry, gas chromatography-ion trap mass spectrometry, gas chromatography time-of-flight mass spectrometry, high performance liquid chromatography etc (Wang *et al*., 2011). Malhat and Nasr (2013) monitored pesticide residues in water samples taken from Nile River, they analysed by similar method of using a gas chromatography fitted with a flame photometric detector.

Empirical Studies

Schmitt and Winger, (1980) cited several instances where sport and commercial fisheries had to be closed because of the occurrence of high discharge of about 90.000kg of chlordane into the James River, during the manifesting process at Hopwell, Verginia between 1966 and 1975 lead to the closure of both commercial and sport fishing in the area. Acute toxicity of some inorganic fertilizers to *O. niloticus* has been studied (Onusinuka and Ufodike 1992), and they reported 96-h LC50 for the fertilizers ranged from $56.23mg1^{-1}$ for $Ca(OH)_2$ to $199\text{-}53mg1\text{-}531^{-1}$ for NPK. They advised that secondary applications of these fertilizers in ponds stocked with *O niloticus* be avoided.

In another study, various plants were used to study the toxicity of plant extracts on fishes, Ayuba and Ofojekwu (2002), also reported acute toxicity, LC_{50} of $204.17mg1^{-1}$ of the root extract of jimson's Weed (*Datura innoxia*) to the African catfish (*Clarias geariepinus*) fingerlings.

Akan *et. al.*, (2013) reported high concentrated of Organophosphate pesticides residue from Alau Dam, Borno State-Nigeria and calls for adequate measures to be taken in order to reduce the high levels of these pesticides so as to preserve the aquatic life in and around the Alau Dam. Several OPPs are extremely poisonous to human and animal life, placing the detection of their residue, an increasing concern.

Agricultural activities have impacted negatively on the River Benue waters. Drains from these activities constantly empty into the waters. Bioaccumulation and bioconcentration of pesticides in the fish species are capable of reaching toxic levels in the fish (even when exposure is low) and subsequently to man.The rapid expansion use of these agricultural chemicals as an integral part of crop production has led to an increasing awareness of the

need to understand their long term consequences for users, food consumers and the environment.The river Benue is primarily an agricultural area with intense agrochemical usage. Agrochemicals in form of pesticides, herbicides and fertilizers are employed annually for vegetables and fruit productions as well as the control of vector-borne diseases of public health. Economic activities within the area include fishing. Fish (fresh and dry) from River Benue serves as the major source of income for most of the inhabitants, and form a source of protein for the inhabitants in and around the metropolis; the river also serve as a major source of municipal water supply for towns and villages around the river.

The present study evaluates the levels of OPPs in sediments, water and fish tissue, in River Benue Makurdi axis, North-central Nigeria.

Regular monitoring of OPPs accumulation in the aquatic ecosystem becomes very necessary to avert any unprecedented health hazard that may occur overtime from consumption of fish and water from the river.

MATERIALS AND METHODS

Materials/Apparatus/Reagents

List of materials, apparatus and reagents used for the determination of organophosphate pesticides residues in sediments, water and fish tissue is contained in Table 3.1. All the materials and reagent were of standard analytical grade.

Table 3.1: Materials/Apparatus/Reagents

MATERIALS/APPARATUS/REAGENTS
Plastic bottles with screw cap, conical flasks
Ice-cold boxes, Spatula, Analytical weigh balance, Ethanol (96%)
Face mask, Pipette, Labels and Markers, Water bath, Syringes,
Volumetric flask, Teflon coated spoon, Aluminum foil, Beakers,
Plastic Gloves, Potassium per magnate(0.1g per litter)
Concentrated Sulphuric acid $20^0C=1.84gml^{-1}$
Ahydrous Sodium Sulphate, ethyl acetate, acetonitrile
Round bottom flask, Rotary evaporator

Study Area

The study was conducted in Makurdi Metropolis of Benue State. Makurdi lies within Longitude $8^0$30'E, $8^0$30'E and Latitude $7^0$30'N, $7^0$43'N. The mean monthly rainfall ranges from 150mm to 180mm and the mean monthly temperatures ranges from 27^0C to 38^0C. Makurdi has an estimated population of 454,000, (United Nations - World Population, 2023). River Benue arises from Adamawa Plateau and flows west across central Nigeria and joins River Niger 483km from the coast, its width varies from about 488 to 976m and its navigable length is more than 965km during the wet season (May to September). It is about 1,370km long and passes through Makurdi (Latitude 70 44^1N and longitude 80 31^1E) (Fig 1). The present research was carried out within the Makurdi axis of the River Benue as main focus point.

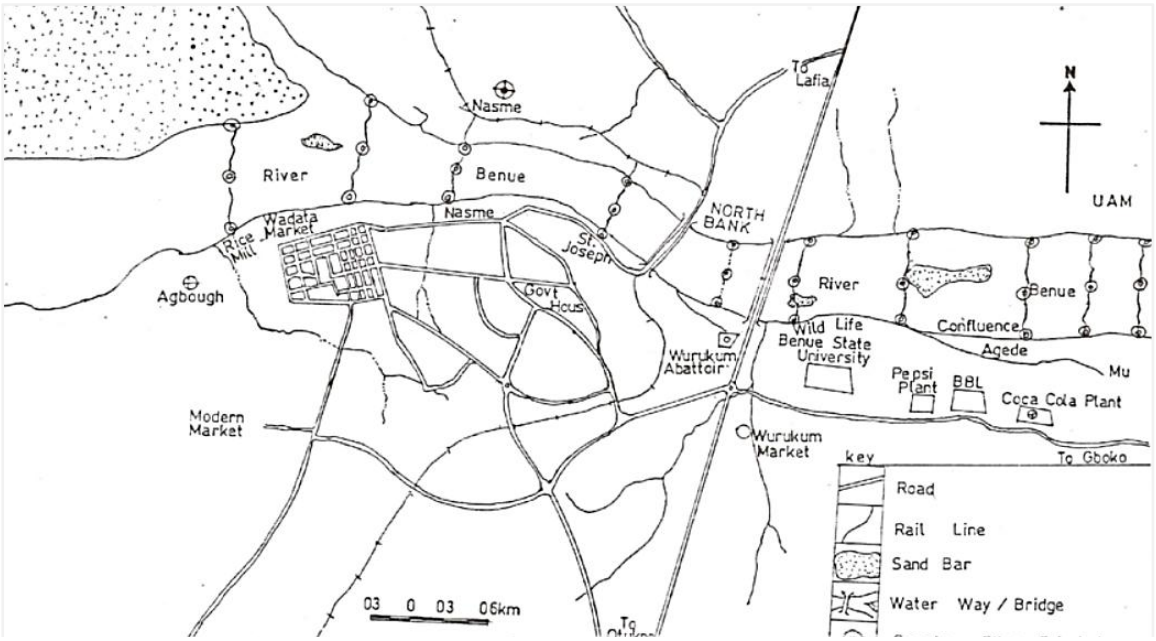

Fig 1: Map of River Benue along the Makurdi axis

METHODS

Pesticide Survey

Survey was conducted to determine the types of pesticides used by famers in the study area. The information was obtained from both farmers and pesticides vendors. Selected pesticides for analysis and their molecular structures are shown in Table 3.2.

Table 3.2: Pesticides and Molecular Structures

Pesticide	Molecular Structure
Phosphine	PH_3
Dichlorovos	$C_4H_7Cl_2O_4P$
Triazovophos	$C_{12}H_{16}N_3P_5$
Methidathion	$C_6H_{11}N_2O_4PS_3$
Fenitrothion	$C_9H_{12}NO_5PS$
Phosphamidon	$C_{10}H_{19}ClNO_5P$
Profenofos	$C_{11}H_{15}BrClO_3P_5$
Malathion	$C_{10}H_{19}O_6PS_2$
Chlorpyrifos	$C_9H_{11}Cl_3NO_3$
Primiphosmethyl	$C_{11}H_{20}N_3O_3PS$

Sample Collection

Water samples were collected at 3 different locations into clean 1L bottles with screw cap preserved in ice-cold boxes from each of the sampling points in rainy season (July-August). Surface Sediment Sample were collected from 3 sites at a depth of 0-20cm along the bank of the river using Teflon coated Spoon and were wrapped in aluminum foil. Fish samples of uniform sizes were bought from fishermen along the river bank in order to avoid the possible error due to size differences. The samples were labeled with an identification number and were transported to the Laboratory.

Sample Extraction and Cleanup Process

Liquid-liquid extraction of the pesticides residue in fish, water and sediments samples were carried out according to the cleanup process by passing the extract to a chromatography column containing an anhydrous sodium sulphate and eluted with the acetonitrile and then concentrated to 5cm^3 of the eluent. The samples were then injected into gas chromatography coupled with electron capture detector (GC-MS), model, for quantification of the chemical residue.

The fish samples (20 g) were weighed into a 150 ml conical flask followed by the addition of 20 g and 5g of anhydrous sodium sulfate and sodium hydrogen carbonate, respectively. 100 ml of 1: l (v/v) ethyl acetate/dichloromethane mixture were transferred into the 20 g fish samples and thoroughly mixed by shaking the conical flask while corked. 20 g of anhydrous sodium sulfate were then added to the content of the conical flask followed by 20 g of sodium hydrogen carbonate. The conical flask were corked tightly and the mixture shaken thoroughly for 10 min. The content was allowed to stand for 3 h.The organic layer were decanted into a 10 mm round bottom flask and evaporated using the rotary evaporator at 40 ^{0}C. The pesticide in the rotary flask were dissolved and collected with 2 ml of ethyl acetate and transferred into a 2 ml vial and ready for the clean-up.

10 mm Portion of deactivated silica gel were weighed and transferred into a 10 mm glass chromatographic column followed by addition of 10 mm of anhydrous sodium sulfate. 10ml of the 1:1 (v/v) ethyl acetate/dichloromethane mixture were used to wet and rinse the column. The extract residue that is sediments, water and fish in 2 ml ethyl acetate were transferred into the column and the extract vial rinsed (three times) with 2 ml ethyl acetate. The column were eluted with 80 ml portion of ethyl acetate/dichloromethane at a rate of 5 ml/min into a conical flask as fraction one. The column were eluted again with 50 ml 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 ^{0}C. Each residue were dissolved and collected in 2 ml ethyl acetate for gas chromatograph analysis.

De-fattening of the Fish Sample Extracts

Fifty (50) ml of 1:1 (v/v) hexane/acetonitrile solution were added to 2 ml pesticide extracted from the fish samples in a 100 ml separator funnel. The separator funnel were shaken gently for 3min while releasing the gas pressure. The separator funnel were allowed to stand for 20min. to allow for phase separation of the organic solvents. The acetonitrile fractions containing the pesticides were collected into a 50 ml beaker while the fat containing hexane solvent phase were discarded. The acetonitrile solvent extract obtained were further cleaned-up using 25 ml of the pure hexane. The acetonitrile fraction were concentrated with rotary evaporator at 40 ^{0}C and the content of the flask dissolve and collected with 2 ml of ethyl acetate into a 2 ml vial. The vial containing the pesticides extracts were stored in the refrigerator at 40^{0}C for GC-MS analysis.

Determination of Pesticide Residues

The SHIMADZU GC/MS (GC- 17A), equipped with fluorescence detector were use for the chromatographic separation and were achieved by using a 35% diphenyl/65% dimethyl polysiloxane column. The oven were programmed as follows: initial temperature 40 ^{0}C, 1.5 min, to 150 ^{0}C, 15.0 min, 5 ^{0}C /min to 200 ^{0}C, 7.5min, 25 °C/min to 290 ^{0}C with a final hold time of 12min and a constant column flow rate of 1 ml/min. The detection of pesticides were 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 ration 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 were operate in MSn mode and perform tandem MS function by injecting ions into the ion trap and destabilizing matrix ions, isolating only the pesticide ions. The retention time, peak area and peak height of the sample were compared with those of the standards for quantization.

Determination of the Lethal Concentration LC_{50} of OPPs on Fish Species Commonly Found in the River Benue

Tilapia (*Orechromis Niloticus*) and cat fish (*Clarias gariepeinus*) are the two fish species most commonly found in the River Benue at the Makurdi axis. These were used for the determination of LC_{50} of three selected pesticides (*Dichlorvos, Methidathion and Chlorpyrifos*). The acute 96 hours toxicity test was carried out under laboratory conditions using the method of Hojque *et al.,* (1993). The fish samples were randomly selected and transferred from the holding tank to test aquaria within 30 minutes after the addition of the pesticides. Aeration was achieved using an electronic aerator during the period exposure of fish samples to the pesticides.

Room temperature was maintained with the entire aquaria exposed to natural light. The fish samples were exposed to each of the five toxicant concentration of 0.10; 0.50; 1.00; 1.50; 2.00 and 2.50; which were renewed after every 48hours in each bioassay. A control was set up which was free of pesticides.

Statistical Analysis

Data collected were subjected to simple statistics (Mean and Standard deviation), analysis of variance (ANOVA) and Pearson correlation matrix using Microsoft Excel and Statistical Package for Social Sciences (SPSS) computer software.

RESULTS AND DISCUSSION

Results

The concentration levels of Organophosphate pesticides (OPPs) in sediments (Table 4.1) ranged from (0.03 to 1.71 µg/kg), concentrations of OPPs residues in the water samples (Table 4.2) ranged from (0.03 to 1.64 µg/kg), these were highest at site 2, with moderate concentration at site 1, while the lowest concentrations were recorded at site 3. The most abundant pesticide residues recorded in fish (Table 4.3) was dichlorvos (1.69 µg/kg), while the lowest was in phosphamidon (0.01 µg/kg). Variations in mean concentration of OPPs in sediments, water and fish samples are shown in Figure 2. Table 4.4 present ANOVA for OPPs Residues in sediments, water and fish samples while Pearson correlation matrix (r) for fish samples from the study area is presented in Table 4. 5.

Results of the LC_{50} of Opps on fish species commonly found in River Benue show that a few of the pesticides concentration caused mortalities at 16 hour test period while majority caused mortalities at 96 hour duration. Mortality declared when fishes failed to respond to touched and death rate increased as the concentration of pesticides and duration of exposure increased. A 100% of matured Tilipia (*O. niloticus*) and catfish (*C gariepenus*) died upon exposure to 2.50 ppm of Dichlorvos. (Table 4.6) for *O. niloticus* and *C gariepenus* respectively. The percentages in mortalities decrease with decrease in concentration for all

the pesticides. The concentration of the pesticides that cause 50% mortalities of Tilapia upon exposure for 96 hours were determine arithmetically to be 1.10; 1.50 and 1.35 ppm respectively for Dichlorvos, Chlopyrifos and Methidathion. While that of cat fish were determine to be 1.10, 1.50 and 1.25 ppm for these pesticides in a similar order as shown by Tilapia (Table 4.7).

Table 4. 1: Concentrations of Organophosphate Pesticides in Sediment

Pesticide	**Sampling Points**			**Mean±SD**
	1	2	3	
Phosphine	1.21	1.41	1.31	1.31±0.1
Dichlorovos	1.67	1.71	1.67	1.68±0.02
Triazovophos	0.24	0.32	0.20	0.25±0.06
Methidathion	0.14	0.20	0.12	0.15±0.04
Fenitrothion	0.44	0.52	0.43	0.46±0.05
Phosphamidon	0.03	0.07	0.14	0.08±0.06
Profenofos	0.22	0.30	0.21	0.24±0.05
Malathion	0.25	0.31	0.23	0.26±0.04
Chlorpyrifos	0.35	0.40	0.32	0.35±0.04
Primiphosmethyl	0.41	0.56	0.43	0.46±0.08

Table 4.2: Concentrations of Organophosphate Pesticides in Water (µg/Kg)

Pesticide	**Sampling Points**			**Mean±SD**
	1	2	3	
Phosphine	1.04	1.16	1.02	1.07±0.04
Dichlorovos	1.62	1.64	1.62	1.60±0.02
Triazovophos	0.11	0.10	0.04	0.08±0.03
Methidathion	0.02	0.01	0.06	0.03±0.02
Fenitrothion	0.43	0.42	0.36	0.40±0.03
Phosphamidon	0.04	0.04	0.20	0.09±0.04
Profenofos	0.10	0.10	0.04	0.08±0.03
Malathion	0.13	0.14	0.05	0.10±0.05
Chlorpyrifos	0.21	0.21	0.13	0.18±0.04
Primiphosmethyl	0.34	0.36	0.30	0.33±0.03

Table 4.3: Concentrations of Organophosphate Pesticides in Fish (µg/Kg)

Pesticide	**Concentration**
Phosphine	1.16
Dichlorovos	1.69
Triazophos	0.13
Methidathion	0.14
Fenitrothion	0.41
Phosphamidon	0.01
Profenofos	0.20
Malathion	0.25
Chlorpyrifos	0.34
Primiphosmethyl	0.55

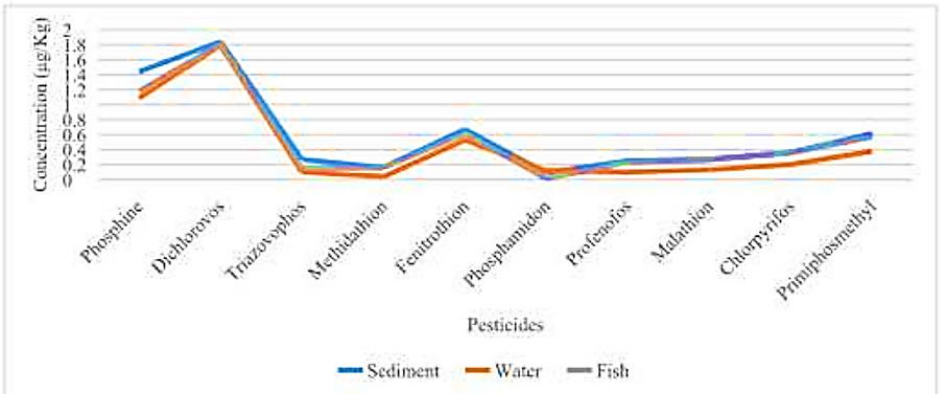

Figure 2: Variations in mean concentrations (µg/kg) of Organophosphate pesticide residues in sediment, water and fish samples.

Table 4.4: ANOVA for Organophosphate Pesticide Residues (OPPs) in Sediment, Water and Fish Samples

Pesticide	Sediment	Water	Fish
Dichlorovos	1.720	0.573	1.610
Triazophos	0.250	0.100	0.140
Methidathion	0.142	0.023	0.150
Fenitrothion	0.450	0.430	0.410
Phosphamidon	0.733	0.115	0.010
Profenofos	0.230	0.103	0.233
Malathion	0.253	0.125	0.260
Chlorpyrifos	0.330	0.200	0.340
Primiphosmethyl	0.405	0.343	0.450

Table 4.5: Pearson correlation matrix (Correlation coefficient (r)) for OPP residues in water, sediment and fish samples from River Benue Makurdi Axis.

Pesticide	Sediment/ Water	Sediment/Fish	Water/Fish
Phosphine	0.757	-0.342	-0.167
Dichlorovos	0.761	-0.400	-0.325
Triazophos	0.790	-0.61	-0.501
Methidathion	-0.221	-0.451	0.770
Fenitrothion	0.771	-0.341	-0.501
Phosphamidon	0.771	0.777	0.762
Profenofos	0.777	-0.434	-0.501
Malathion	0.717	-0.434	-0.646
Chlorpyrifos	0.717	-0. 434	-0.646
Primiphosmethyl	0.777	-0.501	0.434

Level of Significance ($p \leq 0.05$).

Table 4.6: Percentage mortalities of *O niloticus* and *C gariepenus*

Concentration of PPM	Concentration of mortalities of *O niloticus*			Concentrationn of mortalities of *C gariepenus*		
	Dichlorovos	Chlorpyrifos	Methidathion	Dichlorovos	Chlorpyrifos	Methidathion
0.10	20	14	10	20	20	0
0.50	32	26	20	34	30	24
1.00	46	40	36	48	40	36
1.50	64	58	50	70	58	48
2.00	80	67	66	82	72	64
2.50	100	96	86	100	94	86

Table 4.7: 96 hours LC_{50} *O niloticus* and *C gariepenus*

Concentration of PPM	*O niloticus*	*C gariepenus*
Dichlorovos	1.10	1.00
Chlorpyrifos	1.50	1.50
Methidathion	1.35	1.25

Discussion

The occurrence of pesticide residues and their metabolites in various environmental compartments such as aquatic, air, soil and various foods is well documented, and several pesticides have been detected in various environmental matrices and biological tissues, usually at trace concentrations varying from ngL-1 to gL-1. For example, a body of published research data, followed by a significant number of related reviews (Zhang, 2003); (EPA 2014); and (Seria, 2017), has demonstrated increasing scientific interest and global concern about the occurrence, fate and distribution of pesticides in the environment. The ability of a pesticides to hasten the negative effects on fish and other aquatic species is significant. Its toxicity is usually influenced by factors like exposure period, dose rate, and environmental persistence.

In the present study, the most abundant recorded pesticide residue was dichlorvos with mean concentration of 1.64±0.02µg/kg while phosphamidon recorded the lowest concentration level 0.08±0.06µg/kg.

The concentration levels of chlorpyrifos 0.32±0.40µg/kg, dichlorvos 1.62±1.64µg/kg, and fenitrothion 0.43-0.52µg/kg obtained in sediments in this present work were similar to the results reported by Akan, *et al.,* (2013) for Alau Dam, Borno State, where the concentration levels of chlorpyrifos ranged from 0.34 to 1.89 µg/kg for fenithrothion. The present research is also correlated with the results reported by Osuegba, (2021) for River Loko, Nasarawa State, where the concentration levels of chlorpyrifos ranged from 0.31 to 0.41 µg/kg, dichlorovo 1.82 to 1.86 µg/kg, and fenitrothion 0.61 to 0.74 µg/kg. The low concentration of OPPs in water could probably be due to the fact that they are relatively soluble in water, and are mobilized by precipitation, hence less persistence in the environments. Among the detected OPPs residues, dichlorvos recorded the highest concentration (1.68±0.02µg/kg), while methidathion recorded the lowest mean concentration of 0.03±0.02µg/kg (Table 4.2).

The mean concentration of chlorpyrifos in water in this study (0.18±0.04µg/kg) was lower compared to the result reported by Osuegba, (2021) for River Loko (0.203±0.04µg/kg) and that reported for Deomoni River of west Bengal India (Swati, *et al.,* 2015). The concentration of the OPPs detected showed they were all within the WHO FAO set maximum residue limits (MRLs) except Fenitrothion (0.01µg/kg MRL). The Acceptable Daily intake values (ADIs) of chlorpyrifos and Fenitrothion for fish samples are 0.01µg/kg and 0.05µg/kg respectively.

The results obtained from the present study exceeded the ADI values and this may be attributed to the presence of this pesticide in the aquatic environment. The MRL is the maximum amount of the pesticide residue which is found in food substances that will not cause any health effect or hazard (Codex, Commission, 2009).

Studies showed that different fish tissues had accumulated pesticides and the extent of accumulation varied widely from one pesticide to another (Essumanu, & Chokky, (2009), Akan, *et al*., (20130), Swati, *et al.,* (2015); and Pauline, (2016). Bioconcentration is thus influenced by the structure of the compound, its solubility in water, the physiological activity and other vital factors such as temperature, water organic matter content and population density. Organophosphorus pesticides are Lipophilic (fat-soluble), hence, the tendency to concentrate in lipid rich tissues of aquatic organisms including fish. High concentration of dichlorvos in fish sample (1.62µg/kg) may be as a result of the recent use of this pesticide around the study area. Accumulation of these pesticides in fish is a function of their membrane permeability and enzyme system, and may originate from pesticides deposited in the sediments and food in the aquatic environment. The concentrations of all the OPPs obtained in this study were within the acceptable limit for drinking water.

A comparison of the concentration of OPPs (Fig. 2) in the various Samples varied in the order of sediments>fish>water. OPPs with the highest concentration was dichlorvos, which ranged from (1.67-1.71µg/kg) in sediments; (1.62-1.68µg/kg) in water and (1.69µg/kg) in fish. The result of this study is in agreement with the results reported for Loko River, Nasarawa where OPPs concentration in sediments ranged from (1.82 to 1.86µg/kg); (1.81µg/kg) in fish and (1.78 to 1.81 µg/kg) in water (Osuegba, 2021).

Higher levels of OPPs found in the sediments than in fish and water may be attributed to the fact that sediments are important sinks for various pollutants such as pesticides, which under favourable conditions play a significant role in pollutant remobilization in aquatic systems and water sediments interactions. Sediments act as a secondary source of contamination after water in the ecosystem. Sediments are the main reservoirs of environmental pesticides and provide a source from which residues can be released into the atmosphere, groundwater and living organisms.

The lower levels of pesticides residues in the water samples than in sediments and fish could be attributed to the fact that the input of pesticides into the water depends on seasonally different concentrations of suspended matter into which the residues were taken up and transported, dependent on the precipitation events that drive soil erosion activities and suspended solids levels during runoff.

The 96 hour LC_{50} reported in this study for each pesticide is in agreement with the work of Hojque, *et al.,* (1993) who reported a 96hour LC_{50} of 1.6ppm for Chlorpyrifos. The concentration of Chlorpyrifos needed to effect 50% mortality was the highest in each case. No mortality was observed in any of the control which means the laboratory conditions were suitable for the experiments.

Analysis of Variance (ANOVA) shows that the concentration of OPPs in sediments and fish (Table 4.4) were not significantly different ($P \leq 0.05$) except dichlorvos and fenitrothion. Correlations for OPPs (Table 4.5) in sediments and water were almost perfectly positive (0.717-0.777) except for methidathion (-0.0331). For sediments and fish, correlations were weak and negative (-0341 to 0.500). While in water and fish correlation for all the samples were also strong and positive (0.982-0.999).

Organic matter content in sediments and water might have influenced the retention of the organophosphate pesticides molecules.

CONCLUSION

The results of the present research work has led to the following conclusions;

1. The concentration levels of OPPs residues in the order of sediments>fish>water was recorded. Concentrations of the OPPs were however within WHO/FAO set maximum residue limits (MRLs);
2. Pesticides residue in fish tissue exceeded acceptable daily intake values, which could be attributed to the presence of this pesticide in aquatic environment, probably sediments;
3. Of all pesticides studied, Chlorpyrifos was the most abundant OPPs residue in almost all the studied samples;
4. Result of the toxicological effect revealed Dichlorvos, Chlorpyrifos and Feritrothion even at very low concentrations are toxic to fish species. Pesticides residues were relatively found in the experimental fish species, those subjected to toxicity test.
5. The results indicate the usage of these pesticides in the study environments.

Generally, the concentration levels of these OPPs residues suggested the River is relatively affected by human activities such as farming which constitute great hazard to public health, since River Benue is an important source of fish (fresh and dry) consumed by the communities in and outside the study area. These results calls for regular monitoring of OPPs levels in the aquatic ecosystems in order to avert any unprecedented health hazard that might occur overtime from consumption of fish and water from such aquatic environment.

In summary, this present study has provided a valuable insight into the presence and levels of OPPs in the study area. The result highlight the importance of regular and continues monitoring and adherence to strict pesticide regulations to ensure public health safety and minimize potential health risk associated with accumulation of pesticides in the aquatic system.

RECOMMENDATION

1. Further studies are recommended to provide a more comprehensive analysis of a broad range of pesticide concentration levels in the aquatic ecosystems.
2. Fish is one of the major balance nutrient rich food source consumed in the study area and elsewhere, it is proven to be a vector of many toxic substances as the literature suggests. Studies at all levels are needed in order to keep the monitoring process on track. The frequent updates regarding pesticides contamination levels of water systems and bioaccumulation will keep the regulating authorities aware.
3. Provision of guideline as for the information generated through research and sensitization through aggressive enlightenment campaigns on safety guides on the handling and uses of pesticides as well as the health implications for users is crucial.
4. A well planned and enacted legislation and massive pressure from environmentalists is essential for the enforcement and supervision of pesticide use. These will form the basis for public education about their health risk implications; and possibly regulatory legislation.

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