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Risks Assessment of Organochlorines, Organophosphates and Pyrethroids Pesticide Residues in Water within River Benue and Lake Gerio Basin of Adamawa State, Nigeria

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Abstract: *Nigerian farmers particularly from Adamawa state in their quest to increase agricultural production led to increase in the use of pesticides, herbicides, rodenticides and fungicides. These persistent organic chemicals have become integral part of Nigerian farmers. A study on pesticide residue risk assessment in water and farmers in Adamawa state, Nigeria was conducted in four areas of study that comprised of Chigari, Dasin-Hausa, Gurin and lake Gerio respectively, with three objectives. The water samples were analyzed for pesticide residues, hence 19 different residues of organochlorine, organophosphates and pyrethroids were detected by the use of GC-MS device. Recommended chemicals such as HPLC grade Acetone and Acetonitrile and n-hexane were used as solvents while $NaCl_2$ (99.6%) of aqueous solutions and dichloromethane as extrants were utilized. Disperse Liquid-Liquid Extraction Method (DLLME) was used in samples extraction. The most contaminants detected are cypermethrin, permethrin, DDT, bifenthrin and Malathion, and the concentrations of each residue was determined. Generally, about three of water samples from the study areas were found above the EU MRL, only sample obtained from Dasin-Hausa had most of the residues below EU MRL. Therefore, 75% of the samples were found above EU MRL status. The EDI was determined by the use of the Expected Daily Intake formula;* $EDI = \sum_C \times F / D \times W$. *HRI indicated that there is high risk in consuming water for a life time in the study areas. Anova analytical indicated significant association of pesticide and residues across the study areas. Farmers were exposed to these variant residues through oral means which results to high mortality rate among the famers in the study areas due to reported cases of High Blood Pressure, Gastro-intestinal complications, severe fever and frequent dihorrea especially among the old and the young members of the farming communities. Reduce this abstract to a maximum of 250 words.*

Keywords: Pesticide residues, Health risk assessment, Water, Farmers, Adamawa State

Introduction

Adamawa state is an agrarian state where about 70-80% of its population involved either directly or indirectly in agricultural production. The indiscriminate utilization of pesticides as a results of their availability, relatively cheap and easy in application increases pesticides usage by farmers that resulted in occurrence of residues in food (Chowdhury, et al, 2018). Nigerian farmers particularly from Adamawa state in their quest to increase agricultural production led to increase in the use of pesticides, herbicides, rodenticides and fungicides. These persistent organic chemicals have become integral part of Nigerian farmers. These pesticides are been used for diverse reasons ranging from protecting crops from pests, weeds, rodents and fungal diseases to animal husbandry.

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Persistence use of synthetic pesticides such as organochlorine, organophosphates and pyrethroids by farmers in the state led to sporadic presence of their residues in the environments. Thus, it is necessary to re-assure the consumers that water sources are free from undesired pesticide residues. The pollutants such as Aldrin, Alpha-BHC, Endosulfan I, Endosulfan II, Endosulfan sulphate, Alpha – Chlordane, Dieldrin, o, P' – DDT, Heptachlor; Chlorpyriphos, Diazinon, Dichlorovos, Fenthion, Malathion, Chlorpyriphos; Bifenthrin, Cypermethrin, Permethrin and Deltamethrin that are found predominantly in Adamawa state are not target-specific and may eventually cause chronic effect to non-target organisms, since most of these pesticides residues are very persistent and remain for a long period of time due to their stability in structure and lipophilic character such as OCPs (Organochlorine *pesticides*). These pesticides tend to bio-concentrate and bio-magnify in food chain particularly those foods associated with fatty tissues that is leading to vertebrates and non-vertebrates toxicity in all those non-target organisms and even on humans.

Over the past decades, rapid increase of pesticides utilization by the Adamawa farmers was observed which growth in that trend may continue due to socio and technological advancement. In any case, pesticides residues are known to have been associated with human health risk such as severe respiratory and neurological damages or act as a genotoxic, carcinogenic and mutagenic agents and endocrine disruptors. Pesticide residues are also sources of pollution to the environment that constituted danger to aquatic habitat and the edaphic factors that are very vital in degradation and decomposition of organic matter for plant uptake as nutrients. Furthermore, the common effects of pesticide residues in human body are nausea, vomiting, blurred vision, coma, respiratory difficulties, etc. Some pesticide residues are also referred to as carcinogenic, mutagenic and others causes cardio-logical disorder (Raugh et al, 2016). The World Health Organization in collaboration with UNEP, (2020) reported that globally about three (3) million cases of both acute and chronic diseases with some 220,000 cases of deaths are recorded annually. Hence, most of these deaths occurred in developing countries like Nigeria and Adamawa state in particular. Therefore, to ensure water free from harmful pesticide residues, CODEX Alimentarius commission has set maximum residual limit (MRL) use as index that represent maximum concentration of each pesticide residues (mg/L) recommended legally permitted in water and animals products for consumption.

Purpose of the Study

The purpose of the study is to describe the risks of organochlorines, organophosphates and pyrethroids pesticide residues in River Benue and Lake Gerio Basin of Adamawa State, Nigeria. The specific objectives are to:

1. Determine the health risk of Multi-residue Pesticides in water and man from Adamawa state Nigeria;
2. identify the main contributor of pollutants in the water samples; and
3. Evaluate their potential risks based on the present status according to EU MRL.

Materials and Methods

Adamawa state which is located in North Eastern Nigeria on Latitude 7° and 11°N and Longitude 11°and 14°E, Adebayo and Tukur, (2019). The state occupied about 38,823.31 square kilometer, it bordered by Borno state to the North West, Gombe state to the west. It bordered to Cameroon by the east. The state is mountainous topographically and crossed by rivers and valleys. The state is one of the 36 states in Nigeria, which comprises of 21 local governments, the state is an agrarian state where about 70-80% of its population involved either directly or indirectly in agricultural production. The study area was divided into four (Figure.1), were Gurin which is on latitude 9.11670N and on longitude 12.88330E with a distance of 89.5km from Yola the capital of the

state. Dasin-Hausa with a distance of 23km from Yola and Chigari with a distance of 33km finally Lake-Gerio with a distance of 33km from Yola respectively (NBS, 2021). Five liters each of water samples was collected for organochlorine, organophosphates and pyrethroid residues analysis from the main sources of the areas under study

Sample collection

The study areas was divided into four namely Chigari, Dansin-Hausa, Gurin and Lake-Gerio, in each area of study, five (5) liters of water samples from each area of the study was collected from both river and wells located In these areas and was transported to the laboratory and stored in refrigerator at $40^{\circ C}$ in order to avoid breakdown of pesticides before analysis. The water samples were collected in 900ml amber glass bottle that was cleaned-up by non-ionic detergent, rinsed with tap water and also soaked in 10% HNO_3 for at least 24hrs, and rinsed with de-ionized water. The water sample was extracted and prepared using Disperse Liquid-Liquid Extraction Method (DLLME) before injection into GC-MS device for pesticide residue detection.

Chemicals and reagents

HPLC grade Acetone and Acetonitrile 'ACN' (Restek Corporation USA) were purchased from ABJ consolidated Nigeria limited (Nigeria) for the analytical purposes and n-hexane (Marsk, Germany) were used as main solvents. However, sodium chloride of (99.6%), aqueous solution and extrants (dichloromethane) (BDH, Poole, England) were also purchased and used. The certified Standard for the pesticide residue analysis of organochlorine (aldrin, alpha-BHC, o, p,-DDT, dieldrin, endosulfan 1, endosulfan 11, endosulfan sulphate, heptachlor and alpha chlordane). Organophosphate (diazinon, dichlorovos, fenthion, malathion, chlorpyriphos and fenithrothion). Pyrethroids (bifenthrin, permethrin, cypermethrin and deltamethrin) all were acquired from Restek Corporation USA through ABJ consolidated Nigeria Limited. Stock standard solution of the pesticides was prepared contained 1000ppm in n-hexane. It was serially diluted to obtain desired concentration of 10, 20 and 40ng/ml.

Extraction Method of Water samples

Disperse liquid-liquid extraction method (DLLME) technique which was initially introduced by Assadi, et al, (2016) was used in determination of pesticide residues of both organochlorine, organophosphates and pyrethroid in water sample in this study. 50ml volume each of Acetone, Acetonitrile and dichloromethane (1:1:1 v/v/v) was injected into n-hexane solution and introduced in a 2 liters separating funnel which contained 1liter of filtered water and shaken with hand for about 5mins which allowed to settle and formed cloudy solution. After separation, the organic phase was drained into a 250 ml conical flask and the aqueous phase was re-extracted twice with 50ml of n-hexane. The three extracted organic phase were combined and dried through passing it in a glass-funnel that contained anhydrous sodium sulfate. The organic fraction was concentrated by rotary evaporation. 10 ml of dried organic solvent was used as supernatant and injected into GC-MS device for pesticide residue analysis (detection).

The limit of quantification (LOQ) referred to the lowest analytes concentration levels was determined in this study through preparation of standard solutions at estimated concentration. The solution was initially being injected into the GC-MS device and analyzed ten times. However, the average responses and the standard deviation (SD) and limit of detection (LOD) was analyzed and calculated, the LOD for the pesticides detected in water sample were; Organochlorine pesticides (1.205mg/L), Organophosphates pesticides (0.165mg/L) and Pyrethroid pesticides (0.683mg/L).

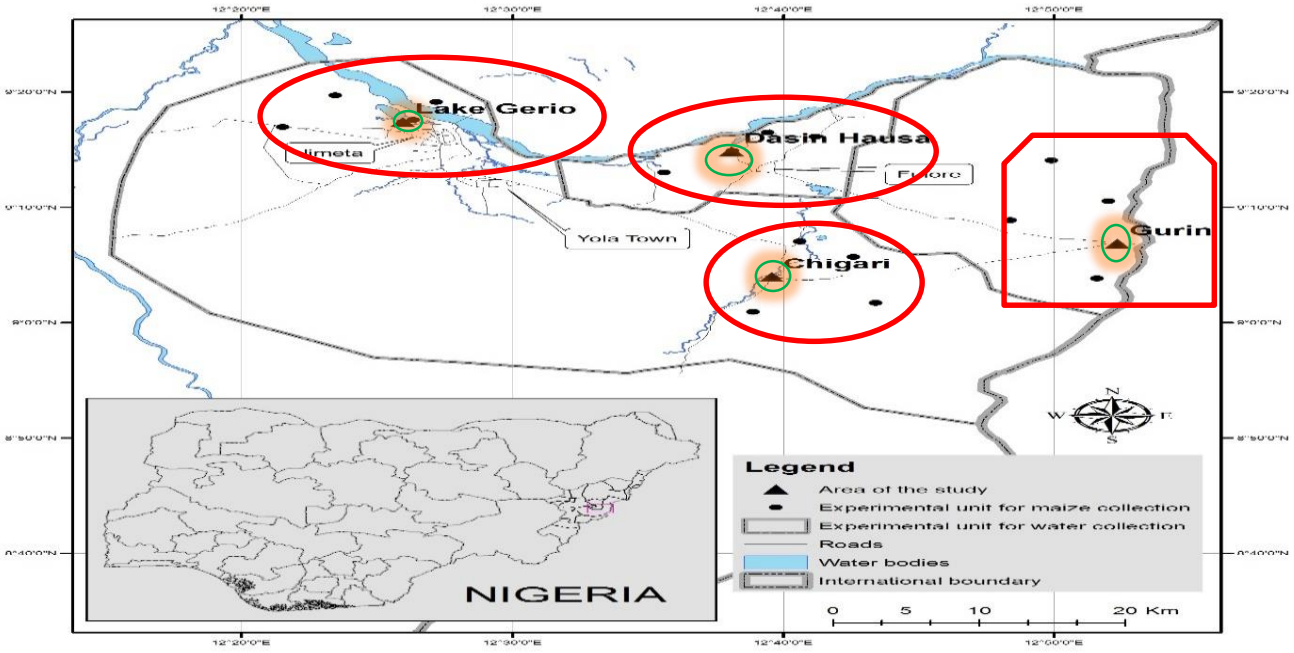

Fig. 1: Map of the study areas in Adamawa state, Nigeria

Recovery Studies

In recovery experiment, the samples of water were spiked with solutions containing mixtures of pesticide standards of both organochlorine, organophosphates and Pyrethroids. Recovery study was conducted in six (6) replicates. The replicates samples was fortified at 10 mg/L which indicated overall recovery range of organochlorine was between 92-100%; recovery of organophosphates between 86-101%; and recovery of pyrethroids between 90-98%. Furthermore, the six (6) points of pesticide residues calibration curve was generated and the linear relationship was evaluated across the range of expected sample concentrations. The pesticide residues was identified by matching the retention time of the sample with its external calibration standard curve. All the cleaning and washing procedures of glass-wares were used in conjunction of USEPA Method 1694 in order to avoid any contamination during the analysis.

Linearity

The range target concentration has direct linear relationship with the analytes concentration responses from the GC-MS instrument which indicated by the value of concentration coefficient (r) of each pesticide. However, the concentration coefficients for the three pesticides in water sample were; organochlorine residues (r = 0.9954), organophosphates residues (r = 0.9987) and pyrethroid residues (r = 0.9588). Therefore, the r values indicated that, all the r values are greater than 0.995. Hence by this, analytical methods were justified as acceptable (valid) to measure the concentrations within the studied concentration range.

Limit of Detection (LOD) and Limit of Quantification (LOQ)

The limit of quantification (LOQ) referred to the lowest analytes concentration levels and was determined through preparation of standard solutions at estimated concentration. The solution was initially being injected into the GC-MS device and analyzed ten times. However, the average responses and the standard deviation (SD) was analyzed and calculated, these include; the limit of

detection (LOD) values obtained from the analysis of these pesticides (organochlorine, organophosphates and pyrethroids). The LOD for the pesticides detected in water sample were; organochlorine pesticides (1.205mg/L), organophosphates pesticides (0.165mg/kg) and pyrethroid pesticides (0.683mg/kg).

GC-MS conditions

The detection and determination of the residues were carried out by injecting 1 μL of the 1.0 cm^3 purified extract into the injection port of a Shimadzu GC –MS QP-2010 gas chromatograph with an electron capture detector (GC-μECD Agilent Technology 7890A). The column (DB-5, 5% phenyl methyl polysiloxan) 30 m length × 0.25mm i.d. × 0.25 μm film thickness. The column temperature was programmed from 50˚C for 1 min, to 205˚C at 30˚C/min, to 240˚C at 1˚C/min, hold 2min at 240˚C. The injection was with split less injector; split vent flow, 22 mL/min; purge flow, 9 mL/min; Helium as carrier gas.

Risk Assessment on community

A structured questionnaire was sampled which contained attributes such as Age, body mean weight, and the amount of water and maize consumed daily as a staple food by the respondents. The Expected Daily Intake (EDI) of various pesticide residues detected from water samples collected from the fields of the study areas was calculated, using the following formula: $EDI = \sum_C \times F / D \times W$

Where $\sum_C$ = Summation of each of the concentrations

F = Daily adult respondents intake mean of water per person/day/ (4Liters)

D = Number of days in a year (365)

W = Mean body weight of adult respondents in the study areas (52.33kg)

Health Risk Index (HRI) was determined using the Expected Daily Intake (EDI) calculated divided by Acceptable Daily Intake (ADI).

Thus: HRI = EDI/ADI. The HRI values that's either less than 1 or greater than1 determined the potentiality levels of exposure of health effects on the consumers (farmers).

Results and Discussion

Analysis of Pesticide Residues in Water from Study Areas

Water samples were collected from different study areas of the main sources which was analyzed. The results indicated that both organochlorine, organophosphates and pyrethroids pesticide residues were detected as indicated on Table 1 below. The results indicated that there is significant relationship between the residue detected and the areas of the study, where organochlorine residues in lake-gerio was detected with higher mean concentration of (0.087ppb). Hence, aldrin is the residue detected with highest mean concentration (0.130ppb) followed by α-BHC (0.048ppb) and dieldrin (0.041ppb) respectively. The area that contained least of organochlorine residues is dasin-hausa with mean concentration of (0.010ppb). Organophosphate residues detected with the highest mean concentration are fenthion (0.013ppb) and diazinon (0.012ppb) respectively. The area that contained highest concentration of organophosphate residues is lake-gerio with mean concentration (0.018ppb) and the area that contained least concentration is dasin-hausa with mean concentration (0.008ppb). Pyrethroid residues detected with highest mean concentration are permethrin (0.018ppb) and cypermethrin (0.016ppb) respectively. The area that contained the highest concentration of pyrethroid residues under study is Chigari with mean concentration (0.019ppb) and the area with least concentration of the residue is Dasin –Hausa with total mean concentration (0.00ppb).

Table 1. Organochlorines, organophosphates and pyrethroids pesticide residues in water sample from different study areas.

S/No.	Pesticides	Area and Residue detected (ppb)				Mean Con.
		Chigari	Dasin	Geriyo	Gurin	(ppb)
	Organochlorines					
1	Aldrin	0.083	0.014	0.346	0.075	0.130
2	Alpha-BHC	0.074	<0.033	0.033	0.084	0.048
3	o, P' – DDT	0.014	0.012	0.022	<0.012	0.012
4	Dieldrin	0.065	0.017	0.058	0.024	0.041
5	Endosulfan I	0.022	0.013	0.072	0.038	0.036
6	Endosulfan II	0.024	0.023	0.032	0.015	0.024
7	Endosulfan sulphate	0.023	<0.023	0.083	0.055	0.040
8	Heptachlor	0.019	<0.019	0.048	<0.019	0.017
	Total Mean Conc. (ppb)	0.041	0.010	0.087	0.036	0.043
	Organophosphates					
1	Chlorpyriphos	<0.013	0.015	0.013	<0.013	0.007
2	Diazinon	0.042	<0.007	0.007	<0.007	0.012
3	Dichlorovos	0.032	<0.032	0.072	0.033	0.010
4	Fenthion	0.013	0.025	<0.013	0.015	0.013
5	Malathion	<0.019	<0.019	<0.019	0.019	0.005
	Total Mean Conc. (ppb)	0.017	0.008	0.018	0.013	0.009
	Pyrethroids					
1	Bifenthrin	<0.019	<0.019	<0.019	0.019	0.005
2	Cypermethrin	0.038	<0.025	0.025	<0.025	0.016
3	Deltamethrin	<0.013	<0.013	0.013	<0.013	0.004
4	Permethrin	0.038	<0.008	0.025	0.008	0.018
	Total Mean Conc. (ppb)	0.019	00	0.016	0.007	0.0104

Risk assessment in Water Samples

The Expected Daily Intake (EDI) was calculated using formula ($\sum_C$ x F/D x MW) which was applied to all 19 pesticide residues detected in water samples from all the four areas under study. HRI was determined by dividing ADI with calculated EDI (HRI=EDI/ADI). The HRI values (≥1 or ≤) indicated the risk involved in consuming the maize sample for a life time.

However, the contaminants found to be risk potentials that are identified in water samples from all the study areas are dichlorodiphenyltrichloroethane (DDT), malathion, cypermethrin, permethrin and bifenthrin which are used as insecticides. The major contaminants are DDT and permethrin, where DDT which is organochlorine origin and permethrin, cypermethrin and bifenthrin are of pyrethroid origin, malathion is of organophosphates. Hence, in a similar study conducted by Zhang, et al (2017) reported in their findings which coincided with this study that DDT, malathion, cypermethrin, bifenthrin and permethrin are both used as insecticides, hence DDT are described as endocrine disruptors, carcinogenic when excessively exposed to it especially during application

through oral, ingestion or skin contact. As in this study where farmers reported to have observed certain symptoms such as skin irritation, abdominal pains, High Blood Pressure etc. From this findings, it indicated that pesticide residues found in the study areas are deleterious which causes ailments and subsequent death to the farmers in the study areas.

Conclusion

Conclusively, water samples in these areas of study is not safe for eg drinking due to presence and persistence nature of high concentration of these pesticide residues identified. However, water samples contained higher risk contaminants with great risk when consumed for a life time.

Table 2. Risk Assessment Table of Water Sample for Adult from Areas under Study

AREAS	**RESIDUES/HRI**					**RISK**
	DDT/HRI	Malathion/HRI	Cypermethrin/HRI	Permethrin/HRI	Bifenthrin/HRI	
Chigari	1.666	___	1.471	1.471	___	**HIGH**
Dasin Hausa	1.95	___	___	___	___	**LOW**
Gurin	___	1.192	___	38.340	3.125	**HIGH**
Lake-Gerio	1.022	___	2.237	2.237	___	**HIGH**

Recommendations

- There are needs to safeguard farmers health through appropriate disseamination of information to both the farmers and consumers s as to reduce mortarlity rate.
- Government should ensure proper handling and disposal of these chemicals by the farmers through enacting new policies at both state and local Government levels so as to reduce environmetal degradation
- Extension services should be invigorated through cheapest channel of communication for effective dissemination of information to the farmers and consumers alike on risk involved in misusage of pesticides during application and storage.

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