Sumerianz Journal of Biotechnology, 2019, Vol. 2, No. 12, pp. 124-133
ISSN(e): 2617-3050, ISSN(p): 2617-3123
Website: https://www.sumerianz.com

Original Article Open Access

Comparative and Quantitative Appraisal of Pesticide Residues in River Water and Soil Samples from Jere Bowl Nigeria

Musa Abubakar*
Department of Basic Science and Technology, Mohamet Lawan College of Agriculture, Maiduguri Borno State, Nigeria

John Abdullahi
Department of Geography, Faculty of Social Science, University of Maiduguri, Borno State, Nigeria

Mu'azu Abdullahi Kofar Na'isa
Department of Planning, Research and Development, Nigerian Institute of Science Laboratory Technology, Ibadan, Nigeria

Gwana Adamu Mohammed
Laboratory Unit, Department of Animal Health and Production Technology, Mohamet Lawan College of Agriculture, Maiduguri, Nigeria

Zanna Wuroma Muhammad
Department of Agricultural Technology, Mohamet Lawan College of Agriculture, Maiduguri, Nigeria

Abstract

This study assessed the concentration levels of five different pesticide residues in water and soil samples that were collected from river Ngadda in Jere bowl, Nigeria. Pooled samples from different locations within five villages were determined by using GC / MS SHMADSU (GC - 17A) with an electron capture detector (ECD) and standard operating procedures were followed. The pesticides (Hexachloro hexahydro dimethanonaphthalene, Dichlorodiphenyl trichloroethene, Cypermethrin, Chlorpyrifos and Dichlorvos) were analysed. Results obtained (µg / g for soil and µg / l for water) revealed a variation in mean concentration levels of the pesticide residues analysed. Bololo, ranged from 9.13 to 38.14 for soil and 1.01 to 15.01 for water. Dusuman; Soil (5.17 to 32.16) and water (5.17 to 32.16). Gongulon; soil (5.27 to 42.10) and water (1.03 to 5.07). Kachallari; soil (17.15 to 24.16) and water (1.11 to 3.7). Masu village; soil (13.13 to 32.19) and water (1.11 to 3.71). The concentration levels were observed to be at alarming levels higher than the maximum residue limits (MRLs) for surface water and soil as described by WHO. The occurrence of the pesticide residues in the river water and soil, are major threats to farmers that are depending on river water for their daily activities and irrigation farming, and the public that is consuming the farm produce. Hence, there are needs for monitoring of pesticides applications and their usage in the said study area and its environs.

Keywords: Concentration levels; Pesticide residues; River Ngadda river water; Soil.

1. Introduction

Generally, to any environmental activities, either natural or human course or both, there are impacts, and these need to be ascertained, assessed and addressed or stated [1]. Over the decades, the public and scientific community have shown interest in pesticides applications and their uses on agricultural farming. Pesticides are seen as means of providing benefits with no justification to any potential risks course to healthcare status.

It is a common, pesticides originally came into use as a means of eliminating pests and limiting their adverse effects on agriculture, household and other aspects of life [2-4].

The benefits of pesticides often come with risks, particularly for farmers and farm workers. These substances are intended to be harmful to living organisms and because they are released into the environment, they pose an exposure and potential health risks to other organisms, including humans [2, 4, 5]. Many of the chemicals are persistent to soil contaminants, whose impact may endure for decades and adversely affect soil conservation. The use of pesticides decreases the general biodiversity in the soil [6]. Pesticide residues in soils expose the crops grown in rotation, additional residues and inhibit beneficial microorganisms to critical levels. Excessive amounts of pesticide residues could alter the soil ecology, threaten the soil flora and fauna, and destroy the metabolic processes of the soil [7]. Pesticide residues in soils enter the food chain through the soil flora and fauna and bioaccumulate in the higher members of the food chain. Disposal of pesticide waste and used containers has been identified as one of the major causes of soil contamination other than for agricultural contamination [8].

There are four major routes through which pesticides reach the water; it may drift outside of the intended area when it is sprayed, it may percolate or leach through the soil, it may be carried to the water as runoff or it may be spilled. They may also be carried to water by eroding soil [9, 10]**.** Fish and other aquatic biota may be harmed by pesticide contaminated water. Pesticide surface runoff into rivers and stream can be highly lethal to aquatic life, sometimes killing all the fish in a particular stream [11]. The chemical residues can pollute surface water as well as

*Corresponding Author

ground water making them unsafe for drinking [12]. The objectives of this study is to determine pesticide residues in water and soil samples from river Ngadda in Jere Bowl, at different locations within five villages and assess the effects of pesticides in soil and water in the study areas.

2. Methodology

Standard operating procedures were followed and observed as described in the methods applied by AOAC [13].

2.1. Study Area

Jere Bowl is situated below 305 m above sea level, north of Maiduguri [14]. It is located between latitude 110° 48' – 110° 58' N and longitude 130° 06' – 130° 20' E in the Sudan – savannah transition zone. Jere Bowl covers an area of about 22,000 ha, out of which a gross area of 15,850 ha was identified as suitable for irrigated agriculture [15]. Jere bowl falls within Jere LGA and it shares boundaries with some local government areas; to the northeast shares border with Nganzai and Mafa, while to the north-west and south-east shares border with Maiduguri and Konduga. The study area was selected based on its proximity, accessibility, relevance of the study and familiarity with the environment. Intensive irrigation activities take place all year round at the banks of the river.

Figure-1. Showed the map of Nigeria, Borno state and Jere Local Government Area

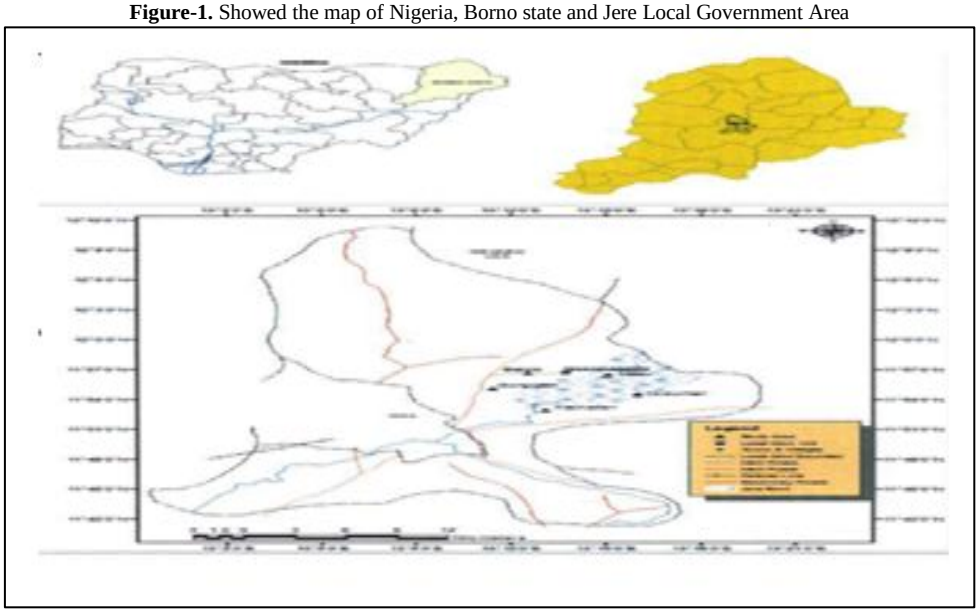
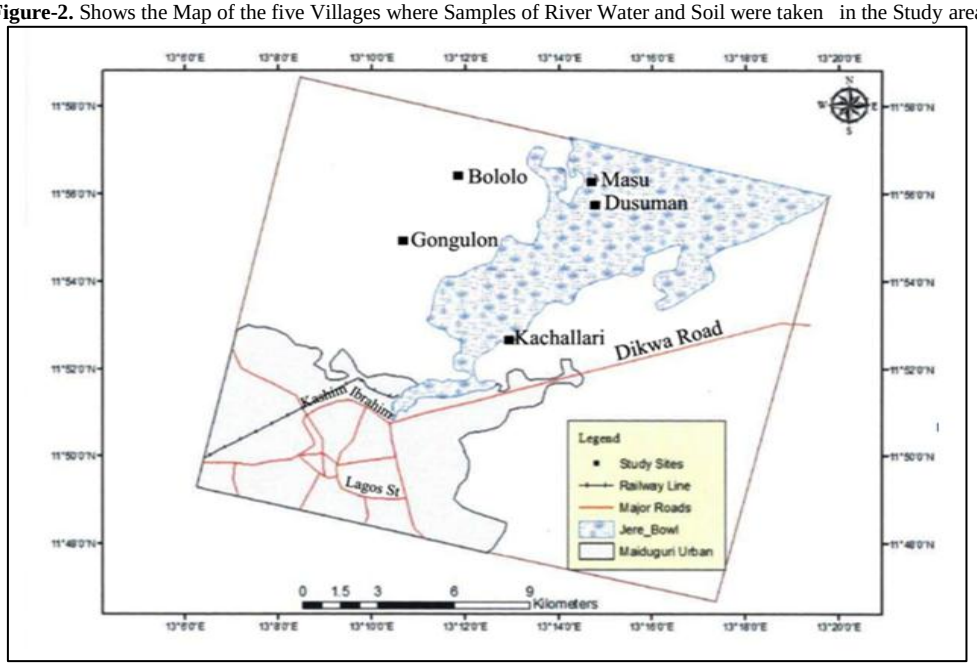


Figure-2. Shows the Map of the five Villages where Samples of River Water and Soil were taken in the Study area



2.2. Materials Used

All the materials and reagents used in the course of conducting this analysis were of analytical grade and standard.

2.3. Methods Applied

Standard operating procedures were followed and observed as described in the methods applied by AOAC [13].

2.3.1. Sampling and Samples Collection (River Water and Soil Samples)

Procedure: - Soil samples were randomly selected and collected from five points from each area at depths of 0.15 cm and 15 to 30 cm, by using spiral Auger of 2.5 cm diameter. The collected soil samples were then pooled together and bulked together to form a composite sample before being placed in clean plastic bags and transported to laboratory. Samples were then air dried. Crushed in to fine particles and sieved through 2 cm nylon sieve as described in the method applied by Gwana, *et al.* [16] and Ashiq, *et al.* [17]. The fine particles were packed in to plastic containers and screwed Capped, labelled with date, name of the person that collected and prepared, serial number for identification. Now are ready for the respective analyses.

2.3.2. Extraction of Soil Sample

Procedure: - The soil samples were extracted using a soil- packed bulb column, and 25 g of each sample was weighed into a glass jar, and fortified at this step, before adding 25 g of pre-cleaned sand and 50 g of granular sodium sulfate. The sample mixture was manually shaken for 30 seconds. It was placed on to roller for 30 seconds. Then allowed to stand for 20 minutes to provide time for the sodium sulfate to absorb any residual moisture from the soil. The sample mixture was then transferred in to a 250 ml bulb column. The sample jar was triple rinsed with small amounts of 5 ml of hexane, then transferred in to the bulb column. The soil content was extracted with 250 ml of acetone hexane (1:1 volume / volume), the elute was collected and concentrated to 100 ml by using a rotary evaporator. The soil extract then subjected to additional clean up as in the method described by Akan, *et al.* [7].

2.3.3. Cleanup of Soil Extracts

The concentrated soil elute was washed by liquid – liquid partitioning with 25 mls saturated sodium sulfate and 300 mls distilled water in a 500 mls seperatory funnel. After shaking, the aliquots' layer was drained into a beaker and hexane was transferred to a 250 mls seperatory funnel as described as the method applied by Fosu, *et al.* [12].

The aqueous layer was returned to the 500 mls seperatory funnel and re-extracted with 40 mls of 15 % dichloromethane in hexane. The organic layer was combined in the 250 ml seperatory funnel and gently washed with 100 mls of distilled water for about 30 seconds. After discarding the aqueous layer, the organic layer was filtered through sodium sulfate, evaporated to near dryness on a rotary evaporated to about 1 ml. The sample extract was quantitatively transferred to a centrifuge tube, concentrated on a nitrogen evaporator to 0.5 ml and diluted to 2.0 ml final volume in hexane prior gas chromatography analysis as in the method described by Akan, *et al.* [7]; Ntow [10].

2.3.4. Collection of River Water Samples

Composite sample of water from the river in each area was collected from four different portions, mixed and pooled together makeup to 2 liters using plastic container. The containers were rinsed twice with the sample to be examined and filled. Out of the pooled sample, 1.5 liters were transferred into plastic bottles. Then it was transported to the laboratory as in the method described by Awofolu [18]; Ntow [10]; Fosu, *et al.* [12].

2.3.5. Extraction of Water Samples

A 1000 mls portion of the filtered water samples were transferred into 2 littres capacity separation flask. Then 30 mls of saturated sodium chloride solution was added to each sample. The samples were thoroughly mixed by inverting the flask three to four times vigorously. A 100 mls of dichloromethane as extraction solvent was then added to each sample and vigorously shaken manually for 2 - 3 minutes, while releasing the pressure intermittently. The phases were allowed to separate for 5 minutes and the dichloromethane extracts were separated from the aqueous layer. The extraction for each water sample was repeated twice with 100 mls of dichloromethane and the organic layer put together and dried over anhydrous sodium Sulphate through filter paper into 50 mls bottom round flasks. The extracts from the water samples were then concentrated on rotary vacuum evaporator to about 1 ml and subjected to cleanup as in the methods described by Ntow [10]; Fosu, *et al.* [12].

2.3.6. Cleanup of Water Samples

Extracts cleanup were done, using polypropylene cartridge columns, packed with 1 g silica gel previously activated for 10 hours in an oven at 1,300 ^{O}C. Two grams' layer of hydrous sodium Sulphate on top of the silica gel were conditioned with 6 mls dichloromethane. The concentrated extracts were then loaded onto the cartridges columns, and 100 mls round bottom flasks placed under the columns to collect the elutes. A 10 mls acetonitrile and 20 mls dichloromethane were then used to elute the cleanup cartridges columns. The total filtrates (elute) collected were concentrated to dryness using the rotary evaporator set at 300 ^{O}C. The residues were re-dissolved in 1 ml of ethyl acetate by pipetting and transferred into 2 ml standard opening vial prior to gas chromatography as in the methods described by Ntow [10]; Fosu, *et al.* [12].

2.3.7. Determination of Pesticide Residues

SHIMADZU – GC / MS (GC – 17), equipped with fluorescence detector was used for the chromatographic separation was achieved by using a 35 % diphenyl and 65 % dimethyl polysiloxane column. The oven was programmed as follows: initial temperature was 40 ^{O}C for 15 minutes to 150 ^{O}C for 15 minutes, 5 ^{O}C for 1 minute to

200 ^{O}C for 7.5 minutes, 25 ^{O}C for a minute to 290 ^{O}C with a final holding time of 12 minutes and a constant column flow rate of 1 ml per minute. The detection of pesticides was performed by using the GC – ion trap MS with optional MSn mode. The scanning mode offered enhances selectivity over either full scanned or selected ion monitoring (SIM). In SIM at the elution time of each pesticide, the ration of the intensity of matrix ions were increase exponentially versus that of the pesticide ions as the concentration of the pesticide approach the detection limit, it decreases the accuracy at lower levels. The GC – ion trap MS was operated in MSn mode and perform tandem MS function by injecting ions into the ion trap, and destabilizing matrix ions, isolating only the pesticide ions. The retention time, peak area and peak height of the sample was compared with those of the standards for quantization as in the method described by Ntow [10]; Akan, *et al.* [7]; Fosu, *et al.* [12].

2.4. Source of Data

The study was conducted in five villages across the Jere Bowl: Bololo, Dusuman, Gongulon, Kachallari and Masu villages irrigated areas. Both primary and secondary sources of data were used.

2.4.1. Primary Data

These were generated from laboratory analysis of soil and water samples collected from irrigated farmlands and rivers.

2.4.2. Secondary Data

The secondary data were obtained from relevant literature.

2.4.3. Data Analysis

Data obtained from this research study was subjected to statistical tools of analysis using graphical presentation, mean for the measurement of central tendency, and standard deviation for measurement of dispersion and or discrepancy within the variables being obtained and its' significance, as described by Stroud and Booth [19].

3. Results

Table 1 showed the mean concentration levels and standard deviation of the pesticide residues in soil from the study areas. The concentration levels (µg / g) of Hexachloro hexahydro dimethanonaphthalene detected in the composite soil samples ranged from 6.11 ± 0.01 to 38.14 ± 0.02, Dichlorodiphenyl trichloroethene (7.11 ± 0.01 to 29.09 ± 0.01), Cypermethrin (5.17 ± 0.01 to 42.10 ± 0.01), Chlorpyrifos (5.27 ± 0.01 to 32.19 ± 0.01), Dichlorvos (6.14 ± 0.01 to 32.16 ± 0.01) respectively. The concentration levels of all the pesticides in the soil samples were observed to be at alarming levels, much higher than the maximum residue limits (MRLs) set for soil by World Health Organization (WHO). This could be attributed to the excessive application of pesticides in the area.

Table 2 showed the mean concentrations and standard deviation of the pesticide residues in river water from the study area. The concentration levels (µg / l) of Hexachloro hexahydro dimethanonaphthalene detected in the composite samples of water ranged from 1.04 ± 0.01 to 2.06 ± 0.02, Dichlorodiphenyl trichloroethene (1.03 ± 0.02 to 2.10 ± 0.01), Chlorpyrifos (3.03 ± 0.01 to 15.01 ± 0.02), Cypermethrin (1.01 ± 0.01 to 3.07 ± 0.01) and Dichlorvos (3.71 ± 0.01 to 13.12 ± 0.02) respectively. The concentration levels of all the pesticides in the river water samples were observed to be at alarming levels, much higher than the maximum residue limits (MRLs) set for surface water by World Health Organization (WHO). This could be attributed to the excessive application of pesticides in the area. Pesticides washed into the river through runoff and erosion from the river banks; also farmers wash empty pesticides containers and sprayers directly into the river.

Table-1. Mean concentration levels of the pesticides in soil samples from the study area

Village	Type of pesticides determined in soil sampled (µg / g)				
	Chlorpyrifos	Cypermethrin	Dichlorodiphenyl Dichlorodiphenyl	Dichlorvos	Hexachloro hexahydro dimethanonaphthalene
Bololo	17.15 ± 0.01	21.12 ± 0.01	9.13 ± 0.01	11.13 ±0.01	38.14 ± 0.02
Dusuman	11.10 ± 0.01	5.17 ± 0.01	7.11 ± 0.01	32.16 ±0.01	10.6 ± 0.01
Gongulon	5.27 ± 0.01	42.10 ± 0.01	14.05 ± 0.01	6.14 ± 0.01	20.04 ± 0.01
Kachallari	24.16 ±0.01	17.15 ± 0.01	19.11 ± 0.01	20.08 ±0.01	20.04 ± 0.01
Masu	32.19 ± 0.01	11.06 ± 0.01	29.09 ± 0.01	19.04 ±0.01	15.12 ± 0.01
*Soil	0.03 µg / g	0.05 µg / g	0.05 µg / g	0.05 µg / g	0.01 µg / g

***Source:** Standard Recommended Values or MRL- Levels, WHO / AOAC, revision 2, section 973 – 42B (b)

Table-2. Mean concentration levels of the pesticide residues in river water sampled from the study area

Village	Type of pesticides determined in soil sampled (µg / g)				
	Chlorpyrifos	Cypermethrin	Dichlorodiphenyl Dichlorodiphenyl	Dichlorvos	Hexachloro hexahydro dimethanonaphthalene
Bololo	15.01 ± 0.02	1.01 ± 0.01	2.10 ± 0.01	13.1 ± 0.02	2.03 ± 0.01
Dusuman	4.40 ± 0.01	3.07 ± 0.01	1.02 ± 0.01	5.13 ± 0.01	1.12 ± 0.01
Gongulon	5.07 ± 0.01	2.01 ± 0.01	1.03 ± 0.02	3.06 ± 0.01	2.02 ± 0.01

Kachallari	3.03 ± 0.01	1.11 ± 0.01	1.69 ± 0.01	3.71 ± 0.01	2.06 ± 0.02
Masu	12.10 ± 0.02	1.46 ± 0.01	2.03 ± 0.01	4.05 ± 0.02	1.04 ± 0.01
*Water	0.05 µg / l	0.05 µg / l	2.0 µg / l	1.0 µg / l	0.03 µg /l

***Source:** Standard Recommended Values or MRL- Levels, WHO / AOAC, revision 2, section 973 – 42B (b)

Figure-3. The concentration (*µg / g*) of pesticide residues in soil sampled per village

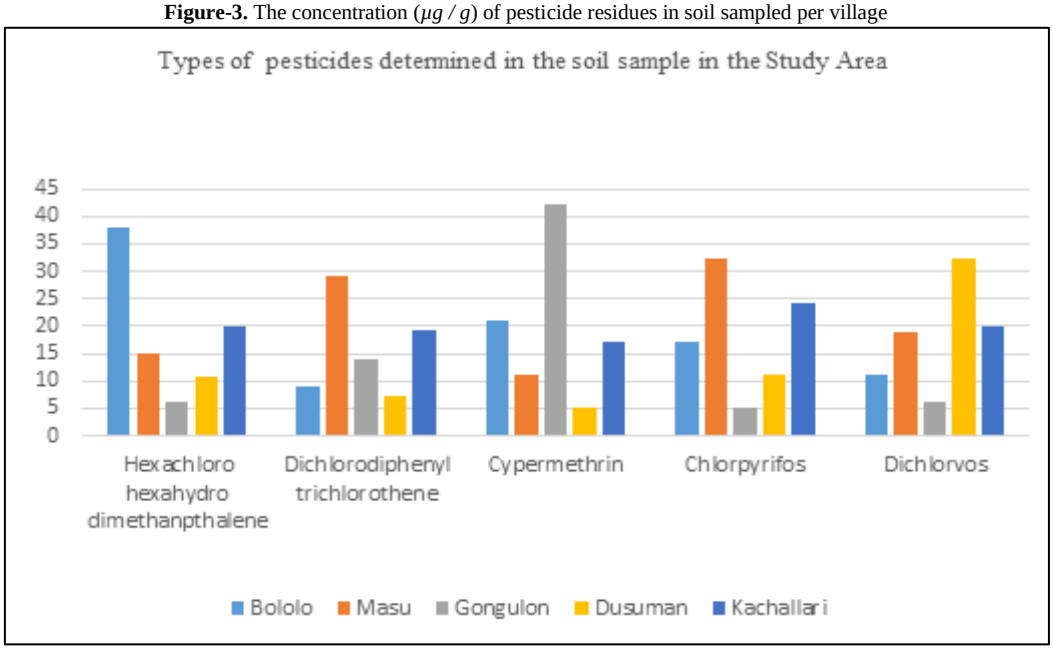
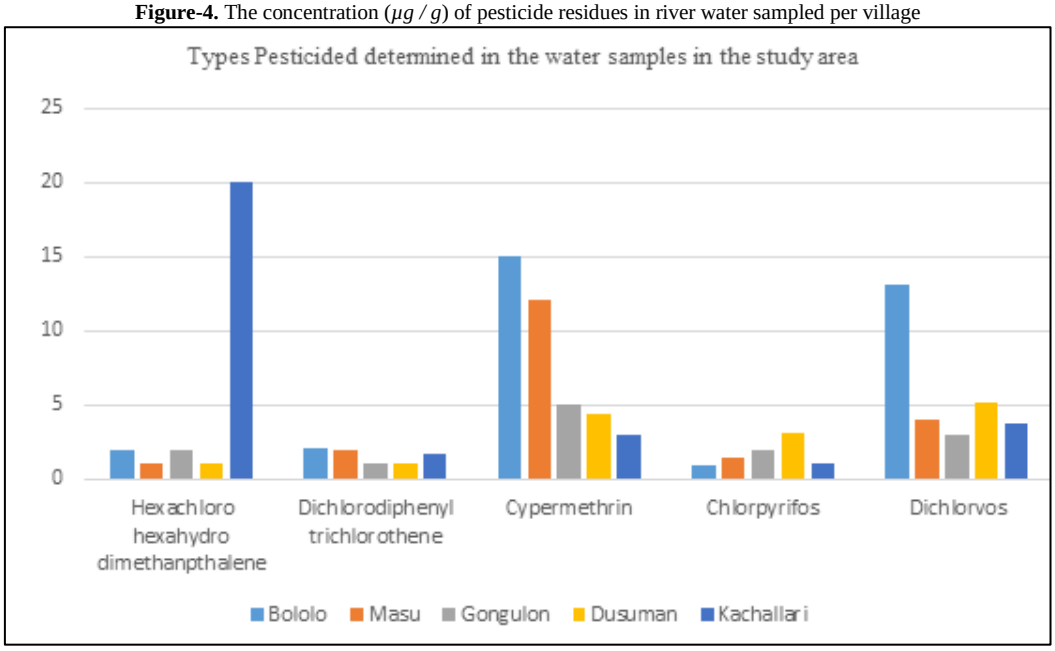


Figure-4. The concentration (*µg / g*) of pesticide residues in river water sampled per village



4. Discussion

Any environmental activities, either natural course or man-made there must be impacts, these need to be assessed, stated and addressed. Some river water and soil sampled, were collected from four villages (Bololo, Dusuman, Gongulon, Kachallari and Masu), at different portions, each mixed and pooled together, from river Ngadda in Jere bowl, Borno state of Nigeria. The samples were analysed to determine and assess pesticide residues. Hexachloro hexahydro dimethanophthalene, Dichlorodiphenyl trichloroethene, Cypermethrin, Chlorpyrifos and Dichlorvos, both qualitatively and quantitatively, and sequential concentration levels order were revealed in the findings of this research study. The observed values were higher at alarming concentration levels exceeded the standard recommended values or minimum residues levels (MRLs levels) by WHO / AOAC. The MRL-Levels for Hexachloro hexahydro dimethanonaphthalene is 0.03 µg /l, Dichlorodiphenyl trichloroethene (2.0 µg / l), Chlorpyrifos (0.05 µg / l), Dichlorvos (1 µg / l) and Cypermethrin (0.05 µg / l in surface water. Also, for soil are; Hexachloro hexahydro dimethanonaphthalene is 0.01 µg / g, Dichlorodiphenyl trichloroethene (0.05 µg / g), Chlorpyrifos (0.03 µg / g), Dichlorvos (0.05 µg / g) and Cypermethrin (0.05 µg / g) as had being prescribed by WHO / AOAC respectively.

Composite soil samples obtained from Bololo village were determined, the results revealed that; soil sample contained moderate amounts of the pesticides at concentration levels ranged from 9.13 to 38.14 µg / g, which exceed the standard recommended values or the minimum residue limit levels (MRLs- levels). Hexachloro hexahydro dimethanophthalene had concentration level of 38.14 µg / g which was the highest, followed by Cypermethrin with the concentration level of 21.12 µg / g, followed by Chlorpyrifos had 17.15 µg / g, Dichlorvos had 11.13 µg / g and least was Dichlorodiphenyl trichloroethene with a concentration level of 9.13 µg / g. That of the pooled sample of river water collected from this village, it revealed that the concentration levels of the pesticides were ranged from 1.01 to 15.01 µg / l, which exceed standard recommended values or the minimum residue limit levels (MRLs- levels) as prescribed by WHO / AOAC. It contained higher amount of Chlorpyrifos which had 15.01 µg / l, followed by Dichlorvos (13.1 µg / l), Dichlorodiphenyl trichloroethene (2.10 µg / l), Hexachloro hexahydro dimethanophthalene (2.03 µg / l) and least was Cypermethrin with the concentration level of 1.01 µg / l respectively.

In comparison, of the pooled and composite samples (river water and soil) obtained from Bololo village, the results revealed that; Hexachloro hexahydro dimethanophthalene had concentration levels in river water (2.03 µg / l) and soil (38.14 µg / g) sampled. The concentration level in soil sample was much higher (x 19 approximately) than that of the river water. For Dichlorodiphenyl trichloroethene had the concentration levels in river water (2.10 µg / l) and soil (9.13 µg / g) sampled. Soil sample had much higher (x 4 approximately) than that of the river water. Cypermethrin in river water and soil (1.01 µg / l and 21.12 µg / l) sampled. Soil sample had most higher (x 21 approximately) than that of the river water. Chlorpyrifos had concentration levels in river water and soil (15.01 µg / l and (17.15 µg / g) sampled. The concentration level of Chlorpyrifos in river water sampled was less than that of the soil sampled. Finally, Dichlorvos concentration levels were 13.10 µg / l and 11.13 for river water and soil sampled. Also, Dichlorvos concentration level in river water sampled was higher than that of the soil sampled. Summarily, amongst the pesticides that determined in river water and soil sampled, four (Hexachloro hexahydro dimethanophthalene, Dichlorodiphenyl trichloroethene, Cypermethrin and Chlorpyrifos) out of the five had higher concentration levels in soil sampled than the river water. While only one pesticide (Dichlorvos) had higher concentration levels in river water sampled than the soil sampled from Bololo village.

The results of the analysis of river water and soil sampled for the pesticides that were obtained from Dusuman village revealed that; composite soil sampled contained moderate amounts of the pesticides at concentration levels ranged from 5.17 to 32.16 µg / g, which exceed standard recommended values or the minimum residue limit levels (MRLs- levels) as prescribed by WHO / AOAC. The highest in amount of pesticides in composite soil sampled was Dichlorvos had a concentration level of 32.16 µg / g, followed by Chlorpyrifos with 11.10 µg / g, Hexachloro hexahydro dimethanophthalene (10.06 µg / g), Dichlorodiphenyl trichloroethene had concentration level of 7.11 µg / g, and the least in terms of concentration level was 5.17 µg / g for Cypermethrin. The pooled sampled of river water collected from this village had revealed that, the concentration levels of the pesticides were ranged from 1.02 to 5.13 µg / l, which exceed standard recommended values or the minimum residue limit levels (MRLs- levels) as prescribed by WHO / AOAC. Dichlorvos had the amount of 5.13 µg / l and was found to be the highest in term of the concentration value, then followed by Chlorpyrifos (4.40 µg / l), Cypermethrin (3.07 µg / l), Hexachloro hexahydro dimethanophthalene (1.12 µg / l) and 1.02 µg / l was for the Dichlorodiphenyl trichloroethene concentration level.

To compare the concentration values between the two samples (river water sampled and soil sampled) that were obtained in Dusuman village; Hexachloro hexahydro dimethanophthalene concentration levels in river water and soil sampled were 1.12 µg / l and 10.6 µg / g. Soil sample had much higher (x 9.5 approximately) than that of the river water. For the Dichlorodiphenyl trichloroethene concentration levels in river water was 1.02 µg / l and that of soil was 7.11 µg / g. The concentration level of soil is much higher (x 7 approximately) than the river water. The concentration levels of Cypermethrin in river water and in soil sampled from Dusuman were 3.02 µg / l and 5.17 µg / g. Soil sample had higher values (x 2 approximately) than that of the river water. The pesticide, Chlorpyrifos concentration levels in river water and in soil sampled were 4.40 µg / l and 11.10 µg / g. Also the concentration level of soil was found to be higher (x 2.5 approximately) than the river water. Lastly, Dichlorvos concentration levels in river water and soil sampled were 5.13 µg / l and 32.16 µg / g. Soil sample had much higher (x 6 approximately) than that of the river water. Hence, all the five pesticides that were determined in soil sampled were found to be much higher than the river water sampled from Dusuman village.

The pooled river water sample and composite soil sample that were collected each from Gongulon village were determined; the results revealed that; soil sample contained higher amounts of the pesticides at concentration levels ranged from 5.27 to 42.10 µg / g, which exceed standard recommended values or the minimum residue limit levels (MRLs- levels) as prescribed by WHO / AOAC. The highest in concentration level in soil sampled was Cypermethrin which value of 42.10 µg / g, followed by Dichlorodiphenyl trichloroethene with 14.05 µg / g, the followed Dichlorvos had 6.14 µg / g, Hexachloro hexahydro dimethanophthalene with 6.11 µg / g and Chlorpyrifos had 5.27 µg / g. Also, the results obtained revealed that the river water sampled collected from Gongulon village contained moderate amounts of the said analytes at alarming concentration levels which ranged from 1.03 to 5.07 µg / l, which also exceed standard recommended values or the minimum residue limit levels (MRLs- levels). Chlorpyrifos which was the highest pesticide determined in concentration level of 5.07 µg / l, followed Dichlorvos had 3.06 µg / l, Hexachloro hexahydro dimethanophthalene had 2.02 µg / l, Dichlorodiphenyl trichloroethene had 2.01 µg / l and finally, Cypermethrin with value of 2.01 µg / l.

When compare the concentration values between the river water sampled and soil sampled, that were obtained in the analysis of the samples from Gongulon village; The pesticide, Hexachloro hexahydro dimethanophthalene concentration levels were 2.02 µg / l in river water sampled and 6.11 µg / g in soil sampled. The analyte in soil sampled was much higher (three times) than river water sampled. Dichlorodiphenyl trichloroethene had the

concentration levels of 2.01 µg / l in the river water sampled and 14.05 µg / g in soil sampled. Soil sampled was seven times of more than the river water sampled in terms of concentration. Cypermethrin concentration levels in river water sampled and soil sampled were 2.01 µg / l and 42.10 µg / g. The soil sampled contained Cypermethrin most higher (approximately 21 times) concentration level than river water sampled. The concentration levels of Chlorpyrifos in river water sampled was 5.07 µg / l and that of the soil sampled was 5.27 µg / g. The analysis revealed that the soil sampled contained Chlorpyrifos more (approximately more 1 times) concentration level than river water sampled. Lastly, Dichlorvos had 3.06 µg / l in river water sampled and the concentration level of 6.14 µg / g in the soil sampled. The concentration level of Dichlorvos in soil sampled was found to be doubled than of the river water sampled. Hence, all the analytes (pesticides) determined in the soil sampled was found to be much higher than that of the river water sampled, which were collected from Gongulon village.

The quantitative analysis of river water and soil sampled collected from Kachallari village for the five pesticides were that, the results obtained of the analytes revealed that, the composite soil sample contained moderate amounts of the of five pesticides at concentration levels ranged from 17.15 to 24.16 µg / g, which exceed standard recommended values or the minimum residue limit levels MRLs- levels as prescribed by WHO / AOAC. The highest among the pesticides in concentration level was Chlorpyrifos with 24.16 µg / g, followed by Dichlorvos (20.08 µg / g), Hexachloro hexahydro dimethanophthalene (20.04 µg / g), Dichlorodiphenyl trichloroethene (19.11 µg / g), and Cypermethrin had the concentration level of 17.15 µg / g. For the river water sampled, the analytes concentration levels ranged from 1.11 to 3.71 µg / l, which exceed standard recommended values or the minimum residue limit levels (MRLs- levels) as prescribed by WHO / AOAC. The pesticide, Dichlorvos concentration level in river water sampled from this village was the highest in terms of concentration with 3.71 µg / l, followed by Chlorpyrifos (3.03 µg / l), Hexachloro hexahydro dimethanophthalene (2.06 µg / l) Dichlorodiphenyl trichloroethene (1.69 µg / l) and the least was Cypermethrin had the concentration level of 1.11 µg / l respectively.

With these results of the analysis obtained from the Kachallari village, when compared; the concentration levels of Hexachloro hexahydro dimethanophthalene, both in river water and the soil sampled were 2.06 µg / l and 20.04 µg / g, the soil sampled had higher (almost 10 times) concentration value more than the river water. Dichlorodiphenyl trichloroethene in the two samples had 1.69 µg / l for river and 19.11 µg / g for soil sampled. The soil oil sampled had higher (almost 11 times) concentration value more than the river water sampled. Cypermethrin had the concentration level of 1.11 µg / l in river water sampled and 17.15 µg / g in the soil sampled. It had much higher concentration level (almost 15.5 times) of the analyte (Cypermethrin) in the soil sampled than the river water sampled. Chlorpyrifos had concentration level of 3.03 µg / l in river water sampled and 24.16 µg / g in the soil sampled. Also Chlorpyrifos had much higher concentration level (approximately 8 times) in the soil sampled than the river water sampled. Dichlorvos concentration level in river water sampled was 3.71 µg / land in the soil sampled was 20.08 µg / g. Soil sampled was five times in concentration level higher than the river water sampled. Hence, in Kachallari village, the five pesticides that were determined in soil sampled were found to be much higher than the river water sampled.

In consideration with the results of the analysis of river water and soil sampled for the pesticides that were obtained from Masu village. It revealed that; composite soil sampled contained much higher amounts of the pesticides at concentration levels ranged from 13.13 to 32.19 µg / g, which exceed the standard recommended values or the minimum residue limit levels (MRLs- levels) as prescribed by WHO / AOAC. The concentration level of the pesticide, Chlorpyrifos, which was the highest in value was found to be 32.19 µg / g, followed by Dichlorodiphenyl trichloroethene with a concentration level of 29.09 µg / g, then followed by Dichlorvos which had 19.04 µg / g, Hexachloro hexahydro dimethanophthalene had 15.14 µg / g and the least was Cypermethrin had a concentration level of 11.06 µg / g. In the analysis of river water sampled from Masu village, the analytes (the five pesticides) concentration levels ranged from 1.01 to 12.10 µg / l, which exceed the standard recommended values or the minimum residue limit levels (MRLs- levels). Chlorpyrifos had 12.10 µg / l in concentration level which was the highest, followed by Dichlorvos with a concentration level of 4.05 µg / l, Dichlorodiphenyl trichloroethene with a concentration level of 2.03 µg / l, Cypermethrin had a concentration level of 1.46 µg / l, and the least in concentration level was Hexachloro hexahydro dimethanophthalene had 11.06 µg / g respectively.

To compare the concentration values between the two samples (river water sampled and soil sampled) that were obtained in Masu village; Hexachloro hexahydro dimethanophthalene concentration levels in river water and soil sampled were 1.04 µg / l and 15.12 µg / g. Soil sample had much higher (approximately 15 times) than that of the river water. For the Dichlorodiphenyl trichloroethene concentration levels in river water was 2.03 µg / l and that of soil was 29.09 µg / g. The concentration level of soil is much higher (approximately 14 times) than the river water. The concentration levels of Cypermethrin in river water and in soil sampled from Musa were 1.46 µg / l and 11.06 µg / g. Soil sample had higher values (approximately 6 times) than that of the river water. The pesticide, Chlorpyrifos concentration levels in river water and in soil sampled were 12.10 µg / l and 32.19 µg / g. Also the concentration level of soil was found to be higher (approximately 3 times) than the river water. Lastly, Dichlorvos concentration levels in river water and soil sampled were 4.05 µg / l and 19.04. Soil sample had much higher (approximately 5 times) than that of the river water. Hence, all the five pesticides that were determined in soil sampled were found to be much higher than the river water sampled from Masu village, and the values exceed that of standard recommended values or minimum recommended levels in soil and water sample by WHO.

In another development, this study revealed that, the analytes (pesticides concerned) determined in each sampled from obtained each village; soil sampled from Bololo had the highest concentration level of the Hexachloro hexahydro dimethanophthalene 38.14 µg / g, seconded by Kachallari village with 20.04 µg / g, followed by Masu vil1age which had 5.13 µg / g, then Dusuman village had 10.6 µg / g, and the least (6.11 µg / g) of analyte was from Gongulon village. when these values that were obtained in the soil sampled from these villages, arranged

sequentially, in descending order of magnitude of their mean concentration levels of the analyte concerned were; Bololo > Kachallari > Musa > Dusuman > Gongulon village.

For the analyte, Dichlorodiphenyl trichloroethene concentration levels in soil sampled from Masu village had highest among the villages with 29.09 µg / g, seconded by Kachallari village with 19.11 µg / g, then followed by Gongulon village with 14.05 µg / g, followed by Bololo village had the concentration level of 9.13 µg / g and the least was from Dusuman village with 7.11 µg / g. Thus, arranged sequential order of magnitude of the mean concentration levels of the analyte concerned, in descending order were; Masu > Kachallari > Gongulon > Bololo > Dusuman village.

The pesticide, Cypermethrin concentration level in soil sampled from Gongulon village had highest among the five villages which was with 42.10 µg / g, then seconded by Bololo village with the concentration level 21.12 µg / g, followed by Kachallari village had 17.15 µg /g, Masu village was with 11.06 µg / g and the least was Dusuman village which had 5.17 µg / g. when these values that were obtained in the soil sampled from these villages, arranged sequentially, in descending order of magnitude of their mean concentration levels of the Cypermethrin concerned were; Gongulon > Bololo > Kachallari > Masu > Dusuman village.

The soil sampled from Masu village had the highest concentration level of the pesticide, Chlorpyrifos with 32.19 µg / g, seconded by Kachallari village with 24.16 µg / g, followed by Bololo vil1age which had 17.15 µg / g, then Dusuman village had 11.10 µg / g, and the least (6.11 µg / g) of analyte was from Gongulon village. when these villages arranged sequentially, in descending order of magnitude of their mean concentration levels of the analyte concerned were; Masu > Kachallari > Bololo > Dusuman > Gongulon village.

Finally, for Dichlorvos concentration levels in soil sampled from Dusuman village had highest among the five villages with 32.16 µg / g, seconded by Kachallari village with 20.08 µg / g, then followed by Masu village with 19.04 µg / g, followed by Bololo village had the concentration level of 11.13 µg / g and the least was from Gongulon village with 6.14 µg / g. Thus, arranged sequential order of magnitude of the mean concentration levels of the analyte concerned, in descending order were; Dusuman > Kachallari > Masu > Bololo > Gongulon village respectively.

Among the results that were obtained from this study, it was revealed that, the five pesticides concerned that were analysed in each river water sampled from each village; Kachallari village had the highest concentration level of the Hexachloro hexahydro dimethanophthalene with 2.06 µg / l, seconded by the Bololo village with 2.03 µg / l, followed by Gongulon vil1age which had 2.02 µg / l, then Dusuman village had 1.12 µg / l, and the least (1.04 µg / l) of analyte was from Masu village. when these values that were obtained in the river water sampled from these villages, arranged sequentially, in descending order of magnitude of their mean concentration levels of the analyte concerned were; Kachallari > Bololo > Gongulon > Dusuman > Masu village.

Another development in this study, it revealed that, the analytes (pesticides concerned) determined in each sampled from obtained each village; the river water sampled from Masu village had the highest concentration level of the Dichlorodiphenyl trichloroethene with 2.03 µg / l, then seconded by Bololo village with 2.10 µg / l, followed by Kachallari vil1age which had 1.69 µg / g, then Gongulon village had 1.03 µg / l, and the least was Dusuman with 1.02 µg / l of the analyte. when these villages were arranged sequentially, in descending order of magnitude of their mean concentration levels of the analyte concerned were; Masu > Bololo > Kachallari > Gongulon > Dusuman village.

In consideration to the pesticide, Cypermethrin concentration level in river water sampled from Dusuman village had highest among the five villages, was with 3.07 µg / l, then seconded by Gongulon village with the concentration level 2.01 µg / l, followed by Masu village had 1.46 µg / l, Kachallari village was with 1.11 µg / l and the least was Bololo village which had 1.01 µg / l. when arranged in sequential order of magnitude, in descending path of their mean concentration levels of the Cypermethrin concerned were; Dusuman > Gongulon > Masu > Kachallari > Bololo village respectively.

For the analyte, Chlorpyrifos concentration levels in river water sampled from Bololo village had the highest among the villages with 15.01 µg / l, thereby Masu village came second with 12.10 µg / l, then followed by Gongulon village with 5.07 µg / l, followed by Dusuman village had the concentration level of 4.40 µg / l and the least was from Kachallari village with 3.03 µg / l. Thus, arranged sequential order of magnitude of their mean concentration levels of the analyte concerned, in descending order were; Bololo > Masu > Gongulon > Dusuman > Kachallari village.

With regard to the river water sampled from these villages, Dichlorvos concentration levels in river water sampled from Bololo village had highest among the five villages with 13.10 µg / l, seconded by Dusuman village with 5.13 µg / l, then followed by Masu village with 4.05 µg / l, followed by Kachallari village had the concentration level of 3.71 µg / l and the least was from Gongulon village with 3.06 µg / l. When arranged sequentially in descending order of magnitude of their mean concentration levels of the analyte concerned were; Bololo > Dusuman > Masu > Kachallari > Gongulon village respectively.

In another consideration to the all of the areas under study, the concentrations levels of the pesticide residues detected values in river water and soil samples, were observed to be high at alarming levels exceeded the MRLs levels as prescribed by WHO / AOAC. The soil may act as an important sign for persistent organic pollutants, including pesticides used presently. The pesticides are said to be hydrophilic in nature and are retained strongly by the soil. Persistent pesticides may slowly breakdown into the soil particles and lead to environmental contaminations, which are closely correlated to agriculture applications. The indiscriminate use of pesticides for long periods may further causes reduction in soil quality. These results that were obtained in this study was in conformity with the findings of Jill [6]. Also supports the work of Glover and Tetteh [8] and Akan, *et al.* [20] who stated that

most of the pesticides were of organophosphorus groups which are persistent and stay in the soil, decomposed slowly and may persist for several years as they are insoluble in water and are retained.

The pesticides interact with the soil and some microorganisms, thus, altering the microbial activity, biochemical reactions and enzymatic activities. These activities, adversely affect the soil vital biochemical reactions including; nitrogen fixation, nitrification and ammonification by deactivating specific soil enzymes. These may lead to decrease in soil qualities. The pesticides may or have influence in mineralization of soil matter also, which is a key to soil property that which determines the soil quality and productivity were by causes significant reduction in soil organic matter. Also earthworms play an important significant role in improving soil fertility by decomposing the organic matter into humus. These earthworms are affected by various agricultural practices and indiscriminate use of pesticides is one of the leading practices adversely affecting them. The present study also consisted with findings of Po-Lud, *et al.* [4], and that of Pal, *et al.* [21], also support the statement made by Okoronko, *et al.* [22] who stated that pesticides that reach the soil can alter the soil microbial diversity, any alteration in the activities of soil microorganisms can eventually lead to the disturbance in soil ecosystem and loss of soil fertility. Jill [6] and Rodrigo, *et al.* [23], stated that pesticides adversely could influence the function of beneficial root colonizing microbes such as bacteria and mycorrhiza, fungi and algae in soil by influencing their growth, colonization and metabolic activities.

This study revealed that in all the areas under study the concentrations of pesticide residues detected in river water samples, the observed values were high at alarming levels exceeded the MRLs levels as prescribed by WHO / AOAC The potential for water pollution was noted during the survey farmers were seen washing pesticide sprayers and empty containers in the river channel. The aquatic systems are likely to suffer more from the pollution because there are sinks of pollutants that enters the water, the effects can also be realized in people since Jere Bowl are sources of livelihood for human communities and support different animal and plant lives. This was in conformity with findings of Fosu, *et al.* [12].

Pesticide residues in water are a major concern as they pose a serious threat to marine ecosystem including humans. The effects of pesticides within an aquatic environment is influenced by their water solubility and uptake ability within some organisms. Unsustainable agriculture and over extraction of water from rivers for irrigation have serious negative consequences on biodiversity and threaten the sustainability of water resources in the Jere Bowl. This finding was consisted with the findings of Nasr [24], and the statement or assertion made by Rodrigo, *et al.* [23] who stated that, pesticides generally move from fields to various water reservoirs by runoff or in drainage induced by rain or irrigation.

Therefore, pesticides and its active metabolites in water would lead to contamination of water bodies and possibly affecting the health of aquatic biota, fishes, amphibians and birds. Many fish and amphibians' killings are caused by dissolved oxygen depletion rather than direct pesticide effect. It may cause bioaccumulation in many animals including human and that affects their health status. Another effect of toxic contaminations is on olfaction in fishes since it can affect activities such as mating, locating food, avoiding predators, reduce their survivor and development. this research study was consisted with findings and reports of most researchers and authors; especially, Essumang, *et al.* [11]; Rodrigo, *et al.* [23]; Glover and Tetteh [8]; Akan, *et al.* [20].

5. Conclusion

Pesticide residues were detected in all the soil and water samples collected from the areas under the study. The concentrations of all the pesticides in the soil and river water sampled were observed to be much higher than the set maximum residue limits (MRLs) as prescribed by WHO / AOAC. Farmers are not adequately enlightened on the application of pesticides and seem to be one of the ways of pollution and may have effect not only on the soil of the areas where pesticides are applied, but pesticides are also washed into aquatic ecosystems by water runoff, soil erosion and washing of sprayers and empty pesticides in the water channels.

Acknowledgement

It is a great pleasure to acknowledge the great role played by, especially, Farmers Association of Nigeria, Jere Chapter, Borno state of Nigeria. The Civilian Joint Task Force (JTF) on civil security matter. The family of Late Mr. Daniel Istafanus Birma of Soil Science Laboratory, Department of Soil Science, Faculty of Agriculture, University of Maiduguri, Maiduguri; Nigeria, for their support and assistance given to us. We owe particular thanks to all those authors and researchers cited in this piece of work and most grateful to all persons who have helped or assisted in one way or the other in the course of conducting this research study. Thanking you and very grateful to you all.

References

[1] Gwana, A. M., Bassey, E. E., Buhari, B. Y., Malah, A. M., Umaru, B. W., Mohammed, L. S., Shettima, U. K., and Halima, M. B., 2017a. "Role of SLT: Environmental impact assessments and statements concept." *International Journal of Environmental Protection and Policy* vol. 5, pp. 1–7.

[2] Andreu, V. and Pico, Y., 2012. "Determination of currently used pesticides in biota." *Anal. Bioanal. Cham.*, vol. 40, pp. 2659-2681.

[3] Musa, A., Wakil, M., and Bukar, A., 2018. "Farmers awareness on the effects of pesticides application on irrigated farmlands in Jere Bowl, Borno State, Nigeria." *Journal of Pure and Applied Science*, vol. 9, pp. 80-91.

[4] Po-Lud, C., Mung-Mu, H., and Tai-Chia, C., 2016. "Recent advances in the determination of pesticides in environmental samples by capillary electrophoresis." *Int. J. Environ. Res. Public Health,* vol. 13, pp. 1-20.

[5] Aktar, W., Senguta, D., and A., C., 2009. "Impact of pesticides use in agriculture: benefits and hazards." *Interdisciplinary Toxicology,* vol. 2, pp. 1-2.

[6] Jill, C., 2010. "Pesticide effects on soil biology montana region Australia." *Leading Edge,* vol. 8, pp. 5-8.

[7] Akan, J. C., Jafiya, L., Mohammed, Z., and Abdulrahman, F. I., 2013. "Determination of some organophosphorus pesticide residues in vegetable and soil samples from alau dam and gomgulon agricultural areas, Borno State, Nigeria." *International Journal of Environmental Monitoring and Analysis,* vol. 1, pp. 58-64.

[8] Glover, M. A. and Tetteh, F. M., 2008. "Effects of pesticide application rate on vegetables and soil " *West African Journal of Applied Ecology,* vol. 12, pp. 1-7.

[9] Bhata, S. C., 2002. *Environmental chemistry*. New Delhi: CBS Publishers and Distribution. p. 442.

[10] Ntow, J. W., 2008. "Pesticide residues in Volta Lake, Ghana." *Research and Management,* vol. 10, pp. 243-248.

[11] Essumang, D. K., Togoh, G. K., and Chokky, L., 2009. "Pesticide residues in the water and fish." *Bulletin of the Chemical Society of Ethiopia,* vol. 2, pp. 19-27.

[12] Fosu, M. B., Okoffo, E. D., and Mensah, M., 2016. "Synthetic pyrethroids pesticide residues in soil and drinking water sources from Cocoa farms in Ghana." *Environment and Pollution,* vol. 5, pp. 45-53.

[13] AOAC, 1990. *Official methods of analysis. Association of official analytical chemists*. 15th Edition ed. Gaithersburg, USA: AOAC Press.

[14] Nyanganji, J. K., 2002. *The morphology and hyrolography of the ngadda catchment and the bama beach ridge*. Frankfurt and Main Publishers.

[15] Jibirin, J. M., 2010. "Forms of potassium and potassium sorption in some fadama soil of Nigeria." *Savannah Journal of Agriculture,* vol. 4, pp. 46-53.

[16] Gwana, A. M., Buhari, B. Y., Bassey, E. E., Adam, A., Mohammed, L. S., Mohammed, L. M., and Hauwa, L. B., 2017b. "Determinations of some selected heavy metals and elements in soil of the college's farm, college of agriculture, maiduguri, north – eastern nigeria, . Special issue. The role of slt: Environmental impact assessment and statement concept." *International Journal of Environmental Protection and Policy,* vol. 5, pp. 17-22.

[17] Ashiq, Hussain, L., Eugenia, P., Lai, Sasya, Thakur, Ganie, S. A., Mohammed Saleem, W., Ani, K., *et al.*, 2013. "Accumulation of heavy metals on soil and vegetable crops grown on sewage and tube well water irrigation." *Academic Journals,* vol. 8, pp. 2187-2193.

[18] Awofolu, O. D. R., 2005. "A survey of trace metals in vegetables, soil and lower animal along some selected major roads in metropolitan, Lagos." *Environmental Monitoring and Assessment,* vol. 105, pp. 431–447.

[19] Stroud, K. A. and Booth, D. J., 2001. *Statistical package Engineering mathematics +www. Palgrave.Com / stroud, pal grave, GB*. london, pp. 1130 -113.

[20] Akan, J. C., Jafiya Mohammed, Z., and I., A. F., 2014. "Determination of some organochlorine pesticide residues in vegetable and soil samples from alau dam and gongulun agricultural sides, Borno State, Nigeria." *Jurnal of Chemical Nuclear Materials and Metallurgical Engineering,* vol. 8, pp. 16-22.

[21] Pal, R., Chakrabarti, R., Chakarabarty, L., and Chowdhury, A., 2006. "Degradation and effects of pesticides on soil micro-biological parameters. A review." *Int. J. Agric. Res.*, vol. 1, pp. 240-258.

[22] Okoronko, N., Igwe, J. C., and Onwuchelcua, E. C., 2005. "Risk and health implication of polluted soil for crop production." *American Journal of Biotechnology,* vol. 4, pp. 1521–1524.

[23] Rodrigo, N. A., Otaran, N., and Otaran, M. A., 2014. "Electrochemically assisted remediation of pesticides in soil and water. A review." *Chem. Rev.*, vol. 1, pp. 8720-8754.

[24] Nasr, M. F., 2013. "Monitoring of organophosphorus residues in water from the Nile River Tributaries, Egypt." *American Journal of Water Resources,* vol. 1, pp. 1-4.