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Organochlorine, Organophosphorus and Pyrethroid Pesticides Residues in Water and Sediment Samples from River Benue in Vinikilang, Yola, Adamawa State, Nigeria Using Gas Chromatography-Mass Spectrometry Equipped with Electron Capture Detector

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Abstract Water and sediment samples from ten (10) different sampling points along river Benue, in Vinikilang, Yola, Adamawa State, Nigeria, were collected for the determination of organochlorine (o, p-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT , p,p'-DDT dieldrin and aldrin), organophosphorus (dichlorvos, diazinon, chlorpyrifos, fenitrothion and Malathion) and pyrethriod (cypermethrin, bifenthrin, permethrin and deltamethrin) pesticide residues. Sample collection and preparation were carried out using standard procedures. The concentrations of all the pesticides in water and sediment samples were determined using GC/MS SHIMADZU (GC-17A) equipped with electron capture detector. The concentrations of organochlorine, organophosphorus and Pyrethriod pesticide residues were significantly higher in the sediment samples than water samples. According to the concentrations and detection frequency, dieldrin and aldrin were the most dominant compounds among the organochlorine pesticide residues. The total concentration of aldrin in the water sample was 2.96 mg/l compared to 11.25 µg/g in the sediment sample and the total concentration of dieldrin in the water sample was 4.36 mg/l compared to 13.37 µg/g in the sediment sample. Chlorpyrifos and dichlovos were the most dominant compounds among the organophosphoruses with the total concentration of Dichlorvos in the water sample being 0.57 mg/l and 22.16 µg/g in the sediment sample. Permethrin and deltamethrin were the dominant compounds among the pyrethroid pesticides. The total concentration of cypermethrin in the water sample was 0.69 mg/l, whereas in the sediment samples, 10.64 µg/g was detected. Results from this study indicates that the water and sediment samples within the study area were contaminated by the studied pesticides. The results also show that there still exists a variety of the studied pesticides in the water and sediment from river Benue, Vinikilang, Yola, Adamawa State. Despite bans and restrictions on the usage of some of these pesticides in Nigeria, the observed concentrations of the Organochlorine, Organophosphorus and Pyrethroid pesticides from the ten sampling points could explain either their persistence in the environment or continued use within the banks and tributary of river Benue.

Keywords: *pesticide, residues, water, sediment, extraction, clean-up*

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1. Introduction

Pesticides use has increased worldwide, particularly in its use to salvage the food supply to the ever increasing global population. Although it is undisputed that pesticides are essential in modern agriculture, there is growing concern about possible environmental contamination from agrochemicals industries, household, rain water runoff from agricultural systems, disposal of outdated stocks, containers and packets and discharge of waste from industries [6,16,19]. These compounds when discharged into aquatic system play an important role in contaminating such systems. Atmospheric transport also represents an important source of pesticides residue accumulation in water bodies [17]. It has been recognized that the persistent and bioaccumulation tendency of these substances, their metabolites and residues in the environment make them not only remain where they are applied but instead partition between the major environmental compartments in accordance with their physicochemical properties and may thereby become transported several kilometers from the point of their original release [1]. Sediment serves as a habitat for benthic biota (such as insects and clams, which are commonly consumed by fish), as both a source and a removal mechanism for some contaminants to and from the stream and as a vehicle for contaminant transport downstream. Aquatic biota also are important in the food web of terrestrial organisms, with some aquatic biota, such as fish, being consumed by people and wildlife.

Benue river is the major tributary of the Niger river and is approximately 1,400 km long. It is one of the largest rivers in Nigeria, lies between longitude 12^0 E and 13^0 E of the Greenwich and latitude 9^0 N and 10^0 N of the equator, at an elevation of 97 meters above sea level in the Southern Guinea Savannah agroecological zone. River Benue is the second most important river in Nigeria. The river Benue originates from northern section of the central hills of the Cameroon Republic, mainstem rises on the Adamawa Plateau in northern Cameroon and certain tributaries rise in the southeastern mountainous regions of Chad. Major tributaries of the Benue are the Gongola river and the Mayo Kébbi, which connects it with the Logone river when flood stage is occurring. Other minor tributaries are the Taraba river and Katsina Ala river. After exiting Cameroon, the Benue river proceeds west, south of the Mandara mountains, passing through Jimeta, near the Nigerian city of Yola, Adamawa State to Makurdi in Benue State, prior to discharging to the Niger river at Lokoja, Kogi State [20]. The Logone floodplain is surrounded by rich grasslands that hosted a large number of grazing animals. The main economic activities around the shores of the river Logone are crop farming and fishing. The major crops include cocoa and cotton. Cultivation of vegetable is particularly done along the bank of the river using irrigation with water from the river. The major agricultural activities around the shores of the river Taraba are fishing, farming of rice, yam and groundnut. Kiri dam is located on river Gongola in Shelleng Local Government Area of Taraba State and is mainly constructed in order to supply water to the Savannah Sugar Company in Numan, Numan Local Government Area of Adamawa State for irrigation purpose. The economic resources are mainly agricultural, and the major crops are groundnuts, maize and guinea corn. Pesticides and fertilizers are applied on farm lands along the major tributaries of river Benue and thus is a major contributor of pesticide load into these tributaries. Fishing is a very important activity on the Mayo Kebbi river. In the surrounding areas, a number of activities threaten the site and others have the potential to do so, some of which include: oil exploration, gold and cement mining, cotton and subsistence agriculture around the firm ground of the wetland area. There are also significant amounts of pesticides used in the cotton industries in Ngorore, Adamawa State. The Mayo Kebbi river can be contaminated by agrochemicals, water runoff and percolation from the cotton fields.

Vinikilang is a fast growing community in Jimeta, Yola, located on the slope of Bagale hill through which river Benue flows. River Benue receives a wide variety of wastes from surrounding agricultural lands which contaminate the river with a variety of pesticides acting as source points. This river is also used for commercial fishing activities. Most farmers within the shores of river Benue and its tributaries are said to use fertilizers, synthetic chemicals and pesticides to increase crop yield and control pests on crops including a number of highly persistent organochlorine and organophosphorus pesticides to check and control pests, diseases, weeds and other plant pathogens in efforts to reduce or eliminate yield losses and preserve high product quality. Lack of knowledge of proper use and side effects of these pesticides among small and large scale farmers has resulted in their misuse. Consequently, the wastes generated flow into river Benue, which may contaminate it with a variety of pesticides. Such contaminants might accumulate in the water, sediments and also bioaccumulate in the various organs of fishes and other aquatic organisms, which may affect humans and other species that depend on the aquatic organism as food.

2. Materials and Methods

2.1. Sampling Points

Water and Sediment samples were collected from ten (10) different sampling points designated S_1 to S_{10}. Samples were collected from a point of higher activities to a point of lower activities. Water and Sediment samples were collected at Greng town designated S_1. Point S_2 was located 1 Km away from point S_1, Point S_3 to S_{10} were located 1Km away from each other, making a total of 10 Km for this study. Water and Sediment samples were collected approximately 10 meters away from the bank of the river.

2.2. Collection of Water Samples

Water samples were collected in 900ml amber glass bottle previously cleaned by washing in non-ionic detergent, rinsed with tap water and later soaked in 10% HNO_3 for 24 hours and finally rinsed with deionised water prior to usage. During sampling, sample bottles were rinsed with sample water three times and then filled to the brim at a depth of one meter below the water surface from each of the ten designated sampling points (S_1 to S_{10}). At each sampling point, water sample was collected in triplicate from three points at a distance of 5 meters from each other and pooled. The samples were labeled and transported to the Chemistry laboratory, University of Maiduguri, stored in the refrigerator at 4°C in order to avoid breakdown of pesticides prior to analysis.

2.3. Collection of Sediment Samples

Sediment samples were collected from river Benue in Vinikilang (points S_1 to S_{10}) using a plastic hand trowel by scooping 1-5cm of the top layer sediment. One kilogram (1kg) of sediment sample was collected at each point, wrapped in a labelled aluminium foil, the labeled samples were stored in an ice-packed cooler and transported to the Chemistry laboratory,University of Maiduguri and stored in a refrigerator at 4°C in order to avoid breakdown of the pesticides prior to analysis.

2.4. Extraction of Water Samples

Liquid–liquid extraction method was used for the determination of pesticide residue according to the procedure described by Pandit *et al.*, [14]. A 50 ml volume of n-hexane was introduced into a 2 litre separating funnel containing 1 litre of filtered water and was shaken manually for 5 min and allowed to settle. After complete separation, the organic phase was drained into a 250 ml Conical Flask, while the aqueous phase was re-extracted twice with 50 ml of n-hexane. The three extracted organic phases were combined and dried by passing through a glass funnel containing anhydrous sodium sulfate. The organic fraction was concentrated using rotary evaporator.

2.5. Extraction of Sediment Samples

Dry Sediment samples were extracted according to Darko *et al.*, [5]. A 10g portion of Sediment sample was transferred into an extraction thimble that had been previously washed with n-hexane and acetone and oven dried. The sample was extracted using 150 ml of n-hexane/acetone mixture 4:1 v/v for eight hours (8hrs) using soxhlet extractor. The extract was evaporated to dryness using a rotary evaporator at 40^{o}C. Each extract was dissolved in 10 ml n-hexane and subjected to clean-up procedure.

2.6. Sample Clean-Up for Sediment

The residue of the extraction step of each Sediment sample was dissolved in 4 ml n-hexane and transferred into a florisil mini-column (8 mm, filled with 3.5g of 7% deactivated florisil with distilled water, and a 1cm layer of anhydrous sodium sulfate was used to cork the florisil from both sides). The florisil column was washed with 10 ml n-hexane before use. The pesticides were eluted from the column with 150 ml of 30% diethyl ether in n-hexane (v/v). The eluate was evaporated at ≤40°C to dryness using a rotary evaporator and dissolved in 1ml of ethyl acetate for Gas Chromatograph analysis [11].

2.7. Determination of Pesticide Residues

The SHIMADZU GC/MS (GC – 17A), equipped with electron capture detector was used for the chromatographic separation and was achieved using a 35% diphenyl/65% dimethyl polysiloxane column. The oven was programmed as follows: initial temperature 40°C, 1.5 mins; to 150°C, 0.0 min. 5°C/min. to 200°C, 7.5 mins; 25°C/mins; to 290°C with a final hold time of 12 mins. and a constant column flow rate of 1mL/min. The detection of pesticides were performed using the GC-ion trap MS with optional MSn mode. The scanning mode offered enhances selectivity over either full scaned or selected ion monitoring (SIM). In SIM, at the elution time of each pesticide, the ratio of the intensity of matrix ions increase exponentially versus that of the pesticide ions as the concentration of the pesticide approach the detection limit, decreasing the accuracy at lower levels. The GC-ion trap MS was operated in MSn mode and performed 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 samples were compared with those of the standards for quantization.

3. Results

The mean concentrations of some organochlorine pesticide residues in water samples from river Benue in Vinikilang, Adamawa State for points S_1 to S_{10} are as presented in Table 1. The concentration of o, p-DDE range from 0.28±0.10 to 1.06± 0.3mg/l; 0.54±0.08 to 1.14±0.54 mg/l p,p'-DDD; 1.10±0. 12 to 2.16±0.34 mg/l o,p'-DDD; 0.15 ± 0.03 to 0.66±0.12 mg/l p,p'-DDT; 2.31±0.44 to 3.75±0.01 mg/l aldrin; 3.65±1.00 to 5.24±0.23 mg/l dieldrin. The mean concentrations of some organochlorine pesticide residues in sediment samples from river Benue in Vinikilang, Adamawa State for points S_1 to S_{10} are as presented in Table 2. The concentration of o, p-DDE range from 0.51±0.02 to 4.73±0.08 µg/g; 0.95±0.08 to 9.29±1.51 µg/g p,p'-DDD; 1.90±0.20 to 11.15±1.60 µg/g o,p'-DDD; 0.15±0.03 to 2.59±0.51 µg/g p,p'-DDT; 2.32±0.45 to 15.70±2.00 µg/g aldrin; 4.02±0.60 to 20.01±2.21 µg/g dieldrin.

Table 1. Mean Concentrations of Some Organochlorine Pesticide Residues in Water Samples from Different Sampling Points, on River Benue in Vinikilang, Adamawa State, Nigeria

	Concentrations (Mg/l)					
Sample	**o, p-DDE**	**p,p'-DDD**	**o,p'-DDD**	**p,p'-DDT**	**aldrin**	**dieldrin**
S1	0.76^{a}±0.13	0.87^{a}±0.20	1.10^{a}±0.12	0.45^{a}±0.10	2.31^{a}±0.44	3.83^{a}±0.50
S2	1.06^{b}±0.30	1.10^{b}±0.20	1.39^{b}±0.40	0.66^{b}±0.12	3.17^{b}±0.42	4.80^{b}±1.00
S3	0.65^{c}±0.22	1.14^{c}±0.54	1.31^{c}±0.31	0.27^{c}±0.10	2.4^{c}±0.30	3.65^{c}±1.00
S4	0.28^{d}±0.10	1.01^{d}±1.00	1.12^{d}±0.1	0.19^{d}±0.03	2.8^{d}±0.40	3.86^{d}±0.30
S5	0.51^{e}±0.20	0.94^{e}±0.33	1.70^{e}±0.30	0.25^{e}±0.05	3.10^{e}±0.50	4.63^{e}±1.00
S6	0.59^{f}±0.20	0.98^{f}±0.21	1.73^{f}±0.20	0.28^{f}±0.05	3.49^{f}±0.23	4.99^{f}±0.40
S7	0.68^{g}±0.14	0.75^{h}±0.10	1.65^{g}±1.00	0.43^{g}±0.10	2.92^{g}±0.21	3.89^{g}±0.33
S8	0.34^{h}±0.11	0.54^{i}±0.08	1.54^{h}±0.02	0.21^{h}±0.04	3.75^{h}±0.01	4.66^{h}±0.03
S9	0.54^{i}±0.30	0.79^{j}±0.20	2.16^{i}±0.34	0.26^{c}±0.10	3.31^{i}±0.40	5.24^{i}±0.23
S10	0.51^{e}±0.22	0.95^{k}±0.10	1.90^{j}±0.20	0.15^{i}±0.03	2.32^{j}±0.50	4.02^{j}±0.60

* Within Columns Mean with different letters are statistically different, P< 0.05.

Table 2. Mean Concentrations of Some Organochlorine Pesticide Residues in Sediment Samples from Different Sampling Points , on River Benue in Vinikilang, Adamawa State, Nigeria

	Concentrations (µg/g)					
Sample	o, p-DDE	p,p'-DDD	o,p'-DDD	p,p'-DDT	aldrin	dieldrin
\S1	$0.51^{a}\pm0.02$	$0.95^{a}\pm0.08$	$2.00^{a}\pm0.16$	$0.15^{a}\pm0.03$	$2.32^{a}\pm0.45$	$4.02^{a}\pm0.60$
S2	$3.89^{b}\pm1.50$	$6.38^{b}\pm1.00$	$8.22^{b}\pm1.08$	$2.14^{b}\pm0.27$	$10.52^{b}\pm2.68$	$13.53^{b}\pm2.37$
S3	$4.12^{c}\pm2.50$	$7.54^{c}\pm2.60$	$8.24^{c}\pm1.70$	$1.60^{c}\pm0.94$	$7.74^{c}\pm1.30$	$11.07^{c}\pm1.40$
S4	$2.62^{d}\pm1.00$	$5.69^{d}\pm1.10$	$9.05^{d}\pm1.70$	$1.70^{d}\pm0.54$	$10.16^{d}\pm1.50$	$14.89^{d}\pm1.30$
S5	$3.66^{e}\pm2.00$	$7.96^{e}\pm1.40$	$9.78^{e}\pm0.60$	$2.59^{e}\pm0.51$	$13.11^{e}\pm1.50$	$15.74^{e}\pm2.64$
S6	$3.40^{f}\pm1.31$	$6.22^{f}\pm0.80$	$11.15^{f}\pm1.60$	$1.89^{f}\pm0.50$	$14.86^{f}\pm2.31$	$17.60^{f}\pm1.24$
S7	$3.23^{g}\pm1.10$	$9.29^{g}\pm1.51$	$9.00^{d}\pm2.50$	$2.06^{g}\pm0.64$	$12.71^{g}\pm3.04$	$16.08^{g}\pm1.60$
S8	$3.62^{h}\pm1.40$	6.51h±0.64	$10.3^{g}\pm2.60$	$1.78^{h}\pm0.34$	$15.70^{h}\pm2.00$	$20.01^{h}\pm2.21$
S9	$4.73^{i}\pm0.80$	$8.59^{g}\pm1.33$	$12.32^{h}\pm1.30$	$2.21^{i}\pm1.10$	$14.30^{i}\pm1.10$	$15.24^{i}\pm0.23$
S10	$0.51^{j}\pm0.22$	$0.95^{a}\pm0.10$	$1.90^{i}\pm0.20$	$0.15^{j}\pm0.03$	$12.32^{j}\pm0.50$	$18.02^{j}\pm0.60$

* Within Columns Mean with different letters are statistically different, P< 0.05.

The mean concentrations of some organophosphorus pesticide residues in water samples from river Benue in Vinikilang, Adamawa State for points S_1 to S_{10} are as presented in Figure 1. The concentration of Dichlorvos ranges from 0.17±0.04 to 1.06±0.60 mg/l; 0.09 ±0.03 to 1.75±0.71 mg/l Diazinon; 0.13±0.20 to 1.17±0.40 mg/l Chlorpyrifos; 0.23±0.10 to 0.91±0.20 mg/l Fenitrothion; 0.17±0.11 to 1.93±0.10 mg/l Malathion and 0.41±0.34 to 0.87±0.40 mg/l Fenthion. For sediment samples as presented in Figure 2, the mean concentration of Dichlorvos ranges from 19.38±2.10 to 25.31±2.60 µg/g; 10.50±3.13 to 26.56±0.70 µg/g Diazinon; 14.79±4.44 to 24.58±3.93 µg/g Chlorpyrifos; 17.99±2.10 to 37.43±5.20 µg/g Fenitrothion; 11.17±2.10 to 26.35±1.00 µg/g, Malathion and 16.26±5.40 to 28.38±2.60 µg/g Fenthion.

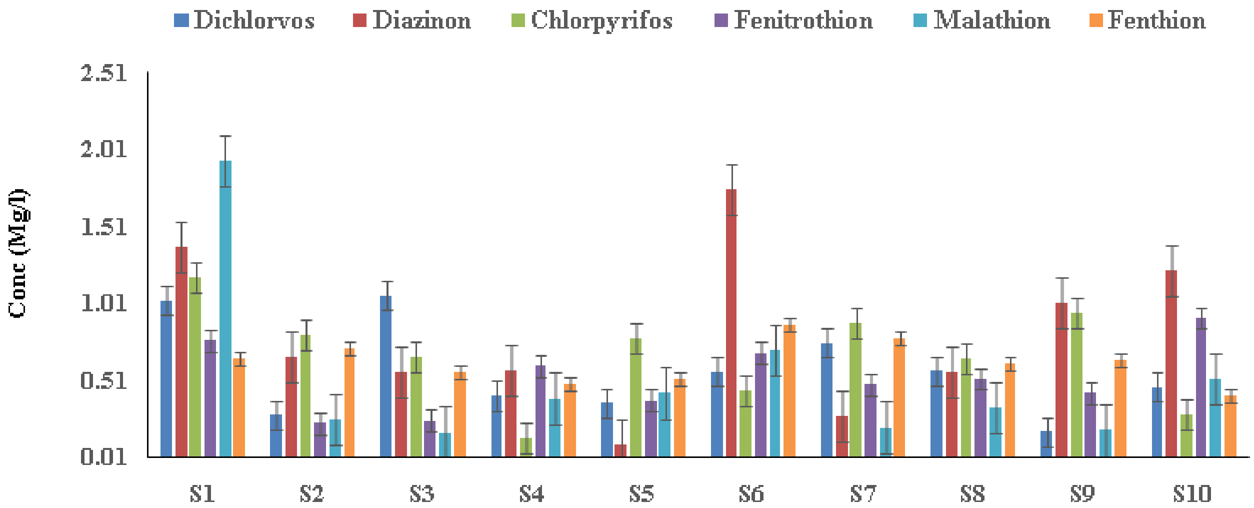

Figure 1. Mean Concentrations of Some Organophosphorus Pesticide Residues in Water Samples from Different sampling Points , on river Benue in Vinikilang, Yola, Adamawa State, Nigeria

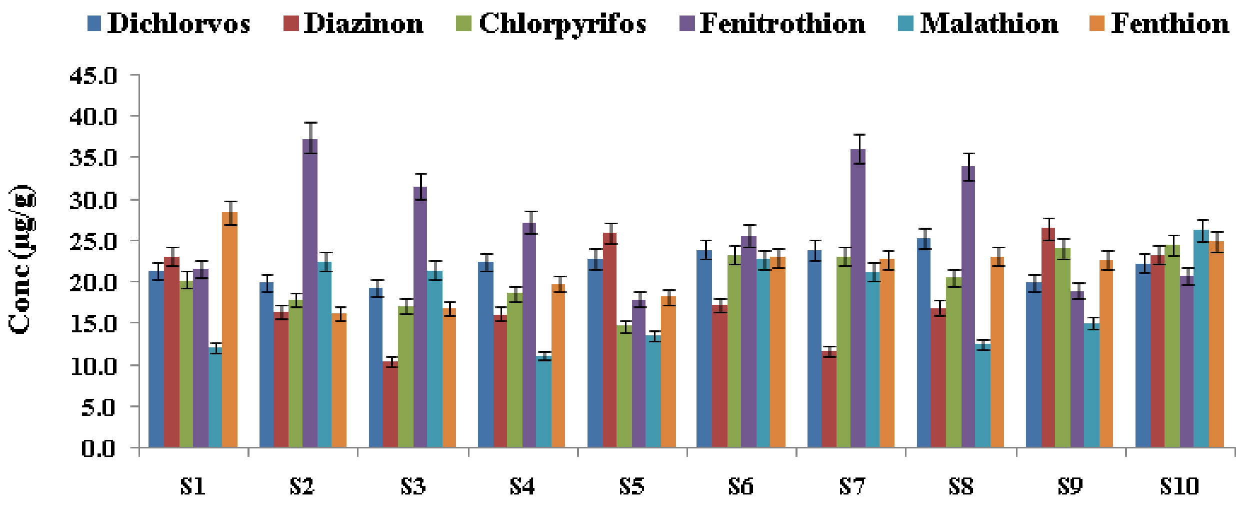

Figure 2. Mean Concentrations of Some Organophosphorus Pesticide Residues in Sediment Samples from Different sampling Points , on river Benue in Vinikilang, Yola, Adamawa State, Nigeria

The mean concentrations of some pyrethriod pesticide residues in water samples from river Benue in Vinikilang, Adamawa State for points S_1 to S_{10} are as presented in Figure 3. The concentration of cypermethrin ranges from 0.48±0.21 to 0.93±0.65mg/l; 0.29±0.15 to 1.36±0.70 mg/l bifenthrin; 0.49±0.10 to 1.52±0.73 mg/l permethrin and 0.28±0.05 to 1.14±0.70 mg/l deltamethrin. The mean concentrations of some Pyrethriod pesticide residues in sediment samples from river Benue in Vinikilang, Adamawa State for points S_1 to S_{10} are as presented in Figure 4. The concentration of Cypermethrin ranges from 9.11±1.02 to 11.93±2.13 µg/g; 2.81±1.05 to 3.98±1.80 µg/g Bifenthrin; 3.26±0.65 to 6.25±2.20 µg/g Permethrin and 3.85±0.80 to 7.11±1.83 µg/g Deltamethrin.

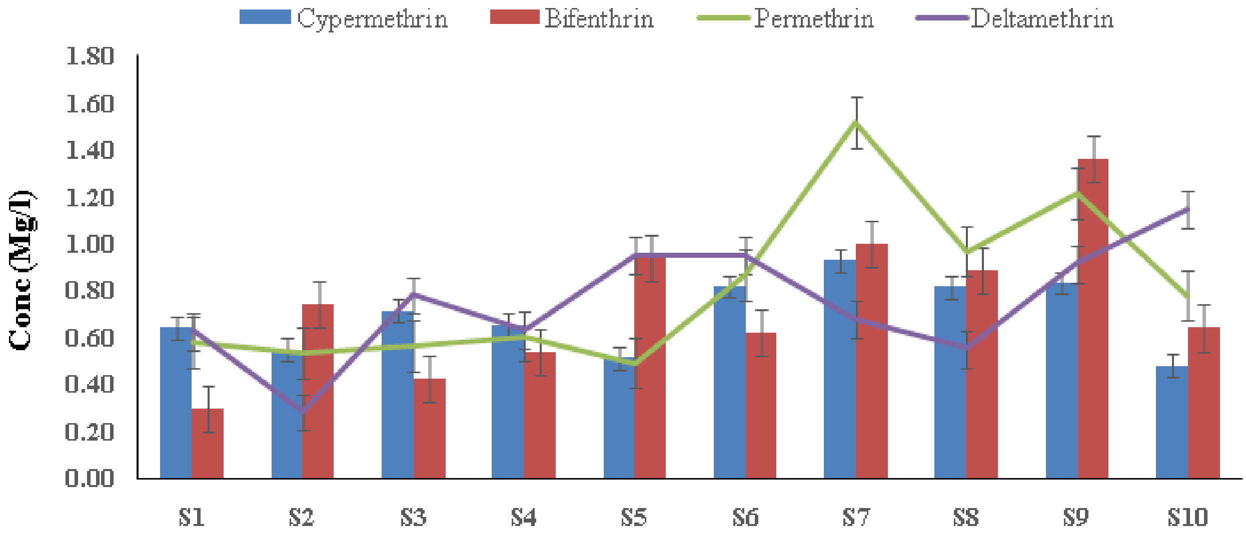

Figure 3. Mean Concentrations of Some Pyrethroid Pesticide Residues in Water Samples from Different sampling Points , on river Benue in vinikilang, Yola, Adamawa, State, Nigeria

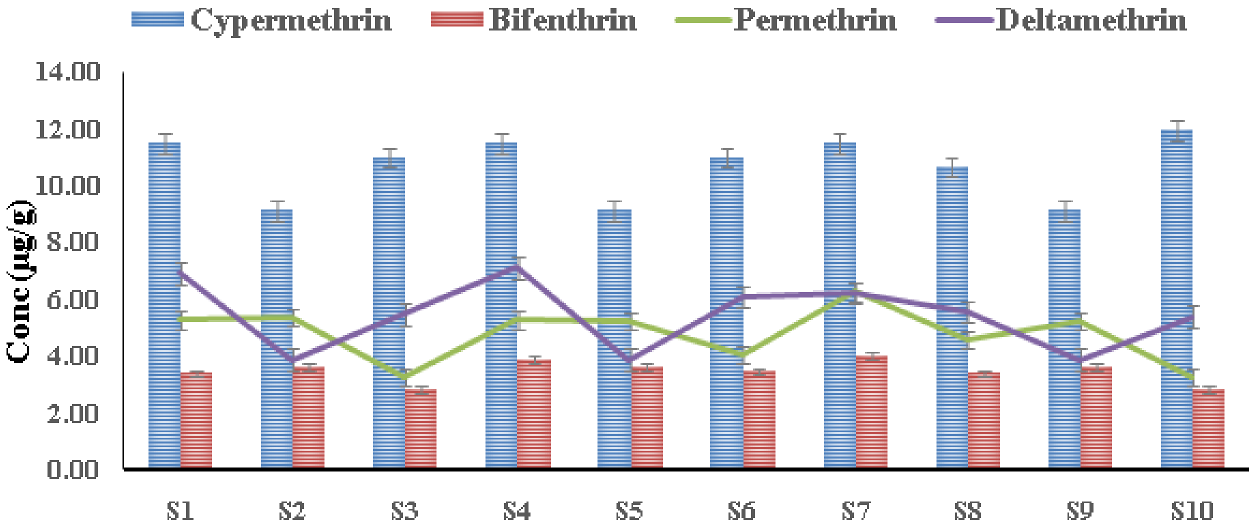

Figure 4. Mean Concentrations of Some Pyrethroid Pesticide Residues in Sediment Samples from Different sampling Points , River Benue in Vinikilang, Adamawa State, Nigeria

Comparison of the concentrations of some Organochlorine Pesticide Residues between Water and Sediment Samples from all the sampling points of River Benue in Vinikilang, Adamawa State, Nigeria.

Figure 5 shows a comparison in the concentrations of organochlorine pesticides between water and sediment samples. The mean concentration of o, p-DDE in the water samples is 0.59 mg/l, while in the sediment sample a total concentration of 3.45 µg/g was recorded. The mean concentration of p,p'-DDD in the water sample was 0.91 mg/l whereas 6.30 µg/g was observed in the sediment sample and in a similar vein, the mean concentration of o,p'-DDD in the water sample is 1.57 mg/l and 9.06 µg/g was recorded in sediment sample. Also, the mean concentration of p,p'-DDT in the water sample is 0.32 mg/l, while 1.89 µg/g was recorded for sediment sample. Figure 5 shows that the mean concentration of aldrin in the water sample was 4.36 mg/l and 13.37 µg/g in the sediment sample. And the mean concentration of dieldrin in the water sample is 2.96 mg/l, while that of sediment sample is 11.25 µg/g.

Figure 6 shows a comparison in the concentrations of organophosphorus pesticides between water and sediment samples. The concentration of dichlorvos in the water sample is 0.57 mg/l, while in the sediment sample, 22.16µg/g was recorded. Diazinon concentration of 0.81 mg/l was recorded in water sample and 18.82 µg/g in the sediment sample. The mean concentration of chlorpyrifos in the water sample is 0.67 mg/l, whereas in the sediment sample a concentration of 20.48µg/g was observed. Also, the mean concentration of fenitrothion in the water sample was 0.52 mg/l, while that of the sediment sample is 27.18µg/g. In addition, the mean concentration of malathion in the water sample is 0.51 mg/l, and that of Sediment is 17.93 µg/g. Fenthion concentration in the water sample was 0.62 mg/l and a concentration of 21.65µg/g was recorded for the sediment sample.

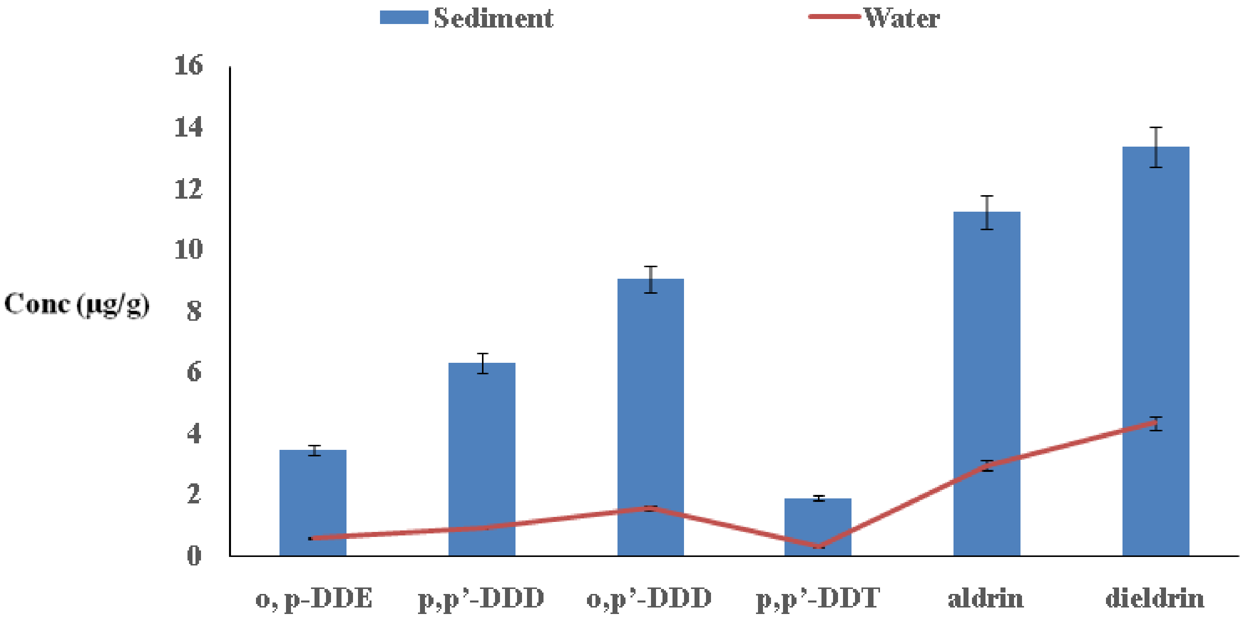

Figure 5. Comparison of the concentrations of Organochlorine Pesticide Residues between Water and Sediment Samples from different points on River Benue Vinikilang, Yola, Adamawa State, Nigeria

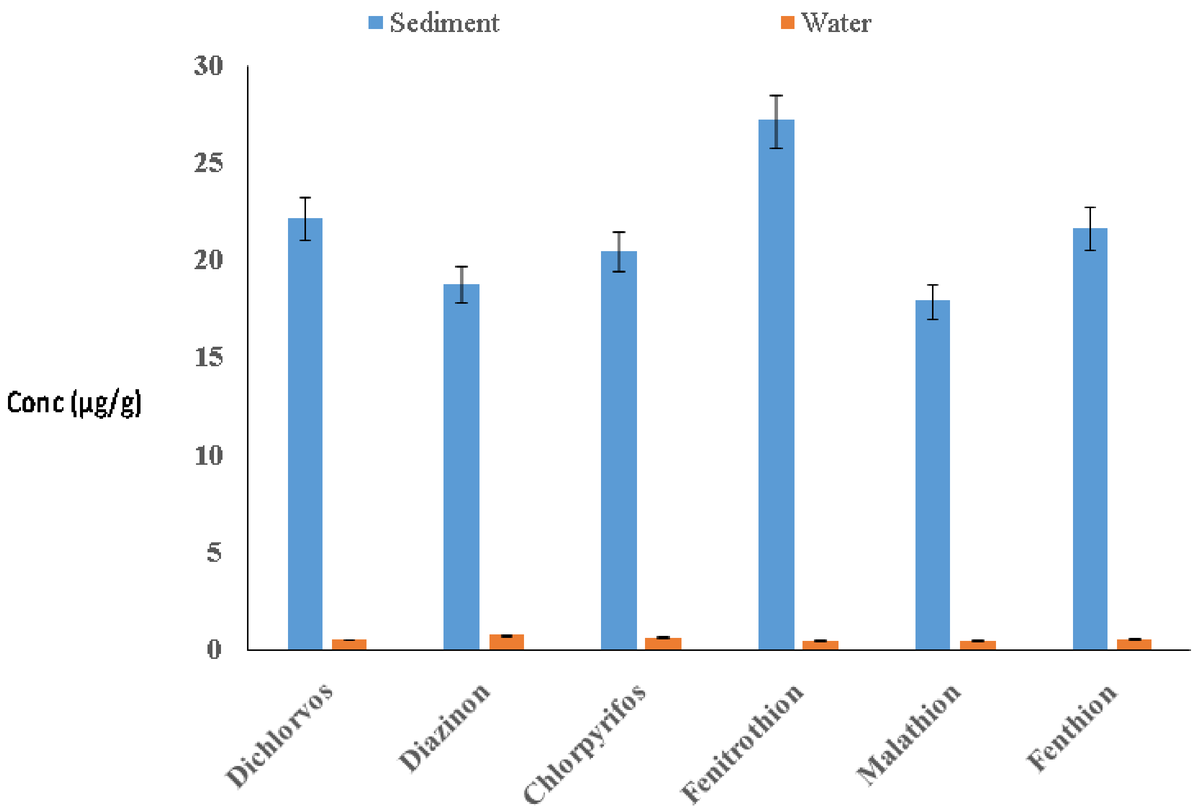

Figure 6. Comparison in the concentrations of Organophosphorus Pesticide Residues between Water and Sediment Samples from different points on River Benue in Vinikilang, Yola, Adamawa State, Nigeria

Figure 7 shows a comparison in the concentrations of pyrethroid pesticides between water and sediment samples. The mean concentration of cypermethrin in the water sample is 0.69 mg/l, whereas in the sediment sample the mean concentration of 10.64µg/g was recorded. The Figure 7 also shows that the mean concentration of bifenthrin in the water sample is 0.74mg/l, while in the sediment sample, 3.45µg/g was recorded. Also, the mean concentration of permethrin in water sample is 0.81 mg/l, while a concentration of 4.76µg/g was recorded for sediment sample. The result also shows that deltamethrin concentration of 0.75 mg/l was recorded in the water sample, while in the sediment sample a concentration of 5.42µg/g was recorded.

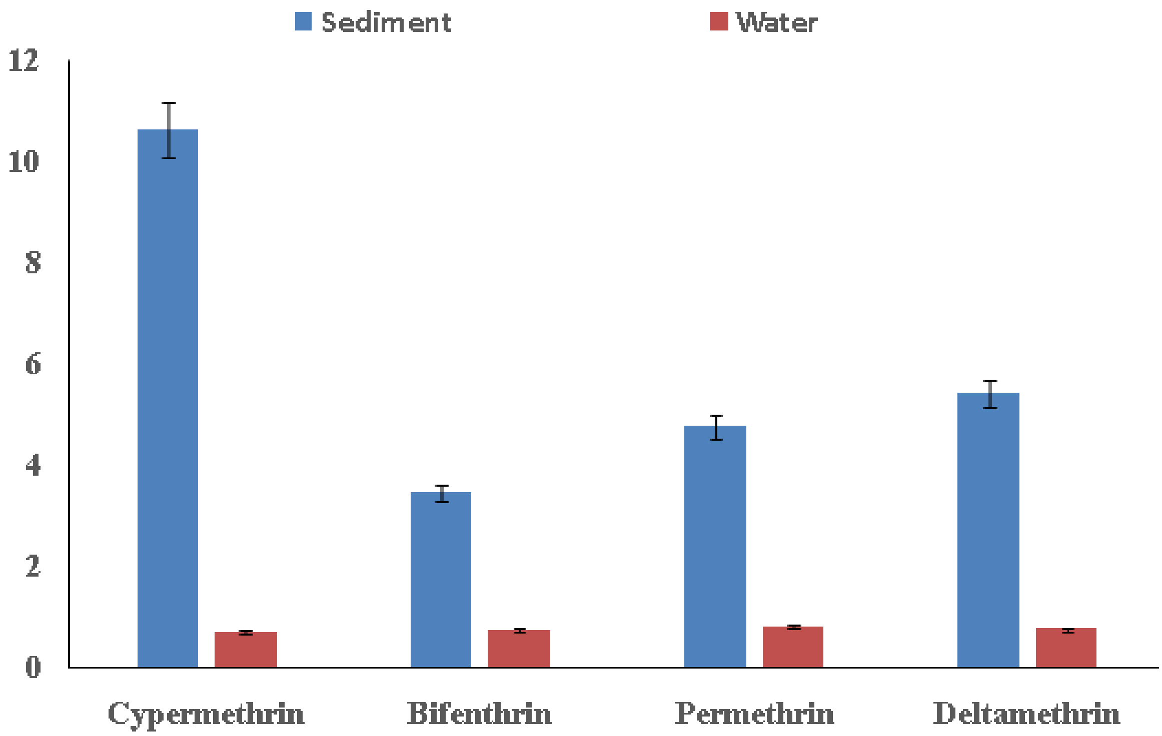

Figure 7. Comparison of the concentrations of Pyrethroid Pesticide Residues between Water and Sediment Samples from different points on River Benue in Vinikilang, Yola, Adamawa State, Nigeria

4. Discussion

Organochlorine pesticide residues (o,p'-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT, aldrin and diedrin) in Water and Sediment Samples from River Benue in Vinikilang, Yola, Adamawa State, Nigeria.

In the water samples the highest concentration of o, p-DDE in the water samples was detected at point S_2 with a value of 1.06± 0.30mg/l, while the lowest concentration was detected at point S_4 with a value of 0.28 ± 0.10 mg/l. For p,p'-DDD the highest concentration of 1.14± 0.54 mg/l was observed at point S_3 with point S_7 showing the lowest concentration of 0.75±0.10 mg/l, o,p'-DDD had the highest concentration at point S_9 with a value of 2.16±0.34 mg/l and the lowest concentration was detected at point S_1 with a value of 1.10±0 12 mg/l. Also, p,p'-DDT highest concentration was observed at point S_2 with a value of 0.66±0.12 mg/l, while the lowest concentration was detected at point S_{10} (0.15 ± 0.03 mg/l). The highest concentration of aldrin in the water samples was detected at point S_8 (3.75±0.01 mg/l) and the lowest concentration was recorded at point S_1 with a value of 2.31±0.44 mg/l. For dieldrin the highest concentration was recorded at point S_9 (5.24±0.23 mg/l), whereas the lowest concentration was observed at point S_3 (3.65±1.00 mg/l).

For sediment samples, the highest concentration of o, p-DDE in the sediment samples was observed at point S_9 with a concentration of 4.73±0.80 µg/g, while the lowest concentration was observed at point S_1 (0.51±0.02 µg/g), For p,p'-DDD, the highest concentration was recorded at point S_7 with a value of 9.29±1.51 µg/g, whereas the lowest concentration was observed at point S_1 (0.95±0.08 µg/g), also for o,p'-DDD, the highest concentration was detected at point S_6 with a value of 11.15±1.60 µg/g and the lowest concentration was observed at point S_{10} (1.90±0.20 µg/g). Also p,p'-DDT recorded the highest concentration at point S_5 with a value of 2.59±0.51 µg/g and the lowest concentration was detected at point S_1 (0.15±0.03 µg/g). Furthermore, the highest concentration of aldrin was detected at point S_8 with a value of 15.70±2.00 µg/g, while the lowest concentration was detected at point S_1 2.32±0.45 µg/g. Also, the highest concentration of dieldrin was recorded at point S_8 20.01±2.21 µg/g, while the lowest concentration was observed at point $S_{1.}$ (4.02±0.60 µg/g).

The total concentrations of p,p'DDT and its metabolites in the water samples were in the range of 0.15±0.03 to 5.24±0.23mg/l, while in sediment samples it ranges from 0.15±0.03 to 20.01±2.21 µg/g. Based on the concentrations and detection frequency, p,p'DDD, aldrin and dieldrin were the most dominant compound among the organochlorine pesticide residues (OCPs). Similar results of OCPs levels in aquatic ecosystem have been reported in recent investigations [2,13]. The concentrations of the degradation products, that is (0.59 mg/l) DDE and (1.57 mg/l) DDDs in all the sample points both in water and sediments were more than the parent compound (0.32 mg/l) DDT, which indicates past usage of the DDT pesticide. DDT normally degrades under aerobic condition to DDE and under anaerobic condition to DDD, thus a higher DDE + DDD/ DDT ratio is an indication of past usage (Tadeo, 2008). Although the use of DDT has been banned in Nigeria since 2008, it's still being used. DDT and its DDE and DDD metabolites persist in the environment and are known to bioaccumulate in aquatic organisms. DDT, DDD, and DDE have all been classified by NAFDAC as probable human carcinogens. The concentration of p,p'DDT (1.89 µg/g) and aldrin (11.25 µg/g), dieldrin (13.37 µg/g) and its metabolites were higher in the sediment samples when compared with water samples as mentioned above. This is because of the hydrophobic characteristic of organochlorine pesticides. It is expected that any organochlorine pesticide present in the study area preferably bind to the particle phase in aquatic system and then accumulated to the sediment through sedimentation process. They have an affinity for particulate matter and one of their main sinks is thought to be river and lake sediments [9]. The concentrations of DDT and its metabolites in the water samples from the ten sampling points were above the set EU maximum residue limit (MRL) of 0.03 Mg/l DDE and 0.02 Mg/l DDDs and DDT. Similarly, the concentrations of DDDs, DDE and DDT detected in the sediment samples were higher than the set EU maximum residue limit (MRL) of 0.3 µg/g DDD, 0.2 µg/g DDT and 0.4 µg/g DDE, hence, the result indicates that the water and sediment samples within the study area were contaminated by DDT, DDE and DDDs.

According to this study, aldrin (11.25 µg/g) and dieldrin (13.37 µg/g) were the most dominant compounds among the organochlorine pesticide in the sediment samples. Other work also reported the higher levels of aldrin and dieldrin in aquatic environments [21]. Dieldrin is a chlorinated cyclodiene that was widely used in Nigeria. The National Agency for Food and Drug Administration and Control (NAFDAC) has banned the sale and supply of 30 different agrochemical products in the country which include dieldrin and aldrin. Due to the toxicity of this persistent pesticide which posed an imminent danger to human health, NAFDAC banned most major uses of dieldrin and aldrin in 2008, but the product is still in use because of its low cost and affordability. Aldrin and dieldrin were detected in measurable concentrations (2.96 Mg/l and 11.25 µg/g), (4.36 Mg/l and 13.37 µg/g) in both water and sediment samples from river Benue, in Vinikilang. The relatively higher concentrations of the two compounds in the sediment samples may be attributed to the fact that both aldrin and dieldrin are not very soluble in water and therefore more likely to adsorb in sediments [10]. The concentration of (dieldrin 4.36 Mg/l and 13.37 µg/g) were slightly significantly higher than that of (aldrin 2.96 Mg/l and 11.25 µg/g) in both water and sediment samples. This could be an indication that there is more dieldrin in the environment compared to aldrin. This trend is supported by the fact that aldrin photolyses to dieldrin in the environment. These results are in agreement with those of the United States Department of Health and Human services [22], which reported that aldrin is readily and rapidly converted into dieldrin in plant and animal tissues. This is so because dieldrin is extremely non-polar and therefore has a strong tendency to adsorb tightly to lipids such as animal fat and plant waxes. It is for this reason that dieldrin bioconcentrates and biomagnifies through the terrestrial and aquatic food webs.

Organophosphorus Pesticide Residues (Dichlorvos, Diazinon, Chlorpyrifos, Malathion, Fenthion and Fenitrothion) in the Water and Sediment Samples from River Benue in Vinikilang, Yola, Adamawa State, Nigeria.

The highest concentration of dichlorvos in water sample was detected at point S_3 with a value of 1.60±0.60 mg/l, while the lowest concentration was observed at point S_9 (0.17±0.04 mg/l). For diazinon, the highest concentration was recorded at point S_6 with a value of 1.75±0.71 mg/l and the lowest concentration at point S_5 (0.09±0.03 m/gl). Also chlorpyrifos had the highest concentration at point S_1 (1.17±0.40 m/gl) whereas the least concentration of chlorpyrifos was observed at point S_4 (0.13±0.20 mg/l), in addition to chlorpyrifos, the highest concentration of fenitrothion was detected at point S_{10} (0.91±0.21 mg/l), with the lowest concentration recorded at point S_2 (0.23±0.10 mg/l). The highest concentration of malathion was recorded at point S_1 with a value of 1.93±0.10 mg/l, while the least value was detected at point S_3 (0.17±0.11 mg/l). For fenthion the highest concentration was observed at point S_6 (0.87±0.40 mg/l), whereas the lowest concentration was detected at point. S_{10} (0.41±0.34 mg/l).

The highest concentration of dichlorvos in the sediment samples was observed at point S_8 (25.31±2.60 µg/g), while point S_3 showed the lowest concentration of 19.38± 2.10 µg/g. Also diazinon recorded the highest concentration at point S_9 with a value of 26.56±0.70 µg/g, while the lowest concentration was observed at point S_3 (10.50±3.13 µg/g). Also, the highest concentration of chlorpyrifos was detected at point S_{10} (24.12±5.81 µg/g), while the lowest concentration was recorded at point S_5 with a value of 14.79±4.44 µg/g. For fenitrothion, the highest concentration of 37.43±5.20 µg/g was observed at point S_2, with the lowest concentration of 17.99±2.10 µg/g at point S_5. Malathion recorded highest concentration at point S_{10} (26.35±1.00 µg/g), while the lowest concentration was observed at point S_4 (11.17±2.10 µg/g). Moreover, the highest concentration of fenthion was detected at point S_1 with a value of 28.38±2.60 µg/g, while the lowest concentration was observed at point S_2 with a value of 16.26±5.40 µg/g.

Organophosphorus pesticides are widely used as agricultural insecticides and also have many uses in households for pest control. The mean concentrations of organophosphorus pesticide residues in the water samples ranged from 0.09±0.03 to 1.93±0.10 mg/l, while that of sediment samples ranged from 10.50±3.13 µg/g to 37.43±5.20 µg/g. According to the concentrations and detection frequency, fenitrothion (37.43±5.20 µg/g), fenthion (28.38±2.60 µg/g) and diazinon (26.56±0.70 µg/g) were the most highest compound among the organophosphorus pesticide residues in the sediment samples. The maximum residue limit (MRL) is the maximum amount of the pesticide residue which is found in food substances that will not cause any health hazard [4,7]. The concentrations of organophosphrous pesticide residues (dichlovos, diazinon, chlorpyrifos and fenitrothion) detected in the water samples fell above the set maximum residue limits (MRLs) of 0.004 Mg/l dichlovos, 0.002 Mg/l for diazion, 0.01 Mg/l for chlorpyrifos and 0.003 Mg/l for fenitrothion. The results therefore suggest that the concentrations of dichlovos, diazinon, chlorpyrifos and fenitrothion residues in the water samples from the study area may pose health hazard to the aquatic organism and by extension, humans that depend on such aquatic organisms for food.

Pyrethroid Pesticide Residues (cypermethrin, bifenthrin, permethrin and deltamethrin) in the Water and Sediment Samples from River Benue in Vinikilang, Yola, Adamawa State, Nigeria.

The highest concentration of cypermethrin in water samples was observed at point S_7 with a value of 0.93±0.65mg/l, whereas the lowest concentration of cypermethrin was detected at point S_{10} (0.48±0.21 mg/l). Similarly, the highest concentrations of bifenthrin of 1.36±0.70 mg/l was detected at point S_9, while the lowest concentration was detected at point S_1 (0.29±0.15 mg/l). Point S_7 recorded the highest concentration of permethrin with a value of 1.52±0.73 mg/l, While, the least concentration was detected at point S_5 (0.49±0.10 mg/l). The maximum concentration of deltamethrin was detected at point S_{10} (1.14±0.70 mg/l), while the lowest concentration was observed at point S_2 (0.28±0.05 mg/l). The maximum concentration of cypermethrin in sediment samples was detected at point S_{10} with a value of 11.93±2.13 µg/g, with the lowest concentration at point S_2 (9.11±1.02 µg/g). Also, the highest concentration of bifenthrin was observed at point S_7 (3.98±1.80 µg/g). However, point S_3 recorded the lowest concentration of bifenthrin (2.81±1.05 µg/g). The highest concentration of permethrin was detected at point S_7 (6.25±2.20 µg/g), while the lowest concentration was observed at point S_3 (3.26±0.65 µg/g). For deltamethrin, the maximum concentration was recorded at point S_4 with a value of 7.11±1.83 µg/g, while the minimum concentration was detected at point at S_2 (3.85±0.80 µg/g).

The concentration of cypermethrin follows same pattern as OCPs and Ops with fluctuation in concentrations between the sampling points. Chronic symptoms after exposure to cypermethrin include brain and locomotory disorders, polyneuropathy and immuno-suppression, which resemble the multiple chemical sensitivity syndromes [12]. Cypermethrin is genotoxic in mouse spleen and bone marrow cells where it induces the chromosomal aberration and sister chromatid exchange [8]. It induces systemic genotoxicity in mammals by causing DNA damage in vital organs like brain, liver, kidney, apart from that in the hematopoietic system [15]. It posses mutagenic activity inducing dominant lethal mutations in male germ cells of mice [18], and it induces chromosomal aberrations and single stranded breaks in DNA in the cultured human lymphocytes. The concentrations of cypermethrin detected in the water and sediment samples from all the sample points fell below the EU maximum residue limits (EU-MRLs) values of 100 Mg/l for water and 200 Mg/kg for sediment [3]. The results therefore, suggest that the concentrations of cypermethrin residues in the water and sediment samples from the study area may not pose health hazard in terms of synthetic cypermethrin pollution.

When Deltamethrin gets on the skin, it can cause skin sensations like tingling, itching, burning, or numbness at that spot. These sensations usually go away within 48 hours, but deltamethrin can be mildly irritating if it gets in the eye and if enough deltamethrin is breathed in, it can cause headaches and dizziness. Although not common, individuals who have ingested large amounts of deltamethrin have experienced nausea, vomiting, abdominal pain and muscle twitches. The concentrations of deltamethrin detected in the water and sediment samples from all the sample points fell below the EU maximum residue limits (EU-MRLs) values of 50 Mg/l for water and 100 Mg/kg for sediment [3]. The results therefore, suggest that the concentrations of deltamethrin residues in the water and sediment samples from river Benue in vinikilang Adamawa State may not pose health hazard in terms of synthetic deltamethrin pollution.

Bifenthrin is hardly soluble in water, so nearly all bifenthrin will stay in the sediment, but it is very harmful for the aquatic life. Even in small concentrations, fish and other aquatic animals are affected by bifenthrin. The concentrations of bifenthrin detected in the water and sediment samples from all the sample points fell below the EU maximum residue limits (EU-MRLs) values of 100 Mg/l for water and 200 Mg/kg for sediment [3]. The results therefore suggest that the concentrations of bifenthrin residues in the water and sediment samples from the study area may not pose health hazard in terms of synthetic bifenthrin pesticide.

In mammals, permethrin has complex effects on the nervous system. As in insects, it causes repetitive nerve impulses. It also inhibits a variety of nervous system enzymes: ATPase, whose inhibition results in increased release of the neurotransmitter acetylcholine [23]. Permethrin inhibits respiration (the process by which cells use sugar as an energy source) in a manner similar to other neurotoxic drugs. It is therefore, not surprising that permethrin causes a wide variety of neurotoxic symptoms. At relatively high doses, these neurotoxic symptoms of permethrin include tremors, incoordination, hyperactivity, paralysis, and an increase in body temperature. Permethrin affects both male and female systems. It binds to receptors for androgen, a male sex hormone, in skin cells from human males [23]. The concentrations of Permethrin detected in the water and sediment samples from all the samples points fell below the EU maximum residue limits (EU-MRLs) values 100 Mg/l for water and 200 Mg/kg for sediment [3]. The results therefore, suggest that the concentrations of permethrin residues in the water and sediment samples from the study area may not pose health hazard in terms of synthetic permethrin pollution.

5. Conclusion

These results indicate that the water and sediment samples within the study area were polluted due to the discharge of toxic pesticides from point and non- point sources. The concentrations of Organochlorine pesticide residues (o,p'-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT, aldrin and diedrin) and Organophosphorus Pesticide Residues (Dichlorvos, Diazinon, Chlorpyrifos, Malathion, Fenthion and Fenitrothion) were higher than the set EU maximum residue limits (MRL) and Pyrethroid Pesticide Residues (cypermethrin, bifenthrin, permethrin and deltamethrin) was lower than the set EU maximum residue limits (MRL). As these toxic substances do not degrade they remain persistent in the environment and also have the ability to accumulate in the food chain which might pose potential hazard in the long run. These results also show that there's still existence of a variety of organochlorine, organophosphorus and pyrethroid pesticides in the water and sediment of river Benue, Vinikiling, Adamawa State, despite the banning of Organochlorine pesticides compounds and restriction on the usage of the other pesticides in Nigeria.

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