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ASSESSMENT OF PESTICIDES RESIDUES IN WATER, SEDIMENT AND FISH PARTS: CASE STUDY OF FISH POND IN ADO-EKITI, NIGERIA

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Abstract – Occurrence, distribution and accumulation of pesticides residues in water, sediment and fish parts from a dam in Nigeria were studied. A gas chromatography coupled with electron capture detector (GC-ECD) was used to quantify the pesticides residues after careful extraction and clean-up. Trace amounts of the analysed pesticides were detected in all the sampled matrixes. High level of variations were reportedin the water and sediments values as observed in the calculated CV% but being more pronounced in sediments. In general, pesticides were obviously higher in the head and muscle than liver with a percentage ratio of 36.8: 33.7:29.5 respectively. Triadimefon, heptachlor, aldrin, chlordane and prochloraz showed evidence of high accumulation in the fish parts.

INTRODUCTION

Pesticides use is indispensable in the area of agricultural production and public health vector control (Musa *et al*., 2011). However, the toxicity of these compounds and their presence in the environment pose great issues. The use of chemical pesticides in crop protection at the moment is inevitable, but the incidence of pesticide residues in food, water and the environment, resulting from the use of these pesticides continues to be a matter of serious controversy (Aiyesanmi and Idowu, 2012), especially when attempts are made to strike a balance between the overall benefits derived from the pesticides and the attendant adverse consequences resulting from their use. The Nigerian experience from available research shows that major pesticides contamination of air, soil and water arises basically from the use of pesticides. Over 95% of all pesticides are imported as finished pre-packed products. Pesticides use in Nigeria includes certain chemicals that for environmental reasons have been partially or completely banned in developed countries. However such chemicals continue to find their way into Nigeria for pest control mainly through illegal traffic. Among these groups of pesticides; the insecticides, specifically organochlorines have enjoyed much research publicity worldwide (Yu *et al*., 2000; Soliman, 2001; Bai *et al*., 2006; Dikshith, 2008; Bempah *et al*., 2011; Kuranchie-Mensah *et al*., 2011). However, this may be due to their peculiar characteristics: low cost, their versatility against various pests, bioaccumulative nature and potential toxic effects to wildlife and humans (Bempah *et al*., 2011).

Fish are used extensively as an indicator for environmental monitoring (Lanfranchi *et al.,* 2006), because they uptake contaminants directly from water and diet. Generally, the ability of fish to metabolize pesticides is moderate; therefore contaminant loading in fish is well reflective of the state of pollution in surrounding environment (Guo *et al*., 2008). Their potential use as biomonitors is significant in the assessment of bioaccumulation and biomagnification of contaminants within the eco-system (Babu *et al*., 5005). This study, therefore, investigated the occurrence, distribution and accumulation of pesticides residues in water, sediment and fish parts from a dam in Ado-Ekiti, Nigeria. The data would enable us to assess the

extent of enrichment and accumulation of the determined residues in the sediments and fish parts.

MATERIALS AND METHODS

Sample collection and preparation

Sampling was conducted in December, 2019. Surface water samples (5 cm below water level) were taken at five different spots along the course of the fish pod by grab method. The samples were stored in pre-cleaned glass sample bottles. The samples were later poured together in a glass sample bottle to obtain composite sample. The glass bottle was covered with screw and caps and was immediately transported to the laboratory and refrigerated at 4 ^{o}C prior to extraction.

Sediment samples were taken at five different locations as in the case of water samples. The samples were taken from the same locations and time for water sampling at a depth of 5 cm using pre-cleaned Ekman grab sampler. The samples were pulled together, taken into a glass bottle and labelled. The collected samples were air-dried, ground, sieved through 2 mm mesh size and stored in glass sample bottle prior analysis.

Five samples of male matured *Clarias gariepinus* were harvested from the fish pond located in Basiri quarters of Ado-Ekiti, Ekiti State, Nigeria. The harvested fish samples were later cleaned and transferred into a frozen container for transportation. The parts (head, liver and muscle) required for the analysis were carefully separated and stored in a deep freezer prior to sample preparation. The parts were later removed from the freezer, washed with deionized water, ground by agate mortar and later blended with an Excella Mixer blender. The homogenized blended samples were stored in glass bottles and kept in a refrigerator at 4^{o} C prior to subsequent analysis.

Reagents used

The reagents used were of spectra purity. They included GC grade n-hexane, dichloromethane, and methylene chloride.

Sample extraction and clean-up

One hundred (100 mL) milliliters of the water sample was transferred into clean 1 l separatory funnel. Forty (40 mL) dichloromethane (DCM) was added to the water and shaken vigorously for about 20 min with occasional venting over the course of each extraction. The mixture was allowed to settle for 30 min to ensure separation of the phases. After separation on standing, the aqueous layer was removed, while the organic layer was filtered into a 250 cm^3 conical flask through anhydrous sodium sulphate (Na_2SO_4) salt that has been prewashed with DCM. The extraction was repeated twice using a 40 ml portion of DCM and all the extracts were combined. The combined organic extracts was concentrated to 2 mL using a rotary evaporator at 40^{o}C.

For sediment and fish samples, method of EPA-600/8-80-038 was employed, where 10.0 g of the weighed samples was extracted after the addition of the surrogate standard solution to the sample and later transferred to the extracting bottle that was cocked with TFE-fluorocarbon. Fifty (50) mL of phosphate buffer was added, followed by pH measurement with the addition of sulphuric acid for pH adjustment to 7 if necessary. One (1.0) g of sodium chloride salt was added to the sample, sealed and shaken so as to dissolve the salt. Twenty (20) mL of the redistilled analytical grade methylene chloride was measured and transferred into the sample. The sample was extracted for about 30 minutes. The extract was filtered into Erlenmeyer flask. The extraction was repeated two more times with fresh solvent and the filtrate was combined. The combined extract was dried by passing through a drying column containing a 10 cm column of anhydrous sodium sulphate (previously rinsed with methylene chloride), and the filtrate was concentrated in the concentrator flask with a stream of nitrogen. The wall of the concentrator flask was rinsed with extracting solvent so as to bring the final volume of the extract to 5.0 mL.

A 30 cm glass stoppered column was filled with 6 g activated florisil (60-100 mesh) and topped with 2 g of anhydrous sodium sulphate. The sample extract was transferred to the Florisil column which was already saturated with n-hexane. The column was eluted with 20 mL eluant (n-hexane). The collected eluent was concentrated on rotary evaporator at 40 ^{o} C and recovered into 2 mL n-hexane. The extract was transferred into glass GC vials for subsequent injection into the GC.

Gas chromatographic conditions

The gas chromatographic conditions for the pesticides were as follows: GC model: HP6890 powered with HP ChemStation Rev. A 09.01[1206]; the carrier gas flow rate was 1.0 mL/min; injector temperature: split injection: 20:1; carrier gas:

hydrogen; inlet temperature: 250 °C; column type: HP 5MS; column dimension: (30 m x 0.25 mm x 0.25 μm); oven programme: initial temperature at 80 °C for 1 min, first ramping 10 °C/min to (200 °C); maintained for 12 min; second ramping at 12 °C/min to 300 °C constant at 1 min; detector: pulse flame photometric detector (PFPD); detector temperature: 300 °C; hydrogen pressure: 22 psi; nitrogen column air: 20 psi; compressed air: 28 psi. The total run time was 31 minutes.

Enrichment coefficient (EC), bioconcentration factor (BCF) and biota-sediment accumulation factor (BSAF)

In order to evaluate the BCF in the fish, the residual pesticides concentration in the fish parts was divided by the residual concentration of pesticides in related water respectively. The enrichment coefficient (EC) was estimated as a ratio between the concentration of the pesticides in the sediments and water respectively. Biota-sediment accumulation (BSAF) was estimated as the pesticides concentration in the fish parts divided by the residual concentration of pesticides in related sediment respectively.

Statistical analysis

The concentration values observed for water, soil sediments and fish parts (head, liver and muscle) were subjected to statistical analysis. The statistical analysis modes used were the descriptive analysis (mean, standard deviation and coefficient of variation in percent); and the inferential analysis (Correlation coefficient, variance and regression coefficient) (Oloyo, 2001). Further, the correlation coefficient values were further subjected to analysis of coefficient of alienation and index of forecasting efficiency (Oloyo, 2001). For the various statistics modes used, the following symbols were used as appropriate: standard deviation (SD); coefficient of variation percent (CV%); correlation coefficient (r_{xy}) setting its critical level at $r_{=0.01}$; variance (r_{xv}^2); regression coefficient (R_{xy}); coefficient of alienation (C_A) and index of forecasting efficiency (IFE). The sample had these representations: water (W), soil sediments (S); for fish we had: head (H), liver (L), muscle (M). Hence in the r_{xy} statistics, the following pairs would be used: W/S, H/L, H/M and L/M respectively.

RESULTS AND DISCUSSION

The ground mean concentration and percentage composition of pesticides in water and sediments is depicted in Table 1. The pesticides concentrations in the water ranged from 0.0006 (aldrin) to 0.238 μg/L (flusilazole, DDT), while the sediments ranged from 0.0006 (aldrin) to 0.435 μg/kg (DDT). The sediments were more contaminated than the water samples with higher concentration of all the pesticides residues except for methoprene and triadimefon. Aldrin and permethrin only showed the same level in water and sediments samples. Low level of spatial distribution exists in the concentrations of most detectable pesticides as shown in the calculated coefficient of variation (1.71 – 39.3%). Triadimenol (61.5%), triadimefon (110%), DDT (41.4%), pyrethrin II (41.6%) and chlordane (84.9%) showed high variability between the water and sediment. The total pesticides load in the sediment was higher than that of the water: water (1.72 μg/L) and sediments (2.19 μg/kg); this gives a ratio of 1.00: 1.27. The difference between the two total values was 0.47 or 21.5%. However, the parameters concentrations were close in some of the parameters as evidenced in some low values of CV%. Glyphosate, metalaxyl, pirimiphos-methyl, flusilazole, boscalid, DDT and guazatine were highest concentrated in the water samples with the % trend of flusilazole = DDT – metalaxyl > guazatine > boscalid > glyphosate > pirimiphos- methyl. In the sediments, DDT and flusilazole were the major constituents of the total pesticides accounting for 19.9% and 11.4% respectively. Metalaxyl (11.0%), boscalid (7.44%), cyproconazole (7.03%), guazatine (6.39%) and glyphosate (5.53%) were also highly concentrated in the sediments.

Table 2 showed the concentration and percentage composition of the pesticides in the fish body parts. The pesticides concentration ranged from 0.001 - 0.175, 0.0002 - 0.102 and 0.002 - 0.188 μg/kg in head, liver and muscle respectively, with DDT as the most concentrated pesticide in the fish parts. The coefficient of variation (CV%) were mostly low in most compounds, except metalaxyl, guazatine, aldrin, heptachlor and chlordane demonstrating the closeness of the parameter values. Five (CV%) had values greater than 40.0; these were from metalaxyl (45.2%), guazatine (59.8%), aldrin (74.2%), heptachlor (75.2%) and chlordane (43.3%) with most concentrated in muscle. The most concentrated pesticides were glyphosate, triadimefon, cyproconazole, pirimiphos-methyl, flusilazole, DDT and boscalid with the mean concentration trend of DDT > flusilazole > boscalid > triadimefon >

Table 1. Grand mean concentration (μg/kg) and percentage composition of pesticides in water and sediments

	Water	% Water	Sediment	% Sediment	CV%
Glyphosate	0.098	5.70	0.121	5.53	14.9
Dichlorvos	0.027	1.57	0.03	1.37	7.44
Pirimicarb	0.02	1.16	0.033	1.51	34.7
Fludioxonil	0.061	3.55	0.064	2.92	3.39
Imidacloprid	0.038	2.21	0.059	2.69	30.6
Fenitrothion	0.038	2.21	0.052	2.37	22.0
Metalaxyl	0.204	11.9	0.241	11.0	11.8
Triadimefon	0.049	2.85	0.0062	0.28	110
Cyproconazole	0.109	6.34	0.154	7.03	24.2
Triadimenol	0.037	2.15	0.094	4.29	61.5
Pirimiphos-methyl	0.09	5.23	0.0922	4.21	1.71
Methoprene	0.084	4.88	0.065	2.97	18.0
Triazophos	0.023	1.34	0.024	1.10	3.01
Flusilazole	0.238	13.8	0.249	11.4	3.19
Pyrethrin 1	0.01	0.58	0.016	0.73	32.6
Piperonyl butoxide	0.0096	0.56	0.017	0.78	39.3
Boscalid	0.125	7.27	0.163	7.44	18.7
DDT	0.238	13.8	0.435	19.9	41.4
Guazatine	0.134	7.79	0.139	6.35	2.59
Aldrin	0.0006	0.04	0.0006	0.03	0.00
Heptachlor	0.019	1.10	0.034	1.55	40.0
Pyrethrin II	0.006	0.35	0.011	0.50	41.6
Prochloraz	0.035	2.03	0.047	2.15	20.7
Gieldrin	0.025	1.45	0.033	1.51	19.5
Permethrin	0.004	0.23	0.004	0.18	0.00
Chlordane	0.001	0.06	0.004	0.18	84.9
TP	1.72	100	2.19	100	17.0

cyproconazole > pirimiphos-methyl glyphosate.

Observations from the study showed that the concentration of these pesticides in the fish parts might be a function of pesticides characteristics and fat content in the fish parts. The total pesticides load in the muscle and head were higher than in the liver: muscle (1.17 μg/kg), head (1.07 μg/kg) and liver (0.938 μg/kg); this gave a percentage ratio of 36.8: 33.7: 29.5 for muscle, head and liver respectively.

In real figure values we have percentage level of these pesticides over total pesticides levels as follows: Head; DDT (16.4%), boscalid (8.60%), triadimefon (6.37%), pirimiphos-methyl (6.54%), cyproconazole (5.98%) and glyphosate (5.42%); Liver; DDT (16.2%), cyproconazole (7.89%), triadimefon (7.46%), pirimiphos-methyl (6.93%), glyphosate (6.82%) and boscalid (6.50%); Muscle; DDT (16.1%), boscalid (8.29%), triadimefon (7.95%); cyproconazole (6.92%), pirimiphos-methyl (6.15%), glyphosate (5.73%). The pesticides levels obtained in the study were comparatively lower to those reported in Alau Dam, Borno State, Nigeria (Fish liver, 0.56 – 2.43 μg/kg) (Akan *et al*., 2013), Elechi Greek Niger Delta, Nigeria (average conc. 30 μg/kg) (Upadhi and Wokoma, 2012). The organophosphorus levels in this study were lower than the level reported in fish for dichlorvos (0.11 - 1.23 μg/kg), chlorpyrifos (0.34 - 1.89 μg/kg) and fenitrothion (0.23 – 1.54 μg/kg) from Alau dam, Nigeria (Akan *et al*., 2013). None of the pesticides exceeded the maximum residue limit of pesticides residues in food as prescribed by Codex Alimentarius Commission (Codex, 2005).

The summary in Table 3 showed the following: the differences between the head and liver (H/L); Head and muscle (H/M); and muscle and liver (M/L) and their percentage differences. In the head and liver comparisons (H/L), the differences ranged from -0.006 (glyphosate) to 0.038 μg/kg (heptachlor). Chlordane, triazophos, pyrethrin I, piperonyl butoxide and chlordane showed similar characteristics by showing similar levels in the head and liver. In differences, only two pesticides had values in H > L as seen in glyphosate [-0.006 μg/kg and - 10.3 (%) difference] and cyproconazole [-0.01 μg/kg and -15.6 (%) difference]. The least difference was dieldrin and permethrin with a value of 0.001 μg/kg (4.55 and 33.3% respectively), while

Table 2. Grand mean concentration (μg/kg) of pesticides in the fish body parts

	Head	%H	Liver	%(L)	Muscle	%M	Mean	SD	CV%
Glyphosate	0.058	5.42	0.064	6.82	0.067	5.73	0.063	0.005	7.27
Dichlorvos	0.025	2.34	0.021	2.24	0.025	2.14	0.024	0.002	9.76
Pirimicarb	0.017	1.59	0.014	1.49	0.016	1.37	0.016	0.002	9.75
Fludioxonil	0.036	3.36	0.034	3.62	0.035	2.99	0.035	0.001	2.86
Imidacloprid	0.032	2.99	0.029	3.09	0.032	2.74	0.031	0.002	5.59
Fenitrothion	0.028	2.62	0.026	2.77	0.029	2.48	0.028	0.002	5.52
Metalaxyl	0.025	2.34	0.021	2.24	0.047	4.02	0.031	0.014	45.2
Triadimefon	0.072	6.73	0.07	7.46	0.093	7.95	0.078	0.013	16.3
Cyproconazole	0.064	5.98	0.074	7.89	0.081	6.92	0.073	0.009	11.7
Triadimenol	0.026	2.43	0.023	2.45	0.027	2.31	0.025	0.002	8.22
Pirimiphos-methyl	0.07	6.54	0.065	6.93	0.072	6.15	0.069	0.004	5.23
Methoprene	0.046	4.30	0.043	4.58	0.048	4.10	0.046	0.003	5.51
Triazophos	0.014	1.31	0.014	1.49	0.015	1.28	0.014	0.001	4.03
Flusilazole	0.118	11.0	0.113	12.0	0.124	10.6	0.118	0.006	4.65
Pyrethrin 1	0.005	0.467	0.005	0.533	0.005	0.427	0.005	0.000	0.00
Piperonyl butoxide	0.007	0.654	0.007	0.746	0.007	0.598	0.007	0.000	0.00
Boscalid	0.092	8.60	0.061	6.50	0.097	8.29	0.083	0.020	23.4
DDT	0.175	16.4	0.152	16.2	0.188	16.1	0.172	0.018	10.6
Guazatine	0.033	3.08	0.023	2.45	0.071	6.07	0.042	0.025	59.8
Aldrin	0.002	0.187	0.0002	0.021	0.002	0.171	0.001	0.001	74.2
Heptachlor	0.051	4.77	0.013	1.39	0.018	1.54	0.027	0.021	75.5
Pyrethrin II	0.006	0.561	0.004	0.426	0.006	0.513	0.005	0.001	21.7
Prochloraz	0.043	4.02	0.038	4.05	0.045	3.85	0.042	0.004	8.58
Dieldrin	0.022	2.06	0.021	2.24	0.019	1.62	0.021	0.002	7.39
Permethrin	0.003	0.280	0.002	0.213	0.002	0.171	0.002	0.001	24.7
Chlordane	0.001	0.093	0.001	0.107	0.002	0.171	0.001	0.001	43.3
TP	1.07	100	0.938	100	1.17	100	1.06	0.118	11.1

heptachlor showed the highest difference with a value of 0.038 μg/kg (74.5%). In the head and muscle (H/M) comparisons, where five pesticides levels had values in head than in muscle, six had the similar values in head and muscle. The pesticides were dichlorvos, imidacloprid, pyrethrin I, piperonyl butoxide, aldrin and pyrethrin II, while the remaining pesticides had values in H > M. The total pesticides also exhibited this properties (Hˆ M) with difference value of (-0.102 μg/kg, -9.52%). The five pesticides that had values in head than muscle were pirimicarb (0.001 μg/kg, difference of 5.88%), fludioxonil (0.00 μg/kg, diff. of 2.78%), heptachlor (0.033 μg/kg, diff. of 64.7%), dieldrin (0.003 μg/kg, diff. 13.6%) and fludioxonil (0.001 μg/kg, diff. 33.3%). In muscle/liver (M/L) comparison, 22 parameters (22/26 or 84.6%) had their values in muscle greater than in liver, three parameters (pyrethrin I, piperonyl butoxide and permethrin, 3/26 or 11.5% had values similar in muscle and liver, while one (1/26 or 3.85%; dieldrin) had value in liver > muscle. The parameter differences (where muscle > liver) in the values ranged from 2.86% to 90.0%, with the least and highest differences being in fludioxonil and aldrin respectively.

The statistical analyses data had been depicted in Table 4. All the samples had been subjected to both descriptive statistics and inferential statistics. For the descriptive statistics, all the mean values were all low and each value being less than 1.00 μg/kg. Actually the mean values ranged as follows: in water/soil sediments we had 0.0691 – 0.0865 ± 0.0731 - 0.1036 μg/kg with corresponding high values of CV% being 106 – 120 respectively. This showed high level of variation in the W/S values but being more pronounced in soil sediments than in water, hence we have CV% of 106 (water) < 120 (soil sediments). In the fish samples, we had mean ranged of 0.0361-0.0451 ± 0.0366 – 0.0445 μg/kg which followed this trend (mean): 0.0361 ± 0.0366 μg/kg (L), 0.0412 ± 0.0401 μg/kg (H) and 0.0451 ± 0.0445 μg/kg (M). There was however a reverse in the CV% as shown: 97.4 (H) < 98.5 (M) < 101 (L). However, the CV% values in H/L, L/M and H/M were generally lower than in W/S.

In the inferential statistics results, all the r_{xy} values were positively high and significantly different at $r_{=0.01}$; the r_{xy} values were 0.9356 (W/S),

0.9681 (H/L), 0.9653 (L/M) and 0.9639 (H/M). The r_{xy} in W/S was lower than all the values in the fish samples. The r_{xy}^2 were all high for each of paired groups, values being 0.8754 (W/S) and 0.9292 – 0.9371 in fish samples. The R_{xy} values were much varied than in the r_{xy} and r_{xy}^2 values. The highest R_{xy} was observed in W/S (1.33). The implication of this was that when water pesticides level increased by 1.00 μg/kg, that of soil would corresponding increase by 1.33 μg/kg showing that pesticides were more resident in soil sediments than in water. For this observation in the fish sample R_{xy} values, we had 1.00/0.8827 μg/kg (H/L), 1.00/1.17 μg/kg (L/M) and 1.00/1.09 μg/kg (H/M). The coefficient of alienation (C_A) values were all generally low: W/S (0.3529) and in fish samples ranged from 0.2508 – 0.2661 with corresponding generally high index forecasting efficiency (IFE): for W/S (0.6471) being lower than in the fish values; fish IFE values ranged from 0.7339 – 0.7492. C_A meant non-relationship and represented error value of prediction of relationship between two compared entities. On the other hand IFE represented the reduction value in the prediction of relationship between two compared entities. When C_A > IFE, relationship prediction is easy and vice versa. However C_A + IFE = 1.00 or 100%. In all the compared pairs, since all the C_A ˆ IFE, it meant prediction of relationship was easy and easily predictable. Because all the IFE values were greater than C_A, it meant any member in a paired group would carry out the functionality of the other member of the pair and vice versa.

The analysed results showed evidence of enrichment of most pesticides in the sediment samples with a range of 0.127 (triadimefon) to 4.00 (chlordane). Figure 1 presents the logarithm of the enrichment coefficient. Chlordane, pyrethrin II, heptachlor, DDT, piperonyl butoxide, pirimicarb and triadimenol were highly accumulated in the sediments as compared to other pesticides (Fig. 1). The EC of ˆ 1 (92.3%) showed accumulation and enrichment of most pesticides except triadimefon and methoprene.

Two key properties of pesticides that control accumulation in sediment and aquatic biota are hydrophobicity and persistence. Generally, pesticides were found to have the potential to accumulate in sediment and aquatic biota if they

Table 3. Comparison of the fish parts highlighting their pairwise differences and their percentages

	Diff (H/L)	%Diff.	Diff (H/M)	%Diff	Diff(M/L)	%Diff
Glyphosate	-0.006	-10.3	-0.009	-15.5	0.003	4.48
Dichlorvos	0.004	16.0	0.00	0.00	0.004	16.0
Pirimicarb	0.003	17.6	0.001	5.88	0.002	12.5
Fludioxonil	0.002	5.56	0.001	2.78	0.001	2.86
Imidacloprid	0.003	9.38	0.00	0.00	0.003	9.38
S1Fenitrothion	0.002	7.14	-0.001	-3.57	0.003	10.3
Metalaxyl	0.004	16.0	-0.022	-88	0.026	55.3
Triadimefon	0.002	2.78	-0.021	-29.2	0.023	24.7
Cyproconazole	-0.01	-15.6	-0.017	-26.6	0.007	8.64
Triadimenol	0.003	11.5	-0.001	-3.85	0.004	14.8
Pirimiphos-methyl	0.005	7.14	-0.002	-2.86	0.007	9.72
Methoprene	0.003	6.52	-0.002	-4.35	0.005	10.4
Triazophos	0.00	0.00	-0.001	-7.14	0.001	6.67
Flusilazole	0.005	4.24	-0.006	-5.08	0.011	8.87
Pyrethrin 1	0.00	0.00	0.00	0.00	0.00	0.00
Piperonyl butoxide	0.00	0.00	0.00	0.00	0.00	0.00
Boscalid	0.031	33.7	-0.005	-5.43	0.036	37.1
DDT	0.023	13.1	-0.013	-7.43	0.036	19.2
Guazatine	0.01	30.3	-0.038	-115	0.048	67.6
Aldrin	0.0018	90.0	0.00	0.00	0.002	90.0
Heptachlor	0.038	74.5	0.033	64.7	0.005	27.8
pyrethrin II	0.002	33.3	0.00	0.00	0.002	33.3
Prochloraz	0.005	11.6	-0.002	-4.65	0.007	15.6
Dieldrin	0.001	4.55	0.003	13.6	-0.002	-10.5
Permethrin	0.001	33.3	0.001	33.3	0.00	0.00
Chlordane	0.00	0.00	-0.001	-100	0.001	50.0
TP	0.1328	12.4	-0.102	-9.52	0.235	20.0

had a water solubility less than 1 mg/L or octanol-water partition coefficient (K_{ow}) greater than 1000 and a soil half-life greater than 30 days (Majewski and Capel, 1995).

The bio-concentration factors (BCFs) of the pesticides in the fish parts with reference to the pesticides concentrations in water from the sampled dam ranged from 0.123 – 3.33, 0.103 – 1.43 and 0.230 – 3.33 in head, liver and muscle with total pesticides BCF of 0.622, 0.544 and 0.681 respectively. Figure 2 further illustrated those residues that were bioconcentrated and extent of their

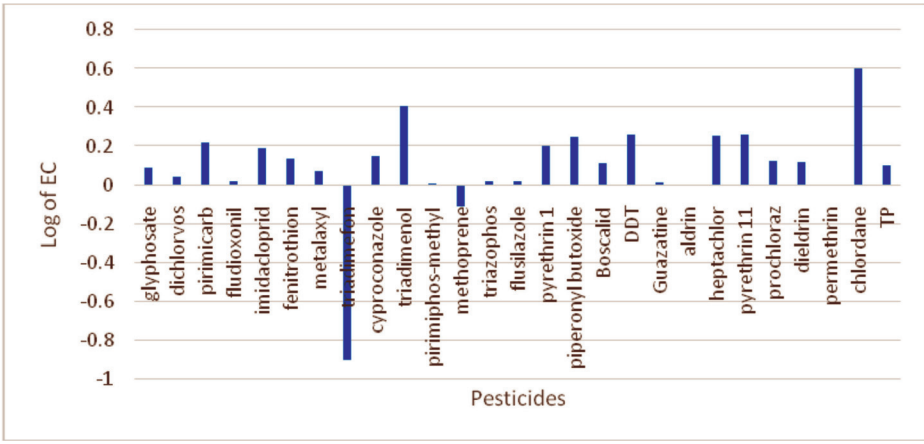

Fig. 1. Pesticides enrichment in the sediments samples

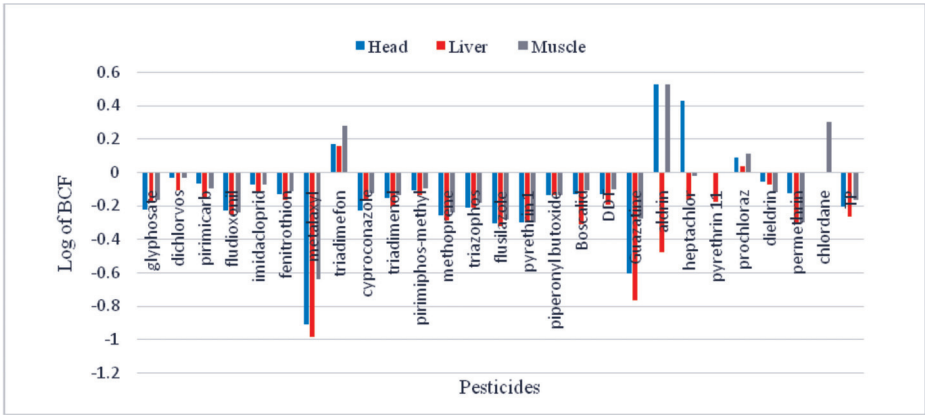

Fig. 2. Log of BCF of pesticides in the fish parts

Table 4. Statistical relationships of pesticides residues in the various samples analysed

Statistics	Water versus soil sediments (W/S)		Head versus liver (H/L)		Liver versus muscles (L/M)		Head versus muscle (H/M)	
	W	S	H	L	L	M	H	M
r_{xy}		0.9356		0.9681		0.9653		0.9639
r_{xy}^2		0.8754		0.9371		0.9317		0.9292
R_{xy}		1.33		0.8827		1.17		1.07
Mean	0.0691	0.0865	0.0412	0.0361	0.0361	0.0451	0.0412	0.0451
SD	0.0731	0.1036	0.0401	0.0366	0.0366	0.0445	0.0401	0.0445
CV%	106	120	97.4	101	101	98.5	97.4	98.5
CA		0.3529		0.2508		0.2613		0.2661
IFE		0.6471		0.7492		0.7387		0.7339
Remarks		Significant		Significant		Significant		Significant

r_{xy} = correlation coefficient; r_{xy}^2 = variance; R_{xy} = regression coefficient; SD = Standard deviation; CV% = coefficient of variation percent; C_A = coefficient of alienation; IFE= Index of forecasting efficiency; Remarks = r_{xy} values were significant at $r_{=0.01}$ at n-2 [26 -2 = 24 (df)].

bioaccumulation. The organochlorine compounds (aldrin, heptachlor and chlordane) revealed evidence of high accumulation in the fish parts as compared to other class of pesticides. This justified previous study on characteristics of OCPs as highly bioaccumulative and biomagnification compounds.

Wassawa and Kiremire (2004)reported that the extent of bioaccumulation of OCPs in fish varies with species due to differences in trophic level habitat, reproductive season exposure, feeding habit and detoxification capacity.

The bio-sediment accumulation factors (BSAFs) values of the pesticides ranged from 0.104 - 11.6, 0.087 – 11.3 and 0.195 – 15.0 in head, liver and muscle respectively, with all the parts showing triadimefon and metalaxyl as the most and least accumulated pesticides residues. In general, BSAFs in the fish parts were in the order of muscle ˆ head ˆ liver. Figure 3 showed the logarithms of BSAFs, which illustrated those residues that were bioaccumulated as a result of the fish feeding on the sediment.

Comparing the accumulation factors of the pesticides in the fish parts, it was observed that muscle recorded highest values of BSAFs in most pesticides than the other parts. This showed that concentration of these pesticides in the fish parts might be a function of the parts, lipid content, uptake and elimination kinetics and physico-chemical properties of water and sediments. The BSAFs of all the pesticides were below 1 except triadimefon (head, liver and muscle), aldrin (head and muscle) and heptachlor (head) indicating high accumulation rate of these three pesticides from the sediments. This revealed that these compounds bioaccumulated highly in the fish. This also revealed the bioaccumulation nature of aldrin and heptachlor which are said to be part of organochlorine compounds (POPs) that exhibit bioconcentration characteristics. The BSAFs reported for DDT (0.349 - 0.432) was comparatively lower to what Alani *et al*. (2013) reported for *p,p'*-DDT (8.70) and *p,p'* –DDE (3.58 -7.83) in young blue crabs. Habitat preferences had been reported to largely affect the kinetics of bioaccumulation process (Zhou *et al*., 1999). Generally, carnivorous fish species showed more bioaccumulation of OCPs and PCBs as compared to herbivorous species. Among the fish species of both group, habitat preference are very important to determine the trends of accumulation.

CONCLUSION

The samples from the studied dam had residues of pesticides, which was an indication of possible agricultural pesticides run-off from nearby environment. The levels detected in the fish parts were generally below Codex Alimentarius Commission maximum residues limits for pesticides in food. The study revealed evidence of bioaccumulation of pesticides in the fish parts with aldrin, heptachlor, chlordane and triadimefon showing the highest. In sediments, chlordane, pyrethrin II, heptachlor, DDT, piperonyl butoxide, pirimicarb and triadimenol showed evidence of high enrichment. On the basis of our findings, the study recommends the needs for continuous survey and monitoring programme for pesticides in order to protect the aquatic environment and human health in general.

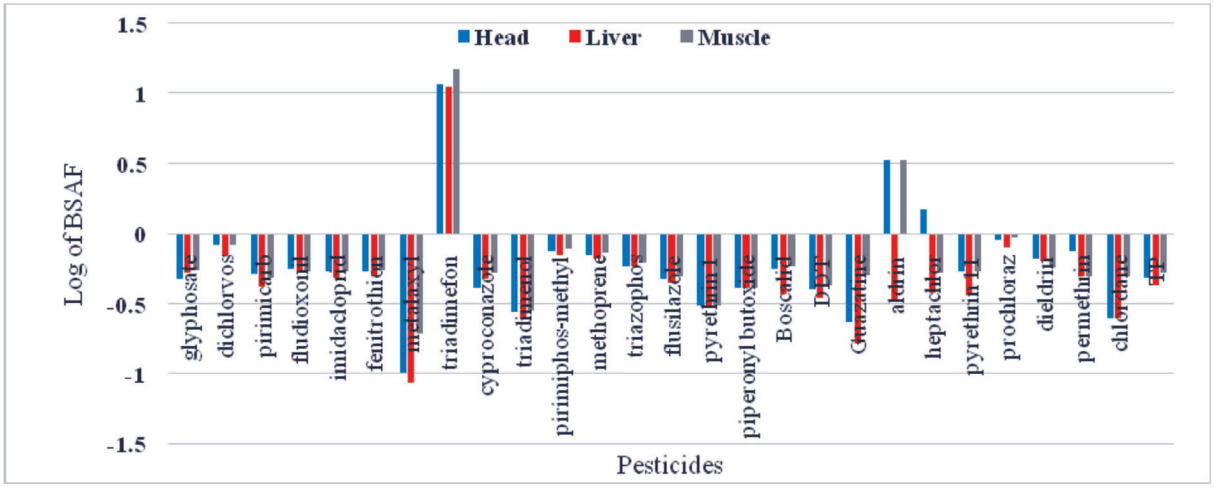

Fig. 3. Log of BSAF of pesticides in the fish part

REFERENCES

Aiyesanmi, A.F. and Idowu, G.A. 2012. Organochlorine pesticides residues in soil of cocoa farms in Ondo State central district, Nigsseria. *Environment and Natural Resources Research*. 2(2): 65-72.

Akan, J.C., Mohammed Z., Jafiya, L. and Audu, S.I. 2013. Organophosphorus pesticide residues in different tissues of fish samples from Alau Dam, Borno state, Nigeria. *World Journal of Fish and Marine Sciences*. 5(5): 519 – 526.

Alani, R., Drouillard, K., Olayinka, K. and Alao, B. 2013. Bioaccumulation of organochlorine pesticide residues in fish and invertebrates of Lagos Lagoon, Nigeria. *American Journal of Scientific and Individual Research.* 4(1): 22-30.

Babu, R., Imagawa, T., Tao, H. and Remesh, R. 2005. Distribution of PCBs, HCHs and DDTs and their ecotoxicological implications in Bay of Bengal, India. *Environment International*. 31(4) : 503-512.

Bai, Y., Zhou, L. and Wang, J. 2006. Organophosphorus pesticide residues in market foods in Shaanxi area, China. *Food Chemistry*. 98 (2) : 240-242.

Bempah, C.K., Donkor, A., Yeboah, P.O. and Osei-Fosu, P. 2011. A preliminary assessment of consumer's exposure to organochlorine pesticides in fruits and vegetables and potential health risk in Accra Metropolis, Ghana. *Food Chemistry*. 128 : 1058-1065.

Chase, C.I. 1976. *Elementary Statistical Procedure*, 2nd edition. McGraw-Hill Kogakusha, Ltd., Tokyo.

Codex. Codex classification of Food and Animal feed (Codex Alimentarius) Pesticides residues in food, Rome, 2005.

Dikshith, T.S.S. 2008. *Safe Use of Chemicals. A Practical Guide,* CRC Press. 312.

Guo, Y., Meng, X.Z., Tang, H.L. and Zeng, E.Y. 2008. Tissue distribution of organochlorine pesticides in fish collected from Pearl river Delta, China: implications for fishery input source and bioaccumulation. *Environmental Pollution* 155 : 150-156.

Kuranchie-mensah, H., Asampson, A., Palm, L.M. and Osei-Fosu, P. 2011. Determination of organochlorine pesticide residues in sediment and water from the Densu river basin, Ghana. *Chemosphere*. 86(3): 286-292.

Lanfranchi, A.L., Menone, M.L., Miglioranza, K.S.B., Janiot, I.J., Aizpun, J.E. and Moreno, V.J. 2006. Striped weakfish (Cynoscion guatucupa): a biomonitor of organochlorine pesticides in estuarine and near-coastal zones. *Marine Pollution Bulletin*. 52: 74-80.

Majewski, M.S. and Capel, P.D. 1995. Pesticides in the atmosphere- distribution, trends and governing factors: Chelas Mich., Ann Arbor Press Inc., p.520. (available from lewis publishers, Boca Raton, Florida.

Mousa, S., Gichuki, J.W., Raburu, P.O and Aura, C.M. 2011. Organochlorine and organophosphorus pesticide residues in water and sediment from Yala/ Nzoia river within lake Victoria basin, Kenya. *Journal of Ecology and Natural Environment.* 3 (12): 392-399.

Oloyo, R.A. 2001. *Fundamentals of Research Methodology and Applied Sciences.* ROA Educational Press, Ilaro, Nigeria.

Soliman, 2001. Changes in concentration of pesticides residues in potatoes during washing and home preparation. *Food Chemistry and Toxicology*. 39(8): 887-891.

Upadhi, F. and Wokoma, O.A., F. 2012. Examination of some pesticides residues in surface water, sediment and fish tissues of Elechi creek, Niger delta, Nigeria. *Research Journal of Environment and Earth Science*. 4(11): 939-944.

Wasswa, J. and Kiremire, B.T. 2004. Pesticide residue distribution in sediment and fish samples from the Uganda side of Lake Victoria. *ANCAP Inaugural Conference Proceedings, Tanzania 7-14.*

Yu et al., 2000. Determination of residues of 20 kinds of organochlorined pesticides in oils, fruits and vegetables by wide-bore capillary gas chromatographic column. *Chinese Journal of Chromatography*. 18(4) : 346-349.

Zhou, H., Cheung, R. and Wong, M. 1999. Bioaccumulation of organochlorines in freshwater fish with different feeding modes cultured in treated wastewater. *Water Research*. 33 : 2747-2756.