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Temporal Distribution of Organochlorine Pesticides in Tissues of Two Fish Species of Tropical Reservoirs: A Case Study of Bui, Ghana

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Abstract
This study analysed tissues distribution of organochlorine pesticides (OCPs) of Alestes nurse and Chrysichthys nigrodigitatus from Bui Reservoir on temporal basis from June, 2017 to May, 2018. GC-ECD was used to identify, quantify pesticide residues. Sixteen OCPs were detected in A. nurse while 14 in C. nigrodigitatus, concentrations range from1.0 – 194.20 ng/g-ww in A. nurse and from1.01 – 370.97 ng/g-ww in C. nigrodigitatus. Among HCHs, α-HCH and γ-HCH dominated in the gonads of A. nurse and C. nigrodigitatus with highest of 156.55 ± 37.65 ng/g-ww and 347.48 ± 23.49 ng/g-ww respectively. In DDTs group methoxychlor and ρ'ρ'DDT predominated in the gonads of A. nurse and C. nigrodigitatus with 25.5 ± 7 ng/g-ww and 9.05 ± 0.8 ng/g-ww respectively. Of cyclodienes endrin II and aldrin were the dominants in gonads (73.5 ± 65.4 ng/g-ww) and gills (26.10 ± 0.17 ng/g-ww) of A. nurse and C. nigrodigitatus respectively. No significant difference ($p>0.05$) in OCP concentrations among tissues but there were significant differences ($p<0.05$) among seasons with wet season accounting for the highest. Results show the use of muscle tissue was adequate in terms of monitoring OCPs in fish while distribution of OCPs were associated with climatic conditions in addition to their chemical properties.
Keywords: cyclodienes; dichlorodiphenyltrichloroethanes hexachlorocyclohexanes; meteorological pollutants; temporal

1. Introduction

Pesticides runoff after rainfall or irrigation events present a significant risk to aquatic ecosystems located adjacent to agricultural areas. The organochlorine pesticides (OCPs) group because of their high persistent, bioaccumulative and toxic nature are of concern to aquatic toxicologists. Once exposure occurs they are likely to get incorporated into the food chain and pose a risk to organisms high up in the chain within the aquatic ecosystem itself and as well as the communities that rely on it for food especially in areas with high fish consumption rates beginning with the planktons, macro invertebrates and vertebrates including fish (Harris and Smith 2016; Tolgyessy, 2013). Aquatic biota are important source of food for humans and therefore a critical aspect of any toxicological assessments. Fish are among the group of aquatic organisms that represent the largest and most diverse group of vertebrates (Yancheva et al., 2015). Fish constitute a significant source of protein and vitamins to humans especially in Ghana where the per capita consumption of fish is estimated as one of the highest in the world (Adum-Kumi et a*l*., 2010). Exposure of fish to OCPs can affect fish behaviour, reduce reproductions rate, disrupt endocrine and immune systems, reduce longevity and lead to stunted growth (Hinck et al., 2009; Kegley *et al*., 1999). Since wild fish are exposed to the pollutants during their entire life cycle, they are susceptible to accumulating these pollutants in their tissues (Schilderman et al., 1999).

Contaminants in general usually do not have uniform distribution in the environment and with pesticides season matters; unlike other classes of chemicals they are used particularly at specific times in the growing season for effective control to be achieved. Depending on the use in the watershed the quantity that may

reach a water body may differ. Large quantities of pesticides are administered in the wet season due to elevated humidity that supports the development of disease-causing organisms (Ibigbami et al., 2015; Saadati et al., 2012). Temporal variation may be significant especially in the case of runoff from storm drain and erosion of contaminated soil from the watershed (Pokethitiyook and Poolpak 2012).

Bui Reservoir is still very young (~ 7 years) compared with most reservoirs in Ghana that are currently considered old (>50 years) and in a stable state in terms of their characteristics and services provision. This study is unique in that it is one of the few studies that have been done on the Bui, and characterisation of OCPs in the aquatic biota provides valuable baseline data for monitoring and managing contamination level in the Reservoir, especially as the irrigated agriculture intensifies in the area with a resultant increase in pesticides uses and transport.

Information on OCP concentrations in some edible fish species have been reported from other freshwater bodies in Ghana such as Lake Bosomtwe (Adu-Kumi et al., 2010; Darko *et al*., 2008), Lake Weija, (Adu-Kumi et al., 2010), Volta Lake (Gbeddy et al., 2015; Kuranchie-Mensah *et al*., 2011; Adu-Kumi *et al*., 2010) and Tono Reservoir (Akoto *et al*., 2016). However, in spite of the importance of Bui Reservoir as a major source of fish protein to large communities across the country and beyond (Alhassan, 2013) no data is available with respect to OCP concentrations in fish from the Reservoir. Consequently, it becomes imperative to measure OCP concentrations in some dominant edible fish species of Bui Reservoir from both ecological and human health perspectives. *Alestes nurse* and *Chrysichthys nigrodigitatus* are commercially important and widely distributed species in rivers and lakes of West Africa (Oronsaye and Nakpodia, 2005; Holden and Reed, 1972). Contaminants in fish are measured in different tissues as tissue type is known to have a substantial effect on the level of uptake of lipophilic pollutants (Zhoa et al., 2014). This study seeks to provide information on the seasonal distribution of OCPs in some tissues of *Alestes nurse* and *Chrysichthys nigrodigitatus* of the Bui Reservoir.

2. Material and Methods

2.1. Study Area

Bui Reservoir is a fairly new reservoir created in 2013 (Obour *et al*., 2015; Alhassan, 2013) situated in the Bono East region of Ghana and it lies within latitudes 8º 37´ - 8º 17´ N and longitudes 2º 15´ W - 2º 25´ W (Figure 1). The Reservoir is served by the Black Volta River that takes it source from the neighboring country Cote d'Ivoire, and flows through farming communities (Gbeddy et al., 2015) with its many tributaries. The watershed of Bui Reservoir covers an area of 123,000 Km^2 (Barrett, 2007). The Reservoir has a maximum surface area of 444 Km^2 and minimum of 288 Km^2 in the wet and dry periods respectively with an average depth of 29 m, a maximum depth of 88 m and has a maximum capacity of 12,570 million cubic metres, and 6,600 million cubic metres at minimum level (Obour et al., 2015; Alhassan, 2013). The dam was constructed primarily for the generation of electricity.

The Reservoir area has a tropical and humid climate with an average annual precipitation that ranges from 1190 – 1310 mm (Kabo-Bah et al., 2016). Being in the transition zone of Ghana the following four hydrological seasons can be distinguished within the catchment area: dry season with virtually little or no rainfall (January - March); pre-wet season with occasional rainfall (April - June); wet season with frequent rainfall (July - September); and post-wet season with little occasional rainfall (October - December) (Abban et al., 2000; Alhassan 2013). The area around the Reservoir has two types of vegetation (Alhassan 2013); the moist semi deciduous forest mostly in the southern and southeastern part and the guinea savannah woodland predominantly in the northeastern. At the eastern part of the Reservoir is a forest and a farming community close to the western part of the Reservoir. The Reservoir is mostly, surrounded by mountains and highland areas thereby increasing the overland flow into the Reservoir.

2.2. Data collection

Fish samples were obtained from fishermen's catch at the major fish landing site of the Reservoir during the four (4) hydrological seasons from June 2017 – May 2018. Fish tissues were analysed for OCPs at the

Pesticides Laboratory, Standard Board Accra, Ghana. Annual rainfall and temperature data for the area for the study period were supplied by the Ghana Meteorological Agency, Bole Synoptic Station.

2.2.1. Sampling protocols

A total of 24 fish 12 each for *A. nurse* and *C. nigrodigitatus* were sampled during each sampling day. As the fish used for this study were from the fishermen's catch there was no need for an approval by an Institutional Animal Care and Use Committee and fish were typical of what was sold on the market and available to consumers. At each sampling event, the fish were sorted and identified using a key by Holden and Reed (1972). Sampled fish were separately wrapped in aluminum foil and kept in a properly labeled plastic Ziploc® bag and then stored in an ice-box cooler under ice conditions and conveyed to the pesticides laboratory and refrigerated at a temperature of < 4 ^{o}C and analysed within 48 hours from the time of collection (EC, 2010).

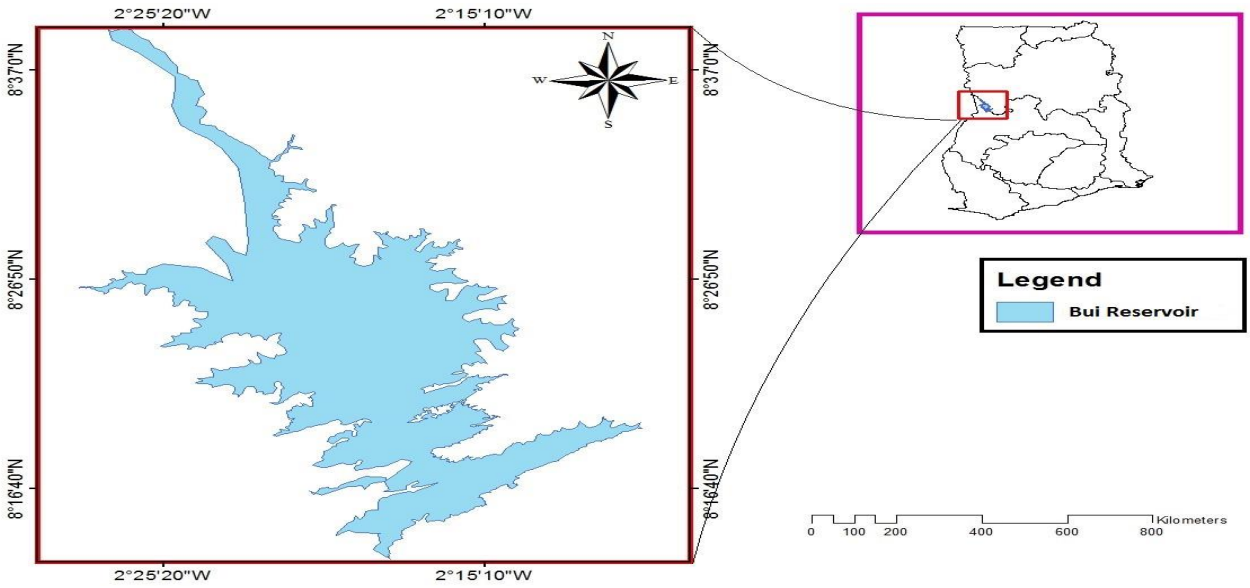

Figure 1: Map of Bui the Reservoir

2.2.2. Tissues isolation from sampled fish of Bui Reservoir

At the laboratory, each fish was gutted with the aid of a dissecting kit by cutting the sample from the pectoral fin to the vent to expose the inner tissues and the tissues of interest harvested, the intestine and gonad were freed and the muscle was cut from the region above the lateral line. The gill was carefully removed around the operculum region. Individual tissues from each fish species were bulked simultaneously to form two pooled samples and encased in aluminum foil wrapper and separately placed in a labeled plastic Ziploc® bag for extraction (Rosseland et al., 2001).

2.2.3. Purification of Solvents, Absorbents, Reagents and Apparatus

All solvents, absorbents, and reagents for the study were purchased from Restek, USA and were of pesticides grade. Standard procedures described in US EPA, Method 8081A (1996) were used to purify solvents, absorbents, glass wool, Whatman® filter papers and reagents.

2.2.4. Method Validation

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

The limits of detection and quantification of pesticides were calculated from several chromatographic runs (7 times) of the lowest values of OCP standards (0.001mg/L) and the calculated standard deviation was multiplied by three (3) and 10 for LOD and LOQ respectively.

2.2.4.2. Method Detection Limit (MDL)

A mixture of the target compounds that is three (3) times the calculated detection limit was prepared. The MDL was assessed in conformity to the method:

MDL = Student's t value (99 % confidence level) × the standard deviation of the replicate measurements (Nallani et al., 2016).

2.2.4.3. Recovery Studies

Recovery studies were conducted to assess the competency of the extraction method applied. The recovery studies were executed in replicates and evaluated by spiking the previously analysed sample with pesticide standard at concentrations approximate to those expected in the sample. The recovery rates were determine from chromatograms and in percentages:

$$\% \text{ Recovery} = [(CS2 - CS1) / CS] \times 100\%$$

Where;

CS1 = value of pesticides in the unspiked sample

CS2 = value of the pesticides in the spiked sample

CS = value of added pesticides

2.2.4.4. Calibration curve

A calibration curve for each analyte was generated by serial dilution the calibration standards to generate different concentrations (at least 6). After running each calibration standard on the instrument a calibration graph (chromatogram) was generated. A regression equation was used to solve for concentration of the sample. Concentrations were reported in the low ppb (part per billion) range – ng/g-ww (wet weight).

2.3. Extraction of analytes from organs of fish of Bui Reservoir

Exactly 10 g of untreated wet fish tissues (gills, gonads, intestines and muscles) was spiked with 1 µL of 50 ng/mL of mixed OCP standards (α-, β-, γ-, δ- HCH, aldrin, dieldrin, α-, β-endosulfan, heptachlor, heptachlor epoxide, chlordane, endrin I, endrin II, α-, β- chlordane, dichlorodiphenyltrichloroethane, methoxychlor). After spiking samples were kept for 24 hours and then ground with 15 g of anhydrous Na_2SO_4 and transferred into a 250 mL sonicating jar. Then 100 mL n-hexane/acetone (3:1 v/v) mixtures was added to the sonicator jar containing the homogenized tissue sample and extraction was carried out for 1 hr. at 45 ^oC in an ultrasonic bath (Branson, 220, Branson Ultrasonic Cleaner. USA). The mixture was then poured into a round bottom flask container through a filter (Whatman® 541) paper held in a funnel. The extraction steps were repeated one more time and the extracts were combined into the same vessel (US EPA Method 3550C 2000).

2.4. Concentration and clean-up of analytes from fish tissues

The analytes in tissues were de-moisturised through a 30 g, 10 – 60 mesh granular Na_2SO_4 fixed in a funnel with good standard Whatman® 541 filter sieve paper. The sodium sulfate was thoroughly rinsed with 10 mL n-hexane before it was transferred into the collection vessel. The extract was reduced in volume using rotary evaporator (BÜCHI Heating Bath B-490) in a water bath to concentrate to 1 mL (US EPA Method 3570C, 2002) and then analyte was redissolved in 5 mL n-hexane and further cleaned up.

Clean-up of the analyte was done using column chromatography. The glass separating column (20 cm length and 1 cm internal diameter) was plugged with glass wool. It was then packed with 5 g of activated silica gel (90% < 45 µm) and overlaid with 2 g each of anhydrous granulated sodium sulfate and activated charcoal (uniform packing of the absorbents were ensured by gently tapping the column). Then conditioned with 10 mL of n-hexane at 2 mL/minute to remove any dirt prior to clean-up and the eluate was disposed. The sample extract was introduce into the column and eluted first with 15 mL n- hexane followed by 5 mL n-hexane to wash down all the analytes into a 100 mL rotary evaporator flask. The collected eluate was evaporated to dryness on a rotary vacuum condenser (BÜCHI Heating Bath B-490) in a water bath at 40 ^oC and re-constituted in 2 mL ethyl acetate (99.9 % purity). The final digest was transferred into a 2 mL vial for subsequent evaluation (US EPA method 3630B, 1996).

2.5. Identification and quantitation of analytes (OCPs) from fish tissue by gas chromatography

The detection and quantification of OCP residues were executed by introducing 1 µL of the 2.0 mL cleaned analytes into the injector pot of a gas chromatograph with a ^{63}Ni electron capture detector (GC-µECD Shimadzu 2010 series) fitted with a ChemStation software. The column consists of a SGE PBX-5 (60 m × 0.25 mm × 0.25 µm). The column temperature was programmed from 90 °C (3 min) at a rate of 25 °C/min to 200 °C, fixed for 15 min, and then at a charge per unit of 30 °C/min to 265 °C held for 5 min. to 275 °C (15 min.) at 3 °C/min. The temperatures of the injector and detector were 250 °C and 300 °C, respectively. The injection was conducted on a splitless injector at 250 °C and the purge activation time was 30 s. The conveyor gas was nitrogen (99.9992, purity) at 1.0 mL/min. and nitrogen gas was used as the make-up gas. The run time was 33 min. Detection of OCP residues was achieved using comparative retention time procedure, while the concentrations of each analyte was assessed by collating the peak areas of reference standard of familiar concentrations (calibration curve). The stock solution of the pesticides standard comprised 1000 ppm in n-hexane was diluted into concentrations of 0.001, 0.01, 0.02, 0.05, 0.1 and 0.5 ppm (mg/L).

2.6. Quality Assurance and Quality Control

To ensure high quality data, blanks samples and blank spikes were incorporated in the assessment. One laboratory blank was analyzed for each five (5) samples. Concentrations of target compounds in the blank sample were 5% less than the lowest concentrations in the unknown samples. Blank spikes were also used to test the GC ECD instrument's data reporting accuracy; peak area, resolution and the detection limit. Spiked samples were processed to check calibration and tuning of the GC ECD. Standard samples were analysed with the same instrument under the same conditions immediately before and immediately after determining the unknown sample, the resulting three spectra outputs agreed. Calibration curves for analytes were prepared and the coefficient of determination (R^2) of the calibration lines were greater than 0.96. Recovery analyses were executed in order to check the proficiency of the investigative protocol using approved procedure. All assessments were conducted in duplicates and the range, average and standard deviation of the concentration were calculated.

2.7. Statistical Analyses

GraphPad Prism version 5.01 was used for the analyses. Prior to statistical analyses data were subjected to normality test using Kolmogorov-Smirnov procedure. Results showed data distributions were not different from a Gaussian distribution. Data points below the detection limit (BDL) at concentrations = <1.0 ng/g-ww were regarded as zero during statistical analysis. Two-way analysis of variance (ANOVA) was applied to evaluate the seasonal distribution of OCPs in the tissues of the fish samples. Bonferroni's post hoc test was employed for multiple range comparisons. The Kruskal-Wallis test was used to assess differences in the distribution of annual rainfall and temperature medians among the seasons and Dunns' post-test was performed for multiple range comparisons. The Student's T-test was used to assess differences in the pesticides concentration between the two selected species of fish. All statistical analyses were performed at an alpha value ($\alpha = 0.05$).

3. Results

3.1. Validation data of GC-ECD method

Validation parameters in this study strengthen the usability of the investigative procedure in the assessments of OCP residues in the tissues of the fish samples. The data obtained for the LOD/MDL ranged from 0.001 – 0.002 ppm and 0.003 – 0.007 ppm for LOQ these indicated the efficiency of the GC-ECD quantification method. Data for recovery studies were between 90 and 103% and were adequate for OCP residues analysis (UNEP, 2002). The coefficients of determination (R^2) between concentration and response (peak area) ratio were between 0.965 and 0.999. These showed strong relationship between concentrations and peak area in the linear range. In all the linear ranged concentrations were between 0.001 and 0.5 mg/L.

3.2. Organochlorine pesticides in the tissues of the fish species

Sixteen (16) OCP residues were detected in the tissues (gills, gonads, intestines and muscles) of *A. nurse* while 14 of them in the tissues of *C. nigrodigitatus* (Tables 1 and 2). The OCPs were grouped into HCHs (α-HCH, β-HCH, γ-HCH and δ-HCH), DDTs (ρ, ρ'-DDT, ρ, ρ'-DDD, and methoxychlor), and cyclodienes (aldrin, α-endosulfan, β-endosulfan, endosulfan sulfate, endrin I, endrin II, dieldrin, heptachlor and trans-chlordane). The order of decreasing concentrations was HCHs > cyclodienes > DDTs for all the tissues of the two fish species.

In the HCHs group, there was no regular pattern of dominance among the isomers in the fish tissues. However, α-HCH dominated in the gonads (156.55 ± 37.65 ng/g-ww) and muscles (117.73 ± 2.42 ng/g-ww) while β-HCH and γ-HCH were the dominant isomers in the gills (36.60 ± 6.00 ng/g-ww) and intestines (156.24 ± 3.88 ng/g-ww) of *A. nurse.* In *C. nigrodigitatus* the highest mean concentrations of the α-HCH were recorded in the gills (34.17 ± 22.92 ng/g-ww), intestines (76.66 ± 4.16 ng/g-ww) and muscles (145.55±94.66 ng/g-ww) while γ-HCH dominated in the gonads (347.48 ± 23.49 ng/g-ww).

Among the members of the DDT group methoxychlor was the primary contaminant in all the tissues of *A. nurse* while ρ, ρ'-DDT dominated the gills, gonads and intestines of *C. nigrodigitatus* with mean concentrations of 1.54 ± 0.05 ng/g-ww, 9.05 ± 0.80 ng/g-ww and 3.52 ± 0.07 ng/g-ww respectively except in the muscles where ρ, ρ'-DDD dominated (Tables 1 and 2).

Of the Cyclodienes high concentration of aldrin was recorded in the gills (9.26 ± 0.66 ng/g-ww) and muscles (4.66 ± 0.05 ng/g-ww) while endrin II and dieldrin had the highest mean concentrations of 73.50 ± 67.40 ng/g-ww and 22.65 ± 10.05 ng/g-ww in the gonads and intestines respectively of *A. nurse*. Aldrin dominance prevailed in all the tissues of *C. nigrodigitatus* (Tables 1 and 2).

Table 1:

Mean concentrations (ng/g-ww) of organochlorine pesticide residues detected in the tissues of *Alestes nurse* of Bui Reservoir (n=3)

Compound	Gill	Gonad	Intestine	Muscle
HCHs				
α-HCH	5.28±3.82	156.55±37.65	4.65±0.75	117.73±2.42
β-HCH	4.07±0.64	18.05±15.55	36.60±6.00	0.54±0.24
γ-HCH	44.96±0.55	29.45±14.95	156.24±3.88	12.64±1.01
δ-HCH	3.56±1.56	3.5±0.15	2.7±0.17	BDL
DDTs				
ρ,ρ'-DDD	BDL	1.45±0.15	1.3±0.00	BDL
ρ,ρ'-DDT	3.56±1.21	6.59±1.05	BDL	BDL
Methoxychlor	22.50±2.50	25.50±7.00	9.30±8.10	13.63±0.05
Cyclodiene				
Aldrin	9.26±0.66	BDL	4.05±2.55	4.66±0.05
α-Endosulfan	BDL	2.40±0.30	BDL	BDL
β-Endosulfan	1.56±0.16	2.30±1.00	0.60±0.10	1.68±0.18
Endosulfan sulfate	0.51±0.11	2.15±0.55	BDL	0.60±0.10
Endrin I	BDL	3.70±1.27	11.4±1.43	2.07±0.17
Endrin II	0.63±0.11	73.5±67.4	9.10±8.00	2.07±0.05
Dieldrin	3.23±0.54	42.15±27.25	22.65±10.05	BDL
Heptachlor	4.81±0.2	BDL	7.65±2.33	1.02±0.02
Trans chlordane	BDL	2.35±0.65	3.45±0.25	0.51±0.10

BDL (Below Detection Limit) = < 0.1

Table 2:
Mean concentrations (ng/g-ww) of organochlorine pesticide residues detected in the tissues of *Chrysichthys nigrodigitatus* of Bui Reservoir (n=3)

Compound	Gill	Gonad	Intestine	Muscle
HCHs				
α-HCH	34.17±22.92	28.94±28.94	76.66±4.16	145.55±94.66
β-HCH	0.74±0.04	2.39±1.03	3.1±0.50	0.55±0.13
γ-HCH	18.23±0.19	347.48±23.49	5.18±0.41	2.11±0.04
δ-HCH	0.61±0.11	BDL	2.09±0.10	3.24±3.24
DDTs				
ρ,ρ'-DDD	BDL	BDL	1.40±0.17	6.3±0.30
ρ,ρ'-DDT	1.54±0.05	9.05±0.80	3.52±0.07	1.17±0.08
Methoxychlor	BDL	3.94±1.21	1.90±0.90	BDL
Cyclodiene				
Aldrin	26.10±0.17	3.41±0.30	25.76±10.03	16.23±0.03
Endosulfan sulfate	BDL	BDL	1.9±0.32	BDL
Endrin I	BDL	1.25±0.21	2.24±1.04	BDL
Endrin II	23.1±6.72	2.63±0.63	14.99±7.79	3.72±0.27
Dieldrin	BDL	BDL	10.5±10.5	BDL
Heptachlor	BDL	BDL	11.17±0.96	6.23±0.39
Trans chlordane	1.69±0.25	BDL	0.96±0.06	BDL

BDL (Below Detection Limit) = < 0.1

3.3. Temporal distribution of organochlorine pesticides in the tissues of *Alestes nurse* and *Chrysichthys nigrodigitatus* of Bui Reservoir

Statistical analyses of temporal (dry, pre-wet, wet and post-wet) and tissues distribution of Σmean OCPs in both *A. nurse* and *C. nigrodigitatus* revealed no significant difference ($p>0.05$) among the tissues but showed significant differences ($p<0.05$) among the seasons with wet season samples accounting for the most contaminated. The temporal distribution of the pollutants in tissues of both fishes were in the following order of decreasing concentrations: wet > dry > pre-wet > post-wet seasons (see Figures 2 and 3).

With regards to annual variations of rainfall and temperature statistical analysis showed significant differences ($p<0.05$) in the median values of both rainfall and temperature among the sampling seasons. The seasonal median values for rainfall and temperature were in the following sequence; wet (139.47 mm) > pre-wet (136.3 mm) > post-wet (25.50 mm) > dry (20.33 mm) and dry (36.33 ^{o}C) > post-wet (34.63 ^{o}C) > pre-wet (32.7 ^{o}C) > wet (29.8 ^{o}C) respectively (see Figures 4 and 5).

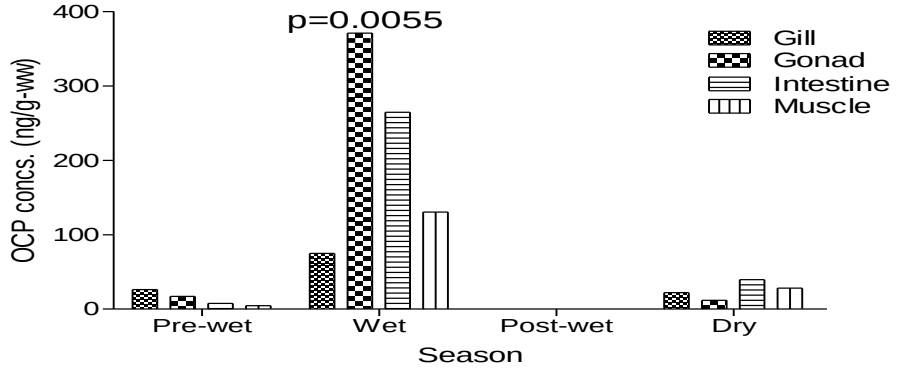

Figure 2: Temporal distribution of organochlorine pesticides in tissues of *Alestes nurse* of Bui Reservoir

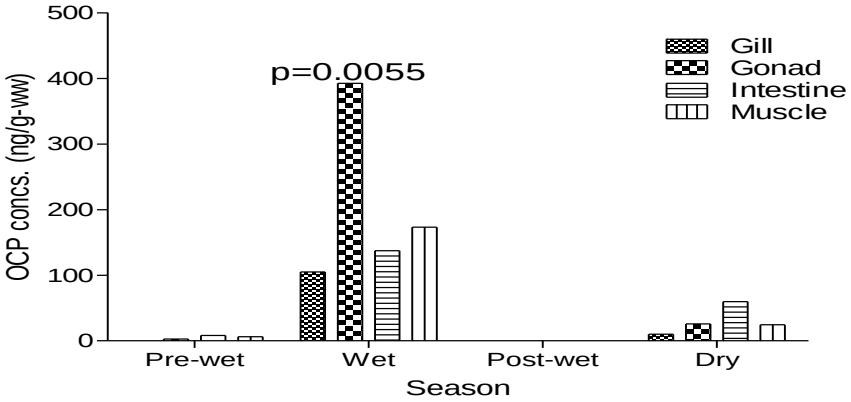

Figure 3: Temporal distribution of organochlorine pesticides in tissues of *Chrysichthys nigrodigitatus* of Bui Reservoir

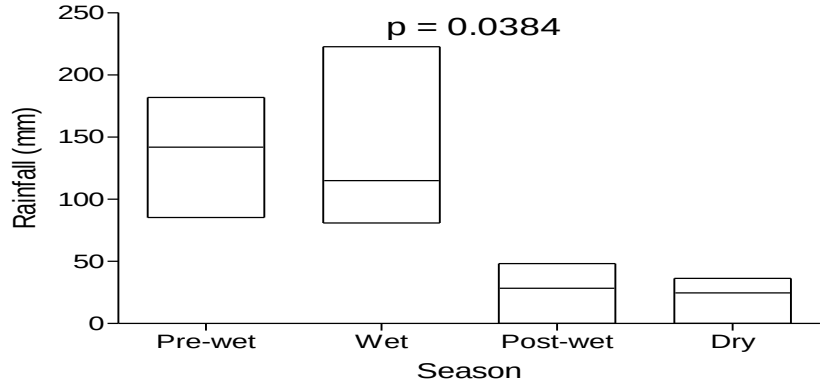

Figure 4: Annual rainfall distribution patterns among the hydrological seasons in the Bui area from June, 2017 to May, 2018.

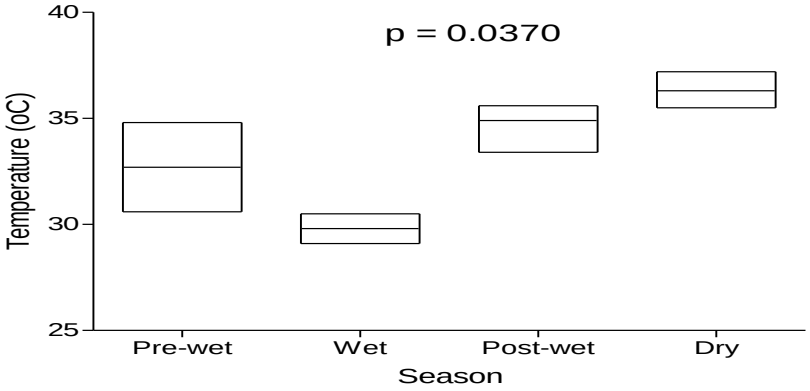

Figure 5: Annual atmospheric temperature patterns among the hydrological seasons in the Bui area from June 2017 to May 2018.

3.4. Species specific bioaccumulation of organochlorine pesticides in *Alestes nurse* and *Chrysichthys nigrodigitatus* of Bui Reservoir

Results of unpaired t-test showed no statistically significant difference ($p>0.05$) in the bioaccumulation of the pesticides between the two fish species.

4. Discussion

4.1. Organochlorine pesticides in the tissues of the fish species of Bui Reservoir

The dominance of α-HCH in most of the tissues of the fishes suggest that the source of the contaminant was technical mixture of HCHs. Technical HCH contains 60 – 70 % α-HCH, 5 – 12 % β-HCH, 10 – 15 % γ-HCH and 6 – 10 % δ-HCH (Sun et al., 2010; Law et al., 2001). It could also be attributed to the transformation of the γ-isomer to α-isomer in these tissues (Zhao et al., 2014). The predominance of the γ-HCH in the intestines of *A. nurse* and the gonads of *C. nigrodigitatus* indicate recent input of purified HCH (Lindane) this is further confirmed as the ratio of α/γ-HCH < 1 (Law et al., 2001). Omwenga et al. (2016) in a similar study of OCPs accumulation in some tissues of *Oreochromis niloticus* from Kiambu fish farm, Kenya, reported high concentrations of γ-HCH in the liver, muscle, gonad and brain. β-isomer preponderance in the intestines of *A. nurse* indicates effective degradation of the compound to the more stable metabolite and may further indicate previous input of HCHs from the watershed.

The prevalence of methoxychlor in the tissues reflect local conditions such as its usage in the watershed as an alternative to ρ, ρ'-DDT. In this study ρ, ρ'-DDE as one of major residues of ρ, ρ'-DDT was not present in the fish tissues. This implies that the metabolite has been converted to the more stable ρ, ρ'-DDD (Ahmed et al., 2015; Omwenga et al., 2016). The relative lower concentrations of ρ, ρ'-DDD recorded in this study indicated slow anaerobic degradation process of the parent pesticide to the refractory isomer. The dominance of ρ, ρ'-DDT instead of its metabolites suggests that there was a fresh use DDT most likely Dicofol in the watershed. Dicofol is a substitute for marketed DDT made up of 20 % DDT and thus a possible source of ρ, ρ'-DDT (Zhou et al., 2006; Qiu et al., 2005; Qiu et al., 2004). Study by Kuranchie-Mensah et al. (2011) reported lower mean concentration (15.95 ± 2.93 ng/g-ww) of DDTs in the muscle of *C. nigrodigitatus* from Lake Volta, Ghana when compared to the value obtained in this study.

The dominance of aldrin instead of dieldrin in most of the fish tissues indicates that there is a renewable source of aldrin in the water. In the environment aldrin is easily and quickly metabolized to dieldrin and aldrin is very similar to dieldrin (Ritter et al., 1995). The degradation of aldrin to dieldrin has probably enhanced the concentration of the latter in the gonads and intestines of *A. nurse*. The non-occurrence of the parent endrin echoes historical use of the compound in the watershed: endrin rapidly degrades in animal tissues to the more stable endrin I and endrin II and very little endrin is bioaccumulated (ATSDR, 1996). Endrin undergoes photo and microbial degradations to produce endrin I and endrin II (endrin aldehyde and endrin ketone respectively) isomers (Bempah and Donkor, 2011; Nollet, 2000). Endosulfan sulfate was the only isomer of endosulfans detected in the intestine of *C. nigrodigitatus* with the mean concentration of 1.90 ± 0.92 ng/g-ww. This suggests biodegradation of both α-endosulfan and β-endosulfan isomers to endosulfan sulfate in the intestine. Furthermore, α and β-endosulfans have aqueous half-lives of just few days but endosulfan sulfate has half-life of several weeks (Vivekanandhan and Duraisamy, 2012).

4.2. Temporal distribution of organochlorine pesticides in the tissues of *Alestes nurse* and *Chrysichthys nigrodigitatus* of Bui Reservoir

The highest OCP concentrations recorded in the wet season can be linked to more pesticides usage by the farmers during wet season and or greater wash-off and severe soil erosion via surface runoff from application sites in the watershed during the more intense rainfall events of the season. Large quantities of pesticides are administered in the wet season due to elevated humidity that supports the development of disease-causing organisms (Ibigbami et al., 2015). Low temperature value recorded during the wet season might have also contributed to elevated concentrations of the contaminants by limiting volatilisation losses (Rissato et al., 2006) and increased atmospheric deposition of the contaminants in the Reservoir (Jongbloed et al., 2000). In the same vein, the higher temperatures during the dry seasons could have accelerated volatilisation of the pollutants and thus the relative less concentration of the contaminants when compared with those of the wet season. Additionally, the lowest value of rainfall that occurred during the dry season could have limited the transportation of the pesticide residues from the watershed through land runoff into the Reservoir. Saadati et al. (2012) in a similar study reported higher OCP concentrations during the wet season than the dry season. The dry season mean OCP concentrations in fish were however higher than

both the pre-wet and post-wet seasons. Evaporative effects as a result of the elevated ambient temperature recorded during the dry season could have favoured the elevation of the contaminant in water and its subsequent absorption by the fish as earlier reported in tissues of *C. nigrodigitatus* (Williams and Ajeyoyu 2015). Normalisation of flow current due to the little occasional rainfall and relative low temperature regimes during the post-wet season may have provided conditions for greater accumulation of the hydrophobic contaminants in the sediments and consequently limiting its availability in the water for uptake by the fish.

4. 3. Species specific bioaccumulation of organochlorine pesticides between *Alestes nurse* and *Chrysichthys nigrodigitatus* of Bui Reservoir

The non-significant difference in bioaccumulation of OCPs between the two species studied might reflect the apparent similarity in the feeding habits of the two species. *A. nurse* is reported to be an indiscriminate feeder that devours assorted edible material available in its habitat (Ogbe et al., 2008; Saliu, 2002). *C. nigrodigitatus* is predominantly omnivorous, also feeding on detritus materials (Oronsaye and Nakpodia, 2005). Saliu (2002) and Offem et al. (2008) described the two species as omnivores

5. Conclusions

The study sought to investigate the temporal dynamics of OCPs in the tissues of *A. nurse* and *C. nigrodigitatus* of a relatively recent tropical reservoir, Bui. OCP concentrations in tissues were highly influenced by the seasons in which the tissue(s) were sampled: the wet season accounted for highest OCP concentrations followed by samples collected in the dry season and pre-wet season. This indicates that the distribution, behaviour and fate of OCPs have close link with meteorological properties beyond their chemical characterization. Contaminants were not detected in tissues sampled during post-wet season. No difference in OCP concentrations among seasons implies that in terms of monitoring OCPs in the Reservoir, use of muscle tissues will be adequate and representative. A study to evaluate the potential health risks of the pesticides in the fish of Bui Reservoir on consumers is necessary from human health point of view.

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